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Many-Electron Effects in the Optical Conductivity of Simple Metals by Kubo Formula[*]

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Starting from the Kubo formula for the optical conductivity, we review, reformulate, and generalize our previous one-electron theory of the optical absorption of solid and liquid alkali metals to include many-body effects due to electron-electron Coulomb interactions. The optical matrix element $\langle \psi_{k'} | \vec{\nabla} | \psi_k \rangle$, which was previously calculated in terms of an "optical pseudopotential," is rederived from a second-order scattering of an electron (quasiparticle in the many-body theory) by the Coulomb field of the ions and the applied photon field. The result is then represented by Feynman graphs similar in the lowest order to the "bremsstrahlung" of quantum electrodynamics, and shown, accordingly, to give rise to four categories of many-electron effects, viz., screening effects (usually incorporated in the one-electron approximation), electron self-energy effects, electron-photon and electron-ion vertex corrections, and final-state interactions. The changes of the one-electron result due to self-energy and to vertex corrections counteract each other in sodium and potassium, leading to no more than 10% net change; accordingly, the only appreciable enhancement comes from final-state interactions involving virtual exchange of plasmons, considered previously by Mahan.

I. INTRODUCTION

In this paper we shall review, reformulate, and generalize our previous calculation[1,2] (hereafter referred to as AI and AII) of the optical conductivity $\sigma(\omega)$ of solid and liquid alkali metals, to include many-body effects due to electron-electron Coulomb interactions. In a subsequent paper, we shall consider a second aspect of many-body effects, namely, that due to *electron-photon-ion interaction* – its effects on the optical effective mass[3] and its implications on photon-induced superconductivity recently introduced by Kumar and Sinha.[4] The calculation to be reported in this paper will be based on the Kubo formula[5,6] and the optical pseudopotential method introduced in AI, since these approaches have been found to be both simple and in reasonable accord in the one-electron approximation with the recent measurements of the optical properties of sodium and potassium by Smith.[7] However, since many calculations of optical properties, both in the one-electron approximation[1,8] and including many-body effects,[9–18] exist in the literature, our emphasis will be on providing a simple and complete picture which will transcend all previous quantitative calculations, and furnish a basis for future investigations in this area. This simple picture – consisting essentially of a second-order scattering involving an electron-ion vertex and an electron-photon vertex similar to the "bremsstrahlung" of quantum electrodynamics – will be derived in Sec. II B.

The difficulty experienced in the calculation of optical properties in recent years seem to stem from two uncertainties. The first is the uncertainty about the optical matrix elements $\langle\psi_{k'}|\vec{\nabla}|\psi_k\rangle$, which determines the oscillator strength between Bloch states $\psi_{k'}$ and ψ_k in the one-electron approximation[1,8]; this was resolved by the introduction of the optical pseudopotential in AI and AII. In the many-body theory, the uncertainty appears to be due to incomplete understanding of the nature of the Feynam graphs (see Fig. 1) to be associated with electron-photon interaction in a metal. This lack of understanding is reflected in current literature in the qualitative prescription of a variety of processes expected to resolve the apparent discrepancy between the one-electron approximation and the experimental results, particularly in the alkali metals.[19] The processes suggested include those by Kohn[9] on multiple electron-hole pair production by photons, by Cohen[10] on the possibility of metallic excitons, by Weiner[11] and Mahan[12] on final-state interactions in which the electron and the hole created by photons interact via virtual exchange of plasmons, by Hopfield[13] and Phillips[14] on plasma resonance, by Foo and Hopfield[15] on phonon effects, and more recently by Beeferman and Ehrenreich[16] on the consideration of electrons and holes as quasiparticles. The situation does not seem to have been made clearer by the introduction of various techniques, e.g., the emphasis on Ward's identities by Geldart and Vosko,[17] or the most recent many-body perturbation method by Young,[18] to mention but a few.

Experimentally, the situation is unresolved, particularly regarding the discrepancy between the optical absorption in sodium and potassium, as measured independently by Mayer and co-workers[19] and more recently by Smith.[7] If the latter is correct, as one is inclined to believe, then we would expect many-body effects due to electron-electron Coulomb interactions to be small in potassium for which the agreement between experiment and one-electron theory is already good.[1,7] In sodium, the discrepancy between the one-electron approximation and experiment seems to be adequately accounted for by the virtual exchange of plasmon considered by Mahan.[12] In order to understand all these from a unified point of view, it is necessary to explore all contributions from electron-electron Coulomb interactions to all orders of perturbation theory, which is our objective in this paper.

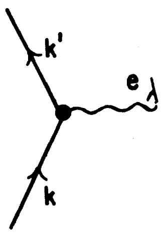

FIG. 1. Feynman graph for the optical matrix element as used in current literature, see, e.g., Ref. 18.

The outline of the present work is as follows. In Sec. II, which will be divided into two parts, we shall review our previous calculation and the Kubo formula in the first part and describe a generalization suitable for many-electron theory in the second part. The many-electron theory, and comparison of the results with experiment will be described in Sec. III. Conclusions will be drawn in Sec. IV.

