

of the samples between the thermocouples in order to avoid radial thermal discontinuities. The points shown in Fig. 8 are the measured values. The curves are calculated from the equation

$$QT = \frac{[(Q_+n_+\mu_+ + Q_-n_-\mu_-)T_+ + Q_{(Pt)}T]}{(n_+\mu_+ + n_-\mu_-)} \quad (2)$$

Q_+ and Q_- are the values either the holes or electrons would have in the absence of the other. The values include a phonon contribution estimated from Figs. 3 and 4. $Q_{(Pt)}$, the absolute thermoelectric power of platinum, is used in order to have the calculated value apply to the silicon-platinum couple. It is important only in the purely intrinsic range where it amounts to something less than a 10 percent correction. The concentrations of holes and electrons, n_+ and n_- , and their mobilities μ_+ and μ_- , have been taken from the data of Morin and Maita.⁶ Values of $|n_+ - n_-|$ are determined

from resistivity measurements in the saturation region taken concurrently with the thermoelectric readings using the thermocouples as potential probes. These are combined with the values of $(n_+n_-)^{+1/2}$ given in Fig. 13 of Morin and Maita. The values of μ_+ and μ_- are taken from the extrapolated values given in their Fig. 12. These represent a major uncertainty. The reasonable agreement shown in Fig. 7 is significant in demonstrating the overall consistency of the data; however, it seems doubtful that the choice of different mass parameters to improve the fit would be meaningful.

ACKNOWLEDGMENTS

We are greatly indebted to C. Herring and F. J. Morin for many useful comments and discussions concerning the ideas presented here. We also wish to acknowledge the important contribution of E. Buehler and E. Kolb in preparing the single crystals of silicon from which our samples were prepared.

Plasma Oscillations in Metals

E. N. ADAMS

Institute for Nuclear Studies, University of Chicago, Chicago, Illinois

(Received July 26, 1954; revised manuscript received February 7, 1955)

The self-consistent field treatment of the electronic wave functions of a solid is used as a basis for a theory of plasma oscillations in a metal. Two procedures are used to calculate the plasma frequency, both being based on the Bohm and Pines method of introducing the plasma oscillators. It is found that band-to-band virtual transitions have a strong effect on the plasma oscillations in a metal. It is concluded that the effective mass treatments are not adequate to treat the electron-plasma interaction, except perhaps in certain semiconductors.

INTRODUCTION

IN the last few years, several papers have appeared which discuss the theory of the formation of an electron plasma¹⁻⁵ in metals. In this paper we would like to treat an aspect of that problem which we believe has been given insufficient attention, *viz.*, the effect of the energy band structure on the plasma frequency.

The effect of the lattice potential on the plasma frequency has heretofore to our knowledge been treated only by Wolff,⁵ who limited his explicit consideration to matrix elements of the electron-electron interaction leading to in-band scattering processes. Wolff estimated for a particular case the effects of interband scattering processes on the plasma frequency and found that they caused a large frequency shift. We will show in the following that for metals band-to-band processes are in general quite important, so that Wolff's quantitative

results are probably limited in applicability to semiconductors.

Although previous work has sought to establish the dispersion relation for plasma waves, we have been content to calculate the plasma frequency for very long wavelength plasma waves. Our results indicate that this frequency is strongly affected by band-band virtual transitions, the effects of which are difficult to calculate accurately. We have not concerned ourselves, therefore, with extending the dispersion relation since we feel that this cannot be done correctly in a treatment which does not make an adequate treatment of band-band transitions.

In carrying out our calculations we have chosen to use the method of Bohm and Pines (BP)^{2,3} for introducing the generalized coordinates of the plasma modes. We made this choice because we feel that their method is basically the simplest we know and leads most directly to the results we want. However, we suspect that certain aspects of their treatment of the auxiliary conditions are incorrect, and believe the problem of the auxiliary con-

¹ D. Bohm and E. P. Gross, Phys. Rev. **75**, 1851, 1854 (1949).

² D. Bohm and D. Pines, Phys. Rev. **85**, 338 (1952).

³ D. Bohm and D. Pines, Phys. Rev. **92**, 609 (1953).

⁴ D. Pines, Phys. Rev. **92**, 626 (1953).

⁵ P. Wolff, Phys. Rev. **92**, 18 (1953).

ditions deserves further study. In the present work we do not solve the problem of satisfying the auxiliary conditions, so our treatment is on that score subject to the same criticism as is that of Bohm and Pines.

In the following sections, we will establish an "in principle" basis for treating the outer electrons of a metal as an electron gas, and then present two somewhat different procedures for calculating the plasma frequency. The first procedure is most easily applied to systems such as semiconductors in which the plasma frequency is small compared to the energy band spacing. It gives results which closely parallel those of Wolff. The second procedure is very much like the treatment of Bohm and Pines. It is most easily applied to systems for which the plasma frequency is large compared to the energy band spacing. Actually in many metals the energy band spacing is comparable to the plasma frequency. Unfortunately neither of our procedures affords an accurate way of calculating the frequency in this case, so we are unable to add very much to Wolff's qualitative discussion of the absorption of plasma quanta which takes place when two bands are in "resonance" via an absorption process. However, we have set the theory up in such a way as to make it clear that shifts in the plasma frequency due to band-band transitions can be large whether or not the exact resonance condition is satisfied.

