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COLLECTIVE OSCILLATIONS OF ELECTRONS IN CRYSTALS

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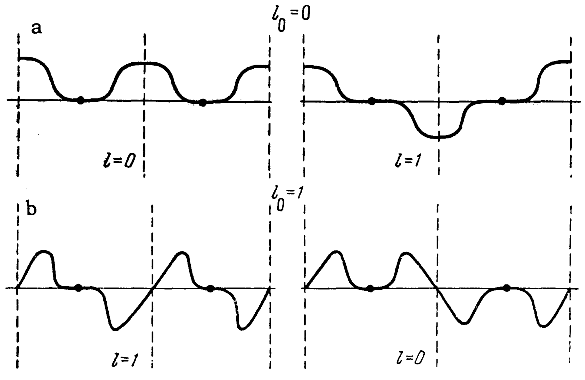
Collective oscillations of electrons distributed with periodic density in a lattice are considered as quasi-hydrodynamic oscillations of a degenerate non-uniform gas of electrons. Properties of the various levels are analyzed and the probabilities of exciting collective oscillations by light and by charged particles are calculated. Quantitative estimates of the position of the levels are compared with data concerning characteristic losses of electrons in thin films.

1. INTRODUCTION

ATTEMPTS have been made to apply the theory of collective oscillations of a plasma to the valence electrons in a crystal by considering them as a degenerate Fermi gas (see, for instance, the review article by Pines[1]). At the present time it is not clear whether such oscillations, "plasmons," are stable enough to be considered as actually existing. There is no doubt that the lifetime of a plasmon is small, and the probability that it will be converted to the excitation of separate electrons and to thermal motion is large. However, the successful interpretation on this basis of certain characteristic energy losses of electrons passing through solid films[1] obliges us to direct ourselves seriously to the problem of the collective oscillations of electrons in crystals and, above all, to attempt to broaden the circle of phenomena under study which are connected with plasmons.



a – Form of the oscillations for even l_0, $l_0 = 0$. For k = 0 only the term $l = 0$ appears; ρ belongs to the type $\rho_l = \rho_0{}^{(s)}$ – in neighboring cells the function is the same. For kd = π principally the term $l = 1$ is represented; ρ belongs to the type $\rho_1{}^{(s)}$ – in neighboring cells the functions differs in sign, $\exp(i\mathbf{k}\cdot\mathbf{d}) = -1$. b – Form of the oscillations for odd l_0, $l_0 = 1$. For k = 0 only the term $l = 1$ appears; ρ belongs to the type $\rho = \rho_1{}^{(a)}$ – in neighboring cells the function is the same. For kd = π principally the terms $l = 0$ and $l = 2$ are represented; ρ belongs to the type $\rho_0{}^{(a)}$ and $\rho_2{}^{(a)}$ – in neighboring cells the functions differ in sign.

The theory of collective oscillations is applied to crystals in a quite elementary way.[1,2] For a uniform degenerate gas of free electrons the following dispersion equations are used:

$$\omega^2 = \omega_p^2 + \langle v^2 \rangle k^2, \qquad \omega_p^2 = 4\pi\rho_0 e^2/m, \tag{1}$$

where ω, k are the frequency and wave number of a plasmon; $\langle v^2 \rangle$ is the average square of the thermal velocity of the electrons,

$$\langle v^2 \rangle = \frac{3}{5} v_{\max}^2 = \frac{3}{5}(3\pi)^{2/3}\frac{\hbar^2}{m^2}\rho_0^{2/3};$$

ρ_0 is the average number density of the electrons; e is the charge and m the mass of an electron. The relation (1) and the condition of its applicability were obtained from a kinetic equation.[3-5] It was shown that the quantum correction is small.[3] This relation is valid (or, a plasmon exists) so long as the plasmon wavelength is sufficiently large in comparison with interelectronic distances, and therefore the term $\langle v^2 \rangle k^2$ in (1) is small in comparison with ω_p^2, which leads to the conditions $k \lesssim k_c \sim \rho_0^{1/6}$. This is a strong condition, because, in the other direction, the effective wavelength can not be materially larger than the lattice constant (see figure a below). Consequently the success of all ideas can be charged in large part to a favorable relation between the numerical coefficients. If the condition derived above is violated, the motion rapidly breaks up into individual excitations of electrons, so that if indeed plasmon levels exist, they ought to be very broad.

In reality the positive charge in a metal is not spread out as in a plasma. Furthermore it is necessary to take the constitution of the atom into account by one means or another. Up to the present time this has, in fact, not been included in the theory but has been dealt with on a different basis. One considers the atom only as the source of a periodic field, or else, proceeding from semiqualitative considerations, assumes that in certain cases, that of Cu, for instance, one must understand by ρ_0 in (1) not only the valence electrons, but should add to these a certain number of electrons from the shell — for Cu, for instance, three times the number of valence electrons, etc.

The problem obviously consists in studying the collective behavior of all of the electrons of the crystal (including the ionic group) from a single point of view, and the theory itself ought to show what part of these participate effectively in a plasmon. The goal of the present paper is to study this question, although only very roughly because of the roughness of the approximation of collective oscillations.

A study has already been made of a plasma in a periodic field on the basis of a classical kinetic equation, in the approximation of a weak periodicity, for a gas of valence electrons.[6] (For an interesting application of the theory of collective oscillations see also Ref. 7). This investigation does not include the ions and is unsatisfactory for our purposes.

