

Electron Interaction in Solids. Collective Approach to the Dielectric Constant

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(Received April 10, 1957)

A quantum theory of the dielectric constant for solids of both low and high polarizability is developed from first principles. In the latter case, the approach used is collective in that the long-range part of the electron interaction is described by the plasmon field. The conditions under which the local field corrections of Lorentz may be neglected are clearly defined. Both the static and frequency-dependent dielectric constant are derived. It is shown that the interaction between electrons may be described in terms of the dielectric constant of the solid provided the electrons in question form a small minority group which can be isolated from the much larger majority electron group. The theory is applied to a calculation of the frequency-dependent longitudinal conductivity and the optical properties of the solid.

1. INTRODUCTION

A SATISFACTORY quantum theory of the dielectric constant in solids should answer three questions. First, under what circumstances is the concept of a dielectric constant meaningful? (Can it be used for all wavelengths, or to describe the interaction between any pair of particles in the solid?) Second, what is the role played by the local field corrections of Lorentz? Third, how do we express the dielectric constant in terms of the electronic wave functions for the solid? In this paper we apply the collective description developed in the preceding paper¹ to a treatment of the dielectric constant. We shall see that the approach is particularly well suited to the problem at hand, and that we are able to obtain a satisfactory answer to the foregoing questions. We derive from first principles both the static and frequency-dependent dielectric constant, and give a critical discussion of the circumstances under which its definition is meaningful.

We begin Sec. 2 with a brief review of the concept of the dielectric constant and the classical description of Lorentz for an insulator. We consider next the possibilities of an individual-particle quantum treatment of the dielectric constant (by means of suitable canonical transformations on the basic Hamiltonian for a set of test charges interacting with the solid). We are thereby able to find the conditions under which the influence of electron interaction on the dielectric constant may be neglected, *viz.*, when $4\pi\alpha \ll 1$, α being the polarizability. When $4\pi\alpha \gtrsim 1$, we are able to take electron interaction into account in an approximation which is equivalent to neglect of the local field corrections. However, we do not find it possible to justify the approximation within the framework of our individual-particle approach.

The development of a collective approach to the static dielectric constant is carried out in Sec. 3. In the region of high polarizability ($4\pi\alpha \gg 1$), it is clear that a treatment of the electron interaction in terms of a plasmon field is the correct one, since this is just the region in which the plasmons are well-defined ele-

mentary excitations of the system. The long-wavelength response of the electrons to the test charge is described by the plasmon field, and the dielectric constant is determined. It is shown that the local field correction may be completely neglected for those solids for which plasmons are a well-defined elementary excitation, and for which the influence of the short-range screened electron interaction on the electronic motion may be regarded as a relatively small perturbation. Where H_{sr} becomes important, we can redefine the dielectric constant by using a representation in which $(H_0 + H_{sr})$ is diagonal. The concept of a dielectric constant is then meaningful, but that of a local field correction is not. In regions of intermediate polarizability ($4\pi\alpha \sim 1$) neither the collective approach nor an individual particle approach which neglects electron interaction is valid. Since, however, the high-polarizability result yields correctly the low-polarizability limit, it probably serves as a useful interpolation formula.

In Sec. 4 we generalize the method of the preceding section to calculate the frequency-dependent dielectric constant. We also discuss the relative role played by the plasmons and the individual electrons in the determination of the dielectric constant.

A knowledge of the dielectric constant at arbitrary frequency enables one to calculate a number of interesting properties of the solid. In Sec. 5 we discuss anew the plasmon dispersion relation in the light of our knowledge of the dielectric constant, and establish the equivalence of the microscopic and macroscopic approach to the determination of the plasmon energy. We then consider the extent to which the interaction between electrons may be described in terms of the dielectric constant of the solid. In Sec. 6 we show that this may be done provided the electrons in question form a small minority group which can be easily isolated from the much larger majority group of electrons. We apply this result to a calculation of the frequency-dependent longitudinal conductivity in Sec. 7.

Essentially the same collective approach may be applied to the interaction of light waves with solids. In Sec. 8, we outline the calculation of the optical properties of solids, and discuss briefly the results. We

¹ P. Nozières and D. Pines, Phys. Rev. **109**, 741 (1958), preceding paper, hereafter referred to as NP I.

summarize our conclusions regarding the dielectric constant and optical properties in Sec. 9.

2. GENERAL CONSIDERATIONS

We consider first the static electronic polarizability. The problem of the dielectric constant may be formulated by introducing test charges in the solid with a density $\rho(\mathbf{x})$. Assume the charges to be infinitely heavy. Call r_k the Fourier components of $\rho(\mathbf{x})$, and further assume that only components with reasonably small k are present. In free space, the charges interact through a simple Coulomb law, with an interaction energy

$$\sum_k \frac{1}{2} M_k^2 r_k r_{-k}.$$

In the solid the electric field of each test charge is screened by the electron cloud, and the Coulomb energy is thereby modified. Under certain conditions, the effective Coulomb energy brought in by the test charges may be written

$$\sum_k \frac{1}{2} M_k^2 r_k r_{-k} / \epsilon(k). \quad (2.1)$$

From elementary electrostatics, we see that $\epsilon(k)$ is the dielectric constant at wavelength k .²

Certain of the limitations on the definition of a dielectric constant may be understood in the following way. Consider the Hamiltonian of the total system which may be written as³

$$H = H_0 + \sum_k \frac{1}{2} M_k^2 (\rho_k + r_k) (\rho_{-k} + r_{-k}). \quad (2.2)$$

Let us suppose that by a suitable canonical transformation we eliminate the interaction term linear in r_k . We then obtain second-order terms, which have the general structure,

$$\sum_{k, k'} g(k, k') r_k r_{k'},$$

where $g(k, k')$ is an operator depending on the electron coordinates. Such terms describe the change in Coulomb energy due to the distortion of the electron cloud. If k^{-1} is larger than the interelectronic spacing, we may neglect the fluctuations of $g(k, k')$ around its expectation value. The expectation value itself is nonzero only when $\mathbf{k}' = \mathbf{k} + \mathbf{K}$, where \mathbf{K} is a vector of the reciprocal lattice. Now, if k is well inside the first Brillouin zone, we may neglect the very rapid fluctuations caused by the terms with nonzero \mathbf{K} . The second-order terms then combine with the original r - r interaction to give a term like (2.1); the dielectric constant may accordingly be defined and determined. Clearly, the concept breaks down for values of k of the order of the first Brillouin-zone size. For such values of k the fluctuations which we neglected become very important, and an average "effective" r - r interaction becomes meaningless.

Before going into the details of the calculation, we

² This definition of $\epsilon(k)$ works equally well for metals and insulators. For an insulator, $\epsilon(0)$ is a finite quantity, while for a metal $\epsilon(k)$ is roughly k_e^2/k^2 , where k_e is the Debye wave vector.

³ We use the notation of NP I.

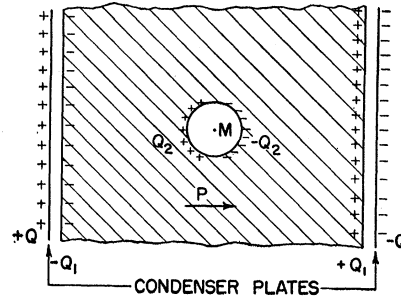


FIG. 1. The Lorentz model for local field corrections. The charge $(Q_2, -Q_2)$ produces \mathbf{E} ; $(Q_1, -Q_1)$ produces \mathbf{E}_1 ; $(Q_2, -Q_2)$ produces \mathbf{E}_2 .

review the macroscopic picture developed by Lorentz⁴ for an insulator. Consider a slab of solid between two condenser plates. The electric field \mathbf{E} and polarization \mathbf{P} are uniform. Around any point M of the solid, draw a sphere of radius small compared to the slab thickness, but large compared to the atomic dimensions, as shown in Fig. 1. The local field \mathbf{E}_M on a charge within the sphere is the sum of (a) the field \mathbf{E} of the charge located on the condenser plates, (b) the field \mathbf{E}_{out} of the polarized matter outside the sphere, and (c) the field \mathbf{E}_3 of the polarized matter inside the sphere.

We know that \mathbf{E}_{out} is the same as that produced by a surface charge density \mathbf{P}_n on the boundary of the solid and the surface of the sphere (\mathbf{P}_n being the component of \mathbf{P} normal to the surface). We may write \mathbf{E}_{out} as

$$\mathbf{E}_{\text{out}} = \mathbf{E}_1 + \mathbf{E}_2,$$

where $\mathbf{E}_1 = -4\pi\mathbf{P}$ is due to charges located on the external surface of the solid, and $\mathbf{E}_2 = \frac{4}{3}\pi\mathbf{P}$ is due to charges on the surface of the sphere. Altogether, the local field \mathbf{E}_M is

$$\mathbf{E}_M = \mathbf{E} + \mathbf{E}_1 + \mathbf{E}_2 + \mathbf{E}_3. \quad (2.3)$$

\mathbf{E}_1 comes from the discontinuity of polarization at the surface of the solid. ($\mathbf{E}_2 + \mathbf{E}_3$) describe the so-called "local field correction" which is produced by the field of polarized matter close to the point M ; this correction involves localized charges, while \mathbf{E}_1 does not. The dielectric constant is defined as

$$1/\epsilon = (\mathbf{E} - 4\pi\mathbf{P})/\mathbf{E}. \quad (2.4)$$

Let us now denote by α the microscopic polarizability,

$$\mathbf{P} = \alpha \mathbf{E}_M.$$

The above set of equations determines ϵ in terms of α .

Suppose we completely neglect the interaction between electrons. We therefore neglect the field of polarized matter, and so take \mathbf{E}_1 , \mathbf{E}_2 and \mathbf{E}_3 , to be zero. We thereby obtain

$$1/\epsilon = 1 - 4\pi\alpha. \quad (2.5)$$

⁴ H. A. Lorentz, *The Theory of Electrons* (Dover Publications, New York, 1952), p. 138.

A possible improvement consists in taking into account \mathbf{E}_1 while neglecting the "local field" corrections \mathbf{E}_2 and \mathbf{E}_3 . We then find the familiar expression

$$\epsilon = 1 + 4\pi\alpha. \quad (2.6)$$

Finally, if we write $\mathbf{E}_2 + \mathbf{E}_3$ as $4\pi P\gamma$ (where γ is some number of order unity), we obtain

$$\epsilon = \frac{1 + 4\pi\alpha(1 - \gamma)}{1 - 4\pi\alpha\gamma}. \quad (2.7)$$

Lorentz has shown that for a set of oscillating individual electrons distributed in a cubic array, \mathbf{E}_3 is zero, γ is equal to $\frac{1}{3}$. Equation (2.7) then leads to the well-known Lorentz-Lorenz formula. We expect this result to be satisfactory if the electrons are closely bound to the ions of a cubic lattice. (In such a case, the electronic polarizability is small.)

If $4\pi\alpha$ is much smaller than 1, ϵ is well represented by $(1 + 4\pi\alpha)$, and a precise knowledge of the local field correction (i.e., of γ) is not necessary. On the other hand, if $4\pi\alpha \gg 1$ (as occurs in metals and semiconductors), (2.7) leads to the rather strange result

$$\epsilon = 1 - (1/\gamma),$$

which is certainly wrong. However, unless we can show that \mathbf{E}_2 and \mathbf{E}_3 cancel one another almost completely (γ being very small), it is not meaningful to keep only \mathbf{E}_1 , thereby neglecting the local field corrections. For a gas of high polarizability, we must accordingly evaluate γ . In what follows, we shall develop the circumstances under which it is very small, and so justify the neglect of local field corrections in such cases.

