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# Calculation of the Interband Optical Conductivity of Sodium and Potassium*

B. I. Bennett and S. H. Vosko
*Department of Physics and Erindale College, University of Toronto,*
*Toronto* 181, *Ontario, Canada*

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The orthogonalized-plane-wave-pseudopotential formalism for an independent-particle model is used in a first-order-perturbation-theory calculation of the interband contribution to the optical conductivity in Na and K. Particular attention is given to the modifications to the transition matrix element that arise owing to the presence of the core. The core manifests itself in two ways: as a direct "core contribution" and as a condition on the pseudopotential to ensure orthogonality of the wave functions between which the interband transitions occur. These effects were found to be important. It is shown that the theory can be summarized by a modified Wilson-Butcher formula utilizing an "effective optical pseudopotential" which incorporates the core effects and depends on the pseudopotential coefficient (110). The theoretical results are sensitive to the magnitude and sign of this coefficient and if one uses a magnitude consistent with Fermi-surface data, the optical data enable one to determine the sign. For Na, Lee's value of +0.25 eV for the coefficient resulted in a good fit to the optical data. In the case of K where the pseudopotential coefficient has not been well established from Fermi-surface measurements the present theory used in conjunction with the optical data indicates a value of approximately −0.16 eV. The results show that the interband optical conductivity can be understood in terms of an independent-particle model which incorporates the Fermi-surface data without introducing large many-body corrections.

## I. INTRODUCTION

In the past decade the optical properties of the alkali metals have been the object of considerable experimental and theoretical interest. In spite of this effort, because of experimental difficulties and a divergence of views among theorists, a consistent satisfactory description of the situation has not emerged. It was in the hope of clarifying the aspect relating to the theory of the interband contribution to the optical absorption that the present work was undertaken.

The recent measurements of the optical constants of the alkali metals by Smith[1] have clarified the experimental situation significantly and reestablished the traditional view of the frequency dependence of the optical conductivity. These measurements do not show any unexpected peaks below the interband threshold as observed by Mayer and co-workers.[2] Also, Smith's measurements cover a wide enough photon-energy range (0.5–4.0 eV) so that the interband contribution to the optical conductivity can be separated from the Drude-free-electron (i.e., intraband) contribution. Powell[3] has performed a detailed statistical analysis on Smith's data and has found that the interband contribution to the optical conductivity can be fit well with a Wilson[4] -Butcher[5] formula as long as the pseudopotential coefficient (110) is treated as a parameter. In particular, Powell found that for Na the magnitude of the pseudopotential coefficient required to fit Smith's optical data is considerably larger than the corresponding pseudopotential coefficient determined from the Fermi-surface data by Lee.[6] In the case of K the situation is not clear cut in that the magnitude of the pseudopotential coefficient required to fit Smith's optical data is within the range of values suggested by various investigators's[7–10] analyses of Fermi-surface data and band-structure calculations.

More recently, Palmer and Schnatterly[11] have measured the optical constants of Na and K over the energy range 1.8–4.4 eV. Their results for K are rather similar to those of Smith; however, their results for Na are significantly different from Smith's. Palmer[12] has suggested that the discrepancy in Na may be due to the rougher surfaces used in the Palmer-Schnatterly[11] experiments. Yamaguchi and Hanyu[13] have measured the optical constants of K in the range 2.07–6.20 eV and obtained results similar to those of Smith. Since the present work will be concerned with the interband conductivity, the necessity of accurately separating it from the total conductivity will limit detailed comparison between theory and experiment to the results of Smith[1] as analyzed by Powell.[3]

Most calculations of the interband conductivity in metals and semiconductors[14] have used an independent- or noninteracting-quasiparticle model (IQPM): "independent" to denote that the basic formula used to calculate the interband conductivity is one for a noninteracting system of electrons; "quasiparticle" to signify that the band structure and the single-particle wave functions used to calculate the transition matrix element are determined with the use of empirical information (e.g., pseudopotential coefficients) which automatically includes some effects of the electron-electron interaction. In fact, one of the restrictions that we impose on the IQPM is that the pseudopotentials used to generate the pseudo-wave-functions must be consistent with the Fermi-surface data. Since Na and K are very good approximations to a nearly free-electron metal, they are ideal to test the validity of the IQPM and to examine our over-all understanding of the theory of the interband contributions to the dielectric functions in metals. In particular their band structures are well known within a few electron volts of the Fermi surface and there is much evidence[15] that their wave functions can be accurately expanded in terms of a small number of orthogonalized plane waves (OPW's). Thus any discrepancy between calculated and experimental values in Na and K reduces to the following theoretical questions: (i) what is the importance of the electron-electron interaction in modifying the basic expression for the interband conductivity in the IQPM; and (ii) what are the modifications of the transition matrix element in the IQPM that arise from the presence of the core, e.g., the use of true wave functions vs pseudo-wave-functions. Estimates of (i) have suggested corrections of less than[16] 15% to as high as 50%.[17] The present work will be concerned with (ii). The ability of the IQPM to reproduce the experimental results will allow some conclusions to be drawn about (i).

With regard to the validity of the IQPM, a recent reexamination of the experimental situation and new calculations of the interband conductivity have resolved a long standing discrepancy between theory and experiment in aluminium.[16,18–20] It was found that the IQPM describes the experiments well when used in conjunction with pseudopotential coefficients determined from Fermi-surface data. Beeferman and Ehrenreich[16] claim that modifications of the transition matrix elements due to the presence of the core (i.e., use of true wave functions instead of pseudo-wave-functions) produced negligible effects. This was not found to be the case in the present work on Na and K.

There have been a number of calculations of the interband conductivity in Na and K using the OPW-pseudopotential formalism.[21–25] A careful examination of these works reveals that they are in error or inadequate. Appelbaum's calculation[21] for Na gives results for the interband conductivity that are approximately a factor 3 smaller than the experimental results.[1,3] It is not clear if this is due to his use of nonorthogonal wave functions to calculate the transition matrix element or to his choice of values for the pseudopotential coefficient (200) that now appears to be much too large, in the light of the more recent work of Lee. Appelbaum's work tends to leave one with the impression that effects due to the presence of the core are unimportant. Our investigation shows that this is not the case. Cutler and co-workers[24,25] do not use the pseudopotential according to its proper definition, thus the numerical values obtained for the interband optical conductivity in their work are questionable. Unfortunately, the work of Animalu and Harrison,[22,23] which has received wide attention, omits an important core contribution and contains an error in mathematical analysis. As a result, Animalu's[23] values of the interband conductivity are unreliable and the Animalu-Harrison[22] definition of the optical pseudopotential is misleading. It will be shown in the present work that the interband conductivity can be expressed in terms of an "effective optical pseudopotential" which depends on the pseudopotential coefficient (110) and various terms arising from the presence of the core which in some respects is similar to their optical pseudopotential. This effective optical pseudopotential can be used to produce a modified Wilson-Butcher formula that gives excellent agreement between experiment and theory for Na and K. A useful feature of this new formula is its sensitivity to the sign of the pseudopotential coefficient (110). Thus, when there is an ambiguity in the sign of this pseudopotential coefficient as determined from Fermi-surface data, it is possible to resolve this ambiguity by use of the interband conductivity.

Section II contains a general outline of the theory with emphasis on the effects due to the presence of the core. Numerical results for the various terms entering the general expression for the interband conductivity are given in Sec. III with a discussion of the distortion that can be produced when attempting to include the nonlocality of the pseudopotential. The modified Wilson-Butcher formula is discussed in Sec. IV.

## II. THEORY

In the independent-particle approximation, the real part of the frequency-dependent optical conductivity for solids with cubic symmetry may be written as

$$\sigma(\omega)=\frac{2\pi e^2}{3m^2\omega\Omega}\sum_{\vec{k}\vec{k}'}\left|\langle\chi_{\vec{k}'}|\vec{p}|\chi_{\vec{k}}\rangle\right|^2 n_{\vec{k}}(1-n_{\vec{k}'}) \times\delta(E_{\vec{k}'}-E_{\vec{k}}-\hbar\omega)\,, \quad (1)$$

where $\omega$ is the frequency of the incident radiation; $\Omega$ is the volume of the system; and $n_{\vec{k}}$ is the Fermi distribution function for electrons with single-particle wave functions $\chi_{\vec{k}}$ and energies $E_{\vec{k}}$, where $\vec{k}$ labels the state in the extended-zone scheme. The wave functions satisfy the single-particle equation

$$H|\chi_{\vec{k}}\rangle = (T+V)|\chi_{\vec{k}}\rangle = E_{\vec{k}}|\chi_{\vec{k}}\rangle\,, \tag{2}$$

where $V$ is an effective single-particle potential, periodic in the lattice, for a conduction electron.

To the order in perturbation theory that will be included, $E_{\vec{k}} \approx \text{const} + \epsilon_{\vec{k}}$, where $\epsilon_{\vec{k}} = \hbar^2\vec{k}^2/2m$. For a solid, the matrix element $\langle\chi_{\vec{k}'}|\vec{p}|\chi_{\vec{k}}\rangle$ vanishes unless $\vec{k}' = \vec{k} + \vec{G}$, where $\vec{G}$ is a reciprocal-lattice vector. Combining this condition with the conservation of energy, as expressed by the $\delta$ function in Eq. (1), i.e., $\epsilon_{\vec{k}'} - \epsilon_{\vec{k}} = \hbar\omega$, for the energy range $\hbar\omega < 4$ eV, the $\vec{G}$'s are restricted to be of the $(2\pi/a_L)(1, 1, 0)$ type with $\vec{k}$ $(< \vec{k}_F)$ in the neighborhood of $k_F$. For the alkali metals and a $\vec{G}$ of this type, $G/k_F \approx 2.28$ so that $n_{\vec{k}'} = 0$. It can be easily seen that $\vec{k}'$ and $\vec{G}$ are nearly parallel and approximately antiparallel to $\vec{k}$. The magnitude of $\vec{k}'$, because of energy conservation, lies in the range $1.3k_F \lesssim k' \lesssim 1.7k_F$. Taking the above into account and converting the sum over $\vec{k}$ into an integral over $\vec{k}$ in Eq. (1) yields

$$\sigma(\omega) = \frac{2\pi e^2}{3m^2\omega(2\pi)^3}\sum_{\vec{G}}\int_{\vec{k}\leq k_F} d\vec{k}\,|\langle\chi_{\vec{k}+\vec{G}}|\vec{p}|\chi_{\vec{k}}\rangle|^2 \times \delta(\epsilon_{\vec{k}+\vec{G}} - \epsilon_{\vec{k}} - \hbar\omega)\,, \tag{1a}$$

where the sum on $\vec{G}$ is restricted to the 12 reciprocal-lattice vectors of the (1, 1, 0) type.