II. ONE-ELECTRON THEORY OF OPTICAL CONDUCTIVITY

A. Kubo Formula

According to the general theory of irreversible processes developed by Kubo,[5] the induced current which is in phase with an oscillating electric field of frequency ω in a cubic or isotropic material is given by the conductivity scalar

$$\sigma(\omega)=\int_0^\infty dt\int_0^\beta d\lambda\, e^{-i\omega t}\langle j_x(0)j_x(t+i\lambda)\rangle\quad . \tag{2.1}$$

Here, $\beta=1/\kappa T$, κ being the Boltzmann constant and T being the absolute temperature of the material; $j_x(t)$ represents the quantum-mechanical current operator in Heisenberg representation, given for a material characterized by a Hamiltonian H as

$$j_x(t)=e^{+iHt/\hbar}j_x(0)\,e^{-iHt/\hbar}\quad , \tag{2.2}$$

$$j_x(0)=(-ie\hbar/m)\nabla_x\equiv(-ie\hbar/m)\frac{\partial}{\partial x}\ , \tag{2.3}$$

in the x direction; and $\langle A\rangle=\sum_k\rho_k\langle\psi_k|A|\psi_k\rangle$ defines the thermal average of an operator A, where

$$\rho_k=e^{-\beta E_k}\Big/\sum\nolimits_m e^{-\beta E_m}\quad , \tag{2.4}$$

E_k and ψ_k being the eigenvalue and eigenfunction of H.

In this completely general form, the Kubo formula (2.1) is too abstract for practical determination of the conductivity in a real metal. Instead, it will be found more convenient to use the form given independently by Greenwood[6]:

$$\sigma(\omega)=\frac{2\pi e^2\hbar^3}{m^2\omega}\sum_{k,k'}|\langle\psi_{k'}|\nabla_x|\psi_k\rangle|^2\times(\rho_k-\rho_{k'})\,\delta(E_{k'}-E_k-\hbar\omega)\ . \tag{2.5}$$

This is known as the Kubo-Greenwood formula. Since, however, it is not altogether obvious that (2.5) reduces exactly to (2.1), it is instructive to briefly demonstrate this explicitly. In (2.5), we have

$$\rho_k-\rho_{k'}=\rho_k(1-e^{-\beta\hbar\omega}),\qquad E_{k'}-E_k=\hbar\omega\ . \tag{2.6}$$

Thus, by using the standard transformation

$$\delta(\omega)=(1/2\pi)\int_{-\infty}^{\infty}e^{i\omega t}\,dt\quad,$$

we obtain from (2. 5)

$$\begin{aligned}\sigma(\omega)&=(\pi/\omega)(1-e^{-\beta\hbar\omega})(\hbar/2\omega)\int_{-\infty}^{\infty}dt\,e^{-i\omega t}\\&\quad\times\sum_{k,k'}\rho_k\langle\psi_k|j_x(0)|\psi_{k'}\rangle\langle\psi_{k'}|j_x(0)|\psi_k\rangle\\&\quad\times e^{-iE_kt/\hbar}\,e^{+iE_{k'}t/\hbar}\\&=(\hbar/\omega)(1-e^{-\beta\hbar\omega})\int_0^{\infty}dt\,e^{-i\omega t}\\&\quad\times\Big\{\sum_{k,k'}\rho_k\langle\psi_k|j_x(0)|\psi_{k'}\rangle\langle\psi_{k'}|j_x(t)|\psi_k\rangle\Big\}\\&=\int_0^{\infty}dt\int_0^{\beta}d\lambda\,e^{-i\omega t}\langle j_x(0)j_x(t+i\lambda)\rangle\ .\end{aligned}$$

This establishes the desired equivalence between (2. 5) and (2. 1). The function $\langle j_x(0)j_x(t)\rangle$ is called *current-current correlation function*. The primary advantage of the form in (2. 5) is that it involves only the stationary states of H.

The reduction of the Kubo-Greenwood formula described in AI and AII was achieved in the framework of the following approximations:

(i) The Hartree-Fock self-consistent-field method. This consists of determining ψ_k and E_k by solving the one-electron Bloch equation

$$H\psi_k=E_k\psi_k\quad,\tag{2.7}$$

where $H\equiv T+V$, T being the kinetic-energy operator $(-\hbar^2/2m)\nabla^2$, and V being the periodic lattice potential representing the effective potential seen by a single valence electron in the metal.

(ii) First-order perturbation solution of (2.7) based on the pseudopotential method, i. e., the pseudopotential transformation

$$|\psi_k\rangle=(1-P)|\phi_k\rangle,\quad P\equiv\textstyle\sum_\alpha|\alpha\rangle\langle\alpha|\ ,\tag{2.8}$$

the summation in P being over the occupied ion core states, is applied to (2.7) to obtain

$$(T+W)|\phi_k\rangle=E_k\,|\phi_k\rangle\quad,\tag{2.9}$$

W being a pseudopotential[20]; then $|\phi_k\rangle$ is determined from this to first order in W by perturbation theory. We find

$$|\phi_{\vec{k}}\rangle=|\vec{k}\rangle+\sum_{\vec{k}'}{}'\,\frac{|\vec{k}'\rangle\langle\vec{k}'|W|\vec{k}\rangle}{T_k-T_{k'}}\quad,\tag{2.10}$$

where $T_k=\hbar^2k^2/2m$ and $\langle\vec{r}\,|\vec{k}\rangle=(1/\Omega^{1/2})\,e^{i\vec{k}\cdot\vec{r}}$ is a plane wave normalized over the volume Ω of the metal, and the prime in the summation implies that the term with $\vec{k}'=\vec{k}$ is to be omitted. In this approximation, we reduce the matrix element that determines the "oscillator" strength

$$\begin{aligned}g_{kk'\lambda}&=(\hbar/2\omega)^{1/2}\vec{e}_\lambda\cdot\langle\psi_{k'}|\,\vec{j}\,|\psi_k\rangle\\&\equiv(\hbar/2\omega)^{1/2}(-ie\hbar/m)\vec{e}_\lambda\cdot\langle\psi_{k'}|\vec{\nabla}|\psi_k\rangle\ ,\end{aligned}\tag{2.11}$$

