

## Optical Conductivity of Simple Metals\*

A. O. E. ANIMALU

*Division of Applied Physics, Stanford University, Stanford, California*

(Received 1 June 1967)

The optical conductivity of simple (nearly-free-electron) metals, in particular the alkali metals, is derived from the Kubo-Greenwood formula by using an expression for the matrix element  $\langle \chi_{k'} | \nabla | \chi_k \rangle$  which we have previously determined to first order in the "optical" pseudopotential. The strength of the interband absorption in the solid alkali metals Li, Na, and K is found to be given approximately by replacing the parameter of the lattice potential determining the band gap in Butcher's formula with the corresponding optical-pseudopotential matrix element. In Na and K, the calculated interband absorption is about 50% of the experimental value; in Li good agreement is obtained. The results in liquid Na are discussed to the effect that an "interband absorption" should be visible in the liquid state under favorable conditions, e.g., under pressure.

### 1. INTRODUCTION

THE purpose of this paper is to describe a calculation of the optical conductivity of simple (nearly-free-electron) metals, in particular the solid and liquid alkali metals, at a finite frequency in an electric field. For simplicity, the self-consistency in the evaluation of the matrix elements involved will be described separately in the next paper<sup>1</sup> (hereafter referred to as AII). The motivation for this computation is the numerical discrepancy between the measured optical absorption of the alkali metals<sup>2</sup> due to interband transitions and that calculated in current literature.<sup>3-6</sup> We shall show how our present theory corrects an error which has existed in these previous calculations and thereby removes nearly 50% of the discrepancy.

In Butcher's original theory of interband transitions in nearly-free-electron metals,<sup>3</sup> and recent improvements, the interband optical absorption is found to be proportional to a matrix element of the screened lattice potential or pseudopotential. Such matrix elements determine the band gap at the Brillouin zone face and hence the distortions of the Fermi surface from the free-electron sphere but have seemed not to account for the strength of the absorption. Hopfield<sup>4</sup> first improved on Butcher's theory by pointing out that although the pseudopotential matrix element entering the Fermi surface may be screened by a *static* Hartree dielectric function, the corresponding matrix element for optical absorption has to be screened by a *dynamic* dielectric function at the frequency of the absorbed photon. He observed, however, that such a correction would be quite small. Next, Overhauser<sup>5</sup> incorporated exchange in the framework of self-consistent, time-dependent,

Hartree-Fock theory, deliberately omitting the screening of the exchange interaction. He thereby restored agreement between theory and experiment in a small photon energy range near the interband threshold but lost over-all qualitative agreement. We feel, in any case, that a proper screening of exchange would lead to results close to the Hartree approximation, and so would leave the discrepancy unresolved.

Appelbaum<sup>6</sup> reformulated the problem in terms of orthogonalized plane waves rather than the simple plane waves of nearly-free-electron theory. However, he appeared to have missed a sizeable correction to the matrix elements arising from orthogonalization. More recently, Animalu and Harrison<sup>7</sup> focused attention upon these orthogonalization terms and pointed out that these terms make additional contributions to the usual pseudopotential matrix elements. They therefore, defined an "optical" pseudopotential matrix element which is different from the usual one determining the Fermi surface. On the basis of this interpretation, we shall develop a general self-consistent theory in AII to deal not only with the optical absorption but also with various electromagnetic phenomena dependent on the emission or absorption of a single photon by the Bloch electron, and derive *inter alia* Hopfield's dynamic screening for the optical pseudopotential.

In Sec. 2 of this paper, the dynamically screened optical pseudopotential will be used to reduce the Kubo-Greenwood formula for the real part of the optical conductivity, and hence to derive expressions for the interband absorption in the solid and the conductivity of the liquid metal. Numerical results will be presented and discussed in Sec. 3.

### 2. THEORY OF THE OPTICAL CONDUCTIVITY

The real part of the optical conductivity of Bloch electrons at a frequency  $\omega$  in an isotropic or cubic

<sup>7</sup> A. O. E. Animalu and W. A. Harrison, *Bull. Am. Phys. Soc.* **12**, 415 (1967). Note: the expression given for  $\langle \psi_f | \nabla | \psi_i \rangle$  in this reference ignored the non-Hermiticity of  $\bar{W}$ , hence the asymmetry in  $\mathbf{k}_f$  and  $\mathbf{k}_i$ ; the correct order of factors in  $\bar{W}$  should be

$$\langle \mathbf{k}_f | \bar{W} | \mathbf{k}_i \rangle = \langle \mathbf{k}_f | W + (\epsilon_f - \epsilon_i) P | \mathbf{k}_i \rangle,$$

where  $W$  always acts to the right. A detailed derivation is included in AII.

\* This work was supported by the Advanced Research Projects Agency through the Center for Materials Research at Stanford University.

<sup>1</sup> A. O. E. Animalu, following paper [*Phys. Rev.* **163**, 562 (1967)] referred to as AII.

<sup>2</sup> *Proceedings of the International Colloquium on Optical Properties and Electronic Structure of Metals and Alloys, Paris, 1965* (North-Holland Publishing Company, Amsterdam, 1966), p. 47. See also H. Mayer and M. H. el Naby, *Z. Physik* **174**, 289 (1963).

