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Plasmon Contribution to the Ultraviolet Absorbing Power of the Alkali Metals

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The absorbing power due to a photon exciting both a plasmon and an intraband transition in a semi-infinite electron gas of metallic density has been found to be of the order of 10^{13} sec^{-1} in the ultraviolet at approximately $\hbar\omega_p+\epsilon_F$. The plasmon absorption appears to give only a small contribution to the ultraviolet absorption spectrum of most metals, but for the alkali metals it is of the same order of magnitude as the previously calculated interband absorbing power. A linear superposition of the Drude, interband, and plasmon conductivities suggests that sodium and potassium may exhibit small broad peaks in their absorption spectra due to plasmon excitations near 8.8 and 5.8 eV, respectively. The calculated plasmon absorption for other free-electron-like metals in the ultraviolet and for an n-doped semiconductor in the infrared is briefly discussed.

I. INTRODUCTION

THE rather surprising optical properties of the alkali metals, namely, the Mayer–El Naby resonance in the near infrared[1,2] and the high absorbing power of sodium and potassium[3,4] in the visible, have been the subject of current theoretical interest.[5] In this paper we show that the ultraviolet spectral region of the alkalies may also exhibit interesting resonant behavior. We have employed the Bohm-Pines formalism[6] for a semi-infinite electron gas of alkali metal density and have calculated the absorbing power for the process where an incident photon excites a plasmon through the intermediary of an intraband transition (electron-hole pair). The conductivity for this process vanishes at energies below the free-electron plasma energy $\hbar\omega_p$ and has a maximum value of the order 10^{13} sec^{-1} at approximately $\hbar\omega_p+\epsilon_F$, where $\omega_p=(4\pi Ne^2/m)^{1/2}$, N is the number of electrons per unit volume, and ϵ_F is the Fermi energy.

The absorption due to this electron-photon-plasmon process was originally considered by Tzoar and Klein.[7] A more general discussion of the propagation of electromagnetic waves in plasmas was given by DuBois, Gilinsky, and Kivelson.[8] The latter authors show from diagrammatic techniques that the important absorption contributions in the high-density and long-wavelength limits come from the two pair final states, namely, the two-free-pair state and the pair-plus-plasmon (bound-pair) state. They also pointed out that the plasmon conductivity is bounded by k_c, the minimum wave vector at which the plasmon can decay into an electron-hole pair. About the same time, Matsudaira[9] used the Bohm-Pines model to calculate the plasmon absorption in a high-density electron gas. The advantages of the Bohn-Pines formalism are (1) the long-range part of the Coulomb interaction ($k\leq k_c$) is explicitly described in terms of the plasmons, which commute with the electrons; (2) the short-range part of the Coulomb interaction ($k>k_c$) is only a slight perturbation to the electron behavior in a high-density gas; and (3) in the high-density limit a small expansion parameter is introduced so that in the presence of a radiation field the photon-bound-pair absorption is of second order, the photon-two-free-pair absorption is of third order, and all other absorption processes are of third or higher order.

Both Matsudaira and DuBois *et al.* ignored the dispersive term in the eigenfrequency ω_k for a plasmon of wave vector $\mathbf{k}$ and thereby replaced ω_k by ω_p. The eigenfrequency for a high-density gas is given from the plasmon dispersion relation by

$$\omega_k=\omega_p+\frac{3\hbar k^2}{5x_0m}+\frac{\hbar^2k^4}{8\omega_pm^2}+\cdots, \tag{1}$$

where $x_0=\hbar\omega_p/\epsilon_F$. The maximum value of the plasmon

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[1] H. Mayer and M. H. El Naby, Z. Physik **174**, 289 (1963).

[2] H. Mayer and B. Hietel, in *Proceedings of the International Colloquium on Optical Properties and Electronic Structure of Metals and Alloys, Paris, 1965*, edited by F. Abeles (North-Holland Publishing Co., Amsterdam, 1966).

[3] H. E. Ives and H. B. Briggs, J. Opt. Soc. Am. **27**, 181 (1937).

[4] H. E. Ives and H. B. Briggs, J. Opt. Soc. Am. **26**, 238 (1936).

[5] For example, see J. C. Phillips, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1966), Vol. 18.

[6] For example, see D. Pines, *The Many-Body Problem* (W. A. Benjamin, Inc., New York, 1961).

[7] N. Tzoar and A. Klein, Phys. Rev. **124**, 1297 (1961).

[8] D. F. DuBois, V. Gilinsky, and M. G. Kivelson, Phys. Rev. **129**, 2376 (1963).

[9] N. Matsudaira, J. Phys. Soc. Japan **17**, 1563 (1962).

wave vector k_c is approximately equal to $\frac{1}{2}x_0\nu_0$, which for a normal electron gas is $0.47r_s^{1/2}\nu_0$, where ν_0 is the Fermi wave vector. For a gas with the density of sodium, r_s is 3.96, k_c is $0.937\nu_0$, and Eq. (1) is a fairly good approximation to order k^2. Then, since $\langle\omega_k\rangle_{\mathrm{av}} \simeq 1.18\omega_p$, a recalculation of the plasmon absorption, which includes the plasmon dispersion, seemed in order.