$\vec{e}_\lambda(\lambda=1, 2)$ being the polarization of the photon field of frequency ω. The result is given by

$$\langle\psi_{k'}|\vec{\nabla}|\psi_k\rangle=\frac{i(\vec{k}\langle\vec{k}\,|\tilde{W}|\vec{k}'\rangle^*-\vec{k}'\langle\vec{k}'\,|\tilde{W}|\vec{k}\rangle)}{T_k-T_{k'}}\ ,\tag{2.12}$$

where $\tilde{W}$, called an "optical" pseudopotential, is defined in terms of an ordinary pseudopotential W by the relation

$$\langle\vec{k}'|\tilde{W}|\vec{k}\rangle\equiv\langle\vec{k}'|W+(T_{k'}-T_k)P|\vec{k}\rangle\ .\tag{2.13}$$

(iii) Low-temperature approximation, i. e., the distribution functions ρ_k are to be evaluated at 0 °K so that

$$\rho_k-\rho_{k'}\to n_k(1-n_{k'})\quad,\tag{2.14}$$

where $n_k=1$ for $k<k_F$,

$\qquad\;\;=0$ for $k>k_F$,

k_F being the Fermi wave number determined by the density of valence electrons.

Then, on gathering results, we obtain the one-electron approximation

$$\begin{aligned}\sigma_0(\omega)&=(2\pi/\hbar)\sum_{k,k',\lambda}|g_{kk'\lambda}|^2\\&\quad\times n_k(1-n_{k'})\,\delta(E_{k'}-E_k-\hbar\omega)\ ,\end{aligned}\tag{2.15}$$

where, for later convenience in generalizing this result to include many-electron effects, we now write $g_{kk'\lambda}$ by virtue of (2. 11) and (2. 12) in the form

$$\begin{aligned}g_{kk'\lambda}&=(\hbar/2\omega)^{1/2}\vec{e}_\lambda\cdot\vec{j}(\vec{k}')\,G_0(k', T_k)\langle\vec{k}'\,|\tilde{W}|\vec{k}\rangle\\&\quad+\langle\vec{k}|\tilde{W}|\vec{k}'\rangle^*G_0(k, T_{k'})(\hbar/2\omega)^{1/2}\vec{e}_\lambda\cdot\vec{j}(\vec{k})\ .\end{aligned}\tag{2.16}$$

Here, $\quad G_0(k, T_{k'})=1/[T_{k'}-T_k]\qquad\qquad$ (2. 17)

defines a free-particle Green's function, and

$$\vec{j}(\vec{k})=e\hbar\vec{k}/m\tag{2.18}$$

defines the matrix element of the current operator in the plane-wave state $\vec{k}$. This is the key result which was evaluated numerically in AI, and recently found to be in reasonable agreement with the optical conductivity of sodium and potassium measured by Smith.[7]

B. Second-Order Scattering Method and Graphical Analysis

Quite another way of interpreting the above results, which will be suitable for immediate generalization to include many-body effects due to electron-electron interaction, is to treat both the pseudopotential W and the electromagnetic coupling $\vec{A}\cdot\vec{j}$ ($\vec{A}$ being the vector potential representing the applied oscillating electric field) as perturbations of the free-electron pseudo-wave-function

$$\phi_k^0(\vec{r}, t) = (1/\Omega^{1/2})\, e^{i(\vec{k}\cdot\vec{r} - \omega_k t)}, \qquad \hbar\omega_k = T_k \quad . \tag{2.19}$$

Then the total scattering of the electron is given by the matrix element $\langle\phi_{k'}^0 | H_I | \phi_k\rangle$, where ϕ_k is the *exact* one-electron scattered pseudo-wave-function determined by the solutions of the equation (in units such that $c = 1$)

$$(T + H_I)\phi_k = i\hbar \frac{\partial\phi_k}{\partial t} \quad , \tag{2.20}$$

$$H_I = W + \vec{A}\cdot\vec{j} + (e^2/2m)\vec{A}^2 \; . \tag{2.21}$$

The solution is formally given by the integral equation

$$\phi_k(\vec{r}, t) = \phi_k^0(\vec{r}, t) + \int d^3r'\, dt'\, G_0(\vec{r}, t; \vec{r}'\, t') \times H_I(\vec{r}', t')\phi_k(\vec{r}', t') \quad , \tag{2.22}$$

where G_0 is the free-electron Green's function or propagator. (We have omitted electron-electron interaction for simplicity at this stage.)