<sup>3</sup> P. N. Butcher, *Proc. Phys. Soc. (London)* **A64**, 765 (1951).

<sup>4</sup> J. J. Hopfield, *Phys. Rev.* **139**, A419 (1965).

<sup>5</sup> A. W. Overhauser, *Phys. Rev.* **156**, 844 (1967).

<sup>6</sup> J. A. Appelbaum, *Phys. Rev.* **144**, 435 (1966).

material is given by the general formula of Kubo<sup>8</sup> and Greenwood<sup>9</sup> in the form used recently (for liquid metals) by Faber<sup>10</sup> and Mott<sup>11</sup>

$$\sigma(\omega) = \frac{2\pi e^2 \hbar^2}{m^2 \omega} \sum_{\mathbf{k}'\mathbf{k}} |\langle X_{\mathbf{k}'} | \nabla_x | X_{\mathbf{k}} \rangle|^2 \times n_{\mathbf{k}'} (1 - n_{\mathbf{k}}) \delta(\hbar\omega_{\mathbf{k}'\mathbf{k}} - \hbar\omega), \quad (2.1)$$

where  $\hbar\omega_{\mathbf{k}'\mathbf{k}}$  is the energy difference between the single-electron Bloch states  $X_{\mathbf{k}'}$  and  $X_{\mathbf{k}}$ ,  $\nabla_x$  being proportional to the current operator in the  $x$  direction, and the  $n$ 's are Fermi distribution functions. By using the expression obtained in Ref. 7 for the matrix element appearing in (2.1), and defining an effective coupling matrix between an electron and a photon (of the electric field)

$$g_{\mathbf{k}'\mathbf{k}\lambda}^{\text{eff}} \equiv (\hbar/2\omega)^{1/2} (ie\hbar/m) \mathbf{e}_\lambda \cdot \langle X_{\mathbf{k}'} | \nabla | X_{\mathbf{k}} \rangle \approx (\hbar/2\omega)^{1/2} (e\hbar/m) \mathbf{e}_\lambda \cdot \left[ \frac{\mathbf{k}' \langle \mathbf{k}' | \tilde{W} | \mathbf{k} \rangle - \mathbf{k} \langle \mathbf{k} | \tilde{W} | \mathbf{k}' \rangle^*}{\hbar\omega_{\mathbf{k}'\mathbf{k}}} \right]. \quad (2.2)$$

We may rewrite (2.1) in the explicit and compact form

$$\sigma(\omega) = (2\pi/\hbar) \sum_{\mathbf{k}'\mathbf{k}\lambda} |g_{\mathbf{k}'\mathbf{k}\lambda}^{\text{eff}}|^2 n_{\mathbf{k}'} (1 - n_{\mathbf{k}}) \delta(\hbar\omega_{\mathbf{k}'\mathbf{k}} - \hbar\omega). \quad (2.3)$$

In (2.2),  $\mathbf{e}_\lambda$  ( $\lambda=1, 2$ ) is the polarization and  $\omega$  is the frequency of the photon in a plane-wave representation of the electric field normalized to a unit volume.  $\tilde{W}$  is the optical pseudopotential,<sup>7</sup> with matrix elements between plane waves

$$\langle \mathbf{k}' | \tilde{W} | \mathbf{k} \rangle = \langle \mathbf{k}' | W + \hbar\omega_{\mathbf{k}'\mathbf{k}} P | \mathbf{k} \rangle, \quad (2.4)$$

where  $W$  is the usual pseudopotential operator (to be understood to act always to the right);  $P = \sum_\alpha |\alpha\rangle \langle \alpha|$  is the usual projection operator of pseudopotential theory, the summation being over the ion core states; and the frequency  $\omega_{\mathbf{k}'\mathbf{k}} \equiv (\epsilon_{\mathbf{k}'} - \epsilon_{\mathbf{k}})/\hbar$ , where  $\epsilon_{\mathbf{k}} \equiv \hbar^2 k^2/2m$  is the energy of a plane-wave state  $|\mathbf{k}\rangle$ . In general,  $\tilde{W}$  is a non-Hermitian operator

$$\langle \mathbf{k}' | \tilde{W} | \mathbf{k} \rangle - \langle \mathbf{k} | \tilde{W} | \mathbf{k}' \rangle^* = +\hbar\omega_{\mathbf{k}'\mathbf{k}} \langle \mathbf{k}' | P | \mathbf{k} \rangle. \quad (2.5)$$

The complete expression (2.2) has to be screened by a *dynamic* dielectric function at the frequency  $\omega = \omega_{\mathbf{k}'\mathbf{k}}$ , as we shall show in AII, in order to achieve the self-consistency suggested by Hopfield.<sup>4</sup>

We proceed now to the integration of (2.3). Since the optical pseudopotential is strictly  $k$  dependent, the anisotropy introduced by crystal symmetry in the integration is, in general, nontrivial. For example, in the ultraviolet and visible spectrum we should consider for the alkali metals the twelve reciprocal lattice vectors:

