

Energy Losses and Collective Excitations in a Crystal*†

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The relation which exists between the Coulomb energy losses of an electron passing through a crystal and the absorption of light by the same crystal is examined in the Born approximation. It is found that at long wavelengths the validity of the Born approximation is the only necessary criterion for the equality of the corresponding averaged matrix elements.

The coupling of an incident electron to the collective modes of a crystal is next considered. The modifications of previous results for the transition probability, required by the presence of a crystal structure, are discussed. When the possibilities for Bragg scattering are extracted, a single function is found to describe the energy losses of a fast incident particle. Although simple band models may be chosen, approximations equivalent to the random-phase approximation lead to a result which retains the possibility of describing observed complex absorption spectra. It is demonstrated how a collective mode of the system may appear when the imaginary part of the polarizability varies from zero sufficiently rapidly.

WE shall consider the energy losses of an electron passing through matter due to its Coulomb interaction with the electrons of the system, and the energy absorbed of a light wave in passing through the same system. It will be shown that in the limit of small momentum transfers from the electron, and long wavelengths of light the average of the matrix elements

governing both processes are identical if the Born approximation is valid.¹

In the first Born approximation the energy loss for an electron with incident velocity \mathbf{v} , per unit time, per unit momentum transfer interval $d^3k/(2\pi)^3$ per unit energy transfer interval $d\omega$ passing through a system going from its ground state $\psi_0(\mathbf{r}_1, \dots, \mathbf{r}_n)$, to an excited state $\psi_\omega(\mathbf{r}_1, \dots, \mathbf{r}_n)$ is²

$$\frac{dE_C(\mathbf{k}, \omega)}{d\tau} = 2\pi e^4 \omega \left| \int d^n \mathbf{r} \psi_\omega^*(\mathbf{r}_1, \dots, \mathbf{r}_n) \sum_i \frac{e^{i\mathbf{k} \cdot \mathbf{r}_i}}{k^2} \psi_0(\mathbf{r}_1, \dots, \mathbf{r}_n) \right|^2 \times \delta(\omega - \mathbf{k} \cdot \mathbf{v}). \quad (1)$$

The matrix elements may be transformed by using the Schrödinger equation obeyed by the many-particle wave functions. This is, of course, equivalent to a derivation of current conservation which follows from the gauge invariance of the equations. Using

$$H\psi_j(\mathbf{r}_1, \dots, \mathbf{r}_n) = \left(\sum_i -\frac{\nabla_i^2}{2m} + V(\mathbf{r}_1, \dots, \mathbf{r}_n, \mathbf{R}_1, \dots, \mathbf{R}_m) \right) \psi_j(\mathbf{r}_1, \dots, \mathbf{r}_n) = E_j \psi_j, \quad (2)$$

where V is the complete potential including electron-electron and electron-nucleus interactions, we obtain

$$(E_j - E_0) \psi_j^*(\mathbf{r}_1, \dots, \mathbf{r}_n) \psi_0(\mathbf{r}_1, \dots, \mathbf{r}_n) = - \sum_i \frac{\nabla_i^2}{2m} \psi_j^*(\mathbf{r}_1, \dots, \mathbf{r}_n) \psi_0(\mathbf{r}_1, \dots, \mathbf{r}_n) + \psi_j^*(\mathbf{r}_1, \dots, \mathbf{r}_n) \sum_i \frac{\nabla_i^2}{2m} \psi_0(\mathbf{r}_1, \dots, \mathbf{r}_n). \quad (3)$$

Equation (1) may then be written

$$\frac{dE_C(\mathbf{k}, \omega)}{d\tau} = \frac{2\pi e^4}{\omega k^2} \left| \int d^n \mathbf{r} \sum_i e^{-i\mathbf{k} \cdot \mathbf{r}_i} \frac{\hat{k}}{2m} [\psi_\omega^*(\mathbf{r}_1, \dots, \mathbf{r}_n) \nabla_i \psi_0(\mathbf{r}_1, \dots, \mathbf{r}_n) - \nabla_i \psi_\omega^*(\mathbf{r}_1, \dots, \mathbf{r}_n) \psi_0(\mathbf{r}_1, \dots, \mathbf{r}_n)] \right|^2 \delta(\omega - \mathbf{k} \cdot \mathbf{v}), \quad (4)$$

where \hat{k} is a unit vector in the direction of \mathbf{k} . Due to the decrease of the wave functions at infinity, the surface terms arising from an integration by parts vanish.

