Characteristic Energy Loss of Electrons Passing through Metal Foils. II. Dispersion Relation and Short Wavelength Cutoff for Plasma Oscillations*†

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Previous work is extended so as to provide a determination of the shortest wavelength at which plasma oscillations can be sustained by a degenerate electron gas. The collective oscillations are treated without introducing collective coordinates, thereby avoiding possible complications associated with subsidiary conditions. Instead the Hartree self-consistent field method is used to provide a direct quantum-mechanical analog to the Bohm-Gross derivation of the dispersion relation. The effect of electron exchange, calculated by replacing the Hartree by the Hartree-Fock method, somewhat decreases the dependence of the plasma frequency on wave number. The maximum wave number corresponds to the momentum just sufficient to cause an electron at the surface of the Fermi sea to make a real transition, absorbing one plasma quantum of energy. This criterion agrees well with Watanabe's measurement of the maximum angle by which electrons undergoing the characteristic energy loss are scattered. The previous work on the intensity of the characteristic energy loss as a function of angle is supplemented by a study near cutoff, where is is shown that the intensity drops rapidly to zero as the maximum angle of scattering is approached. By use of the generalized sum rule of Nozières and Pines it is also possible to study the contribution of one-electron excitation to the differential stopping power. Varying as the fourth power of the angle of scattering, this contribution is negligible at small angles and first becomes dominant as the cutoff is approached.

I. INTRODUCTION

IN a previous paper[1] a qualitative estimate was made of the smallest wavelength, or alternatively, of the largest wave number, at which plasma oscillations can be propagated by a degenerate electron gas. (There and in the present work the usual simplification of a uniform fixed background of positive charge is made.) Although the determination of this cutoff is a problem which can probably be handled satisfactorily within the frame work of the full Bohm-Pines[2] theory of Coulomb interactions, we prefer to give here a more limited treatment which is, however, somewhat simpler and more directly suited to the specific problem at hand. The method is that of the Hartree self-consistent field, and is used in Sec. II to obtain the plasma dispersion relation in a way completely analogous to the classical derivation of Bohm and Gross.[3] The resulting quantum-mechanical dispersion relation is identical to that of Bohm and Pines. Following Bohm and Gross, we remove the time dependence of the self-consistent field by working in a coordinate system moving along with the traveling plasma wave. In Sec. III, on the other hand, we give the corresponding time-dependent calculation, working entirely in the laboratory system. This method of the time-dependent self-consistent field has already been presented by Zyrianov and Eleonskii,[4] and as they point out, also shows promise as a way of treating collective oscillations in nuclei without the introduction of collective coordinates and subsidiary conditions.

One result of both Secs. II and III is simply the dispersion relation already established by Bohm and Pines. The present alternative derivation has, however, the advantage of being free of any possible uncertainties connected with the difficulty of giving a rigorous treatment to the Bohm-Pines subsidiary conditions. An additional advantage of the present simple approach is that it lends itself quite readily to a study of the effect of electron exchange. This is carried out at the end of Sec. II, where the Hartree is replaced by the Hartree-Fock method. It is shown that exchange decreases the dependence of the plasma frequency on wave number.

A serious shortcoming, the neglect of correlations, also appears at this point. This is an inherent approximation in the Hartree-Fock method and is satisfactory in the limit of weak interaction, or high density. In the range of electron densities encountered in normal metals, metals, however, the electron-electron correlations are quite strong and should not be neglected. Since the effect of these correlations is to keep the electrons separated it is clear that the present work overestimates the effect of the exclusion principle on the dispersion relation. A correction for correlation is suggested but not rigorously established. To do so would require a more powerful theory, such as that of Bohm and Pines, which includes correlations from the start.

In the last half of Sec. III the connection is established between the degree of excitation of a plasma oscillator and its amplitude of vibration, and also between the degree of excitation and the average number of excited electrons. The number of excited electrons per plasma quantum is found for all but the very long wavelengths to be relatively small (greater than, but

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† The central result of this investigation has been reported at the March Meeting of the American Physical Society [R. A. Ferrell, Bull. Am. Phys. Soc. Ser. II, 2, 146 (1957)].

[1] R. A. Ferrell, Phys. Rev. **101**, 554 (1956).

[2] D. Bohm and D. Pines, Phys. Rev. **92**, 609 (1953).

[3] D. Bohm and E. P. Gross, Phys. Rev. **75**, 1851 (1949).

[4] P. S. Zyrianov and V. M. Eleonskii, J. Exptl. Theoret. Phys. **30**, 592 (1956) [English translation: Soviet Physics JETP **3**, 620 (1956)]. The present author is indebted to Dr. A. A. Broyles for bringing this article to his attention. *Note added in proof.*—A time-dependent Hartree derivation of the Bohm-Pines dispersion relation similar to that presented in Sec. III of the present paper has recently also been given by M. Nogami (to be published).

of the order of magnitude of unity). This suggests the "momentum-exciton" model which is worked out in a paper which follows. The numerical value of this ratio is also utilized in Sec. IV, where the angular dependence of the eigenloss[5] (characteristic energy loss) intensity is studied in the vicinity of the cutoff. This cutoff results when the wavelength of the plasma oscillation is sufficiently short to convey to individual electrons the momentum needed to enable them to make real transitions. They then absorb energy from the oscillation and damp it out. This cutoff criterion reduces essentially to the requirement that the phase velocity of propagation of the plasma should become small enough to coincide with the velocity of the electrons at the surface of the Fermi sea. This determination can be made more precise and the result is exhibited in Fig. 2 below. The cutoff angle obtained in this way for inelastic electron scattering by the plasma is larger than the Bohm-Pines value by 30–50% for naturally occurring electron densities, and is in good agreement with the measurement of Watanabe on aluminum.[6] Of special theoretical interest is the behavior of the cutoff momentum in the high-density limit. While the Bohm-Pines cutoff parameter varies as r_s, where r_s is the radius of the unit sphere in Bohr radii, the presently determined cutoff parameter has a more complicated dependence. While still passing to zero, it does so more slowly and becomes considerably larger than the Bohm-Pines parameter in the limit $r_s \to 0$.