In Sec. II of this paper we follow the procedure given by Matsudaira to calculate the plasmon conductivity of a high-density electron gas. We assume that the Bohm-Pines Hamiltonian gives a qualitative description at metallic densities and thereby maintain their ordering of zero-, first-, and second-order terms. The plasmon contribution to the optical conductivity arises from the second-order (random-phase) term containing an electron, plasmon, and photon. We wish to point out that Matsudaira introduced a canonical transformation in order to eliminate both the first-order electron-plasmon and electron-photon terms. The absorption cross section which he evaluated, was, therefore, calculated from dressed photons. We have kept the photons in the laboratory system because the electron-photon term describes the intraband and interband absorption which are required for our calculation in Sec. III of the total absorbing power of the alkali metals. However, if ω_k is replaced by ω_p, our expression for the plasmon absorption coincides with that obtained by Matsudaira and DuBois *et al.*

We have found that the inclusion of the dispersive term yields an absorption cross section roughly 30% lower than the dispersionless cross section and shifts the plasmon resonance about 1 eV further into the ultraviolet for a gas with the density of sodium. We estimate that our results for the plasmon conductivity near its peak value are accurate to within 20%. In this region the interband absorption roughly falls as ω^{-3}. The plasmon absorbing power of potassium, for which r_s equals 4.87, is similar to that of sodium.

In Sec. III we apply our results to real metals. In order to ascertain whether the plasmon resonance might be observable in sodium and potassium, we have calculated their total conductivities to second order in the ultraviolet by taking linear superpositions of the Drude, interband, and plasmon contributions. The interband absorption has been given by Butcher,[10] and the intraband absorption is approximated by its Drude value with relaxation time τ. If the electron-photon interaction were eliminated by a canonical transformation, a superposition of absorption processes would no longer be consistent. The plasmon absorption is calculated from second-order perturbation theory where the electron wave function is approximated by plane waves and the dispersive term of the plasmon eigenenergy is included. Our results suggest that a careful experimental study of the optical properties of a bulk alkali metal above its plasma energy may reveal a broad peak in the absorbing power due to the plasmon process when the Drude relaxation time is sufficiently long (approximately 10^{-14} sec). To our knowledge, complete optical measurements (that is, measurements of the index of refraction and extinction coefficient which lead to the complex dielectric constant and to the absorbing power) have not been reported on the alkali metals in this spectral region; however, recent measurements by Sutherland *et al.*[11] have been made at 7.11 eV, on sodium. The plasmon absorption of other free-electron-like metals, like aluminum and magnesium, appears to be too small to detect experimentally, since reported values of their ultraviolet conductivities are at least an order of magnitude higher.

II. FORMULATION AND CALCULATION FOR ELECTRON GAS

We now outline our procedure for calculating the optical conductivity for a semi-infinite electron gas in the presence of an external radiation field. Our discussion can be followed by referring to the summary of the Bohm-Pines theory found in Matsudaira's paper.[9] At the outset we rewrite the Bohm-Pines model Hamiltonian [which includes the plasmon coordinates as shown in Eq. (2.11) in Ref. 9 and introduces subsidiary conditions on the electron wave function] in second quantized form and then employ the first canonical transformation. The resultant Hamiltonian [analogous to Eq. (2.12) in Ref. 9] contains (1) three zero-order uncoupled terms consisting of the electrons (with the short-range interaction included), plasmons, and photons; (2) two first-order terms describing an electron-plasmon and an electron-photon interaction; and (3) three second-order random-phase terms describing an electron–two plasmon, an electron–two photon, and an electron-photon-plasmon interaction. The first-order photon-plasmon term identically vanishes, since the respective unit propagation vectors for the plasmons $\boldsymbol{\varepsilon}_k$ and for the photons $\boldsymbol{\varepsilon}_{l\lambda}$ are orthogonal for this case ($\mathbf{k}=-\mathbf{l}$).

At this stage, Matsudaira introduced a further transformation, containing a superposition of two generating functions, which respectively eliminated the first-order electron-plasmon and electron-photon interaction. However, in our calculation of the optical conductivity to second order for a metal, it is imperative to retain the electron-photon term in order to utilize Butcher's calculation of the first-order interband absorption. We, therefore, introduced a second canonical transformation with the generating operator S_p [given by Eq. (2.16) in Ref. 9] which eliminated only the electron-plasmon interaction.

The canonical transformation operator S_p gives rise to an infinite number of photon absorption mechanisms in the transformed Hamiltonian. However, in the Bohm-Pines scheme, the operator S_p is of order $\alpha=\omega_{\nu+k,\,\nu}/\omega_k$,

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[10] P. N. Butcher, Proc. Phys. Soc. (London) **A64**, 50 (1951).

[11] J. C. Sutherland, E. T. Arakawa, and R. N. Hamm, J. Opt. Soc. Am. **57**, 645 (1967).

where the $\omega_{\nu+k,\,\nu}$ are the electron eigenfrequencies defined by $(\hbar/2m)[(\mathbf{v}+\mathbf{k})^2-(\mathbf{v})^2]$. Since this ordering parameter is much less than 1 for a high-density gas, the higher-order terms in S_p rapidly converge. In this paper we are interested in calculating the absorption of an electron gas and of a metal in the high-density limit at 0°K to second order only. We shall ignore third-order terms, which arise from a photon either creating two electron-hole pairs or creating two plasmons, and also higher-order terms. Two photon processes are also ignored, since the intensity of the incident radiation may be made arbitrarily low. The term, H_{efp} in the transformed system describes the excitation of one plasmon and one electron-hole pair through the absorption of one photon and contains contributions from second-order terms, fourth-order terms, sixth-order terms, etc. H_{efp} is given by

$$H_{efp}=H_{efp}'-i[S_p,H_{ef}']-\tfrac{1}{2}[S_p,[S_p,H_{efp}']]_{efp} +\tfrac{1}{6}i[S_p,[S_p,[S_p,H_{ef}']]]_{efp}+\cdots, \quad (2)$$

where, clearly, the subscript appearing on the commutator relations above second order indicates that portion which yields the net excitation of one plasmon and one free-pair. The second-order random-phase terms, not containing photons, can also be eliminated by a further canonical transformation and can be shown to contribute to the absorption only in the third and higher order (contributing fourth order in H_{efp}). The fourth- and higher-order corrections to H_{efp} are assumed to be negligible in the high-density limit for our calculation to second order. This assumption is the core of the Bohm Pines formulation; that is, the canonical transformation is introduced to eliminate the first-order electron-plasmon interaction, and all electron-plasmon terms emanating from higher-order operations are negligible.

