from the migration of either interstitials or vacancies. The migration of more than a few percent of these defects to dislocations would cause an observable change in the reaction order. Since this is not observed, the probability that the defects migrating in Region III are captured by dislocations is small relative to the probability that they are captured by vacancies:

Case A.—Interstitials migrate in Region III:

$$n_V\sigma_{IV}\gg n_D\sigma_{ID}; \tag{B4}$$

therefore from Eq. (B3) one concludes that interstitials are primarily captured by vacancies.

Case B.—Vacancies migrate in Region III, interstitials having migrated previously:

$$n_V\sigma_{VV}\gg n_D\sigma_{VD}. \tag{B5}$$

Assuming that

$$\sigma_{ID}\approx\sigma_{VD},$$

and

$$\sigma_{IV}\geq\sigma_{VV},$$

then

$$n_V\sigma_{IV}\gg n_D\sigma_{ID}; \tag{B6}$$

therefore, the same conclusion concerning migration of interstitials can be drawn as in Case *A*.

Thus, whenever interstitials migrate, the majority of them should be captured by vacancies.

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Atomic Theory of Electromagnetic Interactions in Dense Materials*

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This theory develops a quantum analog of the classical electron oscillator model. It argues first that the Hamiltonian of long-wave excitations of matter is equivalent to that of an assembly of oscillators under very general assumptions. Next, these oscillators are coupled with the electromagnetic field oscillators and the normal modes of the coupled system are analyzed. The normal modes of longitudinal and transverse excitation have different spectra; the transverse frequencies depend strongly on the wavelength but the longitudinal ones do not. If the "longitudinal photons" are eliminated after the transformation to normal modes, the resulting Coulomb law has the dielectric constant in the denominator. The dielectric response law is expressed as a series of oscillations and also in terms of Van Hove's correlation function. Born-approximation theory of the collisions of fast charged particles with the assembly of normal mode (longitudinal and transverse) oscillators yields the same total cross section as Fermi's macroscopic theory. The transverse excitations include the Čerenkov radiation.

1. INTRODUCTION

THE dielectric constant ϵ of a material is a property relevant to electrodynamic phenomena in which the fields vary but little from one atom to the next. From an atomistic standpoint, ϵ has been interpreted by the classical model in which atomic electrons can perform forced oscillations about their equilibrium positions; no corresponding quantum mechanical theory seems to have been developed.[1]

This paper presents an atomistic theory of dielectric effects which considers three coupled quantum mechanical systems: an aggregate of atoms, the long-wave components of the electromagnetic field, and additional charged particles not included in the aggregate of atoms. The immediate aim is to rederive certain formulas of macroscopic electrodynamics, specifically: (a) the Coulomb interaction $e_1e_2/\epsilon r_{12}$ of charges in a dielectric and the equivalent equation $\mathrm{div}(\epsilon\mathbf{E})=4\pi\rho$, and (b) the probability of energy losses of a charged particle which was calculated macroscopically by Fermi, and, as a function of scattering angle, by Hubbard.[2a,b]

The macroscopic treatment of Coulomb interaction has proved quantitatively successful in the theory of donor levels in semiconductors,[3] even though applied to systems of the order of 100 A only. Inelastic electron collisions in solids have been the object of much recent work.[4] The energy loss spectrum in these collisions is clearly related to the dielectric constant $\epsilon(\omega)$ of each material by the Fermi theory, especially in the form

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[1] The quantum electrodynamics in a medium whose dielectric properties are characterized by a constant ϵ, but are not derived from an atomic model, has been developed by J. M. Jauch and K. M. Watson, Phys. Rev. **74**, 950 and 1485 (1948); **75**, 1249 (1949).

[2] (a) E. Fermi, Phys. Rev. **57**, 485 (1940); J. Hubbard, Proc. Phys. Soc. (London) **A68**, 976 (1955). (b) A theory with similar aims but with a different approach has been developed recently by D. A. Tidman, Nuovo cimento **3**, 503 (1956) and Nuclear Phys. (to be published).

[3] W. Kohn, Phys. Rev. **98**, 1856 (1955). I wish to thank Professor Kohn for calling my attention to this problem and for a discussion of his own approach to an atomistic theory of the interaction.

[4] See, for example, Marton, Leder, and Mendlowitz, *Advances in Electronics and Electron Physics* (Academic Press, Inc., New York, 1955), Vol. 7, p. 183.

given by Budini.[5] Nevertheless the relationship of this spectrum to the Bohm-Pines theory[6] of a quantum-mechanical plasma of metal electrons has not been readily or generally understood. That the relevant properties of the Bohm-Pines plasma are represented by its dielectric constant has been re-emphasized recently.[7] The present work was stimulated by the desire to provide a comprehensive treatment of inelastic collisions. This treatment utilizes those features of the plasma theory that have general applicability. It interlinks the Fermi macroscopic theory, the Bethe quantum theory of collisions with isolated atoms,[8] and Van Hove's correlation function[9] which represents the scattering properties of a system of interacting particles.

The treatment will consist of four steps, namely:

(a) A discussion of long-wave excitations in a macroscopically homogeneous assembly of atoms without long-range interactions. It will be shown that the Hamiltonian of these excitations is equivalent to that of a set of harmonic oscillators, provided that only a small fraction of all atoms is excited, i.e., in the same "small-amplitude" approximation which underlies the classical oscillator theory of polarization. The term "long-wave excitation" is intended here to apply not only to electronic excitations of a crystalline lattice of ions or molecules but to nonlocalized excitations of any macroscopically homogeneous aggregate of atoms or molecules. It thus pertains to liquid or amorphous matter as well as to a crystal, to the excitation of density waves of metal electrons, and also to phonons. It includes processes with sufficient energy to cause a lasting separation of charges, i.e., ionization.

(b) A study of the normal modes of coupled matter and field oscillators with long wavelengths $\lambda\!\!\!^{-}$. The relationship between $\lambda\!\!\!^{-}$ and the eigenfrequencies ω provides a phenomenological quantum mechanical definition of the dielectric constant, as pointed out by Neamtan,[10] through the equation $\epsilon=(c/\omega\lambda\!\!\!^{-})^2$. Whereas Neamtan treated the field-matter coupling as a weak perturbation, thus assuming $\epsilon\sim 1$ and working back to the Kramers-Heisenberg formula, the oscillator character of excitations permits a formally exact treatment of the coupling. The exact secular equation for the normal-mode eigenfrequencies takes the analytical form of the Sellmeyer-Drude dispersion equation. The difference between the longitudinal and transverse field oscillations makes the normal modes correspondingly different for longitudinal and transverse coupled oscillators.[11]

(c) A treatment of "external" electric charges, in addition to the lattice of atoms and to the electromagnetic field. In this case the Hamiltonian terms which couple the external charges with the longitudinal normal modes of the field-matter system may be eliminated, in part, by a well-known procedure of quantum electrodynamics. There results a direct interaction between the external charges, represented by Coulomb's formula with the appropriate dielectric constant. When the time lag in the reaction of matter to external charges has to be considered, one may represent it by a dielectric response function $\epsilon^{-1}(t)$. This function relates to the secular equation for the normal-mode eigenfrequencies and to Van Hove's correlation function[9] among the positions of electrons in the material.

(d) A Born-approximation treatment of inelastic collisions of a fast charged particle with the coupled field-matter system. Longitudinal and transverse normal-mode excitations can be treated separately.[12] Transverse excitations have significant probability only for incident particles of relativistic velocity. Transverse excitations, whose eigenfrequency is substantially shifted owing to coupling with the field, constitute the Čerenkov radiation.

2. LONG-WAVE EXCITATIONS

To develop the quantum analog of the classical electron oscillator model, we rely on considerations utilized previously in the theory of spin waves in magnetized materials.[13] The type of approximations to be used here and the general intent are also related to Tomonaga's quantum mechanical treatment of collective coordinates.[14]

In a system which contains large numbers of identical particles and is macroscopically homogeneous, any particular type of excitation, with energy $\hbar\omega_n$, can usually take place at any one of a large number of equivalent spots. Such a "spot" may, but need not, consist of a cell in a crystal lattice or a molecule in a liquid; the metal electrons contained in a cubic volume of, say, $(10\text{ A})^3$ may also constitute a spot in this sense. The total excitation energy can be indicated, then, as $\sum_n N_n\hbar\omega_n$, where N_n indicates the number of spots with an excitation of type n. If N_n be regarded as an operator with eigenvalues 0, 1, 2, $\cdots$, the expression $\sum_n N_n\hbar\omega_n$ constitutes the relevant part of the Hamiltonian of the

[5] P. Budini, Nuovo cimento **10**, 236 (1953). See also, for the collisions with metal electrons, H. A. Kramers, Physica **13**, 401 (1947).

[6] D. Bohm and D. Pines, Phys. Rev. **92**, 609 (1953); D. Pines, Phys. Rev. **92**, 626 (1953).

[7] J. Hubbard, Proc. Phys. Soc. (London) **A68**, 441 (1955); H. Fröhlich and H. Pelzer, Proc. Phys. Soc. (London) **A68**, 525 (1955).

[8] H. A. Bethe, *Handbuch der Physik* (Verlag Julius Springer, Berlin, 1933), Vol. 24, Part 1, p. 495 ff.

[9] L. Van Hove, Phys. Rev. **95**, 249 (1954).

[10] S. M. Neamtan, Phys. Rev. **92**, 1362 (1953); **94**, 327 (1954).

[11] W. R. Heller and A. Marcus, Phys. Rev. **84**, 809 (1951), calculated excitation energies in a crystal, taking into account the long-range Coulomb interaction. They expressed the energy eigenvalues as functions of a continuously variable angle between the direction of oscillation and the wave vector, which appears to be incorrect. Dr. Heller has kindly informed us that the full implications of the difference between longitudinal and transverse oscillations became clear to him after publication of his paper.

[12] U. Fano, Phys. Rev. **102**, 385 (1956).

[13] T. Holstein and H. Primakoff, Phys. Rev. **58**, 1098 (1940).

[14] S. Tomonaga, Progr. Theoret. Phys. (Japan) **13**, 467, 482 (1955).

system, and has the same appearance as the Hamiltonian of an assembly of harmonic oscillators with frequencies $\omega_1, \omega_2, \cdots \omega_n, \cdots$. Thus the oscillator model reflects, in the first place, the inherent degeneracy of the spectrum of any large, macroscopically homogeneous, system.

In the quantum mechanics of oscillators, the operator N_n is represented in terms of creation-annihilation operators a_n^*, a_n, with the commutation property $a_n a_{n'}^* - a_{n'}^* a_n = \delta_{n'n}$. Proceeding further, one might consider one oscillator for each "spot" i and set $N_n = \sum_i N_{ni} = \sum_i a_{ni}^* a_{ni}$. However, the operator N_{ni} has the whole set of eigenvalues 0, 1, 2, $\cdots$, whereas each spot has only the spectrum of excitation levels $\hbar\omega_1 \cdots \hbar\omega_n \cdots$ without their multiples $2\hbar\omega_n$, $3\hbar\omega_n \cdots$. Accordingly one should more properly set $N_{ni} = \bar{a}_{ni}^* \bar{a}_{ni}$, where the operators $\bar{a}$ have the Fermi-statistics anti-commutation property $\bar{a}_{ni}\bar{a}_{ni}^* + \bar{a}_{ni}^* \bar{a}_{ni} = 1$, and N_{ni} has only the eigenvalues 0 and 1.

In this connection it matters that, under realistic conditions, the electric polarization of a material is proportional to the applied field strength and thus constitutes a weak reaction, adequately represented by the first term of an expansion in powers of the disturbance. The harmonic character of the classical model oscillators derives from the proportionality of the reaction to the disturbance. The corresponding feature in the atomistic picture is that only a minute fraction of the "spots" is excited at any one time. The probability that two identical excitations would accumulate on the same spot is accordingly negligible, and little error is incurred by representing the Hamiltonian of matter excitations in terms of operators N_{ni} having unrealistic eigenvalues 2, 3$\cdots$ in addition to 0 and 1. Similarly, little error is caused by disregarding the fact that excitation of a spot to its nth level usually excludes simultaneous excitation to a different, mth level, and thus assuming that N_{ni} and N_{mi} commute whereas in fact they do not.

This approximation may be cast in mathematical form through the following considerations.[13] The matrices of a_{ni} and a_{ni}^* have rows and columns corresponding to the eigenvalues N_{ni} from 0 to ∞, whereas the matrices of $\bar{a}_{ni}$ and $\bar{a}_{ni}^*$ have only two rows and columns, corresponding to $N_{ni} = 0$, 1. However, the matrix of $(1 - a_{ni}^* a_{ni}) a_{ni}$ coincides with the matrix of $\bar{a}_{ni}$ for $N_{ni} = 0, 1$ and has no nonzero element connecting these eigenvalues with the larger, unrealistic, ones. Thus we introduce no error by replacing $\bar{a}_{ni}$ with $(1 - a_{ni}^* a_{ni}) a_{ni}$ and $\bar{a}_{ni}^*$ with $a_{ni}^* (1 - a_{ni}^* a_{ni})$. The approximation corresponding to the classical oscillator model is introduced next, by dropping $a_{ni}^* a_{ni}$ in the expression $1 - a_{ni}^* a_{ni}$ because its expectation value—the probability of excitation of the particular spot i—is very small. More generally, we shall assume that the Hamiltonian of the system can be expressed in terms of the harmonic oscillator operators a_{ni} and a_{ni}^*, that it has been expanded into powers of these operators, and that all terms of degree higher than bilinear have been disregarded. Thereby a *linear* approximation makes the system equivalent to an assembly of harmonic oscillators, in quantum as in classical mechanics.

The Hamiltonian bilinear in the a_{ni}^*, a_{ni} will generally include cross terms, in particular terms of the form $a_{nj}^* a_{ni}$ which represent a transfer of level-n excitation from spot i to spot j. The cross terms can be removed by a unitary transformation

$$A_r = \sum_{ni} [c_{r,ni} a_{ni} + d_{r,ni} a_{ni}^*], \tag{1}$$

which diagonalizes the Hamiltonian to the form

$$H = \sum_r \hbar\omega_r A_r^* A_r. \tag{2}$$

These equations represent the excitations as normal-mode harmonic oscillations. The summation over the index i corresponds to the ability of excitations to migrate from spot to spot, so that the normal modes are usually spread over the whole material. Often the coupling between excitations of different types, n, m, is not sufficiently strong to wipe out the identity of each type of excitation and the normal-mode frequencies ω_r fall into bands centered near the spot excitation frequencies ω_n.