2. KINETIC EQUATION METHOD

It is a simple matter to write down the kinetic equation for the electron distribution function $f(\mathbf{r}, \mathbf{p}, t)$ for a non-uniform density if one takes into account the external field created by the atomic nuclei. It is possible to start out from the quantum kinetic equation.[3] However, the quantum corrections are small even for electron interactions, and for a gradually varying nuclear field it is known that one can use the classical approximation, so that the external field $U(\mathbf{r})$ enters only in the form $\nabla_{\mathbf{r}} U \cdot \nabla_{\mathbf{p}} f$ (where $\mathbf{r}$ is the coordinate, $\mathbf{p}$ the momentum). As usual, we put

$$f = f^{(0)}(\mathbf{r}, \mathbf{p}) + f^{(1)}(\mathbf{r}, \mathbf{p}, t), \; |f^{(1)}| \ll f^{(0)}$$

Now $f^{(0)}$ depends on $\mathbf{r}$, although comparatively weakly. Consequently the difference between this case and the case $f^{(0)} = f^{(0)}(\mathbf{p})$ boils down to the fact that we have to understand U to be the combined potential of the nucleus and the undisturbed distribution of the electrons, satisfying the equation

$$\nabla^2 U = -4\pi\rho_0, \quad \rho_0 = \int f^{(0)}(\mathbf{r}, \mathbf{p})\, d\mathbf{p}.$$

We now carry out the transition from the distribution in multi-dimensional space to the single-particle approximation:

$$f^{(1)}(\mathbf{r}_1, \mathbf{p}_1;\; \mathbf{r}_2, \mathbf{p}_2;\; t) = f_1(\mathbf{r}_1, \mathbf{p}_1, t)\, f_1(\mathbf{r}_2, \mathbf{p}_2, t),$$

which is equivalent to the Hartree approximation, to which, as Wolff has shown,[8] the theory of plasmons corresponds.

From the kinetic equation for $f_1(\mathbf{r}_1, \mathbf{p}_1, t)$ it is possible, following Silin,[3] to go over to the "quasi-hydrodynamic approximation," in which the first moments of the desired distribution are studied:

$$\int f_1 d\mathbf{p} \equiv \rho_1(\mathbf{r}, t), \quad \int f_1 p_i d\mathbf{p}, \quad \int f_1 p_i p_k d\mathbf{p}, \ldots .$$

A system of equations is obtained for these moments, and the succeeding moments are ignored. This system cannot be simplified as readily as for a uniform plasma,[3] but one general property of its solution — that of periodicity — is important for us.

For the case of electrons in a crystal, a system of equations is obtained which is linear and homogeneous, with coefficients which have the periodicity of the lattice. Consequently one can verify that the solution of this system, for instance the excess density, has the form

$$\rho_1(\mathbf{r}, t) = e^{i\mathbf{k}\mathbf{r}} \rho_{1\mathbf{k}}(\mathbf{r}, t), \tag{2}$$

where $\rho_{1\mathbf{k}}(\mathbf{r}, t)$ has the period of the lattice and $\mathbf{k} = (2\pi n_x/L_x,\; 2\pi n_y/L_y,\; 2\pi n_z/L_z)$; L_x, L_y, L_z are the dimensions of the unit cell, and n_x, n_y, n_z are integers. As a matter of fact, all of the usual arguments which enter, for instance, into the Bloch theory for the wave function of an electron in the periodic field of a crystal, are applicable here. The solutions form a complete orthogonal set of functions of the characteristic oscillations, numbered according to the index $\mathbf{k}$, and the indices of the states $\rho_{1\mathbf{k}}$, determined from the solutions inside the cell. It is obvious that the question of the stability of these new plasmons remains unsolved here also.

3. HYDRODYNAMIC APPROXIMATION

Many of the following results require only a knowledge of the above-mentioned property of periodicity of the functions (2). However for the sake of concreteness, it is convenient to have a method, even though a very approximate one, which would permit one to carry out the calculations to the end. The method of hydrodynamics is one of these.[9] In solving the hydrodynamic equations for an electron gas with Coulomb forces guaranteeing a collective interaction, one can take account of collisions and of thermal motion in the term $\int dp/\rho$ (p is the pressure) for the corresponding equation of state. It is known that this method gave in the classical case an incorrect coefficient of $1/3$ in the correction term $\langle v^2\rangle k^2$ of (1).[3-5] In the case of a uniform degenerate Fermi gas, this method gives a coefficient of $5/9$ in the correction term [see Ref. 10 and Eq. (14) below], which is closer to unity but is still not correct.

The principal equations for a non-uniform degenerate electron gas, neglecting the retardation of the interaction, were written down long ago by Bloch,[9] who made a partial study of their properties for the case of an atom, although he was not engaged in looking for a solution. We will take advantage of this approach for the more general problem.

For plasmons in a crystals, the accounting for the retardation may be essential.

In the linear approximation with respect to the velocity $\mathbf{u}$, for $\rho = \rho_0 + \rho_1$, $|\rho_1| \ll \rho_0$, taking account of the fields $\mathbf{E}$, $\mathbf{H}$ of the electrons themselves and the external fields $\mathbf{E}^{(e)}$, $\mathbf{H}^{(e)}$, we have the following system of equations (the quadratic term $\left(\frac{1}{c}\mathbf{u} \times \mathrm{H}\right)$ is dropped):

$$\frac{\partial\rho_1}{\partial t} = -\operatorname{div}(\rho_0\mathbf{u}),$$

$$m\frac{\partial\mathbf{u}}{\partial t} = -\nabla(D\rho_1) - e\mathbf{E} - e\left\{\mathbf{E}^{(e)} + \left[\frac{1}{c}\,\mathbf{u}\times\mathbf{H}^{(e)}\right]\right\},$$

$$\frac{\partial\mathbf{E}}{\partial t} = 4\pi\rho_0\mathbf{u} + c\,\mathrm{curl}\,\mathbf{H},\ \frac{\partial\mathbf{H}}{\partial t} = -c\,\mathrm{curl}\,\mathbf{E}. \qquad (3)$$

Here the term $-\nabla(D\rho_1)$ arose from the decomposition

$$\int\frac{dp}{\rho} = \int_0^{\rho_0}\frac{dp}{\rho} + \int_{\rho_0}^{\rho_0+\rho_1}\frac{dp}{\rho} = \left(\int\frac{dp}{\rho}\right)_{\rho=\rho_0} + D\rho_1,$$

$$D = \left(\frac{1}{\rho}\,\frac{dp}{d\rho}\right)_{\rho=\rho_0}$$

(for a uniform Fermi gas $D = 5m\langle v^2\rangle/9\rho_0$).