The energy of incident light, with wave vector \mathbf{k} , energy ω , and polarization $\boldsymbol{\eta}$, absorbed per unit time with a flux of one photon per unit area per unit time is

$$\frac{dE_T(\mathbf{k}, \omega)}{d\tau} = \frac{e^2}{2} \left| \int d^n \mathbf{r} \sum_i e^{-i\mathbf{k} \cdot \mathbf{r}_i} \frac{\boldsymbol{\eta}}{2m} [\psi_\omega^*(\mathbf{r}_1, \dots, \mathbf{r}_n) \nabla_i \psi_0(\mathbf{r}_1, \dots, \mathbf{r}_n) - \nabla_i \psi_\omega^*(\mathbf{r}_1, \dots, \mathbf{r}_n) \psi_0(\mathbf{r}_1, \dots, \mathbf{r}_n)] \right|^2. \quad (5)$$

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¹ That an exact relation of this type should exist was suggested to the author by Professor J. Schwinger and Professor E. Wigner in slightly different forms.

² We use the units $\hbar=1$, $e^2=4\pi(e^2)_{\text{cgs}}$.

Thus, the energy losses of an electron are given in terms of the longitudinal component of the current vector, whereas the absorption of light depends upon its transverse components.

Let us examine these components in the limit of $\mathbf{k}\cdot\mathbf{r}\ll 1$ so that we may take only the leading term in the expansion of the exponent.

$$\int d^n\mathcal{V}[\psi_\omega^*(\nabla_i)_\alpha\psi_0 - (\nabla_i)_\alpha\psi_\omega^*\psi_0] \int d^n\mathcal{V}'[\psi_\omega^*(\nabla'_i)_\beta\psi_0 - (\nabla'_i)_\beta\psi_\omega^*\psi_0],$$

does not depend on any direction for an isotropic system. As a diagonal tensor, the component projected parallel to \mathbf{k} equals the component projected perpendicular to \mathbf{k} . For the equality to hold for a single direction of propagation in a crystal, a plane of symmetry equivalent to the direction of propagation is required. However, if we accept only momenta of fixed magnitude but averaged over all directions in the crystal, as may be done experimentally, the two matrix elements again become identical.

We may define the conductivity $\sigma(\omega)$ as the ratio of the power absorbed to the average electric field squared. This definition allows the optical constants of a system to be related to the energy losses of an electron passing through the system:

$$\langle dE_C(\mathbf{k},\omega)/d\tau \rangle = (16\pi^2 e^2/\mathbf{k}^2) \langle \sigma(\omega) \rangle \delta(\omega - \mathbf{k} \cdot \mathbf{v}). \quad (6)$$

The angular brackets indicate an average over angles. It should be noted that, in addition to the Born approximation, no assumption about the electrons of the system, such as the random-phase approximation, was required. One example of the validity of the Born approximation is found by comparing the energy losses in silver up to 6 eV,³ and the optical constants for the corresponding range of wavelengths.⁴

Especially when observing the absorption of energetic photons, it is important to note the restrictions placed on the thickness of the film in order to satisfy the requirement $\mathbf{k} \cdot \mathbf{r} \ll 1$. For propagation normal to the surface of the film, the restriction requires that the wavelength of the incident light be large compared to the film thickness.

COLLECTIVE EXCITATIONS

In a previous paper an expression was derived for the transition rate of a particle with sharp momentum and energy passing through a many-body system.⁵ In the case when a particle is passing through a crystal we may no longer identify the initial wave packet with a sharp momentum state. If the incident wave packet is designated by $\varphi_\alpha(\mathbf{r})$, the arguments given in reference 5 lead to the following result for the transition rate of a particle initially having energy p^0 .

$$1/\tau = 2 \operatorname{Im} \int d^3r d^3r' \varphi_\alpha(\mathbf{r}) \Sigma(\mathbf{r}, \mathbf{r}'; p^0) \varphi_\alpha^*(\mathbf{r}'), \quad (7)$$

³ E. Rudberg, Proc. Roy. Soc. (London) **A127**, 111 (1930).