For a calculation of the optical absorption to second order, the relevant terms of the Hamiltonian in the transformed system are the uncoupled renormalized zero-order terms, the electron-photon term, and the electron-photon-plasmon term, which are given by

$$\begin{aligned}\sum_{\nu}\frac{\hbar^2\nu^2}{2m^*}a^\dagger{}_\nu a_\nu+H_{\mathrm{s.r.}}+V(\mathbf{r})+\sum_{k\leq k_c}[\hbar\omega_k(A^\dagger{}_kA_k+\tfrac{1}{2})-\tfrac{1}{2}NM_k{}^2]+\sum_{l\lambda}\Big[\hbar\omega_{l\lambda}(b^\dagger{}_{l\lambda}b_{l\lambda}+\tfrac{1}{2})+\hbar\frac{(\omega_{l\lambda}{}^2-\omega_p{}^2-c^2l^2)}{4\omega_{l\lambda}}\\ \times(b^\dagger{}_{-l\lambda}b^\dagger{}_{l\lambda}+b_{-l\lambda}b_{l\lambda}-2b^\dagger{}_{l\lambda}b_{l\lambda}-1)\Big]+\sum_{\nu,\nu';\,l\lambda}\left(\frac{2\pi e^2\hbar}{m^2\omega_{l\lambda}}\right)^{1/2}\langle\nu'|e^{i\mathbf{l}\cdot\mathbf{r}}\boldsymbol{\varepsilon}_{l\lambda}\cdot\mathbf{p}|\nu\rangle b_{l\lambda}a^\dagger{}_{\nu'}a_\nu+\sum_{\nu,\nu',\nu'';\,l\lambda k\leq k_c}M_k\left(\frac{\pi e^2\omega_k}{m^2\omega_{l\lambda}}\right)^{1/2}\\ \times A^\dagger{}_{-k}b_{l\lambda}a^\dagger{}_{\nu'}a_\nu\left[\frac{\langle\nu'|e^{i\mathbf{k}\cdot\mathbf{r}}|\nu''\rangle\langle\nu''|e^{i\mathbf{l}\cdot\mathbf{r}}\boldsymbol{\varepsilon}_{l\lambda}\cdot\mathbf{p}|\nu\rangle}{(\omega_k-\omega_{\nu'',\nu'})}-\frac{\langle\nu'|e^{i\mathbf{l}\cdot\mathbf{r}}\boldsymbol{\varepsilon}_{l\lambda}\cdot\mathbf{p}|\nu''\rangle\langle\nu''|e^{i\mathbf{k}\cdot\mathbf{r}}|\nu\rangle}{(\omega_k-\omega_{\nu,\nu''})}\right], \quad (3)\end{aligned}$$

where (1) the kinetic energy of the electrons is characterized by an effective mass m^* which is related to the number of collective coordinates and which does not enter into the calculation of the absorption; (2) $V(\mathbf{r})$ is the periodic electron ion-core potential; (3) the effect of the transformation on the short-range interaction $H_{\mathrm{s.r.}}$ is assumed to be negligibly small; (4) $M_k{}^2$ is the Fourier coefficient of the electron-electron interaction and is defined for the semi-infinite case by $4\pi e^2/k^2$, where the term $k=0$ is cancelled by the positive cores which give charge neutrality; (5) we have used the dispersion relation to diagonalize the unperturbed plasmon Hamiltonian; and (6) $a^\dagger{}_\nu$ and a_ν are the electron creation and annihilation operators, $A^\dagger{}_{-k}$ is the plasmon creation operator, and $b_{l\lambda}$ is the photon destruction operator. Since the system is in the ground state at $T=0$°K, only plasmon creation and photon absorption processes are allowed.

We now restrict ourselves to an electron gas in a uniform positive background, neglect $H_{\mathrm{s.r.}}$ and the subsidiary conditions, and therefore, assume that the electron wave function is given by the Slater determinant of plane waves. For the range of frequencies of interest, the photon wave vector $\mathbf{l}$ is negligible compared to the electron and plasmon wave vectors. We assume the long-wavelength limit and describe the radiation field in the metal by a single wave vector $\mathbf{l}'$, given by the Drude theory with an infinite relaxation time as $(l')^2=(\omega^2/c^2)(1-\omega_p{}^2/\omega^2)$, where $\omega=\omega_{l\lambda}$ is the applied angular frequency. The optical conductivity or absorbing power may be calculated by applying the Golden Rule of quantum mechanics to the perturbations in Eq. (3). In the long-wavelength limit the first-order intraband conductivity vanishes and is replaced by its Drude value with relaxation τ in order to account for collisions. The second-order plasmon conductivity reduces to an expression of the form originally derived by Lindhard,[12] except that one must also integrate over all plasmon vectors:

$$\sigma(\omega)=\frac{2\pi^2e^4}{m^2\omega^3}\sum_{\nu,\,k\leq k_c}\omega_k(\boldsymbol{\varepsilon}_k\cdot\boldsymbol{\varepsilon}_{l\lambda})^2f_\nu[1-f_{\nu+k}] \times\delta(\omega_k+\omega_{\nu+k,\,\nu}-\omega), \quad (4)$$

where f_ν is the Fermi-Dirac occupation number. An inspection of Eq. (4) shows that the plasmon absorption for an isotropic semi-infinite electron gas has the same value for all angles of incidence of the radiation. It is identical to the expressions obtained by DuBois *et al.* and Matsudaira, except that we have replaced ω_p by $\omega_k=\omega_p+3\hbar k^2/5x_0m$. The evaluation of the conductivity