The competition between the Sellmeyer formula, $\epsilon = 1 + 4\pi\alpha$, and the Lorentz one, $3(\epsilon - 1)/(\epsilon + 2) = 4\pi\alpha$, is an old puzzle of the theory of dielectrics. Darwin⁵ has given a very interesting study of the problem, in which he treated by classical analytical mechanics the microscopic motion of the electrons. He reached the conclusion that whenever the electrons were spatially well localized, the Lorentz formula should apply, while for almost free electrons the Sellmeyer formula is valid. Our results will, in fact, confirm these views.

Let us consider what the foregoing approximations correspond to in a Hamiltonian treatment of the problem. Suppose we first neglect the Coulomb interaction between electrons. The Hamiltonian is then

$$H \simeq H_0 + \sum_k \frac{1}{2} M_k^2 \{ 2r_{-k}\rho_k + r_{-k}r_k \}. \quad (2.8)$$

We thereby neglect the field on a given electron of all the other electrons, whose wave function $\Phi(\mathbf{E})$ depends on the applied electric field. The influence of the electrons on a given electron may be split into two parts:

(i) The electric field of the distribution in the absence of an applied field, $\Phi(0)$, which gives rise to a change in the microscopic polarizability, α . This we

expect to be a predominantly short-range process, since the electron interaction is screened. (In fact, it is just due to H_{sr} .) The effect of the field will be small if H_{sr} has but little influence on the electron motion (which is the case for "almost free" electrons). We assume that we deal with such a case, and neglect this effect.

(ii) The field due to the distortion of the electron distribution by the applied field $[\Phi(\mathbf{E}) - \Phi(0)]$. This describes the field of polarized matter and corresponds to the corrections \mathbf{E}_1 , \mathbf{E}_2 , \mathbf{E}_3 , which we just discussed.

Therefore, as long as we can neglect the effect of short-range correlations on α , the neglect of the electron interaction amounts to a neglect of the corrections \mathbf{E}_1 , \mathbf{E}_2 , \mathbf{E}_3 .

The linear interaction term in (2.8) is easily eliminated by a canonical transformation generated by S :

$$S = \sum_k M_k^2 r_{-k} D_k, \quad (2.9)$$

$$(D_k)_{mn} = i(\rho_k)_{mn} / \omega_{mn},$$

where D_k is an electron operator defined in the "one electron" representation. In the second-order terms, quadratic in r_k , we replace the commutator $[\rho_k, D_{k'}]$ by its expectation value⁶ in the ground state, and obtain

$$\sum_k \frac{1}{2} M_k^2 r_k r_{-k} \left\{ \frac{-2M_k^2}{\hbar} \sum_n \frac{|(\rho_k)_{0n}|^2}{\omega_{n0}} \right\}. \quad (2.10)$$

From our previous study, we know that when \mathbf{E}_1 , \mathbf{E}_2 , and \mathbf{E}_3 are neglected the effective interaction is

$$\sum_k \frac{1}{2} M_k^2 r_k r_{-k} [1 - 4\pi\alpha(k)].$$

Equation (2.10) thus defines the microscopic polarizability $\alpha(k)$. We express it in terms of the oscillator strengths by

$$4\pi\alpha(k) = \frac{1}{N} \sum_n f_{n0}(k) \frac{\omega_p^2}{\omega_{n0}^2}. \quad (2.11)$$

When most of the ω_{n0} are larger than ω_p , $4\pi\alpha$ is much smaller than 1, and our neglect of \mathbf{E}_1 , \mathbf{E}_2 , \mathbf{E}_3 is justified. This treatment obviously fails when $4\pi\alpha > 1$.

We may try to improve our treatment by taking into account Coulomb interaction between the electrons. In order to do this, we should modify the operator D_k appearing in S in such a way as to get

$$\frac{i}{\hbar} \left[H_0 + \sum_k \frac{1}{2} M_k^2 \rho_k \rho_{-k}, S \right] = - \sum_k M_k^2 r_{-k} \rho_k. \quad (2.12)$$

Equation (2.12) is in general very difficult to solve. We may, however, obtain a simple solution if we make a combination of the Hartree approximation and the

⁶ Compare the discussion earlier in this section. Let us remark that we automatically neglect the higher order terms. They involve higher powers of r_k and correspond to a nonlinear effect. The concept of a dielectric constant has meaning only for r_k small enough to stay in the linear range, far from saturation.

⁵ C. G. Darwin, Proc. Roy. Soc. (London) A146, 13 (1934).

random-phase approximation, replacing the commutator $[\rho_k, S]$ by its expectation value.⁷ In doing this we are averaging only one factor in the product $\rho_{-k}[\rho_k, S]$, so that we are neglecting exchange terms. We have no way of estimating the accuracy of such an approximation; we make it primarily to investigate its consequences.

We then find that the transformation is generated by

$$S = \sum_k \frac{M_k r_{-k} D_k}{1 + 4\pi\alpha(k)},$$

where D_k is defined by (2.9) and $\alpha(k)$ by (2.11). When we combine the new second-order terms with the original r - r interaction, we obtain the following "effective" r - r interaction

$$\sum_k \frac{M_k^2}{2} \frac{r_k r_{-k}}{1 + 4\pi\alpha(k)}.$$

The dielectric constant is therefore

$$\epsilon(k) = 1 + 4\pi\alpha(k). \quad (2.13)$$

The foregoing approximation thus is equivalent to taking into account the part \mathbf{E}_1 of the field of polarized matter, and ignoring the local field corrections. In cases where \mathbf{E}_2 and \mathbf{E}_3 do not cancel one another, we see *a posteriori* that the approximation is bad. (An example is a cubic array of electrons, for which the Lorentz treatment applies.)

It is physically obvious that the local field corrections \mathbf{E}_2 and \mathbf{E}_3 are necessarily outside the scope of the random-phase approximation. These fields arise from localized charges, therefore from wave packets of density fluctuations ρ_k . In the random-phase approximation, we keep only one ρ_k interacting with r_{-k} and thus cannot describe a localized charge response.

We summarize the results of our individual-particle treatment of the dielectric constant. We found that we could neglect electron interaction altogether when $4\pi\alpha \ll 1$. We further found that a combination of a Hartree approximation with a random-phase approximation yields results which are equivalent to the neglect of local field corrections. We were not able to investigate the validity of this approximation. Therefore, we need to find a better treatment of the polarizability in the region $4\pi\alpha > 1$. As we saw in NP I, this is just the region in which plasmon behavior becomes important. We therefore now consider the polarizability from a collective standpoint by introducing the plasmons to describe the response of the electrons to an external field.

⁷ This approximation is *not* the random-phase approximation of NP I, in which terms which are quadratic in the plasmon field variables are shown to be small. It is more nearly akin to the linearization of the equations of motion for ρ_k , which involves the coupling via H_{sr} as well. A similar approximation has been made by S. Nakajima [*Proceedings of the International Conference on Theoretical Physics, Kyoto and Tokyo, 1953* (Science Council of Japan, Tokyo, 1954)], in the treatment of the electron-phonon interaction.

3. COLLECTIVE APPROACH TO THE STATIC DIELECTRIC CONSTANT

We wish to introduce the collective coordinates (P_k, Q_k) which will describe the plasmon field and hence the long wavelength response of the electrons to the test charge. We do this along the lines of NP I, by extending our basic Hamiltonian (2.2). As we have mentioned there, and as is emphasized by BHP, in choosing our extended Hamiltonian we need be guided only by the twin requirements of "positive definiteness" and "expediency." Thus, H_{ext} should have a lower bound (in which case the lower bound will be the ground state of H) and should be chosen so as to make the resultant problem as simply soluble as possible. We give such a Hamiltonian below. We were led to it by a combination of some physical notion of what form it should take and considerable experience in the practical consequences of various forms for the added terms.

Our starting Hamiltonian was chosen to be⁸

$$H_{\text{ext}} = H_0 + H_{sr} + \sum_{k < k_c} \left\{ \frac{1}{2} |M_k \rho_k + P_k|^2 + \frac{1}{2} M_k^2 r_k r_{-k} + (M_k - \mu_k) r_{-k} (M_k \rho_k + P_k) + \mu_k M_k r_{-k} \rho_k \right\}. \quad (3.1)$$

We are keeping only the long-wavelength part of the test-charge field, since we are interested in the long-wavelength part of the electron response. The quantity μ_k is an, at present, arbitrary constant which we determine later by consistency requirements. We shall then see that $\mu_k \ll M_k$; its physical meaning is better understood after the canonical transformation we now carry out.

Our first transformation is the same transformation as that for electrons alone; it is therefore generated by

$$S = - \sum_{k < k_c} (M_k Q_k \rho_k).$$

We then obtain the following Hamiltonian

$$H_{\text{ext}} = H_0 + H_{\text{field}} + H_{\text{int}} + H_{sr} + U + \sum_{k < k_c} \left\{ (M_k - \mu_k) r_{-k} P_k + \mu_k M_k r_{-k} \rho_k + \frac{1}{2} M_k^2 r_{-k} r_k \right\} \quad (3.2)$$

together with the set of subsidiary conditions

$$(P_k - M_k \rho_k) \Psi = 0, \quad k < k_c. \quad (3.3)$$

Now, the meaning of μ_k is obvious. Almost all of the electron-test charge interaction has been redescribed as a plasmon-test charge interaction. Only the small fraction μ_k/M_k is left as a coupling with the individual

⁸ H_{ext} may be shown to be positive definite in a variety of ways. For instance, in the absence of test charge we note that the Hamiltonian is positive definite. We add to this Hamiltonian a term which is linear in the test charge variable r_k . The response of the system to the test charge will never cancel it completely (see BHP), so that the only effect of the r_k terms might be to increase the ground state energy. To see this another way, note that (3.1) could blow up only if $\langle \rho_k \rangle_{\text{Av}}$ were to become very large and negative; this would, however, cost too much kinetic energy.

particles. The quantity μ_k measures the extent to which the interaction between the test charges and the electrons cannot be described in terms of plasmons. Its introduction is not merely a mathematical artifice; it corresponds to the physical reality that the screening is not perfect.

The next step is to eliminate the two interaction terms by a suitable canonical transformation. In order to do this, it is not necessary that we eliminate H_{int} first. We determine the generating function, S' , for the transformation by the condition

$$\frac{i}{\hbar} \left[H_0 + H_{\text{field}}, S' \right] = - \sum_{k < k_c} \{ (M_k - \mu_k) r_{-k} P_k + \mu_k M_k r_{-k} D_k \}.$$

This is easily solved to give

$$S' = \sum_{k < k_c} \{ - (M_k - \mu_k) r_{-k} Q_{-k} + \mu_k M_k r_{-k} D_k \}, \quad (3.4)$$

where D_k is defined in (2.9). Naturally, the transformation acts also on H_{int} , H_{sr} and U , yielding extra interaction terms linear in r_k . But only the small part $\mu_k M_k r_{-k} D_k$ contributes to the commutators. We may systematically neglect the contribution from U , which we have shown to be very small. The contribution from H_{int} may be written

$$\sum_{\substack{k < k_c \\ l < k_c}} \frac{i}{\hbar} \mu_k M_k r_{-k} Q_l [V_l, D_k].$$

This is a triple interaction between plasmons, individual electrons, and test charges. Its expectation value with respect to electron coordinates is zero. The off-diagonal part involves triple collisions, and has a structure equivalent to the nonlinear interaction U . In the same way that U was negligible compared to $(H_0 + H_{\text{field}})$, this extra nonlinear interaction is negligible compared to the original interaction. A geometrical factor, together with a factor N'/N are responsible for the reduction. The extra interaction arising from H_{sr} leads to greater difficulty. The discussion of such terms is complicated, and we postpone it.

