

Nonlocal effects in absorption edges: Energy-dependent pseudopotentials

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The promotion of electrons between parallel single-particle bands in the neighborhood of zone boundaries is known to constitute a major source of those excitations largely responsible for the dominant structure observed in the optical conductivity $\sigma(\omega)$ of simple polyvalent metals. Departures from parallelism are shown to lead to distinct features in this structure (particularly at interband edges), and the origin and consequences of these departures are investigated particularly insofar as they bear on energy nonlocality in the effective one-electron pseudopotential.

I. INTRODUCTION

Noticeable structure is frequently observed in the optical conductivity $\sigma(\omega)$ of pure polyvalent metals, and has been attributed¹⁻⁴ to singular behavior in the joint density of levels corresponding to the single-particle band structure, the latter generally being accountable (for simple metals) in terms of a weak pseudopotential description. Upon the assumption that a pair of bands (one of which must be occupied) are *exactly* parallel over substantial regions of the zone near its faces, it is possible to show that, in the absence of lifetime effects, $\sigma(\omega)$ will possess striking absorption edges, commencing at photon energies $\hbar\omega$ equal to the band splittings on the zone faces themselves. There is reason to suppose that the assumption of parallelism of the principal bands in the neighborhood of zone faces is essentially correct in metals whose band structures closely resemble nearly-free-electron behavior. However, even when the corresponding pseudopotential $V_{\vec{k}}$ used to interpolate the band structure is taken as completely local, precise parallelism is not to be expected simply because the higher bands in the complete band structure (normally ignored) lead to small second-order distortions. Incorporation of these distortions into a description of the bands using a low-order secular equation can, of course, be achieved by the use of "folded" Fourier components $U_{\vec{k}}$. The $U_{\vec{k}}$ are then weakly energy dependent, a direct consequence of the folding procedure. But in addition, the $V_{\vec{k}}$ (from which the $U_{\vec{k}}$ are constructed) are inherently energy dependent, a nonlocal property characteristic of most pseudopotentials.⁵ It is the purpose of the present paper to extend the theory of Ref. 3 by including, with the aid of a simple model, these (combined) energy dependences in $U_{\vec{k}}$; and we shall show presently that the manifestations of energy nonlocality⁶ can be particularly revealing in the edges themselves (and are, indeed, quite

reminiscent of the broadening produced by scattering effects). To this end, we shall briefly recapitulate in Sec. II the second-order theory of optical absorption in nearly-free-electron polyvalent metals, and in Sec. III develop the modifications necessary to include the major effects stemming from the use of energy-dependent effective potentials. Section IV is devoted to a discussion of the results, and in particular of their bearing on the interpretation of the data taken from real metals (for example those of Mathewson and Myers⁷ on Al), in which discrepancies with theory have already been attributed in part to the possibility of energy dependence in the potentials.

II. OPTICAL CONDUCTIVITY $\sigma(\omega)$

We shall restrict our discussion to metals whose transport coefficients are isotropic.⁸ We suppose the valence bands of the polyvalent metals to have single-particle energies $\epsilon_{n\vec{k}}$ and corresponding Bloch wave functions $\psi_{n\vec{k}}$. In the absence of scattering, the contribution to the optical conductivity $\sigma(\omega)$ from interband excitation may be written (for a volume V of the metal) as

$$\begin{aligned} \sigma_{\text{IB}}(\omega) = & \left(\frac{e^2}{a_0 \hbar} \right) \frac{\pi a_0}{\hbar \omega} \left(\frac{\hbar^2}{2m} \right)^2 \frac{1}{3V} \\ & \times \sum_{\vec{k}, n, n'} f(\epsilon_{n\vec{k}}) [1 - f(\epsilon_{n'\vec{k}})] \\ & \times | \langle \psi_{n'\vec{k}} | \vec{\nabla} | \psi_{n\vec{k}} \rangle |^2 \delta(\epsilon_{n'\vec{k}} - \epsilon_{n\vec{k}} - \hbar\omega), \quad (1) \end{aligned}$$

where the f 's are Fermi-Dirac occupation factors. In the pseudopotential method, the energies $\epsilon_{n\vec{k}}$ follow from a secular equation admitting, by fiat, solutions restricted to the valence bands. Accordingly, the band indices n and n' in Eq. (1) are confined to the spectrum of valence levels, and the energies $\epsilon_{n\vec{k}}$ are taken as solutions to⁹

$$\det(H_{\vec{k}\vec{k}'} - \delta_{\vec{k}\vec{k}'} \epsilon) = 0, \quad (2)$$

where

$$H_{\vec{k}\vec{k}'} = \delta_{\vec{k}\vec{k}'} [\epsilon_{\vec{k}\vec{k}}^0 + V_{\vec{k}\vec{k}}(\vec{k})] + V_{\vec{k}\vec{k}'}(\vec{k}), \quad (3)$$

$$V_{\vec{k}\vec{k}'}(\vec{k}) = \langle \vec{k} + \vec{K} | V | \vec{k} + \vec{K}' \rangle, \quad (4)$$

and

$$\epsilon_{\vec{k}\vec{k}}^0 = (\hbar^2/2m)(\vec{k} + \vec{K})^2 \quad (5)$$

are the free-particle energies. {When the pseudopotential operator V is assumed fully local, it is customary to take the diagonal elements to be zero [i. e., $V_{\vec{k}\vec{k}}(\vec{k}) = V_0 = 0$], a procedure which in principle requires, as we shall see in a moment, the introduction of an effective mass in the free-particle energies.}