With regard to large systems, one is usually interested not as much in the stationary excited states as in quasi-stationary states having some characteristic that lasts perhaps only a little longer than ω_r^{-1}, e.g., in states having a definite momentum or having the excitation concentrated on electrons rather than subdivided among nuclear vibrations. Such quasi-stationary states can be regarded as superpositions of exact energy eigenstates with energies in a band of suitable width, and can be characterized by complex energy eigenvalues $\hbar\omega_r$. The oscillators represented by the approximate Hamiltonian (2) will be assumed to be damped oscillators, having quasi-stationary characteristics to be further specified.

Having relaxed the requirement that the ω_r be exact normal-mode frequencies of excitation, we may utilize the resulting latitude in the choice of the annihilation operators A_r so that they represent collective coordinates[14] appropriate to the intended application. We shall be concerned with the coupling of matter excitations with oscillations of the electromagnetic field. These oscillations can be classified according to their constants, e.g., the momentum $\hbar\mathbf{k}$ and the polarization unit vector $\mathbf{e}_{ks}$, with $s = 1, 2, 3$ and $\mathbf{e}_{k1} = \mathbf{k}/k$. We should, therefore, consider excited states of matter characterized by the same set of momentum and polarization[15] eigenvalues. These excited states will be quasi-stationary in a macroscopically homogeneous and isotropic material, particularly when the momentum is so small

[15] Instead of polarization one may consider, more generally, parity with respect to reflection on planes parallel or perpendicular to $\mathbf{k}$. Thus states with longitudinal excitation are, like $\mathbf{e}_{k1}$, odd under reflection on a plane perpendicular to $\mathbf{k}$, and even for planes parallel to $\mathbf{k}$.

that the material is homogeneous over distances $\sim k^{-1}$. (The momentum $\hbar\mathbf{k}$ is exactly constant, of course, for perfectly crystalline matter.)[16,17] Because electrons and atomic nuclei have masses and velocities of different orders of magnitude, the electronic or vibrational character of an excitation is also quasi-stationary. Unless the interaction between adjacent "spots" is very strong, the quasi-stationary states with momentum $\hbar\mathbf{k}$ will have the same electronic character and direction of oscillation as the excitations at particular spots. The coefficients of the transformation (1) will then be simply

$$c_{r,ni}=e^{-i\mathbf{k}\cdot\mathbf{r}_i}/\sqrt{N},\quad d_{r,ni}=0,$$

where N is the number of equivalent spots per unit volume and $\mathbf{r}_i$ a reference coordinate of the spot i.

In the following we shall deal, for simplicity, only with long-wave (low k) electronic excitations of a homogeneous isotropic material, the relevant Hamiltonian being represented by (2). The index r will be further specified as $n\mathbf{k}s$. Because the material is isotropic (and insofar as long-range Coulomb interactions are still disregarded) the frequency ω_{nks} does not depend on s or on the direction of $\mathbf{k}$. Its dependence on k will not be considered explicitly for small values of k and we shall write simply ω_n for ω_{nks}. The excitations will be represented as harmonic, rather than damped oscillators, until such point where their quasi-stationary character becomes essential.

The creation-annihilation operators may be replaced with oscillator amplitudes and with their conjugated momenta through the formulas[18]

$$\begin{aligned}Q_{nks}&=(\hbar/2\omega_n)^{\frac{1}{2}}(A_{nks}-A_{n-ks}^*),\\ P_{nks}&=i(\hbar\omega_n/2)^{\frac{1}{2}}(A_{nks}^*+A_{n-ks}).\end{aligned}\tag{3}$$

The corresponding form of the Hamiltonian (2), with an additional irrelevant zero-point energy, is

$$H=\sum_n \hbar\omega_n \sum_{ks}[-\tfrac{1}{2}(P_{nks}P_{n-ks}+\omega_n^2 Q_{nks}Q_{n-ks})].\tag{4}$$

Within the limits of the linear (oscillator) approximation, the operator representing the interaction of our material system with another system can be represented as a linear function of the operators a_{ni}, a_{ni}^* or of the A_r, A_r^*. This linear function is further restricted by invariance considerations (selection rules). For example, if the interaction can transfer momentum to the material only in units of $\hbar\mathbf{k}$, the operator will be a linear function only of the A_{nks}^* and A_{n-ks}, or of P_{nks} and Q_{n-ks}, with fixed $\mathbf{k}$ and various n and s. Further, if the operator is even under time reflection it will be a linear function of the Q_{n-ks} only, and, if odd, of the P_{nks} only.

3. COUPLING OF FIELD AND MATTER OSCILLATORS

(a) Representation of the Fields

As a general approach, we follow Fermi's treatment of quantum electrodynamics.[19] However, the fields will be represented in terms of a vector potential only, as in reference 6, without any scalar potential. (A manifestly relativistic formalism would have no advantage, since matter constitutes a special frame of reference.) We set $\mathbf{E}=-(1/c)\partial\mathbf{A}/\partial t$ and $\mathbf{H}=\mathrm{curl}\mathbf{A}$, so that $\mathrm{div}\mathbf{H}=0$ and $c\,\mathrm{curl}\mathbf{E}=-\partial\mathbf{H}/\partial t$ are fulfilled identically, as usual. The Maxwell equation $c\,\mathrm{curl}\mathbf{H}=\partial\mathbf{E}/\partial t+4\pi\mathbf{j}$ yields the wave equation for $\mathbf{A}$, $c^2\,\mathrm{curl}\,\mathrm{curl}\mathbf{A}=-\partial^2\mathbf{A}/\partial t^2+4\pi c\mathbf{j}$, and the remaining equation, $\mathrm{div}\mathbf{E}=4\pi\rho$ must be treated as a *subsidiary condition*, which replaces the two subsidiary conditions of reference 19.

After Fourier analysis in which we take

$$\begin{aligned}\mathbf{A}&=(4\pi)^{\frac{1}{2}}c\textstyle\sum_{ks}q_{ks}\mathbf{e}_{ks}e^{i\mathbf{k}\cdot\mathbf{r}},\\ \mathbf{j}&=\textstyle\sum_{ks}\mathbf{e}_{ks}j_{ks}e^{i\mathbf{k}\cdot\mathbf{r}},\\ \rho&=\textstyle\sum_{k}\rho_k e^{i\mathbf{k}\cdot\mathbf{r}},\end{aligned}\tag{5}$$

where $\mathbf{e}_{ks}$ indicates the polarization vector, as in Sec. 2, and $q_{ks}=-q_{-k,s}^*$ the oscillation amplitude, the wave equation becomes

$$\ddot{q}_{ks}+c^2k^2(1-\delta_{1s})q_{ks}=(4\pi)^{\frac{1}{2}}j_{ks}.\tag{6}$$

Here $c^2k^2(1-\delta_{1s})$ represents the force constant of the field oscillator, which vanishes for the longitudinal field as indicated by the factor $1-\delta_{1s}$. The subsidiary condition takes the form

$$-\dot{q}_{k1}=p_{-k1}=i(4\pi)^{\frac{1}{2}}\rho_k/k.\tag{7}$$

In quantum mechanics the oscillator amplitudes q_{ks} and their conjugate momenta are treated as operators. Instead of the oscillator equation (6), one considers the corresponding Hamiltonian, which, in the absence of

[16] It is appropriate to consider excitations distributed over many atoms whenever the exciting disturbance itself affects many atoms simultaneously and imparts to the material a momentum with $k^{-1}\ll 10^8$ cm^{-1}. (By contrast, if one started from a localized excitation, it becomes appropriate to regard the excitation as distributed only if the mechanisms that transfer excitation from one atom to the next operate much faster than the mechanisms that dissipate the excitation.) An excitation may become localized within a small group of atoms only through a process involving a momentum transfer with $k\gtrsim 10^7$ cm^{-1}. If the momentum received initially by the whole material is small, the excitation may nevertheless become localized at a later stage following a larger momentum exchange between particles *within* the material, especially between electrons and atomic nuclei.

[17] Distributed excitation may also occur in rarefied matter. The super-radiant states of a gas considered by R. H. Dicke, Phys. Rev. 93, 99 (1954), are zero-momentum states, or more properly states with very low momentum.

[18] These operators are not Hermitian because they refer to progressive waves. The signs in (3) and (4) relate to the definition $\mathbf{e}_{-ks}=-\mathbf{e}_{ks}$, from which it also follows that $Q_{nks}^*=-Q_{n-ks}$ and that $-Q_{nks}Q_{n-ks}=Q_{nks}Q_{nks}^*$ is positive. The Hermitian operators $Q_{nks}-Q_{n-ks}$ and $i(Q_{nks}+Q_{n-ks})$ represent the amplitudes of standing excitation waves one-quarter wavelength off phase, similar to those considered in the electrodynamics of reference 19.

[19] E. Fermi, Revs. Modern Phys. 4, 125 (1932).

currents, is[18]

$$H_{\text{field}}=\sum_{\mathbf{k}s}\{-\tfrac{1}{2}[p_{\mathbf{k}s}p_{-\mathbf{k}s}+c^2k^2(1-\delta_{s1})q_{\mathbf{k}s}q_{-\mathbf{k}s}]\}. \quad (8)$$

Similarly, in the absence of charges, $\rho_{\mathbf{k}}=0$, the subsidiary condition reduces to $p_{-\mathbf{k}1}=0$, meaning that only those states of the field exist which are eigenstates of $p_{-\mathbf{k}1}$ corresponding to its eigenvalue zero. (As emphasized in reference 6, $p_{-\mathbf{k}1}$ commutes with H_{field} and therefore has common eigenstates with it.)

(b) Interaction with Matter

If matter is treated according to Sec. 2, the complete Hamiltonian is

$$H=H_{\text{field}}+H_{\text{inter}}+H_{\text{medium}}, \quad (9)$$

with H_{medium} to be taken from (4). We consider the interaction of the field only with the electrons in the medium, disregarding the nuclei for simplicity, and take the nonrelativistic form of the interaction, which gives[20]

$$H_{\text{inter}}=(4\pi)^{\frac{1}{2}}e\sum_{\mathbf{k}s}q_{\mathbf{k}s}\sum_h \mathbf{e}_{\mathbf{k}s}\cdot\tfrac{1}{2}(d\mathbf{r}_h/dt)e^{i\mathbf{k}\cdot\mathbf{r}_h}$$
$$+e^{i\mathbf{k}\cdot\mathbf{r}_h}(d\mathbf{r}_h/dt)+\frac{2\pi e^2}{m}\sum_{\mathbf{k}s\mathbf{k}'s'}\mathbf{e}_{\mathbf{k}s}\cdot\mathbf{e}_{\mathbf{k}'s'}q_{\mathbf{k}s}q_{\mathbf{k}'s'}$$
$$\times\sum_h e^{i(\mathbf{k}+\mathbf{k}')\cdot\mathbf{r}_h}, \quad (10)$$

where $\mathbf{r}_h$ is the position of the hth electron and $d\mathbf{r}_h/dt$ its velocity.

The operator $\sum_h (d\mathbf{r}_h/dt)\exp(i\mathbf{k}\cdot\mathbf{r}_h)$ in (10) can transfer momentum to the medium in units of $\hbar\mathbf{k}$ only, because a shift $\mathbf{r}$ of the origin of electron coordinates multiplies the operator by $\exp(i\mathbf{k}\cdot\mathbf{r})$. This factor is also time-odd because it contains $d\mathbf{r}_h/dt$. For the reasons indicated at the end of Sec. 2, and subject to the approximations of that section, the first term of (10) can then be represented as a sum of operators $P_{n\mathbf{k}s}$, which we write

$$\sum_{\mathbf{k}s}\omega_p q_{\mathbf{k}s}\sum_n (f_n)^{\frac{1}{2}}P_{n\mathbf{k}s}. \quad (11)$$

Here ω_p is a constant having the dimension of a frequency, which we take as equal to the plasma frequency defined by

$$\omega_p{}^2=4\pi\mathfrak{N}e^2/m, \quad (11')$$

($\mathfrak{N}$=electron density); f_n may be regarded as an empirical expansion coefficient, but in the dipole approximation it coincides with the oscillator strength of the nth equivalent oscillator in the medium.[21,22] The oscillator strength f_n could be defined in general as a function of the wave number k but this dependence can often be disregarded for small k (dipole approximation), much like the dependence of the frequency $\omega_{n\mathbf{k}}$ on k.

In the second term of (10) we shall disregard all terms with $\mathbf{k}+\mathbf{k}'\neq 0$, as was done in reference 6. It is not argued here that these terms are negligible; the purpose is only to postpone the study of their influence. (Disregarding these terms we shall arrive at the Sellmeyer-Drude dispersion formula; hence it is surmised that their influence may lead toward the Lorentz-Lorenz result.) With this assumption, the second term of (10) reduces to $-\frac{1}{2}\omega_p{}^2\sum_{\mathbf{k}s}q_{\mathbf{k}s}q_{-\mathbf{k}s}$.

Entering then into (9) Eqs. (8), (10), (11), and (4), we have

$$H=-\sum_{\mathbf{k}s}\tfrac{1}{2}\{p_{\mathbf{k}s}p_{-\mathbf{k}s}+[c^2k^2(1-\delta_{s1})+\omega_p{}^2]q_{\mathbf{k}s}q_{-\mathbf{k}s}$$
$$+\sum_n[-2\omega_p f_n{}^{\frac{1}{2}}q_{\mathbf{k}s}P_{n\mathbf{k}s}+P_{n\mathbf{k}s}P_{n-\mathbf{k}s}$$
$$+\omega_n{}^2Q_{n\mathbf{k}s}Q_{n-\mathbf{k}s}]\}, \quad (12)$$

in which the coupling between field and matter oscillators is confined to those with the same momentum and polarization.