We wish to evaluate the matrix element in Eq. (1) by the OPW-pseudopotential perturbation theory. Following the usual procedure[15] we express $|\chi_{\vec{k}}\rangle$ in terms of a pseudo-wave-function $|\phi_{\vec{k}}\rangle$:

$$|\chi_{\vec{k}}\rangle = A_{\vec{k}}(1-\hat{P})|\phi_{\vec{k}}\rangle\,, \tag{3}$$

where $\hat{P}$ is the core-state projection operator and $A_{\vec{k}}$ is a normalization constant. We will assume the core-state wave functions of a given ion do not overlap neighboring ions so that $\hat{P}^2 = \hat{P}$. To first order in the pseudopotential $W_{\vec{k}}$, the pseudo-wave-function is given by

$$|\phi_{\vec{k}}\rangle = |\vec{k}\rangle + \sum_{\vec{G}'}{}' |\vec{k}+\vec{G}'\rangle \frac{\langle\vec{k}+\vec{G}'|W_{\vec{k}}|\vec{k}\rangle}{\epsilon_{\vec{k}} - \epsilon_{\vec{k}+\vec{G}'}}\,, \tag{4}$$

where the primed summation indicates that $\vec{G}' = 0$ is omitted.

As emphasized by Austin, Heine, and Sham,[26] there is a great deal of arbitrariness in the form of the pseudopotential when considering exact solutions of the pseudoequation. Specifically, the most general form is

$$W_{\vec{k}} = V + \hat{P}X_{\vec{k}}\,, \tag{5}$$

where $X_{\vec{k}}$ is an arbitrary operator which may be $\vec{k}$ dependent. We will not be primarily concerned with a calculation of the pseudopotential from first principles. However, we will show that when considering approximate solutions of the pseudo-Schrödinger-equation some of the arbitrariness in $W_{\vec{k}}$ is removed. As will be seen below, the optical conductivity can be expressed in terms of a matrix element of $W_{\vec{k}}$ whose magnitude is determined from an analysis of the Fermi-surface data.

The matrix element of $\vec{p}$ in Eq. (1) can be expressed to first order in $\hat{P}$ and $W_{\vec{k}}$ by use of Eqs. (3) and (4). The result for $\vec{k}' = \vec{k} + \vec{G} \neq \vec{k}$ is

$$\langle\chi_{\vec{k}'}|\vec{p}|\chi_{\vec{k}}\rangle = A^*_{\vec{k}'}A_{\vec{k}}\left(\frac{\langle\vec{k}'|\hbar\vec{k}'W_{\vec{k}} - \hbar\vec{k}W^\dagger_{\vec{k}'}|\vec{k}\rangle}{\epsilon_{\vec{k}} - \epsilon_{\vec{k}'}} - [\hbar(\vec{k}+\vec{k}')\langle\vec{k}'|\hat{P}|\vec{k}\rangle - \langle\vec{k}'|\hat{P}\vec{p}\hat{P}|\vec{k}\rangle]\right)\,, \tag{6a}$$

where, to this order,

$$A_{\vec{k}} = (1 - \langle\vec{k}|\hat{P}|\vec{k}\rangle)^{-1/2}\,. \tag{6b}$$

The validity of this first-order expansion is dependent on the matrix elements $\langle\vec{k}+\vec{G}|W_{\vec{k}}|\vec{k}\rangle$ for reciprocal-lattice vectors $\vec{G} \geq (2\pi/a_L)(2, 0, 0)$ not being appreciably greater than the matrix elements for the $\vec{G} = (2\pi/a_L)(1, 1, 0)$ type. According to Lee's results this is certainly true for Na.[6] The situation for K is not clear cut.[9] However, the analysis of Dresselhaus *et al.*[10] suggests that the criterion is reasonably satisfied.

The terms in the square brackets of Eq. (6a) are referred to as the "core contributions"[21,24] since they arise solely from the projection operator in Eq. (3). The remaining term of Eq. (6a) requires special consideration because of the possible complexity of $W_{\vec{k}}$ as defined in Eq. (5).

When calculating a matrix element for a transition probability it is essential that the states $\chi_{\vec{k}}$ and $\chi_{\vec{k}'}$ be orthogonal to the order in $P$ and $W_{\vec{k}}$ included. From Eqs. (3) and (4) we see that, to first order in $\hat{P}$ and $W_{\vec{k}}$,

$$\langle\chi_{\vec{k}'}|\chi_{\vec{k}}\rangle = A^*_{\vec{k}'}A_{\vec{k}}\left(\delta_{\vec{k}\vec{k}'} - \langle\vec{k}'|\hat{P}|\vec{k}\rangle + (1-\delta_{\vec{k}\vec{k}'})\frac{\langle\vec{k}'|W_{\vec{k}} - W^\dagger_{\vec{k}'}|\vec{k}\rangle}{\epsilon_{\vec{k}} - \epsilon_{\vec{k}'}}\right)\,. \tag{7}$$

Thus to ensure orthogonality, $W_{\vec{k}}$ must be chosen so that the second and third terms of Eq. (7) cancel. That is, from Eq. (5), for $\vec{k}' \neq \vec{k}$, we see that

$$\langle\vec{k}'|W_{\vec{k}} - W^\dagger_{\vec{k}'}|\vec{k}\rangle = \langle\vec{k}'|\hat{P}X_{\vec{k}} - X^\dagger_{\vec{k}'}\hat{P}|\vec{k}\rangle = (\epsilon_{\vec{k}} - \epsilon_{\vec{k}'})\langle\vec{k}'|\hat{P}|\vec{k}\rangle\,. \tag{8}$$

Therefore, at this point in the calculation we see that $W_{\vec{k}}$ and $W^\dagger_{\vec{k}'}$ may not be chosen to be weak local potentials. On the other hand, the commonly used Phillips-Kleinman, Cohen-Heine, and Austin[26] forms of pseudopotentials do in fact satisfy Eq. (8). Using this condition, Eq. (6a) becomes

$$\langle \chi_{\vec{k}'} | \vec{p} | \chi_{\vec{k}} \rangle = A^*_{\vec{k}'} A_{\vec{k}} \left\{ \left[ \hbar(\vec{k}' - \vec{k}) \frac{\langle \vec{k}' | W_{\vec{k}} | \vec{k} \rangle}{\epsilon_{\vec{k}} - \epsilon_{\vec{k}'}} + \hbar \vec{k} \langle \vec{k}' | \hat{P} | \vec{k} \rangle \right] - [\hbar(\vec{k}' + \vec{k}) \langle \vec{k}' | \hat{P} | \vec{k} \rangle - \langle \vec{k}' | \hat{P} \vec{p} \hat{P} | \vec{k} \rangle ] \right\}, \qquad (9)$$

where we have grouped the terms in the square brackets according to their sources. Although one could simplify the expression we prefer to retain the displayed form to facilitate its interpretation and comparison with previous work.[21,23] We have written the result in terms of $\langle \vec{k}' | W_{\vec{k}} | \vec{k} \rangle$ instead of $\langle \vec{k}' | W^{\dagger}_{\vec{k}'} | \vec{k} \rangle$ since the former is the quantity which enters in an analysis of the Fermi-surface data. Although the above was derived by using pseudopotential theory, the identical result obtains from solving the Schrödinger equation by perturbation theory using OPW functions as the basis functions.[27]

The first square brackets in Eq. (9) give the momentum matrix element as calculated with the pseudo-wave-functions by perturbation theory taking into consideration Eq. (8). The second square brackets give the (core) contribution to the momentum matrix element from the projection operator $(1-\hat{P})$ acting on the zeroth-order parts of the pseudo-wave-functions. We may contrast this result with the classic theory of Wilson[4] and Butcher[5] where the true wave function is expanded in terms of plane waves by use of perturbation theory. In their work only the term corresponding to $\langle \vec{k}' | W_{\vec{k}} | \vec{k} \rangle / (\epsilon_{\vec{k}} - \epsilon_{\vec{k}'})$ would appear in Eq. (9), since the potential in their theory is Hermitian and $\vec{k}$ independent.

The expression given by Eq. (9) for the momentum matrix element has previously been obtained by Animalu[23] and Harrison.[28] However, they incorrectly argue that the term $\langle \vec{k}' | \hat{P} \vec{p} \hat{P} | \vec{k} \rangle$ can be neglected. We will demonstrate that this cannot be done for Na and K. The omission of this term plus an algebraic error results in an expression for $\sigma(\omega)$ involving their "optical pseudopotential." Due to the more complicated structure of this term there has been some disagreement among various authors[16,21,23,28] about its magnitude. Appelbaum,[21] for the case of Na, found it to be nearly the same magnitude as the third term in Eq. (9). More recently Beeferman and Ehrenreich[16] have stated that there is an error of a factor of $\frac{1}{2}$ in Appelbaum's Eq. (10). Because of this disagreement we have made a thorough examination of this term. We find Appelbaum's formula to be correct (see Appendix) and the magnitudes of the terms $\langle \vec{k}' | \hat{P} \vec{p} \hat{P} | \vec{k} \rangle$ and $h(\vec{k}' + \vec{k}) \langle \vec{k}' | \hat{P} | \vec{k} \rangle$ to be approximately the same. Appelbaum found in his calculation for Na that these terms essentially cancel each other. However, we find the degree of cancellation is sensitive to the choice of the core wave functions and the material considered. Thus, we retain the entire "core contribution" in Eq. (9) for our calculations.