The quantity ρ_1 which, like $\mathbf{u}$, is real, gives the quasi-classical approximation to the density matrix; consequently in a system of n particles with unperturbed wave functions $\Psi_j^{(0)}$ and a perturbation $\Psi_j^{(1)}$:

$$\rho \to \sum_{j=1}^{n}\psi_j^*(\mathbf{r})\,\psi_j(\mathbf{r}) \approx \sum(\psi_j^{(0)*} + \psi_j^{(1)*})(\psi_j^{(0)} + \psi_j^{(1)}) = \rho_0 + \rho_1,$$

$$\rho_1 \approx \sum_{j=1}^{n}(\psi_j^{(0)*}\psi_j^{(1)} + \psi_j^{(1)*}\psi_j^{(0)}). \qquad (4)$$

Let us study the free oscillations in the absence of an external field.

The energy of the oscillations is

$$\mathscr{H} = \frac{1}{2}\int d\mathbf{r}\left\{m\rho_0\mathbf{u}^2 + D\rho^2 + \frac{1}{4\pi}(E^2 + H^2)\right\}. \qquad (5)$$

Here and in what follows the index 1 in ρ_1 is dropped.

We introduce a four-component quantity whose first component is a scalar and whose remaining three are vectors (thus in fact we have a ten-component quantity):

$$\mathbf{G} = (G^{(1)}, G^{(2)}, G^{(3)}, G^{(4)}) = (\tilde{\rho}, \tilde{\mathbf{u}}, \tilde{\mathbf{E}}, \tilde{\mathbf{H}}),\quad \tilde{\rho} = \sqrt{D(\mathbf{r})}\,\rho,$$

$$\tilde{\mathbf{u}} = \sqrt{m\rho_0(\mathbf{r})}\,\mathbf{u},\quad \tilde{\mathbf{E}} = \mathbf{E}/\sqrt{4\pi},\quad \tilde{\mathbf{H}} = \mathbf{H}/\sqrt{4\pi}. \qquad (6)$$

If then, with a view to what follows, we multiply the system of equations (3) by i, we can write them in the form

$$i\frac{\partial\mathbf{G}}{\partial t} = \hat{L}\mathbf{G},\quad \mathscr{H} = \frac{1}{2}\int\mathbf{G}^2 dr, \qquad (7a)$$

$$\mathbf{G}_1\mathbf{G}_2 \equiv \sum_{\alpha=1}^{4}G_1^{(\alpha)}G_2^{(\alpha)},\quad \hat{L}\mathbf{G} = \sum_{\beta=1}^{4}L^{(\alpha,\beta)}G^{(\beta)},\quad \omega_p^2(\mathbf{r}) = \frac{4\pi e^2\rho_0(\mathbf{r})}{m}.$$

$$L^{(\alpha,\beta)} = \begin{vmatrix} 0 & -\sqrt{D}\nabla\sqrt{\frac{\rho_0}{m}} & 0 & 0 \\ -\sqrt{\frac{\rho_0}{m}}\nabla D & 0 & -\omega_p(\mathbf{r}) & 0 \\ 0 & \omega_p(\mathbf{r}) & 0 & c\,\mathrm{curl} \\ 0 & 0 & -c\,\mathrm{curl} & 0 \end{vmatrix} \qquad (7b)$$

Thus $\hat{L}$ is a self-adjoint operator. We split all real quantities into two parts:

$$\mathbf{G} = \sum_\lambda(\mathbf{G}_\lambda e^{-i\omega_\lambda t} + \mathbf{G}_\lambda^* e^{i\omega_\lambda t}), \qquad (8)$$

so that for ρ, for instance, we have

$$\rho = \sum_\lambda(\rho_\lambda(\mathbf{r})\,e^{-i\omega_\lambda t} + \rho_\lambda^*(\mathbf{r})\,e^{i\omega_\lambda t}). \qquad (9)$$

It is clear that if ρ_λ corresponds to a transition with the absorption (emission) of a quantum $\hbar\omega_\lambda$, then ρ_λ^* corresponds to a transition with the emission (absorption) of a quantum. In determining by any manner the real oscillation of $\rho(\mathbf{r}, t)$ with the frequency ω_λ, we can split it up into two parts, corresponding to (4), and consider ρ_λ and ρ_λ^* as the quasi-classical approximation for $\sum\Psi_j^{(0)*}\Psi_j^{(1)}$ and $\sum\Psi_j^{(0)}\Psi_j^{(1)*}$, in order, for instance, to use them in quantum-mechanical calculations of different processes.

For $\mathbf{G}_\lambda$ there occur the equations

$$\omega_\lambda\mathbf{G}_\lambda = \hat{L}\mathbf{G}_\lambda. \qquad (10)$$

Thus by using the self-adjointness of operator $\hat{L}$ and the antisymmetry of the real operator $-i\hat{L}$ one can, by the usual method, obtain the properties of orthogonality and normalization.

The value of the constant of normalization is determined from the requirement that the energy of an oscillation with a certain frequency ω_λ is equal to $\hbar\omega_\lambda$. Substituting one term of the sum (8) into

$\mathcal{H}$ (7) we obtain the normalization conditions:

$$\int \mathbf{G}_\lambda^* \mathbf{G}_{\lambda'}\, d\mathbf{r} = \hbar\omega_\lambda \delta_{\lambda\lambda'}, \tag{11a}$$

$$\int \mathbf{G}_\lambda^* \mathbf{G}_{\lambda'}^* d\mathbf{r} = \int \mathbf{G}_\lambda \mathbf{G}_{\lambda'} d\mathbf{r} = 0. \tag{11b}$$