A further result obtained in Sec. IV is the variation as a function of angle of the intensity of the inelastic electron scattering. It is found that the angular dependence determined in reference 1 is modified by a reduction factor which is essentially unity for small angles but drops rapidly to zero as the cutoff angle is approached. In Sec. V, with the help of the generalized sum rule of Nozières and Pines, excitation into the continuum of low-lying one-electron states is studied. The total contribution of these transitions to the differential stopping power is found to be negligible except near the cutoff and beyond. Thus, for angles of scattering less than the cutoff angle, an incident fast electron loses energy almost entirely by collective excitation of the electron plasma.

II. SELF-CONSISTENT FIELD METHOD

Suppose that a running wave of density fluctuation with angular frequency ω and wave vector $\mathbf{k}$ is propagated through a degenerate electron gas, which is assumed to be at rest in the laboratory system (i.e., to have zero average electron momentum). Consider the coordinate system which moves uniformly relative to the laboratory system with velocity equal to the phase velocity $(\omega/k^2)\mathbf{k}$. In this system the density wave is at rest and sets up an electrostatic potential of the form

$$\varphi(x)=2\varphi_0 \cos\mathbf{k}\cdot\mathbf{x}, \tag{1}$$

where φ_0 is a constant. On the other hand, the electrons have an average velocity in the moving system of $-(\omega/k^2)\mathbf{k}$. Aside from the perturbing effect of the sinusoidal potential the electrons occupy states corresponding to a sphere in momentum space of radius equal to the Fermi momentum, but centered at $-(m\omega/k^2)\mathbf{k}$. Let the unperturbed plane waves be designated by $\varphi_i(\mathbf{x})=V^{-\frac{1}{2}}\exp(i\mathbf{k}_i\cdot\mathbf{x})$ (where V is the volume of quantization), and the perturbed wave functions by

$$\psi_i(\mathbf{x})=\varphi_i(\mathbf{x})(1+A_i^{(+)}e^{i\mathbf{k}\cdot\mathbf{x}}+A_i^{(-)}e^{-i\mathbf{k}\cdot\mathbf{x}}). \tag{2}$$

First-order stationary-state perturbation theory[7] gives

$$A_i^{(\pm)}=\frac{-e\varphi_0}{E(\mathbf{k}_i)-E(\mathbf{k}_i\pm\mathbf{k})}, \tag{3}$$

where $E(\mathbf{k}_i)=\hbar^2k_i^2/2m$ is the energy of a free electron of momentum $\hbar\mathbf{k}_i$. Equation (2) thus simplifies to

$$A_i^{(\pm)}=\frac{e\varphi_0/\hbar}{\pm\hbar\mathbf{k}_i\cdot\mathbf{k}/m+\hbar k^2/2m}. \tag{4}$$

According to the above expressions, the contribution of the electrons to the total charge density at the point $\mathbf{x}$ is $-e$ times

$$\textstyle\sum_i|\psi_i(\mathbf{x})|^2\approx V^{-1}\sum_i[1+2A_i\cos(\mathbf{k}\cdot\mathbf{x})],$$

where we have dropped terms higher than the first power in $A_i^{(\pm)}$ and have introduced

$$A_i=A_i^{(+)}+A_i^{(-)}=\frac{-e\varphi_0k^2/m}{(\hbar\mathbf{k}_i\cdot\mathbf{k}/m)^2-\hbar^2k^4/4m^2}. \tag{5}$$

The constant term in the electron density is canceled by the uniform positive background. Hence, according to Poisson's equation, the potential set up by the electrons at point $\mathbf{x}$ is

$$\varphi(\mathbf{x})=2(-4\pi e/k^2V)(\textstyle\sum_iA_i)\cos(\mathbf{k}\cdot\mathbf{x}). \tag{6}$$

This equation is of the same form as Eq. (1). Hence the amplitude of the potential wave, in terms of the perturbations in the electron wave functions, is

$$\varphi_0=-(4\pi e/k^2V)\textstyle\sum_iA_i. \tag{7}$$

If N is the total number of electrons, Eqs. (5) and (7) constitute a set of $N+1$ homogeneous linear equations. The general condition that such a set have a nontrivial solution is the vanishing of the secular determinant. The special case at hand can, however, be handled much more simply. We substitute from Eq. (5) into Eq. (7), and divide by φ_0. (All the A_i's are of the same

[5] The terminology of reference 1 will be assumed throughout.
[6] H. Watanabe, J. Phys. Soc. Japan **11**, 112 (1956).
[7] L. I. Schiff, *Quantum Mechanics* (McGraw-Hill Book Company, Inc., New York, 1955), second edition, p. 153.

sign. Hence φ_0 cannot vanish unless the A_i's all do, which is assumed not to be the case.) We further substitute

$$\hbar k_i/m = \mathbf{v}_i - (\omega/k^2)\mathbf{k},$$

where the velocity vectors $\mathbf{v}_i$ are distributed throughout the volume of a sphere of radius equal to the Fermi momentum divided by the electron mass. Thus the condition for a self-sustaining wave reads

$$\omega_p^2 N^{-1} \sum_i [(\omega - \mathbf{k}\cdot\mathbf{v}_i)^2 - \hbar^2k^4/4m^2]^{-1} = 1. \quad (8)$$

Here we have introduced the customary symbol for the plasma frequency at infinite wavelength, $\omega_p = (4\pi ne^2/m)^{\frac{1}{2}}$. n is the average electron density, N/V.