It is important to note that even when there is nearly complete cancellation between the terms of the core contribution, the term $\hbar \vec{k} \langle \vec{k}' | \hat{P} | \vec{k} \rangle$ in the first square brackets of Eq. (9) remains. Recall that in the pseudopotential theory this term arises from the orthogonality requirement on the true wave functions [Eqs. (7) and (8)]. Its magnitude in Na and K is of the same order as the other term in the first square brackets of Eq. (9). Therefore it must be included. We will see in Sec. III that this term makes a significant contribution to $\sigma(\omega)$. For example, in Na it can produce an increase of $\sigma(\omega)$ by ~ 50%.

The relationship of the present work to that of Appelbaum[21] and Cutler and co-workers[24] can only be made on a qualitative basis, since they give the numerical results for $\sigma(\omega)$ without intermediate results for the momentum matrix element. Appelbaum obtained the momentum matrix elements from numerical solutions of the pseudo-wave-equation in a restricted subspace, using a local approximation for the pseudopotential. As he points out such a procedure does not, in general, yield true wave functions which are orthogonal. His viewpoint is that the degree of nonorthogonality was sufficiently small so that the momentum matrix element could be calculated adequately. This is not borne out by the present work; however, it should be emphasized that Appelbaum solved a rather different model. He included the (200) pseudopotential coefficients with values, in the light of the work of Lee,[6] which were much too large. Miskovsky and Cutler[24] have attempted to investigate the effect of imposing an orthogonality condition on the true wave functions. They find $\sigma(\omega)$ for Na to be larger than Appelbaum's by a factor of 2. However, their results are questionable because they have taken the effective single-particle potential $V$ in Eqs. (2) and (5) to be the small pseudopotential instead of the $W_{\vec{k}}$ of Eq. (5), which is inconsistent since they have used it in an equation for the true wave function instead of the equation for the pseudo-wave-function.

We now turn our attention to expressing $\sigma(\omega)$, Eq. (1a), in terms of Eq. (9). Writing (see Appendix)

$$\langle \vec{k}' | \hat{P} \vec{p} \hat{P} | \vec{k} \rangle = \hbar(\vec{k}' + \vec{k}) S(k', k) + \hbar(\vec{k}' - \vec{k}) B(k', k) \qquad (10)$$

and noting that $\vec{k}' = \vec{k} + \vec{G}$, Eq. (9) becomes

$$\langle \chi_{\vec{k}+\vec{G}} | \vec{p} | \chi_{\vec{k}} \rangle = A^*_{\vec{k}+\vec{G}} A_{\vec{k}} \left[ \left( \hbar \vec{G} \frac{\langle \vec{k} + \vec{G} | W_{\vec{k}} | \vec{k} \rangle}{\epsilon_{\vec{k}} - \epsilon_{\vec{k}+\vec{G}}} \right.\right.$$

$$+\hbar\vec{k}\,\langle\vec{k}+\vec{G}|\,\hat{P}|\vec{k}\,\rangle\Big)+\{\hbar\vec{G}B(|\vec{k}+\vec{G}|,\,|\vec{k}|\,)$$
$$+\hbar(\vec{G}+2\vec{k})\,[S(|\vec{k}+\vec{G}|,\,|\vec{k}|\,)-\langle\vec{k}+\vec{G}|\,\hat{P}|\vec{k}\,\rangle]\}\Big]\,. \tag{11}$$

The relative importance of the various terms in Eq. (11) can readily be seen by expressing $\vec{k}$ in terms of its components parallel and perpendicular to $\vec{G}$ ($\vec{k}=\vec{k}_{\parallel}+\vec{k}_{\perp}$), and simultaneously noting that the component of $\vec{k}$ parallel to $\vec{G}$ is fixed for a definite $\hbar\omega$ by the $\delta$ function in Eq. (1a), that is,

$$\vec{k}\cdot\vec{G}/G^2=\tfrac{1}{2}(\hbar\omega/\epsilon_{\vec{G}}-1)\,, \tag{12a}$$

and thus

$$\vec{k}=\tfrac{1}{2}(\hbar\omega/\epsilon_{\vec{G}}-1)\vec{G}+\vec{k}_{\perp}\,, \tag{12b}$$

$$\vec{G}+2\vec{k}=(\hbar\omega/\epsilon_{\vec{G}})\vec{G}+2\vec{k}_{\perp}\,, \tag{12c}$$

$$k_{\perp}^2=k^2-(\vec{k}\cdot\vec{G})^2/G^2=k^2-\tfrac{1}{4}(\hbar\omega/\epsilon_{\vec{G}}-1)^2G^2\,. \tag{12d}$$

Using Eqs. (12a)–(12c) in Eq. (11) yields

$$\langle\chi_{\vec{k}+\vec{G}}|\vec{p}|\chi_{\vec{k}}\rangle=-(A^*_{\vec{k}+\vec{G}}A_{\vec{k}}/\hbar\omega)\{\hbar\vec{G}[\mathcal{W}_G+\tfrac{1}{2}(1-\hbar\omega/\epsilon_{\vec{G}})\hbar\omega P_G-\hbar\omega B_G-(\hbar\omega/\epsilon_{\vec{G}})\hbar\omega(S_G-P_G)]-\hbar\vec{k}_{\perp}[\hbar\omega(2S_G-P_G)]\}\,, \tag{13}$$

where the matrix elements in Eq. (11) have been evaluated in accordance with the $\delta$ function in Eq. (1a) and abbreviated by $\mathcal{W}_G$, $P_G$, $S_G$, and $B_G$, and their $k$ and $\omega$ dependence is suppressed for convenience. They are to be regarded as functions of $k$ for each value of $\omega$, in particular,

$$\mathcal{W}_G(k;\omega)\equiv\langle\vec{k}+\vec{G}|\,W_{\vec{k}}|\vec{k}\,\rangle\,, \tag{14a}$$

$$P_G(k;\omega)\equiv\langle\vec{k}+\vec{G}|\,\hat{P}|\vec{k}\,\rangle\,, \tag{14b}$$

$$S_G(k;\omega)\equiv S(|\vec{k}+\vec{G}|,\,|\vec{k}|\,)\,, \tag{14c}$$

$$B_G(k;\omega)\equiv B(|\vec{k}+\vec{G}|,\,|\vec{k}|\,)\,, \tag{14d}$$

with

$$|\vec{k}+\vec{G}|=k(1+\hbar\omega/\epsilon_{\vec{k}})^{1/2} \tag{14e}$$

and

$$\cos(\vec{k},\vec{k}+\vec{G})=\left(1-\frac{\epsilon_{\vec{G}}-\hbar\omega}{2\epsilon_{\vec{k}}}\right)\Big/\left(1+\frac{\hbar\omega}{\epsilon_{\vec{k}}}\right)^{1/2}\,. \tag{14f}$$

Their range of variation for each $\omega$ are shown in Figs. 1–4. It is worth noting that for $\hbar\omega$ in the range threshold to 4 eV, $\hbar\omega/\epsilon_{\vec{G}}$ ranges in value from ~0.12–0.25 in Na and ~0.12–0.40 in K. Substituting Eq. (13) into Eq. (1a) and noting the symmetry of the integrand, each $\vec{G}$ vector gives an identical contribution. Therefore we replace the sum on $\vec{G}$ by a factor of 12 and perform the angular integrations to obtain

$$\sigma(\omega)=\frac{4e^2\epsilon_G}{\pi\hbar(\hbar\omega)^3}\int_{k_m}^{k_F}dk\,\frac{k}{G}\,(A_{\vec{k}+\vec{G}}A_{\vec{k}})^2M^2(k;\omega)\,, \tag{15}$$

where

$$k_m=\tfrac{1}{2}G\,(1-\hbar\omega/\epsilon_{\vec{G}})\le k_F\,, \tag{16a}$$

$$M^2(k;\omega)=M^2_{\parallel}(k;\omega)+M^2_{\perp}(k;\omega)\,, \tag{16b}$$

$$M_{\parallel}(k;\omega)=\mathcal{W}_G+\tfrac{1}{2}(1+\hbar\omega/\epsilon_{\vec{G}})\hbar\omega P_G-\hbar\omega[B_G+(\hbar\omega/\epsilon_{\vec{G}})S_G]\,, \tag{16c}$$

and

$$M_{\perp}(k;\omega)=\hbar\omega(2S_G-P_G)[(k^2-k_m^2)/G^2]^{1/2}\,. \tag{16d}$$

This result for $\sigma(\omega)$ differs from Animalu's Eq. (2.9) (first paper of Ref. 23), in three respects: (i) Equation (15) retains the normalization factors $A$, from Eq. (6b); (ii) the contribution from the $\langle\vec{k}'|\hat{P}\vec{p}\hat{P}|\vec{k}\rangle$ term as indicated by $S_G$ and $B_G$ has been included; (iii) we have corrected a mathematical error in Animalu's analysis. In particular he argues incorrectly that part of the integrand in his Eq. (2.8) cancels due to the symmetry of the $\vec{G}$ vectors, although he does retain this term when deriving Eq. (2.10) for a liquid metal.

