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

4. CONCLUSION

We have shown that the optical pseudopotential gives reasonable results for the optical conductivity in simple (nearly-free-electron) metals. It would also appear from the works of Mueller[23] and Heine[24] that, if indeed the *s-d* interaction in transition metals is weak, then an effective electron-photon coupling matrix could be constructed along the lines suggested in AII and the theory would also be applicable to transition metals.

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

ACKNOWLEDGMENTS

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[22] N. W. Ashcroft and J. Lekner, Phys. Rev. **145**, 83 (1966).
[23] F. M. Mueller, Phys. Rev. **153**, 659 (1967).
[24] V. Heine, Phys. Rev. **153**, 673 (1967).
[25] See, for example, C. N. Berglund and W. E. Spicer, Phys. Rev. **136**, A1030 (1964); **136**, A1044 (1964); also Ref. 2, p. 285.

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Self-Consistent Theory of Optical Transitions in Simple Metals*

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

1. INTRODUCTION

IN the past, efforts have been made to solve the Schrödinger equation for a Bloch (conduction) electron moving in the static periodic potential of a metal under an applied electromagnetic field by using the semiclassical effective-Hamiltonian method and/or the effective-mass approximation.[1] These approaches do not, however, take into account the mixing of states from different bands and the modification of the coupling between the electron and the applied field due to the self-consistent field of the conduction electrons. Consequently, they are inadequate for performing a realistic calculation of the *transition probabilities* for various processes dependent on the emission or absorption of a photon by the electron, upon which we wish to focus attention in this paper.

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

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[*] This work was supported by the Advanced Research Project Agency through the Center for Materials Research at Stanford University.
[1] For a review see, e.g., J. Callaway, *Energy Band Theory* (Academic Press Inc., New York), 1964, pp. 233–306.
[2] H. Mayer and B. Hietel, in *Proceedings of the International Colloquium and Optical Properties and Electronic Structures of Metals and Alloys, Paris, 1965* (North-Holland Publishing Company, Amsterdam, 1966), p. 47.
[3] W. E. Spicer, Phys. Rev. **154**, 385 (1967).

and effective-Hamiltonian approaches in computing transition probabilities in order to include self-consistently the collective effects due to electron-electron interactions in the presence of an external perturbing field. The few such attempts which have been made in the recent literature include the resonance studies by Phillips,[4] the electron-electron effects in photoemission by Hopfield,[5] and the most recent studies of plasmon effects by Mahan.[6] Another effect which has proven to be of considerable importance in optical transitions (particularly in the alkali metals) comes from the fact that the pseudopotential entering the optical transition probability is different from the usual one determining energy bands and electron-phonon interaction. This has been called the "optical" pseudopotential[7,8]: It depends explicitly on the frequency of the absorbed photon. We have shown in a previous paper[8] that the difference between the optical and the regular pseudopotential accounted for nearly a factor of 2 between the observed and the calculated interband optical absorption, in the alkali metals.

Our objective in this paper is to show, firstly in Sec. 2, how the optical pseudopotential arises quite naturally in the second-quantized Hamiltonian for the assembly of Bloch electrons in an applied electromagnetic field. Secondly, we show, in Sec. 3, how the effect of electron-electron interaction can be incorporated self-consistently in terms of the dynamic Hartree dielectric function at the frequency of the absorbed or emitted photon, and reduces to the result previously obtained by Hopfield[5] for an ordinary pseudopotential. The simple reduced Hamiltonian obtained in this way not only gives the transition probabilities directly but is also useful as a starting point for investigating various problems. As an example we shall use the Hamiltonian in deriving the effective mass of a Bloch electron in an electromagnetic field in Sec. 4: This is a self-energy effect due to continuous emission and reabsorption of photons.

It would appear, therefore, that we have obtained a general and quantitative form of the theory of optical transitions in simple metals, which has the advantage that we do not have to perform a preliminary energy-band-structure computation. The calculation of an optical pseudopotential, as we have shown in a previous paper,[8] entails no more labor than the usual regular pseudopotential. We must point out, however, that the present theory cannot account for special effects due to the shape of the bands, e.g., critical points,[4] although it is useful for calculating the appropriate oscillator strengths involved.