We now calculate the second-order terms quadratic in r_k (replacing all electron operators by their expectation value). We get

$$\sum_{k < k_c} \left\{ - \frac{(M_k - \mu_k)^2}{2} \frac{\mu_k^2}{2} \sum_n \frac{2M_k^2}{\hbar} \frac{|(\rho_k)_{0n}|^2}{\omega_{n0}} \right\} r_k r_{-k}. \quad (3.5)$$

To obtain the dielectric constant explicitly, we must find μ_k . We determine it by the following consistency requirement: in the elimination of the electron-test charge and plasmon-test charge interactions in H_{ext} , test-charge variables must not be introduced in the subsidiary conditions. In other words, after the final transformation, test charges and electrons must be

entirely separated, both in the Hamiltonian and in the subsidiary conditions. Since our treatment of the Hamiltonian is accurate to second order in r_k , we need cancel only the linear terms in r_k in the subsidiary conditions (one has always one more degree of accuracy in the Hamiltonian than in the wave function). On averaging the electron operators multiplying r_k , we obtain the following consistency relation

$$M_k - \mu_k = \mu_k \left\{ \frac{2M_k^2}{\hbar} \sum_n \frac{|(\rho_k)_{0n}|^2}{\omega_{n0}} \right\}, \quad (k < k_c). \quad (3.6)$$

Using (2.11), we see that

$$\mu_k = \frac{M_k}{1 + 4\pi\alpha(k)}, \quad (k < k_c). \quad (3.7)$$

For a gas of high polarizability, μ_k is effectively much smaller than M_k . Combining the second-order terms (3.5) with the original interaction, and using (3.6), we obtain the final screened (r - r) interaction:

$$\sum_{k < k_c} \frac{M_k^2 r_k r_{-k}}{2 \epsilon(k)},$$

$$\epsilon(k) = 1 + 4\pi\alpha(k) = 1 + \frac{4\pi e^2}{m} \sum_n \frac{f_{n0}(k)}{\omega_{n0}^2}. \quad (3.8)$$

We remark that $M_k = \epsilon(k)\mu_k$. This is not an accident, since μ_k describes that part of the test charge-electron interaction attributed to individual particles. It therefore measures what is left of the original Coulomb interaction after screening. This is just the definition of $1/\epsilon(k)$.

Almost all the (r - r) interaction was cancelled by second-order terms arising from the plasmons, which were calculated rigorously. This emphasizes the main advantage of the collective description. We redescribe most of the long-range density fluctuations in terms of P_k and Q_k for which the random-phase approximation is rigorously true:

$$[P_k, Q_l] = -i\hbar \delta_{k,l}.$$

Equation (3.8) corresponds to no local field corrections (complete cancellation of \mathbf{E}_2 and \mathbf{E}_3). Our only approximation concerned terms of order μ_k arising from H_{sr} . These may yield an appreciable correction to $\epsilon(k)$, but they cannot change its order of magnitude, $\epsilon(k) \sim M_k/\mu_k$. Since the only possible local field correction must proceed from this short-range effect, we may conclude that these corrections are much smaller than the one predicted by the Lorentz formula (which would lead to $\epsilon = -2$).

The importance of the local field corrections depends on how much influence H_{sr} has on the electron motion. If H_{sr} is only a small perturbation, whose effect is small compared to that of H_0 , the terms arising from it in the preceding canonical transformation will be negligible

compared to those arising from H_0 [which determine the screened (r - r) interaction]. In this case we expect the local field corrections to be negligible, and we have $\epsilon = 1 + 4\pi\alpha$. Such a case occurs, for instance, if all ω_{n0} are much smaller than the plasma frequency ω (see Sec. 7 of NP I), as happens for free electrons. This is just the conclusion reached by Darwin⁵ for the case in question, that of nonlocalized electrons.

If, on the contrary, H_{sr} is important in determining the electron behavior, the correction may be sizable, so that $\epsilon(k)$ will only be of the order of magnitude of $[1 + 4\pi\alpha(k)]$. In this case, just as in NP I, we may overcome the difficulty by a change of representation. As we pointed out in Sec. 7 of NP I, when the effect of H_{sr} is large, the natural representation in terms of the physical actual eigenstates is the one in which $(H_0 + H_{sr})$ is diagonal. Let us therefore switch to such a representation, whose basis we call Φ_M . The treatment of the dielectric constant goes along exactly as before, but we no longer need worry about H_{sr} . The dielectric constant is therefore given rigorously by

$$\epsilon(k) = 1 + \frac{1}{N} \sum_M f_{0M}(k) \frac{\omega_p^2}{\omega_{M0}^2}, \quad k \ll k_c. \quad (3.9)$$

For values of k larger than k_c , there is no collective mode, and the dielectric constant must be calculated by a direct perturbation treatment, as was done at the beginning of this section. We obtain

$$\frac{1}{\epsilon(k)} = 1 - \frac{1}{N} \sum_M f_{0M}(k) \omega_p^2 / \omega_{M0}^2, \quad k \gg k_c. \quad (3.10)$$

This is now a rigorous result since we have absorbed the effect of H_{sr} into the representation. When k is of order k_c , (3.9) and (3.10) do not agree. This may be due to the fact that for such values the effect of the random-phase term U becomes important. However, we may expect that (3.9) will serve as a useful interpolation formula, since it is accurate for both limiting regions.

We pay for the rigor of the foregoing results by the fact that we no longer have a simple physical interpretation of what is going on. In (3.9), the quantity $(\epsilon - 1)/4\pi$ is not the microscopic polarizability because it already takes into account the short-range part of the electron correlations. In other words, \mathbf{E}_2 and \mathbf{E}_3 are automatically included. Accordingly, we do not know how to separate what is due to local field corrections, and what is not. We do not even know what the microscopic polarizability $\alpha(k)$ is, since in the present case the short-range electric field of the equilibrium distribution of electrons modifies α strongly. Equation (2.11) is then incorrect. As far as local field corrections are concerned, we can only conclude that in such a case they are sizeable, although they do not change the order of magnitude of ϵ . It is interesting to see physically why the local field correction is so drastically reduced compared to that of Lorenz-Lorentz. Let us go back to the Lorentz

picture for an insulator (Fig. 1). The electric field at point M may still be written as

$$\begin{aligned} \mathbf{E}_M &= \mathbf{E} + \mathbf{E}_1 + \mathbf{E}_2 + \mathbf{E}_3, \\ \mathbf{E}_1 &= -4\pi\mathbf{P}, \\ \mathbf{E}_2 + \mathbf{E}_3 &= 4\pi\mathbf{P}\gamma, \end{aligned} \quad (3.11)$$

where γ is a number of order 1. Now the field \mathbf{E}_1 arises from free charges located at the outer boundary of the solid. This field is related to a macroscopic boundary condition of electrostatics, and is not screened: it gives a contribution to the polarization \mathbf{P}

$$P_1 = \alpha(0)\mathbf{E}_1, \quad (3.12)$$

where $\alpha(0)$ is the polarizability for zero momentum, which may be very large. On the other hand, \mathbf{E}_2 and \mathbf{E}_3 arise from the microscopic field of the neighboring electrons on the one which we are considering. Due to the collective behavior, this field is screened within a radius of order k_c^{-1} . Hence, \mathbf{E}_2 and \mathbf{E}_3 arise from particles very close to M . When calculating the polarization produced by $(\mathbf{E}_2 + \mathbf{E}_3)$, we should, therefore, use the polarizability at a wavelength of order k_c , and *not* at zero wavelength; i.e.,

$$\mathbf{P}_{2+3} \sim \alpha(k_c)(\mathbf{E}_2 + \mathbf{E}_3). \quad (3.13)$$

We know that $\alpha(k_c)$ is much smaller than $\alpha(0)$ and is of order $1/4\pi$. These considerations are summed up in the following equation determining \mathbf{P} :

$$4\pi\mathbf{P} = 4\pi\alpha(0)[\mathbf{E} - 4\pi\mathbf{P}] + 4\pi\alpha(k_c)[4\pi\mathbf{P}\gamma]. \quad (3.14)$$

From (3.14) it is trivial to obtain the dielectric constant

$$\epsilon(0) = 1 + \frac{4\pi\alpha(0)}{1 - 4\pi\alpha(k_c)\gamma}. \quad (3.15)$$

A typical value of $4\pi\alpha(k_c)\gamma$ will be $\frac{1}{3}$. We see that the local field correction does not change the order of magnitude of ϵ . If the screening radius k_c is of the order of the interelectronic spacing, the effect of the short-range Coulomb interaction is small, and we expect $4\pi\alpha(k_c)\gamma$ to be much smaller than 1. In this case there are no local field corrections at all.

The drastic reduction of the local field corrections when $4\pi\alpha(k)$ is much larger than 1 is due to the fact that the fluctuations of the long wavelengths ρ_k 's are frozen by the subsidiary conditions: one cannot have localized charge leading to a local field. This emphasizes the need for a collective treatment.

4. FREQUENCY-DEPENDENT DIELECTRIC CONSTANT

We now generalize the discussion of the preceding section to the case of a nonzero frequency, Ω . Let us assume that the test charge r_k is oscillating with a frequency Ω .

$$\dot{r}_k = i\Omega r_k.$$

We may guarantee that the r_k have this equation of motion by adding a new term, H_{tc} , to the Hamiltonian such that

$$[H_{tc}, r_k] = \hbar \Omega r_k. \quad (4.1)$$

The r_k now constitute a set of commuting operators. We use the same approach as in Sec. III, and our result will be subject to the same limitations.

First, suppose we neglect the electron Coulomb interaction, and calculate $\epsilon(k, \Omega)$ by a simple perturbation treatment. In this approximation, the Hamiltonian of the system is

$$H = H_0 + H_{tc} + \sum_k \frac{1}{2} M_k^2 [2\rho_k r_{-k} + r_k r_{-k}]. \quad (4.2)$$

A straightforward calculation yields the following result (which is just a special case of the Kramers-Heisenberg formula):

$$\frac{1}{\epsilon(k, \Omega)} = 1 - 4\pi\alpha(k, \Omega),$$

$$4\pi\alpha(k, \Omega) = \frac{1}{N} \sum_n f_{0n}(k) \frac{\omega_p^2}{\omega_{n0}^2 - \Omega^2}. \quad (4.3)$$

We know that (4.3) is accurate only when $4\pi\alpha$ is much smaller than 1. When $4\pi\alpha \gg 1$, we must go over to a collective approach.

We see already in (4.3) that difficulties arise when $\omega_{n0} \sim \Omega$. The difficulties are of the same sort we encountered in NP I when $\omega \sim \omega_{n0}$, and may be resolved in similar fashion. Thus, where $\omega_{n0} = \Omega$, resonant absorption of energy from the test charge takes place. Such absorption may be described in terms of the conductivity $\sigma(\Omega)$, which we calculate in Sec. 7. We could explicitly omit such terms in our various transformations by a procedure analogous to that followed in NP I. However, as was obvious from the treatment there, such a prescription is equivalent to taking principal parts in the sum over excited states n , and we shall understand that to be done in (4.3) and what follows. As was the case in NP I, we do not expect this procedure to work when Ω is of the order of the average ω_{n0} . In this case, taking principal parts cuts out too many electronic excitations. Put more physically, the indeterminacy in frequency due to power absorption is then too large to permit an accurate definition of $\epsilon(k, \Omega)$.