Our chief qualitative conclusion is that even in a "free electron" metal-like sodium, the band-band transitions should affect the plasma frequency strongly, so it is not generally correct to apply to metals the results of Bohm and Pines obtained for a free electron gas.

1. REDUCTION OF OUTER ELECTRON PROBLEM

We want to begin by discussing in a formal way how we can reduce the Schrödinger equation for the outer electrons. Since we are interested in treating correctly the field of the atomic cores, we will need to make use of some kind of self-consistent field (SCF) method to get inner-shell wave functions. We will want to use the energy band type solutions since we are concerned here with typically metallic properties.

For the simple calculations we will do, it is immaterial whether we suppose the use of the Hartree (H), Hartree-Fock-Slater (HFS), or some other⁶ SCF procedure. However, we wish to comment on those characteristics of the SCF wave functions which would be most desirable if we were carrying through a complete configuration interaction calculation. Feasibility of mathematical treatment requires two things. First our one-electron wave functions should form a complete orthonormal set; second our inner-core wave functions should be so good that we need consider only a single configuration for the inner shell. In most cases the simple Hartree SCF wave function satisfies only the first of these conditions, but the HFS wave functions satisfy

both. Thus the HFS set of SCF wave functions would be suitable for providing a "frame of reference" in the function space.

It is possible to conceive that some SCF procedure other than the HFS procedure would be best⁶ for determining the one-electron wave functions which define the "fixed frame." Certainly the simple HFS method has the disadvantage that the dependence of energy on wave number is peculiar at the Fermi surface,⁷ and that feature would be objectionable in some parts of the calculation. We have not made a study to determine the best way of choosing a SCF principle in general, but will merely suggest one which satisfies the two requirements of orthonormality and of giving good inner shell wave functions and has in addition one other desirable feature which will be discussed below. The suggested principle uses the following one-electron Hamiltonian for determining the one-electron wave functions:

$$H\psi(x) = [p^2/2m + V(x) + A_c(x)]\psi(x). \quad (1.1)$$

The Schrödinger type Eq. (1.1) describes the motion of an electron in the average field $V(x)$ of the nuclei and all the other electrons plus an exchange potential $A_c(x)$ due to the core alone. This exchange potential suffices to insure that the core wave functions are substantially the same as the HFS wave functions, since exchange with the outer electrons should not have much effect on the wave functions of the core electrons. At the same time it is easy to show that the eigensolutions of (1.1) have the desired orthogonality properties.

Equation (1.1) is just the HFS equation with exchange among the outer electrons removed. In the SCF approximation it will lead, therefore, to an estimate of the ground state energy which is poorer than that obtained by the more usual HFS procedure. Nevertheless, once committed to going beyond HFS, we would prefer to treat the exchange among the valence electrons explicitly. The reason for such a preference is that the HFS procedure introduces a strong correlation between positions of electrons of parallel spin and no correlation between positions of electrons of antiparallel spin, and thus introduces a preferential lowering of the energy of high spin states which is at least partly spurious. In a number of physical phenomena the crux of the problem is just to understand the competition between Coulomb correlation and exchange to lower the energy. In such cases we prefer to study the two effects on the same footing, somewhat in the manner of Pines,⁴ rather than to start from wave functions which overestimate one effect and ignore the other.

So much for the starting wave functions. We now wish to see how to construct an approximation to the true ground state wave function which is better than the SCF ground-state wave function. The first step is to calculate the matrix of the energy in a representation

⁶ J. C. Slater, *Phys. Rev.* **81**, 385 (1951).

⁷ F. Seitz, *The Modern Theory of Solids* (McGraw-Hill Book Company, Inc., New York, 1940), p. 340.

using antisymmetrized products of the SCF wave functions. One must calculate the expectation value of the energy for each configuration which is to be included in the calculation. Having done so one can for each configuration write the diagonal matrix element as an expression consisting of (a) a sum of SCF parameters for the occupied states, (b) a sum of Coulomb and exchange integrals for the lowest SCF configuration, (c) a sum of Coulomb and exchange integrals which take account of the difference in charge distribution between the configuration of reference and the SCF ground-state configuration. We will neglect the terms (c) in our subsequent discussion, since the ground state should consist chiefly of configurations which are relatively low, and the terms (c) should be small for all these low configurations. In any case the terms we wish to take account of are very much larger than the terms (c).

Thus we see that for our purposes the energy of a configuration (c) will be of the form

$$E(c) = \sum_{\mu}^{(c)} E_{\mu} + \sum_{\mu\nu}^{(c)} E_{\mu\nu}^{(x)}. \quad (1.2)$$

In (1.2) the configuration (c) refers only to the outer electrons; the inner shell configuration being always the same, we need not mention the inner electrons any more. The energy $E_{\mu\nu}^{(x)}$ is just the exchange energy between electrons μ and ν . The Coulomb and exchange interaction between outer and inner electrons and between inner and inner electrons is completely taken account of in the SCF parameters E_{μ} . The zero of energy in (1.2) has been chosen so as to get rid of the Coulomb and exchange integrals (b).