2. SECOND QUANTIZATION OF THE HAMILTONIAN

Consider a system of Bloch (conduction) electrons moving in a periodic crystal potential $U(\mathbf{r})$, under an applied electromagnetic field described by a vector potential $\mathbf{A}(\mathbf{r},t)$, in the Lorentz gauge ($\nabla\cdot\mathbf{A}=0$). The full Hamiltonian for the system may be written in the second-quantized form

$$H=\int d^3r\,\psi^\dagger(\mathbf{r}t)\left[-\frac{\hbar^2\nabla^2}{2m}+U(\mathbf{r})\right]\psi(\mathbf{r}t)+\frac{1}{2}\int d^3rd^3r'\psi^\dagger(\mathbf{r}t)\psi^\dagger(\mathbf{r}'t)\frac{e^2}{|\mathbf{r}-\mathbf{r}'|}\psi(\mathbf{r}'t)\psi(\mathbf{r}t)$$

$$+(ihe/mc)\int d^3r\psi^\dagger(\mathbf{r}t)\mathbf{A}(\mathbf{r},t)\cdot\nabla\psi(\mathbf{r}t)+(e^2/2mc^2)\int d^3r\psi^\dagger(\mathbf{r}t)\mathbf{A}^2(\mathbf{r},t)\psi(\mathbf{r}t)+H_{\text{field}}\,,\quad(2.1)$$

where the last term is the energy of the free electromagnetic field, and all the other terms have their usual meaning. We introduce creation and annihilation operators for the photons of the field and for the electrons by writing

$$\mathbf{A}(\mathbf{r}t)=\left(\frac{h}{2V\omega_{Q\lambda}}\right)^{1/2}\sum_{Q\lambda}\mathbf{e}_{Q\lambda}(b_{Q\lambda}e^{+i\mathbf{Q}\cdot\mathbf{r}}+b_{-Q\lambda}{}^\dagger e^{-i\mathbf{Q}\cdot\mathbf{r}})\,,\quad(2.2)$$

$$\psi(\mathbf{r}t)=\sum_k c_k\chi_k(\mathbf{r})\,,\quad \psi^\dagger(\mathbf{r}t)=\sum c_k{}^\dagger\chi_k{}^*(\mathbf{r})\,,\quad(2.3)$$

where $\mathbf{e}_{Q\lambda}$ ($\lambda=1$, 2) is the polarization, $\omega_{Q\lambda}$ is the frequency of the photon, V is the normalization volume, and $\{\chi_k\}$ is a complete orthonormal set of functions in $\mathbf{r}$ space. Then (2.1) becomes

$$H=\sum_{k'k}E_{k'k}c_{k'}{}^\dagger c_k+\tfrac{1}{2}\sum_{k'p',kp}V_{k'p',kp}c_{k'}{}^\dagger c_{p'}{}^\dagger c_kc_p$$

$$+\sum_{k'kQ\lambda}g_{k'kQ\lambda}(b_{Q\lambda}+b_{-Q\lambda}{}^\dagger)c_{k'}{}^\dagger c_k+\sum\hbar\omega_{Q\lambda}b_{Q\lambda}{}^\dagger b_{Q\lambda}$$

$$+(\text{terms of the form } b_{Q\lambda}{}^\dagger b_{Q\lambda}c_{k'}{}^\dagger c_k)\,,\quad(2.4)$$

where

$$E_{k'k}=\int\chi_{k'}{}^*(\mathbf{r})\times[-(\hbar^2/2m)\nabla^2+U(\mathbf{r})]\chi_k(\mathbf{r})d^3r\,,\quad(2.5)$$

$$V_{k'p',kp}=\int\chi_{k'}{}^*(\mathbf{r})\chi_{p'}{}^*(\mathbf{r}')\frac{e^2}{|\mathbf{r}-\mathbf{r}'|}\times\chi_k(\mathbf{r}')\chi_p(\mathbf{r})d^3rd^3r'\,,\quad(2.6)$$

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[4] J. C. Phillips, Solid State Phys. **18**, 56 (1966).

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

[6] G. D. Mahan, Phys. Letters **24A**, 708 (1967).

[7] A. O. E. Animalu and W. A. Harrison, Bull. Am. Phys. Soc. **12**, 415 (1967).

[8] A. O. E. Animalu, preceding paper, Phys. Rev. **163**, 557 (1967).

and

$$g_{k'kQ\lambda}=(\hbar/2V\omega_{Q\lambda})^{1/2}(ie\hbar/mc)$$

$$\cdot\mathbf{e}_{Q\lambda}\int\chi_{k'}{}^{*}(\mathbf{r})(e^{+i\mathbf{Q}\cdot\mathbf{r}}\boldsymbol{\nabla})\chi_k(\mathbf{r})d^3r. \quad (2.7)$$

The last set of terms in the electron and photon operators may be described as "anharmonic" terms in the essentially Frölich-type Hamiltonian (2.4): These biquadratic terms represent the scattering of photons by the Bloch electrons as in the Compton effect, and so will not concern us further. In any case, for the interesting cases of weak fields, terms of order A^2 are small. The formal expression (2.4) becomes useful if we can determine the complete set of functions $\{\chi_k\}$ and hence the matrix elements in (2.5), (2.6), and (2.7) explicitly.