$\mathbf{G} = \pm(2\pi/a)(1,1,0)$ ,  $\pm(2\pi/a)(1,0,1)$ ,  $\pm(2\pi/a)(0,1,1)$ ,  $\pm(2\pi/a)(-1,1,0)$ ,  $\pm(2\pi/a)(-1,0,1)$ , and  $\pm(2\pi/a) \times (0, -1, 1)$ , all of which satisfy  $|\mathbf{k} \pm \mathbf{G}| > k_F$ , since  $G/k_F \approx 2.28$ . For any pair of  $\mathbf{G}$ 's, say  $\pm(2\pi/a)(1,1,0)$ , the argument of the energy  $\delta$  function in (2.3) is

$$y^\pm \equiv (\hbar^2/2m)(|\mathbf{k} \pm \mathbf{G}|^2 - k^2) - \hbar\omega = (\hbar^2/2m)(\pm 2\mathbf{k} \cdot \mathbf{G} + G^2) - \hbar\omega. \quad (2.6)$$

Similarly, by using (2.5) we obtain for each pair of  $\mathbf{G}$ 's

$$|\mathbf{k}' \langle \mathbf{k}' | \tilde{W} | \mathbf{k} \rangle - \mathbf{k} \langle \mathbf{k} | \tilde{W} | \mathbf{k}' \rangle^*|^2 = G^2 |\langle \mathbf{k}' | \tilde{W} | \mathbf{k} \rangle|^2 + (\hbar\omega)^2 k^2 |\langle \mathbf{k}' | P | \mathbf{k} \rangle|^2 \pm 2(\hbar\omega) \mathbf{k} \cdot \mathbf{G} \langle \mathbf{k}' | \tilde{W} | \mathbf{k} \rangle \langle \mathbf{k} | P | \mathbf{k}' \rangle. \quad (2.7)$$

The insertion of the  $\pm$  sign in (2.6) and (2.7) makes explicit the momentum conservation:  $\mathbf{k}' = \mathbf{k} + \mathbf{G}$ , with  $k \leq k_F$  and  $k' > k_F$  irrespective of the sense in which the angle between  $\mathbf{k}$  and  $\mathbf{G}$  is described. For brevity we shall write subsequently,

$$\langle \mathbf{k}' | \tilde{W} | \mathbf{k} \rangle \equiv \tilde{W}_G \quad \text{and} \quad \langle \mathbf{k}' | P | \mathbf{k} \rangle \equiv P_G,$$

noting, of course, that both  $\tilde{W}_G$  and  $P_G$  depend on the state  $k$ . Also for a given value of  $k$ ,  $G$ , and  $\omega$ , we must conserve energy by setting  $k' = [k^2 + (2m\omega/\hbar)]^{1/2}$  and defining the angle between  $\mathbf{k}$  and  $\mathbf{k}'$  in the usual way as  $\cos^{-1}[(k'^2 + k^2 - G^2)/2kk']$ . Thus,  $\tilde{W}_G$  and  $P_G$  also depend implicitly on  $\omega$  *but not* on the sign of  $\mathbf{G}$  in each pair of  $\mathbf{G}$ 's. However, the term  $(\hbar\omega)P_G$  does not become indefinitely large, since  $P_G$  drops off rapidly as  $\omega$  increases.

On substituting (2.7) in (2.3) and changing the summation over  $\mathbf{k}$  into an integration, we obtain at 0°K

$$\sigma(\omega) = \frac{1}{3} \frac{e^2}{2\pi m^2 \omega^3} \sum_G \int \{G^2 |\tilde{W}_G|^2 + (\hbar\omega)^2 k^2 |P_G|^2 \pm 2(\hbar\omega) k G \tilde{W}_G P_G z\} k^2 \delta(y^\pm) dk dz, \quad (2.8)$$

where  $z \equiv \mathbf{k} \cdot \mathbf{G}/kG$  is the angle between  $\mathbf{k}$  and  $\mathbf{G}$ , the factor  $\frac{1}{3}$  is due to the isotropy of  $\sigma(\omega)$  in a cubic system, and the summation is over *pairs* of  $\mathbf{G}$ 's as discussed above. On performing the integration over  $z$  for each pair of  $\mathbf{G}$ 's, the last (third) term in the integrand contributes zero and we find

$$\sigma(\omega) = \frac{e^2}{6\pi m \hbar^2 \omega^3} \sum_G \int_{k_m}^{k_F} G k \times \{ |\tilde{W}_G|^2 + (\hbar\omega)^2 (k/G)^2 |P_G|^2 \} dk, \quad (2.9)$$

where

$$k_m = [G^2 - (2m\omega/\hbar)]/2G \leq k_F.$$

This is the general expression for the interband absorption in a cubic nearly-free-electron metal which we shall evaluate numerically in the next section.

For the liquid metal, there is no special anisotropy introduced by the momentum condition  $\mathbf{k}' = \mathbf{k} + \mathbf{q}$ .

<sup>8</sup> R. Kubo, J. Phys. Soc. Japan **12**, 570 (1957).

<sup>9</sup> D. A. Greenwood, Proc. Phys. Soc. (London) **A71**, 585 (1958).

<sup>10</sup> T. E. Faber, in *Proceedings of the International Colloquium on Optical Properties and Electronic Structure of Metals and Alloys, Paris, 1965* (North-Holland Publishing Company, Amsterdam, 1966), p. 259; Advan. Phys. **15**, 547 (1966).