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[12] J. Lindhard, Kgl. Danske Videnskab. Selskab, Mat.-Fys. Medd. 28, 8 (1954).

is straightforward.

$$\sigma(z)=0,\quad z\leq 0$$

$$\sigma(z)=\frac{3}{128}\frac{x_0^5}{\hbar x^3}\epsilon_F[h_1(z)+g_1(z)],\quad 0\leq z\leq\frac{6}{5x_0}K_c^2$$

$$\sigma(z)=\frac{3}{128}\frac{x_0^5}{\hbar x^3}\epsilon_F[h_2(z)+g_2(z)],$$
$$\frac{6}{5x_0}K_c^2\leq z\leq 2K_c-\frac{K_c^2}{y_2}\qquad(5)$$

$$\sigma(z)=\frac{3}{128}\frac{x_0^5}{\hbar x^3}\epsilon_F[h_3(z)+g_3(z)],$$
$$2K_c-\frac{K_c^2}{y_2}\leq z\leq 2K_c+\frac{K_c^2}{y_1}$$

and

$$\sigma(z)=0,\quad z\geq 2K_c+\frac{K_c^2}{y_1},$$

where

$$h_1(z)=\Big[\frac{1}{2}\Big(1+\frac{z}{2y_1}\Big)(K_2^2-K_1^2)-\frac{z^2}{4}\ln\frac{K_2}{K_1}-\frac{1}{16y_1^2}$$
$$\times(K_2^4-K_1^4)+\frac{z}{2}(K_3^2-K_2^2)-\frac{3}{10x_0}(K_3^4-K_2^4)\Big],$$

$$g_1(z)=\frac{6}{5x_0^2}\Big[\frac{1}{4}\Big(1+\frac{z}{2y_1}\Big)(K_2^4-K_1^4)-\frac{z^2}{8}(K_2^2-K_1^2)$$
$$-\frac{1}{24y_1^2}(K_2^6-K_1^6)+\frac{z}{4}(K_3^4-K_2^4)-\frac{1}{5x_0}(K_3^6-K_2^6)\Big],$$

$$h_2(z)=\Big[\frac{1}{2}\Big(1+\frac{z}{2y_1}\Big)(K_2^2-K_1^2)-\frac{z^2}{4}\ln\frac{K_2}{K_1}-\frac{1}{16y_1^2}$$
$$\times(K_2^4-K_1^4)+\frac{z}{2}(K_c^2-K_2^2)-\frac{3}{10x_0}(K_c^4-K_2^4)\Big],$$

$$g_2(z)=\frac{6}{5x_0^2}\Big[\frac{1}{4}\Big(1+\frac{z}{2y_1}\Big)(K_2^4-K_1^4)-\frac{z^2}{8}(K_2^2-K_1^2)$$
$$-\frac{1}{24y_1^2}(K_2^6-K_1^6)+\frac{z}{4}(K_c^4-K_2^4)-\frac{1}{5x_0}(K_c^6-K_2^6)\Big],$$

$$h_3(z)=\Big[\frac{1}{2}\Big(1+\frac{z}{2y_1}\Big)(K_c^2-K_1^2)-\frac{z^2}{4}\ln\frac{K_c}{K_1}\qquad(6)$$
$$-\frac{1}{16y_1^2}(K_c^4-K_1^4)\Big],$$

$$g_3(z)=\frac{6}{5x_0^2}\Big[\frac{1}{4}\Big(1+\frac{z}{2y_1}\Big)(K_c^4-K_1^4)-\frac{z^2}{8}(K_c^2-K_1^2)$$
$$-\frac{1}{24y_1^2}(K_c^6-K_1^6)\Big],$$

$$x=\hbar\omega/\epsilon_F,$$
$$y_1=[1+6/5x_0]^{-1},$$
$$y_2=[1-6/5x_0]^{-1},$$
$$K_c=k_c/\nu_0,$$
$$z=\hbar(\omega-\omega_p)/\epsilon_F,$$
$$K_1=(y_1^2+y_1z)^{1/2}-y_1,$$
$$K_2=y_2-(y_2^2-y_2z)^{1/2},\quad \text{for } y_2 \text{ positive}$$
$$K_2=y_2+(y_2^2-y_2z)^{1/2},\quad \text{for } y_2 \text{ negative}$$
$$K_3=(\tfrac{5}{6}x_0z)^{1/2}.$$

These equations are valid in the region where the surface, $2K-K^2/y_2$, does not exhibit a maximum for a value of K less than the critical plasmon cutoff K_c. Also, K_c must be less than or equal to 2. The above expressions reduce to Matusdaira's results, when $K_s\leq 1$, if ω_k is replaced by ω_p, y_1 and y_2 are replaced by 1, and g_1, g_2, g_3, and the last terms in h_1 and h_2 are replaced by zero. For $K_c>1$, the dispersionless plasmon conductivity given by Matsudaira does not hold.