We choose a representation in which (2.5) is diagonal so that the χ's are solutions of the single-electron Bloch equation (without electron-electron interactions);

$$[-\hbar^2\nabla^2/2m+U(\mathbf{r})]\chi_k=E_k\chi_k. \quad (2.8)$$

If, as in the effective Hamiltonian method, we were to determine the Bloch functions by performing a full energy-band calculation, the evaluation of the matrix elements in (2.6) and (2.7) would be quite complicated. Instead, we perform a pseudopotential transformation

$$|\chi_k\rangle=(1-P)|\varphi_k\rangle, \quad (2.9)$$

where

$$P=\sum_{\alpha}|\alpha\rangle\langle\alpha| \quad (2.10)$$

is a projection operator ($P^2=P$) onto the core states, the summation being over the occupied core electron orbitals in the system. This leads, without any approximation, to the pseudopotential equation

$$[-\hbar^2\nabla^2/2m+W]|\varphi_k\rangle=E_k|\varphi_k\rangle, \quad (2.11)$$

where W is a weak pseudopotential operator,[9] the precise form of which does not matter until actual numerical computation is required. We make explicit the dependence of W on the energy of the state k by writing $W(k)$ subsequently.

We now make an approximation, by determining $|\varphi_k\rangle$ in (2.11) to first order in W by perturbation theory, and substituting the result in (2.8) to obtain

$$|\chi_k\rangle=a_0\Bigg\{|\mathbf{k}\rangle-P|\mathbf{k}\rangle+\sum_{k''}{}'|\mathbf{k}''\rangle$$

$$\times\frac{\langle\mathbf{k}''|W(k)|\mathbf{k}\rangle}{\epsilon_k-\epsilon_{k''}}+\cdots\Bigg\}, \quad (2.12)$$

where a_0 is a normalization constant, and $\epsilon_k\equiv\hbar^2k^2/2m$ is the energy of the plane-wave state $|\mathbf{k}\rangle$. Since the φ_k's are, in general, nonorthogonal, we must check to any desired order in W that the χ's are orthogonal. By using (2.12), together with the relation $P^2=P$ when necessary, and the fact that, in general, W satisfies the non-Hermiticity relation

$$\langle\mathbf{k}'|W(k)|\mathbf{k}\rangle-\langle\mathbf{k}|W(k')|\mathbf{k}'\rangle^{*}$$

$$=-(\epsilon_{k'}-\epsilon_k)\langle\mathbf{k}'|P|\mathbf{k}\rangle, \quad (2.13)$$

we obtain orthogonality between the χ's:

$$\langle\chi_{k'}|\chi_k\rangle=|a_0|^2\delta_{k'k}+O(W^2), \quad (2.14)$$

provided that we also treat $\langle\mathbf{k}'|P|\mathbf{k}\rangle$ as a first order quantity. For our present purpose, it is convenient to rewrite (2.12) in the more compact form by replacing $P|\mathbf{k}\rangle$ by $\sum_{k''}|\mathbf{k}''\rangle\langle\mathbf{k}''|P|\mathbf{k}\rangle$ to obtain

$$|\chi_k\rangle=a_0'|\mathbf{k}\rangle+a_0\sum_{k''}{}'|\mathbf{k}''\rangle$$

$$\times\langle\mathbf{k}''|\tilde{W}(k)|\mathbf{k}\rangle/(\epsilon_k-\epsilon_{k''})+\cdots, \quad (2.15)$$

where a_0' is a new constant incorporating the diagonal term $\langle\mathbf{k}|P|\mathbf{k}\rangle$ and $\tilde{W}$ is the Animalu-Harrison "optical" pseudopotential[7] defined by

$$\langle\mathbf{k}''|\tilde{W}(k)|\mathbf{k}\rangle=\langle\mathbf{k}''|W(k)+(\epsilon_{k''}-\epsilon_k)P|\mathbf{k}\rangle. \quad (2.16)$$

It depends on the energy of both states but has been labeled here by the energy of the state in $W(k)$. The definition of $\tilde{W}$ is not compelling, but it enables us to give a simple physical interpretation to the final results.

By using (2.15) in (2.7), retaining only first-order terms, and noting that $\mathbf{e}_{Q\lambda}\cdot\mathbf{Q}=0$ in the Lorentz gauge, we obtain

$$g_{k'kQ\lambda}=\left(\frac{\hbar}{2V\omega_{Q\lambda}}\right)^{1/2}(e\hbar/mc)\mathbf{e}_{Q\lambda}\cdot\Bigg[\frac{\mathbf{k}'\langle\mathbf{k}'-\mathbf{Q}|\tilde{W}(k)|\mathbf{k}\rangle}{\epsilon_{\mathbf{k}}-\epsilon_{\mathbf{k}'-\mathbf{Q}}}$$

$$-\mathbf{k}\langle\mathbf{k}+\mathbf{Q}|\tilde{W}(k')|\mathbf{k}'\rangle^{*}/(\epsilon_{\mathbf{k}+\mathbf{Q}}-\epsilon_{\mathbf{k}'})\Bigg]. \quad (2.17)$$

This result follows less directly from (2.12) provided we recognize that

$$\langle k'|P\boldsymbol{\nabla}P|k\rangle=\sum_{\alpha}\sum_{\alpha'}\langle k'|\alpha\rangle\langle\alpha|\boldsymbol{\nabla}|\alpha'\rangle\langle\alpha'|k\rangle,$$

is logically a second-order quantity, since $\boldsymbol{\nabla}P\neq P\boldsymbol{\nabla}$.