⁴ H. Fröhlich and H. Pelzer, Proc. Phys. Soc. (London) **A68**, 525 (1955).

⁵ S. Engelsberg, Phys. Rev. **123**, 1130 (1961).

where the self-energy $\Sigma(\mathbf{r}, \mathbf{r}'; p^0)$ is no longer a function of $\mathbf{r} - \mathbf{r}'$. If we restrict the discussion to monatomic crystals with a Bravais lattice, the wave packet may be written in terms of its Fourier components

$$\varphi_\alpha(\mathbf{r}) = \sum_{\mathbf{K}} a_{\mathbf{K}} \frac{\exp(-i\mathbf{p} \cdot \mathbf{r} - i\mathbf{K} \cdot \mathbf{r})}{\mathcal{V}^{\frac{1}{2}}}. \quad (8)$$

The sum over \mathbf{K} extends over all reciprocal lattice vectors of the crystal, each satisfying

$$\exp(i\mathbf{K} \cdot \mathbf{R}) = 1.$$

\mathbf{R} is any vector which joins two equivalent points of the crystal, \mathcal{V} is the volume of the crystal, and \mathbf{p} is the momentum of the incident particle when it is far from the crystal. We utilize the translational symmetries the crystal does maintain in choosing the Fourier expansion of the self-energy.

$$\Sigma(\mathbf{r}, \mathbf{r}'; p^0) = \sum_{\mathbf{K}} \int \frac{d^3k}{(2\pi)^3} \times \exp[i\mathbf{k} \cdot (\mathbf{r} - \mathbf{r}') - i\mathbf{K} \cdot \mathbf{r}] \Sigma(\mathbf{k}, \mathbf{K}, p^0). \quad (9)$$

The transition rate which results is

$$\begin{aligned} \frac{1}{\tau} = & 2 \operatorname{Im} \left(\sum_{\mathbf{K}} |a_{\mathbf{K}}|^2 \Sigma(\mathbf{p} + \mathbf{K}, 0, p^0) \right. \\ & \left. + \sum_{\mathbf{K}, \mathbf{A} \neq 0} a_{\mathbf{K}-\mathbf{A}} a_{\mathbf{K}}^* \Sigma(\mathbf{p} + \mathbf{K}, \mathbf{A}, p^0) \right). \quad (10) \end{aligned}$$

We expect that if the particle moves fast enough it essentially averages over the crystal and thus picks out the static or zero reciprocal lattice vector term of the interaction. This statement may be made more plausible by considering the expression for the self-energy which neglects vertex corrections,

$$\Sigma(x, x') = ie^2 D(x, x') G(x, x'). \quad (11)$$

G is the Green's function for the incident particle and D is the interacting field Green's function as defined previously.⁵ By using a representation for D and G similar to that used for Σ in Eq. (9), we obtain

$$\begin{aligned} \Sigma(\mathbf{p}, \mathbf{A}, p^0) = & -ie^2 \sum_{\mathbf{K}} \int \frac{d^4k}{(2\pi)^4} \\ & \times D(\mathbf{k}, \mathbf{K}, \omega) G(\mathbf{p} - \mathbf{k}, \mathbf{A} - \mathbf{K}, p^0 - \omega). \quad (12) \end{aligned}$$

The incident particle Green's function satisfies an equation of the form

$$\left(p^0 - \frac{(\mathbf{p} - \mathbf{\Lambda})^2}{2m}\right) G(\mathbf{p}, \mathbf{\Lambda}, p^0) + \sum_{\mathbf{\Lambda}'} [\Sigma(\mathbf{p} - \mathbf{\Lambda}', \mathbf{\Lambda} - \mathbf{\Lambda}', p^0) G(\mathbf{p}, \mathbf{\Lambda}', p^0)] = \delta_{\mathbf{\Lambda}, 0}. \quad (13)$$

With the attitude that only zero reciprocal lattice vectors will be important, we obtain the approximate solutions

$$G(\mathbf{p}, 0, p^0) \approx \frac{1}{p^0 - p^2/2m - \Sigma(\mathbf{p}, 0, p^0)}, \quad (14)$$

$$G(\mathbf{p}, \mathbf{\Lambda} \neq 0, p^0) \approx - \frac{\Sigma(\mathbf{p}, \mathbf{\Lambda}, p^0)}{[p^0 - (\mathbf{p} - \mathbf{\Lambda})^2/2m + \Sigma(\mathbf{p} - \mathbf{\Lambda}, 0, p^0)][p^0 - p^2/2m + \Sigma(\mathbf{p}, 0, p^0)]}.$$