In the subsidiary equation (7) the Fourier coefficients $\rho_{\mathbf{k}}$ are given by $-e\sum_h\exp(-i\mathbf{k}\cdot\mathbf{r}_h)$. This operator should be a linear function of the operators $Q_{n\mathbf{k}1}$, for the reasons indicated at the end of Sec. 2, and one verifies, as in reference 21, that

$$i(4\pi)^{\frac{1}{2}}\rho_{\mathbf{k}}/k=\omega_p\sum_n f_n{}^{\frac{1}{2}}Q_{n\mathbf{k}1}.$$

The subsidiary condition becomes then

$$\Omega_{\mathbf{k}}=p_{-\mathbf{k}1}-\omega_p\sum_n f_n{}^{\frac{1}{2}}Q_{n\mathbf{k}1}=0, \quad (13)$$

and requires that only those states of the combined system exist which are eigenstates of $\Omega_{\mathbf{k}}$ corresponding to its eigenvalue zero. It is seen from (13) and (12) that $[\Omega_{\mathbf{k}},H]=0$.

In the usual procedure of quantum electrodynamics, the subsidiary condition is eliminated by a change of variables represented by a unitary transformation which replaces every operator O with SOS^{-1}. For our

[20] The second term of (10) drops out in the relativistic form, but in its place one must consider virtual transitions to negative energy states.

[21] If one considers first the electrons belonging to "spot" i much smaller than k^{-1}, $\mathbf{r}_h$ in the exponent can be replaced with $\mathbf{r}_i$. The operator $d\mathbf{r}_h/dt$ can be correspondingly represented by $\sum_n i\omega_n x_n(a_{ni}{}^*-a_{ni})\mathbf{e}$, where $x_n\mathbf{e}$ is the dipole matrix element for transition to the nth excited state of a spot with polarization $\mathbf{e}$. The $\sum_i(a_{ni}{}^*-a_{ni})\exp(i\mathbf{k}\cdot\mathbf{r}_i)\mathbf{e}\cdot\mathbf{e}_{ks}$ yields $N^{\frac{1}{2}}(A_{n\mathbf{k}s}{}^*+A_{n-\mathbf{k}s})$, where N is the number of spots. The dipole matrix element and the oscillator strength are related by $\omega_n x_n=m^{-\frac{1}{2}}(\frac{1}{2}\hbar\omega_n)^{\frac{1}{2}}(\mathfrak{N}f_n/N)^{\frac{1}{2}}$, where the $\mathfrak{N}/N$ is the number of electrons per spot. Equation (11) follows from (10) using these formulas and the definition (3). Note that the electron density $\mathfrak{N}$ in (11') may be intended to include all electrons in the medium or, for example, only the optical electrons; the definition of f_n is correspondingly modified, so that the sum rule $\Sigma_n f_n=1$ holds when the sum extends to the transitions of all electrons included in $\mathfrak{N}$. Applications involve in fact only the product $\omega_p{}^2f_n$ which is independent of such conventions.

[22] From the standpoint of Tomonaga's theory (reference 14), one would consider $\sum_h \mathbf{e}_{\mathbf{k}s}\cdot[(d\mathbf{r}_h/dt)\exp(i\mathbf{k}\cdot\mathbf{r}_h)+\exp(i\mathbf{k}\cdot\mathbf{r}_h)(d\mathbf{r}_h/dt)]$ as a collective momentum $\pi_{\mathbf{k}s}$ of the medium. However, the oscillations of the corresponding coordinate are anharmonic. The expansion $\pi_{\mathbf{k}s}\propto\sum_n f_n{}^{\frac{1}{2}}P_{n\mathbf{k}s}$ constitutes a process of harmonic analysis which goes beyond the initial Tomonaga theory and is approximately equivalent to solving the Schrödinger equation for the excitation of individual "spots" of the medium. This problem does not arise in Tomonaga's application to an electron plasma because the plasma, in absence of long-range interactions, is capable only of a single type of oscillation, with zero frequency.

problem $S=\exp(-i\hbar^{-1}\omega_p\sum_{\mathbf{k}}q_{-\mathbf{k}1}\sum_n f_n^{\frac{1}{2}}Q_{n\mathbf{k}1})$, which replaces p_{-k1} with $p_{-k1}+\omega_p\sum_n f_n^{\frac{1}{2}}Q_{n\mathbf{k}1}$ and $P_{n\mathbf{k}1}$ with $P_{n\mathbf{k}1}+\omega_p f_n^{\frac{1}{2}}q_{-\mathbf{k}1}$. The condition (13) reduces to $p_{-\mathbf{k}1}=0$ and the Hamiltonian SHS^{-1} no longer contains the variable $q_{\mathbf{k}1}$ but only the momenta $p_{\mathbf{k}1}$. The subsidiary condition simply states, then, that the longitudinal oscillators possess no energy, just as in the case of the no-charge Hamiltonian (8). On the other hand, the transformation S introduces in the Hamiltonian H a term affecting the matter oscillators with $s=1$, with equal $\mathbf{k}$ and all n. This energy term represents the Coulomb interaction between electronic oscillations at different points of the medium. Our treatment has assumed implicitly that the short wave longitudinal field oscillators (with $k^{-1}\lesssim 10^{-7}$ cm) had been eliminated in advance by a change of variable and replaced by a screened Coulomb interaction, as in reference 6, because the short-range portion of the Coulomb interaction has an essential influence on the excitation spectrum at each spot. Here we consider only the coupling of the *long-wave* longitudinal matter oscillators with the longitudinal field oscillators of equal wavelength, a coupling which is equivalent to the long-range tail of the Coulomb interaction.

(c) Normal-Mode Equation

Instead of carrying out first the change of variables represented by S and then seeking the normal modes of the longitudinal matter oscillators which are thereby coupled, we combine these operations by seeking directly the normal modes of the matter and field oscillators. This single operation[23] can be applied equally to the longitudinal and to the transverse oscillators.

Because the coupling term in (12) contains the momentum instead of the amplitude of the matter oscillators, it is convenient to interchange momenta and amplitudes by introducing the new variables

$$\bar{Q}_{n\mathbf{k}s}=P_{n-\mathbf{k}s}/\omega_n,\quad \bar{P}_{n\mathbf{k}s}=-\omega_n Q_{n-\mathbf{k}s}. \tag{14}$$

The Hamiltonian (12) becomes now

$$\begin{aligned}H=-\sum_{\mathbf{k}sn}\tfrac{1}{2}\{&p_{\mathbf{k}s}p_{-\mathbf{k}s}+P_{n\mathbf{k}s}\bar{P}_{n-\mathbf{k}s}\\&+[c^2k^2(1-\delta_{s1})+\omega_p{}^2]q_{\mathbf{k}s}q_{-\mathbf{k}s}\\&-2\omega_p\omega_n f_n^{\frac{1}{2}}q_{\mathbf{k}s}\bar{Q}_{n-\mathbf{k}s}+\omega_n{}^2\bar{Q}_{n\mathbf{k}s}\bar{Q}_{n-\mathbf{k}s}\}.\end{aligned} \tag{15}$$

The normal modes, which diagonalize the bilinear expression consisting of the last three terms of (15), are the eigenvectors of the homogeneous system of equations

$$\begin{aligned}-\partial H/\partial q_{-\mathbf{k}s}&=[c^2k^2(1-\delta_{s1})+\omega_p{}^2]q_{\mathbf{k}s}\\&\quad-\textstyle\sum_n\omega_p\omega_n f_n^{\frac{1}{2}}\bar{Q}_{n\mathbf{k}s}=\omega^2 q_{\mathbf{k}s},\\-\partial H/\partial\bar{Q}_{n-\mathbf{k}s}&=-\omega_p\omega_n f_n^{\frac{1}{2}}q_{\mathbf{k}s}+\omega_n{}^2\bar{Q}_{n\mathbf{k}s}=\omega^2\bar{Q}_{n\mathbf{k}s}.\end{aligned} \tag{16}$$

[23] This operation has been carried out, in a different context, and discussed in much detail by N. van Kampen, Kgl. Danske Videnskab, Mat.-fys. Medd. **26**, No. 15 (1953).

From the second equation it follows that

$$\bar{Q}_{n\mathbf{k}s}=-\omega_p\omega_n f_n^{\frac{1}{2}}q_{\mathbf{k}s}/(\omega^2-\omega_n{}^2). \tag{17}$$

Substitution into the first equation of the system (16) shows that the solutions of this system correspond to the roots of the secular equation

$$c^2k^2(1-\delta_{s1})+\omega_p{}^2+\omega_p{}^2\textstyle\sum_n\dot{\omega}_n{}^2 f_n/(\omega^2-\omega_n{}^2)=\omega^2, \tag{18}$$

that is, since $\sum_n f_n=1$,

$$c^2k^2(1-\delta_{s1})=\omega^2[1-\omega_p{}^2\textstyle\sum_n f_n/(\omega^2-\omega_n{}^2)]. \tag{19}$$

The expression in square brackets coincides with the Sellmeyer-Drude formula for the dielectric constant of a medium containing undamped oscillators with frequencies ω_n. At this point we take into account that the matter oscillators are assumed to be damped, with complex ω_n. This is done appropriately, as shown in Appendix A, by replacing $\omega^2-\omega_n{}^2=(\omega-\omega_n)(\omega+\omega_n)$ in (19) with $(\omega-\omega_n)(\omega+\omega_n{}^*)=\omega^2-|\omega_n|^2-\omega(\omega_n-\omega_n{}^*)$. Thus we set

$$\epsilon(\omega)=1-\omega_p{}^2\sum_n\frac{f_n}{\omega^2-|\omega_n|^2-\omega(\omega_n-\omega_n{}^*)} \tag{20}$$

and replace the secular equation (19) with

$$c^2k^2(1-\delta_{s1})=\omega^2\epsilon(\omega). \tag{21}$$

In (20) and (21), ω_n and f_n may be regarded, if necessary, as functions of k instead of having the value corresponding to $k=0$.

Notice that: (1) the structure of the secular equation (19) or (21) is characteristic of all systems where one oscillator is coupled a number of other oscillators not coupled among themselves; (2) Eq. (21) for $s\neq 1$ coincides with Neamtan's[10] quantum mechanical definition of ϵ as the ratio c^2k^2/ω^2, where $\hbar\omega$ is the energy eigenvalue for a photon of momentum $\hbar k$ as modified by interaction with matter; (3) Neamtan's calculation of this eigenvalue by perturbation technique (Kramers-Heisenberg approximation, to second order in the electron charge e) replaces the "exact" equation (21) with the approximation $c^2k^2=\omega^2\epsilon(ck)$. (The "exact" formulation has been made possible, here, as in the classical theory, by the oscillator approximation of matter properties. The perturbation treatment is adequate only for $\epsilon\sim 1$, i.e., when the field is weakly perturbed by the presence of matter.)

(d) Discussion of the Spectrum

The spectrum of normal modes $\Omega_1, \Omega_2, \cdots\Omega_\alpha\cdots$ is simplest when the spectrum of matter oscillators consists of well-separated "lines" $\omega_1, \omega_2, \cdots\omega_n\cdots$ with negligible damping. We discuss the spectrum Ω_α by a graphical construction shown in Fig. 1. Figure 1(a) shows plots of the familiar anomalous dispersion curve $\epsilon(\omega)$ for two situations, respectively of moderately

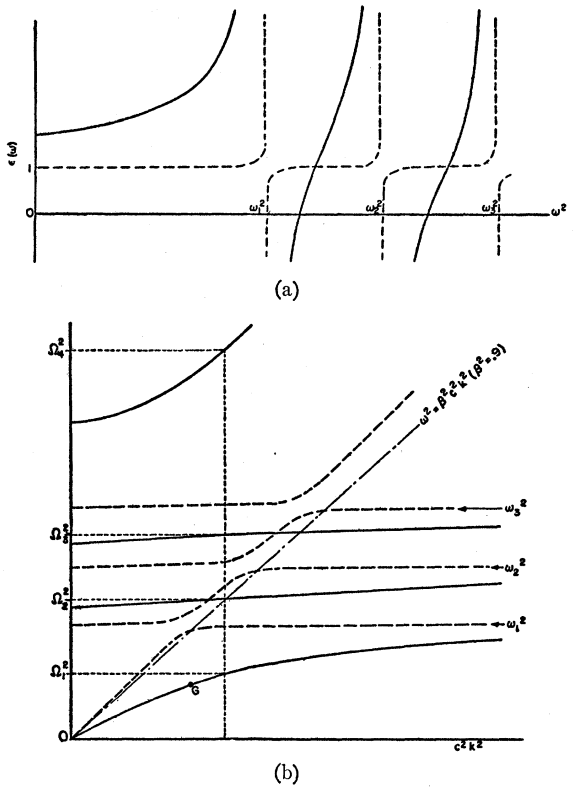

FIG. 1. (a) Schematic plot of $\epsilon(\omega)$; $f_1=\frac{1}{3}, f_2=\frac{1}{3}, f_3=\frac{1}{3}$; — — — $\omega_p^2/\omega_1^2=0.01$; ——— $\omega_p^2/\omega_1^2=1.0$. (b) Level diagram of normal modes for same input data as in (a). - - - Construction of normal mode eigenvalues Ω_α^2 for a transversal mode with given k. (The line ·—·—· is discussed in Sec. 6.)

strong and weak density of matter oscillators. Extreme schematizations are made by taking only three matter oscillators well spaced in frequency, with no damping. The curves of Fig. 1(b) are constructed by taking as ordinate the abscissa of Fig. 1(a) and as abscissa the product $\omega^2\epsilon(\omega)$ of the abscissa and ordinate of Fig. 1(a).

Figure 1(b) will be regarded as a *level diagram* of the normal modes. The "levels" Ω_α^2 are the roots of the Eq. (21), $\omega^2\epsilon(\omega)=c^2k^2(1-\delta_{s1})$. To find these roots, one enters into Fig. 1(b) at the abscissa c^2k^2 for $s=2$, 3 and at 0 for $s=1$, and one reads the corresponding Ω_1^2, Ω_2^2, $\cdots$ of the many-branched curve. For the transverse modes, $s=2$, 3, one visualizes quantum-mechanically a field oscillator whose frequency level equals ck when unperturbed but is "repelled" by the frequencies ω_1, ω_2, $\cdots$ of the matter oscillators.

Visible light traveling in a transparent refractive medium like glass, where ω_1 is rather high, corresponds to a point of the diagram such as G. The field oscillation is then accompanied by an electronic oscillation of the medium having comparable intensity; for a given k, Ω_1 is about $\frac{2}{3}$ of the corresponding vacuum value ck. We have here an example of tight coupling.