In carrying out the collective approach, we adopt as our starting Hamiltonian⁹

$$H_{\text{ext}} = H_0 + H_{\text{field}} + H_{\text{int}} + H_{\text{sr}} + U,$$

$$+ H_{tc} + \sum_{k < k_c} \{ (M_k - \mu_k) r_{-k} P_k + \mu_k M_k r_{-k} \rho_k + \frac{1}{2} M_k^2 r_{-k} r_k \}. \quad (4.4)$$

H_{ext} differs from (3.2) only in the addition of H_{tc} . Again,

⁹ The H_{field} which appears in (3.2) and (4.4) involves the free-plasma frequency ω_p , and not the corrected one, ω . This is important for the derivations of this section.

μ_k is an arbitrary constant which we shall determine later. Simultaneously with (4.4) we must consider the set of subsidiary conditions, (3.3).

Our goal is now to find a canonical transformation which eliminates from (4.4) the plasmon-test charge and electron-test charge interactions, and which, at the same time, does not introduce test-charge variables into the subsidiary conditions (3.3). Let S be the generator of this transformation. We must have

$$\frac{i}{\hbar} [H_0 + H_{\text{field}} + H_{\text{int}} + H_{\text{sr}} + U + H_{tc}, S] = - \sum_{k < k_c} \{ (M_k - \mu_k) r_{-k} P_k + \mu_k M_k r_{-k} \rho_k \}. \quad (4.5)$$

To satisfy (4.5) we try an S of the general form

$$S = \sum_{k < k_c} (\alpha_k P_k + \beta_k Q_{-k} + F_k) r_{-k}, \quad (4.6)$$

where α_k and β_k are numbers, while F_k is an unknown electron operator.

The new features in the calculation arise from the commutator of F_k with U , H_{sr} , and H_{int} . We first remark that we may always neglect the terms arising from U , (since we have shown in Sec. 6 of NP I that U is very small). Next we do not have to consider the terms arising from H_{sr} . Either H_{sr} does not influence the electron motion appreciably, and the corresponding terms are negligible; or H_{sr} has a large effect on the eigenstates, and we then take it automatically into account by switching to the many-body representation in which $(H_0 + H_{\text{sr}})$ is diagonal. Consider now the terms arising from H_{int} which are of the type:

$$\frac{i}{\hbar} \sum_{\substack{k < k_c \\ l < k_c}} [V_k, F_l] Q_k r_{-l}.$$

These terms differ from the analogous terms in the static case because the commutator $[V_k, F_l]$ has a finite expectation value. We keep the terms involving $[V_k, F_l]_{00}$, and neglect again the triple collisions between electrons, plasmons, and test charges. With these approximations, it is just a matter of algebra to find the coefficients α_k , β_k , and the operator F_k :

$$\alpha_k = \frac{i}{\Omega} \left\{ \frac{M_k}{\epsilon(k, \Omega)} - \mu_k \right\},$$

$$\beta_k = M_k \left\{ \frac{1 - \epsilon(k, \Omega)}{\epsilon(k, \Omega)} \right\},$$

$$(F_k)_{mn} = \frac{i\mu_k M_k}{\Omega} - \frac{iM_k^2}{\Omega \epsilon(k, \Omega)} \frac{\omega_{mn}}{\omega_{mn} + \Omega} (\rho_k)_{mn}. \quad (4.7)$$

Here $\epsilon(k, \Omega)$ is defined from the $\alpha(k, \Omega)$ given in (4.3):

$$\epsilon(k, \Omega) = 1 + 4\pi\alpha(k, \Omega). \quad (4.8)$$

The next step is to determine μ_k by the requirement that r_k does not enter the subsidiary conditions. Again,

we replace the commutator $[\rho_k, F_l]$ by its expectation value. We then find that this requirement is satisfied for *any* choice of μ_k .¹⁰ Since the only approximations in our treatment arise from the term F_k of the generator S , we choose μ_k so as to have an F_k as small as possible. For very low frequency Ω (much smaller than the average ω_{n0}), the most convenient μ_k is $M_k/\epsilon(k, \Omega)$, as in the static case. [With such a choice, Ω disappears from the denominator of $(F_k)_{mn}$.] For high frequencies, on the contrary, the best choice is $\mu_k=0$, and we shall make that choice in the following. When $\mu_k=0$, the second-order terms are trivially calculated. When combined with the original (r - r) interaction, they yield the following screened interaction:

$$\sum_{k < k_c} \frac{M_k^2 r_k r_{-k}}{2\epsilon(k, \Omega)},$$

$\epsilon(k, \Omega)$ is therefore the dielectric constant at wavelength k and frequency Ω .

The derivation of the basic formula,

$$\epsilon(k, \Omega) = 1 + \frac{1}{N} \sum_n f_{0n}(k) \frac{\omega_p^2}{\omega_{n0}^2 - \Omega^2}, \quad (4.9)$$

completes the aim of this section. However, before going on to a discussion of the meaning of (4.9) it is desirable to have a clearer picture of the physical origin of the expression. Thus, in our derivation, the contributions from the plasmons and the electrons to the screening of the test charges were intermingled. We can, however, separate them in the following way.

Let us first isolate plasmons and electrons, that is, first eliminate H_{int} from (4.4). Since our treatment may be carried out for any choice of μ_k , we take a simple choice, $\mu_k=0$. Our Hamiltonian (4.4) is then

$$H_{\text{ext}} = H_0 + \sum_{k < k_c} \frac{P_k P_{-k} + \omega_p^2 Q_k Q_{-k}}{2} + H_{\text{int}} + H_{\text{sr}} + H_{\text{tc}} \\ + \sum_{k < k_c} (M_k r_{-k} P_k + \frac{1}{2} M_k^2 r_{-k} r_k). \quad (4.10)$$

We eliminate H_{int} exactly as in Sec. 5 of NP I, without considering the test charges. We then get the following Hamiltonian:

$$H_{\text{ext}} = H_0 + H_{\text{sr}} + H_{\text{rp}} + H_{\text{field}} + H_{\text{tc}} \\ + \sum_{k < k_c} \{M_k r_{-k} P_k + M_k r_{-k} B_k + \frac{1}{2} M_k^2 r_{-k} r_k\}, \quad (4.11)$$

where B_k is defined in (5.5) of NP I. The test charges

¹⁰ In fact, this is not surprising: two Hamiltonians with different values of μ_k only differ by a term $\Delta\mu_k(M_{k\rho k} - P_k)r_{-k}$. ($M_{k\rho k} - P_k$) is the operator of the subsidiary condition, which rigorously commutes with H_{ext} . One may therefore change the value of μ_k by a canonical transformation, generated by $(i\Delta\mu_k/\Omega)(M_{k\rho k} - P_k)r_{-k}$, which acts only on H_{tc} . Since we can change μ_k at will, the results must be independent of its choice. This is not possible in the static case, where $\Omega=0$. In order to keep α_k and P_k finite, we must then choose $\mu_k = M_k/\epsilon(k, \Omega)$.

now interact with electrons through a screened Coulomb interaction. The plasmons are independent of the electrons (they do not appear in the subsidiary condition). We may therefore eliminate independently the plasmon-test charge interaction. This is done *rigorously* by a canonical transformation generated by

$$S = \sum_{k < k_c} \left\{ -M_k r_{-k} Q_{-k} \frac{\omega^2}{\omega^2 - \Omega^2} - i M_k r_{-k} P_k \frac{\Omega}{\omega^2 - \Omega^2} \right\}. \quad (4.12)$$

The resultant Hamiltonian is

$$H_{\text{ext}} = H_{\text{field}} + H_0 + H_{\text{sr}} + H_{\text{rp}} + H_{\text{tc}} \\ + \sum_{k < k_c} \left\{ \frac{M_k^2}{2} r_{-k} r_k \frac{\Omega^2}{\Omega^2 - \omega^2} + M_k r_{-k} B_k \right\}, \quad (4.13)$$

which must be considered together with the subsidiary conditions (5.15) of NP I. We should like to emphasize that the only approximations involved in obtaining (4.13) are those required to eliminate H_{int} , that is, the approximation of well-defined independent plasmons.

What have we accomplished at this point? We have determined the role that plasmons play in screening the initial interaction between test charges. We see that the screening is not complete, although nearly so for low frequencies. We could characterize this lack of complete screening by a dielectric constant, $\epsilon_{\text{coll}}(k, \Omega)$, defined by

$$\frac{1}{\epsilon_{\text{coll}}(k, \Omega)} = \frac{\Omega^2}{\Omega^2 - \omega^2}. \quad (4.14)$$

Since the test charges are still interacting with individual electrons in (4.13), there is also an "individual particle" contribution to $1/\epsilon$, which we could obtain by eliminating $M_k r_{-k} B_k$ from (4.13). It is in fact simpler to get it from the total $1/\epsilon$ calculated in (4.8) using

$$\frac{1}{\epsilon_{\text{ind}}(k, \Omega)} = \frac{1}{\epsilon(k, \Omega)} \frac{1}{\epsilon_{\text{coll}}(k, \Omega)}. \quad (4.15)$$

With the aid of the dispersion relation, and Eqs. (4.8) and (4.15), it is straightforward to show that

$$\frac{\epsilon_{\text{coll}}(k, \Omega)}{\epsilon_{\text{ind}}(k, \Omega)} = \frac{\sum_n f_{0n}(k) \omega_{n0}^2 / [(\omega^2 - \omega_{n0}^2)(\Omega^2 - \omega_{n0}^2)]}{\sum_n f_{0n}(k) \Omega^2 / [(\omega^2 - \omega_{n0}^2)(\Omega^2 - \omega_{n0}^2)]}. \quad (4.16)$$

We see from (4.16) that when Ω is much smaller than the average ω_{n0} , $1/\epsilon_{\text{ind}}$ is much larger than $1/\epsilon_{\text{coll}}$; in such a case, the screened interaction is determined mainly by the individual particles. (In other words, the screening due to the plasmons is essentially complete.) On the contrary, when Ω is much larger than the average ω_{n0} , the term $1/\epsilon_{\text{coll}}$ is preponderant, and the dielectric constant depends almost entirely on collective plasmon properties. (At such high frequencies, the individual-particle excitations do not follow the test-charge oscillation.) The fact that at high frequency

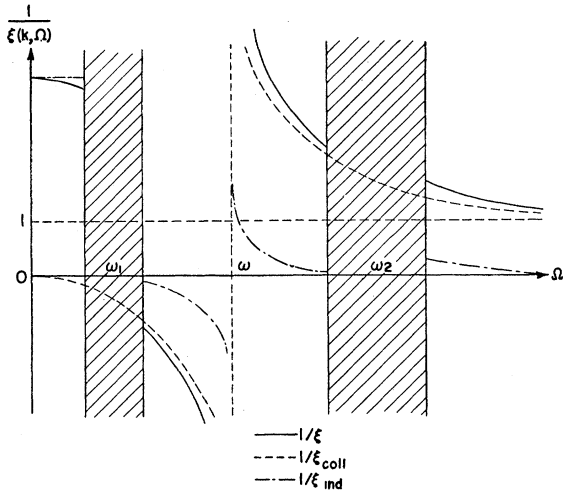


FIG. 2. Schematic representation of the frequency-dependent dielectric constant. The shaded area represents the ranges of Ω where we do not trust our results.

the individual part of $1/\epsilon$ is negligible shows that in such circumstances the electron-test charge interaction appearing in (4.13),

$$\sum_{k < k_c} M_{k\gamma-k} B_{k\gamma}$$

is negligible. At high frequencies (of the order of ω_p) one might expect some difficulty with the nature of the individual-particle excitation spectrum, since the subsidiary conditions then act to reduce the number of degrees of freedom. However, when the plasmons are well-defined, they determine entirely the dielectric constant at such frequencies, so that the above difficulty does not arise.

Let us now discuss in a closer way the behavior of $1/\epsilon(k, \Omega)$ as a function of the frequency Ω . Consider a solid in which the excited states Φ_n form two groups: a group of low-energy states for which $\omega_{n0} \sim \omega_1 \ll \omega$, and a group of high-energy states for which $\omega_{n0} \sim \omega_2 \gg \omega$.