A feature of Eq. (15) is its possibility of determining the sign of $\mathcal{W}_G$ when its magnitude is known from Fermi-surface data. The magnitude of this quantity, at least in the case of Na, is claimed to be well determined[6]; however, its sign is ambiguous. The remaining quantities in the expression are well defined after some choice for core wave functions is made. Therefore the effect on $\sigma(\omega)$ of constructive or destructive interference between the terms in $M_{\parallel}(k,\omega)$ of Eq. (16c) may enable one to deduce the appropriate sign for $\mathcal{W}_G$, as well as providing one with an estimate of its magnitude.

The relationship of the expression for $\sigma(\omega)$ given in Eqs. (15) and (16) to the Wilson-Butcher[4,5] formula for $\sigma(\omega)$ deserves special attention because of the success the latter has had in fitting the experimental results in the interband region.[3] To obtain the $\omega$ dependence given by the Wilson-Butcher formula requires $(A_{\vec{k}+\vec{G}}A_{\vec{k}})^2M^2(k,\omega)$ to be essentially constant. We first note that over the $\omega$ range of interest $(A_{\vec{k}+\vec{G}}A_{\vec{k}})^2$ is, in fact, nearly constant taking on the values 1.17 and 1.36 for Na and K, respectively. The fact that the components $M_{\parallel}$ and $M_{\perp}$ of $M$ depend on $k$ and $\omega$, both explicitly and implicitly through $P_G$, $S_G$, and $B_G$ [see Eqs. (16b)–(16d)], does not preclude $M(k;\omega)$ remaining relatively constant. We will see in Sec. III that this does in fact occur for both Na and K so that Eq. (15) is consistent with the Wilson-Butcher dependence of $\sigma$ on $\omega$ observed. However, it must be stressed that $(A_{\vec{k}+\vec{G}}A_{\vec{k}})M$ is not equal to the pseudopotential determined from Fermi-surface

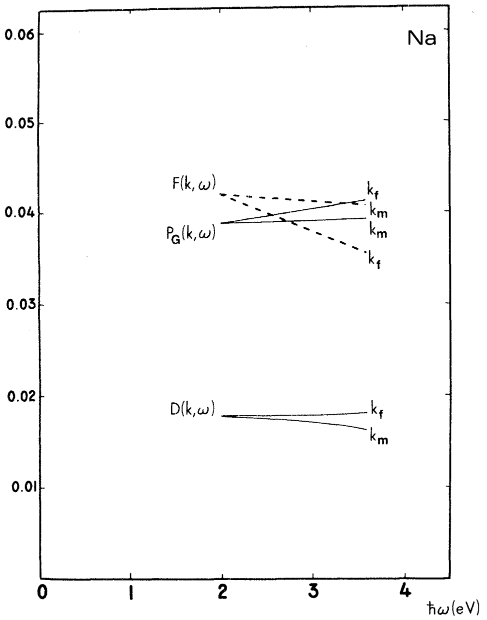

FIG. 1. Functions $F(k, \omega)$, $D(k, \omega)$, and $P_G(k, \omega)$ for Na. The curves labeled $k_F$ and $k_m$ locate the extremes of the range of the function for fixed $\hbar\omega$.

data. On the basis of the $k$ dependence obtained from the numerical evaluation of $\mathcal{W}_G$, $P_G$, $S_G$, and $B_G$ in Sec. III a modified Wilson-Butcher formula for $\sigma(\omega)$ will be derived in Sec. IV.

## III. NUMERICAL RESULTS AND DISCUSSION

The objective of this section is to obtain an understanding of the magnitude and the $\omega$ dependence of $\sigma$ produced by Eqs. (15) and (16) with particular emphasis on the sensitivity of the final result to the choice of form (i.e., $\vec{k}$ dependence) and numerical value of the pseudopotential factor $\mathcal{W}_G(k; \omega)$. Since all the quantities in the integrand of Eq. (15) are well behaved, the integration over $k$ (numerical or otherwise) for a fixed $\omega$ is trivial given $M^2(k, \omega)$. (As noted previously, $A_{\vec{k}+\vec{G}}A_{\vec{k}}$ is essentially constant over the range of $k$ and $\omega$ under consideration.) Thus the problem is to investigate the $k$ dependence of $\mathcal{W}_G$, $P_G$, $S_G$, and $B_G$ due to their dependence on the core wave function and energies. Given a set of core wave functions, $P_G$, $S_G$, and $B_G$ are straightforward to evaluate (see Appendix). On the other hand, $\mathcal{W}_G$, the most important quantity, is rather delicate and, as will be seen later, requires special attention. From Eqs. (16c) and (16d) we see that the relevant quantities to evaluate are

$$D(k; \omega) \equiv \tfrac{1}{2}(1 + \hbar\omega/\epsilon_{\vec{G}})P_G(k; \omega) - [B_G(k; \omega) + (\hbar\omega/\epsilon_{\vec{G}})S_G(k; \omega)] \tag{17a}$$

and

$$F(k; \omega) \equiv [2S_G(k; \omega) - P_G(k; \omega)] \; . \tag{17b}$$

We have calculated $D(k; \omega)$ and $F(k; \omega)$ using a variety of core-state wave functions and have found the results to be insensitive to the choice. In general, for fixed $\omega$, $D(k; \omega)$ and $F(k; \omega)$ vary monotonically as $k$ ranges from $k_m$ [see Eq. (16a)] to $k_F$. Plots of $D(k; \omega)$ and $F(k; \omega)$ for $k = k_m$ and $k = k_F$ are given in Figs. 1 and 2 and compared with $P_G(k; \omega)$, the quantity which enters the Animalu-Harrison theory. The Roothan-Hartree-Fock wave functions[29] for the neutral atoms were used for the core states. From the figures it is clear that $D(k, \omega)$ and $F(k, \omega)$ have a small fluctuation about their mean value for each $\omega$. The magnitude of $D(k, \omega)$ indicates the potential for it to interfere with $\mathcal{W}_G(k, \omega)$ in $M_{\parallel}(k, \omega) = \mathcal{W}_G(k, \omega) + \hbar\omega D(k, \omega)$. This should be compared with the optical pseudopotential of Animalu and Harrison,[22,23] i.e., $\mathcal{W}_G(k, \omega) + \hbar\omega P_G(k, \omega)$. Since $D(k, \omega)$ is considerably smaller than $P_G(k, \omega)$, the degree for potential interference is reduced; however, it remains very important in interpreting the optical measurements. The difference in the theories has two sources: (a) They neglected the term which gives rise to $B_G$ and $S_G$ in Eq. (17a); and (b) there is the analytic error mentioned in Sec. II below Eq. (16d). In particular in Na, $S_G \approx P_G$ and $|B_G| \lesssim \frac{1}{30} P_G$ so that $D \approx \frac{1}{2} P_G$ and $F \approx P_G$. That is, the core contribution [see Eqs. (6a) and (9)] is essentially zero for Na. On the other hand in K, $S_G \approx 1.5\, P_G$ and $|B_G| \approx \frac{1}{15} P_G$ so that $D \lesssim \frac{1}{2} P_G$ and $F \approx 2P_G$, making $M_{\perp}$ relatively more important than in Na. There-

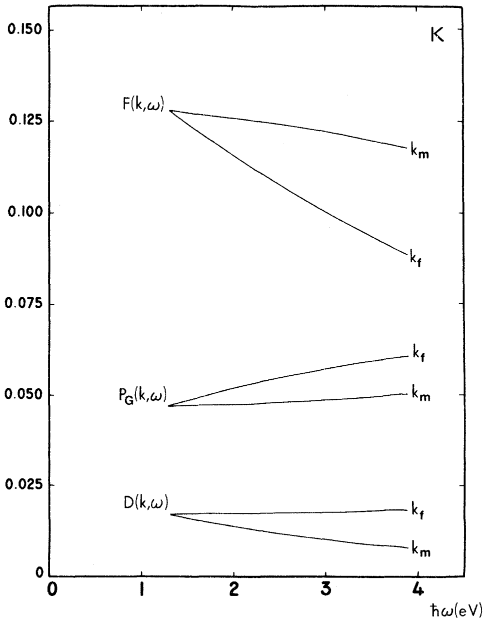

FIG. 2. Functions $F(k, \omega)$, $D(k, \omega)$, and $P_G(k, \omega)$ for K. The curves labeled $k_F$ and $k_m$ locate the extremes of the range of the function for fixed $\hbar\omega$.

fore, the core contributions are more important in K than in Na.

The quantity $\mathcal{W}_G$ is extremely difficult to calculate from first principles. Some appreciation for the problem can be gained by noting that the Fourier coefficient of the single-particle potential $V_{\vec{G}}$ is $\sim -3$ eV, while the corresponding pseudopotential[15] is $\sim \frac{1}{20} |V_{\vec{G}}|$. Because of this, our viewpoint is to obtain $\mathcal{W}_G$ as far as possible from analyses of Fermi-surface data such as given by de Haas–van Alphen experiments. Since the pseudopotential that is obtained from fits of the Fermi surface incorporates a number of many-body effects there remains the question of whether these many-body effects[30] enter the optical absorption in precisely the same way. Hopfield[31] showed that one major difference was to screen the bare weak potential with the dielectric function $|\epsilon(\vec{G}, \omega)|$ instead of $\epsilon(\vec{G}, 0)$. In the random-phase approximation, to which the theory of Sec. II is equivalent, the difference between $|\epsilon(\vec{G}, \omega)|$ and $\epsilon(\vec{G}, 0)$ is negligible and since we are not considering higher-order electron-electron corrections to $\sigma(\omega)$ we assume that the pseudopotential including many-body corrections that enters the optical absorption is the same as determined from Fermi-surface studies.