On the other hand, the coupling is weak on the far right side of Fig. 1. Transverse matter excitations with $\hbar\omega_n$ of the order of 5–10 ev and with $k>10^5$ cm^{-1} are practically unperturbed by the field oscillators, because for this k the photon energy $\hbar ck$ is much larger than 10 ev. These excitations are strongly coupled with field oscillations of nearly equal frequency only at the surface of the medium, or at other inhomogeneities, where the momentum $\hbar\mathbf{k}$ is not conserved. Indeed light with photon energy near $\hbar\omega_n$ incident from vacuum on the surface of a medium, with photon momentum $\hbar\omega_n/c$, excites in the medium not field oscillations but damped matter oscillations with excitation energy $\hbar\omega_n$ and momentum $\gg\hbar\omega_n/c$. This is the ordinary light absorption process.

Notice the gaps in the spectrum above ω_1^2, ω_2^2, etc., which arise because c^2k^2 is non-negative. It is well known that light of frequency just above a resonance, where $\epsilon<0$, cannot penetrate a material from the outside but is kept out by "metallic" reflection. In metals the first resonance lies at $\omega_1=0$ and the gap extends to rather high frequencies.

For longitudinal oscillations, the factor $(1-\delta_{s1})$ in (21) vanishes and we must find the eigenvalues at the abscissa $\omega^2\epsilon(\omega)=0$. The eigenvalue $\Omega_0=0$ is rejected because of the subsidiary condition (13), as shown in (f) below. That the eigenfrequencies of longitudinal oscillations are the roots of $\epsilon(\omega)=0$, and lie at the upper edge of metallic reflection bands, is rather well known.[7]

For $\omega_p^2 f_n \ll \omega_{n+1}^2-\omega_n^2$, there is a root near ω_n which is determined approximately by setting $\omega=\omega_n$ in all terms on the right of (20) with $n'\neq n$. Disregarding the damping, i.e., for ω_n real, the result is

$$\Omega_n^2 \sim \omega_n^2+\omega_p^2 f_n\left[1-\omega_p^2\sum_{n'\neq n}\frac{f_{n'}}{\omega_n^2-\omega_{n'}^2}\right]^{-1}. \quad (22)$$

In metals, where $\omega_1=0$, and in any case when ω_1 is small, the lowest eigenvalue Ω_α equals approximately the "plasma frequency" $\omega_p f_1^{\frac{1}{2}}$ which is, for condensed matter, of the order of 10 ev/$\hbar$. For larger values of ω_n, the shift $\Omega_n-\omega_n$ is approximately $\frac{1}{2}\omega_n^{-1}\omega_p^2 f_n[\cdots]^{-1}$, i.e., inversely proportional to ω_n itself. The upward shift of the longitudinal oscillation frequencies reflects the Coulomb repulsion between oscillator layers in opposite phase half a wavelength apart in the lattice (see Fig. 2); this effect is well known for the longitudinal infrared vibrations of ionic lattices.[24]

When $\omega_p^2 f_n$ increases to become comparable to $\omega_{n+1}^2-\omega_n^2$, the eigenvalue Ω_n rises to approach ω_{n+1}. The nature of the corresponding eigenfunction is changed in this situation. For $\omega_p^2 f_n \gg \omega_{n+1}^2-\omega_n^2$, the eigenfunction of a level way above ω_{n+1} may resemble the zero-coupling eigenfunction of the level ω_n, thus

[24] For transverse oscillations the corresponding effect is not electrostatic but magnetic and is accordingly smaller by a factor of order $(v/c)^2\sim 1/137^2$. The qualitative situation is here altogether different owing to resonance or near resonance with the photon energy levels in empty space.

indicating that eigenvalues have, in effect, crossed.[25] In metals, the plasma oscillation eigenvalue, which corresponds to a zero-coupling eigenvalue ~ 0, may lie at $\hbar\Omega_\alpha \sim 10$–$15$ ev, above other eigenvalues corresponding to inter-band transitions with zero-coupling eigenvalues $\hbar\omega_n$ of a few ev.

We face here the problem of understanding the analytical behavior of $\epsilon(\omega)$ under various circumstances. Information on the roots of $\epsilon(\omega)=0$ is provided by observational data on the spectrum of longitudinal oscillations[4] (see Sec. 6). Information on the spectral regions where the real or imaginary parts of $\epsilon(\omega)$ are large, i.e., on the spectrum of zero-coupling eigenvalues ω_n, is provided by optical data on the anomalous dispersion and absorption. (This spectrum coincides, as shown above, with the spectrum of *transverse* normal modes with $10^5 \lesssim k \lesssim 10^7$ cm^{-1} and is usually called *the* band spectrum of the material.) The problem of correlating these two types of information, under conditions of damping and strong coupling more complex than those assumed in Fig. 1 is just recently being approached.[26]

(e) Normal-Mode Eigenfunctions

In a normal mode of coupled oscillation with amplitude $\mathcal{Q}_{\alpha k s}$, the field and matter oscillators are excited with relative amplitudes and phases represented by the matrix $L_{\alpha n}(n=0, 1\cdots\infty)$ in the linear relationship

$$\mathcal{Q}_{\alpha k s}=L_{\alpha 0}q_{k s}+\sum_{n=1}^{\infty}L_{\alpha n}\bar{Q}_{n k s}. \tag{23}$$

Each row of this matrix is the eigenvector of the system (16) corresponding to an eigenvalue Ω_α. The matrix is orthogonal because the bilinear form in the Hamiltonian (15) is symmetric, but not necessarily real if the matter oscillators are treated as damped. Disregarding again this aspect, which should be treated as in Appendix A, we see that (18) represents a relationship among elements of the matrix L, namely,

$$L_{\alpha n}=-\omega_p\omega_n f_n^{\frac{1}{2}}(\Omega_\alpha^2-\omega_n^2)^{-1}L_{\alpha 0}. \tag{24}$$

The value of $L_{\alpha 0}$ remains to be determined by the orthogonality (i.e., normalization) condition. Instead of calculating the normalization factor directly, we utilize the following property of transformation matrices. If $\Omega_\alpha^2\delta_{\alpha\beta}=\sum_{nn'}L_{\alpha n}V_{nn'}(L^{-1})_{n'\beta}$, we have $L_{\alpha n}(L^{-1})_{n\alpha}=(L_{\alpha n})^2=\partial(\Omega_\alpha^2)/\partial V_{nn}$. In (15), V_{00} is represented by $c^2k^2(1-\delta_{s1})+\omega_p^2$. Here ω_p^2 is a constant and doesn't vary, and $c^2k^2(1-\delta_{s1})$ must equal $\Omega_\alpha^2\epsilon(\Omega_\alpha)$

[25] The crossing of energy levels in the presence of damping has been studied by W. Lamb, Phys. Rev. **85**, 259 (1952); see in particular pp. 272–273.

[26] See, e.g., the discussion by D. Pines in *Solid State Physics* (Academic Press, Inc., New York, 1955), Vol. 1, p. 400 ff.; also R. A. Ferrell, Phys. Rev. **101**, 554 (1956).

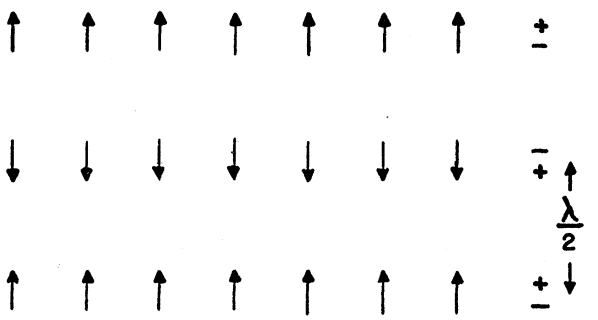

FIG. 2. Diagram of polarization layers in long-wave longitudinal excitations.

because of the secular equation (21). It follows that

$$L_{\alpha 0}=(L^{-1})_{0\alpha}=\left\{\left[\frac{d\omega^2\epsilon(\omega)}{d(\omega^2)}\right]_{\omega=\Omega_\alpha}\right\}^{-\frac{1}{2}}, \tag{25}$$

i.e., the admixture of the field oscillation in each normal mode can be expressed in terms of the dielectric constant. In particular, for the longitudinal normal mode $\alpha=0$, $\Omega_0=0$, we have

$$(L_{00})_{s=1}=[\epsilon(0)]^{-\frac{1}{2}}. \tag{26}$$

(f) Subsidiary Condition

Because of (14), (23), (24), and (25), (13) reduces to

$$\begin{aligned}\mathcal{P}_{-k1}&-\omega_p\sum_n\frac{f_n^{\frac{1}{2}}}{\omega_n}\bar{P}_{n-k1}\\ &=\sum_\alpha\left[(L^{-1})_{0\alpha}-\omega_p\sum\frac{f_n^{\frac{1}{2}}}{\omega_n}(L^{-1})_{n\alpha}\right]\mathcal{P}_{\alpha-k1}\\ &=\sum_\alpha(L^{-1})_{0\alpha}\left(1-\omega_p^2\sum_n\frac{f_n}{\Omega_\alpha^2-\omega_n^2}\right)\mathcal{P}_{\alpha-k1}\\ &=\sum_\alpha(L^{-1})_{0\alpha}\epsilon(\Omega_\alpha)\mathcal{P}_{\alpha-k1}=0.\end{aligned} \tag{27}$$

Now, for $s=1$ and $\alpha\neq 0$, we have $\epsilon(\Omega_\alpha)=0$, and (27) reduces further to

$$\mathcal{P}_{0-k1}=0. \tag{28}$$

Since the Hamiltonian term corresponding to $s=1$ and $\alpha=0$ is $\sum_k \mathcal{P}_{0k1}\mathcal{P}_{0-k1}$, the subsidiary condition (28) requires simply that there be no energy in the longitudinal mode with $\alpha=0$. This result parallels the initial requirement that there be no energy in the longitudinal components of the field in the absence of matter [$p_{-k1}=0$ for the Hamiltonian (8)].

4. COULOMB INTERACTION IN DENSE MATERIALS

Consider a number of particles with charge e and mass m (taken for simplicity to be those of electrons) at positions $\mathbf{r}_j$ in a material medium. The portion of their Hamiltonian which does not involve long-range

electromagnetic interaction we take as $\sum_j (p_j^2/2m) + V(\mathbf{r}_1 \cdots \mathbf{r}_j \cdots)$. In addition to this portion there will be an interaction H_{inter} as given by (10), with $\mathbf{r}_h$ replaced with $\mathbf{r}_j$. The total Hamiltonian for the particles, the field and the medium is

$$H=\sum_i \frac{p_j^2}{2m}+V + (4\pi)^{\frac{1}{2}}e \sum_{\mathbf{ks}} q_{\mathbf{ks}}\mathbf{e}_{\mathbf{ks}}\cdot\sum_j \tfrac{1}{2}(\dot{\mathbf{r}}_j e^{i\mathbf{k}\cdot\mathbf{r}_j}+e^{i\mathbf{k}\cdot\mathbf{r}_j}\dot{\mathbf{r}}_j) + \frac{2\pi e^2}{m}\sum_{\mathbf{ks}\mathbf{k}'s'} e_{\mathbf{ks}}\cdot e_{\mathbf{k}'s'} q_{\mathbf{ks}} q_{\mathbf{k}'s'} \sum_j e^{i(\mathbf{k}+\mathbf{k}')\cdot\mathbf{r}_j} - \tfrac{1}{2}\sum_{\alpha\mathbf{ks}} (\mathcal{P}_{\alpha\mathbf{ks}}\mathcal{P}_{\alpha-\mathbf{ks}}+\Omega_\alpha^2 \mathcal{Q}_{\alpha\mathbf{ks}}\mathcal{Q}_{\alpha-\mathbf{ks}}), \quad (29)$$

where the last sum represents the field-medium Hamiltonian (15) diagonalized by the transformation (23). The Hamiltonian (29) must be considered in conjunction with the subsidiary condition (7). The portion of ρ_k which pertains to the charges in the medium is taken into account by the introduction of the normal mode coordinates, so that (7) has the form, related to (27) and (28),

$$[\epsilon(0)]^{\frac{1}{2}}\mathcal{P}_{0-\mathbf{k}1} - i(4\pi)^{\frac{1}{2}}e\sum_j e^{-i\mathbf{k}\cdot\mathbf{r}_j}/k = 0. \quad (30)$$

We apply here the general procedure, outlined at the end of Sec. 3(b), to eliminate the subsidiary condition. The necessary transformation, which leaves every $\mathcal{P}$ unchanged except those with $\alpha=0$ and $s=1$, is

$$S=\exp\{-\hbar^{-1}[\epsilon(0)]^{-\frac{1}{2}}\sum_{\mathbf{k}} \mathcal{Q}_{0-\mathbf{k}1}(4\pi)^{\frac{1}{2}} \times e\sum_j \exp[-i\mathbf{k}\cdot\mathbf{r}_j/k]\}. \quad (31)$$

This transformation reduces (30) once more to

$$[\epsilon(0)]^{-\frac{1}{2}}\mathcal{P}_{0-\mathbf{k}1}=0 \quad (32)$$

and the terms with $\alpha=0$ and $s=1$ in (29) to

$$-\tfrac{1}{2}\sum_{\mathbf{k}}\left[\mathcal{P}_{0\mathbf{k}1}\mathcal{P}_{0-\mathbf{k}1}+2\mathcal{P}_{0\mathbf{k}1} i(4\pi)^{\frac{1}{2}}e\frac{\sum_j e^{-i\mathbf{k}\cdot\mathbf{r}_j}}{[\epsilon(0)]^{\frac{1}{2}}k} + 4\pi e^2\frac{|\sum_j e^{-i\mathbf{k}\cdot\mathbf{r}_j}|^2}{\epsilon(0)k^2}\right]. \quad (33)$$

The first two terms of (33) vanish, in effect, because of (32). The last term is the well-known representation of the Fourier components of a Coulomb interaction between charged particles at positions $\mathbf{r}_1$, $\mathbf{r}_2 \cdots \mathbf{r}_j \cdots$, divided by the zero-frequency dielectric constant, as expected from macroscopic electrostatics.

The transformation (31) also changes $\mathbf{p}_j$ in (29) into

$$\mathbf{p}_j - (4\pi)^{\frac{1}{2}}e[\epsilon(0)]^{\frac{1}{2}}\sum_{\mathbf{k}} \mathbf{e}_{-\mathbf{k}1}\mathcal{Q}_{0-\mathbf{k}1}\exp[-i\mathbf{k}\cdot\mathbf{r}_j].$$

This change cancels a portion of the interaction terms which contain

$$q_{\mathbf{k}1}=[\epsilon(0)]^{-\frac{1}{2}}\mathcal{Q}_{0\mathbf{k}1}+\sum_{\alpha>0}(L^{-1})_{0\alpha}\mathcal{Q}_{\alpha k1}, \quad (34)$$

namely the first term on the right in the expression of each $q_{\mathbf{k}1}$.