If the $\mathbf{G}_\lambda$ are understood to be quantities, already normalized, which form a complete set of functions, then an arbitrary state is determined by the set of coefficients a_λ in the expansion

$$\mathbf{G}(\mathbf{r}, t) = \sum_\lambda (a_\lambda \mathbf{G}_\lambda e^{-i\omega_\lambda t} + a_\lambda^* \mathbf{G}_\lambda^* e^{i\omega_\lambda t}), \tag{8a}$$

so that the energy turns out to be

$$\mathcal{H} = \sum_\lambda |a_\lambda|^2 \hbar\omega_\lambda. \tag{12}$$

Thus for a uniform plasma, in which $\rho_0 = \text{const}$, $\omega_p = \text{const}$, we have "free plasmons:"

$$\rho = \rho_\mathbf{k} e^{i(\mathbf{k}\cdot\mathbf{r}-\omega t)}, \quad \mathbf{u} = \mathbf{u}_\mathbf{k} e^{i(\mathbf{k}\cdot\mathbf{r}-\omega t)}, \tag{13}$$

etc. Substituting into (10) and (12) we find two types of solutions: if $\omega^2 = \omega_p^2 + c^2k^2$, then $\mathbf{H} = (c/\omega)(\mathbf{k}\times\mathbf{E})$, $\mathbf{E} = im\omega\mathbf{u}/e$ (transverse waves),

$$u_\mathbf{k} = \sqrt{2\pi\hbar e^2/(m\omega V)}, \quad \rho_\mathbf{k} = 0. \tag{14a}$$

If however $\omega^2 \neq \omega_p^2 + c^2k^2$, then $\mathbf{H} = 0$, $\mathbf{E} = im\omega\mathbf{u}/e$, $\mathbf{k}\cdot\mathbf{u} = ku$ (longitudinal waves),

$$\omega^2 = \omega_p^2 + {}^5/_9 \langle v^2 \rangle k^2,$$

$$u_\mathbf{k} = \sqrt{\frac{2\pi\hbar e^2}{m\omega V}\,\frac{\omega}{\omega_p}}, \quad \rho_\mathbf{k} = \frac{k\rho_0}{\omega} u_\mathbf{k} = \sqrt{\frac{\hbar k^2 \rho_0}{2m\omega V}}, \tag{14b}$$

where V is the normalization volume. The dispersion relation obtained by this method has an incorrect factor of $^5/_9$ in the correction term.

CHARACTER OF THE FUNCTIONS FOR A CRYSTAL

In a crystal, ρ, $\mathbf{u}$, $\mathbf{E}$, and $\mathbf{H}$ have to be determined from a numerical solution of (10), where ρ_0, within the limits of one cell, is taken according to the Thomas-Fermi method. ρ_0 has been determined many times for different elements and different degrees of compression (see Refs. 11 and 12, for example).

We will use the cell method,[13,14] which was developed and used to find the wave functions of electrons in crystals. If we make use of the continuity of the functions and their derivatives in going across the boundaries of the cells, in conformance with the condition of periodicity (2) (which is valid for all components of $\mathbf{G}$), we can write the following boundary conditions, for example, for ρ: for any point $\mathbf{r}_0$ the surface of the cell has to be[14]

$$\rho(\mathbf{r}_0) = e^{i\mathbf{k}\cdot\mathbf{d}} \rho(\mathbf{r}_0 - \mathbf{d}), \quad \frac{\partial\rho(\mathbf{r}_0)}{\partial n} = -e^{i\mathbf{k}\cdot\mathbf{d}} \frac{\partial\rho(\mathbf{r}_0 - \mathbf{d})}{\partial n}, \tag{15}$$

where $\mathbf{d}$ is a vector connecting the two opposite faces of the cell. We will set $\mathbf{d}$ equal to the lattice constant. $\partial/\partial n$ is the derivative taken normal to the faces.

If we consider waves having the character of longitudinal waves [and going over to longitudinal waves for $\rho_0 \to \text{const}$; see (14b)], we can neglect retardation and set $\mathbf{E} = -\text{grad}\, \Phi$. In this case the coefficients of (10) in each cell will have spherical symmetry and a solution inside the cell can be sought in the form of an expansion in the spherical functions $Y_{lm}(\vartheta, \varphi)$ (normalized to unity),

$$\rho = \sum_{l,m} a_{lm}(\mathbf{k}) \rho_l(r) Y_{lm}(\vartheta\varphi), \tag{16}$$

in which we assume that the polar axis is directed along $\mathbf{k}$. For $m \neq 0$ waves appear which have the character of transverse oscillations and go over to transverse electromagnetic waves for $\rho_0 \to \text{const}$ in a uniform plasma (14a). Generally speaking it is no longer possible here to ignore the magnetic field of the waves and the retardation. However, the waves which most interest us are those having principally a longitudinal character, that is, containing a weak admixture of terms with $m \neq 0$. Consequently we will consider that the average field of distant cells is small in comparison with the field

$$\mathbf{E} = -\text{grad}\, \Phi, \quad \Phi = -e \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}',$$

so long as the a_{lm} for $m \neq 0$ are comparatively small. Since $\rho(\mathbf{r}_0 - \mathbf{d}) = \sum a_{lm} \rho_l(r_0) \times Y_{lm}(\pi - \vartheta, \pi + \varphi) = \sum a_{lm} \rho_l(r_0)(-1)^l Y_{lm}(\vartheta, \varphi)$, then (15) has the form

$$\sum_{lm} a_{lm}(\mathbf{k}) \rho_l(r_0) \{1 - (-1)^l e^{i\mathbf{k}\cdot\mathbf{d}}\} Y_{lm}(\vartheta\varphi) = 0, \tag{17a}$$

$$\sum_{lm} a_{lm}(\mathbf{k}) \frac{\partial\rho_l(r_0)}{\partial n} \{1 + (-1)^l e^{i\mathbf{k}\cdot\mathbf{d}}\} Y_{lm}(\vartheta\varphi) = 0 \tag{17b}$$

for all ϑ and φ ($r_0 = r_0(\vartheta, \varphi)$). As we see, principally the states with $k = 0$ are important for us. In this case there remains in (17a) only a sum over odd l, in (17b) — over even l. Consequently for $k = 0$ any solution $\rho_l(r) Y_{lm}(\vartheta, \varphi)$ of (10), taken by itself, will satisfy the conditions (17) if we subject ρ_l to the requirement $\rho_l'(r_0) = 0$ for even l and to the requirement $\rho_l(r_0) = 0$ for odd l. We note that for any l the radial equations, for instance for ρ_l, have in general many solutions differing in their "radial quantum number" n_r; however it is apparently necessary to take only the lowest of these into account, since the remaining ones will correspond to too large a gradient of ρ, for which it is already known a plasmon cannot exist and breaks up into individual excitations of electrons.