Having gotten the matrix elements of the energy which are diagonal in configurations, we next have to treat the matrix elements which lead to configuration interaction. These will have the property that, except for some small exchange terms, they connect only configurations which differ in the quantum numbers of just two electrons, and in fact, it is for this reason that we are able to replace the inner shells by an equivalent potential. Now the SCF energy eigenvalues take account of the matrix elements of the electron-electron interaction which are diagonal in the configuration. These matrix elements involve only the particular Fourier components of the interaction with wave vectors equal to the wave vectors \mathbf{K} of the reciprocal lattice. No matrix elements which lead to scattering between configurations have been taken into account, of course. If we include the exchange energy in the SCF energy parameters (as would be done in the HFS procedure), we would have as our perturbation just those matrix elements of the electron-electron interaction which mix configurations.

If we do not include the exchange energy in the SCF eigenvalues, though, we must retain the diagonal matrix elements when computing exchange but not otherwise. The last case may be treated formally by simply using the electron-electron interaction with the Fourier com-

ponents \mathbf{K} removed. The deletion of this discrete set of Fourier components does not affect the calculated value of any quantity except the diagonal-in-configuration nonexchange matrix element of the Coulomb interaction, and it causes the value of this quantity to be zero. That is exactly what we want.

Making use of the "crystal momentum representation,"⁸ we can now write down the configuration interaction problem in a Hamiltonian form with the simple Hamiltonian

$$H = \sum_{\mu} E(p_{\mu}) + \sum_{k,\mu\nu}'' (2\pi e^2/k^2) \times \mathbf{q}(p_{\mu}, k) \mathbf{q}(p_{\nu}, -k) e^{ik \cdot x_{\mu\nu}} \quad (1.3)$$

in which \mathbf{q} denotes the effective charge. The first prime on the second summation in (1.3) refers to the fact that k does not take on the value zero nor that of any reciprocal lattice vector. The second prime is a reminder that $\mu \neq \nu$. Greek indices are used to denote electrons. p_{μ} denotes the "crystal momentum" of the μ th electron, x_{μ} denotes the "crystal coordinate" which is conjugate to p_{μ} , $x_{\mu} \equiv i\hbar \partial / \partial p_{\mu}$, $x_{\mu\nu}$ denotes $x_{\mu} - x_{\nu}$. The quantity $\mathbf{q}(p, k)$ is a matrix in the bands. Its matrix elements are given in terms of the SCF wave functions by

$$\mathbf{q}_{nn'}(p, k) = (\psi_{n, p+\hbar k}, e^{ik \cdot x} \psi_{n', p}). \quad (1.4)$$

The states we have to work with are those properly antisymmetrized eigenstates of (1.3) in which no electrons occupy the states which were previously assigned to the inner shell electrons. In the remainder of the paper we will omit the double prime on such summations as that in (1.3) since it plays no role in our considerations, which concern only scattering matrix elements.

2. PLASMA FREQUENCY: APPROXIMATION OF WOLFF

In the previous section we have described a certain Hamiltonian procedure for treating the electron-electron interaction problem in a representation based on SCF solutions of the many electron problem. In this section we will attempt to deduce the plasma frequency for very-long-wavelength plasma waves. We will use a mathematical method which is the exact analog of the BP method, except that we will use the language of perturbation theory to describe certain approximate stages of the calculation. Following BP, we introduce auxiliary quantized oscillators with the associated operators p_k, q_k which satisfy

$$[p_k, q_{k'}] = (\hbar/i) \delta_{kk'}, \quad (2.1)$$

$$p_{k^+} = p_{-k}, \quad q_{k^+} = q_{-k}.$$

We will not be concerned with deciding just how many oscillators should be introduced, but will refer to BP for a discussion of that question. The treatment we will make will apply only to small k values in any case.

To introduce the oscillator coordinates into the

⁸ E. N. Adams, J. Chem. Phys. **21**, 2013 (1953).

Hamiltonian (1.3), we replace (1.3) by

$$H = \sum_{\mu} \mathbf{E}(\mathbf{p}_{\mu}) + \sum_{k\mu\nu}^{(l)} (2\pi e^2/k^2) \mathbf{q}(\mathbf{p}_{\mu}, k) \mathbf{q}(\mathbf{p}_{\nu}, -k) e^{ik \cdot x_{\mu\nu}} \\ + \frac{1}{2} \sum_{k}^{(s)} \{ \mathbf{p}_k - (4\pi e^2/k^2)^{\frac{1}{2}} \sum_{\mu} \mathbf{q}(\mathbf{p}_{\mu}, k) e^{ik \cdot x_{\mu}} \} \\ \times \{ \mathbf{p}_k^+ - (4\pi e^2/k^2)^{\frac{1}{2}} \sum_{\nu} \mathbf{q}(\mathbf{p}_{\nu}, -k) e^{-ik \cdot x_{\nu}} \}. \quad (2.2)$$

The notation (l) , (s) for the regions of summation of k is used to indicate that the wave numbers in the two regions are "large" and "small" respectively as discussed in BP. Clearly the Hamiltonian (2.2) has the same matrix elements as the Hamiltonian (1.3) between wave functions which satisfy the auxiliary conditions,

$$\Omega_k \psi \equiv \mathbf{p}_k^+ \psi = 0. \quad (2.3)$$

We may therefore adopt for the Hamiltonian the expression given by (2.2) instead of (1.3), provided that we use it in a function space in which all functions satisfy (2.3).