Since the structure in $\sigma(\omega)$ is dominated by the behavior of the bands near zone boundaries, as discussed above, it is sufficient to fix attention on a pair of bands (say $n=1$ and 2) associated with a chosen reciprocal-lattice vector \vec{K} , and given by solutions to

$$\begin{vmatrix} \epsilon_{\vec{k}} - \epsilon + U_{\vec{0}\vec{0}}(\epsilon) & U_{\vec{0}\vec{K}}(\epsilon) \\ U_{\vec{K}\vec{0}}(\epsilon) & \epsilon_{\vec{k}-\vec{K}} - \epsilon + U_{\vec{K}\vec{K}}(\epsilon) \end{vmatrix} = 0, \quad (6)$$

where

$$U_{\vec{k}\vec{k}'}(\vec{k}, \epsilon) = V_{\vec{k}\vec{k}'}(\vec{k}, \epsilon) + \sum_{\vec{R}'' \neq \vec{R}, \vec{R}'} \frac{V_{\vec{k}\vec{k}'}(\vec{k}, \epsilon) V_{\vec{R}''\vec{R}'}(\vec{k}, \epsilon)}{\epsilon - \epsilon_{\vec{R}''\vec{R}'}} + \dots \quad (7)$$

is a "folded" Fourier component. In the analysis of Fermi-surface data ($\epsilon = \epsilon_F$), it is quite common practice (though not universal) to overlook the \vec{k} dependence explicitly displayed in Eq. (7), a procedure that has at least *a posteriori* justification for many simple metals. We will also adopt this procedure, concentrating here on energy-dependent effects which, as is clear from Eq. (7), are partly a consequence of "folding down" the starting secular equation, and partly the intrinsic energy dependence of the $V_{\vec{k}\vec{k}'}$. By ignoring the spatial non-locality [i. e., $U_{\vec{k}\vec{k}'}(\epsilon) = U_{\vec{R}\vec{R}'}$], it is readily shown,³ provided that the current matrix element in Eq. (1) can be written

$$\langle \psi_{2\vec{k}} | \vec{\nabla} | \psi_{1\vec{k}} \rangle = \frac{1}{2} i \vec{K} \left(\frac{2U_{\vec{k}\vec{k}}}{\hbar\omega} \right), \quad (8)$$

that $\sigma(\omega)$ (for $\hbar\omega$ in the neighborhood of a particular edge) can be cast in the form

$$\sigma(\omega) = \sigma_a \sum_{\vec{K}} (a_0 K) \left| \frac{2U_{\vec{k}\vec{k}}}{\hbar\omega} \right|^2 \left[1 - \left(\frac{2U_{\vec{k}\vec{k}}}{\hbar\omega} \right)^2 \right]^{-1/2}, \quad (9)$$

$$[\sigma_a = e^2/24\pi a_0 \hbar \approx 5.48 \times 10^{14} \text{ sec}^{-1}],$$

where the sum extends over the equivalent reciprocal-lattice vectors. Aside from the evident low-order nature of Eq. (9), the approximation em-

bodied in Eq. (8) amounts to an assertion that the current carried by the true valence eigenfunctions is given well enough by calculating it as if it were indeed carried by the pseudowave functions. This clearly merits further discussion,¹⁰ but in the present work we are concerned with a quite separate point, namely the extent to which possible modification of the *structure* in $\sigma(\omega)$ can arise solely as a consequence of the energy dependence of V . It is recognized (and in some cases expected) that a more detailed treatment of the current matrix elements can lead to overall corrections to the magnitude¹¹ of $\sigma(\omega)$.

III. ENERGY-DEPENDENT POTENTIALS

In what follows, we shall assume that the folded pseudopotential coefficients U_K are known at some reference energy, the Fermi energy ϵ_F being a choice of some practical importance. For energies differing from ϵ_F (but not differing too greatly), we shall take

$$U_{\vec{k}\vec{k}'}(\epsilon) = U_{\vec{k}\vec{k}'}(\epsilon_F) + \alpha_{\vec{k}\vec{k}'}(\epsilon - \epsilon_F) + \dots \quad (10)$$

(| $\epsilon - \epsilon_F$ | / $\epsilon_F \ll 1$).

We note [especially from Eq. (7)] that the $\alpha_{\vec{k}\vec{k}'}$ can be calculated, provided that the energy dependence of each $V_{\vec{k}\vec{k}'}$ is known. Since the interpolation of *a priori* band-structure calculations by a few pseudopotential coefficients determined at a set of points of high symmetry reveals discrepancies (at other points in the zone) which are generally small, we may take the $\alpha_{\vec{k}\vec{k}'}$ as first-order quantities, and discard in the following calculations all second- and higher-order products. Accordingly, if we choose $U_{\vec{k}\vec{k}}(\epsilon_F) = 0$, then with the notation

$$\alpha_0 = \alpha_{\vec{0}\vec{0}} = \alpha_{\vec{K}\vec{K}}, \quad \alpha_{\vec{K}} = \alpha_{\vec{0}\vec{K}} = \alpha_{\vec{K}\vec{0}}$$