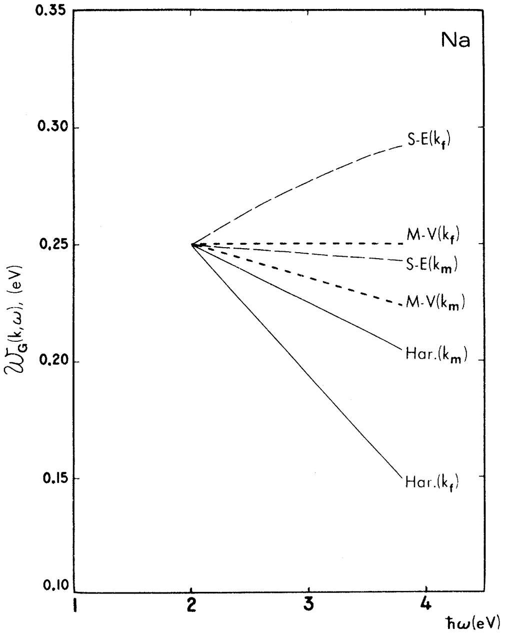

FIG. 3. $\mathcal{W}_G(k, \omega)$ as defined in Eqs. (14a) and (18) for Na, with $V$ equal to the semiempirical (S–E) or Hartree (Har.) potential and $C$ adjusted so that $\langle \vec{k}_F + \vec{G} | W_{\vec{k}_F} | \vec{k}_F \rangle_B = 0.25$ eV. In the curves labeled M–V, both $V_{110}$ and $C$ were adjusted so that the backscattering matrix element takes on the required value at $\hbar\omega_0$ and the variation of $\mathcal{W}_G(\vec{k}_F, \omega)$ vs $\omega$ is minimized.

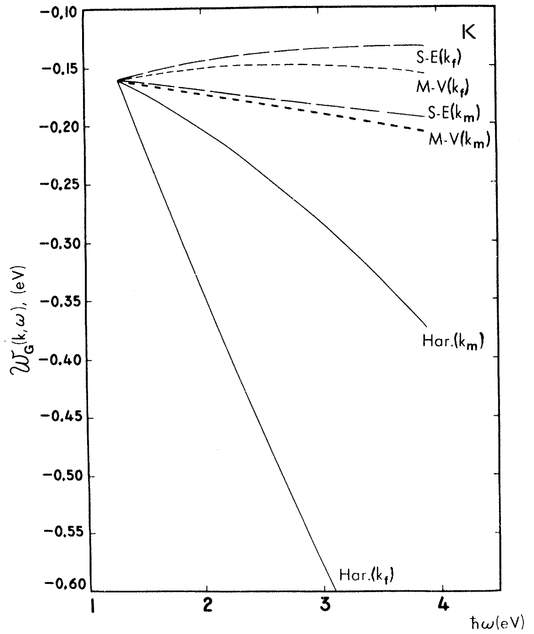

FIG. 4. $\mathcal{W}_G(\vec{k}, \omega)$ as defined in Eqs. (14a) and (18) for K. The same comments given for Fig. 3 hold here except that $\langle \vec{k}_F + \vec{G} | W_{\vec{k}_F} | \vec{k}_F \rangle_B = -0.16$ eV.

For Na, Lee[6] found that the Fermi-surface data could be fit with a local pseudopotential although the data could not distinguish between the values $\mathcal{W}_{110} = (+0.25 \pm 0.01)$ eV and $\mathcal{W}_{110} = (-0.21 \pm 0.01)$ eV. However, for K the situation is less clear. Lee and Falicov[9] found that a local pseudopotential was inadequate to account in detail for the measured Fermi surface and resorted to a nonlocal pseudopotential with at least 87 plane waves required in the pseudo-wave-function. Their result for $\mathcal{W}_{110}$ is $(0.05 \pm 0.05)$ eV. More recently, Dresselhaus *et al.*[10] have fit the measured Fermi surface using only 19 plane waves in the pseudo-wave-function and a $\vec{k}$ dependent pseudopotential. For our purposes it is sufficient to note that their value for $\mathcal{W}_{110}$ is 0.196 eV for $\vec{k}_F$ in the (1, 1, 0) direction, and for $\vec{k}$'s of interest in Eq. (15) $\mathcal{W}_{110}$ deviates by at most $-15\%$ from this value. On the other hand, there is evidence for negative values of $\mathcal{W}_{110}$ of this magnitude.[32] Thus for K we can only conclude that $|\mathcal{W}_{110}| \lesssim 0.20$ eV and attempt to obtain additional information on $\mathcal{W}_{110}$ from the optical data.

On the basis of the Fermi-surface analyses it is logical to assume that $\mathcal{W}_G(k; \omega)$ is a constant and to proceed to the calculation of $\sigma(\omega)$ by Eq. (15). However, a theoretical justification is required for the very weak $k$ dependence we are advocating, because of the fact that $W_{\vec{k}}$ should satisfy the nonlocality condition given in Eq. (8) which produces a $k$ dependence in $\mathcal{W}_G(k; \omega)$ and because of previous calculations[23] which have included strong $k$ and $\omega$

dependence in $w_G(k;\omega)$. There are a number of choices possible for $W_{\vec{k}}$ which satisfy Eq. (8). Since the final physical result should not depend on the particular choice made for $W_{\vec{k}}$, we shall follow Animalu[23] and take, in accordance with Eq. (8),

$$W_{\vec{k}} = V + \hat{P}(\epsilon_{\vec{k}} + C - H)\ , \tag{18}$$

where $C$ may be regarded as a constant adjustable parameter and $H$ is the Hamiltonian of Eq. (2). Animalu[23] took $V$ to be the Hartree potential due to the cores and assumed that the Herman-Skillman atomic wave functions and energies produced an adequate representation of the operators $\hat{P}$ and $\hat{P}H$. He then adjusted $C$ so that the backward-scattering matrix element $\langle \vec{k}_F + \vec{G} \,|\, W_{\vec{k}_F} \,|\, \vec{k}_F \rangle$ with $\vec{k}_F$ in the [110] direction takes on a prescribed value. (Henceforth this particular matrix element will be denoted by $\langle \vec{k}_F + \vec{G} \,|\, W_{\vec{k}_F} \,|\, \vec{k}_F \rangle_B$.) This completes Animalu's definition of $W_{\vec{k}}$ and the corresponding $w_G(k;\omega)$ can be calculated from Eq. (14a) for the $k$ values required in Eq. (15) for each value of $\omega$. It is worthwhile to point out that the general theorem of Austin, Heine, and Sham[26] on the arbitrariness of pseudopotentials [see Eq. (5)] is no guarantee that Animalu's prescription will produce a $\vec{k}$ dependence for the matrix element $\langle \vec{k} + \vec{G} \,|\, W_{\vec{k}} \,|\, \vec{k} \rangle$ by fitting it for a specific $\vec{k} = \vec{k}_F$ without accurate estimates of $V_{110}$ and $\hat{P}H$. A more meaningful approach is to regard both $V_{110}$ and $C$ as adjustable parameters and that their values be balanced so that the $\vec{k}$ dependence of $\langle \vec{k} + \vec{G} \,|\, W_{\vec{k}} \,|\, \vec{k} \rangle$ be similar to that indicated by the Fermi-surface data.

Our viewpoint that $V_{110}$ and $C$ should be taken as adjustable parameters is based on the fact that the single-particle potential $V(\vec{r})$ is not known to sufficient accuracy to obtain $V_{110}$ to better than 5 to 10% even for Na and K where particularily good potentials are available. This can be seen from Table I where we tabulate $V_{110}$ for the Hartree potentials and the semiempirical potentials.[33–35] The semiempirical potentials are one-electron local potentials determined by fitting atomic spectroscopic data. In a sense they include exchange and correlation effects between the valence electron and the core. Therefore they may be regarded as the "best" local one-electron potentials available for the problem at hand. From Table I we see that the difference between the Hartree and semiempirical $V_{110}$'s are ~ 1 eV which is of order five times $w_{110}$! Thus to regard $V_{110}$ as fixed, especially at the Hartree value, when attempting to obtain $\langle \vec{k} + \vec{G} \,|\, W_{\vec{k}} \,|\, \vec{k} \rangle$ by prescribing it for a specific $\vec{k} = \vec{k}_F$ is not justified.

TABLE I. Pseudopotential parameters.

| | Na | K |
|---|---|---|
| $a_L$ | 4.295 Å | 5.329 Å |
| $\epsilon_F$ | 3.14 eV | 2.04 eV |
| $\hbar\omega_0$ | 2.00 eV | 1.30 eV |
| $\langle \vec{k}_F + \vec{G} \,\|\, W_{\vec{k}_F} \,\|\, \vec{k}_F \rangle_B$ | 0.25 eV | −0.16 eV |
| $V_{110}$ (Har.) | −2.31 eV | −2.76 eV |
| $C$ (Har.) | −48.37 eV | −49.46 eV |
| $V_{110}$ (semiempirical) | −3.15 eV | −3.73 eV |
| $C$ (semiempirical) | 2.20 eV | −3.80 eV |
| $V_{110}$ (M-V) | −3.81 eV | −4.56 eV |
| $C$ (M-V) | −9.71 eV | −10.74 eV |

To illustrate the effect of allowing $V_{110}$ to vary we have calculated $w_G(k;\omega)$ for two sets of values for $V_{110}$ and $C$. In the example labeled "Har.," the Animalu prescription of only adjusting $C$ was followed. In the second example, referred to as M-V, both $V_{110}$ and $C$ were adjusted so that $\langle \vec{k}_F + \vec{G} \,|\, W_{\vec{k}_F} \,|\, \vec{k}_F \rangle_B$ takes on a prescribed value and the variation of $\langle \vec{k}_F + \vec{G} \,|\, W_{\vec{k}_F} \,|\, \vec{k}_F \rangle$ as a function of the orientation of $\vec{k}_F$ is minimized. The latter condition is equivalent to minimizing the variation of $w_G(k_F;\omega)$ as a function of $\omega$. In both Har. and M-V, Clementi's[29] neutral-atom results were used for the core-state wave functions and energies in constructing $\hat{P}$ and $\hat{P}H$. The results for $w_G(k;\omega)$, $k = k_F$ and $k_m$, are shown in Figs. 3 and 4 and the values of the parameters $V_{110}$ and $C$ are given in Table I. It was found that $w_G(k;\omega)$ varies monotonically with $k$ for fixed $\omega$. For Na, Lee's[6] value of 0.25 eV for the back-scattering matrix element was used. The value − 0.16 eV used for K was deduced from fitting the optical data (see below). From Fig. 3 we see that $w_G(k_F,\omega)$ for Har. varies considerably outside of the limits Lee put on the Na matrix element, i.e., $(0.25 \pm 0.01)$ eV. The situation in K is even more irregular in that $w_G(k_F,\omega)$ for Har. varies by a factor of ~ 5 in the $\omega$ range of interest. There is no justification for a variation of this magnitude. It should be emphasized that this large variation in $w_G(k_F;\omega)$ that occurs in K is characteristic of the Har. value for $V_{110}$ and is not dependent on the choice of − 0.16 eV for the back-scattering matrix element. Similar variations occur for any value in the range − 0.20 to + 0.20 eV for the back-scattering matrix element with the Har. value for $V_{110}$. These results clearly establish that the Animalu prescription for constructing $W_{\vec{k}}$ is not reliable. Also it is seen that it is possible to construct a $W_{\vec{k}}$ which satisfies Eq. (8) and produces essentially constant values of $w_G(k_F;\omega)$.