We now make a unitary transformation in the manner of BP to a new representation in which we will be able to introduce the so-called "random phase approximation" (RPA). The desired transformation is made by means of the unitary operator

$$u_1 = \exp(is_1/\hbar), \\ s_1 = - \sum_{k\mu} (4\pi e^2/k^2)^{\frac{1}{2}} q_k e^{ik \cdot x_{\mu}}. \quad (2.4)$$

Before writing down the results of the transformation (2.4) on H , we will describe the RPA briefly. The essence of the approximation is to say that for finite k such a sum of phase factors as $\sum_{\mu} e^{ik \cdot x_{\mu}}$ is small compared to n , the value of the sum when $k=0$. The BP assumptions imply that the value of such a sum should vanish essentially like k , so that for small k we may in certain cases neglect these sums. The basis for the approximation is the supposition that in the true wave function the only configurations which are very probable are those for which the electrons are rather evenly distributed. We will not go into the matter here since it is discussed thoroughly in BP.

For brevity we will call that term in the Hamiltonian involving the sum (l) over large values of k , H_{SR} . Further, in treating the sum (s) we will make use of the approximation, valid⁸ for small k ,

$$1 - \mathbf{q}(\mathbf{p}_{\mu}, k) \approx -ik \cdot \mathbf{X}(\mathbf{p}_{\mu}), \quad (2.5)$$

where $\mathbf{X}(\mathbf{p})$ is a matrix in the bands. Its general matrix element can be expressed in terms of the modulating function of the Bloch wave by

$$X_{nn'}(\mathbf{p}) \equiv (u_{np}, \partial u_{n'p} / \partial \mathbf{p}).$$

We will also use the following relations:

$$u_1 \mathbf{E}[\mathbf{p}_{\mu}] u_1^{-1} = \mathbf{E}[\mathbf{p}_{\mu} + \sum_k (4\pi e^2/k^2)^{\frac{1}{2}} ik q_k e^{ik \cdot x_{\mu}}]. \quad (2.6)$$

$\mathbf{E}[\mathbf{p}]_{nn}$ is the energy eigenvalue for a Bloch state of momentum \mathbf{p} in the n th band.

$$u_1 \Omega_k u_1^{-1} = \mathbf{p}_k + (4\pi e^2/k^2)^{\frac{1}{2}} \sum_{\mu} e^{ik \cdot x_{\mu}}. \quad (2.7)$$

By means of the aforementioned equations we can now reexpress the Hamiltonian (2.2) in the new representation defined by the unitary transformation (2.4). We have, in the approximation to which we will work,

$$u_1 H u_1^{-1} = \sum_{\mu} [\mathbf{E}(\mathbf{p}_{\mu}) + \sum_k^{(s)} (4\pi e^2/k^2)^{\frac{1}{2}} \\ \times \{ i\mathbf{k} \cdot \mathbf{v}(\mathbf{p}_{\mu}) / 2, e^{ik \cdot x_{\mu}} \} q_k + (1/2m) \sum_k^{(s)} \\ \times (4\pi e^2/k \cdot l) \alpha(\mathbf{p}_{\mu}) : \mathbf{k} \mathbf{l} e^{i(k \cdot l) \cdot x_{\mu}} q_k q_l^+ + \dots] \\ + H_{SR} + \frac{1}{2} \sum_k^{(s)} [\mathbf{p}_k - (4\pi e^2/k^2)^{\frac{1}{2}} \\ \times \sum_{\mu} ik \cdot \mathbf{X}(\mathbf{p}_{\mu}) e^{ik \cdot x_{\mu}}] \\ \times [\mathbf{p}_k^+ + (4\pi e^2/k^2)^{\frac{1}{2}} \sum_{\nu} ik \cdot \mathbf{X}(\mathbf{p}_{\nu}) e^{ik \cdot x_{\nu}}]. \quad (2.8)$$

In (2.8) we have used the notation

$$\alpha(\mathbf{p}) = m \partial^2 E(\mathbf{p}) / \partial \mathbf{p} \partial \mathbf{p}, \\ \mathbf{v}(\mathbf{p}_{\mu}) = \partial E(\mathbf{p}_{\mu}) / \partial \mathbf{p}_{\mu}. \quad (2.9)$$

Using the RPA, we may neglect those terms in (2.8) which involve $q_k q_l^+ (k \neq l)$. We will also neglect for the moment the terms involving $k \cdot \mathbf{X}$ and H_{SR} and look at the partial problem defined by the Hamiltonian,

$$H_0 = \sum_{\mu} [\mathbf{E}(\mathbf{p}_{\mu}) + \sum_k^{(s)} (4\pi e^2/k^2)^{\frac{1}{2}} \{ \frac{1}{2} ik \cdot \mathbf{v}(\mathbf{p}_{\mu}), e^{ik \cdot x_{\mu}} \} q_k] \\ + \frac{1}{2} \sum_k^{(s)} [\mathbf{p}_k \mathbf{p}_k^+ + \omega_0 k^2 q_k q_k^+] \quad (2.10)$$

with auxiliary conditions $u_1 \Omega_k u_1^{-1} \psi = 0$. In (2.10) we have introduced the notation

$$\omega_0 k^2 = (4\pi e^2/m) \sum_{\mu} \alpha(\mathbf{p}_{\mu}) : \mathbf{k} \mathbf{k} / k^2, \quad (2.11)$$

and used curly brackets to denote the anticommutator.