and

$$e = \epsilon - \epsilon_F,$$

Eq. (6) becomes

$$\begin{vmatrix} e_{\vec{k}} - e & u_{\vec{k}} + e\alpha_{\vec{k}} \\ u_{\vec{k}} + e\alpha_{\vec{k}} & e_{\vec{k}-\vec{K}} - e \end{vmatrix} = 0, \quad (11)$$

where

$$e_{\vec{k}} = (m/m^*)(\epsilon_{\vec{k}}^0 - \epsilon_F)$$

and

$$m/m^* = 1/(1 - \alpha_0). \quad (12)$$

We have also defined

$$u_{\vec{k}} = (m/m^*)U_{\vec{k}}$$

so that, with Eq. (12), the effects of the energy dependence of the average of the pseudopotential are incorporated in an effective mass. The solutions to Eq. (12) are most easily given by writing

$$\vec{k} = \frac{1}{2} \vec{K} - \vec{q} \quad (13)$$

in terms of which

$$e = [(m/4m^*)\epsilon_{\vec{K}} + e_{\vec{q}}] + \alpha_{\vec{K}} u_{\vec{K}} \pm \{[(\hbar^2/2m^*)\vec{K} \cdot \vec{q}]^2 + u_{\vec{K}}^2 + (2u_{\vec{K}})\alpha_{\vec{K}}[(m/4m^*)\epsilon_{\vec{K}} + e_{\vec{q}}]\}^{1/2}, \quad (14)$$

where $\epsilon_{\vec{K}} = \hbar^2 K^2/2m$. We shall also resolve \vec{q} into its components perpendicular (\perp) and parallel (\parallel) to \vec{K} :

$$\vec{q} = \vec{q}_{\perp} + \vec{q}_{\parallel}.$$

With the aid of the notation

$$\beta = \epsilon_{\vec{K}} / |2U_{\vec{K}}|, \quad x = \left(\frac{1}{4} \epsilon_{\vec{K}} - \epsilon_{\vec{F}} + \frac{\hbar^2 q_{\perp}^2}{2m} \right) / |2U_{\vec{K}}| = \frac{\beta}{4} \left[1 - \left(\frac{2k_{\vec{F}}}{K} \right)^2 + \left(\frac{2q_{\perp}}{K} \right)^2 \right],$$

$$y = \frac{\hbar^2}{2m} q_{\parallel}^2 / |2U_{\vec{K}}| = \frac{\beta}{4} \left(\frac{2q_{\parallel}}{K} \right)^2,$$

and

$$\tilde{\alpha}_{\vec{K}} = \alpha_{\vec{K}} U_{\vec{K}} |U_{\vec{K}}|^{-1}, \quad (15)$$

we may rewrite Eq. (14) as

$$|2u_{\vec{K}}|^{-1} e = (m^*/m) |2U_{\vec{K}}| e = (x + y) + \frac{1}{2} \tilde{\alpha}_{\vec{K}} \pm \left[\frac{1}{4} + y(\tilde{\alpha}_{\vec{K}} + \beta) + \tilde{\alpha}_{\vec{K}} x \right]^{1/2}. \quad (16)$$

The two bands represented here are shown in Fig. 1, and are directly compared with those corresponding to the use of energy-independent potentials ($\alpha_{\vec{K}} = \alpha_0 = 0$). Note in particular that, for fixed y (or q_{\parallel}), the separation between the two bands, namely,

$$|2u_{\vec{K}}|^{-1} \Delta e = [1 + 4y(\tilde{\alpha}_{\vec{K}} + \beta) + 4\tilde{\alpha}_{\vec{K}} x]^{1/2} \quad (17)$$

is no longer independent of x (or q_{\perp}), as is clearly the case for $\alpha_{\vec{K}} = 0$. This departure from parallelism in the elementary two-band model is one immediate consequence of energy nonlocality. The other is a general scaling of the energy eigenvalues by the factor $(1 + \alpha_0)$, an effect noted by others,¹² particularly in the context of band effective masses. It may also be seen from Eq. (17) that the \vec{k} space surface of constant energy difference (a plane when $\alpha_{\vec{K}} = 0$) is now a conic section of revolution about \vec{K} .

Interband absorption commences at an energy which is now straightforward to determine. When $\alpha_{\vec{K}} = \alpha_0 = 0$, (energy-independent potentials), the levels associated with the onset of interband absorption are those in the neighborhood of the zone face ($q_{\parallel} = 0, y = 0$). The same situation obtains when $\alpha_{\vec{K}}, \alpha_0 \neq 0$, the essential difference arising through the slight changes in q_{\perp} values corresponding to a given choice of q_{\parallel} . In fact, the limiting values on q_{\perp} (those for $q_{\parallel} = 0$) are given by setting

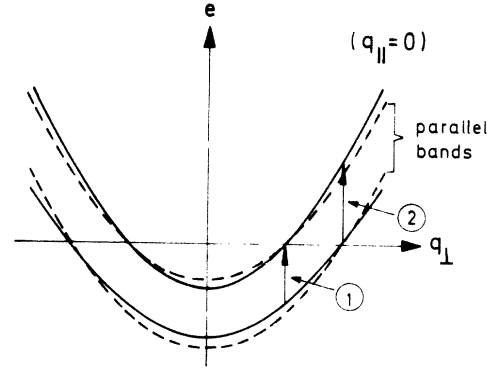


FIG. 1. Band structure corresponding to Eq. (16) [or (14)] and plotted in the zone plane ($q_{\parallel} = 0$ or $k = \frac{1}{2} \vec{K}$). The dashed lines represent (within the same model) the bands appropriate to an energy-independent pseudopotential. Agreement between the two sets of bands occurs at the Fermi energy (or $e = 0$ here), where the $U_{\vec{K}}$ and U_0 are defined. It is the smaller of the energy differences labeled 1 and 2 which determines the onset of interband absorption.