In the above calculations the operators $\hat{P}$ and $\hat{P}H$ were constructed from neutral-atom core-state wave functions and energies instead of those appropriate to a solid. To put the whole theory on a firmer foundation we have also calculated $\hat{P}$ and $\hat{P}H$ with core states and energies that are appropriate to the metal.[36] In these calculations the single-particle potential $V(\vec{r})$ consisted of two parts: The conduction-electron–ion interactions were represented by the semiempirical potentials; and the effect of the electron-electron interaction between conduction electrons was approximated by a Hartree potential due to a uniform charge distribution. Since the semiempirical potential gives an excellent representation of the electron-ion interaction and the Hartree term gives the most important contribution to the single-particle potential due to the conduction-electron–electron interactions, this calculation should produce a reliable picture of the true situation. This would be reflected in the results by $C$ being a small number (a few electron volts) when $V_{110}$ is held fixed to the value given by the semiempirical potential (i.e., $C$ is the only adjustable parameter in fitting $\langle \vec{k}_F+\vec{G}\,|\,W_{\vec{k}_F}\,|\,\vec{k}_F\rangle_B$). From Table I, we see that this is indeed the case. Also from the curves labeled S-E in Figs. 3 and 4 we see that the variation in $\mathcal{W}_G(k_F;\,\omega)$ over the $\omega$ range of interest is less than 20% in both Na and K. This variation could be reduced by making a small adjustment ($\lesssim 10\%$) to the semiempirical value of $V_{110}$ and readjusting $C$ accordingly.

To summarize, we have shown that is possible, and in fact follows naturally from careful calculations with semiempirical potentials, to obtain representations of $\langle \vec{k}+\vec{G}\,|\,W_{\vec{k}}\,|\,\vec{k}\rangle$ that satisfy Eq. (8) and give values for $\langle \vec{k}_F+\vec{G}\,|\,W_{\vec{k}_F}\,|\,\vec{k}_F\rangle$ for all orientations of $\vec{k}_F$ that are in accordance with Fermi-surface data.

With the above results for $D(k;\,\omega)$, $F(k;\,\omega)$, and $\mathcal{W}_G(k;\,\omega)$ it is straightforward to calculate $\sigma(\omega)$ from Eq. (15). We begin with Na, because the possible values for the pseudopotential matrix elements are well established. The resulting $\sigma(\omega)$'s for $\langle \vec{k}_F+\vec{G}\,|\,W_{\vec{k}_F}\,|\,\vec{k}_F\rangle_B = 0.25$ eV are given in Fig. 5 for three $\mathcal{W}_G(k;\,\omega)$'s: The Har. and S-E curves correspond to those of Fig. 3 and const. corresponds to $\mathcal{W}_G(k;\,\omega) = \text{constant} = 0.25$ eV. The agreement between the theoretical curves S-E and const. with the experimental results is very good, especially when one considers that Powell[3] allowed the interband threshold to fall below 2 eV in his analysis. This has the effect of making the experimental interband contribution for $\hbar\omega \geq 2$ eV smaller than if the analysis had been done with the threshold fixed at 2 eV. The resulting $\sigma(\omega)$ for Animalu's procedure (i.e., Har.) for obtaining $\mathcal{W}_G(k;\,\omega)$ are considerably below the experimental values. The reason for this is clear from Fig. 3, where one sees that $\mathcal{W}_G(k;\,\omega)$ – Har. falls off by ~30% as $\hbar\omega$ goes from 2 to 4 eV. Calculations of $\sigma(\omega)$ for $\langle \vec{k}_F+\vec{G}\,|\,W_{\vec{k}_F}\,|\,\vec{k}_F\rangle_B = -0.21$ eV gave values which were approximately a factor three times smaller than those for +0.25 eV. This is due to the difference in interference that occurs between $\mathcal{W}_G(k;\,\omega)$ and $\hbar\omega D(k;\,\omega)$ in the two cases. From Fig. 1 we see that $\hbar\omega D(k;\,\omega)$ is of order of magnitude 0.05 eV; thus the ratio of the effective matrix elements which enter Eq. (15) for the two cases is approximately 1.8.

Recalling the discussion given above on the analysis of the Fermi surface for K, we were forced to use the optical data to deduce a value of $\langle \vec{k}_F+\vec{G}\,|\,W_{\vec{k}_F}\,|\,\vec{k}_F\rangle_B$. Powell[6] found that the interband conductivity could be fit with a Wilson-Butcher expression with the magnitude of the matrix element equal to 0.15 eV. From an examination of Eq. (15) and Fig. 2 it becomes clear that the effective matrix element $A_{\vec{k}+\vec{G}}A_{\vec{k}}\,M(k;\,\omega)$ can reach a value in this vicinity by $-0.15\ \text{eV} \gtrsim \mathcal{W}_G(k;\,\omega) \gtrsim -0.20$ eV and $0 \lesssim \mathcal{W}_G(k;\,\omega) \lesssim 0.10$ eV. Calculations of $\sigma(\omega)$ for $\mathcal{W}_G(k;\,\omega) = \text{constant}$ in these ranges were carried out. It was found that only $\mathcal{W}_G$ in the range $-0.15$ to $-0.16$ eV fit the experimental results over the whole photon energy. The $\mathcal{W}_G(k;\,\omega)$ corresponding to the S-E and Har. were also tried. The S-E $\mathcal{W}_G(k;\,\omega)$ gave a good fit for $\langle \vec{k}_F+\vec{G}\,|\,W_{\vec{k}_F}\,|\times\vec{k}_F\rangle_B = -0.16$ eV. On the other hand it was not possible to fit the experimental results with any $\mathcal{W}_G(k;\,\omega)$ calculated by the Har. scheme. The resulting curves for $\sigma(\omega)$ are given in Fig. 6. It is

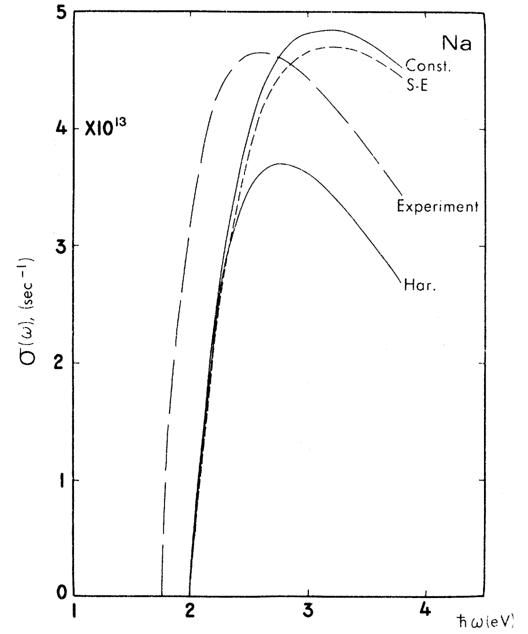

FIG. 5. Interband contribution to the optical conductivity for Na. The theoretical curves are obtained by use of semiempirical (S-E) and Hartree (Har.) potentials, along with those resulting from $\mathcal{W}_G(k,\,\omega) = 0.25$ eV (const.). The experimental curve is from Smith (Ref. 1) as analyzed by Powell (Ref. 3). It should be pointed out that Powell treats the threshold energy as an adjustable parameter when fitting the data with the Wilson-Butcher formula.