For this partial problem we will go beyond our original program and derive the dispersion relation for the plasma waves. We want to show that the Hamiltonian (2.10) gives exactly the dispersion relation of Wolff,⁵ so that effectively the approximation which he makes is to neglect the terms in $(k \cdot \mathbf{X})$. To get the dispersion relation for the plasma waves we first introduce the creation-destruction operators for the plasma waves through the usual type of relations:

$$q_k = (\hbar/2\omega_0 k)^{\frac{1}{2}} (a_k + a_{-k}^+), \\ \mathbf{p}_k = (\hbar\omega_0 k/2)^{\frac{1}{2}} (a_k - a_{-k}^+) / i. \quad (2.12)$$

Using (2.12) we rewrite (2.10).

$$H_0 = \sum_{\mu} E(\mathbf{p}_{\mu}) + \sum_{\mu} \sum_k^{(s)} (2\pi e^2 \hbar / \omega_0 k^2)^{\frac{1}{2}} \{ i\mathbf{k} \cdot \mathbf{v}(\mathbf{p}_{\mu}) / 2, e^{ik \cdot x_{\mu}} \} \\ \times (a_k + a_{-k}^+) + \sum_k^{(s)} \hbar\omega_0 k \cdot (N_k + \frac{1}{2}). \quad (2.13)$$

To get the dispersion relation of Wolff, we need only calculate the effect of the interaction term in the second order of perturbation theory, ignoring the Pauli principle in the intermediate states. Writing

$$\alpha(\mathbf{p}_{\mu}) : \mathbf{k} \mathbf{k} / k^2 \equiv \alpha_k(\mu), \\ [\mathbf{v}(\mathbf{p}_{\mu}) \cdot \mathbf{k}] / k \equiv v_k(\mu), \quad (2.14)$$

we can write the second-order energy as

$$\Delta E = - \sum_{\mu} [\sum_k \frac{1}{2} m v_k^2(\mu) / \sum_{\nu} \alpha_k(\nu)] + \sum_k (N_R + \frac{1}{2}) \\ \times \hbar\omega_0 k [\sum_{\mu} k^2 v_k(\mu)^2 \alpha_k(\mu) / 2\omega_0 k^2 (\alpha_k)]. \quad (2.15)$$

The first of the terms in (2.15) represents an eigenvalue renormalization. If the energy surfaces are spheres ($\alpha_k(\mu) = \text{const}$) we get the BP result that the mass of the electron is reduced by the relative amount ($n'/3n$) with n' the number of oscillators per unit volume.

The second term of (2.15) represents a frequency shift. It agrees with the formula (21) of Wolff,⁵ so we are justified in regarding our procedure as essentially the same as his. It is easily shown that (2.15) agrees with the BP formulas if the energy surfaces are spherical.

We will now return to (2.8) and re-examine the terms in the energy which we have not yet taken into account. These extra terms are given by

$$H_1 = \sum'_{\mu k} (4\pi e^2/k^2)^{1/2} \mathbf{p}_k \cdot \mathbf{X}(\mathbf{p}_\mu) e^{-i\mathbf{k} \cdot \mathbf{x}_\mu} + \sum_{k\mu\nu} (s) \times (2\pi e^2/k^2) [\mathbf{k} \cdot \mathbf{X}(\mathbf{p}_\mu)] [\mathbf{k} \cdot \mathbf{X}(\mathbf{k}_\nu)] e^{i\mathbf{k} \cdot \mathbf{x}_{\mu\nu}}. \quad (2.16)$$

The second term in (2.16) is a residual long wavelength interaction between the electrons. If the bands are far apart so that $\mathbf{k} \cdot \mathbf{X}(\mathbf{p}_\mu)$ are small, this last term represents an interaction very much weaker than the original Coulomb interaction, and may properly be ignored. Probably there are many cases in which it cannot be ignored. We will return to this question later.

The first term describes an interaction between electrons and plasma quanta which can cause the electrons to scatter from one band to the other. There will be a frequency shift due to this term and we will estimate the shift by means of perturbation theory also. We will here omit the eigenvalue renormalization term and give only the expression for the frequency shift. We assume notationally that only the n band is occupied with electrons.

$$\delta\omega/\omega = 4\pi e^2 \sum_{\mu, n'} |k \cdot \mathbf{X}_{nn'}(\mathbf{p}_\mu)|^2 E_{nn'}(\mathbf{p}_\mu) / k^2 [E_{nn'}^2(\mathbf{p}_\mu) - (\hbar\omega_k)^2]. \quad (2.17)$$

The sum over bands n' in (2.17) should be taken only over those bands which are unoccupied in order to be consistent with the "fixed frame" treatment of the inner shells.