The main result (33) may be further developed to utilize a value of ϵ more appropriate than the zero-frequency one. If the charges perform a periodic, or quasi-periodic motion, with frequency ω, the appropriate value of ϵ is $\epsilon(\omega)$. This value is often smaller than $\epsilon(0)$ in that it discounts the contribution of matter oscillators with low frequencies $\omega_n<\omega$. A quantum mechanical analog of this treatment consists of applying to the Hamiltonian (29) additional transformations having the same form as (31) but with $\mathcal{Q}_{0-\mathbf{k}1}$ replaced with $\mathcal{Q}_{1-\mathbf{k}1}$, $\mathcal{Q}_{2-\mathbf{k}1}$, etc. These transformations have the following effects: (a) to reduce the interaction terms in (29) by subtracting from $q_{\mathbf{k}1}$ the additional terms indicated in (34) with $\alpha=1, 2\cdots$; (b) to replace them, in part, with additional Coulomb interactions similar to the last term in (33) with $[\epsilon(0)]^{-1}$ replaced with $[(L^{-1})_{01}]^2$, $[(L^{-1})_{02}]^2$, $\cdots$; (c) to introduce new coupling terms, analogous to the middle term of (33). Notice that, whereas the interaction terms in (29) couple the particle velocities to the oscillator amplitudes, and may be properly treated as perturbations when the particles are slow, the middle term of (23) couples, on the contrary, the particle position to the oscillator velocity, represented by $\mathcal{P}$ and will be properly treated as a perturbation when the oscillator is "slow." Thus the decision on performing additional transformations analogous to (31) constitutes a choice between alternate zero-approximation Hamiltonians.

5. DIELECTRIC RESPONSE AND VAN HOVE'S PAIR DISTRIBUTION FUNCTION

Macroscopically, when a density of "external" charge ρ_{ext} is placed in a dielectric medium, an additional density ρ_{med} is induced in the medium by polarization. The resulting total electric field $\mathbf{E}_{\text{tot}}$ consists of two parts $\mathbf{E}_{\text{ext}}$ and $\mathbf{E}_{\text{med}}$, such that $\text{div}\mathbf{E}_{\text{ext}}=4\pi\rho_{\text{ext}}$ and $\text{div}\mathbf{E}_{\text{med}}=4\pi\rho_{\text{med}}$. The relationship between $\mathbf{E}_{\text{tot}}$ and $\mathbf{E}_{\text{ext}}$ is represented in terms of the dielectric constant $\mathbf{E}_{\text{tot}}=\epsilon^{-1}\mathbf{E}_{\text{ext}}$, and similarly we have $\rho_{\text{tot}}=\epsilon^{-1}\rho_{\text{ext}}$. Because of time lag in the polarization, ϵ^{-1} is actually an operator and one must properly write

$$\mathbf{E}_{\text{tot}}(t)=\int_{-\infty}^{t}\epsilon^{-1}(t-t')\mathbf{E}_{\text{ext}}(t')dt', \qquad \rho_{\text{tot}}(t)=\int_{-\infty}^{t}\epsilon^{-1}(t-t')\rho_{\text{ext}}(t')dt'. \quad (35)$$

We want to show how this phenomenological dielectric response function may be derived by quantum me-

chanics and how it is the Fourier transform of $1/\epsilon(\omega)$, where $\epsilon(\omega)$ is the same as in the secular equation (21).

The $\mathbf{k}$th Fourier component of a conservative field $\mathbf{E}$ is $(4\pi)^{\frac{1}{2}}p_{-\mathbf{k}1}\mathbf{e}_{\mathbf{k}1}$ according to (5) and (7). We seek the expectation value of this quantity at the time t, assuming that $\langle p_{-\mathbf{k}1}\rangle$ vanishes in the initial state of the medium but that a pulsed charge distribution $\rho_{\mathbf{k}}\delta(t)$ has been applied as a perturbation at $t=0$.

If a system with Hamiltonian H is subjected to a time dependent perturbation $V(t')$, the interaction representation of an operator F at the time t is, to first order in the perturbation,

$$F+i\hbar^{-1}\int_{-\infty}^{t}dt'[\exp(i\hbar^{-1}Ht')V(t')\exp(-i\hbar^{-1}Ht'),F]. \tag{36}$$

The system field+medium of Sec. 3 is coupled to external charges by a Hamiltonian term

$$V(t)=\sum_{\mathbf{k}'s}(4\pi)^{\frac{1}{2}}q_{\mathbf{k}'s}\mathbf{e}_{\mathbf{k}'s}\cdot\mathbf{j}_{-\mathbf{k}'s}(t).$$

The pulsed charge distribution involves (because of the continuity equation) the current

$$\mathbf{j}_{-\mathbf{k}'s}=\delta_{-\mathbf{k}'\mathbf{k}}\delta_{s1}\mathbf{e}_{\mathbf{k}1}i\rho_{\mathbf{k}}k^{-1}\delta'(t).$$

We enter then in (36) the resulting expression for $V(t')$, and $F=(4\pi)^{\frac{1}{2}}p_{-\mathbf{k}1}\mathbf{e}_{\mathbf{k}1}$, leaving out the first term because its expectation value vanishes. The integration in (36) is of the type $\int_{-\infty}^{t}f(t-t')\delta'(t')dt'=f(0)\delta(t)+f'(t)\,\mathrm{St}(t)$, where the step function $\mathrm{St}(t)$ is 1 for $t>0$ and 0 for $t<0$. Since $\dot{q}_{-\mathbf{k}1}=-p_{\mathbf{k}1}$, (36) reduces to the operator

$$4\pi i\rho_{\mathbf{k}}k^{-1}\mathbf{e}_{\mathbf{k}1}i\hbar^{-1}\{[q_{-\mathbf{k}1},p_{-\mathbf{k}1}]\delta(t) +[p_{\mathbf{k}1},\exp(i\hbar^{-1}Ht)p_{-\mathbf{k}1}\exp(-i\hbar^{-1}Ht)]\,\mathrm{St}(t)\}. \tag{37}$$

The first term in the braces contributes the expectation value of $\mathbf{E}_{\mathrm{ext}}$, namely $-4\pi i\rho_{\mathbf{k}}k^{-1}\mathbf{e}_{\mathbf{k}1}\delta(t)$; the second term must represent the effect of the medium. The expectation value of the second term may be expressed as a correlation function $\langle[p_{\mathbf{k}1}(0),p_{-\mathbf{k}1}(t)]\rangle\mathrm{St}(t)$ between $p_{\mathbf{k}1}$ and $p_{-\mathbf{k}1}$ taken at an interval t apart. If $p_{\mathbf{k}1}$ and $p_{-\mathbf{k}1}$ are represented in terms of normal modes, by a transformation reciprocal to (23), each term of $p_{-\mathbf{k}1}(t)=\sum_{\alpha}(L^{-1})_{0\alpha}\mathcal{P}_{\alpha-\mathbf{k}1}(t)$ varies as a harmonic oscillator which we treat here, again for simplicity, without regard to damping.[27] The cross products $\mathcal{P}_{\alpha\mathbf{k}1}\mathcal{P}_{\beta-\mathbf{k}1}$ with $\alpha\neq\beta$, have expectation value zero, and those with $\beta=\alpha$ have the expectation value $\hbar\Omega_{\alpha}/2$, owing to (3). The expectation value of (37) is then

$$\frac{4\pi\rho_{k}}{ik}\mathbf{e}_{\mathbf{k}1}\{\delta(t)-\sum_{\alpha}[(L^{-1})_{0\alpha}]^{2}\Omega_{\alpha}\sin\Omega_{\alpha}t\,\mathrm{St}(t)\}, \tag{38}$$

where $(L^{-1})_{0\alpha}$ is given by (25).

According to the formulation of this problem, the expression in the braces should represent the response function $\epsilon^{-1}(t-t')$. Its Fourier transform is

$$1+\sum_{\alpha}\left\{\left[\frac{d\omega^{2}\epsilon(\omega)}{d(\omega^{2})}\right]_{\Omega_{\alpha}}\right\}^{-1}\left(\frac{\Omega_{\alpha}^{2}}{\omega^{2}-\Omega_{\alpha}^{2}}\right). \tag{39}$$

This function has the same poles as $[\epsilon(\omega)]^{-1}$, namely at $\omega^{2}=\Omega_{\alpha}^{2}$ for $\alpha\neq0$, the same residues at these points, namely $\{[d\epsilon/d(\omega^{2})]_{\Omega_{\alpha}}\}^{-1}$, and the same value at infinity, namely 1. Therefore it coincides with $[\epsilon(\omega)]^{-1}$,[28] and we can write

$$\delta(t)-\sum_{\alpha}[(L^{-1})_{0\alpha}]^{2}\Omega_{\alpha}\sin\Omega_{\alpha}t\,\mathrm{St}(t)=\epsilon^{-1}(t) =\frac{1}{2\pi}\int_{-\infty}^{\infty}e^{i\omega t}\frac{d\omega}{\epsilon(\omega)}. \tag{40}$$

Alternately, the correlation function $\langle[p_{\mathbf{k}1}(0),p_{-\mathbf{k}1}(t)]\rangle$ in the expectation value of (37) can be expressed in terms of the coordinates of the electrons in the medium, without introducing coupled oscillators at all. To this end, we utilize the subsidiary condition (7), where we enter $\rho_{\mathbf{k}}=e\sum_{h}\exp(-i\mathbf{k}\cdot\mathbf{r}_{h})$, as in the derivation of (13). Thus we find, instead of (40),

$$\epsilon^{-1}(t)=\delta(t)+\frac{4\pi e^{2}}{k^{2}}i\hbar^{-1}\sum_{hj}\langle[e^{i\mathbf{k}\cdot\mathbf{r}_{h}(0)},e^{-i\mathbf{k}\cdot\mathbf{r}_{j}(t)}]\rangle\,\mathrm{St}(t). \tag{41}$$

This formula does not actually depend on $\mathbf{k}$, because in the small-k (i.e., dipole) approximation the expectation value is simply proportional to k^{2}.

Equation (41) may be derived still more directly by the standard procedure of electrodynamics, which eliminates the subsidiary condition and the longitudinal field oscillators at the start and introduces instead the direct Coulomb interaction between the "external" charges and the electrons of the medium so that $V(t)=(4\pi e^{2}/k^{2})\sum_{h}\exp[i\mathbf{k}\cdot\mathbf{r}_{h}]\rho_{k}\delta(t)$. One calculates then the expectation value of the $\mathbf{k}$th Fourier component of the electron density, $\sum_{j}\exp(-i\mathbf{k}\cdot\mathbf{r}_{j})$, at the time t.

The expectation value $\sum_{hj}\langle e^{i\mathbf{k}\cdot\mathbf{r}_{h}(0)}e^{-i\mathbf{k}\cdot\mathbf{r}_{j}(t)}\rangle$ has been described by Van Hove[9] as a Fourier component of the pair distribution function

$$G(\mathbf{r},t)=\mathfrak{N}^{-1}\left\langle\sum_{hj}\int d\mathbf{r}'\delta(\mathbf{r}+\mathbf{r}_{h}(0)-\mathbf{r}')\delta(\mathbf{r}'-\mathbf{r}_{j}(t))\right\rangle. \tag{42}$$

In terms of this distribution function, (41) takes the form

$$\epsilon^{-1}(t)=\delta(t)+\frac{4\pi e^{2}\mathfrak{N}}{k^{2}\hbar}\int d\mathbf{r}e^{-i\mathbf{k}\cdot\mathbf{r}} \times i[G(\mathbf{r},t)-G(\mathbf{r},t)^{*}]\,\mathrm{St}(t). \tag{43}$$

[27] The damping should be treated as in Appendix A, leading directly to the final result (40).

[28] E.g., E. T. Whittaker and G. N. Watson, *Modern Analysis* (Cambridge University Press, Cambridge, 1946), Chap. 7.

A different dielectric response function may be defined as

$$\epsilon(t)=\frac{1}{2\pi}\int_{-\infty}^{\infty}e^{i\omega t}\epsilon(\omega)d\omega=\delta(t)+\omega_p^2\sum_n f_n\frac{\sin\omega_n t}{\omega_n}, \quad (40')$$

i.e., replacing $1/\epsilon(\omega)$ with $\epsilon(\omega)$. This function can be expressed as a correlation function, following in reverse the procedure for deriving (38). The result is formally identically with (41) except that $\mathbf{r}_j(t)$ is now defined as $\exp(i\hbar^{-1}H_{\text{medium}}t)\mathbf{r}_j\exp(-i\hbar^{-1}H_{\text{medium}}t)$ instead of $\exp(i\hbar^{-1}Ht)\mathbf{r}_j\exp(i\hbar^{-1}Ht)$. That is, the expression on the right of (41) represents either $\epsilon(t)$ or $\epsilon^{-1}(t)$ depending on whether one considers the variations of $\mathbf{r}_j(t)$ induced only by forces within the medium or, respectively, by the joint action of medium and electromagnetic field.

To summarize, we have on the one hand the treatment of Sec. 2 and 3 indicating that $\epsilon^{-1}(t)$ is represented by a series of damped oscillations, whose frequencies Ω_α are related to the frequencies of matter oscillators, without long-range interactions, as roots of the secular equation for longitudinal coupled oscillations, $\epsilon(\omega)=0$. On the other hand, the Van Hove approach gives less information but provides a definition of ϵ in terms of the mechanics of particles of the medium, which is subject to no specific assumption. In particular it involves no restriction to long waves. If k is not small, $\epsilon^{-1}(t)$ in (41) or (43) is no longer independent of k, but it may be convenient to consider in general the function $\epsilon^{-1}(t,k)$ as given by these formulas, and also its transform $[\epsilon(\omega,k)]^{-1}$ which is, according to (43) the Fourier transform in space and time of

$$\delta(t)\delta(\mathbf{r})+\frac{\mathfrak{N}e^2}{\hbar}\int d\mathbf{r}'\frac{i[G(\mathbf{r}',t)-G(\mathbf{r}',t)^*]}{|\mathbf{r}-\mathbf{r}'|}\mathrm{St}(t). \quad (43')$$

The two approaches can be combined by starting from the definition (41) of $\epsilon^{-1}(t)$ and then Fourier-analyzing the time dependence of the operator $\sum_h\exp[i\mathbf{k}\cdot\mathbf{r}_h(t)]$. This analysis can be carried out, in turn, either by a collective coordinate procedure in the manner of Tomonaga[14,22] or starting from the schematization of Sec. 2. Further, the long-range interactions between particle oscillations may be treated either as direct Coulomb interactions or as effects of coupling with longitudinal field oscillators according to Sec. 3. The explicit introduction of longitudinal field oscillators brings out the correspondence between the roles of $\epsilon(\omega)$ in determining the spectra of longitudinal and transverse oscillations.