<sup>11</sup> N. F. Mott, Phil. Mag. **13**, 989 (1966).

TABLE I. Static and dynamic dielectric function in Na.<sup>a</sup>

$\hbar\omega$ (eV)	$\hbar\omega/E_F$	$\epsilon_{\text{HF}}(q,0)$	$ \epsilon_{\text{HF}}(q,\omega) $	$\epsilon_{\text{HF}}^R(q,\omega)$	$\epsilon_{\text{HF}}^I(q,\omega)$
2.39	0.74	1.1053	1.1235	1.1229	0.0377
3.36	1.04	1.1053	1.1158	1.1142	0.0600
4.34	1.34	1.1053	1.1037	1.1009	0.0784
5.31	1.64	1.1053	1.0884	1.0844	0.0929
7.90	2.44	1.1053	1.0389	1.0328	0.1124

<sup>a</sup> Note: The dielectric functions are evaluated for  $q=(2\pi/a)\sqrt{2}$  in the frequency range above the interband threshold,  $\hbar\omega\sim 2.1$  eV.  $\epsilon_{\text{HF}}^R$  and  $\epsilon_{\text{HF}}^I$  are, respectively, the real and imaginary parts of  $\epsilon_{\text{HF}}(q,\omega)$ .

Thus from (2.8) we find

$$\sigma(\omega) = \frac{e^2\Omega_0}{48\pi^4 m \hbar^2 \omega^3} \int_0^\infty a(q) q^3 dq \int_{k_m}^{k_F} k \times \{ |\tilde{w}_q|^2 + (\hbar\omega)^2 (k/q)^2 |P_q|^2 + [(2m\omega/\hbar q^2) - 1](\hbar\omega)\tilde{w}_q P_q \} dk, \quad (2.10)$$

where  $k_m$  is defined similarly as in (2.9),  $\Omega_0$  is the atomic volume and we have set  $|\langle \mathbf{k}' | \tilde{W} | \mathbf{k} \rangle|^2 \equiv a(q) |\tilde{w}_q|^2$ ,  $a(q)$  being the usual liquid metal interference function. We see that the last (third) term in (2.7) does not vanish in this case. The evaluation of (2.10) entails no more labor than the usual first-principle pseudopotential calculation for  $\tilde{w}_q$ ,  $P_q$  being obtained as a byproduct in such a calculation.

In practice, the contribution from the second term in the integrand of (2.9) is no more than about 5–15%, and so for the solid we obtain the approximate result

$$\sigma(\omega) \approx \frac{e^2}{6\pi m \hbar^2 \omega^3} \sum_{\mathbf{G}} \int_{k_m}^{k_F} Gk |\tilde{W}_{\mathbf{G}}|^2 dk \quad (2.11)$$

$$\approx \sum_{\mathbf{G}} \frac{e^2 m |\tilde{W}_{\mathbf{G}}|^2 (\omega - \omega_{\mathbf{G}}^-)(\omega_{\mathbf{G}}^+ - \omega)}{12\pi G \hbar^4 \omega^3}, \quad (2.12)$$

where  $\omega_{\mathbf{G}}^\pm = (\hbar/2m)G(G \pm 2k_F)$ , and in the last step we have taken  $\tilde{W}_{\mathbf{G}}$  out of the integrand by evaluating it at the upper limit,  $k_F$ . If we now consider the twelve  $\mathbf{G}$  vectors of the {110} set for the alkali metals, we see that (2.12) is equivalent to Butcher's formula.<sup>3,5</sup> However, the parameter of the lattice potential determining the band gap is here replaced by the corresponding optical-pseudopotential matrix element. The result (2.11) is equivalent to ignoring the non-Hermiticity of  $\tilde{W}$ .

From (2.11), we obtain for the liquid metal a similar approximation which we write in the form (changing the order of integration)

$$\sigma(\omega) \approx \frac{e^2\Omega_0}{48\pi^3 m \hbar^2 \omega^3} \int_{k_0}^{k_F} k dk \int_{k'-k}^{k'+k} |\tilde{w}_q|^2 a(q) q^3 dq, \quad (2.13)$$

where

$$k' = (k^2 + (2m\omega/\hbar))^{1/2}$$

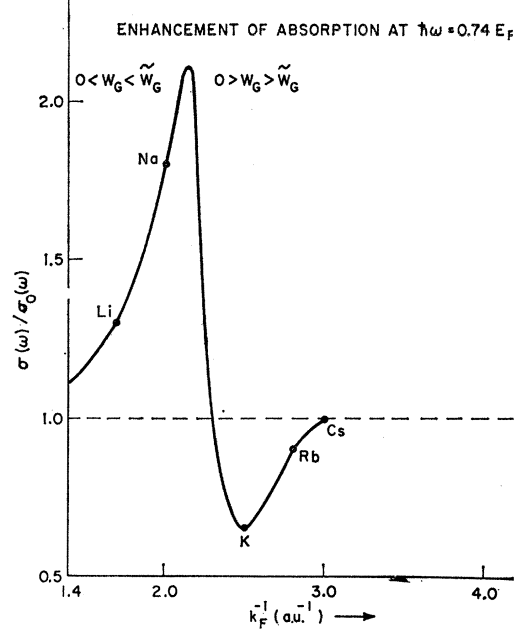


FIG. 1. Enhancement of absorption at  $\hbar\omega=0.74E_F$ . Note: A smooth curve has been drawn through the points marked Li, Na, K, Rb, and Cs which are the actual calculated values.

as before, and

$$k_0 = (k_F^2 - (2m\omega/\hbar))^{1/2}$$

for  $k_F > (2m\omega/\hbar)$ , = 0 otherwise. This expression is the explicit form of the formula used recently by Wilson and Rice.<sup>12</sup> These special results can now be seen from the perspective of our general theory.