We note that if $(\mathbf{p} - \mathbf{\Lambda})^2 \neq \mathbf{p}^2$, integrations over energy will reduce $G(\mathbf{\Lambda} \neq 0)$ with respect to $G(\mathbf{\Lambda} = 0)$ by the factor

$$\Sigma/[(\mathbf{p} \cdot \mathbf{\Lambda}/m) - (\mathbf{\Lambda}^2/2m)],$$

when the energy dependence of Σ is neglected. These arguments are based in principle on the dominance of the kinetic energy as compared to the interaction energy. Thus, the factor $\Sigma/(\mathbf{p} \cdot \mathbf{\Lambda}/m)$ is enough to ensure that for a fast incident particle the terms with $\mathbf{\Lambda} \neq 0$ may be neglected. When the condition for Bragg scattering of the incident particle $(\mathbf{p} - \mathbf{\Lambda})^2 = \mathbf{p}^2$ is satisfied the approximation scheme used above leads to singularities and must be modified. However, if we are not interested in the elastic Bragg scattering we may restrict our considerations to $G(\mathbf{p}, 0, p^0)$.

In our discussion of approximations to the function $D(\mathbf{k}, \mathbf{K}, \omega)$ we will use a scheme applicable to the collective excitation arising from the Coulomb interactions of the electrons of the crystal. Since there are directions

fixed in space determined by the crystal, the Coulomb and transverse electromagnetic field are coupled. This coupling will be neglected, since its effects are smaller than the Coulomb effects by the ratio of the Fermi velocity to the velocity of light. D may be defined by the equation

$$\nabla^2 D(x, x') = \delta U_{\text{eff}}(x)/\delta U(x'), \quad (15)$$

where U_{eff} is the effective field acting at a point and U is the applied external field,

$$U_{\text{eff}}(x) = U(x) + e \int d^4 x' \mathcal{D}(x - x') \langle \rho(x') \rangle$$

$$= U(x) - ie^2 \int d^4 x' \mathcal{D}(x - x') G(x', x'^+). \quad (16)$$

The high-density approximation is used to obtain the inverse dielectric function.⁶

$$\epsilon^{-1}(x, x') = \frac{\delta U_{\text{eff}}(x)}{\delta U(x')} = \delta(x - x') + ie^2 \int d^4 x_1 d^4 x_2 d^4 x_3 \mathcal{D}(x - x_1) G(x_1, x_2) \frac{\delta G^{-1}(x_2, x_3)}{\delta U(x')} G(x_3, x_1)$$

$$\approx \delta(x - x') - ie^2 \int d^4 x_1 d^4 x_2 \mathcal{D}(x - x_1) G(x_1, x_2) \epsilon^{-1}(x_2, x') G(x_2, x_1). \quad (17)$$

The dependence of G^{-1} on U has only been accounted for through the term U_{eff} . Since \mathcal{D} satisfies the equation

$$\nabla^2 \mathcal{D}(x - x') = -\delta(x - x'),$$

the approximation made in Eq. (17) may be written

$$\nabla^2 \epsilon^{-1}(x, x') - ie^2 \int d^4 x_1 G(x, x_1) \epsilon^{-1}(x_1, x') G(x_1, x) = \nabla^2 \delta(x - x'). \quad (18)$$

Defining the polarizability P by the equation

$$\nabla^2 \epsilon^{-1}(x, x') - \int d^4 x_1 P(x, x_1) \epsilon^{-1}(x_1, x') = \nabla^2 \delta(x - x'). \quad (19)$$

the present approximation scheme gives

$$P(x, x') = -ie^2 G(x, x') G(x', x). \quad (20)$$

⁶ P. C. Martin and J. Schwinger, Phys. Rev. **115**, 1342 (1959).