6. INELASTIC SCATTERING OF CHARGED PARTICLES

(a) Scattering Formula

We wish to calculate in Born approximation the probability of collisions between a fast charged particle and the system of field+material medium considered in Sec. 3. In order that the results of Sec. 3 be applicable, the calculation will be restricted to collisions with small momentum transfer $\hbar\mathbf{q}$, such that $q^{-1}\gg10^{-8}$ cm. The collisions result from the interaction between the incident particle and the field, the field itself being already coupled to the medium.

The probability of collision per unit path is represented by a differential scattering coefficient $d\tau_\mathbf{q}$ which we express in the form

$$d\tau_\mathbf{q}=\frac{2}{\hbar v}\,\mathrm{Im}\left\{\sum_\alpha\frac{V_{-\mathbf{q},0\alpha}V_{\mathbf{q},\alpha0}}{\hbar(\Omega_\alpha-\omega)}\right\}dN_\mathbf{q}. \quad (44)$$

Here $\hbar\omega$ is the energy lost by the particle as a result of the momentum transfer $\hbar\mathbf{q}$ and $\hbar\Omega_\alpha$ is the excitation energy of the field+medium; $V_{\mathbf{q},\alpha0}$ is the matrix element of the interaction energy, and $dN_\mathbf{q}$ the number of final states of the scattered particle. The "imaginary part" symbol Im is introduced to specify the proper analytical treatment of the singularity at $\Omega_\alpha=\omega$.[29] Equation (44) is obtained from (2.24) of reference 29 with the following modifications: (1) Because it is understood, from Sec. 2, that Ω_α has a negative imaginary part,[30] we need not introduce explicitly a convergence factor $i\epsilon$ and take the limit $\epsilon=0$. (2) For the same reason, the product of matrix elements is not reduced to real form, nor is the Im{ } worked out explicitly; on the contrary, we aim at expressing the inelastic collision probability as the imaginary part of a more general parameter of field+medium, as is often done in the macroscopic description of dissipative effects. (3) The interaction operator R of reference 29 is replaced in Born approximation with the interaction energy operator. (4) The normalization volume L^3 has been divided out here because we calculate a scattering coefficient instead of a cross section. (5) A factor $\hbar^{-1}$, which is taken as 1 in reference 29, has been entered explicitly in (44). (6) The cross section has been summed over final states by introducing $\sum_\alpha$ and $dN_\mathbf{q}$.

(b) Interaction Matrix Elements and Normalization Factors

The incident particle will be treated relativistically, by a Dirac equation, and its interaction Hamiltonian is somewhat simpler than (10), namely,

$$V=(4\pi)^{\frac{1}{2}}eL^{-\frac{3}{2}}\sum_{\mathbf{k}s}q_{\mathbf{k}s}\mathbf{e}_{\mathbf{k}s}\cdot\boldsymbol{\alpha}ce^{i\mathbf{k}\cdot\mathbf{r}}. \quad (45)$$

Here $c\boldsymbol{\alpha}$ represents the particle velocity and the normalization volume has been taken as L^3, instead of unity as in preceding sections, to emphasize the dimensional aspect of the calculation.

In the calculation of the matrix element $V_{\mathbf{q},\alpha0}$, the integration over $d\mathbf{r}$ yields 1 for $\mathbf{k}=-\mathbf{q}$ and 0 otherwise.

[29] See, e.g., M. Gell-Mann and M. L. Goldberger, Phys. Rev. **91**, 398 (1953); see also the similar convention in reference 23.

[30] The sign of $\Omega_\alpha-\omega$ is adjusted so that Im{ } be positive.

To calculate the matrix element of the field oscillator amplitude q_{ks}, one expands into normal modes

$$q_{ks}=\sum_\alpha (L^{-1})_{0\alpha}\mathfrak{Q}_{\alpha ks}$$

and then utilizes (25) and a formula analogous to (3). One finds

$$(q_{qs})_{0\alpha}(q_{qs'})_{\alpha 0}=-\delta_{ss'}\frac{\hbar}{2\Omega_\alpha}[(L^{-1})_{0\alpha}]^2$$
$$=-\delta_{ss'}\frac{\hbar}{2\Omega_\alpha}\left\{\left[\frac{d\omega^2\epsilon(\omega)}{d(\omega^2)}\right]_{\Omega_\alpha}\right\}^{-1}. \quad (46)$$

The matrix elements of the operator $\boldsymbol{\alpha}$ must be averaged over the initial orientation of the particle spin and summed over the final one. Provided the momentum transfer is much smaller than the momentum of the incident particle, one finds as the average value the classical result

$$\langle(\mathbf{e}_{-qs}\cdot\boldsymbol{\alpha})_{-q}(\mathbf{e}_{-qs}\cdot\boldsymbol{\alpha})_q\rangle=-(\mathbf{e}_{qs}\cdot\boldsymbol{\beta})^2,$$

where $\boldsymbol{\beta}=\mathbf{v}/c$ denotes the incident particle velocity.

The number of states dN_q includes the volume element $d\mathbf{q}$ which is conveniently represented in cylindrical coordinates with $\mathbf{v}$ as an axis and φ as an azimuth about it. Since the energy and momentum changes of the particle are related by[31]

$$\mathbf{q}\cdot\mathbf{v}=\omega, \quad (47)$$

in our approximation, we have

$$dN_q=(2\pi)^{-3}L^3d\mathbf{q}=(2\pi)^{-3}L^3v^{-1}d\omega d(q^2/2)d\varphi. \quad (48)$$

(c) Differential Scattering Coefficient

Entering these results into (44) yields

$$d\tau_q=\frac{2}{\hbar v}\frac{4\pi e^2}{L^3}\sum_s \mathrm{Im}\left\{\sum_\alpha \frac{1}{2\Omega_\alpha(\Omega_\alpha-\omega)}\left[\frac{d\omega^2\epsilon(\omega)}{d(\omega^2)}\right]^{-1}_{\Omega_\alpha}\right\}$$
$$\times(\mathbf{e}_{qs}\cdot\boldsymbol{\beta})^2c^2\frac{L^3d\omega d(q^2)d\varphi}{(2\pi)^3 2v}. \quad (49)$$

Considerations similar to those applied to the $\sum_\alpha$ in (39) show that[32]

$$\mathrm{Im}\{\textstyle\sum_\alpha\cdots\}=\mathrm{Im}\{[c^2q^2(1-\delta_{s1})-\omega^2\epsilon(\omega)]^{-1}\}. \quad (50)$$

[31] Because the momentum change $\Delta\mathbf{p}=\hbar\mathbf{q}$ is small, we express the energy change as $\hbar\omega=(dE/d\mathbf{p})\cdot\hbar\mathbf{q}=\mathbf{v}\cdot\hbar\mathbf{q}$.

[32] This result holds only for Im{ } and not for { }. The scattering coefficient (44) can also be represented in terms of a correlation function, as in reference 9. The results thus obtained are related to those of this paper by the substitution

$$\mathrm{Im}\{[c^2q^2(1-\delta_{s1})-\omega^2\epsilon(\omega)]^{-1}\}=\mathrm{Im}\{\textstyle\sum_\alpha(q_{-qs})_{0\alpha}(q_{qs})_{\alpha 0}/(\Omega_\alpha-\omega)\}$$
$$=\tfrac{1}{2}\int_{-\infty}^{\infty}dt\exp(-i\omega t)\langle q_{-qs}(0)q_{qs}(t)\rangle. \quad (50')$$

This substitution, taken in reverse, expresses the Fourier transform of the correlation $\langle q_{-qs}(0)q_{qs}(t)\rangle$ in terms of the Fourier transform of the response function $\epsilon(t)$ of (41′), and thus expresses the main result of our whole calculation as a relationship between two correlation functions.

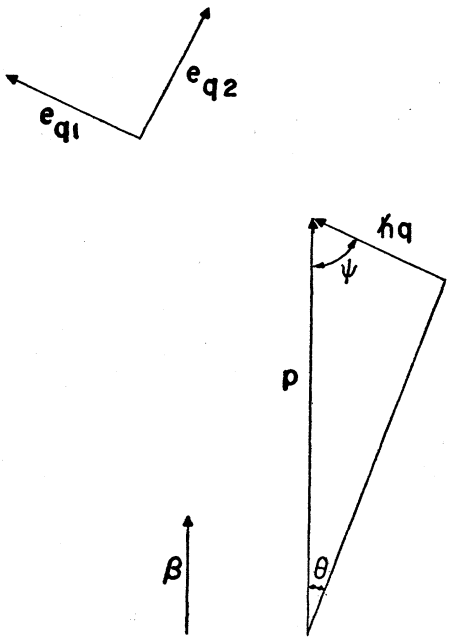

FIG. 3. Momentum transfer and polarization diagram.

Putting the polarization vector $\mathbf{e}_{q2}$ in the plane $(\boldsymbol{\beta},\mathbf{q})$, as shown in Fig. 3, and considering (47), we find

$$(\mathbf{e}_{qs}\cdot\boldsymbol{\beta})^2=\frac{\omega^2}{c^2q^2}\delta_{s1}+\left(\beta^2-\frac{\omega^2}{c^2q^2}\right)\delta_{s2}, \quad (51)$$

where the two terms correspond respectively to the longitudinal and transverse excitations. By means of (50) and (51) and integration over $d\varphi$, (49) reduces to

$$d\tau=\frac{e^2}{\pi\hbar v^2}\mathrm{Im}\left\{-\frac{1}{\epsilon(\omega)}+\frac{\beta^2c^2q^2-\omega^2}{c^2q^2-\omega^2\epsilon(\omega)}\right\}\frac{d(q^2)}{q^2}d\omega. \quad (52)$$

(d) Longitudinal Excitations

The first term of (52) yields a probability distribution of different energy losses, represented by $\mathrm{Im}[-1/\epsilon(\omega)]d\omega$, independent of the distribution of momentum transfers, $q^{-2}d(q^2)=2dq/q$. The spectrum on energy losses peaks at $\hbar\omega\sim\hbar\Omega_\alpha$ in correspondence to the normal modes of longitudinal oscillation.[5,7] As discussed in Sec. 3(d), this spectrum departs very substantially from the spectrum of energy levels $\hbar\omega_n$ of the medium without field coupling, especially when $\omega_p^2f_n\gtrsim\omega_{n+1}^2-\omega_n^2$.

The energy-momentum equation (48) fixes a lower limit on q which depends on ω, namely $q_{\min}=\omega/v$; this limit is attained when $\mathbf{q}$ is parallel to $\mathbf{v}$, i.e., the incident particle is slightly decelerated but not deflected. The deflection angle θ depends both on q and on $q_{\min}$, i.e., on ω, and also on the momentum $\mathbf{p}$ of the incident particle. In the dipole approximation we have $\theta^2=\hbar^2\times(q^2-q_{\min}^2)/p^2$ and the angular distribution of

scattering

$$\frac{d(q^2)}{q^2}=\frac{d(\theta^2)}{[(\hbar^2\omega^2/p^2v^2)+\theta^2]}, \tag{53}$$

which was previously known from semiclassical calculation[2] and quantum-mechanically for collisions with atoms,[8,12] and which has been derived by Ferrell[26] from the theory of plasma excitations.

The probability of longitudinal excitations $\hbar\omega$, irrespective of deflection or momentum transfer, is obtained by integrating (53). The lower limit $q_{\min}$ to the integral yields $\log(v^2/\omega^2)$. At the upper limit the dipole approximation breaks down and one must take into account the dependence of $\epsilon(\omega)$ on q, discussed at the end of Sec. 5. This functional dependence is not known in any detail, except for atomic H,[8,33] whereas in the dipole approximation $\epsilon(\omega)$ is known to some extent from optical experiments. The total probability of all longitudinal excitations results by further integration over $d\omega$ and is still more poorly known.

Within the dipole approximation, however, one can consider the probability of all longitudinal excitations with a deflection no larger than some limit $\Theta_{\max}$ such that $\hbar/p\Theta_{\max}\sim q_{\max}^{-1}\gg 10^{-8}$ cm. This probability is

$$\tau_{\text{long}}(\theta\leqslant\Theta_{\max})$$
$$=\frac{e^2}{\pi\hbar v^2}\operatorname{Im}\int_0^\infty -\frac{d\omega}{\epsilon(\omega)}\int_0^{\Theta_{\max}}\frac{d(\theta^2)}{(\hbar^2\omega^2/p^2v^2)+\theta^2}$$
$$=\frac{e^2}{\pi\hbar v^2}\operatorname{Im}\int_0^\infty -\frac{d\omega}{\epsilon(\omega)}\ln\left(\frac{p^2v^2\Theta_{\max}^2}{\hbar^2\omega^2}\right). \tag{54}$$

Of greater practical interest is the expectation value of the energy dissipated in longitudinal excitations (including ionizations) per unit path, obtained by multiplying with $\hbar\omega$ before integration,

$$\frac{dW_{\text{long}}}{dx}=\frac{e^2}{\pi v^2}\operatorname{Im}\left\{\int_0^\infty -\frac{\omega d\omega}{\epsilon(\omega)}\int_{q_{\min}}\frac{d(q^2)}{q^2}\right\}. \tag{55}$$

This expression is more tractable because one can integrate in (55) over ω *at constant* q analytically. Utilizing the symmetry property of (20), $\epsilon(-\omega)=\epsilon^*(\omega)$, and (40), one finds

$$\operatorname{Im}\int_0^\infty -\frac{\omega d\omega}{\epsilon(\omega)}=\tfrac{1}{2}\int_{-\infty}^\infty\frac{i\omega d\omega}{\epsilon(\omega)}=\pi\left[\frac{d\epsilon^{-1}(t)}{dt}\right]_{t=0}=\frac{\pi}{2}\omega_p^2, \tag{56}$$

irrespective of the value of q. Because the lower limit $q_{\min}=\omega/v$ depends on ω, one may define an effective limit $\tilde{\omega}/v$ by

$$\operatorname{Im}\int_0^\infty -\frac{\omega d\omega}{\epsilon(\omega)}\ln\omega=\frac{\pi}{2}\omega_p^2\ln\tilde{\omega}. \tag{57}$$

[33] U. Fano, Phys. Rev. **95**, 1198 (1954).