$e = 0$, ($\epsilon = \epsilon_{\vec{F}}$) in Eq. (6). Once these are known, the excitation energies follow immediately, and (again to first order in $\alpha_{\vec{K}}, \alpha_0$) interband absorption for a zone face labeled by \vec{K} begins at

$$\hbar\omega_{\text{edge}} = |2u_{\vec{K}}| (1 + \alpha_{\vec{K}}) = |2U_{\vec{K}}| (1 + \alpha_0 + \alpha_{\vec{K}}) \quad (18)$$

or

$$\hbar\omega_{\text{edge}} = |2u_{\vec{K}}| (1 - \alpha_{\vec{K}}) = |2U_{\vec{K}}| (1 + \alpha_0 - \alpha_{\vec{K}}),$$

whichever is the smaller. It follows that the spread in energies associated with the "edge," as a consequence of the energy dependence of the effective potential, is

$$\Delta(\hbar\omega_{\text{edge}}) = |4U_{\vec{K}}\alpha_{\vec{K}}|. \quad (19)$$

We turn next to a discussion of the form $\sigma(\omega)$ takes when the solutions (16) are used in conjunction with Eq. (1). For the reasons discussed above, we shall continue to set (as in Refs. 3 and 4)

$$\langle \psi_{2\vec{K}} | \vec{\nabla} | \psi_{1\vec{K}} \rangle = \frac{1}{2} i \vec{K} |2u_{\vec{K}}/\hbar\omega|.$$

Then the contribution to $\sigma_{\text{IB}}(\omega)$ from the bands ($n = 1, 2$) in the neighborhood of a zone plane labeled by K is

$$\sigma_{\text{IB}}(\omega) = \sigma_a \frac{\epsilon_{\vec{K}}}{\hbar\omega} \frac{2a_0}{\pi} \frac{\hbar^2}{2m} \times \int_{\text{zone}} d\vec{q}_{\perp} f_1(1 - f_2) \left| \frac{2u_{\vec{K}}}{\hbar\omega} \right|^2 \delta(\epsilon_{2\vec{q}} - \epsilon_{1\vec{q}} - \hbar\omega),$$

where the occupation factors

$$f_i = f(\epsilon_{i,q})$$

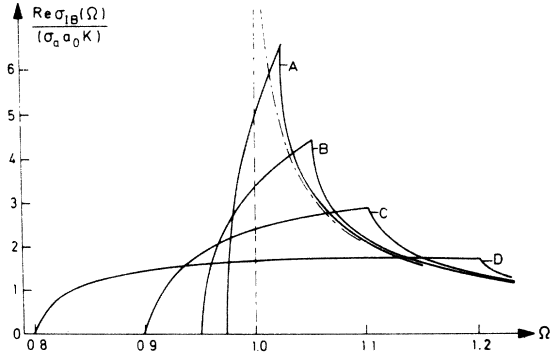


FIG. 2. Form of the interband optical conductivity from a pair of nearly-parallel bands [Eqs. (24) and (25)]. The four full curves shown correspond to progressively large values of $\alpha_{\bar{K}}$; namely, A (0.025), B (0.05), C (0.1), D (0.20). The dot-dashed curve is the limiting case ($\alpha_{\bar{K}} = 0$) corresponding to one of the contributing terms in Eq. (9). Note how quickly the peak height falls with increasing $\alpha_{\bar{K}}$. When $|\alpha_{\bar{K}}| > \frac{2}{5}(\sqrt{2}-1)(1+\alpha_0)$, the maximum of $\sigma(\Omega)$ is no longer at the cusp. For the sake of clarity, the Drude or intraband contribution is omitted. In the same units, and at high enough frequency the contribution would be $[(2k_F/K)(8/\pi) |\epsilon_F/2U_K|^2 \Omega^{-2}(\hbar/\tau)/\epsilon_F]$. $[m/m_{\text{opt}}(1+2\alpha_0)]$.

are assumed (for normal conditions) to be sufficiently close to step functions. Further, if we write

$$d\vec{q} = \frac{1}{4} \pi K^3 d(2q_{\perp}/K) d(2q_{\parallel}/K) d(2q_{\parallel}/K),$$

then

$$\begin{aligned} \sigma_{\text{IB}}(\omega) &= \sigma_a(a_0 K) \left| \frac{2U_{\bar{K}}}{\hbar\omega} \right|^2 \frac{\epsilon_{\bar{K}}^2}{2\hbar\omega} \\ &\times \iint d\left(\frac{2q_{\perp}}{K}\right) d\left(\frac{2q_{\parallel}}{K}\right) d\left(\frac{2q_{\parallel}}{K}\right) \\ &\times f_1(1-f_2) \delta(\epsilon_{2\bar{q}} - \epsilon_{1\bar{q}} - \hbar\omega). \end{aligned}$$