Equation (8) is just the dispersion relation first derived by Bohm and Pines [Eq. (57) of reference 2]. It formally differs from the classical dispersion relation [Eq. (9) of reference 3] only in the appearance of the additional term[8] $-\hbar^2k^4/4m^2$, which vanishes in the classical limit as $\hbar \to 0$. (Of course, the distribution of velocities is much different in the degenerate and nondegenerate cases. In this respect the degenerate case is simpler, because of the absence of the Boltzmann tail which in principle produces a singularity in the dispersion relation and requires a treatment of electron trapping at all wavelengths.) As Bohm and Pines observe, it is a straightforward matter to obtain from Eq. (8) an expansion for ω in powers of k. Although they present expressions to fourth order in k, we repeat the calculation here, since there is an additional fourth-order term which they do not seem to have included. Designating the velocity average by $\langle\ \rangle$, we find for the coefficient of ω_p^2 in Eq. (6) (odd powers of velocity average to zero).

$$\langle [(\omega - \mathbf{k}\cdot\mathbf{v}_i)^2 - \hbar^2k^4/4m^2]^{-1}\rangle = \omega^{-2} + \omega^{-4}k^2\langle v^2\rangle + \omega^{-6}k^4\langle v^4\rangle + \omega^{-4}\hbar^2k^4/4m^2 + \cdots.$$

Substituting into Eq. (8), multiplying by ω_p^2, solving by iteration, and introducing $\Delta v^2 \equiv (\langle v^4\rangle - \langle v^2\rangle^2)^{\frac{1}{2}}$, we obtain

$$\omega^2 = \omega_p^2 + k^2\langle v^2\rangle + \omega_p^{-2}k^4(\Delta v^2)^2 + \hbar^2k^4/4m^2 + \cdots. \quad (9)$$

It is convenient to introduce the Fermi momentum $\hbar k_0 = mv_0$, the Fermi energy $E_0 = \hbar^2k_0^2/2m$, and the ratio of the Fermi energy to the plasma quantum of energy, $\gamma = E_0/\hbar\omega_p$. Then Eq. (9) reads

$$\omega^2 = \omega_p^2[1 + 4\gamma^2\langle v^2/v_0^2\rangle(k/k_0)^2 + 16\gamma^4(\Delta v^2/v_0^2)^2(k/k_0)^4 + \gamma^2(k/k_0)^4 + \cdots]. \quad (10)$$

Substituting $\langle v^2/v_0^2\rangle = \frac{3}{5}$ and $(\Delta v^2/v_0^2) = 12/175$ and taking the square root gives

$$\omega/\omega_p = 1 + \frac{6}{5}\gamma^2(k/k_0)^2 + \left(-\frac{6}{35}\gamma^4 + \frac{1}{2}\gamma^2\right)(k/k_0)^4 + \cdots. \quad (11)$$

The coefficient of $(k/k_0)^2$ is the same as Bohm and Pines's, but for the coefficient of $(k/k_0)^4$ they have only $\gamma^2/2$. Our coefficient is consequently smaller than theirs by the factor $(1 - 12\gamma^2/35) = (1 - 0.385/r_s)$, where $r_s = (3/4\pi a_0^3 n)^{\frac{1}{3}}$ is the radius of the unit sphere in Bohr radii. Here we have used the free electron expressions

$$E_0 = 3.67 \text{ ry}/r_s^2, \quad (12a)$$

$$\hbar\omega_p = 3.46 \text{ ry}/r_s^{\frac{3}{2}}, \quad (12b)$$

which yield

$$\gamma = 1.061 r_s^{-\frac{1}{2}}. \quad (12c)$$

Recently, by studying the dependence of the characteristic energy loss, $\hbar\omega$, of 25-kev electrons passing through metal foils as a function of scattering angle, $\hbar k/p$, where p is the momentum of the incident electrons, Watanabe[6] was able to establish experimentally the value of the $(k/k_0)^2$ and $(k/k_0)^4$ coefficients in Eq. (9). (For additional discussion of this experiment, see the review articles by Pines.[9,10]) He was able to measure $(k/k_0)^2$ coefficients for several metals, and these will be discussed further below. For the moment, we want to consider briefly the $(k/k_0)^4$ coefficients he found for the two metals aluminum and magnesium. In both cases, his experimental values are somewhat smaller than $\gamma^2/2$. The correction of the preceding paragraph, however, reduces $\gamma^2/2$ by 19% and 15% in the cases of Al and Mg, respectively, and thereby brings the experimental and theoretical values into agreement, within experimental error (which is, to be sure, rather large). A word of caution must, however, be injected at this point concerning the significance of this agreement. In the following paragraphs is shown that there are non-negligible exchange corrections to the Bohm-Pines dispersion relation. The effect of exchange on the $(k/k_0)^2$ coefficient of ω/ω_p is estimated, but evaluation of the $(k/k_0)^4$ exchange correction is not attempted. Since the effect of exchange always appears in higher order in k/k_0, the dominant $(k/k_0)^4$ term, $(\gamma^2/2)(k/k_0)^4$, will be unaffected. For this reason it is unlikely that inclusion of exchange will significantly alter the value of the theoretical fourth-order coefficient. Agreement with the experimental value cannot be definitely established without a quantitative estimate of the effects both of exchange and of the positive-ion lattice on the fourth-order coefficient.

To take into account the effect of electron exchange on the second-order coefficient, we simply replace the

[8] This term is of considerable importance for the short wavelengths and is essential to a correct treatment of the cutoff. A Hartree-type derivation of the dispersion relation which uses the Bohm-Gross transformation and is similar to the present work has already been given by Wolff [P. A. Wolff, Phys. Rev. **92**, 18 (1953)]. But to solve the Hartree equations Wolff uses the WKB method, which is not valid for short wavelengths. He therefore does not find this nonclassical term in the body of his paper. It is, however, implicit in Eqs. (6b) of his Appendix B, which is equivalent to the present treatment. He also discusses there the effect of exchange. (See reference 13.)