The quantity $\hbar\tilde{\omega}$ is determined experimentally and is often indicated by ZI. The upper limit of the integral over q^2 need not be discussed here and is denoted by $q_{\max}^2$, independent of ω. With these conventions, the "longitudinal stopping power" (55) is

$$\frac{dW_{\text{long}}}{dx}=\frac{e^2}{\pi v^2}\frac{\pi}{2}\omega_p^2\ln\left(\frac{q_{\max}^2v^2}{\tilde{\omega}^2}\right)=\frac{2\pi\mathfrak{N}e^4}{mv^2}\ln\left(\frac{q_{\max}^2v^2}{\tilde{\omega}^2}\right). \tag{58}$$

This result takes into account the so-called "zero-energy density effect." It differs from the corresponding results obtained by ordinary atomic theory[8] by including the effective frequency $\tilde{\omega}$ instead of another parameter $\bar{\omega}$ defined by $\operatorname{Im}\int_0^\infty\epsilon(\omega)\omega d\omega\ln\omega=\frac{1}{2}\pi\omega_p^2\ln\bar{\omega}$.[34] The difference between $\tilde{\omega}$ and $\bar{\omega}$ reflects the upward shift of the longitudinal oscillation frequencies discussed in Sec. 3 and due to long-range Coulomb interactions. (The experiments on stopping power determine $\bar{\omega}$ rather than $\tilde{\omega}$.) As v approaches the light velocity, (58) approaches a minimum value, except for variations of $q_{\max}$ with which we are not concerned. That is, there is no "relativistic rise" in the probability of longitudinal excitations with small momentum transfer. A nonrelativistic treatment of the incident particle gives the same result as a relativistic one.[12]

Notice, finally, that the probability of longitudinal excitations, as given by (52), can also be derived directly from the Bethe theory,[8] without introducing explicitly any consideration of interactions within the medium. The cross section for excitation of a level with energy $\hbar\Omega_\alpha$ is given by Bethe in the form

$$(2\pi e^4/mv^2)(dQ/Q^2)|F_\alpha(q)|^2,$$

where $Q=\hbar^2q^2/2m$ and $F_\alpha(q)$ is the matrix element of $\sum_h\exp(i\mathbf{q}\cdot\mathbf{r}_h)$ connecting the ground state and the state α. If we agree to extend the $\sum_h$ over all electrons in a unit volume, the cross section is changed into the probability $d\tau_\alpha$ per unit path. The probability of an energy loss $\hbar\omega$ is expressed by replacing $|F_\alpha(q)|^2$ in Bethe's formula with

$$\sum_\alpha|F_\alpha(q)|^2\delta(\Omega_\alpha-\omega)=(2\pi)^{-1}\int_{-\infty}^\infty dt\sum_\alpha|F_\alpha(q)|^2\times\exp[i(\Omega_\alpha-\omega)t].$$

One may then apply the closure theorem according to Van Hove,[9] after which the result can be expressed in terms of the dielectric constant by means of (41).

[34] The formulas

$$\tilde{\omega}=\prod_n\omega_n^{f_n},\quad\text{or}\quad\ln\tilde{\omega}=\sum_n f_n\ln\omega_n,$$

follow by taking $\epsilon(\omega)$ in the form (20). Similar formulas,

$$\bar{\omega}=\prod_\alpha\Omega_\alpha^{F_\alpha},\quad\ln\bar{\omega}=\sum_\alpha F_\alpha\ln\Omega_\alpha,$$

with $F_\alpha=\{\omega_p^2[d\epsilon/d(\omega^2)]_{\Omega_\alpha}\}^{-1}$, follow by taking $[\epsilon(\omega)]^{-1}$ in the form (39). Note that $\sum_\alpha F_\alpha=1$, so that the F_α's may be regarded as modified oscillator strengths.

(e) Transverse Excitations

For these processes the distribution of energy losses $\hbar\omega$ and of momentum transfers $\hbar\mathbf{q}$ may be discussed with reference to the diagram in Fig. 1(b). Each collision with a given ω and q is represented in the diagram by a point with coordinates $c^2k^2=c^2q^2$ and ω^2. The relationship (47) between ω and $\mathbf{q}$ requires that the representative points lie on the lower right side of the straight line $\omega^2=v^2q^2$ with slope $\beta^2=v^2/c^2$. On this line, the numerator of the second term in (52), which represents $c^2q^2(\mathbf{e}_{q2}\cdot\boldsymbol{\beta})^2$ vanishes because the particle velocity has no component transverse to a deceleration without deflection.

The mechanism of transverse excitations by a fast particle is electromagnetic and as such becomes important only when the particle approaches the light velocity. Indeed most of the diagram in Fig. 1(b) is excluded when the slope β^2 is small, the more so because excitations with large q are unlikely anyhow as discussed below.

Under the conditions of Fig. 1, namely matter oscillators with well-separated frequencies ω_n and small damping, the points representing energy and momentum transfers (ω,q) are confined to the lines in the graph which represent the eigenvalues of the secular equation (21), $c^2q^2-\omega^2\epsilon(\omega)=0$, i.e., the poles of the second term in (52). Energy-wise, the eigenvalues are very close to the excitation energies $\hbar\omega_n$ of matter uncoupled with the field whenever the field-matter coupling constitutes a small perturbation, i.e., for $\omega_p^2f_n\ll c^2q^2-\omega_n^2$. This condition is always fullfiled for large q. In this event the result (52) reduces to that of ordinary atomic theory[12] by expansion of $[c^2q^2-\omega^2\epsilon(\omega)]^{-1}$ into powers of $\mathrm{Im}\epsilon(\omega)/[c^2q^2-\omega^2\,\mathrm{Re}\epsilon(\omega)]$, with $\mathrm{Re}\epsilon(\omega)\sim1$; the leading term is proportional to $(c^2q^2-\omega^2)^{-2}$ and itself vanishes rapidly as q increases.

On the other hand, when $\omega_pf_n^{\frac{1}{2}}$ and cq are of the order of ω_n, the eigenvalues depart substantially from the unperturbed values ω_n. As soon as this departure is much larger than the line width corresponding to the damping of ω_n, the transverse excitations will be nearly undamped and constitute the Čerenkov radiation. As shown in Fig. 3, the angle of emission of this radiation is

$$\psi=\arcsin\left(\frac{\mathbf{e}_{q1}\cdot\boldsymbol{\beta}}{\beta}\right)=\arccos\left(\frac{1}{\beta[\epsilon(\omega)]^{\frac{1}{2}}}\right) \quad (59)$$

and does not vanish, even when ω approaches 0, provided β and $\epsilon(0)$ are sufficiently large.

Even when the coupling constant $\omega_pf_n^{\frac{1}{2}}$ is very small, it plays a role when β is so close to 1 that the dot-dashed line in Fig. 1 intersects the weak-coupling broken line in its brief curved portion near $(c^2q^2=\omega_n^2,\omega_n^2)$. The curvature is due to the coupling; in its absence the probability of inelastic collision would diverge in the limit $\beta=1$.[12] (This divergence is reflected in the indefinite relativistic rise of the stopping power in calculations that do not take into account the "density effect.")

The qualitative analysis of transverse excitations becomes more difficult under conditions where the diagram of Fig. 1 is unrealistic, namely when the line width of matter oscillations or the coupling constant $\omega_pf_n^{\frac{1}{2}}$, or both, become of the order of the line separations $\omega_{n+1}-\omega_n$. Budini[5] and Sternheimer[35] pointed out that tighly coupled transverse excitations will not appear as Čerenkov radiations if the damping is too strong.

In any event, it remains true that transitions with $c^2q^2\gg\omega^2$ are quite infrequent, because the imaginary part of the second term of (52) approaches zero rapidly as c^2q^2 becomes very large. The transverse interaction mechanism becomes important again only for very large values of q and ω, when the energy taken up by an electron in the medium is itself relativistic, that is, in a quite different type of collision with which we are not concerned.

We can then calculate an integrated probability of transverse excitations within the dipole approximation, without having to set an explicit limitation to the deflection angle as was done for longitudinal excitations in (54). We have

$$\begin{aligned}\tau_{\mathrm{trans}}&=\frac{e^2}{\pi\hbar v^2}\,\mathrm{Im}\int_0^\infty d\omega\int_{\omega^2/v^2}^\infty\frac{\beta^2c^2q^2-\omega^2}{c^2q^2-\omega^2\epsilon(\omega)}\,\frac{d(q^2)}{q^2}\\&=\frac{e^2}{\pi\hbar v^2}\,\mathrm{Im}\int_0^\infty d\omega\lim_{A=\infty}\left\{\frac{1}{\epsilon(\omega)}\ln(1+A)\right.\\&\qquad\left.+\left[\beta^2-\frac{1}{\epsilon(\omega)}\right]\ln\left[1+\frac{A}{1-\beta^2\epsilon(\omega)}\right]\right\}\\&=\frac{e^2}{\pi\hbar v^2}\,\mathrm{Im}\int_0^\infty d\omega\left[\beta^2-\frac{1}{\epsilon(\omega)}\right]\ln\left(\frac{1}{1-\beta^2\epsilon(\omega)}\right), \quad (60)\end{aligned}$$

where a term $\beta^2\lim_{A\to\infty}A$ has been deleted from the integrand because it is real. The corresponding expectation value of the energy loss is

$$\begin{aligned}\frac{dW_{\mathrm{trans}}}{dx}&=\frac{e^2}{\pi v^2}\,\mathrm{Im}\int_0^\infty\omega d\omega\left[\beta^2-\frac{1}{\epsilon(\omega)}\right]\ln\left(\frac{1}{1-\beta^2\epsilon(\omega)}\right)\\&=\frac{e^2}{2\pi iv^2}\int_{-\infty}^\infty\omega d\omega\left[\beta-\frac{1}{\epsilon(\omega)}\right]\ln\left(\frac{1}{1-\beta^2\epsilon(\omega)}\right), \quad (61)\end{aligned}$$

the latter because $\epsilon(-\omega)=\epsilon^*(\omega)$.

[35] R. M. Sternheimer 88, 851 (1952). Sternheimer and Budini utilized approximations equivalent to the solution (22) of the longitudinal problem, which implies no strong mixing of different modes of oscillation of matter. See also Appendix B.

(f) Connection with the Theory of the "Density Effect"

Equations (54) and (60) together, or (58) and (61), are readily seen to be equivalent to the results of the Fermi theory.[2,5] Note that $\hbar/p\Theta_{\max}$ in (54) is equivalent to the cutoff radius ρ of the Fermi theory, and that $-1/\epsilon(\omega)$ in (54) through (57) can be replaced with $\beta^2-1/\epsilon(\omega)$ because β^2 is real and does not contribute to the result.

All these formulas reduce to those of the ordinary atomic theory[8,12] of collisions if one takes $\epsilon(\omega)=1+i\,\mathrm{Im}\epsilon(\omega)$ and expands into powers of $\mathrm{Im}\epsilon(\omega)$ to first order.

To separate out the contribution of the Čerenkov radiation to (60) and (61), one may rewrite these formulas according to Budini,[5,36] setting $\epsilon=a+ib$ and separating out the real and imaginary parts, especially in the logarithmic factor.[37]

Various expressions for the equations of the density effect theory are given in Appendix B.

7. CONCLUSIONS

Whereas electrodynamic processes in dense materials had been previously interpreted in somewhat fragmentary fashion, the various points of view are now seen to fit well together in a single formulation, starting from an atomistic, quantum mechanical description of matter and of the electromagnetic field.

In particular, as surmised from the classical model, the rather high frequency of the plasma oscillations of metal electrons represents a special case of the general upward shift of all frequencies of longitudinal long-wave electric oscillations. This shift results from long-range Coulomb interactions, which affect all longitudinal collective oscillations whether "plasma" or "interband," and has no direct analog for transverse oscillations. Because the plasma oscillations constitute a special case of longitudinal collective oscillation, it may be a matter of semantics whether a longitudinal excitation observed in some particular material should be attributed to plasma effect. The angular distribution of inelastic electron scattering and the dependence of the excitation energy on the momentum transfer $\hbar\mathbf{q}$ (which becomes appreciable when $q\sim10^7$ cm^{-1})[38] do not readily provide criteria for classifying the excitation.

[36] P. Budini and L. Taffara, Nuovo cimento **3**, 23 (1956).

[37] The treatment in Sec. 3 of reference 5 does not stress that the spectrum is different for transverse and longitudinal excitations. The zeros of $\epsilon(\omega)$ are poles of the integrand for the longitudinal excitation formulas, and indeed $\mathrm{Im}[-1/\epsilon(\omega)]$ peaks near these zeros. This is not the case for the transverse excitation formulas because the logarithms vanish when $\epsilon(\omega)=0$.

[38] H. Watanabe, J. Phys. Soc. Japan **11**, 112 (1956) has observed a variation $\Omega_\alpha(q)\sim\Omega_\alpha(0)+a^2q^2+b^2q^4$ with $a\sim10^{-7}$ cm and $b\ll a$, for q up to $\sim10^8$ cm^{-1}. At the Electron Physics conference of the University of Maryland (April 23–25, 1956), Watanabe, Pines, and others pointed out that the rapid convergence of the expansion in powers of q^2 is readily explained by plasma oscillation theories, whereas other theories would not lead to the same result, according to Pines.

The following points appear to deserve further study:

(1) The foundations of the oscillator model of matter excitations. The discussion of Sec. 2 is admittedly sketchy and aims only at pointing out that the model rests on very general assumptions. It remains to be determined more closely how well the necessary assumptions are fulfilled in realistic conditions and what can be said about the parameters of the model (spectral distribution and damping of the oscillators) for various types of matter.

(2) Extension of the Tomonaga theory,[14] particularly in the directions indicated in reference 22, at the end of Sec. 5, and in reference 32, to link up firmly with the treatment based on the oscillator model.