And finally, if we change to the variables x and y defined above, we arrive at

$$\sigma_{\text{IB}}(\omega) = \sigma_a(a_0 K) \left| \frac{2U_{\bar{K}}}{\hbar\omega} \right|^2 I,$$

where, with the supplementary definition

$$\Omega = \hbar\omega / |2U_{\bar{K}}| (1 + \alpha_0) = \hbar\omega / |2u_{\bar{K}}|, \quad (20)$$

we have

$$\begin{aligned} I(\Omega) &= \frac{1}{(1 + \alpha_0)^2} \frac{1}{\Omega} \beta^{1/2} \int dx \int \frac{dy}{y^{1/2}} \\ &\delta(\Omega - [1 + 4y(\bar{\alpha}_{\bar{K}} + \beta) + 4\bar{\alpha}_{\bar{K}}x]^{1/2}), \quad (21) \end{aligned}$$

with the implied understanding that the limits on integration now include the requirements imposed by the factor $f_1(1-f_2)$. From Eqs. (11) or (14) we see that, for fixed y , the range of integration for x is set by¹³

$$y - \frac{1}{2}(1 + 4\beta y)^{1/2} < -x < y + \frac{1}{2}(1 + 4\beta y)^{1/2}, \quad (22)$$

whereas for y itself, the range is (apart from second-order corrections³)

$$0 < y < \frac{1}{4} \beta(2k_F/K - 1)^2.$$

Integrating the δ function in Eq. (21) is a straightforward procedure, and the result is

$$\begin{aligned} I(\Omega) &= [1/(1 + \alpha_0)^2] [1/2\bar{\alpha}_{\bar{K}}] [(\Omega^2 + 2\bar{\alpha}_{\bar{K}}\Omega - 1)^{1/2} \Theta(\Omega - \Omega_1) \\ &- (\Omega^2 - 2\bar{\alpha}_{\bar{K}}\Omega - 1)^{1/2} \Theta(\Omega - \Omega_2)], \quad (23) \end{aligned}$$

where

$$\Omega_1 = 1 - \bar{\alpha}_{\bar{K}}, \quad \Omega_2 = 1 + \bar{\alpha}_{\bar{K}}.$$

It is apparent that Eq. (23) is independent of the sign of $\alpha_{\bar{K}}$ (and hence of $U_{\bar{K}}$). Accordingly, we may write the conductivity as

$$\begin{aligned} \sigma_{\text{IB}}(\Omega) &= \sigma_a(a_0 K)(1 + \alpha_0)^{-4} \frac{1}{\Omega^2} \frac{1}{2|\alpha_{\bar{K}}|} \\ &[(\Omega + |\alpha_{\bar{K}}|)^2 - 1]^{1/2}, \quad (24) \end{aligned}$$

$$1 - |\alpha_{\bar{K}}| < \Omega < 1 + |\alpha_{\bar{K}}|$$

and

$$\begin{aligned} \sigma_{\text{IB}}(\Omega) &= \sigma_a(a_0 K)(1 + \alpha_0)^{-4} \frac{1}{\Omega} \\ &\times 2/\{[(\Omega + |\alpha_{\bar{K}}|)^2 - 1]^{1/2} + [(\Omega - |\alpha_{\bar{K}}|)^2 - 1]^{1/2}\}, \quad (25) \end{aligned}$$

$$1 + |\alpha_{\bar{K}}| < \Omega < \Omega_0,$$

where $\Omega_0 = \beta(2k_F/K - 1)$. Equations (24) and (25) are the main results and should be compared directly with Eq. (10) in Ref. 3. Similarly, Fig. 5 of Ref. 3 should be compared with Fig. 2 in this paper, in which $\sigma_{\text{IB}}(\Omega)$ is plotted. Before turning to a detailed discussion of these results, we observe at this point that, whereas the overall sign of $\alpha_{\bar{K}}$ (as noted) does not affect the form of the result, the sign of α_0 is of some consequence.

IV. DISCUSSION

The physical origin of the absorption edge described by Eqs. (24) and (25) can be readily traced to the singularity in the joint density of levels corresponding to the two bands of Eq. (14). Let $S_{12}(\vec{k}, \hbar\omega)$ be the surface of constant energy difference defined by the locus of \vec{k} vectors satisfying

$$\epsilon_{2\vec{k}} - \epsilon_{1\vec{k}} = \hbar\omega.$$

Then the contribution to Eq. (1) from those levels in the vicinity of a given zone plane may be written³

$$\sigma_{\text{IB}}(\omega) = \sigma_a \left(\frac{\epsilon_{\bar{K}}}{\hbar\omega} \right) \frac{2a_0}{\pi} \frac{\hbar^2}{2m}$$

$$\times \int_{S_{12}} \frac{dS_{12}(\vec{k}, \hbar\omega)}{|\nabla_{\vec{k}}(\epsilon_{2\vec{k}} - \epsilon_{1\vec{k}} - \hbar\omega)|} f_1(1-f_2) \left| \frac{2U_{\vec{k}}}{\hbar\omega} \right|^2 \quad (26)$$