Those solutions with $k = 0$ form a basis. For $k \neq 0$ each of these generates its own branch of solutions. Thus if $kd \ll 1$, then expanding $\exp(i\mathbf{k}\cdot\mathbf{d})$ in a series and keeping only the first terms, we can seek a solution in the form of a sum of several first harmonics with coefficients $a_{lm}^{l_0 m_0}(\mathbf{k})$, where the new indices $l_0 m_0$ indicate to which branch the solution belongs, or which harmonic remains when $k \to 0$. It is easily shown that, if for $\mathbf{k} = 0$ a certain $a_{lm}^{l_0 m_0}$ is different from zero (and equal to unity), we find that for $\mathbf{k} \neq 0$ the adjacent harmonic will have $a_{lm}(\mathbf{k}) \sim kd$, the next one $a_{lm}(\mathbf{k}) \sim (kd)^2$, etc.

Let us for simplicity replace the cell by a sphere, $r_0 = \mathrm{const}$, for example. We will study the case $l_0 = 0$, $a_{lm}^{00}(0) = \delta_{l_0}$, i.e., the branch arising from the state $l = l_0 = 0$. We will look for ρ in the form of a linear combination of the three first harmonics, all with $m = 0$:

$$\rho_{\mathbf{k}}(r) = \sum_{l=0}^{2} a_{l0}^{0}(\mathbf{k})\, \rho_l^{(s)}(r)\, Y_{l0}(\vartheta\varphi) \tag{18}$$

(the index s indicates that ρ has to satisfy a "symmetrical" boundary condition $\rho_l^{(s)\prime}(r_0) = 0$). Condition (17b) drops out here. It is impossible to satisfy (17a) for all ϑ, φ, however. We satisfy it, for example, (a) for $\vartheta = 0$, (b) on the average over the sphere. Here, in calculating the normalization, all three coefficients $a_{l_0}^{0}$ are determined; it turns out that for $kd > 0$, a_{00}^{0} decreases; a_{10}^{0} increases, at first linearly with kd, while a_{20}^{0} increases quadratically. For $kd = \pi$ only a_{10}^{0} is different from zero [in this approximation see Eq. (18)], then it decreases and for $kd = \pi/2$ the second harmonic is maximum.

Let us now study the branch which for $k = 0$ starts with the state $l = 1$, $m = 0$, that is $a_{lm}^{10}(0) = \delta_{l_1}\delta_{m_0}$. Proceeding similarly, we imagine $\rho_l = \rho_l^{(a)}$ to be of an "antisymmetric" type, $\rho_l^{(a)}(r_0) = 0$. It is clear that here the functions have more nodes, and the energy of this state has to be considerably larger than for $l_0 = 0$ (as is substantiated by a calculation; see Sec. 8). For small k, a_{10}^{10} decreases as kd, and a_{00}^{10} and a_{20}^{10} increase linearly. For $kd = \pi$ a_{10}^{10} vanishes, and a_{00}^{10} and a_{20}^{10} have the same order of magnitude. If one does not replace the cell by a sphere, then the generation of longitudinal waves with $m = 0$ becomes generally impossible. For all orders of $(kd)^2 \sim d^2/\lambda^2$, transverse waves are mixed in with waves having a longitudinal character, and conversely.

We obtain the solution in another cell with integral indices $\boldsymbol{\nu} = (\nu_1, \nu_2, \nu_3)$ by multiplying the solution found in one cell by an exponential factor. Introducing for normalization purposes the factor $N^{-1/2}$, where N is the number of cells in the normalization volume V [$\rho_{l n_r}$ is normalized inside the cell in conformance with (11a)], and writing out all the indices, we have

$$\rho_{kn_i} = N^{-1/2} e^{i\mathbf{k}\cdot\boldsymbol{\nu}d} \sum_{lm} a_{lm}^{(n_i)}(k)\, \rho_{ln_r}^{(p_{n_i})}(r)\, Y_{lm}(\vartheta, \varphi), \tag{19}$$

where n_i denotes the combination of indices of an "internal state" in the cell, $n_i = (n_r, l_0, m_0)$, that is it indicates to which branch the solution belongs, and the index p_{n_i} denotes the type of boundary condition for ρ: for even l we have $p_{n_i} = s$, $\rho'(r_0) = 0$; for odd l_0, $p_{n_i} \equiv a$, $\rho(r_0) = 0$. All that has been said has to be repeated for the remaining functions $G^{(\alpha)}$, for which all the indices of the different functions $G^{(\alpha)}$ coincide. In practice we do not take the index n_r into account (see below).

The nature of typical solutions is shown schematically in the figure. The solution for $k = 0$, $l_0 = l = 0$ formally is in conflict with the condition $\int \rho d\mathbf{r} = 0$; however this condition would be fulfilled for a k different from zero but arbitrarily small. If one goes over to a uniform plasma $\rho_0 \to \mathrm{const}$, then this solution goes over to the usual longitudinal oscillations. The reduction of ρ to zero in the center of the cell is related to the fact that oscillations of arbitrarily small energy do not penetrate into the depth of the atomic shell.

These collective oscillations have essentially the character of excitons. An excitation inside one cell (also representing a collective oscillations) is propagated in the form of a wave throughout the entire crystal.

5. EXCITATION OF THE OSCILLATIONS

If a system of solutions is known for a crystal, then the change of state under the influence of an external field can be found by the usual method.