[9] D. Pines, *Solid State Physics* (Academic Press, Inc., New York, 1955), Vol. 1, p. 437.

[10] D. Pines, Revs. Modern Phys. **28**, 184 (1956).

above Hartree self-consistent field method by the Hartree-Fock method. The wave function for the N-electron system is a product of two Slater determinants of the one-electron wave functions ψ_i. (Since none of the interactions involved in the present problem is spin-dependent, we are free to consider the spin "up" electrons as distinguishable from those with spin "down".) The Hartree-Fock equation for $\psi_i(\mathbf{x})$ is the free-electron time-independent Schrödinger equation (we continue to work in the moving coordinate system), perturbed by $-e\varphi(\mathbf{x})$ the energy of interaction with the Hartree field, and in addition by the integral operator

$$-\tfrac{1}{2}\sum_j \psi_j(\mathbf{x})\int d^3\mathbf{x}'\psi_j^*(\mathbf{x}')\frac{e^2}{|\mathbf{x}-\mathbf{x}'|}\cdot .$$

The centered dot indicates that the expression is to be multiplied by $\psi_i(\mathbf{x}')$ before the integration over $\mathbf{x}'$ is carried out. The summation is over all electrons, while the factor of one-half allows for the fact that only half of these can exchange. The above operator can be expressed in powers of the $A_j^{(\pm)}$ by substituting the ψ_j from Eq. (2). The term independent of the $A_j^{(\pm)}$ is known, from the work of Pines,[11] to affect the free-electron motion only very slightly, provided electron-electron correlation is taken into account. We therefore neglect this term, as well as those quadratic in the $A_j^{(\pm)}$. The effect of the remaining linear terms on the one-electron function ψ_i can be taken into account by perturbation theory.

This calculation is carried out in Appendix I [which contains Eqs. (13)–(23)]. The result depends on E_{ex}, the exchange energy per electron,[12] and is given by[13]

$$\omega^2=\omega_p^2+k^2\langle v^2\rangle+E_{ex}k^2/m. \tag{23a}$$

Solving for ω in terms of ω_p, one obtains in place of Eq. (11)

$$\omega/\omega_p=1+\frac{6}{5}\gamma^2\left(1+\frac{5}{6}\frac{E_{ex}}{E_0}\right)(k/k_0)^2. \tag{24}$$

According to reference 12

$$E_{ex}=-0.916\ \text{ry}/r_s. \tag{25}$$

Substituting from Eq. (12a), we find for the correction factor due to exchange

$$1+\tfrac{5}{6}(E_{ex}/E_0)=1-0.208r_s. \tag{26}$$

Thus we see that exchange reduces the value of the dispersion coefficient and thereby decreases the dependence of the plasma frequency on wave number.

Before applying the correction factor of Eq. (26) to normal metals it is necessary to examine the range of validity of the present Hartree-Fock calculation. An inherent approximation in the Hartree-Fock method is the neglect of correlation. Such an approximation is justified for weak interaction, or high density. Therefore Eqs. (24) and (26) can be relied upon for electron densities corresponding to $r_s\ll 1$, and we conclude that exchange has no effect on the dispersion coefficient in the high-density limit.

For the electron densities encountered in normal metals, corresponding to values of r_s greater than unity, electron-electron correlation is important and its neglect is not justified. Since the correlation tends to keep the electrons separated so that the Pauli exclusion principle will have less influence, it is clear that the present calculation errors in overestimating the effect of exchange. For these comparatively low densities exchange can be handled correctly only by means of a more powerful theory, such as that of Bohm and Pines, which takes into account correlation. The reader should consult the work of these authors (reference 2) for a discussion of this and related questions. In particular it should be mentioned that the random-phase approximation used by Bohm and Pines is closely related to our Hartree self-consistent field calculation. The Hartree calculation can be considered as an exact treatment of the Hamiltonian obtained by neglecting all terms in the Fourier expansion of the Coulomb interaction except those corresponding to a given momentum transfer. This might be called the "strong-random-phase approximation." It is not clear that it is identical to the Bohm-Pines random-phase approximation, which neglects terms in the kinetic energy part of the Hamiltonian. In any case, the results are identical, at least in regard to the dispersion relation for plasma oscillation. As Bohm and Pines state, when one makes such a random-phase approximation, "no 'exchange' contributions to the dispersion relation appear up to order k^4." The present Hartree-Fock calculation is an attempt to go beyond these approximations and include the effect of interactions corresponding to momentum transfers other than that associated with the wavelength of the plasma oscillation being studied. Our procedure suffers, however, from neglect of correlation and we can only conjecture here what the correct result for normal electron densities would be. By virtue of the correlation each electron is surrounded by a screening cloud, so that electron-electron collisions only take place for close collisions. The sum in Eq. (21) of Appendix I should therefore be restricted to large momentum differences, which simply replaces the Coulomb exchange energy by the exchange energy for a screened Coulomb potential. According to Appendix I of reference 11, this is equivalent to reducing E_{ex} by the factor $g(\beta)=1-4\beta/3+\beta^2/2-\beta^4/48$, where β is determined below from Eq. (43) and Fig. 2 of Sec. IV. It must be emphasized that this correction for correlation is in no

[11] D. Pines, Phys. Rev. **92**, 626 (1953).
[12] F. Seitz, *The Modern Theory of Solids* (McGraw-Hill Book Company, Inc., New York, 1940), p. 341.
[13] This result agrees with an estimate given by Pines [reference 10, Eq. (22)], except for sign, the short-range modification discussed below, and the trivial omission of the mass factor. Wolff (reference 8), has noted that exchange contributes a $(k/k_0)^2$ term to the dispersion relation, but does not give a numerical result.

way proved in the present work. The exchange correction to the coefficient of $(k/k_0)^2$, which we call the "dispersion coefficient," is therefore conjectured to be, instead of Eq. (26),

$$1+\tfrac{5}{6}(E_{ex}/E_0)=1-0.208r_s g(\beta). \quad (27)$$

Numerical values for the dispersion coefficient both with and without the exchange correction are listed in Table I for the four values of electron density corresponding to the metals measured by Watanabe.[6] The experimental values were obtained by multiplying Watanabe's parameter a by 2γ.