The above expressions for $\sigma(\omega)$ in Eq. (5), which are valid for a high-density electron gas, are now assumed to hold for metallic densities. We have recalculated the dispersionless plasmon conductivity[13] to take into account the corrections to Matsudaira's formulas which must be made to extend their validity to $k_c>\nu_0$. A comparison of the plasmon absorbing power with and without the dispersion in the plasma frequency is given in Fig. 1 for the free-electron values of lithium, sodium, and potassium, $r_s=3.22$, 3.96, 4.87 and $\hbar\omega_p=8.20$, 5.99, 4.36 eV, respectively. The dispersion in the plasma frequency shifts the peak to higher energy (approximately $\hbar\omega_p+\epsilon_F$) and reduces the absorbing power by approxi-

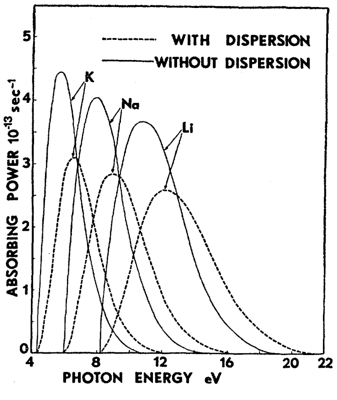

FIG. 1. The calculated plasmon absorbing power with and without plasmon dispersion for electron gases of alkali metal densities as a function of incident photon energy.

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[13] The corrected formulas for the dispersionless plasmon conductivity along with a detailed formulation of the plasmon problem are contained in the Ph.D. thesis of R. J. Esposito [Temple University, 1968 (unpublished)].

mately 30%. The absorbing power due to this process is of the order of 10^{13} sec^{-1}. Although it is an order of magnitude below ordinary metallic (nonalkali) absorption, it is the same order as the calculated alkali interband absorption in the ultraviolet.

In the above calculations we have employed three approximations which affect the accuracy of our results at metallic densities. These are (1) the assumption that the Bohm-Pines expansion parameter is sufficiently small and leads to a proper prescription of term ordering in the Hamiltonian; (2) the neglect of terms of order k^4 and higher in ω_k; and (3) the neglect of the effects of $H_{\text{s.r.}}$ and the subsidiary conditions on the electron wave function. We now discuss the validity of our approximations. The Bohm-Pines prescription for term ordering appears to be valid for $r_s \lesssim 4$, since the random-phase terms can be still treated as perturbations.[14] The average ordering parameter $\langle\alpha\rangle_{\text{av}}$ [averaged over all electron wave vectors not taking into account the frequency selection rule in Eq. (4)] ranges from zero to 0.33 (0.36, 0.40) for lithium (sodium, potassium) as k goes from zero to k_c. However, as a result of this δ function only a range of values for the plasmon wave vector **k** contribute to the conductivity, and α has a maximum for each frequency. For example, in the sodium calculation with dispersion for $\hbar\omega \simeq 6.6$ eV, $0.09\nu_0 \leq k \leq 0.56\nu_0$, and $\alpha < 0.1$; for $\hbar\omega \simeq 8.9$ eV (absorption peak of Fig. 1), $0.36\nu_0 \leq k \leq k_c$, and $\alpha < 0.4$; for $\hbar\omega \simeq 11.4$ eV, $0.58\nu_0 \leq k \leq k_c$ and $\alpha < 0.7$, where $k_c = 0.937\nu_0$. For $\hbar\omega > 7.8$ eV $(z > 1.2K_c^2/x_0)$ the conductivity is sensitive to k_c. This suggests that any corrections to $\sigma(\omega)$ must include some contributions from $H_{\text{s.r.}}$ which become noticeable only for $k_c \sim \nu_0$. Therefore, our neglect of terms fourth order and higher in the electron-photon-plasmon contribution to the conductivity means that we are making approximately a 20% error in the representation near the resonance. Near the high-frequency cutoff value the ordering parameter is large and $\alpha_{\max} \simeq 1.2$. Also, for $k \sim k_c$, the terms of order k^4 and higher in Eq. (1) will contribute about 20% to the value of ω_k and affect our results only in the high-frequency fall-off region.

Let us point out that we do not invoke "the random phase approximation" in the Bohm-Pines scheme. (Such an approximation neglects the random-phase terms and, in our case, all contributions to the plasmon conductivity.) In fact, we have calculated the random-phase terms themselves to second order in an expansion parameter which is valid at metallic densities for most of the plasmon **k** space. Our neglect of the effect of $H_{\text{s.r.}}$ and the subsidiary conditions on the wave function is questionable at metallic densities and introduces an approximation of the same order as the random phase approximation. For example, the Bohm-Pines subsidiary condition appears to be equivalent to the form of the ground-state wave function for the Sawada[15] Hamiltonian. The Sawada model treats the short-range and long-range Coulomb interactions with equal weight, but neglects *a priori* in the high-density limit certain very small terms in the original Hamiltonian and commutation rules. Thus, the difference in the two pictures for a high-density gas is the following: The Bohm-Pines model explicitly introduces the plasmons as the elementary excitations and treats the remainder of the Coulomb interaction ($H_{\text{s.r.}}$ and random-phase terms) as small perturbations; whereas the Sawada model removes some random-phase terms (corresponding to scatterings of excited states to excited states) at the beginning, correctly treats the short-range part of the Coulomb interaction in this approximation, and evidences a plasmon set of solutions. The approximations made in each picture are valid in the high-density limit, perhaps with the Sawada treatment being on firmer ground as it provides the basis for the Bohm-Pines assumptions. Both pictures lead to equivalent results at metallic densities in the random phase approximation,[14,16] this time with the Bohm-Pines picture possibly having the edge. For example, at $r_s \sim 2$, the ratio of the average potential energy per particle to the average kinetic energy per particle, which Sawada used as an ordering parameter, is about 1, and in the random phase approximation the pair distribution function becomes unphysically negative.[17] On the other hand, the Bohm-Pines model appears to give reasonable results for $r_s \lesssim 4$ if a Slater determinant of plane waves is chosen, as we have indicated in the above paragraph. At $r_s \lesssim 4$ Pines[18] has shown that the neglect of $H_{\text{s.r.}}$ and the subsidiary conditions on the wave function is not a very poor assumption. Thus, despite the speculative nature of our approximations, we believe that our results near the plasmon resonance should be accurate to within 20%, or at the very least, should show the general trend of the plasmon conductivity. Indeed, since we have neglected $H_{\text{s.r.}}$ and the subsidiary conditions, our calculation is expected to hold to second order only. Any more accurate calculation of the conductivity must include a more appropriate wave function (including some effect from $H_{\text{s.r.}}$), the higher-order corrections in ω_k, and the third-order terms which correspond to other absorption processes.