In the presence of an external electric field $E^{(e)}$, equation (3) can be written in a form corresponding to Eq. (7a):

$$i\,\frac{\partial G}{\partial t} = \hat{L}G + K,$$

$$K = \left(0;\; -\frac{\omega_p(\mathbf{r})}{\sqrt{4\pi}}\,\mathbf{E}^{(e)};\; 0;\; 0\right). \tag{20}$$

Usually the external field is periodic, with a frequency ω_0. We resolve it into components of the type $\exp(-i\omega_0 t)$ and $\exp(i\omega_0 t)$, which give rise to corresponding components in G, and study one of these components, for instance $G \sim \exp(-i\omega_0 t)$. We expand the desired solution in terms of the basic system of functions — the solutions $G_\lambda^{(0)}$ of

Eq. (10):

$$\mathbf{G} = \sum_\lambda a_\lambda(t)\, e^{-i\omega_\lambda t}\, \mathbf{G}_\lambda^{(0)}(\mathbf{r}). \qquad (21a)$$

Substituting in (20), multiplying by $\mathbf{G}_\lambda^{(0)*}$, integrating over space and using (11a) we obtain

$$\frac{d}{dt} a_\lambda = -\frac{i}{\hbar\omega_\lambda} \int \mathbf{G}_\lambda^{(0)*}\, \mathbf{K}(\mathbf{r}, t)\, d\mathbf{r}\, e^{i\omega_\lambda t}. \qquad (21b)$$

Let $\mathbf{K} = \mathbf{K}^{(0)}(\mathbf{r})\, e^{-i\omega_0 t}$. Integrating from the initial condition $a_\lambda = 0$ for $t = 0$ we obtain:

$$a_\lambda(t) = I\,[e^{i(\omega_\lambda - \omega_0)t} - 1]/i\,(\omega_\lambda - \omega_0),$$

$$I = -\frac{i}{\hbar\omega_\lambda} \int \mathbf{G}_\lambda^{(0)*}(\mathbf{r})\, \mathbf{K}^{(0)}(\mathbf{r})\, d\mathbf{r} = I_1 + I_2,$$

$$I_1 = -\frac{ie}{\hbar c} \int \rho_0 \mathbf{u}_\lambda^* \mathbf{A}\, d\mathbf{r}, \qquad I_2 = \frac{ie}{\hbar} \int \rho_\lambda^* \Phi\, d\mathbf{r}, \qquad (22)$$

where $\mathbf{E}^{(e)}$ is expressed in terms of vector and scalar potentials, $\mathbf{E}^{(e)} = -\nabla\Phi - \dot{\mathbf{A}}/c$.

According to (12) the weight of the state λ at the instant t is $|a_\lambda(t)|^2$. The probability of transition to this state per unit time is

$$W_\lambda = \lim_{t\to\infty} \frac{d}{dt} |a_\lambda(t)|^2 = 2\pi\, |I_1 + I_2|^2\, \delta(\omega_\lambda - \omega_0). \qquad (23)$$

6. INTERACTION WITH LIGHT

Let us study the absorption of light. For $\mathfrak{N}$ quanta in the volume V let

$$\Phi = 0,\quad \mathbf{A} = \mathbf{A}_0 \exp(i(\mathbf{k}_0\cdot\mathbf{r} - \omega_0 t)),\quad A_0^2 = 2\pi\hbar\omega_0\mathfrak{N}/Vk_0^2.$$

We assume that $\mathbf{A}_0$ is directed along the z axis, $\mathbf{A}_0 = A_0 \operatorname{grad} z$. Using the first equation of (3), we have

$$\int \rho_0 \mathbf{u}_\lambda^* \mathbf{A}_0\, d\mathbf{r} = i\omega_\lambda A_0 \int \rho_\lambda^* z\, d\mathbf{r}.$$

Hence according to (19):

$$|I_1|^2 = \frac{e^2\omega_\lambda^2}{\hbar^2 c^2} A_0^2 \qquad (24)$$

$$\times \left| \sum_\nu N^{-1/2} e^{i(\mathbf{k}_0 - \mathbf{k}, \nu)d} \sum_{lm} a_{lm}^{l_0 m_0}(k) \int \rho_l^* Y_{lm}^*(\vartheta\varphi)\, e^{i\mathbf{k}_0\mathbf{r}}\, r\cos\vartheta\, d\mathbf{r} \right|^2,$$

where the integral is extended throughout the volume of one cell. Since

$$\sum \exp[i(\mathbf{k}_0 - \mathbf{k})\cdot\boldsymbol{\nu} d] = N\delta_{\mathbf{k}\mathbf{k}_0},$$

and, for light, for $\hbar\omega_0 = \hbar\omega_\lambda \sim 5$ to 30 ev, $k_0 d \ll 1$, then the exponential factor in the integral can be dropped. Consequently, just as for ordinary excitons, a plasmon is excited with a k that is practically zero. Only dipole oscillations with $l = 1$ give a contribution For $k = 0$ such oscillations are present only if $l_0 = 1$. Energetically this branch is situated below the branch $l_0 = 0$. Substituting the value of A_0, multiplying by the number of initial photon states $(2\pi)^{-3} V d\mathbf{k}_0$ and introducing the spectrum of the incident light

$$S_0(\omega_0)\, d\omega_0 d\Omega \ \mathrm{erg\cdot cm^{-2} sec^{-1}} = \mathfrak{N} c\hbar\omega_0 (2\pi)^{-3}\, d\mathbf{k}_0,$$

we obtain, after integration over ω_0, the following expression for the total absorption of energy per unit time, $\hbar\omega_0 W = S$:

$$S_{\mathrm{erg/sec}} = N 3\pi \frac{e^2}{\hbar c} \omega_0 S_0(\omega_0)\, d\Omega \left| \int_0^{r_0} \rho_1^{l_0}(r)\, r^3 dr \right|^2 |a_{10}^{l_0 m_0}(0)|^2. \qquad (25)$$

Thus only transverse oscillations with $l = 1$, $m = 0$ can be excited (we recall that here the z axis is directed along the field $\mathbf{A}_0$, and not along $\mathbf{k}$, as in Sec. 4). If we designate

$$\left| \frac{4\pi}{3} \int_0^{r_0} \rho_1(r)\, \frac{r}{r_0}\, r^2 dr \right| = n_{\mathrm{eff}}, \qquad (26)$$