### 3. NUMERICAL RESULTS AND DISCUSSION

#### General Results

We begin the presentation of numerical results by making some general qualitative observations which follow from the formulas derived in the preceding section. We compare the approximate result (2.12) with the usual one

$$\sigma_0(\omega) = \frac{e^2 m |W_{\mathbf{G}}|^2 (\omega - \omega_{\mathbf{G}}^-)(\omega_{\mathbf{G}}^+ - \omega)}{\pi G \hbar^4 \omega^3}, \quad (3.1)$$

where  $W_{\mathbf{G}}$  is the usual pseudopotential matrix element screened by a static dielectric function and determining the band gap at the (110) Brillouin zone face in the alkali metals. We see that the absorption is "enhanced" by a factor

$$F(\hbar\omega) \equiv \sigma(\omega)/\sigma_0(\omega) \approx |\tilde{W}_{\mathbf{G}}|^2 / |W_{\mathbf{G}}|^2. \quad (3.2)$$

Since  $\tilde{W}_{\mathbf{G}}$  differs from  $W_{\mathbf{G}}$  by the extra non-negative factor  $\hbar\omega P_{\mathbf{G}}$  (Note:  $P^2 = P$ ), it follows that if  $W_{\mathbf{G}} > 0$  as in Li<sup>13</sup> and Na,<sup>14,15</sup> then  $\tilde{W}_{\mathbf{G}} > W_{\mathbf{G}}$  so that  $F(\hbar\omega) > 1$ . If,

<sup>12</sup> E. G. Wilson and S. A. Rice, Phys. Rev. **145**, 55 (1966).

<sup>13</sup> F. S. Ham, Phys. Rev. **128**, 82 (1962); **128**, 1524 (1962).

<sup>14</sup> N. W. Ashcroft, Phys. Rev. **140**, A935 (1965).

<sup>15</sup> M. J. G. Lee, Proc. Roy. Soc. (London) **295A**, 440 (1966).

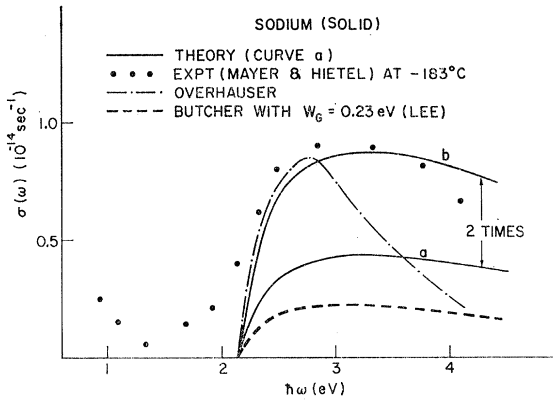


FIG. 2.  $\sigma(\omega)$  in solid Na due to interband transitions. Note: The theoretical curve *a* has been multiplied by a factor of 2 in order to obtain curve *b*.

on the other hand,  $W_G < 0$  as in K, Rb, and Cs,<sup>13,14</sup> then  $\tilde{W}_G < W_G$  so that  $F(\hbar\omega) < 1$ . The present theory, therefore, has the appropriate qualitative features suggested by Overhauser<sup>5</sup> but not for the reasons (time-dependent, Hartree-Fock screening) given by him. The actual number obtained by evaluating the exact expression (2.9) is compared with (3.1) in Fig. 1 at  $\hbar\omega = 0.74E_F$ , i.e.,  $\hbar\omega$  (eV) = 3.48 (Li), 2.39 (Na), 1.56 (K), 1.37 (Rb), and 1.17 (Cs).

To demonstrate that the enhancement is not due to dynamic screening we show in Table I the calculated values of  $\mathcal{E}_{\text{HF}}(q, \omega)$  and  $\mathcal{E}_{\text{HF}}(q, 0)$  at fixed  $q = G \equiv 2\pi\sqrt{2}/a$  in solid Na ( $a$  is the lattice constant). The screening of exchange was incorporated in Hubbard's approximation (which should be about right): This simply requires replacing the Coulomb interaction  $4\pi e^2/q^2$  by  $(4\pi e^2/q^2) \times [1 - f(q)]$ , with  $f(q) = 1/2(k_F^2 + q^2 + k_s^2)$ ,  $1/k_s$  being taken here as the Thomas-Fermi screening length, in the standard expressions for the dielectric function given in text books (see, e.g., Pines<sup>16</sup>). There is hardly any significant difference between the two in the ultraviolet and visible range of photon energies, a fact previously noted by Hopfield.<sup>4</sup>

There is no adjustable parameter in the theory. However, we have noted that whereas the effective mass<sup>13</sup>  $m^*$  entering the screening of  $W_G$  is 1.3 in Li, 1.096 in Na, and 0.88 in K, it is the free-electron mass, (i.e.,  $m^* = m$ ) which enters the dynamic screening of the optical-pseudopotential matrix element  $\tilde{W}_G$  in the nearly-free-electron model used here. It would be of interest to see the effect of such a parameter in the calculation: This will be done below in connection with Li where the difference might be expected to be significant in the computation of  $\sigma(\omega)$ .