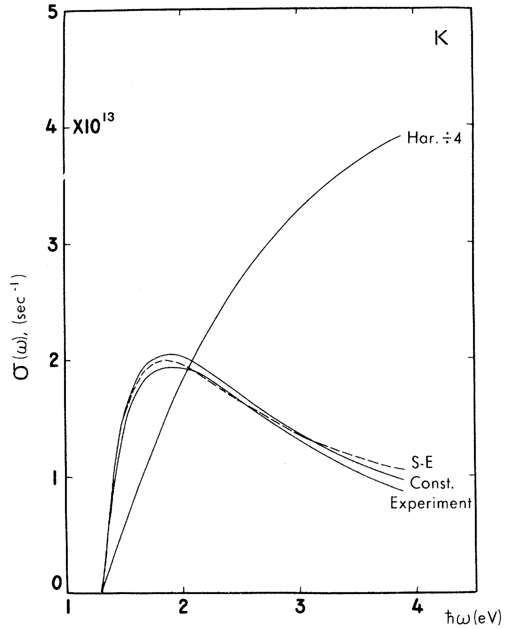

FIG. 6. Interband contribution to the optical conductivity for K. The same comments given for Fig. 5 hold here except that $\mathcal{W}_G(k, \omega) = -0.16$ eV for the curve labeled const.

worth emphasizing that the destructive interference that occurs between $\mathcal{W}_G(k; \omega)$ and $\hbar\omega D(k; \omega)$ when $\mathcal{W}_G(k; \omega)$ is negative is essential in fitting the experimental results with Eq. (15). The reason for this is that as $\hbar\omega$ increases the contribution from $M_\perp(k; \omega)$ increases rapidly to approximately 25% of the experimental value at $\hbar\omega \approx 4$ eV and unless this is compensated by a decrease in $M_\parallel(k; \omega)$ the whole effective matrix element does not remain nearly constant as Powell's analysis requires. This explains why a fit cannot be obtained with positive $\mathcal{W}_G(k; \omega)$, unless one insists it has a very special $k$ and $\omega$ dependence, i.e., $\mathcal{W}_G(k; \omega)$ drops from 0.10 to 0.05 eV as $\hbar\omega$ goes from 2 to 4 eV. There is no indication from the Fermi-surface data that such a wide variation in $\langle \vec{k}_F + \vec{G} | W_{\vec{k}_F} | \vec{k}_F \rangle$ does in fact occur. Thus the first-order OPW-pseudopotential perturbation theory of $\sigma(\omega)$ in combination with the optical data points to a fairly unique value for the pseudopotential parameter $\mathcal{W}_{110}$ in K. The accuracy of this determination is quite sensitive to the validity of the former and accuracy of the measurements.

The results obtained above for K should be compared with those of Dresselhaus *et al.*[10] who found that the Fermi-surface data and the interband optical conductivity could be fit with a nonlocal $k$-dependent pseudopotential that included the two sets of reciprocal-lattice vectors [110] and [200]. Their value for $\langle \vec{k}_F + \vec{G} | W_{\vec{k}_F} | \vec{k}_F \rangle_B$ is +0.196 eV in contrast to our result of $-0.16$ eV. However, their calculations do not include the effect of core orthogonalization in calculating the matrix element $\langle \chi_{\vec{k}'} | \vec{p} | \chi_{\vec{k}} \rangle$ [see Eqs. (9) and (15)], which have been found to produce substantial contributions in our work. On the other hand, they do include the effect of the [200] reciprocal-lattice vectors which would be a higher-order correction to the perturbation theory used in the present work.

## IV. MODIFIED WILSON-BUTCHER FORMULA

In the calculations presented in Sec. III the integration over $k$ in Eq. (15) was performed numerically so that the effects of the $k$ dependence in $\mathcal{W}_G(k; \omega)$, $D(k; \omega)$, and $F(k; \omega)$ of Eqs. (14a), (17a), and (17b) could be investigated and understood. From those results it is clear that until definite evidence is brought forward to the contrary the most reasonable choice for $\mathcal{W}_G(k; \omega)$ is a constant equal to the value required to fit the Fermi-surface data. The variation of $D(k; \omega)$ and $F(k; \omega)$ with $k$ for fixed $\omega$ can be seen from Figs. 1 and 2 to be small enough so that they can be replaced by their mean values $D_0(\omega)$ and $F_0(\omega)$ in Eq. (15). Thus, combining Eqs. (17a) and (17b) with Eq. (15) yields

$$\sigma(\omega) \approx \frac{4e^2 \epsilon_G}{\pi\hbar(\hbar\omega)^3} \int_{k_m}^{k_F} dk \frac{k}{G} A^4_{k_F} \left( [\mathcal{W}_G + \hbar\omega\, D_0(\omega)]^2 + [\hbar\omega F_0(\omega)]^2 \frac{k^2 - k_m^2}{G^2} \right) . \tag{19}$$

The integration over $k$ is now trivial and gives a modified Wilson-Butcher formula for $\sigma(\omega)$:

$$\sigma(\omega) \approx \frac{e^2}{\hbar} \frac{G}{2\pi} \frac{(\hbar\omega - \hbar\omega_0)(\hbar\omega_i - \hbar\omega)}{(\hbar\omega)^3 \epsilon_{\vec{G}}} O^2(\omega) , \tag{20}$$

where $O(\omega)$ is the effective optical pseudopotential:

$$O(\omega) = A^2_{k_F} \left( [\mathcal{W}_G + \hbar\omega D_0(\omega)]^2 + \frac{(\hbar\omega - \hbar\omega_0)(\hbar\omega_i - \hbar\omega)}{8\epsilon^2_{\vec{G}}} [\hbar\omega F_0(\omega)]^2 \right)^{1/2} ; \tag{21}$$

$\hbar\omega_0$ and $\hbar\omega_i$ are the low and high threshold energies given by

$$\hbar\omega_0 = \epsilon_{\vec{G}}(1 - 2k_F/G) , \tag{22a}$$

$$\hbar\omega_i = \epsilon_{\vec{G}}(1 + 2k_F/G) . \tag{22b}$$

From Figs. 1 and 2 we see that $D_0(\omega)$ and $F_0(\omega)$ can be approximated accurately by the linear interpolations

$$D_0(\omega) = d_0 + d_1(\hbar\omega - \hbar\omega_0)/\hbar\omega_0 , \tag{23}$$

$$F_0(\omega) = f_0 + f_1(\hbar\omega - \hbar\omega_0)/\hbar\omega_0 . \tag{24}$$

Values for $d_0$, $d_1$, $f_0$, $f_1$, and $A^2_{k_F}$ are given in Table II. Using these results in Eq. (20) for $\sigma(\omega)$ gives values that are within 5% of those obtained by

TABLE II. Expansion parameters for $D_0(\omega)$ and $F_0(\omega)$.

| | Na | K |
|---|---|---|
| $d_0$ | 0.0177 | 0.0169 |
| $d_1$ | $-5.6\times10^{-4}$ | $-2.0\times10^{-3}$ |
| $f_0$ | 0.0420 | 0.1275 |
| $f_1$ | $-0.0041$ | $-0.0122$ |
| $A^2_{k_F}$ | 1.0825 | 1.1669 |

a numerical integration of Eq. (15). It is important to realize that the effective optical pseudopotential can be substantially different from the pseudopotential matrix element $w_G$.

## V. CONCLUSION

The OPW-pseudopotential formalism has been used to derive an expression for the interband contribution to the optical conductivity which has a structure similar to the Wilson-Butcher formula. The primary difference between the two formulas is the replacement of the potential parameter in the Wilson-Butcher expression by an effective optical pseudopotential (which is significantly different from that of Animalu and Harrison). One evaluates this quantity by using the results of de Haas–van Alphen experiments and wave functions for the electronic core states. The theoretical values for $\sigma(\omega)$ obtained in this manner are in good agreement with the experimental measurements of Smith.[1] In particular, the results for Na, where the pseudopotential coefficients are well established, suggest that the many-body corrections beyond those included in the pseudopotential coefficients are small ($\lesssim 15\%$). For K, although one can fit the optical data using a (110) pseudopotential coefficient commensurate with Fermi-surface data, the question of higher-order corrections due to a (200) pseudopotential coefficient must be resolved before one may comment about any additional many-body corrections.

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## APPENDIX

In this Appendix the matrix elements $\langle\vec{k}'|\hat{P}|\vec{k}\rangle$ and $\langle\vec{k}'|\hat{P}\vec{p}\hat{P}|\vec{k}\rangle$ are reduced to their elemental constituents, with particular emphasis on the latter matrix element. All results are given in terms of the radial parts of the core-state wave functions. The core eigenkets and wave functions are designated by $|\vec{l}t\rangle$ and $\chi_t(\vec{r}-\vec{L})\equiv\langle\vec{r}|\vec{l}t\rangle$, respectively, where $t$ stands for the usual atom quantum numbers $n$, $l$, $m$, $\sigma$, and $\vec{l}$, the lattice site $\vec{L}$. Then the core-projection operator may be written

$$\hat{P}\equiv\sum_{\vec{l}t}|\vec{l}t\rangle\langle\vec{l}t| , \tag{A1}$$

where the sums $\vec{l}$ and $t$ extend over all the lattice sites of the system and all the core states, respectively. The matrix element of $\hat{P}$ between plane-wave states that satisfy periodic-boundary conditions and are normalized over the crystal volume $\Omega$ may be expressed in standard form

$$\langle\vec{k}'|\hat{P}|\vec{k}\rangle=\Delta(\vec{k}',\vec{k})\sum_{nl}b_{nl}(k')b_{nl}(k)P_l(\hat{k}'\cdot\hat{k}) , \tag{A2}$$

where $\Delta(\vec{k}',\vec{k})$ is the generalized Kronecker $\Delta$ defined by

$$\Delta(\vec{k}',\vec{k})=\sum_{\vec{G}'}\delta_{\vec{k}',\vec{k}+\vec{G}'} ; \tag{A3}$$

$$b_{nl}(k)=[4\pi(2l+1)/\Omega_0]^{1/2}\int_0^\infty dr\, r^2 j_l(kr)R_{nl}(r) ; \tag{A4}$$

$\Omega_0$ is the primitive-cell volume; $j_l(kr)$ is the usual spherical Bessel function; $R_{nl}(r)$ is the normalized radial part of the core state; and $P_l(\hat{k}'\cdot\hat{k})$ is the standard Legendre polynomial of the cosine of the angle between the vectors $\vec{k}'$ and $\vec{k}$. Specializing Eq. (A2) to Na and K, where the cores contain $l=0$ and $l=1$ states only, allows $P_G(k;\omega)$ of Eq. (14b) to be written as

$$P_G(k;\omega)=\sum_n b_{n0}(|\vec{k}+\vec{G}|)b_{n0}(k) + \sum_n b_{n1}(|\vec{k}+\vec{G}|)b_{n1}(k)\cos(\vec{k},\vec{k}+\vec{G}) , \tag{A5}$$

where $|\vec{k}+\vec{G}|$ and $\cos(\vec{k},\vec{k}+\vec{G})$ are given in terms of $k$ and $\omega$ by Eqs. (14e) and (14f).