When Fourier representations of the form given in Eq. (9) are chosen, Eq. (19) becomes

$$\sum_{\mathbf{A}} [(\mathbf{k}-\mathbf{A})^2 \delta_{\mathbf{K},\mathbf{A}} - P(\mathbf{k}-\mathbf{A}, \mathbf{K}-\mathbf{A}, \omega)] \epsilon^{-1}(\mathbf{k}, \mathbf{A}, \omega) = \mathbf{k}^2 \delta_{\mathbf{K},0}. \quad (21)$$

We again look for solutions in which the dominant contribution is from the zero reciprocal lattice vector.

$$\epsilon^{-1}(\mathbf{k}, 0, \omega) \approx \mathbf{k}^2 / [\mathbf{k}^2 - P(\mathbf{k}, 0, \omega)],$$

$$\epsilon^{-1}(\mathbf{k}, \mathbf{K} \neq 0, \omega) \approx \frac{\mathbf{k}^2 P(\mathbf{k}, \mathbf{K}, \omega)}{[\mathbf{k}^2 - P(\mathbf{k}, 0, \omega)][(\mathbf{k}-\mathbf{K})^2 - P(\mathbf{k}-\mathbf{K}, 0, \omega)]}. \quad (22)$$

The limit of a uniform positively-charged background corresponds to \mathbf{K} going to infinity. Any collective excitation we find must probe many atoms, which may be written as the condition $(\mathbf{k}/\mathbf{K})^2 \ll 1$. It may be shown that the leading term of $P(\mathbf{k}, \mathbf{K}, \omega)$ in an expansion for small $|\mathbf{k}|$ goes as \mathbf{k}^2 . Therefore, since $\epsilon^{-1}(\mathbf{k}, \mathbf{K} \neq 0, \omega) \approx (\mathbf{k}^2/\mathbf{K}^2)\epsilon^{-1}(\mathbf{k}, 0, \omega)$, we may neglect contributions of $\epsilon^{-1}(\mathbf{k}, \mathbf{K} \neq 0, \omega)$ to collective excitations. Of course, to include the complete spectrum of excitations of the crystal, these terms must be retained, for they give rise to the Bragg scattering of the excitations when the condition $(\mathbf{k}-\mathbf{K})^2 = \mathbf{k}^2$ is satisfied.⁷

For the evaluation of the polarizability, the single-particle Green's function for the electrons in the crystal is written in terms of the wave functions satisfying a Hartree equation:

$$[-\nabla^2/2m + V_I(\mathbf{r}) + V_e(\mathbf{r})]\varphi_m(\mathbf{k}, \mathbf{r}) = E_m(\mathbf{k})\varphi_m(\mathbf{k}, \mathbf{r}), \quad (23)$$

where \mathbf{k} is the reduced wave vector which lies within the

first Brillouin zone, the index m refers to the energy band, V_I is the ionic potential, and V_e is the Hartree potential caused by the electrons

$$V_e(\mathbf{r}) = e^2 \int d^3\mathbf{r}' \mathcal{D}(\mathbf{r}-\mathbf{r}')n(\mathbf{r}'), \quad (24)$$

with the electron density n given in terms of the wave functions,

$$n(\mathbf{r}) = 2 \sum_{m < c} \int_0^{p_f} \frac{d^3k}{(2\pi)^3} \varphi_m^*(\mathbf{k}, \mathbf{r}) \varphi_m(\mathbf{k}, \mathbf{r}); \quad (25)$$

"fBz" means that the integration extends over the first Brillouin zone. The limits on the summation and integration require the inclusion of all electrons below the Fermi level. For a system at zero temperature, the Hartree Green's function is written

$$G(x, x') = \frac{1}{i} \sum_{m > c} \int_{\text{fBz}} \frac{d^3k}{(2\pi)^3} \varphi_m(\mathbf{k}, \mathbf{r})^* \varphi_m(\mathbf{k}, \mathbf{r}') e^{-iE_m(\mathbf{k})(t-t')}; \quad t > t'$$

$$= -\frac{1}{i} \sum_{m < c} \int_0^{p_f} \frac{d^3k}{(2\pi)^3} \varphi_m(\mathbf{k}, \mathbf{r})^* \varphi_m(\mathbf{k}, \mathbf{r}') e^{-iE_m(\mathbf{k})(t-t')}; \quad t < t'. \quad (26)$$