(the effective number of oscillating electrons), then S takes the usual form[15] for the absorption of light by N atoms, for each of which the effective square of the matrix element of the coordinate is

$$|x_{ab}|_{\mathrm{eff}}^2 \sim r_0^2 n_{\mathrm{eff}}^2. \qquad (27)$$

However such an absorption indicates that it takes place very rapidly: setting $N = \frac{1}{d^3} T\Sigma$, where T is the width of the crystal and Σ is the area of the surface being irradiated, we find for the ratio of the intensities of the incident and absorbed light ($r_0 \sim d$):

$$\frac{S}{S_0\, d\omega_0\, d\Omega\Sigma} \sim \frac{e^2}{\hbar c} \frac{\omega_0}{d\omega_0} \frac{T}{d}.$$

Thus even over a distance much smaller than $137d \sim c/\omega_0 \sim 1/k_0$ the absorption will be total. Consequently even on the surface of a crystal a light wave very rapidly goes over into a transverse plasmon wave, in which the principal component of ρ is a dipole oscillation (in each cell) in the direction of the external electric field. According to the statements made in Sec. 4, there will be present in this oscillation, with a relative weight $(k_0 d)^2 \sim (e^2/\hbar c)^2$, an added wave with $l_0 = 1$, $l = 0$, for which the average value of ρ will not vanish, i.e., a wave of longitudinal type.

7. EXCITATION BY FAST CHARGED PARTICLES

Let a particle with charge e_1, mass M, momentum $\mathbf{p}_0$ and energy $E_0 = \hbar^2 p_0^2/2M$ strike the crystal, and as the result of exciting a plasmon make a transition to a state with momentum $\mathbf{p}_f$ and energy E_f. This will produce a charge density for the transition, expressed in terms of the initial and final wave functions of the particle,

$$\psi = V^{-1/2} e^{i(\mathbf{p}\cdot\mathbf{r}-Et)/\hbar}. \tag{28}$$

There will arise a perturbation potential

$$\Phi = e_1 \int \frac{d\mathbf{r}'}{|\mathbf{r}-\mathbf{r}'|}\, \psi_f^*(\mathbf{r}', t)\, \psi_0(\mathbf{r}', t)$$

$$= \frac{4\pi e_1 \hbar^2}{V\,|\mathbf{p}_f - \mathbf{p}_0|^2}\, e^{\frac{i}{\hbar}(\mathbf{p}_0-\mathbf{p}_f,\, \mathbf{r}) - i\omega_{0f}t}. \tag{29}$$

Here

$$\hbar\omega_{0f} = E_f - E_0 = v_0 \hbar\, |\mathbf{p}_0 - \mathbf{p}_f| \cos\theta,$$

$\mathbf{v}_0 = (\mathbf{p}_f + \mathbf{p}_0)/2M$ is the average particle velocity, which for a fast particle is the same as the initial velocity, and θ is the angle between the outgoing momentum and $\mathbf{v}_0$.

Substituting Φ into (22) and (23), one can split up the integral over the whole crystal into a sum (over ν) of integrals over the separate cells, since ρ differs from one cell to another only by the factor $\exp(i\,\mathbf{k}\cdot\boldsymbol{\nu}\, d)$. The sum gives $\hbar\mathbf{k}_0 = \mathbf{p}_0 - \mathbf{p}_f$, and after multiplying by the number of final states $(2\pi)^{-3} V\, d\mathbf{k}$ or $(2\pi h)^{-3} V\, d\mathbf{p}_f$ and integrating with respect to $\mathbf{k}$ or $\mathbf{p}_f$ we obtain

$$W = 4N \frac{e_1^2 e^2}{\hbar^2} \int \frac{d\,\mathbf{k}}{k^4}\, \delta(\omega(k) - kv_0\cos\theta) \left| \int e^{i\mathbf{k}\cdot\mathbf{r}} \rho^*(\mathbf{r})\, d\mathbf{r} \right|^2, \tag{30}$$

where the integral over $\mathbf{r}$ is taken within the limits of one cell.

For the case of a uniform plasma we substitute ρ from (13) and (14b) (here V has to be replaced by the volume V/N of one cell) and obtain

$$W = \frac{e_1^2 \omega_p}{\hbar} \int_0^{k_c} \frac{dk}{k^2} \int_{-1}^{1} d\cos\theta\, \delta(\omega(k) - kv_0 \cos\theta)$$

$$\approx \frac{1}{2} \frac{m v_0 e_1^2}{\hbar^2} \frac{\hbar\omega_p}{E_0} \ln \frac{v_0 k_c}{\omega_p}, \tag{31}$$

where we have ignored the difference between ω_p and $\omega(k)$. This is the usual formula, which has also been obtained by other methods.[1]

For the case of a crystal the integral over the cell in (30) has the form

$$\int e^{-i\mathbf{k}\cdot\mathbf{r}} \sum_{lm} a_{lm}^{l_0 m_0}(\mathrm{k})\, \rho_l^{l_0}(r)\, Y_{lm}(\vartheta, \varphi)\, d\mathbf{r}.$$

We will restrict ourselves to a study of such small k that $kd \ll 1$. Since, as is apparent from (31), the upper limit in the integral with respect to k appears logarithmically, we can ignore it for a small portion of the scattering of the order of $\ln(k_c/k_{\max})/\ln(k_c v_0/\omega_p)$. For M = m (excitation by an electron)

$$k_c v_0/\omega_p \sim \sqrt{\hbar^2 E_0/me^4} \gg 1.$$

We will exclude it from a consideration of very large angles of scattering: probably $\cos\theta > (e^2/\hbar c)\sqrt{mc^2/E_0}$. Setting $\exp(i\,\mathbf{k}\cdot\mathbf{r}) \approx 1 + i\,\mathbf{k}\cdot\mathbf{r}$ and directing the z axis along $\mathbf{k}$ we obtain the probability of exciting a plasmon with a given k, l_0, and m_0 (integrated with respect to the angle θ between $\mathbf{k}$ and $\mathbf{v}_0$):

$$W_{k, l_0, m_0}\, dk = \frac{2e^2 e_1^2}{\hbar^2 v_0} \frac{dk}{k^3} \frac{4\pi}{3} r_0^3$$

$$\times \left\{ \left| a_{00}^{l_0 m_0}(k)\, \overline{\rho_0^{l_0}} \right|^2 + \frac{\omega_1^2 r_0^2}{3v_0^2} \left| a_{10}^{l_0 m_0}(k)\, \overline{\rho_l^{l_0} \frac{r}{r_0}} \right|^2 \right\}. \tag{32}$$