It is not immediately obvious whether or not the shift given by (2.17) is significantly large in the general case. In order to get some basis for an opinion we can see what (2.17) gives in several limiting cases. The special cases we will discuss are those in which either (a) $\hbar\omega_k \gg |E_{nn'}|$ for those states n' which make an important contribution to the sum, or (b) $|E_{nn'}| \gg \hbar\omega_k$ for all important states, or (c) $E_{nn'} \sim \hbar\omega_k$ for some of the important states.

In case (a) we get

$$\delta\omega/\omega \approx -4\pi e^2 \sum_{\mu, n'} |k \cdot \mathbf{X}_{nn'}|^2 E_{nn'} / [k^2 (\hbar\omega_k)^2]. \quad (2.18)$$

Using the commutation relation

$$X_{nn'} = (\hbar/mi) P_{nn'} / E_{nn'}, \quad (2.19)$$

we can write (2.18) in the form

$$\delta\omega/\omega \approx - (4\pi e^2/m) \sum_{\mu, n'} |k \cdot P_{nn'}|^2 / (k_m^2 E_{nn'} \omega_k^2). \quad (2.20)$$

We could do such a sum over n' explicitly if the summation were over all bands ($n' \neq n$), since by the f sum rule

$$(2/m) \sum_{n'} |k \cdot P_{nn'}|^2 / (k^2 m E_{nn'}) = \alpha_k - 1. \quad (2.21)$$

Actually we are supposed to sum only over bands n' which are unoccupied, hence higher in energy than the band n which is of interest. Nevertheless, we may use (2.21) to get an estimate of the order of magnitude of the frequency shift (2.20). The estimate so obtained is

$$\delta\omega/\omega = \sum_{\mu} (\alpha_k(\mu) - 1) / \sum_{\mu} 2\alpha_k. \quad (2.22)$$

The estimate (2.22) indicates that even when the plasma frequency is large there may be a substantial percentage shift as a result of the band-band interaction. According to (2.22) the shift is positive and amounts to just 50 percent when $|\alpha_k| \gg 1$. When $|\alpha_k|$ is of the order of unity, the predicted shift may have any sign and size. This last feature of (2.22) must not be taken seriously, since it is clear from (2.20) that in perturbation approximation the frequency shift is always positive. The strongest statement we can make is that the shift is always positive as long as the assumption (a) is met, and (2.22) gives a lower limit on the amount of the shift.

In case (b) we assume that $\hbar\omega_k$ is small. Such a situation can be met, for example, in semiconductors. In such a case it is clear from (2.17) that the plasma frequency is always reduced by the band-band processes. The relative shift is obtained from the expression (2.20) by reducing each term in the sum by the factor $(\hbar\omega_k)^2 / E_{nn'}^2$. But this factor is very small by assumption, so one can probably neglect the shift in most cases (b).

In case (c) we have the possibility of a sort of resonance behavior, so the shift cannot be accurately estimated by the formula (2.17) at all. There is no reason, however, to suppose that the shift is especially small, if the matrix elements \mathbf{X} are large. We cannot tell what sign to expect for the shift in this case.

The band-band transitions will also affect the dispersion relation. Inasmuch as we have been unable to get a generally accurate formula for the frequency at long wavelength, it would be pointless to give our approximate formula for the correction to the dispersion relation.

To summarize the situation, we can say that there are several terms which can have a large effect on the plasma frequency but which were not explicitly treated by Wolff. (Wolff estimated the effect of these terms for certain of the transition metals and decided that it is large.) One of these terms gives the frequency shift which we have estimated crudely by (2.17) and found normally to be large in a metal. The other kind of term is the second term of (2.16) which we cannot readily treat using our present approach, but which is probably large in many cases. We conclude that Wolff's dispersion relation is probably not valid in metals because of the band-band interaction terms of the first sort.

In order to establish what the situation is as regards the terms (2.16), we will have to do another calculation.

3. PLASMA FREQUENCY: APPROXIMATION OF BOHN AND PINES

We will now do an analogous calculation to the one of Sec. 2, except that we will use the exact transformation of BP so that the terms (2.16) do not occur. Thus, starting with the Hamiltonian (2.2) we will make the unitary transformation generated by the unitary operator u_2 constructed in the usual way from S_2 :

$$S_2 = -\sum_{k\mu} (4\pi e^2/k^2)^{1/2} \mathbf{q}(\mathbf{p}_\mu, \mathbf{k}) e^{i\mathbf{k}\cdot\mathbf{x}_\mu} q_{\mathbf{k}}. \quad (3.1)$$