The summation and integration in the expression for $G(t > t')$ are taken over all unfilled states. The wave functions may be written as the product of a plane wave and a Bloch function which is periodic in the lattice

$$\varphi_m(\mathbf{k}, \mathbf{r}) = e^{-i\mathbf{k} \cdot \mathbf{r}} u_m(\mathbf{k}, \mathbf{r}). \quad (27)$$

The Bloch functions satisfy the completeness relations

$$\sum_m \int_{\text{fBz}} \frac{d^3k}{(2\pi)^3} u_m(\mathbf{k}, \mathbf{r})^* u_m(\mathbf{k}, \mathbf{r}') = \delta(\mathbf{r}-\mathbf{r}'), \quad \frac{1}{\Omega} \int_{\Omega} d^3r u_m(\mathbf{k}, \mathbf{r})^* u_l(\mathbf{k}, \mathbf{r}) = \delta_{m,l}, \quad (28)$$

where the spatial integration is restricted to a unit lattice cell of volume Ω . Approximations (20) and (26) permit the evaluation for the polarizability in the limit of $|\mathbf{k}|$ going to zero.⁸

$$\lim_{\mathbf{k}^2 \rightarrow 0} \text{Re} \frac{P(\mathbf{k}, 0, \omega)}{\mathbf{k}^2} = \frac{n_e e^2}{\omega^2} \left\langle \frac{1}{m^*} \right\rangle + \frac{4e^2}{m^2 \mathbf{k}^2} \sum_{m_1 < c, m_2 > c} \int_0^{p_f} \frac{d^3p}{(2\pi)^3} \frac{|\mathbf{k} \cdot \mathbf{M}_{12}(\mathbf{p})|^2}{[E_{m_2}(\mathbf{p}) - E_{m_1}(\mathbf{p})][\omega^2 - (E_{m_2}(\mathbf{p} + \mathbf{k}) - E_{m_1}(\mathbf{p}))^2]}. \quad (29)$$

⁷ D. S. Falk, Phys. Rev. **118**, 105 (1960).

⁸ J. Hubbard, Proc. Phys. Soc. (London) **A68**, 976 (1955), and H. Kanazawa, Progr. Theoret. Phys. **13**, 227 (1955), have obtained this result using other techniques.

The average effective mass is defined by

$$n_c \left\langle \frac{1}{m^*} \right\rangle = \sum_c \frac{1}{k^2} \int_0^{p_f} \frac{d^3 p}{(2\pi)^3} (\mathbf{k} \cdot \nabla_p)^2 E_c(\mathbf{p}) \frac{2}{\Omega} \int_{\Omega} d^3 r u_c(\mathbf{p}, \mathbf{r})^* u_c(\mathbf{p}, \mathbf{r}). \quad (30)$$

c denotes the unfilled bands of the crystal. The dipole moment between two bands is

$$\mathbf{M}_{12}(\mathbf{p}) = 1/\Omega \int_{\Omega} d^3 r [\nabla_r u_{m_2}(\mathbf{p}, \mathbf{r})^*] u_{m_1}(\mathbf{p}, \mathbf{r}). \quad (31)$$

The imaginary part of the polarizability for frequencies greater than zero is given by

$$\begin{aligned} \lim_{k^2 \rightarrow 0} \text{Im} P(\mathbf{k}, 0, \omega) = & -2\pi e^2 \sum_c \int_{\text{fBz}} \frac{d^3 p}{(2\pi)^3} \left| \frac{1}{\Omega} \int_{\Omega} d^3 r |u_c(\mathbf{p}, \mathbf{r})|^2 \right|^2 \delta[E_c(\mathbf{p} + \mathbf{k}) - E_c(\mathbf{p}) - \omega] \\ & - \frac{2\pi e^2}{m^2 \omega^2} \sum_{m_2 > c, m_1 < c} \int_0^{p_f} \frac{d^3 p}{(2\pi)^3} |\mathbf{k} \cdot \mathbf{M}_{12}(\mathbf{p})|^2 \delta[E_{m_2}(\mathbf{p} + \mathbf{k}) - E_{m_1}(\mathbf{p}) - \omega]. \end{aligned} \quad (32)$$

In Eqs. (29) and (32) the first term represents the intra-band contributions arising through electron transitions from below the Fermi level to above it in the unfilled bands. The behavior of these terms is identical with behavior obtained for the uniform high-density electron gas.⁹ However, even when simple assumptions are made about the band structure and dipole moments, the second or so-called interband terms can lead to extremely complex energy-loss spectra.