It will be noted from Table I that the exchange correction computed above by no means improves the agreement between theory and experiment. It is only weakly dependent on r_s and amounts roughly to a 10% reduction in the dispersion coefficient. The agreement is best in the case of beryllium. The dispersion coefficients for the other metals should theoretically be smaller than the beryllium coefficient, whereas experimentally they are larger. The discrepancy is worst in the cases of germanium and magnesium, where it amounts to about a factor of two. It is natural to suppose that the discrepancy is due to departures, caused by the positive-ion lattice, from free-electron behavior. An extension of the Bohm-Pines theory to include the effect of lattice on the dispersion coefficient has been made by Nozières and Pines.[14] The present Hartree-Fock approach, or rather that of the next section, may also be extended to take the effect of the lattice into account.[15] It would be highly desirable to have a quantitative estimate of the extent to which the lattice affects the dispersion. In general this would require detailed knowledge of the Bloch waves and the energy-band structure of the metals. Only in the case of the alkali metals can a relatively simple theoretical treatment be expected. Unfortunately it is just these metals which are most difficult to handle experimentally.

TABLE I. Theoretical and experimental (Watanabe, reference 6) values of the eigenloss and of the dispersion coefficient for various metals. The entries under "Exch." are computed from a conjectured formula for the correction due to electron exchange, and are not rigorously established in the present work.

		Eigenloss		Dispersion coefficient Theory		
Metal	r_s	$\hbar\omega_p$	Exp.	No exch.	Exch.	Exp.
Be	1.88	18.2	19.0	0.72	0.64	0.65±0.06
Al	2.07	15.7	15.0	0.65	0.58	0.74±0.07
Ge	2.08	15.6	16.5	0.65	0.58	1.22±0.22
Mg	2.65	10.9	10.5	0.51	0.44	0.81±0.05

III. TIME-DEPENDENT SELF-CONSISTENT FIELD

The method of Bohm and Gross, used in the preceding section, of working in a moving coordinate system is not generally applicable to the problem of calculating the frequency of collective oscillation of a system of many particles. Only in the case of a free interacting gas does it seem to be useful. Treating the plasma oscillations in metals more realistically and taking the lattice into account would already select out the laboratory system as preferred. The Bohm-Gross transformation would be of no advantage in this case, since in the moving coordinate system the lattice would set up a rapidly fluctuating time-dependent potential. Therefore, it is necessary in the general case to work in the laboratory system and to cope directly with the time dependence of the self-consistent field set up by the collective oscillations. A procedure for accomplishing this has been provided by Zyrianov and Eleonskii,[4] who have noted that it is possible to make a very simple generalization of Hartree's equation to the time-dependent case. In this section we sketch briefly the derivation of the plasma dispersion relation by this method, and show that it is equivalent to the derivation given in Sec. II. In addition we derive a relation between the amplitude of the oscillating self-consistent field and the quantum number of excitation of the corresponding plasma oscillator (i.e., the number of plasmons present). This result will be used in Sec. IV to study the short-wavelength cutoff in the excitation of plasmons by electron scattering.

The one-electron wave functions are now time-dependent. If the unperturbed plane waves are designated by

$$\varphi_i(\mathbf{x},t)=V^{-\frac{1}{2}}\exp\{i[\mathbf{k}_i\cdot\mathbf{x}-E(\mathbf{k}_i)t/\hbar]\},$$

the perturbed wave functions will have the form

$$\psi_i(\mathbf{x},t)=\varphi_i(\mathbf{x},t) \times[1+A_i^{(+)}e^{i(\mathbf{k}\cdot\mathbf{x}-\omega t)}+A_i^{(-)}e^{-i(\mathbf{k}\cdot\mathbf{x}-\omega t)}]. \quad (28)$$

The self-consistent potential is in the form of the traveling wave $\varphi(\mathbf{x},t)=2\varphi_0\cos(\mathbf{k}\cdot\mathbf{x}-\omega t)$. The Hamiltonian operator which acts on the individual electrons is therefore time dependent and of the form H_0+H', where $H'=-e\varphi(\mathbf{x},t)$ and H_0 is the free-electron kinetic-energy operator. The time-dependent generalization of Hartree's equation is consequently

$$i\hbar\partial\psi(\mathbf{x},t)/\partial t=(H_0+H')\psi(\mathbf{x},t). \quad (29)$$

Substitution of Eq. (28) into Eq. (29) and collection of first-order terms yields

$$A_i^{(\pm)}=\frac{-e\varphi_0}{E(\mathbf{k}_i)-E(\mathbf{k}_i\pm\mathbf{k})\pm\hbar\omega} =\frac{e\varphi_0/\hbar}{\pm\hbar\mathbf{k}_i\cdot\mathbf{k}/m\mp\omega+\hbar k^2/2m}. \quad (30)$$

Recalling that the present electron momentum $\hbar\mathbf{k}_i$ differs from that of Eq. (4) by the term $(m\omega/k^2)\mathbf{k}$, one sees that Eqs. (30) and (4) are identical. Thus the

[14] P. Nozières and D. Pines (to be published). See also D. Pines, reference 10.