To simplify the matrix element $\langle\vec{k}'|\hat{P}\vec{p}\hat{P}|\vec{k}\rangle$ we note that the matrix element of $\vec{p}$ between core states centered on different lattice sites vanishes, i.e.,

$$\langle\vec{l}'t'|\vec{p}|\vec{l}t\rangle=\delta_{\vec{l}',\vec{l}}\langle\vec{l}t'|\vec{p}|\vec{l}t\rangle . \tag{A6}$$

Thus

$$\langle\vec{k}'|\hat{P}\vec{p}\hat{P}|\vec{k}\rangle=\Delta(\vec{k}',\vec{k})N\langle\vec{k}'|\hat{P}_0\vec{p}\hat{P}_0|\vec{k}\rangle , \tag{A7}$$

where $N$ is the number of lattice sites in the crystal and $\hat{P}_0$ is the core-projection operator for a single site which may be expressed as sum of projection operators each corresponding to a particular angular momentum:

$$\hat{P}_0=\sum_l \hat{P}_0(l) , \tag{A8}$$

where

$$\hat{P}_0(l)=\sum_{nm}|nlm\rangle\langle nlm| . \tag{A9}$$

Since the momentum operator $\vec{p}$ is a vector operator with odd parity its matrix elements vanish unless $\Delta l=\pm1$. Noting that the cores of Na and K contain $s$ and $p$ states [i.e., $\hat{P}_0=\hat{P}_0(s)+\hat{P}_0(p)$], it follows that

$$\langle \vec{k}' | \hat{P}\vec{p}\hat{P} | \vec{k} \rangle = \Delta(\vec{k}', \vec{k}) N [\langle \vec{k}' | \hat{P}_0(p)\vec{p}\hat{P}_0(s) | \vec{k} \rangle + \langle \vec{k}' | \hat{P}_0(s)\vec{p}\hat{P}_0(p) | \vec{k} \rangle] . \tag{A10}$$

The evaluation of these matrix elements is considerably simplified by transforming the $p$ states from a $\{nlm\}$ representation to the Cartesian representation $\{nl\alpha\}$, where $\alpha = 1, 2, 3$ corresponding to $(x, y, z)$. The normalized $p$-wave functions in the Cartesian representation are

$$\langle \vec{r} | nl\alpha \rangle = (3/4\pi)^{1/2} (x_\alpha / r) R_{n1}(r) \tag{A11}$$

and the projection operator $\hat{P}_0(p)$ may be written

$$\hat{P}_0(p) = \sum_{n\alpha} | n1\alpha \rangle \langle n1\alpha | . \tag{A12}$$

Substituting this form for $\hat{P}_0(p)$ in the first term on the right-hand side of (A10) gives

$$\langle \vec{k}' | \hat{P}_0(p)\vec{p}\hat{P}_0(s) | \vec{k} \rangle = \sum_{nn'\alpha} \langle \vec{k}' | n'1\alpha \rangle \langle n'1\alpha | \vec{p} | n0 \rangle \times \langle n0 | \vec{k} \rangle . \tag{A13}$$

The individual matrix elements in (A13) follow directly from their definitions:

$$\langle \vec{k}' | n'1\alpha \rangle = \Omega^{-1/2} \int d\vec{r}\, e^{-i\vec{k}'\cdot\vec{r}} (x_\alpha / r) R_{n'1}(r) \left(\frac{3}{4\pi}\right)^{1/2} = -iN^{-1/2} \frac{k'_\alpha b_{n'1}(k')}{k'} \;; \tag{A14}$$

$$\langle n'1\alpha | p_\beta | n0 \rangle = \int d\vec{r} \left(\frac{3}{4\pi}\right)^{1/2} \left(\frac{x_\alpha}{r}\right) R_{n'1}(r) \frac{\hbar}{i} \frac{\partial}{\partial x_\beta} R_{n0}(r) \left(\frac{1}{4\pi}\right)^{1/2} = \delta_{\alpha\beta} \frac{-i\hbar}{\sqrt{3}} \int_0^\infty dr\, r^2 R_{n'1}(r) \frac{d}{dr} R_{n0}(r) \;; \tag{A15}$$

and

$$\langle n0 | \vec{k} \rangle = N^{-1/2} b_{n0}(k) . \tag{A16}$$

Combining Eqs. (A13) to (A16) yields

$$N\langle \vec{k}' | \hat{P}_0(p)\vec{p}\hat{P}_0(s) | \vec{k} \rangle = -\hbar\vec{k}' \sum_{nn'} \frac{b_{n'1}(k') I_{n'n} b_{n0}(k)}{\sqrt{3}\, k'} , \tag{A17}$$

where

$$I_{n'n} \equiv \int_0^\infty dr\, r^2 R_{n'1}(r) \frac{d}{dr} R_{n0}(r) . \tag{A18}$$

If the radial functions $R_{nl}(r)$ are solutions of a radial differential equation with a local potential and energy eigenvalues $\epsilon_{nl}$, then Eq. (A18) can be transformed into

$$I_{n'n} = (m/\hbar^2)(\epsilon_{n0} - \epsilon_{n'1}) \int_0^\infty dr\, r^2 R_{n'1}(r) r R_{n0}(r) . \tag{A18a}$$

Noting that the operators $\hat{P}_0(s)$, $\vec{p}$, and $\hat{P}_0(p)$ are Hermitian and that the right-hand side of (A17) is real, we can immediately obtain the second term on the right-hand side of Eq. (A10) from Eq. (A17):

$$N\langle \vec{k}' | \hat{P}_0(s)\vec{p}\hat{P}_0(p) | \vec{k} \rangle = N\langle \vec{k} | \hat{P}_0(p)\vec{p}\hat{P}_0(s) | \vec{k}' \rangle^* = -\hbar\vec{k} \sum_{nn'} \frac{b_{n'1}(k) I_{n'n} b_{n0}(k')}{\sqrt{3}\, k} . \tag{A19}$$

For the purposes of combining with the other terms in Eq. (9) it is convenient to express the matrix element $\langle \vec{k}' | \hat{P}\vec{p}\hat{P} | \vec{k} \rangle$ as a linear combination of terms with the vector form $\hbar(\vec{k}' + \vec{k})$ and $\hbar(\vec{k}' - \vec{k})$. Using Eqs. (A10), (A17), and (A19), this may be achieved by writing

$$\langle \vec{k}' | \hat{P}\vec{p}\hat{P} | \vec{k} \rangle = \hbar(\vec{k}' + \vec{k}) S(k', k) + \hbar(\vec{k}' - \vec{k}) B(k', k) , \tag{A20}$$

where

$$S(k', k) \equiv -\frac{1}{2\sqrt{3}} \sum_{nn'} I_{n'n} \left(\frac{b_{n'1}(k') b_{n0}(k)}{k'} + \frac{b_{n'1}(k) b_{n0}(k')}{k}\right) \tag{A21}$$

and

$$B(k', k) \equiv -\frac{1}{2\sqrt{3}} \sum_{nn'} I_{n'n} \left(\frac{b_{n'1}(k') b_{n0}(k)}{k'} - \frac{b_{n'1}(k) b_{n0}(k')}{k}\right) . \tag{A22}$$

$S_G(k; \omega)$ and $B_G(k; \omega)$ of Eqs. (14c) and (14d) are obtained from these expressions by substituting Eq. (14e) for $k' = |\vec{k} + \vec{G}|$.

Concerning the relative order of magnitude of the terms $\hbar(\vec{k}' + \vec{k}) \langle \vec{k}' | \hat{P} | \vec{k} \rangle$ and $\langle \vec{k}' | \hat{P}\vec{p}\hat{P} | \vec{k} \rangle$ we see from Eqs. (A2), and (A20)–(A22) that both quantities are bilinear in the $b_{nl}$'s. Thus the ratio of their magnitudes reduces to the value of the $(I_{n'n}/k)$ which we see from Eq. (A18) is order unity since $I_{n'n}$ is of order an atomic wave vector and thus approximately equal to $k$.

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# Electronic and Nuclear-Magnetic-Resonance Properties of the Liquid Metals

P. Jena* and N. C. Halder†
*Department of Physics, State University of New York, Albany, New York* 12203

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The electronic structure of liquid metals has been studied by investigating the temperature dependence of the electron density of states, electron effective mass, Knight shift, and coefficient of electrical resistivity. The values of the effective mass have been successfully used to interpret the change of the Knight shift upon melting. The temperature coefficient of electrical resistivity, calculated using the temperature-dependent effective mass and the Ziman theory, shows substantially improved agreement with experiment.

## I. INTRODUCTION

In this paper we present a study of the temperature dependence of the electronic structure of some liquid metals. The electron density of states, electron effective mass, change of Knight shift upon melting, and temperature coefficient of resistivity have been calculated, and comparisons have been made with the most recent experimental measurements. We also examine the two points of view regarding the electronic structure of liquid metals that have been expressed in the literature. In one[1] of these the electrons in a liquid metal are regarded as nearly free (NFE) with a simple parabolic dispersion relation ($E \propto k^2$); whereas in the other[2] the electrons are regarded as not being free, the density of states exhibiting some remnant of the kinks that occur in the spectrum of the solid due to the Brillouin-zone boundaries. Some information concerning the variation of the electronic structure with temperature can be obtained by a systematic study of the density of states and the other quantities mentioned above.

Ballentine[3] has calculated the energy spectrum and the density of states for a number of liquid metals following the Green's-function approach of Edwards[2] and using the local model potential of Animalu and Heine.[4] He did not study the effect of temperature. He concluded that in general the electrons cannot be regarded as being free. However, he observed that if the position of the first peak of the liquid interference function was near