Now, on iterating (2.22) we obtain

$$\langle\phi_{k'}^0 | H_I | \phi_k\rangle = \langle\phi_{k'}^0 | H_I | \phi_k^0\rangle + \int d^3r\, dt \int d^3r'\, dt'\, \phi_{k'}^{0*}(\vec{r}, t) H_I(\vec{r}, t) \times G_0(\vec{r}, t; \vec{r}', t') H_I(\vec{r}', t')\phi_k^0(\vec{r}', t') + \cdots \; . \tag{2.23}$$

From this expansion, we are to pick terms that are linear in W and $\vec{A}\cdot\vec{j}$, which are the lowest-order contribution to the optical absorption. Clearly, the first term on the right-hand side of (2.23) does not contribute. The lowest-order contribution from the second term to the optical absorption comes from the two cross terms, on substituting (2.21),

$$g_{kk'\lambda}^{(a)} = \int d^3r\, dt \int d^3r'\, dt'\, \phi_{k'}^{0*}(\vec{r}, t) \times \vec{A}(\vec{r}, t)\cdot\vec{j}\, G_0(\vec{r}, t; \vec{r}', t') \times W(\vec{r}')\phi_k^0(\vec{r}', t') \quad , \tag{2.24a}$$

$$g_{kk'\lambda}^{(b)} = \int d^3r\, dt \int d^3r'\, dt'\, \phi_{k'}^{0*}(\vec{r}, t) \times W(\vec{r}) G_0(\vec{r}, t; \vec{r}', t') \times \vec{A}(\vec{r}', t')\cdot\vec{j}\,\phi_k^0(\vec{r}', t') \quad . \tag{2.24b}$$

In order to see that these two contributions correspond to the two terms appearing in (2.16), we normalize $\vec{A}$ in the form

$$\vec{A} = (\hbar/2\omega)^{1/2}\vec{e}_\lambda e^{i\omega t} \tag{2.25}$$

and introduce the Fourier transform $G_0(k, \omega')$ of the Green's function through the form (since G_0 is a function of $\vec{r}' - \vec{r}$ and $t' - t$ only)

$$G_0(\vec{r}, t) = (1/\Omega)\textstyle\sum_{\vec{k}} e^{i\vec{k}\cdot\vec{r}}(1/2\pi) \times \int d\omega'\, e^{i\omega' t} G_0(\vec{k}, \omega') \quad . \tag{2.26}$$

On substituting in (2.24) and performing the integrations, we obtain

$$\begin{aligned} g_{kk'\lambda}^{(a)} &= \frac{1}{\Omega}\sum_{\vec{p}} \int \frac{d\omega'}{2\pi}\left(\frac{\hbar}{2\omega}\right)^{1/2} \vec{e}_\lambda\cdot\vec{j}(\vec{k}') \\ &\quad \times \delta(\vec{k}' - \vec{p})\delta(\omega' - \omega_{k'} + \omega) G_0(p, \omega') \\ &\quad \times \langle\vec{p}| W |\vec{k}\rangle \delta(\omega' - \omega_k) \\ &= \left(\frac{\hbar}{2\omega}\right)^{1/2} \vec{e}_\lambda\cdot\vec{j}(\vec{k}') G_0(k', \hbar\omega_k) \\ &\quad \times \langle\vec{k}'| W |\vec{k}\rangle \delta(\omega_k - \omega_{k'} + \omega) \quad . \end{aligned} \tag{2.27}$$

This is identical with (2.16), but for the fact that W rather than $\tilde{W}$ is involved in (2.27), and the energy δ function. The discrepancy is due to the fact that we have evaluated the matrix elements defined by (2.23) between pseudowaves ϕ_k, rather than the true wave functions ψ_k. It is clear that when we make the appropriate modification, then W in (2.27) becomes replaced by $\tilde{W}$ in this order.

The crucial point revealed in the present multiple-scattering approach is that the lowest-order contribution (i.e., order $\tilde{W}$) to the optical matrix element in a metal (Fig. 1) is basically a *second-order scattering process*, involving the scattering of an incoming electron by the Coulomb field of the ions (represented by $\tilde{W}$), a propagation, and then scattering by the photon field into a final excited state. This is a familiar process in quantum electrodynamics (cf. bremsstrahlung),[21] and may accordingly be represented by the Feynman graph shown in Fig. 2(a) which corresponds to $g_{kk'\lambda}^{(a)}$. Similarly, Fig. 2(b) represents the "time-reversed" or "conjugate" graph corresponding to $g_{kk'\lambda}^{(b)}$. The sum of the two graphs gives the lowest-order contribution to the optical matrix element in one-electron approximation. The important features of the graphical analysis can be summed up as rules for calculating the matrix

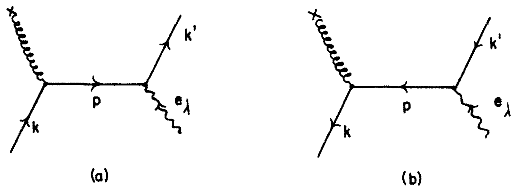

FIG. 2. Contributions to the optical matrix elements, $g_{kk'\lambda}^{(a)}$ and $g_{kk'\lambda}^{(b)}$ in the lowest order according to the multiple scattering analysis [Eq. (2.24)]: These are similar in structure to the Feynman graph for the bremsstrahlung (Ref. 21). Full lines represent electron propagators, curly lines represent electron-ion interaction given by the optical pseudopotential, and wavy lines represent electron-photon interaction.