(i) In the range $\Omega \ll \omega_1$, ϵ is essentially the static dielectric constant. It is determined mainly by the low-energy excited states of the electrons.

(ii) In the range $\omega_1 \ll \Omega \ll \omega_2$, ϵ is approximately equal to ϵ_{coll} , being given by

$$\epsilon \cong 1 - (\omega^2/\Omega^2). \quad (4.17)$$

It is almost entirely determined by plasmons.

(iii) In the range $\Omega \gg \omega_2$, one finds

$$\epsilon = 1 - (\omega_p^2/\Omega^2). \quad (4.18)$$

This differs from ϵ_{coll} by the small amount $(\omega^2 - \omega_p^2)/\Omega^2$. In this case ϵ is again determined mainly by plasmons. If, however, one prefers to discuss the behavior of $4\pi\alpha$ rather than of ϵ , we see that at such frequencies, the part $-\omega^2/\Omega^2$ arises from plasmons, while the part $(\omega^2 - \omega_p^2)/\Omega^2$ arises from the high-energy excited states of the individual electrons.

(iv) Finally, in the ranges $\Omega \sim \omega_1$ or $\Omega \sim \omega_2$, we encounter difficulties with our use of principal parts, and we cannot define ϵ accurately.

The foregoing results are summarized in Fig. 2.

When the dielectric constant is determined mainly by individual electrons, the discussion of the local field corrections of the preceding section applies. Where it is determined by the plasmons, no local field corrections can appear. For instance, in an ionized gas, where the excitation frequencies are small, the dielectric constant is simply $1 - \omega_p^2/\Omega^2$, as indicated by Darwin.⁵

5. PLASMON DISPERSION RELATION

Let us reconsider the dispersion relation for plasmons, obtained in NP I, in the light of our determination of the dielectric constant. We found that the plasmon frequency ω is determined by

$$1 = \frac{4\pi e^2}{m} \sum_n \frac{f_{0n}}{\omega^2 - \omega_{n0}^2}. \quad (5.1)$$

On comparing (5.1) and (4.9) we see that the dielectric constant vanishes when $\Omega = \omega$. This result is a consequence of simple electrostatics, since a longitudinal wave may only propagate when $\epsilon(k, \Omega) = 0$. The vanishing of the dielectric constant at the plasmon frequency was used by Hubbard¹¹ and by Fröhlich and Pelzer¹² to determine the plasmon energy.

The great advantage of the microscopic treatment is that it allows a discussion of the local field corrections which enter ϵ . These appear in our Hamiltonian as extra short-range terms whose importance we are in a position to evaluate. In a sense, then, we need never worry about the influence of local field corrections on the plasmon energy. Either the contributions from H_{sr} are negligible, and we have no local field correction, or they are important, and we include H_{sr} in our basic representation. The ω_{n0} in (5.1) and (4.9) are then the appropriate "many-electron" excitation frequencies.

We are now able to interpret in a simple way the effect of the core electrons on the plasma frequency. Let us consider again the dispersion relation (9.5) of NP I:

$$\frac{4\pi e^2}{m} \sum_{\mu(\text{core})} \frac{f_{0\mu}(k)}{\omega^2 - \omega_{0\mu}^2} + \sum_{\mu(\text{val})} \frac{f_{0\mu}(k)}{\omega^2 - \omega_{0\mu}^2} = 1. \quad (5.2)$$

We see from (4.3) that the first term, involving excited states of the core, is just $[-4\pi\alpha_{\text{core}}(k, \omega)]$, where $\alpha_{\text{core}}(k, \omega)$ is the polarizability of the core electrons, at frequency ω and momentum k . The dispersion relation may therefore be written as

$$\frac{4\pi e^2}{m\epsilon_{\text{core}}(k, \omega)} \sum_{\mu(\text{val})} \frac{f_{0\mu}(k)}{\omega^2 - \omega_{0\mu}^2} = 1. \quad (5.3)$$

¹¹ J. Hubbard, Proc. Phys. Soc. (London) **A68**, 441 (1955).

¹² H. Fröhlich and H. Pelzer, Proc. Phys. Soc. (London) **A68**, 525 (1955).

This shows that the core acts only through its dielectric constant, modifying the effective valence-electron Coulomb interaction. When α_{core} is small, this way of presenting the result is more natural, and better fitted for comparison with experiment (α_{core} may be inferred directly from experiment). On the contrary, when α_{core} is very large, we would do better to include the core into the plasmons, and treat it as we do the valence shell. Of course, there are intermediate cases; for instance, the d electrons in transition metals. We then may think of the collective mode in two ways: either as a plasma of s and d electrons, where the d electrons are strongly coupled with the plasmons, or as a plasma of s electrons alone, but embedded in a highly polarizable gas of d electrons. The two points of view are equivalent, and neither makes possible a simply convergent calculation.

6. INTERACTION BETWEEN A SMALL GROUP OF ELECTRONS

We now consider under what circumstances we may generalize to electrons the concept of a dielectric constant which we have introduced for infinitely heavy test charges. In order to render the concept of a medium, and hence a dielectric constant, meaningful, we must consider only a small fraction of the electrons as our "test charges." Let us accordingly isolate a group of minority carriers, \tilde{N} in number, whose density fluctuation is $\tilde{\rho}_k$, individual electron Hamiltonian \tilde{H}_0 , etc.¹³ We take $\tilde{N} \ll N$, and assume in this section that the operators, ρ_k , H_0 , etc., refer only to the majority carriers. We remark that in isolating a group of minority carriers, we automatically neglect all effects associated with the indistinguishability of the minority and majority carriers (e.g., exchange effects in their interaction).

We may then write our initial Hamiltonian as

$$H = H_0 + \tilde{H}_0 + \sum_k \frac{1}{2} M_k^2 (\rho_k + \tilde{\rho}_k) (\rho_{-k} + \tilde{\rho}_{-k}). \quad (6.1)$$

The situation is quite similar to that encountered in Sec. 4 for test charges. There are two new complications. First, the density fluctuations $\tilde{\rho}_k$ no longer carry out simple oscillatory motion. If we choose the eigenstates Φ_μ of \tilde{H}_0 as the basis representation for the minority-carrier operators, we have

$$(\tilde{H}_0, \tilde{\rho}_k)_{\mu\nu} = \tilde{\hbar} \Omega_{\mu\nu} (\tilde{\rho}_k)_{\mu\nu}.$$

Second, there is a short-range majority-minority interaction which may influence the excitation spectrum of the minority carriers. In other words, the minority electrons are not infinitely heavy, and may recoil when interacting with the majority electrons.

We shall be primarily interested in low minority excitation frequencies, $\Omega_{\mu\nu}$. We therefore wish to

generalize our low-frequency test-charge treatment, in which μ_k was taken to be $M_k/\epsilon(k, \Omega)$. (The high excitation-frequency case is treated, in quite similar fashion, by taking $\mu_k = 0$.) We first define a screened minority density fluctuation, $\tilde{\rho}_k^s$ by

$$(\tilde{\rho}_k^s)_{\mu\nu} = (\tilde{\rho}_k)_{\mu\nu} / \epsilon(k, \Omega_{\mu\nu}). \quad (6.2)$$

In place of (6.1), we introduce the following extended Hamiltonian:

$$\begin{aligned} H_{\text{ext}} = & H_0 + \tilde{H}_0 + \sum_{k > k_c} \frac{1}{2} M_k^2 (\rho_k + \tilde{\rho}_k) (\rho_{-k} + \tilde{\rho}_{-k}) \\ & + \sum_{k < k_c} \frac{1}{2} (M_k \rho_k + P_k) (M_k \rho_{-k} + P_{-k}) \\ & + \sum_{k < k_c} \{ M_k (\tilde{\rho}_k - \tilde{\rho}_k^s) P_{-k} + M_k^2 \tilde{\rho}_k \rho_{-k} \\ & \quad + \frac{1}{2} M_k^2 \tilde{\rho}_k \tilde{\rho}_{-k} \}. \end{aligned} \quad (6.3)$$

We then introduce plasmons which involve only the majority carriers. (Since there are very few minority carriers, this cannot alter the plasmon behavior.) After the first canonical transformation generated by

$$S = \sum_{k < k_c} (-M_k Q_k \rho_k),$$

Eq. (6.3) becomes:

$$\begin{aligned} H_{\text{ext}} = & H_0 + \sum_{k > k_c} \frac{1}{2} M_k^2 (\rho_k + \tilde{\rho}_k) (\rho_{-k} + \tilde{\rho}_{-k}) \\ & + \sum_{k < k_c} \frac{1}{2} (P_k P_{-k} + \omega_p^2 Q_k Q_{-k}) + H_{\text{int}} + U \\ & + \tilde{H}_0 + \sum_{k < k_c} M_k (\tilde{\rho}_k - \tilde{\rho}_k^s) P_{-k} + M_k^2 \tilde{\rho}_k \rho_{-k} \\ & \quad + \frac{1}{2} M_k^2 \tilde{\rho}_k \tilde{\rho}_{-k}. \end{aligned} \quad (6.4)$$

Equation (6.4) is the simple analog of Eq. (4.4).

Consider the short-range terms of (6.4). They may modify the dynamics of the electrons and, so, change the dispersion of the solid. We already know how to take into account when necessary the majority-majority short-range interaction by including it in the basic representation for the majority electrons. The minority-minority interaction is certainly exceedingly small for small \tilde{N} .¹⁴ Difficulties may arise with the short-range minority-majority correlations. The magnitude of k_c is usually such that the screening radius is of order of the interelectronic spacing and we expect such correlations to be relatively unimportant. However, they may modify the $\Omega_{\mu\nu}$, and a more involved treatment is required to take this effect into account. In what follows, we neglect these possible corrections to the $\Omega_{\mu\nu}$.

We may now eliminate the majority-minority and

¹³ This notation for minority carriers should not be confused with that introduced in NP I for the separation of the principal parts of certain operators. No such separation involving principal parts is carried out explicitly in this paper or in NP III.

¹⁴ A word of caution should be injected at this point. In making the foregoing statements we have assumed that the minority carriers are not strongly spatially correlated with each other. Such correlations may occur where there is an energy gap in the excitation spectrum, that is, with excitons and superconductors. We discuss this situation in detail in NP III.

the plasmon-minority electron interaction from (6.4). We thereby transform to a new set of "dressed" minority electrons which carry a cloud of virtual majority electrons and virtual plasmons. The desired canonical transformation is generated by an S , such that:

$$\begin{aligned} & \frac{i}{\hbar} [H_0 + \tilde{H}_0 + H_{\text{field}} + H_{\text{int}} + \sum_{k < k_c} M_k^2 \tilde{\rho}_k \tilde{\rho}_{-k}, S] \\ &= - \sum_{k < k_c} \{ M_k (\tilde{\rho}_k - \tilde{\rho}_k^s) P_{-k} + M_k^2 \tilde{\rho}_k^s \rho_{-k} \}. \end{aligned} \quad (6.5)$$

On purely physical grounds, we expect that in (6.5) the contribution from the long-range minority-minority interaction will be negligible if we take \tilde{N} small enough. (The screening is not affected by the interaction between distant carriers.) We obtain our results neglecting this contribution, and later discuss its importance.