Here the term with $\sin^2\theta$ is dropped in comparison with $\cos^2\theta = \omega_1^2/k^2 v_0^2$ and it is considered that in the term $\delta(\omega(k) - kv_0\cos\theta)$ it is in general necessary to write $\omega_{l_0}(k)$ in place of $\omega(k)$. The bar on top denotes an averaging over the cell. Hence, only longitudinal waves with m = 0 are excited. The first term in the brackets corresponds to an ordinary longitudinal plasmon (the average density does not vanish), the second to a longitudinal dipole oscillation in the cell. Since small k play a role, the first, principal term appears if $l_0 = m_0 = 0$, that is if a plasmon is excited in the lower band. But a non-vanishing $\overline{\rho}$ can also be involved in oscillations with $l \neq 0$. Thus for small values $kd a_{00}^{1m_0}(k) \sim kd a_{1m_0}^{1m_0}(k)$ (see Sec. 4). Hence for $l_0 = 1$ this term is $(kd)^2$ times smaller than the principal term. It is possible to write

$$\{\ \} \approx \left\{ \left| a_{00}^{00}\, \overline{\rho_0^0} \right|^2 \delta_{l_0 0}\delta_{m_0 0} + k^2 d^2 \left| a_{10}^{1m_0} \overline{\rho_0^1} \right|^2 \delta_{l_0 1} \right.$$

$$\left. + \frac{\omega_1^2 r_0^2}{3v_0^2} \left| \overline{a_{10}^{10} \rho_1^1 \frac{r}{r_0}} \right|^2 \delta_{l_0 1} \delta_{m_0 0} \right\}. \tag{32a}$$

The role of the different terms for different k depends essentially on how k enters into the normalization factor. For a uniform plasma the first term in curly brackets is equal to $3\hbar k^2 \rho_0/(2mr_0^3\omega_p)$. Thus one can set

$$\left| a_{00}^{00}(k)\, \overline{\rho_0^0} \right|^2 = \frac{3}{r_0^3} \frac{\hbar k^2}{2m} \frac{\rho_{0\,\mathrm{eff}}}{\omega_0} b_0,$$

where b_0 is a number of order unity, and $\rho_{0\,\mathrm{eff}}$ can be considered equal to $\rho_0(r_0)$. Then for the lower band the total probability is

$$W_{00} = \frac{m v_0 e_1^2}{2\hbar^2} \frac{\hbar\omega_p(r_0)}{E_0} b_0 \ln \frac{v_0 k_{\max}}{\omega_0}. \tag{33}$$

The excitation of higher levels for longitudinally polarized dipole oscillations ($l_0 = 1$, $m_0 = 0$), if they exist, can take place with a probability of order $(kd)^2$ relative to the probability of the principal process, in the form of characteristic losses for scattering through large angles θ, in which the following relation ought to be satisfied:

$$\cos\theta \sim \omega_{l_0m_0}/kv_0 > \omega_{l_0m_0}r_0/v_0.$$

8. QUANTITATIVE ESTIMATES

It is possible to estimate the energy of a level by using, for example, a variational method for an almost-longitudinal plasmon, when the retardation of the interaction can be ignored. These calculations have been carried out by D. G. Sannikov for the case of Cu. By selecting test functions in the form of polynomials for ρ and for the velocity potential φ in the cell, which satisfied the boundary conditions appropriate to a given l_0, and then varying three undetermined parameters, it was possible to obtain eigenvalues of the energy $\hbar\omega_l$ for different l. The unperturbed density was substituted from Ref. 12.

The radius of the cell was taken to correspond to the normal density of copper, $\xi_0 = r_0/\mu = 9.4$. The following values were obtained, which represent upper limits, since a variational method was used:

1. $l_0 = 0$; $l = 0$, $\hbar\omega = 30$ ev (which corresponds to the beginning of the band, k = 0); $l = 1$, $\hbar\omega = 27$ ev (which corresponds approximately to kd = π).

2. $l_0 = 1$; $l = 1$, $\hbar\omega = 58$ ev (which corresponds to the beginning of the band, k = 0); $l = 0$, $\hbar\omega = 74$ ev (which corresponds approximately to kd = π).

The relatively small width of the lower band (~ 3 ev) corresponds to the fact the plasma is uniform ($\langle v^2\rangle k_c^2 \ll \omega_p^2$). It indicates that the study of collective oscillations in crystals carried out above is developed within the confines of the usual theory of plasmons. The lower band corresponds to optically inactive oscillations in the sense that it cannot be immediately excited by light. Certainly, however, a more complicated process on the part of an interstitial electron is possible, as a result of which light can excite a plasmon of such a type. This has been the object of a separate study.[16]

The characteristic value of the energy losses in Cu is considered to be about 23 ev (Ref. 1). One can identify the band $l_0 = 0$ with this figure. It follows consequently from (32) and (32a) that just this band can be excited by a charged particle. The existence of longitudinal oscillations with $l = 1$ has to be regarded as extremely improbable; this band is very broad, plasmon oscillations with energies of ~ 60 ev will very rapidly go over into excitations of separate electrons. Certainly the application of the Thomas-Fermi method can in general give rise to certain doubts. Here, however, the method is not addressed to such fine effects as the chemical bond or the compressibility, where it is excessively crude, but to energies which exceed the energy of the chemical bond by one or two orders of magnitude; we expect that the results derived above are approximately correct. As a matter of fact it is known that the Thomas-Fermi method gives values for the energies of atomic electrons which are not too far out of line. For a study of other possible optical effects see Ref. 16.

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