When we neglect the processes mentioned before, the imaginary part of $\epsilon^{-1}(\mathbf{k}, 0, \omega)$ will give the various modes the incident particle will couple to, and the intensity with which the modes will be excited. Therefore, we should like to investigate $\text{Im}[\mathbf{k}^2 - P(\mathbf{k}, 0, \omega)]^{-1}$. The vanishing of $\text{Im} P$ implies a sharp collective excitation when the condition $\mathbf{k}^2 = \text{Re} P(\mathbf{k}, 0, \omega)$ is satisfied. For a uniform high-density electron gas a single sharp collective mode, the plasmon, results. However, in a crystal the existence of band levels make any number of collective excitations possible. The only restriction will be that between each pair of poles of ϵ^{-1} there will be a nonsharp absorption region. These statements may be made clearer by considering the dispersion relation satisfied by the polarizability of crystals with reflection invariance,

$$P(\mathbf{k}, 0, \omega) = \int_0^\infty \frac{d\omega'^2}{\pi} \frac{\text{Im} P(\mathbf{k}, 0, \omega')}{\omega'^2 - \omega^2 - i\delta}, \quad \delta \rightarrow 0^+. \quad (33)$$

This dispersion relation is satisfied by approximations (29) and (32). It can be derived exactly by using a Lehmann representation for $\epsilon^{-1}(\mathbf{k}, 0, z)$ and taking its inverse. A problem arises in the exact derivation since the structure of the function does not forbid the occurrence of a zero of $\epsilon^{-1}(z)$ on the imaginary z axis,

⁹ P. Nozieres and D. Pines, Phys. Rev. **113**, 1254 (1959).

thus preventing an inversion. By appealing to the physical argument that the system cannot perfectly shield any of the spatial Fourier components of an arbitrarily strong applied field, such zeroes are ruled out. The existence of the dispersion relation (33) demands the polarizability have certain properties. Since $\text{Im} P$ is less than or equal to zero, $\text{Re} P$ is a monotonic decreasing function of ω when ω is greater than zero and $\text{Im} P$ is equal to zero. For ω such that $\text{Im} P$ is nonzero, the polarizability as a function of complex frequencies will have a branch line along the real axis. In the limit of ω going to infinity, $\text{Re} P$ decreases to zero. Suppose there were an absorption band such that $\text{Im} P$ jumped discontinuously from zero to some constant value at the frequency ω_1 and cut off abruptly at ω_2 . Equation (33) then indicates that $\text{Re} P$ will go to minus infinity at ω_1 and start decreasing from plus infinity at ω_2 . Such logarithmic singularities will occur whenever there are discontinuous jumps of $\text{Im} P$ to or from zero. When $\text{Im} P$ changes continuously to zero the magnitude of $\text{Re} P$ can be made to assume arbitrarily large values by choosing an $|\text{Im} P|$ which decreases rapidly enough. Consider the contribution of one additional absorption band. By allowing $\text{Im} P$ to rise rapidly enough, the effect of lower frequency absorption regions can be canceled to make $\text{Re} P$ go negative. If $\text{Re} P$ starts sufficiently positive, due to the previous absorption region, we find a solution to $\mathbf{k}^2 = \text{Re} P(\mathbf{k}, 0, \omega)$ at an energy between the previous band and the region being considered. It is now possible for the additional band by decreasing rapidly enough to enhance $\text{Re} P/\mathbf{k}^2$ to a value greater than one with a resulting collective excitation at an energy greater than the cutoff of the absorption region. If there is an absorption band in which $|\text{Im} P|$ decreases rapidly towards zero but thereafter maintains a small almost constant value, $\text{Im}(\epsilon^{-1})$ will show a

resonance structure. In this case there will be a nonzero width to the collective state. These arguments may be paraphrased by the statement that the addition of an absorptive band which changes rapidly enough will give rise to an additional collective mode.