[15] Some work along this line has already been carried out by R. D. Myers (private communication).

requirement of self-consistency is the same as before, and results in the same dispersion relation.[16] (There is only a minor change in the Hartree field set up by the electrons; the additional time factors in the wave functions result in a running instead of a standing wave.) Zyrianov and Eleonskii have already sketched a somewhat different derivation in their note, and as a matter of fact, give an extension of the dispersion relation to any interaction which perturbs the particle plane waves only slightly. They also briefly discuss the extension of the time-dependent method to include the effect of exchange. We do not need to go into this here, since the work is straightforward and the results are the same as those of Sec. II.

Now that we have found a solution to the time-dependent Schrödinger equation corresponding to a collective oscillation of the system, it is desirable to determine the degree of excitation which the solution describes. The wave function for the complete system, Ψ, in terms of the one-electron wave functions, ψ_i, is given by

$$\Psi = A\prod_i \psi_i(\mathbf{x}_i,t), \tag{31}$$

where A is the antisymmetrizing operator. It is clear that if the ψ_i are substituted from Eq. (28) into Eq. (31) and multiplied out, a large number of terms (i.e., Slater determinants) will be obtained. If these are collected according to the power of $e^{-i\omega t}$ which accompanies them, then Ψ will assume the form of a generalized wave packet, in which each stationary-state wave function appears in the superposition with its own time factor. The time factor is simply the exponential function of $-it/\hbar$ times the energy eigenvalue associated with the stationary state of the system. The wave packet peaks at a certain energy of excitation. Significantly larger energies will not be present with appreciable probability in the expansion because the additional factors of $e^{-i\omega t}$ bring in further factors of $A_i^{(+)}$. (It is assumed that $A_i^{(\pm)}\ll 1$.) On the other hand, an energy appreciably smaller than the mean energy is improbable because of the smaller number of terms in Eq. (31) which correspond to such an energy. The situation is similar to the competition between the Boltzmann factor and the entropy, so familiar in statistical mechanics. In the present case, the most probable energy of excitation, which we write as $\nu\hbar\omega$, is easily determined from the equation

$$\begin{aligned}\nu &= (\hbar\omega)^{-1}\left[\left(\Psi, i\hbar\frac{\partial}{\partial t}\Psi\right)-\left(\Psi, i\hbar\frac{\partial}{\partial t}\Psi\right)\Big|_{A_i^{(\pm)}=0}\right]\\ &= (\hbar\omega)^{-1}\sum_i\left[\left(\psi_i, i\hbar\frac{\partial}{\partial t}\psi_i\right)-\left(\varphi_i, i\hbar\frac{\partial}{\partial t}\varphi_i\right)\right]\\ &= \sum_i(|A_i^{(+)}|^2-|A_i^{(-)}|^2).\end{aligned} \tag{32}$$

In arriving at this result it is first necessary to normalize the ψ_i by dividing by $(1+|A_i^{(+)}|^2+|A_i^{(-)}|^2)^{\frac{1}{2}}$. In addition, use is made of the orthogonality of ψ_i and ψ_j for $i\neq j$. The latter follows from Eq. (29), which can be used to show that (ψ_i,ψ_j) is a constant independent of time. It follows that the constant must equal zero except in the special case of resonance, $E_i-E_j=\pm\hbar\omega$, which does not arise in the present problem. *Note added in proof.*—The ψ_i defined by Eq. (28) are not strictly solutions of Eq. (29), since solving Eq. (29) to second order furnishes an additional time-dependent factor to every ψ_i. The contribution which these factors make to Eq. (32) is canceled by the total interaction energy, which must be subtracted whenever the Hartree-Fock method is strictly adhered to, so as not to count the pairwise interactions twice. Equation (32) can, of course, also be derived by simply adding to the total kinetic energy the total interaction energy.

It is desirable to note at this point that the degree of excitation or number of plasmons,[17] ν, can be calculated in an alternative way which exhibits more clearly the fact that the Pauli exclusion principle has been satisfied. It might be claimed that the term in ψ_i which contains the factor $A_i^{(+)}e^{i\mathbf{k}\cdot\mathbf{x}}$ should not contribute if the state $\mathbf{k}_j=\mathbf{k}_i+\mathbf{k}$ is already occupied. Similarly, the term in ψ_j containing $A_j^{(-)}e^{-i\mathbf{k}\cdot\mathbf{x}}$ should be omitted. But the energy denominators in the expressions for $A_i^{(+)}$ and $A_j^{(-)}$ are identical except for sign. Therefore these two contributions do indeed cancel from Eq. (32). The same is true for the quantity $\sum_i A_i = \sum_i(A_i^{(+)}+A_i^{(-)})$, which appears in Eqs. (6) and (7) of the preceding section.

Returning to Eq. (32), substituting from Eq. (30), and from $\omega_p^2=4\pi Ne^2/mV$, we find

$$\nu = (V\varphi_0^2k^2/2\pi\hbar\omega_p)G(\omega,\mathbf{k}), \tag{33}$$

where

$$G(\omega,\mathbf{k}) = N^{-1}\sum_i \frac{(\omega-\mathbf{k}\cdot\mathbf{v}_i)\omega_p^3}{[(\omega-\mathbf{k}\cdot\mathbf{v}_i)^2-\hbar^2k^4/4m^2]^2}.$$