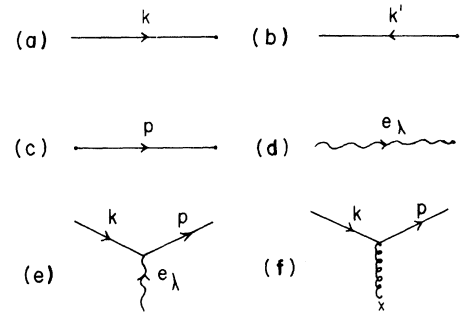

FIG. 3. (a) Incoming (initial) electron of momentum $\hbar\vec{k}$ and energy $\hbar\omega_k$; (b) outgoing (final) electron of momentum $\hbar\vec{k}'$ and energy $\hbar\omega_k$; (c) internal electron line, with which we associate a factor

$$\frac{1}{\Omega}\sum_{\vec{p}}\int\frac{d\omega'}{2\pi}\,G_0(\vec{p},\omega');$$

(d) incoming (initial) photon, contributing a factor $(\hbar/2\omega)^{1/2}\vec{e}_\lambda$; (e) electron-photon vertex $\vec{j}(\vec{k})\delta(\vec{k}-\vec{p})\delta(\omega_k-\omega_p-\omega)$; (f) electron-ion vertex $\langle\vec{k}|\,\tilde{W}\,|\vec{p}\rangle\,\delta(\omega_k-\omega_p)$(note that a Coulomb field does not conserve momentum).

element associated with each graph in momentum space as shown in Fig. 3.

In this formulation, many-body effects now correspond to the familiar processes of quantum electrodynamics, giving rise to the renormalization of various quantities[22] due to electron self-energy effects, electron-photon vertex correction, the electron-ion vertex correction and final-state interactions. These are shown in Figs. 4(a)–4(c) as modifications of the skeleton graph corresponding to Fig. 2(a). Similar modifications corresponding to Fig. 2(b) have been omitted for brevity. These, and their implications on the optical conductivity, will be explored in Sec. III.

An aspect of many-body effect which is usually included in the one-electron approximation in the framework of time-dependent Hartree-Fock theory is shown in Fig. 5(a). This is the *polarization* of the electron gas due to the excitation of electron-hole pairs from the Fermi sea by the ions. Below the electron plasma frequency, this leads to the screening of the bare electron-ion pseudopotential by the electron gas discussed in AII. Above the plasma frequency, it leads to the plasma resonance considered by Hopfield[13] and Phillips.[14] If the electron-hole pair excitation is taken into account to all orders of perturbation theory within the random-phase approximation, the effect would be to replace the bare electron-ion vertex in Fig. 5(a) by an effective vertex [represented by the thick curly electron-ion line in Fig. 5(a)], determined by the solution of the integral equation shown in Fig. 5(b). The result in local screening approximation is

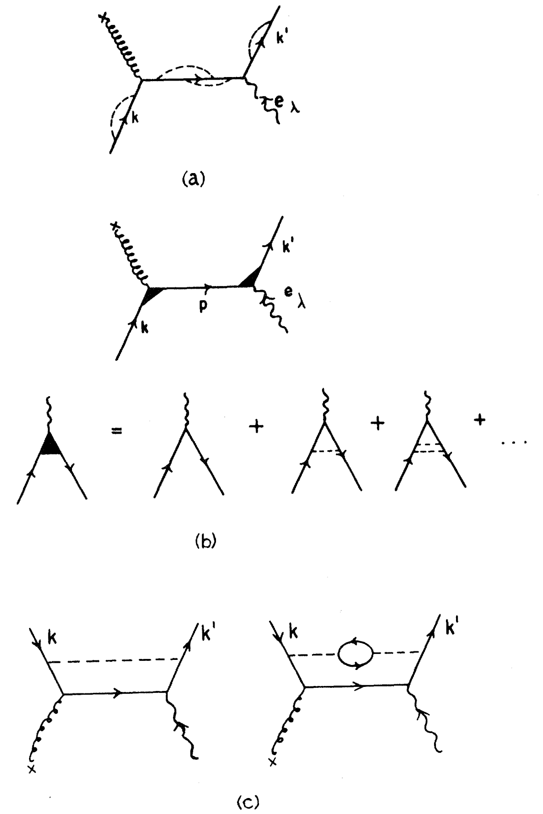

FIG. 4. (a) Modification of optical matrix element due to electron-electron Coulomb interaction (this gives rise to electron self-energy effects); (b) corrections at the electron-ion vertex and at the electron-photon vertex due to the "bridging" of the initial and final electron lines by Coulomb interaction; (c) final-state interactions without and with electron-hole pair excitation.