and it is clear that the possibility of singular behavior in $\sigma_{IB}(\omega)$ is controlled both by the vanishing of $|\nabla_{\vec{k}}(\epsilon_{2\vec{k}} - \epsilon_{1\vec{k}} - \hbar\omega)|$ and the extent of $S_{12}(\vec{k}, \hbar\omega)$ over which this may occur. In the case of energy-independent potentials, S_{12} is a plane surface (perpendicular to \vec{K}) over which $|\nabla_{\vec{k}}(\epsilon_{2\vec{k}} - \epsilon_{1\vec{k}} - \hbar\omega)|$ takes the (constant) value $(2\epsilon_{\vec{k}}/K) [(1 - 2U_{\vec{k}}/\hbar\omega)^2]^{1/2}$. The divergence, at threshold ($\hbar\omega = |2U_{\vec{k}}|$) is immediately apparent. However, when $\alpha_{\vec{k}} \neq 0$, $S_{12}(\vec{k}, \hbar\omega)$ is no longer planar, $|\nabla_{\vec{k}}(\epsilon_{2\vec{k}} - \epsilon_{1\vec{k}} - \hbar\omega)|^{-1}$ cannot be removed from the integral in Eq. (26), and any singular tendency associated with the integrand is compensated by the behavior of the surface element. Accordingly, the result is finite although, as can be seen from Fig. 2, a steeply rising curve for small $\alpha_{\vec{k}}$. The maximum occurs at $|2U_{\vec{k}}|(1 + \alpha_0 + |\tilde{\alpha}_{\vec{k}}|)$ and the corresponding value of σ is

$$\sigma_{\max}(\omega) = \sigma_a(a_0 K) |\alpha_{\vec{k}}|^{-1/2}, \quad (27)$$

a potentially useful relation connecting the peak height to quantities characterizing the energy dependences of the effective potential.¹⁴ In this respect, the role played by $|\alpha_{\vec{k}}|^{-1/2}$ is not dissimilar to that of thermal or collisional smearing of absorption edges in the energy-independent potential analysis.¹⁵ Scattering effects within the present model can also be included in a phenomenological relaxation-time approximation. Following the steps leading to Eq. (19) of Ref. 3 [or (6) of Ref. (4)], we find for the real part of the conductivity

$$\begin{aligned} \sigma_{IB}(\Omega) &= \frac{\sigma_a(a_0 K)}{(1 + \alpha_0)^4} \frac{\beta^{1/2}}{\pi} \Omega^2 \\ &\times \int dx \int dy y^{-1/2} [1 + 4y(\tilde{\alpha}_{\vec{k}} + \beta) + 4\tilde{\alpha}_{\vec{k}} x]^{-1/2} \\ &\times \{ [1 + 4y(\tilde{\alpha}_{\vec{k}} + \beta) + 4\tilde{\alpha}_{\vec{k}} x] - \Omega^2 - \delta^2 \}^2 + 4\Omega^2 \delta^2 \}^{-1}, \end{aligned} \quad (28)$$

where δ incorporates the relaxation time τ in the combination

$$\delta = (\hbar/\tau) |2U_{\vec{k}}| (1 + \alpha_0).$$

Equation (28) can be integrated numerically,¹⁶ and leads to results of the type shown in Fig. 3. In accordance with expectation, the cusp-like and threshold features of the infinite relaxation time result ($\delta = 0$) are seen to be smoothed out, the peak height is generally decreased, but the area under the curve is essentially unaltered. The latter result is, of course, related directly to the optical effective mass m_{opt} , which in the present model is most conveniently discussed in terms of the sum rule on the entire (Drude and interband) transverse conductivity, the interband contribution to which $[\sigma_{IB}(\omega)]$ satisfies¹⁷

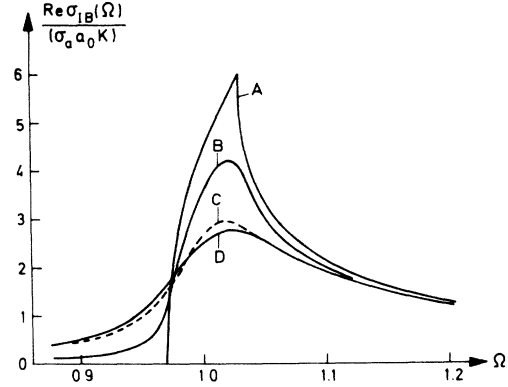


FIG. 3. Effects of scattering for the $\sigma(\omega)$ curves appropriate to $|\alpha_{\vec{k}}| = 0.03$, and values of $\delta = (\hbar/\tau) |2u_{\vec{k}}|$: A ($\delta = 0$); B ($\delta = 0.009$); D ($\delta = 0.036$). Curve C is included to show the relative effects of scattering and energy-dependence. It corresponds to the case $|\alpha_{\vec{k}}| = 0$ and $\delta = 0.036$.