In the matrix element of the electron-electron interaction in (2.6), the only terms which survive to first order in W are the free-electron-gas results, which we write in the form that will be used later in Sec. 3 for deriving the screening in the random-phase approximation,

$$V_{k'p',kp}=(4\pi e^2/|\mathbf{k}'-\mathbf{k}|^2)\delta_{\mathbf{k}'-\mathbf{k},\mathbf{p}'-\mathbf{p}} \quad (2.18)$$

for the direct Coulomb interaction, and

$$V_{k'p',pk}=[4\pi e^2/(|\mathbf{k}-\mathbf{p}|^2+k_s^2)]\delta_{\mathbf{k}-\mathbf{p},\mathbf{k}'-\mathbf{p}'} \quad (2.19)$$

for the exchange part, $1/k_s$ being a screening length. The screening of the exchange is incorporated here for completeness: It does not detract from our general results.

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[9] J. C. Phillips and L. Kleinman, Phys. Rev. 116, 287 (1959).

The conservation of momentum requires

$$\mathbf{k}'=\mathbf{k}+\mathbf{q}+\mathbf{Q}\,, \tag{2.20}$$

where $\hbar\mathbf{q}$ is the momentum imparted to the electron by collision with an ion.

On gathering results, the final form of (2.4) becomes

$$H=\sum_k E_k c_k{}^\dagger c_k+\tfrac{1}{2}\sum_{k'kqQ} V(\mathbf{q}+\mathbf{Q})c_{\mathbf{k}+\mathbf{q}+\mathbf{Q}}{}^\dagger c_{\mathbf{k}'-\mathbf{q}-\mathbf{Q}}{}^\dagger c_{\mathbf{k}'}c_{\mathbf{k}}$$
$$+\sum_{k'kQ\lambda} g_{k'kQ\lambda}(b_{Q\lambda}+b_{-Q\lambda}{}^\dagger)c_{k'}{}^\dagger c_k$$
$$+\sum_{Q\lambda}\hbar\omega_{Q\lambda}b_{Q\lambda}{}^\dagger b_{Q\lambda}\,, \tag{2.21}$$

where we have dropped the exchange term momentarily so that $V(\mathbf{q}+\mathbf{Q})\equiv 4\pi e^2/|\mathbf{q}+\mathbf{Q}|^2$.

It is useful to assess the simplification achieved in the second-quantized formalism. Firstly, we have prescribed *ab initio* the interaction between a single electron and a single photon in terms of the familiar pseudopotential theory: This has made it easy to spotlight the fact that the pseudopotential required for electromagnetic phenomena is different from the regular one determining, for example, the shape of the Fermi surface and electron-phonon interaction. The transition probability for various processes dependent on the mixing of two Bloch states $\chi_{k'}$ and χ_k and the absorption or emission of a single photon is simply proportional to $g_{k'k,Q\lambda}{}^* g_{kk',-Q\lambda}$. which can be evaluated self-consistently, as described in Sec. 3, without recourse to any detailed band-structure calculation: This is the real advantage over the effective Hamiltonian (*single*-band) formalism. The Hamiltonian itself can be used for various purposes such as the one described in Sec. 4 and for calculating photon-assisted tunneling currents in simple metals. Finally, the formalism is applicable to the regular solid or amorphous materials (e.g., liquid metals), to a lattice distorted by phonons or vacancies, and to alloys, for we can write

$$\langle\mathbf{k}'|\tilde{W}|\mathbf{k}\rangle=S(|\mathbf{k}'-\mathbf{k}|)\langle\mathbf{k}'|\tilde{w}|\mathbf{k}\rangle\,,$$

where

$$S(|\mathbf{k}'-\mathbf{k}|)\equiv\frac{1}{N}\sum_j\exp[-i(\mathbf{k}'-\mathbf{k})\cdot\mathbf{R}_j]$$

is the usual structure factor of diffraction theory which takes completely into account the dependence of $\tilde{W}$ on the positions $\mathbf{R}_j$ of the N ions in the system, and $\langle\mathbf{k}'|\tilde{w}|\mathbf{k}\rangle$ is the matrix element of the potential associated with a single ion.