With these simplifications, the problem is now completely equivalent to that encountered in Sec. 4. The generating function S is obtained by a simple transposition of Eq. (4.7):

$$S = \sum_{k < k_c} \{ M_k (\tilde{\rho}_k^s - \tilde{\rho}_k) Q_k + G_k \}, \quad (6.6)$$

where G_k is an operator depending on both minority and majority electrons, defined by¹⁵

$$(G_k)_{mn, \mu\nu} = \left\{ \frac{i M_k^2}{\epsilon(k, \Omega_{\mu\nu}) (\omega_{mn} + \Omega_{\mu\nu})} \right\} (\rho_k)_{mn} (\tilde{\rho}_{-k})_{\mu\nu}. \quad (6.7)$$

[In order to satisfy (6.5), we again neglect the off-diagonal "random phase" terms arising from H_{int} .]

Let us now consider the second-order terms which arise from the action of S upon the minority-majority and plasmon-majority interactions. These are

$$\begin{aligned} & \sum_{k < k_c, l < k_c} \left\{ -\frac{1}{2} M_k^2 (\tilde{\rho}_k - \tilde{\rho}_k^s) (\tilde{\rho}_{-k} - \tilde{\rho}_{-k}^s) \right. \\ & \quad + \frac{i}{2\hbar} M_k^2 [\rho_{-k}, G_l] \tilde{\rho}_k^s \\ & \quad - \frac{i}{2\hbar} M_k M_l [(\tilde{\rho}_k^s - \tilde{\rho}_k), (\tilde{\rho}_l^s - \tilde{\rho}_l)] P_{-k} Q_l \\ & \quad \left. + \frac{i}{2\hbar} M_k^2 [\tilde{\rho}_k^s, G_l] \rho_{-k} \right\}. \end{aligned} \quad (6.8)$$

The last two terms involve only one minority carrier at a time. They correspond to a change in the behavior of an individual minority electron due to collisions with

¹⁵ We now have simultaneously two representations, one of the majority carrier operators, in terms of the eigenstates Φ_n of H_0 (or eventually $H_0 + H_{\text{sr}}$), and one of the minority carrier operators, in terms of the eigenstates Φ_μ of \tilde{H}_0 . The two representations must not be confused. A matrix element of S should have four indices, $S_{\mu\nu, mn}$.

two plasmons, or with two electrons. They have the structure of a random-phase term and are certainly negligible. (Their diagonal part with respect to minority electrons corresponds to the reaction of these on the majority carriers, which is exceedingly small.) The first two terms of (6.8) describe the screening of the minority-minority interaction. Again, we neglect the fluctuations of the majority carriers, and replace the commutator $[\rho_{-k}, G_l]$ by its expectation value. With these approximations, (6.8) yields the following effective long-range interaction between "dressed" minority carriers:

$$\sum_{k < k_c} \frac{1}{2} M_k^2 \tilde{\rho}_k \tilde{\rho}_{-k}^s. \quad (6.9)$$

We therefore obtain the very natural result that the matrix elements for the transition $\mu \rightarrow \nu$ is screened by the dielectric constant at frequency $\Omega_{\mu\nu}$. Such a result is in accord with the correspondence principle and our physical intuition.

We now return to the terms arising from the commutators of S with the long-range minority-minority electron interaction. They are

$$-\frac{i}{\hbar} \sum_{k < k_c} \frac{1}{2} M_k^2 \{ [S, \tilde{\rho}_k] \tilde{\rho}_{-k} + \tilde{\rho}_{-k} [S, \tilde{\rho}_k] \}. \quad (6.10)$$

If we replace the commutator, $[S, \tilde{\rho}_k]$ by its diagonal part, the resultant term leads to a screened energy smaller than (6.9) by a factor of $[\omega_p^2 / \langle \omega_{n0}^2 \rangle_{\mu\nu}] (\tilde{N}/N)$, which is certainly negligible for a sufficiently small (\tilde{N}/N) . The off-diagonal part of the commutators gives rise to exchange terms between minority electrons, which are likewise of order (\tilde{N}/N) compared to the terms we have kept. We can understand simply why the long-range interaction between minority carriers is ineffective. For $\Omega_{\mu\nu}$ larger than the minority carrier $\tilde{\omega}_p$, the effect of the Coulomb interaction is negligible compared with the effect of \tilde{H}_0 . This is not the case for $\Omega_{\mu\nu}$ smaller than $\tilde{\omega}_p$, but for such frequencies the dielectric constant, ϵ , is independent of the response of the minority carriers.

We summarize the approximations we have made to obtain the effective interaction between minority carriers, (6.9). First, we have neglected the influence of the screened long-range density fluctuations of the majority electrons, since we kept only the expectation value of commutators like $[\rho_{-k}, G_l]$ in (6.8). Such an approximation is excellent for sufficiently small k , and we expect it to work well throughout the region of k of interest. Second, we neglected the effect of the short-range, and screened long-range majority-minority interaction on the energy levels of individual minority carriers. However, the corresponding change in $\Omega_{\mu\nu}$, even though it may be appreciable, will not influence our result, (6.9) in the low-frequency region, since ϵ is frequency-independent in that region.

We should like to emphasize the limitations of our result, (6.9). It is valid only for a very small number

of carriers, and must be used only to the lowest order in $\tilde{\rho}_k$. For instance, we may use it to calculate the screened exchange energy,

$$E_{\text{exch}}^{\text{sc}} = \sum_{k < k_c} \sum_{\mu} \frac{1}{2} M_k^2 \frac{|\tilde{\rho}_k|_{0\mu}^2}{\epsilon(\Omega_{\mu 0})}. \quad (6.11)$$

We may also use it to obtain the transition probability for the scattering of two minority carriers, using time-dependent perturbation theory. On the other hand, it may be used to calculate correlation effects only under very special circumstances, in which the direct correlations between minority carriers are more important than the screened correlations with the majority carrier fluctuations. For this to happen, the strength of the minority-majority interaction must be down by a factor of at least \tilde{N}/N compared to the minority-minority interaction since there are so few minority carriers. Such an effect does occur for the conduction electrons in semiconductors.

7. FREQUENCY-DEPENDENT LONGITUDINAL CONDUCTIVITY

As an application of the results of the preceding section, we calculate the conductivity of the electron gas. To do this, we introduce into the solid a test charge r_k , oscillating at frequency Ω , and calculate the rate at which the test charge loses energy. An absorption process will excite the electrons from state Ψ_0 to state Ψ_n , such that $\omega_{n0}(k) = \Omega$. If we can neglect the effect of H_{rp} and of the subsidiary conditions on the excited state Ψ_n , the states Ψ_0 and Ψ_n are simply eigenstates Φ_0 and Φ_n of $(H_0 + H_{\text{sr}})$. We may expect that the effect of the subsidiary conditions will be negligible for low individual electron excitation frequencies, $\omega_{n0} \ll \omega_p$. When ω_{n0} is large, however, the density of excited states might reflect the reduction in the number of degrees of freedom due to the subsidiary conditions. We carry out the calculation with the assumption that this effect is small. (A similar approximation was made in our treatment of plasmon damping in NP I.)

Let us furthermore assume that H_{sr} is a relatively small perturbation on the electron motion, so that Φ_n corresponds to the excitation of a given electron. There will only be a few electrons for which $\omega_{n0}(k)$ lies between $(\Omega - \eta)$ and $(\Omega + \eta)$. We treat these electrons as our "minority carriers", and denote their density fluctuation by $\delta\rho_k$. In the minority group, we also include the test charges. The $\tilde{\rho}_k$ of Sec. 6 is therefore

$$\tilde{\rho}_k = \delta\rho_k + r_k. \quad (7.1)$$

The damping of the test-charge oscillation then appears as a scattering within the minority group.

In order to treat the scattering correctly, we must first decouple completely the minority group from the majority carriers. We do this by the techniques of Sec. 6. A simple application of (6.9) gives the following "effective" interaction between test charge and "res-

onating" electrons:

$$H_{\text{scat}} = \frac{M_k^2}{\epsilon(\Omega)} \{ r_k \delta\rho_{-k} + r_{-k} \delta\rho_k \}. \quad (7.2)$$

From (7.2) we obtain the transition probability for excitation of any electron [only one term of (7.2) conserves energy]. We express the result in terms of the oscillator strengths of the electrons*:

$$W(k, \Omega) = \frac{4\pi^2 e^2}{m} \frac{M_k^2}{|\epsilon(k, \Omega)|^2} \frac{r_k r_{-k}}{\hbar\Omega} \sum_n f_{0n}(k) \delta(\Omega - \omega_{n0}). \quad (7.3)$$

The rate of energy loss is simply $\hbar\Omega W(k, \Omega)$. It is also equal to σE^2 , where \mathbf{E} is the electric field of the test charges. We get \mathbf{E} from Poisson's equation:

$$\mathbf{E} = \frac{4\pi e}{k^2} \frac{i\mathbf{k}}{\epsilon(k, \Omega)} (r_k - r_{-k}). \quad (7.4)$$

From (7.4) we obtain the rate of energy loss of the test charges*:

$$\hbar\Omega W(k, \Omega) = \frac{8\pi M_k^2}{|\epsilon(k, \Omega)|^2} r_k r_{-k} \sigma. \quad (7.5)$$

We remark that in σ the dielectric constant disappears, as we should expect, since σ is a "local" property. (This emphasizes the need for a complete decoupling of the minority group before calculating transition probabilities.) We finally obtain

$$\sigma(k, \Omega) = \frac{\pi e^2}{2m} \sum_n f_{0n}(k) \delta(\Omega - \omega_{n0}). \quad (7.6)$$

This resembles closely the usual expression for the transverse optical conductivity, differing only in that longitudinal oscillator strengths replace transverse ones. For isotropic solids in the limit of low k , the conductivity is therefore isotropic.

The lifetime of plasmons is simply related to the conductivity. Comparing (8.1) of NP I with (7.6), we see that

$$1/\tau_{p1} = 4\pi\sigma(k, \omega). \quad (7.7)$$

This simple relation was obtained earlier by Wolff¹⁶ and Kanazawa.¹⁷ Equation (7.7) may be obtained from a macroscopic argument, and is true even if our determination of τ_{p1} and σ fails because of the effect of the subsidiary conditions.

Finally when the test charge oscillates at the plasma frequency, $\omega(k)$, strong absorption occurs because of the emission of plasmons. The calculation of plasmon ex-

* Note added in proof.—In the case of large damping (Ω of the order of the average ω_{n0}) ϵ in Eqs. (7.2) to (7.5) should be replaced by the complex dielectric constant, $\epsilon^* = \epsilon - 4\pi i\sigma/\Omega$.

¹⁶ P. A. Wolff, Phys. Rev. **92**, 18 (1953).