Finally, at high frequencies above the interband threshold, the term  $(\hbar\omega)P_G$  in  $\tilde{W}_G$  drops rapidly and  $\tilde{W}_G$  is different from  $W_G$  but not necessarily less than  $W_G$  in K, Rb, and Cs, as shown below.

<sup>16</sup> D. Pines, *Elementary Excitations in Solids* (W. A. Benjamin, Inc., New York, 1963), p. 143.

### The Optical Pseudopotential

The procedure for computing an optical pseudopotential follows the one outlined by Harrison in his book.<sup>17</sup> We have, however, made some simplification in the computation of the usual pseudopotential matrix element by writing

$$W_q \equiv \langle \mathbf{k} + \mathbf{q} | W | \mathbf{k} \rangle = V_q + \sum_{\alpha} (\hbar^2 \mathbf{k}^2 / 2m + |E_{\alpha}| + C) \times \langle \mathbf{k} + \mathbf{q} | \alpha \rangle \langle \alpha | \mathbf{k} \rangle, \quad (3.3)$$

where the core energies  $E_{\alpha}$  and the core functions are Herman and Skillman<sup>18</sup> neutral-atom values, and  $C$  is a constant adjusted to obtain the observed band gap at  $q = G = (2\pi/a)\sqrt{2}$  (e.g., for  $W_G = 0.23$  eV in Na,  $C = -2.52$  Ry). In (3.3),  $V_q$  is given by Eq. 8-60 and each contribution to  $P_q \equiv \langle \mathbf{k} + \mathbf{q} | P | \mathbf{k} \rangle = \sum_{\alpha} \langle \mathbf{k} + \mathbf{q} | \alpha \rangle \times \langle \alpha | \mathbf{k} \rangle$ , by Eq. 8-63 of Ref. 17. To compute  $\tilde{W}_q$  we simply add  $(\hbar\omega)P_q$  to (3.3).

For the screening of  $W_q$  we used the approximation of dividing (3.3) by the static Hartree-Fock dielectric function, which ignores the  $k$  dependence but introduces only slight error<sup>19</sup>; for  $\tilde{W}_q$  dynamic screening was used

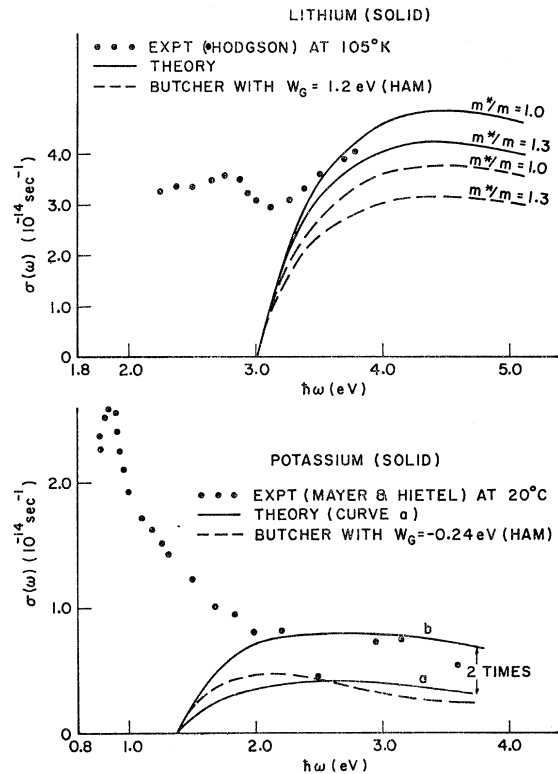


FIG. 3.  $\sigma(\omega)$  in solid Li and K due to interband transitions. Note: The actual theoretical curve corresponds to  $m^*/m = 1.0$  in Li.

<sup>17</sup> W. A. Harrison, *Pseudopotentials in the Theory of Metals* (W. A. Benjamin, Inc., New York, 1966).

<sup>18</sup> F. Harman and S. Skillman, *Atomic Structure Calculations* (Prentice-Hall, Inc., Englewood Cliffs, New Jersey, 1963).

<sup>19</sup> A. O. E. Animalu, *Phil. Mag.* **11**, 379 (1965).