3. DYNAMICAL SCREENING OF THE ELECTRON-PHOTON INTERACTION

In Sec. 2 we determined the coupling matrix $g_{k'kQ\lambda}$ between the electron and a single photon of the electromagnetic field in terms of an optical pseudopotential $\tilde{W}$ constructed from the single-electron Bloch equation (2.8) which does *not* include electron-electron interaction. Consequently, $\tilde{W}$ in the defining expression (2.17) is *unscreened*. In this section we shall determine, in the framework of self-consistent, time-dependent, Hartree-Fock theory, the influence of electron-electron interactions on each Fourier component $g_{kqQ\lambda}$ (note that $\mathbf{k}'=\mathbf{k}+\mathbf{q}+\mathbf{Q}$) of the coupling matrix. We write

$$g_{kqQ\lambda}{}^{\text{eff}}=g_{kqQ\lambda}+g_{kqQ\lambda}{}^{\text{sc}}\,, \tag{3.1}$$

where the second term is the modification due to the self-consistent field of the conduction electrons.

For simplicity we ignore exchange in the meantime, and use the equation of motion method. We may remark here that we would get the same result from the Schrödinger equation *but* we would have to go to second order in the density matrix. In the equation-of-motion method using the second-quantized formalism, the desired result will be obtained by considering no more than the linear response of the electron-hole pair, $\rho_{kqQ}=c_{\mathbf{k}}{}^\dagger c_{\mathbf{k}+\mathbf{q}+\mathbf{Q}}$, to the perturbation due to a single-photon mode (i.e., fixed Q and λ)

$$H_{\text{int}}=\sum_{kq} g_{kqQ\lambda}(b_{Q\lambda}+b_{-Q\lambda}{}^\dagger)\rho_{kqQ}{}^\dagger\,. \tag{3.2}$$

[Note that $b_{Q\lambda}(t)=b_{Q\lambda}(0)\,e^{-i\omega_{Q\lambda}t}$.]

The equation of motion of the electron-hole pair is

$$[H,\rho_{kqQ}]=-i\hbar\partial\rho_{kqQ}/\partial t\,. \tag{3.3}$$

The electron-density fluctution is

$$\rho_{qQ}=\sum_k c_{\mathbf{k}}{}^\dagger c_{\mathbf{k}+\mathbf{q}+\mathbf{Q}}\,. \tag{3.4}$$

We seek an oscillating solution of (3.3) at a frequency $\omega\equiv\omega_{Q\lambda}$ associated with the mode (Q,λ), for if the electron-density fluctuation is to respond to (2.3) with this frequency, then each electron-hole pair must do likewise. Thus, from (3.3)

$$-\hbar(\omega+i\delta)\langle\rho_{kqQ}\rangle=\langle[H,\rho_{kqQ}]\rangle\,, \tag{3.5}$$

where the small positive number δ corresponds to adiabatic turning on the interaction (3.2), and the expectation value is taken in the ground state.

In the random phase approximation (RPA),[10] we obtain

$$-\hbar(\omega+i\delta)\langle\rho_{kqQ}\rangle=(E_{\mathbf{k}}-E_{\mathbf{k}+\mathbf{q}+\mathbf{Q}})\langle\rho_{kqQ}\rangle+(n_{\mathbf{k}}-n_{\mathbf{k}+\mathbf{q}+\mathbf{Q}})$$
$$\times\{v(\mathbf{q}+\mathbf{Q})\langle\rho_{qQ}\rangle+g_{kqQ\lambda}(\langle b_{Q\lambda}\rangle+\langle b_{-Q\lambda}{}^\dagger\rangle)\} \tag{3.6}$$

where $n_{\mathbf{k}}$ is the Fermi distribution. The Bloch energies E_k for a nearly free electron metal can be written

$$E_k=\epsilon_k+\langle\mathbf{k}|W|\mathbf{k}\rangle+O(W^2)\,, \tag{3.7}$$

so that, on regarding $\langle\rho_{kqQ}\rangle$ as first order, we have to retain only the zero order in (3.7). Thus, on rearranging (3.6) we derive

$$\langle\rho_{qkQ}\rangle=-\frac{n_{\mathbf{k}}-n_{\mathbf{k}+\mathbf{q}+\mathbf{Q}}}{\epsilon_{\mathbf{k}}-\epsilon_{\mathbf{k}+\mathbf{q}+\mathbf{Q}}+h(\omega+i\delta)}\{v(\mathbf{q}+\mathbf{Q})\langle\rho_{qQ}\rangle$$
$$+g_{kqQ\lambda}(\langle b_{Q\lambda}\rangle+\langle b_{-Q\lambda}{}^\dagger\rangle)\}\,. \tag{3.8}$$

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[10] D. Pines, *Elementary Excitations in Solids* (W. A. Benjamin, Inc., New York, 1963), pp. 138–143.