The optical absorbing power can also be calculated from the Hamiltonian obtained by Matsudaira after the first canonical transformation [Eq. (2.12) in Ref. 9] by straightforward perturbation theory. The resulting expression for the plasmon absorption is similar to Eq. (5) only for ω close to ω_p. We find that our choice of second-order and higher-order terms in the second canon-

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[14] P. Nozieres and D. Pines, Phys. Rev. **111**, 442 (1958).

[15] K. Sawada, K. A. Brueckner, N. Fukuda, and R. Brout, Phys. Rev. **108**, 507 (1957).

[16] J. Hubbard, Proc. Roy. Soc. (London) **A243**, 336 (1957).

[17] A. J. Glick and R. A. Ferrell, Ann. Phys. (N. Y.) **11**, 359 (1960).

[18] D. Pines, Phys. Rev. **92**, 626 (1953).

ically transformed system is consistent with the first transformed system; but, the introduction of the second canonical transformation offers a better perturbation scheme, because it eliminates at the outset the first-order electron-plasmon interaction.

III. DISCUSSION AND APPLICATION TO FREE-ELECTRON-LIKE METALS

We now assume that the Bohm-Pines prescription serves as an adequate approximation for a free-electron-like metal. In this case the long-range electron-electron interaction ($k \leq k_c$) is treated by the introduction of the plasmon coordinates, the short-range electron-electron interaction is assumed to be comparatively small, and an appropriate periodic potential $V(\mathbf{r})$ describes the electron-ion core interaction. The electron-photon term now describes both the intraband and interband absorption. The plasmon absorption in the ultraviolet should be experimentally observable if it is not masked by the interband absorption. The relatively low interband absorption of the alkali metals indicates that they offer the best chance for observing the plasmon absorption. In this section, we assume that the total absorption (conductivity) to second order in the high-density limit is given by a superposition of the intraband, interband, and plasmon conductivity. This superposition makes evident the consistency of our choice in eliminating only the first-order electron-plasmon term by a canonical transformation. The intraband contribution is replaced by its Drude value with relaxation time τ. For simplicity, the Slater determinant of plane waves and the long-wavelength limit for the photons are used in the calculated plasmon absorption of the alkali metals. The former assumption means that the only permitted second-order process is that of a photon decaying into a plasmon with an accompanying intraband transition. The process of a photon exciting a plasmon with an accompanying interband transition and higher-order processes are not considered. An effective mass M (different from m^*) replaces the normal electron mass in ω_p, so that ω_p is equal to the experimental plasma frequency. The same effective mass M is also used for the Drude contribution.

The optical constants of sodium have been reported by several investigators, namely, by Ives and Briggs[3] from 2.15 to 4.89 eV, by Mayer and Hietel[2] from 0.5 to 4.2 eV (in fairly good agreement with the previous authors), and by Sutherland *et al.*[11] between 6.2 and 7.1 eV. Sutherland also reported the index of refraction n to 30 eV and found the extinction coefficient k between 6.0 and 30 eV to be less than 0.04. However, detailed measurements above 7.1 eV of the absorbing power of sodium, which is related to the optical constants by

$$\sigma(\omega) = nk\omega/2\pi, \qquad (7)$$

have not been made to our knowledge. Our Kramers-Kronig analysis of the data for the index of refraction did not produce values of the extinction coefficient consistent with experiment after several simplifying extrapolations were tried. The plasma energy for sodium was extrapolated by Sutherland to occur at 5.69 eV in agreement with electron characteristic loss studies; earlier transmission measurements by Wood and Lukens[19] indicated the plasma edge at 5.91 eV. We assume throughout that all the above studies, which were made on thin films, give results which are indicative of the bulk optical properties.