TABLE II. Orders of magnitude of the contributions to  $\bar{W}_q$  for  $G=q=2\pi\sqrt{2}/a$ .<sup>a</sup>

	Li	Na	K	Rb	Cs
$k_F$ (a.u.)	0.589	0.488	0.395	0.369	0.341
$W_G$ (eV)	1.2	0.23	-0.24	-0.43	-0.50
$C$ (Ry)	1.516	-2.521	-2.918	-3.567	-3.775
$\langle \mathbf{k}_F + \mathbf{G}   P   \mathbf{k}_F \rangle$	0.0606	0.0410	0.0478	0.0422	0.0425

<sup>a</sup>  $2|W_G|$  is the observed band gap across the (110) Brillouin zone face,  $P = \sum_{\alpha} |\alpha\rangle\langle\alpha|$ , and the adjustable constant  $C$  is defined in Eq. (3.3).

in the same manner. The latter approximation is the more desirable, since it is the entire expression (2.2) that should be screened as shown in AII.

Orders of magnitude of the contributions to  $\bar{W}_q$  for  $q=2\pi\sqrt{2}/a$  are given in Table II. Extrapolation of  $P_q$  in this table is dangerous since, in general, it varies with frequency: The value given is at zero frequency and for back-scattering, which is the appropriate limiting value of the matrix elements entering the optical absorption. Although the computation of  $P_q$  is generally reliable, it becomes more tedious for the heavier alkali metals, Rb and Cs: For these two elements we found that no reliable value of  $V_q$  in (3.3) could be obtained (the reliability being tested by the limit of  $W_q$  as  $q \rightarrow 0$ ) without taking a prohibitively large mesh of integration. On this account the final results are given only for Li,

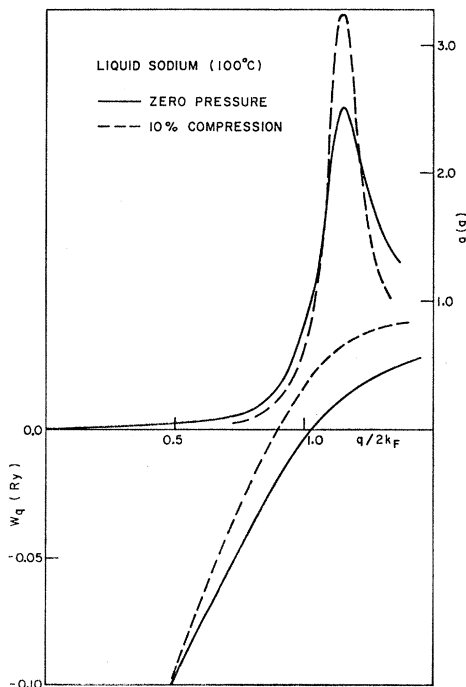


FIG. 4. Pseudopotential  $W_q$  and the interference function  $a(q)$  in liquid Na at 100°C. Note:  $W_q$  has been adjusted to give  $W_G = 0.23$  (eV) in solid Na, where  $G/2k_F \approx 1.14$ . The peak in  $a(q)$  occurs at  $q/2k_F \approx 1.16$ . The net effect of pressure is to exaggerate the structure in the product  $a(q)|\bar{W}_q|^2$  appearing in the integrand of (2.10).

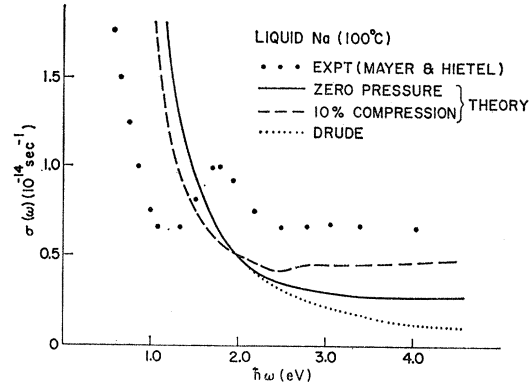


FIG. 5.  $\sigma(\omega)$  in liquid Na at 100°C. Note: The Drude curve is derived by assuming Ziman's relaxation time (cf. Ref. 12).

Na, and K which were accurately determined to better than 5%.

#### Numerical Results: $\sigma(\omega)$

The interband absorption in the solid was calculated in two ways: (i) from the exact expression (2.9), and (ii) from the approximation similar to (2.12) in which we replaced  $[\bar{W}_G|^2 + (\hbar\omega)^2(k/G)^2|P_G|^2]$  in (2.9) by its value at  $k=k_F$ . The results are close for small  $\hbar\omega$ , since in practice, the range  $k_m < k < k_F$  is extremely close to  $k_F$  (e.g., for  $\hbar\omega/E_F = 0.74$ ,  $k_m/k_F = 0.98$ ). A similar procedure was used for the conductivity of liquid Na as given by (2.10). For the same reason the  $q$  integration which is the more sensitive is performed last.

In Fig. 2 the results for solid Na are shown and compared with experiments<sup>2</sup> and with the earlier results due to Overhauser.<sup>5</sup> We see that the calculated value is about 50% of the experimental value. A similar conclusion applies to solid K [Fig. 3(b)]. In Li [Fig. 3(a)] the agreement between theory and experiment<sup>20</sup> is quite good. Recently, Mahan<sup>21</sup> has demonstrated on the basis of the optical pseudopotential leading to the result in Fig. 2, that additional enhancement by about 50% comes from electron-hole scattering via virtual exchange of plasmons. We presume a similar explanation to apply to K although the situation is not clear on account of the "anomalous" peak overlapping the interband absorption, the origin of which is not yet understood. In Li which is less free-electron-like, such an effect, if present, would spoil the good agreement obtained here.