We proceed to deduce the self-consistent term $g_{kqQ\lambda}{}^{\mathrm{sc}}$ in (3.1). This is given by Poisson's equation[11]

$$g_{kqQ\lambda}{}^{\mathrm{sc}}(\langle b_{Q\lambda}\rangle+\langle b_{-Q\lambda}{}^{\dagger}\rangle)=v(\mathbf{q}+\mathbf{Q})\langle\rho_{qQ}\rangle\,. \qquad (3.9)$$

If we now use the definitions (3.1) and (3.9) to eliminate $v(\mathbf{q}+\mathbf{Q})\langle\rho_{qQ}\rangle$ from (3.8), we get

$$\langle\rho_{kqQ}\rangle=-\frac{n_{\mathbf{k}}-n_{\mathbf{k}+\mathbf{q}+\mathbf{Q}}}{\epsilon_{\mathbf{k}}-\epsilon_{\mathbf{k}+\mathbf{q}+\mathbf{Q}}+\hbar(\omega+i\delta)}\times g_{kqQ\lambda}{}^{\mathrm{eff}}(\langle b_{Q\lambda}\rangle+\langle b_{-Q\lambda}{}^{\dagger}\rangle)\,. \qquad (3.10)$$

Equations (3.9) and (3.10) have to be solved self-consistently. Our procedure for doing this is to sum over k in (3.10) and feed the result into the right-hand side of (3.9), then add the *unscreened* term $g_{kqQ\lambda}(\langle b_{Q\lambda}\rangle+\langle b_{-Q\lambda}{}^{\dagger}\rangle)$ to both sides of the resulting equation. The result is an integral equation for $g_{kqQ\lambda}{}^{\mathrm{eff}}$;

$$g_{kqQ\lambda}{}^{\mathrm{eff}}=g_{kqQ\lambda}-v(\mathbf{q}+\mathbf{Q})\times\sum_{p}\frac{n_{\mathbf{p}}-n_{\mathbf{p}+\mathbf{q}+\mathbf{Q}}}{\epsilon_{\mathbf{p}}-\epsilon_{\mathbf{p}+\mathbf{q}+\mathbf{Q}}+\hbar(\omega+i\delta)}g_{pqQ\lambda}{}^{\mathrm{eff}}\,, \qquad (3.11)$$

where we have dropped the common factor $(\langle b_{Q\lambda}\rangle+\langle b_{-Q\lambda}{}^{\dagger}\rangle)$ multiplying both sides of the equation. This is the analog of the integral equation given by Sham and Ziman[12] for the effective electron-phonon interaction matrix. The most general form of (3.11) including exchange (screened or unscreened) is

$$g_{k'kQ\lambda}{}^{\mathrm{eff}}=g_{kk'Q\lambda}-\sum_{\mathbf{p}\neq\mathbf{p}'}\frac{n_{\mathbf{p}}-n_{\mathbf{p}'}}{\epsilon_{\mathbf{p}}-\epsilon_{\mathbf{p}'}+\hbar(\omega+i\delta)}g_{pp'Q\lambda}{}^{\mathrm{eff}}\times\{v(kpk'p')-v_{\mathrm{ex}}(kpp'k')\}\,, \qquad (3.12)$$

where $\mathbf{k}'=\mathbf{k}+\mathbf{q}+\mathbf{Q}$, $\mathbf{p}'=\mathbf{p}+\mathbf{q}+\mathbf{Q}$, and

$$v(kpk'p')=(4\pi e^2/|\mathbf{q}+\mathbf{Q}|^2)\delta_{\mathbf{k}'-\mathbf{k},\mathbf{p}'-\mathbf{p}}\,, \qquad (3.13)$$

$$v_{\mathrm{ex}}(kpp'k')=[2\pi e^2/(|\mathbf{p}-\mathbf{k}|^2+k_s{}^2)]\delta_{\mathbf{p}-\mathbf{k},\mathbf{p}'-\mathbf{k}'}\,. \qquad (3.14)$$

Note that $g_{kk'Q\lambda}$ is strictly k-dependent, so that the solution of this equation follows along the lines suggested elsewhere[13] for the special case where the exchange is replaced by a suitable local potential.

The qualitative feature of (3.11) and (3.12) can be seen by ignoring the k dependence of $g_{kk'Q\lambda}$, e.g., by evaluating it *once* at a fixed $k=k_F$, say. Then we can factor out $g_{kqQ\lambda}{}^{\mathrm{eff}}$ from the summation over $\mathbf{p}$ in (3.11) to obtain

$$g_{kqQ\lambda}{}^{\mathrm{eff}}\approx g_{kqQ\lambda}/\epsilon_H(\mathbf{q}+\mathbf{Q},\,\omega)\,, \qquad (3.15)$$

where

$$\epsilon_H(\mathbf{q}+\mathbf{Q},\,\omega)=1+v(\mathbf{q}+\mathbf{Q})\times\sum_{p}\frac{n_{\mathbf{p}}-n_{\mathbf{p}+\mathbf{q}+\mathbf{Q}}}{\epsilon_{\mathbf{p}}-\epsilon_{\mathbf{p}+\mathbf{q}+\mathbf{Q}}+\hbar(\omega+i\delta)} \qquad (3.16)$$

is the Hartree dynamic dielectric function.