¹⁷ H. Kanazawa, Progr. Theoret. Phys. Japan **13**, 227 (1955).

citation by, for instance, a moving charge, is straightforward, and has been dealt with elsewhere.^{11,12}

8. OPTICAL PROPERTIES OF SOLIDS

In the preceding sections we have obtained the longitudinal polarizability and conductivity. In this section we use the same collective approach to the transverse polarizability and conductivity, and hence optical properties of the solid. Bohm and Pines¹⁸ have given a treatment of this problem for the case of free electrons, and what follows is simply a generalization of their results to the case of electrons in a periodic lattice. A somewhat different approach has been proposed by Fano.¹⁹

The Hamiltonian for the system of electrons interacting with the electromagnetic field may be written²⁰:

$$H = H_0 + \frac{1}{2} \sum_{\mathbf{k}} M_{\mathbf{k}}^2 \rho_{\mathbf{k}\rho - \mathbf{k}} + \sum_{i, \mathbf{k}\mu} \frac{(4\pi e^2)^{\frac{1}{2}}}{m} (\boldsymbol{\epsilon}_{\mathbf{k}\mu} \cdot \mathbf{p}_i) e^{-i\mathbf{k} \cdot \mathbf{x}_i} Q_{\mathbf{k}\mu} + \frac{1}{2} \sum_{\mathbf{k}, \mu} [P_{\mathbf{k}\mu}^* P_{\mathbf{k}\mu} + (\omega_p^2 + c^2 k^2) Q_{\mathbf{k}\mu}^* Q_{\mathbf{k}\mu}] + \sum_{\mathbf{k}, \mu, \nu} \frac{2\pi e^2}{m} \boldsymbol{\epsilon}_{\mathbf{k}\mu} \cdot \boldsymbol{\epsilon}_{\nu} \rho_{\mathbf{k} + \nu} Q_{\mathbf{k}\mu} Q_{\nu}, \quad (8.1)$$

where $Q_{\mathbf{k}\mu}$ is the Fourier component of the electromagnetic field with wave vector \mathbf{k} , polarization $\boldsymbol{\epsilon}_{\mathbf{k}\mu}$ (perpendicular to \mathbf{k}), and where $P_{\mathbf{k}\mu}$ is the conjugate momentum of $Q_{\mathbf{k}\mu}$. $P_{\mathbf{k}\mu}$ and $Q_{\mathbf{k}\mu}$ are assumed to satisfy the reality condition:

$$\begin{aligned} (Q_{\mathbf{k}\mu})^* &= Q_{-\mathbf{k} \mu}, \\ (P_{\mathbf{k}\mu})^* &= P_{-\mathbf{k} \mu}. \end{aligned} \quad (8.2)$$

In (8.1) we may neglect the long-range part of the Coulomb interaction. Most of it will be described in terms of longitudinal plasmons, and could lead only to a very weak coupling with transverse photons (only "three-particle" transitions will have a nonzero matrix element). As for the short-range Coulomb interaction, either its effect on the electron motion is small, and we may neglect it, or it is large, and we take it into account by including H_{sr} in the basic representation of the electron operators (absorbing H_{sr} into H_0). We remark that (8.1) is very similar to the Hamiltonian obtained for plasmons in Sec. 4 of NP I: it differs only by the replacement of ω_p^2 by $(\omega_p^2 + c^2 k^2)$, and of $\boldsymbol{\epsilon}_{\mathbf{k}}$ by the transverse $\boldsymbol{\epsilon}_{\mathbf{k}\mu}$. This resemblance comes from the fact that the plasmons are simply longitudinal photons.

The last term of (8.1) describes a nonlinear interaction between photons and electrons. It is directly analogous to the random-phase term U of NP I. It is

known to be important only for very high-energy phenomena (for instance, the Compton effect). We therefore neglect it. The only problem left is then to eliminate the linear photon-electron interaction in (8.1). We achieve this by the same techniques as those used in NP I for the plasmon case, working in the representation Φ_n where H_0 [or, if necessary, $(H_0 + H_{sr})$] is diagonal.

Let us therefore write the Hamiltonian as

$$H = H_0 + \frac{1}{2} \sum_{\mathbf{k}, \mu} (P_{\mathbf{k}\mu}^* P_{\mathbf{k}\mu} + \omega_{\mathbf{k}, \mu}^2 Q_{\mathbf{k}\mu}^* Q_{\mathbf{k}\mu}) + \sum_{\mathbf{k}\mu} V_{\mathbf{k}\mu} Q_{\mathbf{k}\mu} + \frac{1}{2} \sum_{\mathbf{k}, \mu} (\omega_p^2 + c^2 k^2 - \omega_{\mathbf{k}\mu}^2) Q_{\mathbf{k}\mu}^* Q_{\mathbf{k}\mu}, \quad (8.3)$$

where $V_{\mathbf{k}\mu}$ is defined by

$$V_{\mathbf{k}\mu} = \sum_i \frac{(4\pi e^2)^{\frac{1}{2}}}{m} (\boldsymbol{\epsilon}_{\mathbf{k}\mu} \cdot \mathbf{p}_i) e^{-i\mathbf{k} \cdot \mathbf{x}_i}.$$

(We have dropped the electron Coulomb interaction, which we shall not take explicitly into account in the following calculation.) In order to eliminate the interaction term, we perform the canonical transformation generated by

$$S = \sum_{\mathbf{k}, \mu} (A_{\mathbf{k}\mu} P_{-\mathbf{k}\mu} + B_{\mathbf{k}\mu} Q_{\mathbf{k}\mu}), \quad (8.4)$$

where the operators $A_{\mathbf{k}\mu}$ and $B_{\mathbf{k}\mu}$ are defined by

$$\begin{aligned} (A_{\mathbf{k}\mu})_{mn} &= (V_{\mathbf{k}\mu})_{mn} / (\omega_{\mathbf{k}\mu}^2 - \omega_{mn}^2), \\ (B_{\mathbf{k}\mu})_{mn} &= -i\omega_{mn} (V_{\mathbf{k}\mu})_{mn} / (\omega_{\mathbf{k}\mu}^2 - \omega_{mn}^2). \end{aligned} \quad (8.5)$$

As in NP I, we take the principal part of any divergent expression, and treat later the energy-conserving transitions, which give rise to the conductivity. We choose the corrected frequency $\omega_{\mathbf{k}\mu}$ such that the second-order terms cancel the last term of (8.3). This leads to the following dispersion relation

$$\omega_{\mathbf{k}\mu}^2 = \omega_p^2 + c^2 k^2 + \frac{2}{\hbar} \sum_n \left\{ \frac{|(V_{\mathbf{k}\mu})_{0n}|^2 \omega_{n0}}{\omega_{\mathbf{k}\mu}^2 - \omega_{n0}^2} \right\}. \quad (8.6)$$

The final Hamiltonian is simply

$$H = H_0 + \frac{1}{2} \sum_{\mathbf{k}, \mu} (P_{\mathbf{k}\mu}^* P_{\mathbf{k}\mu} + \omega_{\mathbf{k}\mu}^2 Q_{\mathbf{k}\mu}^* Q_{\mathbf{k}\mu}) - \frac{1}{4} \sum_{\mathbf{k}\mu} (V_{\mathbf{k}\mu} A_{-\mathbf{k}\mu} + A_{-\mathbf{k}\mu} V_{\mathbf{k}\mu}). \quad (8.7)$$

Let us first consider the last term of (8.7) which describes the screened magnetic interaction of the electrons brought about by the exchange of virtual photons. The nonscreened interaction should be

$$-\frac{1}{2} \sum_{\mathbf{k}, \mu} \frac{V_{\mathbf{k}\mu} V_{-\mathbf{k}\mu}}{c^2 k^2}. \quad (8.8)$$

The screening therefore consists of the replacement of $V_{\mathbf{k}\mu}$ by $c\mathbf{k}A_{\mathbf{k}\mu}$. From (8.5), we see that the screening

¹⁸ D. Bohm and D. Pines, Phys. Rev. **82**, 625 (1951), hereafter referred to as BP I.

¹⁹ U. Fano, Phys. Rev. **103**, 1202 (1956).

²⁰ See, for instance, BP I, Eq. (8).

radius k_s^{-1} is roughly defined by $ck_s = \omega_p$. This result is quite analogous to the one obtained in NP I. There, we were dealing with electric longitudinal interactions and found a very effective screening, within a range $k_c^{-1} \sim v_0/\omega_p$. In this section, we are dealing with magnetic transverse interactions, whose strength is very small (of order v_0/c smaller than the electric ones). On the other hand, their screening is much less drastic, within a range $k_s^{-1} \sim (c/v_0)k_c^{-1}$. This explains why, for very long wavelengths, the screened longitudinal and transverse interactions are of the same order of magnitude (to go from $V_{k\mu}$ to the V_k of NP I, one just has to change $\epsilon_{k\mu}$ into ϵ_k , and $\omega_{k\mu}$ into ω_k . When $k \ll \omega_p/c$, this is not much of a change²¹).

Let us now turn to the dispersion relation (8.6) which we write explicitly:

$$c^2 k^2 = \omega_{k\mu}^2 - \omega_p^2 - \frac{2\omega_p^2}{\hbar m N} \times \sum_n \frac{|\langle \sum_i (\epsilon_{k\mu} \cdot \mathbf{p}_i) e^{-i\mathbf{k} \cdot \mathbf{x}_i} \rangle_{0n}|^2 \omega_{n0}}{\omega_{k\mu}^2 - \omega_{n0}^2}. \quad (8.9)$$

In the last term of (8.9), the intraband transitions give a contribution at most of order $\omega_p^2(v_0^2/c^2)$, which is completely negligible. The contribution from the interband transitions is most conveniently described in terms of the following transverse oscillator strengths:

$$f_{0n}^{\text{inter}}(k, \mu) = \frac{2}{\hbar m} \frac{|\langle \sum_i (\epsilon_{k\mu} \cdot \mathbf{p}_i) e^{-i\mathbf{k} \cdot \mathbf{x}_i} \rangle_{0n}|^2}{\omega_{n0}}, \quad (8.10)$$

$$f_{0n}^{\text{intra}}(k, \mu) = \sum_{\alpha, \beta} \frac{m}{\hbar^2} (\epsilon_{k\mu})_\alpha \cdot (\epsilon_{k\mu})_\beta \frac{\partial^2 E}{\partial \kappa_\alpha \partial \kappa_\beta}.$$

It is shown in the appendix that these quantities satisfy the usual f -sum rule: $\sum_n f_{0n}(k, \mu) = N$. Using again the fact that, for an intraband transition, $\omega_{n0}^2/\omega_{k\mu}^2$ is negligibly small, we may write (8.9) as

$$c^2 k^2 = \omega_{k\mu}^2 - \frac{\omega_p^2}{N} \sum_n f_{0n}(k, \mu) \frac{\omega_{k\mu}^2}{\omega_{k\mu}^2 - \omega_{n0}^2}. \quad (8.11)$$

In this form, the analogy of (8.11) with the plasmon dispersion relation is obvious. Equation (8.11) is a well-known result, which is discussed in many places.²²

In order to link our microscopic result with the usual macroscopic treatment, we use the familiar relation

$$c^2 k^2 = \omega_{k\mu}^2 \epsilon(\omega_{k\mu}). \quad (8.12)$$

²¹ The magnetic and electric screened interactions nevertheless keep their respectively transverse and longitudinal character. No mixing of their effects occurs, except in high-order transitions. For instance, the longitudinal dielectric constant is negligibly affected by the magnetic screened interaction between electrons.

²² See, for instance, F. Seitz, *Modern Theory of Solids* (McGraw-Hill Book Company, Inc., New York, 1940). A very detailed discussion is given by Fano (reference 19).

Comparing (8.11) and (8.12), we obtain

$$\epsilon(\omega_{k\mu}) - 1 = \frac{1}{N} \sum_n \frac{f_{0n}(k, \mu) \omega_p^2}{\omega_{k\mu}^2 - \omega_{n0}^2}. \quad (8.13)$$

The transverse dielectric constant $\epsilon(\omega_{k\mu})$ given in (8.13) is very similar to the longitudinal $\epsilon(\Omega, k)$ given in Sec. 4. When $k \ll \omega_p/c$, the transverse and longitudinal ϵ are of the same order of magnitude (and would be equal for an isotropic solid). On the contrary, when $k \gg \omega_p/c$, the transverse polarizability $[\epsilon(\omega_{k\mu}) - 1]$ is drastically reduced, while the longitudinal one is still very large.