$$1 - \frac{m}{m_{opt}} = \left(\frac{1}{2a_0 k_F} \right) \frac{1}{4\sigma_a} \int_0^\infty \frac{\hbar d\omega}{\epsilon_F} \sigma_{IB}(\omega) \quad (29)$$

or alternatively, [using, Eq. (20)]

$$1 - \frac{m}{m_{opt}} = \left(\frac{1}{2a_0 k_F} \right) \frac{1 + \alpha_0}{4\sigma_a} \left| \frac{2U_{\vec{k}}}{\epsilon_F} \right| \int_0^\infty d\Omega \sigma_{IB}(\Omega). \quad (30)$$

Using Eqs. (24) and (28), we can immediately calculate that contribution to the right-hand side of Eq. (30) which is linear¹⁸ in $U_{\vec{k}}$. For a single zone plane, this is simply

$$S_{\vec{k}}^{(1)} = \frac{\pi}{8} \left(\frac{K}{2k_F} \right) \left| \frac{2U_{\vec{k}}}{\epsilon_F} \right| \frac{1}{(1 + \alpha_0)^3} + O(\alpha_{\vec{k}}^2)$$

and to this order in $U_{\vec{k}}$

$$1 - \frac{m}{m_{opt}} = \sum_{\{\vec{k}\}} S_{\vec{k}}^{(1)},$$

where the sum extends over the set of reciprocal-lattice vectors whose associated zone planes cut the Fermi surface. It must be remembered that we are regarding α_0 as a first-order quantity, so the corrections (from energy dependence) to m_{opt} are essentially of second order. In view of the assumption made in connection with the calculation of the current matrix element, these can have little significance.

Finally, it remains to comment on the relation of the results presented here to the experimentally determined optical conductivities. By way of example, consider the case of Al for which Mathewson and Myers have noted, on the basis of careful measurements of the temperature dependence of its $\sigma(\omega)$, that the location of the edge *appears*¹⁹ to differ slightly from the value expected from an analysis of Fermi-surface data. These differences remain after appropriate corrections for dynamic ef-

fects in the lattice (chiefly the Debye-Waller factor), and have been ascribed to possible energy dependences in the $U_{\vec{k}}$. In the fitting of Fourier components of the pseudopotential to Fermi-surface dimensions, the value of m^* (or α_0) are not determined. This can be readily perceived from the generalization to higher dimension of Eq. (11), with the stipulation that at the Fermi energy, $e=0$, and that solutions are sought not for energy but wave vector. Thus it is $u_{\vec{k}}$ rather than $U_{\vec{k}}$ that is extracted from the analysis of Fermi-surface structure. But if $\alpha_{\vec{k}}=0$, it is precisely the $u_{\vec{k}}$ that fix the locations of the absorption edges in $\sigma(\omega)$ [see Eq. (18)]. It follows that deviations from these locations are a reflection of the values taken by the $|\alpha_{\vec{k}}|$. In the case of Al²⁰ we can deduce from the data of Mathewson and Myers that for $\vec{K}=(2, 0, 0)$

the corresponding value of $|\alpha_{\vec{k}}|$ is in the range

$$0.021 < |\alpha_{\vec{k}}| < 0.047 .$$

Values of $\alpha_{\vec{k}}$ taken from recent band-structure calculations^{21,22} are comparable to these experimental results, and it is therefore reasonable to conclude that not only can optical measurements provide estimates of pseudopotential coefficients, but high-precision data can in addition yield information on their energy dependences.

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¹W. A. Harrison, Phys. Rev. **147**, 467 (1966).

²A. I. Golovashkin, A. I. Kopeliovich, and G. P. Motulevich, Zh. Eksp. Teor. Fiz. **53**, 2053 (1967) [Sov. Phys.-JETP **26**, 1161 (1967)].

³N. W. Ashcroft and K. Sturm, Phys. Rev. B **3**, 1898 (1971).

⁴M. J. Kelly and N. W. Ashcroft, Phys. Rev. B **8**, 2445 (1973).

⁵A full discussion of the origin and importance of nonlocal effects in pseudopotentials may be found in the article by V. Heine, Solid State Phys. **24**, 1 (1970).

⁶There is also a nonlocality in momentum \vec{k} which we take to be subsumed, if noticeable, into an additional-contribution to the energy nonlocality. The fact that so many of the simple metal Fermi surfaces can be parameterized by \vec{k} -independent Fourier components $u_{\vec{k}}(\epsilon_F)$ suggests that this approximation is reasonable.

⁷A. G. Mathewson and H. P. Myers, J. Phys. F **2**, 403 (1972).

⁸The modifications required to deal with noncubic simple metals are straightforward and can be extracted from Ref. 4.

⁹In the heavy (but simple) metals, spin-orbit coupling can have noticeable effects on the band structure; these will be the subject of a further communication.

¹⁰The point has received some attention (in connection with "optical pseudopotentials") from J. Appelbaum, Phys. Rev. **144**, 435 (1966); A. O. E. Animalu, Phys. Rev. **163**, 557 (1967); M. J. Kelly, thesis (Victoria University, Wellington, 1970) (unpublished); and J. Hammerberg (private communication).

¹¹It should be noted, however, that Eq. (8), or its modification when scattering is included [Eq. (19) of Ref. 3], can lead to good agreement with the data (in some simple metals) with regard to location of structure and overall magnitude.