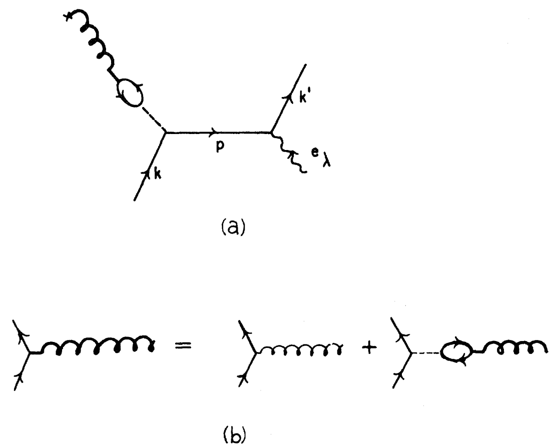

FIG. 5. Excitation of electron-hole pairs by the ion, leading to the screening of the bare electron-ion interaction. The net effect is to replace the bare optical pseudopotential matrix element, shown as a thin curly line in (b), by an effective screened optical pseudopotential matrix element [Eq. (2.28)], shown as a thick curly line in (a) and in the integral equation (b).

$$\langle \vec{k}' | \tilde{W}^{\text{eff}} | \vec{k} \rangle = \langle \vec{k}' | \tilde{W} | \vec{k} \rangle / \epsilon(\vec{k}' - \vec{k}, \omega) \quad , \qquad (2.28)$$

where $\epsilon(q, \omega)$ is the Hartree-Fock *dynamic* dielectric function with suitably screened exchange interaction. Thus, in the one-electron approximation, the conductivity is

$$\sigma_0(\omega) = \frac{2\pi}{\hbar} \sum_{k, k', \lambda} | g^{\text{eff}}_{kk', \lambda} |^2 + n_k (1 - n_{k'}) \delta(T_k - T_{k'} + \hbar\omega) , \qquad (2.29)$$

where $g^{\text{eff}}_{kk',\lambda}$ is given by (2.16) with $\tilde{W}$ replaced by $\tilde{W}^{\text{eff}}$ in (2.28). The fact that the pseudopotential that enters the optical conductivity should be screened with a dynamic Hartree-Fock dielectric function was first pointed out by Hopfield.[13]

III. MANY-BODY EFFECTS

A. General Considerations

Let us now turn to the many-body theory. We have noted above that in addition to the screening effects due to electron-hole pair excitations, there are many-body effects due to the electron self-energy, electron-ion, electron-photon vertex corrections, and final-state interactions, as shown in Figs. 4(a)–4(c). The effects shown in Figs. 4(a) and 4(b) modify the optical matrix elements and the energy δ function entering the definition of $\sigma(\omega)$ in the following way: We rewrite Eq. (2.20) in a form that includes the electron-electron interactions and vertex corrections as

$$(T + M + \overline{H}_I) \overline{\phi}_k = i\hbar \frac{\partial \overline{\phi}_k}{\partial t} \quad , \qquad (3.1)$$

where $(T + M)\overline{\phi}^{\,0}_k = E_k \overline{\phi}^{\,0}_k$ (3.2)

defines "unperturbed" Landau quasiparticle states $\overline{\phi}^{\,0}_k$, M being the self-energy due to electron-electron interaction, and

$$\overline{H}_I = \Lambda_0 \tilde{W}^{\text{eff}} + \vec{A} \cdot \vec{\Lambda} + O(\vec{A}^2) \qquad (3.3)$$

is modified interaction term, Λ_0 and $\vec{\Lambda}$ being the proper vertex parts for scalar and vector coupling.[23] To recover the one-electron approximation, we simply set $\Lambda_0 = 1$, $\vec{\Lambda} = \vec{j}$, and $M = 0$.

On carrying out the scattering analysis described in Sec. II B and extracting the two terms contributing to optical absorption, we see that the optical matrix takes the form

$$\begin{aligned} \overline{g}^{\text{eff}}_{kk',\lambda} = {} & (\hbar/2\omega)^{1/2} \vec{e}_\lambda \cdot \vec{\Lambda}(\vec{k}') \overline{G}_0(k', E_k) \Lambda_0 \\ & \times \langle \vec{k}' | \tilde{W}^{\text{eff}} | \vec{k} \rangle + \Lambda_0 \langle \vec{k} | \tilde{W}^{\text{eff}} | \vec{k}' \rangle^* \\ & \times G_0(k, E_{k'}) (\hbar/2\omega)^{1/2} \vec{e}_\lambda \cdot \vec{\Lambda}(\vec{k}) \quad , \end{aligned} \qquad (3.4)$$

where $\overline{G}_0$ is the quasiparticle Green's function given approximately by [Ref. 23, p. 257, Eq. (6-61)]

$$\overline{G}_0(k, E_{k'}) = z_k^{1/2} z_{k'}^{1/2} / [E_{k'} - E_k] \quad , \qquad (3.5)$$

z_k and $z_{k'}$ being quasiparticle renormalization factors and E_k being the quasiparticle excitation energy. Thus, we find the modified result

$$\sigma(\omega) = (2\pi/\hbar) \sum_{k, k', \lambda} | \overline{g}^{\text{eff}}_{kk', \lambda} |^2 n_k (1 - n_{k'}) \delta(E_k - E_{k'} + \hbar\omega) \; ; \qquad (3.6)$$

where

$$\begin{aligned} \overline{g}^{\text{eff}}_{kk',\lambda} = {} & z_k^{1/2} z_{k'}^{1/2} (\hbar/2\omega)^{1/2} \vec{e}_\lambda \cdot \vec{\Lambda}(\vec{k}) \Lambda_0(\vec{k}) \langle \vec{k} | \tilde{W}^{\text{eff}} | k' \rangle / \\ & [E_k - E_{k'}] + z_k^{1/2} z_{k'}^{1/2} (\hbar/2\omega)^{1/2} \vec{e}_\lambda \cdot \vec{\Lambda}(\vec{k}') \\ & \times \Lambda_0(\vec{k}') \langle \vec{k} | \tilde{W}^{\text{eff}} | \vec{k}' \rangle / [E_{k'} - E_k] . \end{aligned} \qquad (3.7)$$

This is the result we are after. In principle, it includes the electron-electron many-body effects, to all orders in the Coulomb interaction and first order in $\tilde{W}^{\text{eff}}$. In the remainder of this section, we shall evaluate the various parameters in this expression in suitable approximations and compare the results, wherever possible, with previous calculations and with experiment. The modification of (3.7) due to the final-state interactions of Fig. 4(c) will also be discussed.