In order to appreciate the meaning of (3.15) let us consider the very special case when $Q\rightarrow 0$ in (2.17) corresponding to a pure electric field. Then (3.15) takes the form

$$g_{k'k\lambda}{}^{\mathrm{eff}}\approx\left(\frac{\hbar}{2V\omega}\right)^{1/2}\left(\frac{e\hbar}{mc}\right)\mathbf{e}_{\lambda}\times\left[\frac{\mathbf{k}'\langle k'|\tilde{W}(k)|\mathbf{k}\rangle-\mathbf{k}\langle\mathbf{k}|\tilde{W}(k')|\mathbf{k}'\rangle^{*}}{\epsilon_H(q,\omega)}\right]\Big/\hbar\omega_{kk'}\,, \qquad (3.17)$$

where $\mathbf{k}'=\mathbf{k}+\mathbf{q}$ and $\omega_{k'k}=(\epsilon_{k'}-\epsilon_k)/\hbar$. If, in addition, we neglect the non-Hermiticity of $\tilde{W}$ in (3.17) so that $\langle\mathbf{k}'|\tilde{W}(k)|\mathbf{k}\rangle=\langle\mathbf{k}|\tilde{W}(k')|\mathbf{k}'\rangle^{*}$, then the term in square brackets becomes $\mathbf{q}\langle\mathbf{k}'|\tilde{W}(k)|\mathbf{k}\rangle/\epsilon_H(q,\omega)$. This has an obvious interpretation in terms of an effective dynamically screened optical pseudopotential;

$$\langle\mathbf{k}'|\tilde{W}_{\mathrm{eff}}(k)|\mathbf{k}\rangle\approx\langle\mathbf{k}'|\tilde{W}(k)|\mathbf{k}\rangle/\epsilon_H(q,\omega)\,, \qquad (3.18)$$

giving in (3.17)

$$g_{k'k\lambda}{}^{\mathrm{eff}}\approx(\hbar/2V\omega)^{1/2})e\hbar/mc)\mathbf{e}_{\lambda}\times\mathbf{q}\langle\mathbf{k}'|\tilde{W}_{\mathrm{eff}}(k)|\mathbf{k}\rangle/\hbar\omega_{k'k}\,. \qquad (3.19)$$

The screening corresponds to the optical frequency $\omega=\omega_{k'k}$ of the external field, as required by energy conservation in an optical transition. Thus, at zero field, (3.18) reduces by virtue of (2.16) to the usual result

$$\langle\mathbf{k}'|W_{\mathrm{eff}}(k)|\mathbf{k}\rangle\approx\langle\mathbf{k}'|W(k)|\mathbf{k}\rangle/\epsilon_H(q,0)\,, \qquad (3.20)$$

where W_{eff} is the statically screened regular pseudopotential determining, for example, the shape of the Fermi surface.

The result (3.18) has been previously suggested by Hopfield[5] in connection with photoemission. However, he derived his results with the usual pseudopotential rather than an optical one. The differences between the static and the dynamic dielectric functions have been discussed in Ref. 8 and in textbooks (see e.g., Ref. 10, p. 143). More recently, Phillips[14] has discussed the effect of the dynamic screening in the enhancement of indirect interband optical absorption in metals.

4. AN EFFECTIVE-MASS THEOREM

In this section we shall prove a general theorem about the effective mass of Bloch electrons in an electromagnetic field. We precede our derivation by an illustration in the context of the current theory of the "optical" effective mass[15] $m_{\mathrm{op}}{}^{*}$. The expression for $m_{\mathrm{op}}{}^{*}$ is given most commonly in terms of the so-called f-sum rule (which can be derived from the $\mathbf{k}\cdot\mathbf{p}$ method of band-structure calculation) for an isotropic material

$$m/m^{*}(k)=1+\sum_{k'}f_{k'k}\,, \qquad (4.1)$$

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[11] This equation becomes an obvious definition if we had written the interaction terms (3.2) in the conventional form in terms of an external potential $\varphi_{\mathrm{ex}}\rho^{+}$ and determined the screening term φ^{sc} from $\nabla^2\varphi^{\mathrm{sc}}=-4\pi e^2\rho$ by taking the Fourier transform.

[12] L. J. Sham and J. M. Ziman, Solid State Phys. **15**, 221 (1963).

[13] A. O. E. Animalu, Phil. Mag. **10**, 379 (1965).