By using an effective mass approximation and a constant dipole moment, the interband contribution to the imaginary part of the polarizability [Eq. (32)] may be calculated. As long as the density of states at one of the ends of the two bands being considered does not go to zero continuously, $\text{Im } P$ will have a discontinuous jump. By choosing alternative simple band schemes one may reproduce practically any behavior of $\text{Im } P$ desired. Although parameters may be adjusted in the band

scheme to agree with the observed energy losses, the test of the model is, of course, one that also predicts other physical properties unrelated to the energy losses by invariance arguments.

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Sputtering Experiments in the Rutherford Collision Region*

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Sputtering experiments have been conducted by bombarding the (110) plane and the (100) plane of single crystals of copper by deuterons incident normally with energies from 0.8 to 2.5 Mev from a Van de Graaff accelerator. Electron micrographs showed that surface etch pits were formed by bombardment, even at these high energies. Measurements of optical transmission of the sputtered film collected on a quartz tube indicated a deviation from a cosine distribution in the energy range investigated. For 800-keV deuterons bombarding a (100) plane in Cu, the absolute value of the sputtering ratio was $S = 1.1 \times 10^{-3}$ atom/ion at 25° with respect to the surface normal and 5.8×10^{-4} at angles larger than 40° ; and $S < 0.9 \times 10^{-3}$ atom/ion at 25° for 1.5-Mev deuterons. For 0.80- and 2.5-Mev deuterons bombarding a (110) plane, $S < 5 \times 10^{-2}$ atom/ion. These data agree with the calculations of Goldman and Simon and of Pease within a factor of 2, but disagree with those reported by Pleshivtsev by 2 to 4 orders of magnitude. The sputtering ratio was found to decrease with increasing ion energy, in qualitative agreement with the theoretical predictions but contrary to the findings of Pleshivtsev.

SPUTTERING phenomena have been studied by many authors¹ in the hard-sphere collision region and to a lesser extent in the region of weakly screened Coulomb collisions. For the energy region above 100 keV where for light incident ions ($Z_1 \leq 2$) bombarding targets with $Z_2 < 40$ the Rutherford scattering predominates, the only data for "back" sputtering² known to the author are preliminary results reported by Pleshivtsev.³ However there exists a discrepancy of 3 to 4 orders of magnitude between sputtering ratios reported by this author for deuterons bombarding a copper target and the theoretical predictions for the same system, such

as those of Goldman and Simon,⁴ Goldman, Harrison, and Coveyou,⁵ Harrison,⁶ and Pease.⁷ It seemed interesting, therefore, to check the experimental result by experiments in the Rutherford collision region. Such collisions, which displace target atoms, occur when the energy E of the incident ions is greater than a limiting energy⁸

$$E_B = 4E_R^2 Z_1^2 Z_2^2 (Z_1^{\frac{2}{3}} + Z_2^{\frac{2}{3}}) \frac{M_1}{M_2} \frac{1}{E_d}, \quad (1)$$

where M_1 , Z_1 and M_2 , Z_2 are the mass and the atomic number of the incident ion and the target atom, respectively, $E_R = 13.6$ eV is the Rydberg energy for hydrogen, and E_d is the energy required to displace an atom from its lattice site. For many metals the values

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¹ M. Kaminsky, review article for *Ergeb. exakt. Naturwiss.* (to be published). For data up to 1955, see the article by G. K. Wehner, *Advances in Electronics and Electron Physics*, edited by L. Marton (Academic Press Inc., New York, 1955), Vol. 7, p. 289.

² It is necessary to discriminate between "back" and "forward" sputtering. In "back" sputtering the target particles leave from the surface that is struck by the incident ion beam, while in "forward" sputtering they leave from the opposite surface [see experiments by M. W. Thompson, *Phil. Mag.* 4, 139 (1959)].

³ N. V. Pleshivtsev, *Soviet Phys.—JETP* 37, 882 (1960).

⁴ D. T. Goldman and A. Simon, *Phys. Rev.* 111, 383 (1958).

⁵ D. T. Goldman, D. E. Harrison, and R. R. Coveyou, Oak Ridge National Laboratory Report 2729, 1959 (unpublished).

⁶ D. E. Harrison, *J. Chem. Phys.* 32, 1332 (1960).

⁷ R. S. Pease, *Rend. S.I.F.*, XIII 158 (1959).

⁸ N. Bohr, *Kgl. Danske Videnskab. Selskab. Mat.-fys. Medd.* 18, 8 (1948).