B. Proper Vertex Parts

The proper vertex functions Λ_0 and $\vec{\Lambda}(\vec{k})$ have been studied by a number of authors.[23–26] As first noted by Heine *et al.*[24] the factor $z_k^{1/2} z_{k'}^{1/2} \Lambda_0 \times (k) \langle \vec{k} | \tilde{W}^{\text{eff}} | \vec{k}' \rangle$ in (3.7) represents the appropriate matrix element of the effective pseudopotential seen by the Landau quasiparticle in a metal, and in sodium $z_{k_F} \simeq 0.71$. Watabe and Yasuhara[25] have noted, however, that Λ_0 depends not only on the wave vector $\vec{k}$ but also on the energy of the state $\vec{k}$ and on the frequency ω appearing in the dielectric screening function $\epsilon(\vec{k}' - \vec{k}, \omega)$ in the definition of $\langle \vec{k} | \tilde{W}^{\text{eff}} | \vec{k}' \rangle$. They found that in the optical frequency range in sodium $\Lambda_0(k_F, \omega) \simeq 1.557$, while $\Lambda_0(k_F, 0) \simeq 1.19$; in other words, the *dynamic* vertex part (which is the appropriate one in our case) is larger than the *static* vertex part. Thus, for sodium,

$$(z_k z_{k'})^{1/2} \Lambda_0(k, \omega) \simeq z_{k_F} \Lambda_0(k_F, \omega) \simeq 1.11 \; . \qquad (3.8)$$

This is only 11% enhancement of the optical matrix element (3.7) or about 20% enhancement of the zeroth-order one-electron conductivity $\sigma_0(\omega)$ given by (2.29). In both Refs. 24 and 25 the estimates were based on the calculation performed by Rice.[26]

As regards the vector vertex part $\vec{\Lambda}(\vec{k})$ in (3.7), it has been shown by Nozières [Ref. 23, p. 255, Eq. (6-51)] to be given exactly by the Bethe-Salpeter equation

$$\vec{\Lambda}(\vec{k}, \omega) = \vec{j}(\vec{k}) + \sum_{\vec{k}', \omega'} {}^0 I(k\omega, k'\omega')$$

$$\times \overline{G}_0(k', \omega')\, \overline{G}_0(k', \omega')\, \vec{\Lambda}(\vec{k}', \omega') \ , \qquad (3.9)$$

where $\vec{j}(\vec{k})$ is given by (2.18) and ${}^0I(k\omega, k'\omega')$ is the irreducible interaction between two quasiparticles. The result expected from an exact solution of this equation will not be very different from that given by the Born approximation, which corresponds to one of the so-called *Ward identities*[23]

$$\vec{\Lambda}(\vec{k}) = \vec{j}(\vec{k}) + \textstyle\sum_{k'} f(\vec{k}, \vec{k}')\delta(\mu - E_{k'})\vec{j}(\vec{k}') \ , \qquad (3.10)$$

where μ is the chemical potential and $f(\vec{k}, \vec{k}')$ is the parameter of the Landau-Fermi liquid theory reprepresenting the phenomenological interaction between quasiparticles. Physically, $\vec{\Lambda}(\vec{k})$ is usually interpreted as the "current" carried by a quasiparticle, the second term in (3.10) being the effect due to the "back flow" of quasiparticles (Ref. 23, p. 10, Fig. 2).

It is convenient to introduce a quasiparticle effective mass m^* (due to electron-electron but not electron-phonon interaction) by writing (3.10) in the form

$$\vec{\Lambda}(\vec{k}) = e\hbar\vec{k}/m^* \ . \qquad (3.11)$$

We see therefore that the net effect of the vector vertex correction [at the electron-photon vertex in Fig. 4(b)] on $\sigma(\omega)$ is to replace the bare mass m by m^* in the expression for $\vec{j}(\vec{k})$. According to Rice,[26] m^* in the alkali metals, sodium in particular, is no more than 10–15% larger than the bare mass. Consequently, in sodium, the enhancement of $\sigma_0(\omega)$ due to the *scalar* vertex part Λ_0 nearly cancels exactly the effect of the *vector* vertex part $\vec{\Lambda}$.