[14] Reference 2 p. 22.

[15] M. H. Cohen, and V. Heine, Advan. Phys. **7**, 395 (1958).

by the expression

$$1/m_{\mathrm{op}}^* = \frac{1}{N} \sum_k n_k / m^*(k) , \qquad (4.2)$$

where n_k is the Fermi distribution, N is the number of conduction electrons per unit volume, and $f_{k'k}$ is the "oscillator strength" for transitions from state k to state k';

$$f_{k'k} = \frac{2\hbar}{m\omega_{k'k}} \left| \int \chi_{k'}^* \nabla \chi_k d^3\mathbf{r} \right|^2 , \qquad (4.3)$$

where $\hbar\omega_{k'k}$ is the energy difference between the Bloch states χ_k and $\chi_{k'}$. From the expression (2.17) which defines $g_{k'kQ\lambda}$ in the limit as $Q \rightarrow 0$, we obtain

$$\langle \chi_{k'} | \nabla | \chi_k \rangle = i[\mathbf{k}' \langle \mathbf{k}' | \tilde{W}(k) | \mathbf{k} \rangle - \mathbf{k} \langle \mathbf{k} | \tilde{W}(k') | \mathbf{k}' \rangle^*] / \hbar\omega_{k'k} , \qquad (4.4)$$

where $\hbar\omega_{k'k} = \epsilon_{k'} - \epsilon_k$. The present formalism can therefore be used to evaluate oscillator strength directly in nearly-free-electron metals without recourse to energy-band calculations. However, the pseudopotential needed is different from that determining, for example, electron-phonon interaction and the energy-band structure. In addition, (4.4) can be evaluated self-consistently by replacing $\tilde{W}$ and $\tilde{W}_{\mathrm{eff}}$ given by (3.18).

For the complete problem we have, in general, a Green's function

$$G(k,\bar{E}) = 1/[\bar{E} - E_k - \sum (k,\bar{E})] , \qquad (4.5)$$

where $\sum (k,\bar{E})$ is the self-energy, so that we can define an effective "electromagnetic" mass by

$$(1/\hbar) \partial\bar{E}/\partial k |_{k=k_F} = \hbar k_F / m_{\mathrm{e-m}}^* , \qquad (4.6)$$

and find, from the poles of (4.5),

$$m_{\mathrm{e-m}}^* = m_B (1 - \partial \sum / \partial \bar{E}) |_{k=k_F} , \qquad (4.7)$$

where m_B is the zero-field Bloch effective mass. This is our effective-mass theorem. This is the analog of the so-called "thermal" mass in the electron-phonon interaction.[16] It does not seem at the present time to have any more general meaning than the optical effective mass introduced above. But it is evidently the proper mass to be used in describing the influence of the field on the dynamical properties of the Bloch electron. No attempt will be made here to compute this mass explicitly; in practice, it should follow the procedure for the electron-phonon case exactly.[16]

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[16] See, e.g., A. O. E. Animalu, F. Bonsignori, and V. Bortolani, Nuovo Cimento **44B**, 83 (1966).

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Fermi Surface of Lead from Kohn Anomalies

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The dispersion relations for phonons in lead determined by neutron spectrometry exhibit a large number of Kohn anomalies, which may all be related to the Fermi surface in a consistent manner by considering both electron transitions diametrically across the Fermi surface and nondiametral transitions between points with parallel tangent planes. Factors affecting the size and shape of anomalies are reviewed. The detailed interpretation of anomalies leads to a mapping of the Fermi surface, and the result may be compared with that of Anderson and Gold, who used the de Haas–van Alphen method. There is fair agreement, with significant particular differences. The sizes of anomalies have been interpreted in terms of a screened ion-electron interaction.

1. INTRODUCTION

SINCE Kohn[1] pointed out that the phonon-electron interaction changes abruptly along surfaces in the wave-vector space of phonons which are directly related to the Fermi surface, and that this change may be observable as kinks in phonon dispersion curves, such anomalies have been observed in some metals. Brockhouse *et al.*[2] were the first to see the effect, in lead. As they pointed out, the investigation of the Fermi surface via phonons and neutrons is a potentially interesting complement to other methods. The neutron method does not require particularly pure samples or low temperatures, and the interpretation of data is mostly just a matter of geometrical constructions. But it is rather elaborate and, with present neutron sources and spectrometers, applicable only to metals that exhibit relatively large anomalies and are especially amenable to neutron spectrometry, and in fact has not previously been used for a comprehensive study of a Fermi surface. The anomalies in lead seemed to be sufficiently pro-

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[1] W. Kohn, Phys. Rev. Letters **2**, 393 (1959).

[2] B. N. Brockhouse, K. R. Rao, and A. D. B. Woods, Phys. Rev. Letters **7**, 93 (1961).