It is straightforward to establish the following equations:

$$\begin{aligned} u_2 \Omega_k u_2^{-1} &= p_k^+ + (4\pi e^2/k^2)^{1/2} \sum_{\mu} \mathbf{q}(\mathbf{p}_\mu, -\mathbf{k}) e^{-i\mathbf{k}\cdot\mathbf{x}_\mu}, \quad (3.2) \\ u_2 \mathbf{E}(\mathbf{p}_\mu) u_2^{-1} &= \mathbf{E}(\mathbf{p}_\mu) + (1/2m) \sum_{\mathbf{k}} (4\pi e^2/k^2)^{1/2} \\ &\quad \times \{i\mathbf{k}\cdot\mathbf{P}(\mathbf{p}_\mu), \mathbf{q}(\mathbf{p}_\mu, \mathbf{k}) e^{i\mathbf{k}\cdot\mathbf{x}_\mu}\} q_{\mathbf{k}} \\ &\quad + \sum_{\mu k l} (2\pi e^2/mkl) (\mathbf{k}\cdot\mathbf{l}) \mathbf{q}(\mathbf{p}_\mu, \mathbf{k}) \\ &\quad \times \mathbf{q}(\mathbf{p}_\mu, -\mathbf{l}) e^{i(\mathbf{k}-\mathbf{l})\cdot\mathbf{x}_\mu} q_{\mathbf{l}}. \quad (3.3) \end{aligned}$$

In (3.3), the operator $P(\mathbf{p})$ is a matrix in the bands. Its matrix elements are given in terms of the SCF functions by

$$P_{nn'}(\mathbf{p}) = (mi/\hbar) X_{nn'}(\mathbf{p}) [E_n(\mathbf{p}) - E_{n'}(\mathbf{p})].$$

By means of Eqs. (3.2), (3.3), and the RPA we can get for the transformed Hamiltonian the form

$$H = \sum_{\mu} \mathbf{E}(\mathbf{p}_\mu) + H_I + \frac{1}{2} \sum_{\mathbf{k}} k^{(s)} (p_k^2 + \omega_0^2 q_k^2) + H_{SR}. \quad (3.4)$$

In (3.4), $\omega_0^2 \equiv (4\pi e^2/m)$ is the plasma frequency for a free electron gas having the same mean electron density as our metal, and H_I is given to sufficient approximation by

$$H_I \doteq (1/2m) \sum_{k\mu}' (4\pi e^2/k^2)^{1/2} \{i\mathbf{k}\cdot\mathbf{P}(\mathbf{p}_\mu), e^{i\mathbf{k}\cdot\mathbf{x}_\mu}\} q_{\mathbf{k}}. \quad (3.5)$$

Besides the RPA we have made a further approximation and dropped all terms which would not affect the plasma frequency in lower order than order k^2 .

The Hamiltonian (3.4) is just that of BP with the difference that we sum only over "outer" electrons, and we have been able to make a slight simplification in the matrix elements which occur in H_I . We will not be interested in calculating anything like the BP dispersion relation, however. We wish merely to estimate the effect of band-band transitions on the plasma frequency for long wavelength plasma waves.

We can again estimate the frequency shift by means of second-order perturbation theory. We obtain in the same manner as previously,

$$\delta\omega_k/\omega_0 = (1/m\omega_0) \sum_{\mu n'} |k \cdot P_{nn'}(\mathbf{p}_\mu)|^2 E_{nn'}(\mathbf{p}_\mu) / [E_{nn'}^2 - \hbar^2 \omega_0^2] k^2. \quad (3.6)$$

Formula (3.6) is, of course, unreliable unless the shift it gives is relatively small.

We will now examine as before the limiting cases (a) $\hbar\omega_0 \gg |E_{nn'}|$, (b) $\hbar\omega_0 \ll |E_{nn'}|$. We will begin with (b) this time and use the f sum rule just as we did in case (a) of Sec. 2. Such a procedure yields the formula,

$$\delta\omega_k/\omega_0 \approx (1/2n) \sum_{\mu} [\alpha_k(\mathbf{p}_\mu) - 1]. \quad (3.7)$$

It is not immediately clear that (3.7) gives anything like the result that was obtained in Sec. 2. However, in view of the fact that (3.7) is a perturbation theory result, we are justified in rewriting (3.7) in the form

$$\begin{aligned} \omega_0 + \delta\omega_k &= \{1 + \sum_{\mu} [\alpha_k(\mathbf{p}_\mu) - 1]/n\}^{1/2} 2\omega_0 \\ &= \langle\alpha_k\rangle^{1/2} \omega_0. \quad (3.8) \end{aligned}$$

Equation (3.8) is identical with the zero-order result of Wolff. While it cannot be said that we have verified Wolff's result, the agreement of (3.8) with Wolff's result is not disappointing. It should be noted, however, that the agreement is not as complete as it appears at first sight. In the first place, to get (3.8) we have summed over all intermediate bands n' in contravention of the Pauli principle and in clear violation of the restrictions on our "fixed frame of reference" in the function space. In the second place, we obtain the result (3.7) taking all terms into account, while the result of Wolff was obtained with the neglect of the terms (2.16). If (3.8) were really a valid result, we might conclude that the agreement between (3.8) and Wolff's result (2.11) justifies the neglect of the terms (2.16). Although that interpretation of our results is not justified, we take the view that, while the terms (2.16) may not be insignificant, the procedure of Sec. 2 is the most satisfactory one to use when $\hbar\omega_0 \ll |E_{nn'}|$. Thus we think Wolff's results may be useful in semiconductors.

We now return to case (a) $\hbar\omega_0 \gg |E_{nn'}|$. We see that the shift predicted by (3.6) is relatively much smaller than that we found for case (b) and normally positive. Thus if the plasma frequency is very high the band-band transitions would not affect it very much and the frequency should be similar to what it would be if the electrons were free.