The internal photoelectric absorption of the alkali metals was calculated by Butcher,[10] who used the one-electron approximation with plane waves and a nearly-free-electron energy spectrum. This model yields for the alkali metals a single adjustable parameter, the Fourier coefficient of the self-consistent potential V_{110} which is chosen to fit the experimental data from which the Drude contribution has been subtracted. A choice of $V_{110}=0.323$ eV for sodium produces reasonably good agreement with the measurements of Ives and Briggs. Appelbaum[20] noted that when Butcher's model is fitted to the observed absorbing power in the visible spectral region, V_{110} is higher than those values of the pseudopotential form factor inferred from band calculations (between 0.11 and 0.24 eV) and de Haas–van Alphen studies of the Fermi surface (between 0.18 and 0.25 eV).[21] Appelbaum refined Butcher's calculation by using orthogonalized plane waves and a more realistic band structure given by a pseudopotential calculation with two adjustable band gap parameters. However, he found that the more sophisticated calculation yielded an interband absorption not only smaller than the experimental values for a reasonable choice of pseudopotential form factors but also smaller than Butcher's predictions for the same V_{110}. A later study of interband matrix elements by Overhauser[22] included not only the direct electronic interaction with the photon field, but also the Hartree-Fock potential arising from the transverse collective motion of all the electrons responding to the applied photon field. For a band gap energy ($2V_{110}$) of 0.500 eV this calculation agrees fairly well with Mayer and Hietel's data between 2 and 3 eV. However, the rapid fall-off in Overhauser's calculated absorbing power above 3 eV does not agree with experiment.

In order to estimate the interband absorption of sodium in the ultraviolet, we assume that Butcher's calculation for $V_{110}=0.323$ eV, in spite of its shortcomings, can be employed, since it fits the experimental data of Briggs and Ives. The plasmon absorbing power of sodium was calculated from Eq. (5), where the normal electron mass was replaced by an effective mass $M=1.03m$ to produce agreement with the experimental

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[19] R. W. Wood and C. Lukens, Phys. Rev. **54**, 332 (1938).

[20] J. A. Appelbaum, Phys. Rev. **144**, 435 (1966).

[21] Recent band studies and Fermi-surface measurements for the alkali metals are discussed in Refs. 20 and 22. Also, see N. W. Ashcroft, Phys. Rev. **140**, 935 (1965).

[22] A. W. Overhauser, Phys. Rev. **156**, 844 (1967).

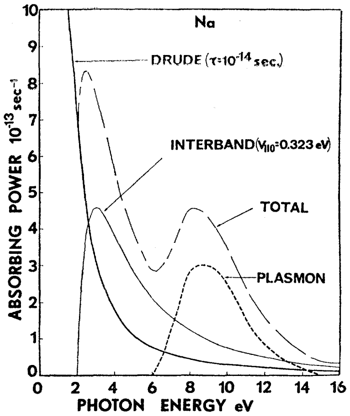

FIG. 2. The calculated absorbing power of sodium as a function of incident photon energy.

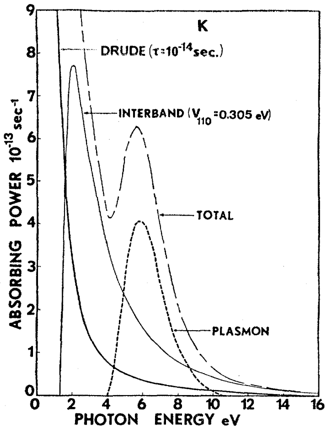

FIG. 3. The calculated absorbing power of potassium as a function of incident photon energy.

plasma frequency of Wood and Lukens. It then follows that the electron values for the plasma absorption are $\epsilon_F=3.09$ eV, $x_0=1.89$, $r_s=4.06$, and $K_c=0.945$. The calculated Drude (for a relaxation time of 10^{-14} sec), interband (based on Ives and Briggs's data), and plasmon absorbing powers are given in Fig. 2. The effective electron mass M was used in the calculation for the Drude contribution and the free-electron mass for the interband contribution. The Mayer–El Naby resonance in the near infrared is not shown. If one assumes that the total conductivity can be determined from a superposition of the three absorption mechanisms, a peak in the ultraviolet conductivity due to the plasmons should be experimentally observable near 8.8 eV when the intraband relaxation is sufficiently long (perhaps even for relaxation times as short as 10^{-16} sec). If the plasma energy is set equal to 5.69 eV, the calculated plasmon peak is shifted to slightly lower energy, but the general features of Fig. 2 remain the same. Sutherland's results indicate some structure in ϵ_2 between 6.20 and 7.11 eV and may provide some evidence for the onset of plasmon absorption. However, it is difficult to distinguish between interband and plasmon absorption in this spectral region, and the Butcher model does not properly take into account the band structure. Our calculated total conductivity at 7.11 eV is 3.5×10^{13} sec^{-1} (3.0×10^{13} sec^{-1} for very long τ), whereas the conductivity from Sutherland's data is $(2.4\pm0.9)\times10^{13}$ sec^{-1}.

The optical constants of potassium were also reported by Ives and Briggs[4] from 2.15 to 4.89 eV. Their values are in good agreement with the later measurements of Mayer and El Naby[1] from 0.62 to 3.40 eV. Several different values of the plasma energy have been reported by optical techniques, these are at 3.76,[23] 3.94,[19] and 4.25 eV.[2] The value at 3.94 eV, which we choose for our calculation, is in good agreement with Ives-Briggs's data and with electron energy loss experiments. Butcher's choice of $V_{110}=0.305$ eV for potassium produces reasonably good agreement with the observed internal photoelectric absorption in the visible spectral region. Experimental evidence indicates that V_{110} is about 0.20 eV. Hopfield[24] expanded the electron wave function to second order in the electron-ion potential for potassium and found a peak slightly above 4 eV in the imaginary part of the dielectric constant, in rough agreement with Butcher's calculation. The parameters for the plasmon absorption which agree with the experimental plasma frequency are $M=1.22m$, $\epsilon_F=1.73$ eV, $x_0=2.28$, $r_s=5.95$, and $K_c=1.14$. The Drude, interband, and plasmon absorption for potassium are given in Fig. 3. A superposition of the three ultraviolet conductivities reveals that the plasmon absorption should be observable near 5.8 eV. If the plasma energy is chosen to be 4.25 eV, the plasmon resonance would be close to its free-electron value with dispersion shown in Fig. 1 and still should be experimentally observable. If the value of 3.76 eV is chosen, the resonance will occur in a region of higher interband absorption but is resolvable in our model.