C. Quasiparticle Self-Energy Effect

Another source of modification of $\sigma(\omega)$ due to electron-electron Coulomb interaction comes from the quasiparticle energy E_k which appeared as energy denominator in (3.7) and in the energy δ function $\delta(E_k - E_{k'} + \hbar\omega)$ in (3.6). Now, the quasiparticle energy is given by the poles of the quasiparticle Green's function, i.e., by the equation

$$E_k = T_k + M(k, E_k) \ , \qquad (3.12)$$

where M is the self-energy operator introduced earlier in Eq. (3.2), and is given by Rice[26] as

$$M(k, E) = -\sum_q \int \frac{dE'}{2\pi i}\, \frac{\upsilon(q) G_0(\vec{k}+\vec{q}, E+E')}{\epsilon(q, E')} \ . \qquad (3.13)$$

In this expression, the unperturbed one-particle Green's function must be written in the form

$$G_0(\vec{k}, E) = n_k/(E - T_k - i\eta) + (1 - n_k)/(E - T_k + i\eta) \ ,$$

where the limit $\eta \to 0$ is to be taken after the energy integration has been performed, and $\upsilon(q) = 4\pi e^2/q^2$.

It is of interest to discuss the *shift* in the threshold energy for interband optical transition due to the use of the quasiparticle excitation energy in the δ function appearing in (3.6) rather than T_k (the free-particle energy) appearing in (2.29). A reliable estimate, not unlike the one used by Ashcroft and Wilkins,[27] for $M(k, E)$, shows that the shift in the interband threshold in alkali metals has the functional form

$$\delta\omega_0 \simeq -\frac{2e^2}{\pi\hbar}\,\frac{1-x^2}{4x}\ln\left|\frac{1+x}{1-x}\right| \ , \qquad (3.14)$$

to the right (i.e., higher-frequency region) beyond ω_0 given by

$$\hbar\omega_0 = (\hbar^2/2m)K(K - 2k_F) \ . \qquad (3.15)$$

Here, K is the magnitude of the (110) reciprocal-lattice vector, $K = 2.28k_F$, and in (3.14) $x = |k_F - K|/k_F > 1$, so that $\delta\omega_0 > 0$. Thus, as is the case in all previous calculations, we find no evidence for the anomalously low threshold found experiment by Mayer and co-workers.[19] On the other hand, this negative result favors the recent results obtained independently by Smith.[7]

D. Final-State Interactions

Finally, we turn to precesses in which an outgoing electron interacts with an incoming one via its Coulomb field, with or without electron-hole pair excitation, as shown in the two graphs of Fig. 4 (c). These graphs represent the so-called final-state interactions considered by Mahan.[12] The contribution of such processes to the optical matrix elements of Eq. (3.7), to all orders in electron-hole pair excitation, can be evaluated from the first of the two graphs of Fig. 4(c), by replacing the bare Coulomb interaction $\upsilon(q)$ by a dynamically screened interaction $v(q)/\epsilon(q, \omega)$. We may write this as an extra term, $\delta\overline{g}^{\,\mathrm{eff}}_{kk'\lambda}$, to be added to (3.7)

$$\delta\overline{g}^{\,\mathrm{eff}}_{kk'\lambda} = \int \frac{d^3q}{(2\pi)^3}\, \overline{g}^{\,\mathrm{eff}}_{k+qk'\lambda}\, \xi(k, k'; q) \ , \qquad (3.16),$$

where $\xi(k, k'; q) = \dfrac{d\omega'}{2\pi}\, \dfrac{\upsilon(q)}{\epsilon(q, \omega')}\, \overline{G}_0(\vec{k}, E_{k+q})$

$$\times \overline{G}_0(\vec{k}' + \vec{q}, E_{k'} + \hbar\omega) \ . \qquad (3.17)$$

All corrections due to quasiparticle self-energy in the final-state interaction have been included in this term.

Two cases of the above general result were distinquished in Mahan's paper.[12] One case arises if $v(q)$ is screened by the static dielectric function $\epsilon(q, \omega \sim 0)$, and the other, arises from the poles of $1/\epsilon(q, \omega)$: The latter is found to correspond to processes in which a virtual plasmon is exchanged between the initial and final electron states. Both of these are automatically included in (3.16). There is no compelling reason to isolate the two terms in our general expression (3.17), but it is pertinent to note that, at least in the static case, the factors in (3.17) are precisely those appearing in Mahan's expression for the conductivity.[12] However, whereas our correction enters the expression for $\sigma(\omega)$, through the square of optical matrix element $|\bar{g}^{\text{eff}}_{kk'\lambda}+\delta\bar{g}^{\text{eff}}_{kk'\lambda}|^2$ as required by (3.6), Mahan's correction is included as a *linear* term in $\sigma(\omega)$, which we consider to be in error.

Thus, in place of Mahan's result, $\sigma/\sigma_0 \simeq 1.45$, we should have typically

$$\sigma/\sigma_0 \simeq (1+z^2_{k_F}\times 0.45)^2 \simeq 1.49 \quad \text{for} \quad z_{k_F}\simeq 0.71$$

in sodium. The two results are not very different. These results were compared with experiment in AI and led to significant improvement in the agreement between theory and experiment.

IV. CONCLUSIONS

In this paper we have reformulated the optical effects in simple metals in a form in which various electron-electron interaction effects can be sorted out. Although no substantially new result was obtained, our analysis has provided a basis for confidence in the present interpretation of optical properties in the alkali metals based on the one-electron "optical" pseudopotential method of AI, and many-body effects. Perhaps the most important contribution of the present work is the interpretation of various previous works in terms of an inclusive theory. In a subsequent paper, we shall show how the present approach can be used to resolve the apparent difference between the so-called optical and thermal effective masses.[3]

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