Since the dispersion relation [Eq. (8)] determines ω_p in terms of ω and $\mathbf{k}$, G can be considered a function only of the latter two quantities. The general behavior of this function will be discussed in the next section. Let us here study only the limit of $k\to 0$, where $G\approx 1$. Then the energy of excitation is

$$\nu\hbar\omega_p = V\varphi_0^2k^2/2\pi. \tag{34}$$

This result is in complete agreement, as must be expected for the long-wavelength limit, with the following simple classical calculation: According to Poisson's equation the charge density is $(k^2/4\pi)\varphi(\mathbf{x},t)$. The total

[16] The Bohm-Pines dispersion relation can also be derived from the Lindhard theory of the dielectric constant [J. Lindhard, Kgl. Danske Videnskab. Selskab, Mat.-fys. Medd. 28, No. 8 (1954)]. The condition that a plasma oscillation of a given wavelength and frequency should be self-sustaining is that the dielectric constant, $K(\omega,\mathbf{k})$, should vanish. This follows from the equation $\mathbf{D}=K\mathbf{E}$ when the electric displacement $\mathbf{D}$ vanishes but there is present a nonzero fluctuating electric field $\mathbf{E}$. See also J. Hubbard, Proc. Phys. Soc. (London) A68, 441 and 976 (1955).

[17] The term "plasmon" has been introduced by D. Pines (reference 10) for the quantum of energy in a plasma oscillation.

potential energy is therefore

$$\frac{1}{2}\int\frac{k^2}{4\pi}\varphi(\mathbf{x},t)\varphi(\mathbf{x},t)d^3\mathbf{x}$$
$$=\frac{\varphi_0^2k^2}{2\pi}\int\cos^2(\mathbf{k}\cdot\mathbf{x}-\omega t)d^3\mathbf{x}=V\varphi_0^2k^2/4\pi.$$

This is exactly one-half the total energy of excitation, as must be the case for a harmonic oscillator.

We are now in a position to investigate the validity of the assumption $A_i^{(\pm)}\ll 1$. As a rough measure of $A_i^{(\pm)}$, consider the quantity $e\varphi_0/\hbar\omega_p$. From Eq. (34), we have

$$\left(\frac{e\varphi_0}{\hbar\omega_p}\right)^2=\frac{\nu\mathrm{ry}}{\pi\hbar\omega_p}\left(\frac{\lambda}{L}\right)^2\frac{a_0}{L}\ll 1, \tag{35}$$

where $\lambda=2\pi/k$ is the wavelength, a_0 is the Bohr radius, and the cube of quantization has edge of length L. The inequality is always satisfied if the excitations to be studied are restricted by $\nu\ll L/a_0$. This is, however, no real restriction and can be alleviated by using a larger volume of quantization. In the limit of an infinite number of electrons occupying an infinite volume, the above perturbation treatment of the self-consistent field equations is completely rigorous.

We conclude this section by studying the collective nature of the plasma oscillations. More specifically, we ask the question, how many electrons are excited per plasmon? Designating the expectation value for the number of electrons to be found outside the Fermi sea by ν', we have

$$\nu'=\sum_i{}'|A_i^{(+)}|^2+\sum_i{}''|A_i^{(-)}|^2, \tag{36}$$

where the primed and double-primed summations are performed over regions of the Fermi sea restricted by the exclusion principle. According to reference 1, Sec. III, the number of terms in each of these restricted sums is, for small k/k_0, (where k_0 is the Fermi wave number) approximately $3Nk/4k_0$. According to Eq. (30) $A_i^{(\pm)}$ is accurately given for small k by $\mp e\varphi_0/\hbar\omega_p$. Thus the number of plasmons per excited electron is

$$\frac{\nu}{\nu'}=\frac{V\varphi_0^2k^2}{2\pi\hbar\omega_p}\frac{2k_0}{3Nk}\left(\frac{\hbar\omega_p}{e\varphi_0}\right)^2=\frac{8\gamma}{3}\frac{k}{k_0}. \tag{37}$$

This ratio is very small for long-wavelength plasma oscillations. In this case each plasmon corresponds to the excitation of a very large number of electrons. On the other hand, as one passes to shorter wavelengths the smaller energy denominators in $A_i^{(+)}$ cause the first term in Eq. (36) to predominate over the second. Eventually (at the cutoff—see Sec. IV), the second term can be neglected compared to the first. The same approximation applies to Eq. (32), so that the ratio ν/ν' becomes in this case unity. In this limit only one excited electron will be found on the average outside the Fermi sea, for each plasmon of excitation. This simple result suggests an idealized quantum-mechanical model for the electron plasma, in which the ground state is represented by the unmodified Fermi sea and the excited state of one short-wavelength plasmon is represented by one-electron excitation.[18] It should be emphasized that a small ν/ν' ratio is in no way essential to or connected with the collective nature of the oscillations. The latter is due solely to the large number of electrons which are available to participate in the oscillations. At the short-wavelength limit, for example, a large fraction of all the electrons in the system participate. This is not inconsistent with the fact that, in this case, if a measurement of the electron momenta were carried out, only one electron per plasmon would be found with momentum in excess of the Fermi value. Speaking somewhat more pictorially, for a collective oscillation to be possible it is only necessary for an excited particle to be able to interact with the others in the system, so as to be able to pass along its excitation. It is not necessary for more than one particle to be excited at the same time. This is especially evident in a recent treatment of nuclear collective oscillations by one-nucleon excitation.[19]

IV. SHORT-WAVELENGTH CUTOFF

Equation (8) of Sec. II can be employed to calculate the plasma frequency for a given wavelength provided the summand is a well-behaved function of $\mathbf{v}_i$. This ceases to be the case when the energy denominator vanishes in at least one of the $A_i^{(+)}$ of Eq. (30). Then the excitation of some of the electrons conserves energy. This results in real transitions, which damp out the plasma oscillation. Letting p and v be the components of the electron momentum and velocity in the direction of propagation of the plasma wave, and using a crude approximation for the energy of transition, ΔE, we have

$$\Delta E\approx(\partial E/\partial p)\hbar k=v\hbar k. \tag{38}$$

Introducing the phase velocity of the plasma wave, $V=\omega/k$, and requiring conservation of energy upon absorption of a plasmon by an electron we find $v\hbar k\approx\hbar\omega$, or

$$v\approx V. \tag{39}$$

This equation is well known in classical plasma theory[3] as the condition for Landau trapping, and indicates that those waves will be damped whose propagation