¹²See, for example, N. W. Ashcroft, thesis (Cambridge University, 1964) (unpublished); D. Weaire, Proc. Phys. Soc. Lond. **92**, 956 (1967); R. W. Shaw, J. Phys. C **2**, 2350 (1969), and V. Heine and R. O. Jones, *ibid.* **2**, 719 (1969).

¹³Note that at the Fermi energy ($e=0$), the effects of $\alpha_{\vec{k}}$

and α_0 are, of course, absent.

¹⁴When $|\alpha_{\vec{k}}| > \frac{2}{5}(\sqrt{2}-1)(1+\alpha_0)$, the maximum in σ is to the right of the cusp, and has the value $\sigma_{\max} = \sigma_a(a_0K)^{\frac{1}{2}} |\alpha_{\vec{k}}|^{-1} (1/x_0^2) (\frac{1}{2}x_0^2 + \alpha_{\vec{k}}x_0)^{1/2}$, where $x_0 = -\frac{3}{2}\alpha_{\vec{k}} + \sqrt{2}(1+\alpha_0)$.

¹⁵If the phenomenological relaxation time is taken as τ , then it is easy to show from Eq. (9) that the maximum value of σ for a single zone plane is approximately $\sigma_{\max} = \sigma_a(a_0K) |2\hbar/U_{\vec{k}}\tau|^{-1/2}$, and comparing this with Eqs. (19) and (28) leads to the result that scattering effects and energy-dependent broadening are roughly equivalent when $|\alpha_{\vec{k}}U_{\vec{k}}| \sim 2\hbar/\tau$. It should also be noted that, whereas the effects of $\alpha_{\vec{k}}$ are striking in the absorption edges of polyvalent metals, they will be much less noticeable in monovalent metals. The scaling due to α_0 will be present in both classes.

¹⁶A reasonable approximation to Eq. (28) can be obtained by noting that the last term in the integrand is sharply peaked for small δ (in Al, $\delta \sim 0.04$) at $(1+4y(\tilde{\alpha}_{\vec{k}} + \alpha_0) + 4x\tilde{\alpha}_{\vec{k}})^{1/2} = (\Omega^2 + \delta^2)^{1/2}$ so that

$$\sigma_{\text{B}}(\Omega) = \sigma_a(a_0K) \left(\frac{\beta^{1/2}}{(1+\alpha_0)^4\pi\Omega} \right) \int dx \int \frac{dy}{y^{1/2}} \\ \times 4\delta \{ [1+4y(\tilde{\alpha}_{\vec{k}} + \beta) + 4x\tilde{\alpha}_{\vec{k}}] - \Omega^2 - \delta^2 \}^{-1/2}$$

which can be integrated directly, and which also leads to the results shown in Fig. 3.

¹⁷See Eq. (38) of Ref. 3.

¹⁸The contributions quadratic in $U_{\vec{k}}$ are also straightforward to obtain, and suffer similar corrections.

¹⁹It must be remembered that the analysis of Ref. 7 is carried out within the energy-independent pseudopotential model. The location of the peaks in $\sigma(\omega)$ are determined by adjusting $u_{\vec{k}}$ and τ in an equation such as (19) of Ref. 3. Notice, therefore, that if the value of $\alpha_{\vec{k}}$ is such that the location of a corresponding peak in $\sigma(\omega)$ is in fact *not* dominated by scattering (but rather by energy-dependent effects), then the values of τ so deduced (and the consequent extraction of $u_{\vec{k}}$) can be slightly in error.

²⁰Note that in the analysis of the Fermi surface of Al [N. W. Ashcroft, Philos. Mag. **8**, 2055 (1963)], a secular equation of fourth order was used. Thus, the

folded Fourier components used here (second-order secular equations) differ slightly from those appropriate to the Fermi-surface determination, even in absence of any energy-dependent effects; but these differences are quite small.

²¹If band-structure calculations provide L_1 and L'_2 (at an average energy ϵ_L^0); X_1 and X'_4 (at an average energy ϵ_X^0); and W_3 , W_1 , and W_2 (at an average energy ϵ_W^0); then from $U_{111}(\epsilon_L^0) = \frac{1}{2}(L_1 - L'_2)$ and $U_{111}(\epsilon_W^0) = \frac{1}{4}(W_1 - W_2)$, we deduce α_{111} ; and from $U_{200}(\epsilon_X^0) = \frac{1}{2}(X_1 - X'_4)$ and $U_{200}(\epsilon_W^0) = \frac{1}{4}(W_1 + W'_2 - 2W_3)$, we deduce α_{200} . By this means, we find from the band structures of Smrka

[Czeck. J. Phys. B 20, 241 (1970)], values of 0.014 and 0.012; of Segall [Phys. Rev. 124, 1797 (1961)], values of 0.03 and 0.074; of Greisen [Phys. Status Solidi. 25, 753 (1968)], values of 0.013 and 0.019; and of Arberman and von Barth (unpublished) values of 0.024 and 0.036, for α_{111} and α_{200} , respectively.

²²Representative values of $\alpha_{\vec{k}}$ and α_0 can be obtained from an examination of various model potential formulations of the pseudopotential. See, for example, R. W. Shaw and W. A. Harrison, Phys. Rev. 163, 604 (1967); R. W. Shaw, J. Phys. C 2, 2350 (1969); and M. L. Cohen and V. Heine, Solid State Phys. 24, 37 (1970).