The results for liquid Na are given in Figs. 4 and 5. In Fig. 4 the pseudopotential and the interference functions entering (2.10) are shown side by side at zero pressure and at 10% compression. The objective in considering the two cases is clear from Fig. 4 where the 10% compression introduces more structure in the product  $a(q)|\bar{W}_q|^2$  and consequently demonstrates in Fig. 5 that an "interband" absorption peak should be visible in the liquid state under favorable conditions:

<sup>20</sup> Reference 2, p. 60.

<sup>21</sup> G. D. Mahan, Phys. Letters 24A, 708 (1967).

i.e., by putting the specimen under pressure or by increasing the temperature since the latter produces similar increase in  $a(q)$ , and using a metal or alloy where the zero of the pseudopotential does not fall on the major peak in  $a(q)$ . The interference functions used were calculated from the expression given by Ashcroft and Lekner<sup>22</sup>: The hard core radius of 3.1 (a.u.) was kept fixed, but the packing density  $\eta$  was adjusted appropriately, e.g., at 10% compression,  $\eta=0.50$ , whereas,  $\eta=0.45$  at zero pressure.

#### 4. CONCLUSION

We have shown that the optical pseudopotential gives reasonable results for the optical conductivity in simple (nearly-free-electron) metals. It would also appear from the works of Mueller<sup>23</sup> and Heine<sup>24</sup> that, if

<sup>22</sup> N. W. Ashcroft and J. Lekner, *Phys. Rev.* **145**, 83 (1966).

<sup>23</sup> F. M. Mueller, *Phys. Rev.* **153**, 659 (1967).

<sup>24</sup> V. Heine, *Phys. Rev.* **153**, 673 (1967).

indeed the  $s$ - $d$  interaction in transition metals is weak, then an effective electron-photon coupling matrix could be constructed along the lines suggested in AII and the theory would also be applicable to transition metals.

An important correction which the use of an "optical"-pseudopotential matrix element has revealed is that the assumption of constant matrix element currently made by Spicer and co-workers<sup>25</sup> in analyzing photoemission experiments needs to be reexamined. This question will be considered in greater detail in a subsequent paper.

#### ACKNOWLEDGMENTS

I wish to thank Professor W. A. Harrison for suggesting this problem and Dr. Neville Smith and Robert Shaw for helpful conversations. The cooperation of Stanford University computers is gratefully acknowledged.

<sup>25</sup> See, for example, C. N. Berglund and W. E. Spicer, *Phys. Rev.* **136**, A1030 (1964); **136**, A1044 (1964); also Ref. 2, p. 285.

## Self-Consistent Theory of Optical Transitions in Simple Metals\*

A. O. E. ANIMALU

*Division of Applied Physics, Stanford University, Stanford, California*

(Received 1 June 1967)

It is shown that the interaction of Bloch (conduction) electrons moving in the periodic lattice potential of a metal with an electromagnetic field is adequately described by a simple reduced Hamiltonian in which the coupling between a single electron and a single photon is represented by a dynamically screened "optical pseudopotential". Thus, realistic calculation of the transition probabilities for various processes, particularly photoemission and absorption, including the collective effects due to the self-consistent field of the electrons, can be performed without recourse to detailed energy-band-structure computation in simple (nearly-free-electron) metals. Furthermore, a simple Hamiltonian of this type can be used quite generally for other purposes, for example, in calculating the self-energy of the Bloch electron due to emission and reabsorption of single photons. An expression is given for the effective mass of the Bloch electron in an electromagnetic field.

### 1. INTRODUCTION

IN the past, efforts have been made to solve the Schrödinger equation for a Bloch (conduction) electron moving in the static periodic potential of a metal under an applied electromagnetic field by using the semiclassical effective-Hamiltonian method and/or the effective-mass approximation.<sup>1</sup> These approaches do not, however, take into account the mixing of states from different bands and the modification of the coupling between the electron and the applied field due to the self-consistent field of the conduction electrons. Consequently, they are inadequate for performing a realistic calculation of the *transition probabilities* for

various processes dependent on the emission or absorption of a photon by the electron, upon which we wish to focus attention in this paper.

The mixing of states from different bands in high static fields responsible for Zener tunneling and magnetic breakthrough is well known and relatively well understood.<sup>1</sup> The situation in a space and time *varying* field is perhaps the least clear at the moment. An example of this is the optical absorption due to interband transitions in metals, particularly the alkali metals which have roused considerable attention recently.<sup>2</sup> In a recent review of photoemission studies, Spicer<sup>3</sup> has emphasized the need for going beyond the effective-mass

\* This work was supported by the Advanced Research Project Agency through the Center for Materials Research at Stanford University.

<sup>1</sup> For a review see, e.g., J. Callaway, *Energy Band Theory* (Academic Press Inc., New York), 1964, pp. 233-306.

<sup>2</sup> H. Mayer and B. Hietel, in *Proceedings of the International Colloquium and Optical Properties and Electronic Structures of Metals and Alloys, Paris, 1965* (North-Holland Publishing Company, Amsterdam, 1966), p. 47.

<sup>3</sup> W. E. Spicer, *Phys. Rev.* **154**, 385 (1967).