(3) Extension of the theory of Sec. 3 to take into account the off-diagonal terms of the second (quadratic) interaction term in (10), which couple oscillators with different momenta.

(4) Extended analysis of the level diagram in Fig. 1 to conditions of still stronger coupling $\omega_p^2 f_n$ and strong damping, i.e., deeper study of the complex function $\epsilon(\omega)$ for various types of material [see end of Sec. 3(d)].

(5) Extension to shorter wave excitations, treating in greater detail the transition from long-range to short-range interactions and from long-wave to short-wave excitations, for which the collective aspects become irrelevant.

(6) Consideration of the effects of exchange between "external" particles and the particles of the medium, which were disregarded in this paper.

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APPENDIX A

The complex-frequency formalism serves to treat in abbreviated form the coupling of the collective coordinate $\bar{Q}_{nks}$ with other coordinates $x_{n\nu}$ of the medium which oscillate with frequencies near ω_n. The entire system of coupled oscillators is conservative and the complex formalism is to be introduced only toward the end of the calculation.

Consider, then, an oscillator with amplitude Q_n and *real* frequency $\tilde{\omega}_n$, coupled with oscillators x_n with force constants $\omega_{n\nu}^2=\tilde{\omega}_n^2+\nu\delta$, with ν integer and running from $-\infty$ to ∞ and with δ small and to be set eventually at zero. The coupling constant between Q_n and each of the $x_{n\nu}$ is assumed independent of ν and is called β_n. The influence of all other oscillators upon Q_n must eventually express itself in terms of β_n alone, or rather in terms of $\tilde{\beta}_n^2=\lim_{\delta=0}(\beta_n^2/\delta)$. The normal-mode frequencies of these coupled oscillators are found, through equations analogous to (16), (17) and (18), to be the

roots of the secular equation

$$\omega^2-\tilde{\omega}_n^2-\sum_\nu \frac{\beta_n^2}{\omega^2-\tilde{\omega}_n^2-\nu\delta}=\omega^2-\tilde{\omega}_n^2-\bar{\beta}_n^2\pi\cot\left[\pi\frac{\omega^2-\tilde{\omega}_n^2}{\delta}\right]$$
$$=\omega^2-\tilde{\omega}_n^2-\bar{\beta}_n^2\Lambda=0. \quad \text{(A1)}$$

As a function of ω^2, Λ varies from $-\infty$ to ∞ in every interval δ, so that each interval includes a root $\omega_{n\nu}^2$ of (A1).

If the Hamiltonian (15) is generalized to include the coupling of each matter oscillator $\bar{Q}_{nks}$ to other oscillators $x_{n\nu}$, one finds, instead of (20),

$$\epsilon(\omega)=1-\omega_p^2\sum_n f_n\frac{1-\bar{\beta}_n^2\Lambda/\omega^2}{\omega^2-\tilde{\omega}_n^2-\bar{\beta}_n^2\Lambda}, \quad \text{(A2)}$$

where the effect of this further coupling is represented by $\bar{\beta}_n^2\Lambda$. This new expression may be brought to the usual form of a dispersion equation, in terms of the normal mode frequencies $\omega_{n\nu}$, by representing the function $\epsilon(\omega)$ in terms of the residues at its poles $\omega^2=\omega_{n\nu}^2$,

$$\epsilon(\omega)=1-\omega_p^2\sum_n f_n\sum_\nu\frac{1-\bar{\beta}_n^2\Lambda(\omega_{n\nu}^2)/\omega_{n\nu}^2}{\omega^2-\omega_{n\nu}^2}$$
$$\times\left[\left(-\bar{\beta}_n^2\frac{d\Lambda}{d(\omega^2)}\right)_{\omega_{n\nu}^2}\right]^{-1}. \quad \text{(A3)}$$

Since $\bar{\beta}_n^2\Lambda(\omega_{n\nu}^2)=\omega_{n\nu}^2-\tilde{\omega}_n^2$ and $-d(\cot x)/dx=1+\cot^2 x$, (A3) reduces to

$$\epsilon(\omega)=1-\omega_p^2\sum_n f_n\sum_\nu\frac{1-(\omega_{n\nu}^2-\tilde{\omega}_n^2)/\omega_{n\nu}^2}{\omega^2-\omega_{n\nu}^2}$$
$$\times\frac{\bar{\beta}_n^2\delta}{(\omega_{n\nu}^2-\tilde{\omega}_n^2)^2+\pi^2\bar{\beta}_n^4}$$
$$=1-\omega_p^2\sum_n f_n\int_0^\infty d(\omega_{n\nu}^2)\frac{1-(\omega_{n\nu}^2-\tilde{\omega}_n^2)/\omega_{n\nu}^2}{\omega^2-\omega_{n\nu}^2}$$
$$\times\frac{\bar{\beta}_n^2}{(\omega_{n\nu}^2-\tilde{\omega}_n^2)+\pi^2\bar{\beta}_n^4} \quad \text{(A4)}$$

where the interval δ has become a differential. Thus we have returned to the Sellmeyer-Drude dispersion formula with oscillator strengths distributed continuously in $\omega_{n\nu}^2$ according to

$$f_n\left[1-\frac{\omega_{n\nu}^2-\tilde{\omega}_n^2}{\omega_{n\nu}^2}\right]\frac{\bar{\beta}_n^2}{(\omega_{n\nu}^2-\tilde{\omega}_n^2)^2+\pi^2\bar{\beta}_n^4}, \quad \text{(A5)}$$

that is, in the shape of the intensity spectrum of a single damped oscillator with frequency $\tilde{\omega}_n$ and "line width" $\pi\bar{\beta}_n^2/\tilde{\omega}_n$. The distortion of the line shape, represented by the factor in brackets, as well as the effect of tail cutoff at $\omega_{n\nu}^2=0$ will be disregarded in the approximation $\pi\bar{\beta}_n^2\ll\tilde{\omega}_n^2$.

When the real dielectric constant expression (A4) is entered in the secular equation (21), the system field +oscillators $\bar{Q}_{nks}$+oscillators $x_{n\nu}$ turns out to have a continuous distribution of real normal mode frequencies, whereas the complex expression (20) yields a discrete distribution of complex frequencies. It remains to be shown that the two distributions are equivalent for realistic applications. (Remember that a system with a continuous spectrum of stationary states would require an infinite time to settle in a stationary state, so one needs consider only its transient states.)

A complex variable may be introduced in (A4) when one considers more closely the mathematical definition of the resonance denominator $(\omega^2-\omega_{n\nu}^2)^{-1}$. This definition should in fact be specified when the denominator is first introduced in (17) or (A2). Typically, when an oscillator of frequency ω_0 is impulse-excited, the Fourier transform of its sinusodial amplitude variations is properly defined as $\lim_{\tau=0}[\omega_0^2-(\omega-i\tau)^2]^{-1}$. We replace then ω^2 in (A4) with $\omega-i\tau$ and carry out the integral over $\omega_{n\nu}^2$, extending it to $-\infty$ and disregarding the factor $[1-\cdots]$ in the numerator, as noted above. The result is

$$\epsilon(\omega)=1-\omega_p^2\sum_n\frac{f_n}{(\omega-i\tau)^2-\tilde{\omega}_n^2+i\pi\bar{\beta}_n^2\omega/|\omega|}, \quad \text{(A6)}$$

which reduces to (20) in the limit $\tau=0$ and in the approximation $\pi\bar{\beta}_n^2\ll\tilde{\omega}_n^2$ in which we set $|\omega_n|^2=\tilde{\omega}_n^2$ and $\omega_n-\tilde{\omega}_n^*=\pi\bar{\beta}^2/|\omega|$.

APPENDIX B. FORMULAS FOR DENSITY EFFECT CALCULATIONS

When the stopping power is resolved into a longitudinal and a transverse component, given respectively by (58) and (61), the density effect calculation splits up accordingly.

The longitudinal, or "zero-energy," density effect has been discussed below Eq. (58). Information regarding the effective frequency $\tilde{\omega}$ for specified materials, from experimental or theoretical data, is still quite inadequate.[39] Also inadequate is the information[40] on the relationship between the effective frequencies $\tilde{\omega}$ and $\tilde{\omega}$ [34] for specified chemical substances, or, more specifically, on the dependence of $\tilde{\omega}$ on the density of the substance. (Note that $\tilde{\omega}$ is the zero-density limit of $\tilde{\omega}$.)

For the transverse stopping power, the integral in (61) is usually evaluated by shifting the path of integration toward $\omega=i\infty$. Integration from $-\infty$ to ∞ along a half-circle of infinitely large radius in the upper complex plane contributes to dW_{trans}/dx the amount

$$\left(\frac{e^2}{2v^2}\right)\omega_p^2\left[\ln\left(\frac{1}{1-\beta^2}\right)-\beta^2\right], \quad \text{(B1)}$$

[39] See, e.g., D. O. Caldwell, Phys. Rev. **100**, 291 (1955).
[40] R. M. Sternheimer, Phys. Rev. **93**, 351 (1954).

which one finds from atomic theory.[12] This amount stems entirely from the second term of the large-ω expansion $\epsilon^{-1}=1+\omega_p^2/\omega^2+\cdots$ and is simply proportional to the density of electrons in the material. In addition, if β^2 and $\epsilon(0)$ are so large that $1-\beta^2\epsilon(0)<0$, the values of $\ln(1-\beta^2\epsilon)$ at $\omega=0\pm\delta$ differ by $2\pi i$ and one must regard the plane of the complex variable ω as cut along the imaginary axis from $\omega=0$ to $\omega=il$, where l is the single root of $1-\beta^2\epsilon(il)=0$. Integration along this cut yields the high-energy density-effect correction to be subtracted from (B1),

$$\frac{e^2}{v^2}\int_0^l\left[\beta^2-\frac{1}{\epsilon(iy)}\right]ydy, \tag{B2}$$

so that

$$\frac{dW_{\text{trans}}}{dx}=\frac{e^2}{v^2}\left\{\tfrac{1}{2}\omega_p^2\left[\ln\left(\frac{1}{1-\beta^2}\right)-\beta^2\right]-\int_0^l\left[\beta^2-\frac{1}{\epsilon(iy)}\right]ydy\right\}. \tag{B3}$$

This formula should prove convenient because $1/\epsilon(iy)$ is a smooth monotonically increasing function of y,[41] suitable for numerical evaluation. Alternately, the integration path in (B3) can be brought back to the positive real axis of ω, utilizing a formula of complex variable integration,[42] which yields

$$\frac{dW_{\text{trans}}}{dx}=\frac{e^2}{v^2}\left\{\tfrac{1}{2}\omega_p^2\left[\ln\left(\frac{1}{1-\beta^2}\right)-\beta^2\right]+\tfrac{1}{2}l^2(1-\beta^2)-\frac{1}{\pi}\int_0^\infty\omega d\omega\,\mathrm{Im}\left(-\frac{1}{\epsilon(\omega)}\right)\ln\left(\frac{\omega^2+l^2}{\omega^2}\right)\right\}. \tag{B4}$$

This formula may be condensed, by means of (56), to

$$\frac{dW_{\text{trans}}}{dx}=\frac{e^2}{2v^2}\omega_p^2\left\{\frac{2}{\pi\omega_p^2}\int_0^\infty\omega d\omega\,\mathrm{Im}\left(-\frac{1}{\epsilon(\omega)}\right)\times\ln\left(\frac{\omega^2}{(\omega^2+l^2)(1-\beta^2)}\right)+\frac{l^2}{\omega_p^2}(1-\beta^2)-\beta^2\right\}, \tag{B5}$$

which might be convenient for numerical calculation if data become available on the function $\mathrm{Im}[-1/\epsilon(\omega)]$, which measures the differential probability of longitudinal excitations.[43]

If $1/\epsilon$ is represented, according to (39) and to reference 34, as $1+\omega_p^2\sum_\alpha F_\alpha/(\omega^2-\Omega_\alpha^2)$, (B4) and (B5) reduce to

$$\frac{dW_{\text{trans}}}{dx}=\frac{e^2}{2v^2}\omega_p^2\left\{\ln\left(\frac{1}{1-\beta^2}\right)-\beta^2+\frac{l^2}{\omega_p^2}(1-\beta^2)-\sum_\alpha F_\alpha\ln\left(\frac{\Omega_\alpha^2+l^2}{\Omega_\alpha^2}\right)\right\} \tag{B6}$$

$$=\frac{e^2}{2v^2}\omega_p^2\left\{\sum_\alpha F_\alpha\ln\left(\frac{\Omega_\alpha^2}{(\Omega_\alpha^2+l^2)(1-\beta^2)}\right)-\beta^2+\frac{l^2}{\omega_p^2}(1-\beta^2)\right\}. \tag{B7}$$

Equations (B4) and (B6) clearly reduce to (B1) in the limit $l=0$ [no density effect, $\beta^2\leq 1/\epsilon(0)$]. The last two terms in the braces of (B6), which represent the density effect, differ from (1) of reference 35 only by the replacement of the usual oscillator strengths f_n with the F_α and of ω_n with Ω_α.[43] (This difference probably lies within the limits of accuracy of the calculations of reference 35 which assume a coarse distribution of oscillator strengths and frequencies.) In the limiting case where the stopping power is fully saturated by the density effect [$\beta\sim 1$, l large, $\epsilon(il)\sim 1-\omega_p^2/l^2$, $(l^2/\omega_p^2)(1-\beta^2)\sim 1$], (B5) and (B7) easily reduce to

$$\left(\frac{dW_{\text{trans}}}{dx}\right)_{\max}=\frac{e^2}{2v^2}\omega_p^2\left\{\ln\left(\frac{\tilde{\omega}^2}{\omega_p^2}\right)+1-\beta^2\right\} \tag{B8}$$

owing to (57).

[41] G. C. Wick, Ricerca sci. **12**, 858 (1941).

[42] For a function $f(\omega)$ which: (*a*) has no singularity in the upper half-plane, (*b*) vanishes at $\omega=\infty$, and (*c*) equals $f^*(-\omega)$, one finds

$$f(iy)=(2\pi i)^{-1}\int_{-\infty}^{\infty}f(\omega)d\omega[(\omega-iy)^{-1}+(\omega+iy)^{-1}]=(2/\pi)\int_0^\infty\omega d\omega\,\mathrm{Im}f(\omega)/(\omega^2+y^2).$$

We take $f=1-1/\epsilon$.

[43] This relationship to the spectrum of longitudinal excitations has no immediate physical meaning, in view of the remark in reference 36.