As in Sec. 2, we conclude that when $|E_{nn'}| \sim \hbar\omega_0$, the shift is difficult to predict and may be large.

4. SUMMARY AND CONCLUSIONS

We would like now to summarize the tentative conclusions which we draw from the calculations of Secs. 2 and 3. First we conclude that for the case that the plasma frequency is small the results of Wolff are probably valid. In that case the procedure of Sec. 2 is probably the simplest to follow in studying the plasma since it gives rather good results in zero order. In the case that the plasma frequency is larger, however, the procedure of Sec. 3 is probably the simplest to use, since the equations indicate that the behavior is much more free-electron-like.

The strength of the band-band interactions brings into question the adequacy of the "fixed frame" treat-

ment. In a metal for which ω_0 is large, the inner-shell electrons are capable of interacting strongly with the plasma waves and thus in turn perturbing them. We will discuss this question further below, but it should be said here that the whole matter could stand further examination.

The treatment that we have made is based in principle on a limited configuration interaction calculation according to which all inner-shell states are completely occupied. Strictly speaking, the prohibition against exciting electrons from inner shells must be maintained even in virtual processes if we are to justify the Hamiltonian formalism which we used. Actually, since the electron-electron interaction is so strong, it might be better to seek a procedure which treats the inner shells more accurately, but we have not been able to imagine one which does not have drawbacks. The difficulty which results when too many bands are brought into the purview of the calculation is somewhat obscured by our method of calculation, but it lies in the fact that the exclusion principle must eventually be satisfied. In the BP treatment, which we have followed, the problem of satisfying the Pauli principle cannot be separated from the problem of satisfying the auxiliary conditions. As we bring in more electrons it becomes harder to satisfy the auxiliary conditions, and at the same time more important to do so. We note that in the BP papers³ the auxiliary conditions were simply ignored. That may well be the reason that BP failed to obtain the effect of exchange⁵ on the plasma frequency.

The entire question of the correct way to treat the auxiliary conditions is too complicated for us to go into here, and we do not know the answer anyhow. However, if our practice of ignoring the Pauli principle and auxiliary conditions in intermediate states can be justified, we can see that the manner of treatment of inner shells is optional. Equation (2.11) shows that closed shell electrons contribute nothing to the plasma frequency since the sum of the $\alpha \cdot (p_\mu)$ over a band will vanish. Further, if the electrons are in bands lying so deep that the level spacing is large compared to $\hbar\omega$, then the argument of Sec. 2 shows that the band-band virtual transitions of the electrons will have only a small effect on the plasma frequency. On this basis we can say the results of our calculation are insensitive to the particular way in which we separate the electrons into "inner" and "outer" provided that all electrons which lie below the Fermi surface by not more than a small multiple of $\hbar\omega$ are treated as "outer" electrons.

As an application of our ideas we will comment on the plasma frequency in sodium, because we think it presents a particular point of interest. Since the effective mass of the sodium electrons is close to unity,

the plasma frequency will be found to be the same, in the first approximation, whether one adopts the method of calculation of Sec. 2 or of Sec. 3. Indeed, the reputation of sodium as a "free electron" metal might lead us to expect that this first approximation value of the frequency should be close to the actual plasma frequency for sodium. Actually our theory suggests that such need not be the case. From the matrix point of view the small deviation of the effective mass from unity in sodium is a consequence of the cancellation between terms in the f sum going through higher bands and terms going through lower bands. Our rough estimate (3.6) shows that the dipole matrix elements are weighted differently in the formula for the frequency shift than in the f sum, so the rather complete cancellation found in the f sum is no longer to be expected. Since the dipole matrix elements in sodium are not abnormally small and since the plasma energy is comparable with the interband spacing the imbalance of cancellation in (3.6) should be substantial and the frequency shift large. Moreover, if we observe the Pauli principle in a manner consistent with our "fixed frame" treatment of the inner shells, the sum in (3.6) should be extended only over bands n' of higher energy, and the imbalance is complete. Thus we must be prepared to find that the observed plasma frequency differs substantially from that calculated on the free electron gas model. Unfortunately it is difficult to make an accurate estimate of the expected shift.

While the case of sodium is of special interest because it illustrates that even the best "free electron" metal cannot be treated as an electron gas for the purpose of forming a plasma, our conclusion is actually quite general that in metals the effective mass approximation is inadequate for treating the electron-plasma interaction. We think that semiconductors provide the only possibility of cases for which the effective mass treatment is adequate.

In our opinion the published theories of the electron plasma in metals are unsatisfactory as regards the treatment of the exclusion principle. However, it seems possible that the exclusion principle only affects the frequency of waves of finite wavelength since the effect of density waves of sufficiently long wavelength should be nearly equivalent to a static perturbation and the effect of a static perturbing potential on the one electron wave functions is not affected by the exclusion principle. For that reason, we believe that the considerations of this paper have some chance to be valid, even in view of their incompleteness.

While this manuscript was in preparation the writer has had the pleasure of a number of conversations on the subject with J. McClure, D. Pines, and M. Cohen.