Let us now turn back to (8.3), and consider the real transitions for which $\omega_{k\mu}^2 = \omega_{n0}^2$. They give rise to the conductivity. We evaluate the lifetime τ of the photon $Q_{k\mu}$ by usual time-dependent perturbation method. We find²³

$$-\frac{1}{\tau} = -\frac{\pi \omega_p^2}{2N} \sum_n f_{0n}(k, \mu) \delta(\omega_{k\mu} - \omega_{n0}), \quad (8.14)$$

which is the simple transverse analog of the plasmon lifetime calculated in NP I. From τ , it is a straightforward matter to calculate the rate of energy loss from the photon field, and hence the conductivity, $\sigma(k, \mu)$, which is

$$\sigma(k, \mu) = \frac{1}{4\pi\tau} = \frac{\pi e^2}{2m} \sum_n f_{0n}(k, \mu) \delta(\omega_{k\mu} - \omega_{n0}). \quad (8.15)$$

Equation (8.15) generalizes to transverse modes the longitudinal result obtained in Sec. 7.

We have now completed the determination from first principles of the macroscopic properties of the solid: we know the polarizability and the conductivity both for transverse and longitudinal modes, at various wavelengths and frequencies. Let us again emphasize the similarity of the transverse and longitudinal results, which differ from one another only through the replacement of longitudinal f_{0n} and $\omega(k)$ by their transverse analogues.

9. CONCLUSION

On first beholding the familiar expression for the static dielectric constant (3.8), coming as it does after a lengthy and sometimes involved derivation, the reader may well be inclined to wonder what all the fuss is about. Certainly (3.8) may be derived in a wide variety of ways. However, the conditions under which it is valid have been a subject of much debate, and it is for that reason that we have gone into the matter in so much detail.

The collective approach which we have developed

²³ Equation (8.14) is not exact for intraband transitions. Since these can never conserve the energy, this does not matter. Notice that the validity of (8.14) depends also on the assumption that the individual-particle excitation spectrum is not appreciably affected by the subsidiary conditions.

is most useful when $4\pi\alpha \gg 1$; this is also the region of greatest uncertainty about the nature of possible local field corrections. In this region of high polarizability, we find that (3.8) is rigorous, provided we work in a representation in which $(H_0 + H_{sr})$ is diagonal, so that the oscillator strengths and energy differences which appear there are calculated in this many-body representation [compare (3.9)]. Here the question of a local field correction does not arise, but the many-body eigenstates and oscillator strengths raise new problems. Fortunately, in many cases H_{sr} is of sufficiently short range that it may be treated as a relatively small perturbation. In such cases again we have no local field correction, and further more the f_{0n} and ω_{n0} of (3.8), being now associated with only one-electron transitions, should be calculable with no further intrinsic difficulties.

Examples of simple, highly polarizable solids, for which (3.8) applies, are those solids for which the plasmons are a well-defined mode of excitation possessing an energy near $\hbar\omega_p$. Thus, on comparing the conditions for the validity of (3.8), and the "existence" and "convergence" criteria for plasmons developed in NP I, we find they are essentially identical. We furthermore know that H_{sr} is a small perturbation when most of the ω_{n0} are smaller than ω_p , i.e., when the plasma frequency ω is very close to the free electron ω_p . Hence we should expect (3.8) to be quite accurate in the alkali and alkaline earth metals, in Al, and in Si and Ge. We also expect it to be quite successful in a wide variety of compounds.

The conditions under which our basic formula for the dielectric constant fails, and local field corrections become important are considerably less clear. Local field corrections could arise when $4\pi\alpha \ll 1$, but in this very low-polarizability region, they represent a small correction to the already small polarizability. The intermediate-polarizability region, $4\pi\alpha \lesssim 1$, combined with fairly well localized charges (e.g., the Lorentz insulator), would seem a prospect for possible local field corrections, principally because our calculation is not accurate in this domain. On the other hand, it should also be noted that one might expect (3.8) to furnish a fairly accurate interpolation formula throughout the region of intermediate polarizability, since it works in both the limits of high and low polarizability. As we saw, we also can have important local field corrections when $4\pi\alpha \gg 1$, if k_e is small enough that H_{sr} perturbs strongly the electron motion. However, such corrections do not change the order of magnitude of α , and are far smaller than those predicted by the Lorentz formula.

To sum up, we find that for a highly polarizable electron system (and hence a nonlocalized group of electrons), the local field corrections are small. For a group of tightly-bound electrons (which display an accordingly low polarizability) the Lorentz field correction exists, but the dielectric constant is only slightly altered. Thus, our calculations substantiate the classical work of Darwin.⁵

With a knowledge of the dielectric constant and conductivity at various wavelengths and frequencies, we are able to deal with a large class of problems in solid state physics, namely, those where the electron interaction enters only through its average effect. For instance, the effective interaction between minority carriers derived in Sec. 6 depends only on the macroscopic $\epsilon(\Omega, k)$. Other applications include the energy loss of fast particles (which will be described in more detail in NP IV), and the screened interaction of ions in a metal, which is closely related to the propagation of sound waves.²⁴ Quite generally, our derivation of ϵ and σ provides a link between the macroscopic approach (for instance, the Fermi dielectric approach to the characteristic energy-loss problem), and the microscopic approach from first principles (as in the BP treatment of the energy loss).

The usefulness of the macroscopic concepts (ϵ and σ) depends on the neglect of the electronic fluctuations. Whenever these fluctuations are important, our averaging processes fail. This happens, for instance, when k^{-1} is of the order of the interatomic spacing, or when Ω is of the order of the individual electron excitation frequencies. In such cases, our treatment does not converge, and, in fact, the macroscopic quantities ϵ and σ lose most of their physical meaning. A detailed treatment of the microscopic correlations is then necessary.

It should be noted that the concept of a dielectric constant is generally quite meaningful at frequencies near the plasma frequency. We therefore expect that in this range of frequencies, the interaction of electrons goes through a resonance, due to exchange of virtual plasmons. Such an effect might occur for the d - d interaction in transition metals, and be of importance for the study of ferromagnetic effects.²⁵ Another possible field of application of the present results might be ferroelectricity, where theoretical treatments have, in general, been obscured by the uncertain knowledge of the local field corrections. It is our hope that the considerations developed in this paper may prove to be a useful guide for the construction of a satisfactory theory of ferroelectrics.

This paper constitutes an attempt to recognize that many properties of solids do not depend on a detailed solution of the many-body problem, and to formulate carefully the conditions under which this is true. We have seen that in the "well-behaved" ranges of k and Ω , one may describe the effect of the electric and magnetic interactions of electrons using macroscopic polarizabilities and conductivities. This result promises a considerable simplification in the treatment of electrons in

²⁴ Thus the methods developed in this paper could be applied to a derivation of the sound-wave dispersion relation in metals. The results obtained will be completely equivalent to those found by J. Bardeen and D. Pines [Phys. Rev. **99**, 1140 (1955)].

²⁵ A similar effect may occur in the interaction between transition-metal impurities in metals.

solids and will form one of the major topics of the following paper.

APPENDIX

Let us study more closely the oscillator strengths defined in (8.10). Since the relevant values of k are very small ($< \omega_p/c$), we may replace (8.10) by its limit for $k=0$. For the interband oscillator strengths, ω_{n0} is independent of k . We then see from (8.10) that the transverse oscillator strength $f_{0n}(k, \mu)$ is just equal to the corresponding longitudinal $f_{0n}(\mathbf{e}_{k\mu})$, in the limit of small k . The interband oscillator strengths depend only on the polarization of the wave, and not on its direction of propagation.

In (8.10) we defined the intraband $f_{0n}(k, \mu)$ as being equal to the longitudinal $f_{0n}(\mathbf{e}_{k\mu})$. The f -sum rule for the transverse $f_{0n}(k, \mu)$ is then a trivial consequence of the sum rule for the longitudinal $f_{0n}(\mathbf{e}_{k\mu})$. If, however, we had defined the intraband oscillator strength by the

same expression as the interband one,

$$f_{0n}^{\text{intra}}(k, \mu) = \frac{2}{\hbar m} \frac{|\sum_i (\mathbf{e}_{k\mu} \cdot \mathbf{p}_i e^{-i\mathbf{k} \cdot \mathbf{x}_i})_{0n}|^2}{\omega_{n0}}, \quad (\text{A1})$$

we would not have an f -sum rule. Using (A1) in place of (8.10), one finds that

$$\sum_n f_{0n}(k, \mu) = N - \sum_{n(\text{intra})} \sum_{\alpha, \beta} A_{\alpha} A_{\beta} \left(\frac{m}{m^*} \right)_{\alpha\beta} \quad (\text{A2})$$

where the vector \mathbf{A} is given by

$$\mathbf{A} = \frac{(\mathbf{e}_{k\mu} \times \mathbf{e}_k) \times \nabla_{\mathbf{k}} E}{\mathbf{e}_k \cdot \nabla_{\mathbf{k}} E}. \quad (\text{A3})$$

For a longitudinal polarization $\mathbf{e}_{k\mu}$, $\mathbf{A}=0$ and the two definitions of the intraband oscillator strength are equivalent. It is not so, however, in the transverse case.

Superexchange Interaction Energy for $\text{Fe}^{3+}\text{-O}^{2-}\text{-Fe}^{3+}$ Linkages

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(Received September 11, 1957)

The superexchange interaction energy for an $\text{Fe}^{3+}\text{-O}^{2-}\text{-Fe}^{3+}$ linkage is considered for seven oxides in which Fe^{3+} is the only magnetic ion present, and for magnetite. The superexchange energy may be estimated from the value of T_C/n , where T_C is the Curie temperature and n is the number of $\text{Fe}^{3+}\text{-O}^{2-}\text{-Fe}^{3+}$ interactions per Fe^{3+} ion per formula unit. The average value of T_C/n is 115° (range 106 to 132°). The only compounds considered are antiferromagnetic oxides in which Fe^{3+} ions are present in one set of crystallographically equivalent positions and ferrimagnetic oxides in which Fe^{3+} ions are present in two different sets of crystallographically equivalent positions. No distinct correlation of superexchange energy with $\text{Fe}^{3+}\text{-O}^{2-}$ distances or with the included angle in the linkages is evident. Superexchange coupling is considered only for contact distances and for included angles substantially greater than 90° .

INTRODUCTION

KRAMERS¹ first suggested that the coupling of magnetic moments of transition-metal ions in oxides could take place through excited states of intervening oxygen ions. The nature of this coupling, which is known as superexchange² interaction, has been investigated in more detail by Van Vleck³ and Anderson.⁴ Néel⁵ has shown that the antiferromagnetism of transition-metal oxides and the spontaneous magnetization of iron spinels (ferrites), which he has called ferrimagnetism, may be understood on the basis of negative exchange (antiferromagnetic) interaction.

Thus far, attempts to estimate the exchange energy have not yielded entirely satisfactory results. Theo-

retical treatment of the problem is difficult and experimental data have been inadequate. Weisz⁶ found a semiempirical relationship of the exchange energy to the magnetic moment of M , the M -O distances and the M -O- M angle, where M is a transition-metal ion. However, his relationship depends on the structure type involved.

The Curie temperature,⁷ T_C , of a material may be considered to be the most direct measure of the interaction energy between magnetic ions. The number, n , of M -O- M interactions per magnetic ion per formula

⁶ R. S. Weisz, Phys. Rev. **81**, 626 (1951); Ceram. Age **59**, 35 (1952).

⁷ The Curie temperature, T_C , will denote the temperature below which order appears in the orientation of the moments of the magnetic ions. Usually T_C corresponds to the appearance of spontaneous magnetization as a consequence of order in ferro- or ferrimagnetic materials, whereas the Néel temperature, T_N , designates the appearance of order in antiferromagnetic materials which have zero spontaneous magnetization.

¹ H. A. Kramers, Physica **1**, 182 (1934).

² Superexchange hereafter will be called exchange for brevity.

³ J. H. Van Vleck, J. phys. radium **12**, 262 (1951).

⁴ P. W. Anderson, Phys. Rev. **79**, 350 (1950).

⁵ L. Néel, Ann. phys. **3**, 137 (1948).