Since the expected plasmon absorption for lithium occurs at energies far removed from reported measurements of the optical constants, it will not be discussed further at this time. For the case of the heavier alkali metals, the random-phase terms are no longer second order ($k_c>v_0$), and the replacement of the electron wave function in the calculation of the plasmon absorption by plane waves is a more questionable approximation than for the case of the lighter alkali metals. However, if we assume that our approximations are valid for rubidium and cesium, we find that the calculated plasmon absorption for rubidium, $\hbar\omega_p=3.09$ eV and $K_c=1.37$, shows a peak of 6.5×10^{13} sec^{-1} at 4.5 eV. The experimental conductivity of rubidium, which was

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[23] J. Bösenberg and H. Raether, Phys. Rev. Letters **18**, 397 (1967).

[24] J. J. Hopfield, Phys. Rev. **139**, A419 (1965).

reported by Ives and Briggs,[25] rises from 5.87×10^{13} $\sec^{-1}$ at 4.10 eV to 6.83×10^{13} $\sec^{-1}$ at 4.89 eV. Their results in the near ultraviolet are in fairly good agreement with the preliminary data of Mayer and Hietel; however, the agreement is not good in the visible spectral region. The two groups are in better agreement for cesium, and their results indicate a rise in the conductivity at their ultraviolet limits above 4.0 eV. The calculated plasmon absorption for cesium, $\hbar\omega_p=2.86$ eV and $K_c=1.39$, peaks at 4.25 eV with the value of 6.38×10^{13} $\sec^{-1}$, which is roughly 40% of the experimental value. Although a more accurate model is certainly required, the absorption from our rather elementary model of an electron gas of heavy alkali metal density indicates that the plasmon absorption may be important for rubidium and cesium.

Several other free-electron-like metals were also investigated; however, the plasmon absorption is completely masked by the interband absorption. The calculated plasmon absorption for aluminum, $r_s=2.34$, is above 2.0×10^{13} $\sec^{-1}$ between 20 and 26 eV. The peak value is 2.4×10^{13} $\sec^{-1}$ and occurs at 22 eV. Transmission measurements through thin aluminum films, subjected to the atmosphere, yield a conductivity of roughly 10^{14} $\sec^{-1}$ over this energy region.[26] A bulk plasmon resonance does not seem evident from the data, although there is some scatter in the values for the extinction coefficient. For very thin films the plasmon dispersion relation reveals that the oscillations should be a function of film thickness and plasmon wave vector.[27] The conductivity determined by a Kramers-Kronig analysis of the reflectivity from a bulk aluminum specimen is also roughly 10^{14} $\sec^{-1}$ in the far ultraviolet.[28] Our calculations for magnesium, $r_s=2.99$, give a peak of 2.8×10^{13} $\sec^{-1}$ near 15.5 eV. The experimental conductivity of magneisum is about an order of magnitude higher in this region.[26] It thus appears that for metals, the alkalis offer the best choice for the observation of the ultraviolet plasmon absorption.

As a last example, we consider the plasmon absorption in the infrared due to the conduction-band electrons in a heavily n-doped semiconductor. Such a group of electrons constitute a very high-density electron gas, $r_s\leq1$.[29] An n-doped InSb specimen at room temperature may exhibit the following parameters[30]: $N=1.82\times10^{18}$ cm^{-3}, $M=0.041m$, a host dielectric constant equal to 14.7, $\hbar\omega_p=0.0654$ eV, $\epsilon_F=0.13$ eV, $K_c=0.252$, and a relaxation time equal to 2.9×10^{-13} sec. The peak in the calculated plasmon conductivity for this specimen occurs at about 0.10 eV and has a value of roughly 10^{10} $\sec^{-1}$. The Drude conductivity at room temperature is approximately 10^{12} $\sec^{-1}$ at this energy and completely masks the plasmon conductivity. Depending upon the material, the onset of interband absorption may also be important. In general, the conduction-band plasmon absorption for a doped semiconductor or semimetal will not be observable in the infrared, unless one chooses a material with idealized electronic parameters, including a very long intraband relaxation time at low temperatures.

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[25] H. E. Ives and H. B. Briggs, J. Opt. Soc. Am. **27**, 395 (1937).

[26] W. R. Hunter, J. Opt. Soc. Am. **54**, 208 (1964); W. R. Hunter, in *Proceedings of the International Colloquium on Optical Properties and Electronic Structure of Metals and Alloys, Paris, 1965*, edited by F. Abeles (North-Holland Publishing Co., Amsterdam, 1966), p. 136.

[27] H. Kanazawa, Progr. Theoret. Phys. (Kyoto) **26**, 851 (1961). For experimental studies on thin films, see T. Sasaki and A. Ejiri, in *Proceedings of the International Colloquium on Optical Properties and Electronic Structure of Metals and Alloys, Paris, 1965*, edited by F. Abeles (North-Holland Publishing Co., Amsterdam, 1966), p. 417.

[28] H. Ehrenreich, H. Philipp, and B. Segall, Phys. Rev. **132**, 1918 (1963).

[29] P. Nozieres and D. Pines, Phys. Rev. **109**, 1062 (1958).

[30] For example, see B. Lax and G. W. Wright, Phys. Rev. Letters **4**, 16 (1960).