[18] The consequences of this model have been reported by J. J. Quinn and the present author [Bull. Am. Phys. Soc. Ser. II, **1**, 44(1956)]. See also a paper which follows. *Note added in proof.*—Using the present self-consistent field treatment as a guide it has proved possible to include in this "momentum-exciton" model the effects of three-, five-, etc., electron excitation. By taking into account Feynman graphs in which the excitation makes a "jog" and travels backwards as well as forwards in time, one can derive the Bohm-Pines dispersion relation and the other results of the present paper without the necessity of working in the classical limit and invoking the *correspondence principle.*

[19] R. A. Ferrell and W. M. Visscher, Phys. Rev. **102**, 450 (1956); **104**, 475 (1956).

velocities coincide with some of the electron velocities of translation. In the present case of the degenerate electron gas v is limited by the Fermi value, v_0. On the other hand, V is roughly proportional to wavelength, (since ω is only weakly dependent on wavelength and can be approximated by ω_p), and increases without limit as one passes to very long wavelengths. Thus, damping only occurs for the short wavelengths, and first sets in for $v_0\hbar k_0(k/k_0)\approx\hbar\omega_p$. Designating the cutoff ratio by $k/k_0=\beta$, and noting that $v_0\hbar k_0$ is twice the Fermi energy, E_0, we have

$$\beta\approx(2\gamma)^{-1}=0.471\sqrt{r_s}. \tag{40}$$

This can be compared with Pines' expression,[20] obtained from the Bohm-Pines theory,

$$\beta_{\mathrm{BP}}=0.353\sqrt{r_s}. \tag{41}$$

Equation (40) gives a cutoff ratio 33% larger than does Eq. (41). No real inconsistency exists between these two expressions. Equation (41) refers to the optimal number of collective variables to be introduced into the Bohm-Pines theory, so as to best describe, (with a certain variational trial wave function), the long-range correlations in the ground state. There is nothing in the Bohm-Pines theory *a priori* to prevent shorter wavelength plasma oscillations from taking place, even though no variables have been introduced to describe them.

A cutoff determination which is more accurate than Eq. (40) is obtained when ΔE of Eq. (38) is equated to the actual transition energy, $(2\beta+\beta^2)E_0$, and when the functional dependence of ω on k is taken into account. Figure 1 shows a plot of the transition energy and of $\hbar\omega$[21] for the case $r_s=2$ (nearly aluminum, for which $r_s=2.07$). The continuum is due to electrons of less than the maximum velocity of v_0. As k/k_0 is increased the cutoff is encountered at the moment that the $\hbar\omega$ curve touches the continuum. The dashed line represents the approximate expression, Eq. (11). As seen from the figure, this terminated series expansion fails adequately to reproduce the fairly rapid rise in $\hbar\omega$ near the cutoff.[22] The actual cutoff ratio is 0.73 while the approximate value is 0.68, corresponding to an error of about 7%. [Equation (40) gives the slightly worse value of 0.666.] Fortunately, accurate values for β as a function of r_s can be obtained from the exact Bohm-Pines dispersion relation much more readily than the function $\omega(k)$ itself. It is only necessary in Eq. (8) to replace $\hbar\omega$ by $\Delta E=(2\beta+\beta^2)E_0$ and k by βk_0. Since ω_p is a function of r_s the resulting expression is a relation between β and r_s. Breaking the summand up into partial fractions and letting u_iv_0 be the component of the electron velocity along k, we have

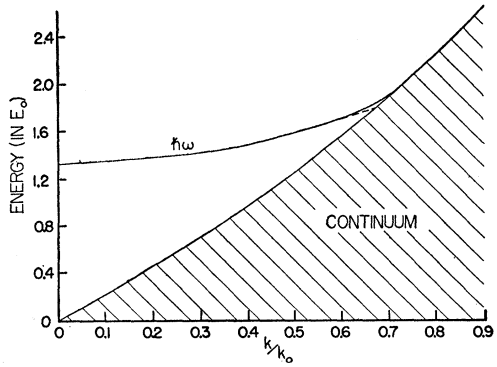

FIG. 1. Collective and individual electron excitation energies (in units of the Fermi energy), as functions of momentum (in units of the Fermi momentum) for $r_s=2$. The dashed curve represents the three-term approximation to the series expansion of the Bohm-Pines dispersion relation. The cutoff occurs for the momentum at which the collective excitation merges with and is in resonance with the continuum of individual electron excitation energies.

$$\begin{aligned}1&=\frac{m\omega_p^2}{k^2}N^{-1}\sum_i\left(\frac{1}{\hbar\omega-\hbar kv_0u_i-\hbar^2k^2/2m}\right.\\&\qquad\left.-\frac{1}{\hbar\omega-\hbar kv_0u_i+\hbar^2k^2/2m}\right)\\&=\left(\frac{\hbar\omega_p}{E_0}\right)^2\frac{1}{4\beta^3}N^{-1}\sum_i\left(\frac{1}{1-u_i}-\frac{1}{1-u_i+\beta}\right)\\&=\frac{3}{16\gamma^2\beta^3}\int_{-1}^{+1}\left(\frac{1}{1-u}-\frac{1}{1-u+\beta}\right)(1-u^2)du\\&=(3/16\gamma^2\beta^2)[(2+\beta)\ln(1+2/\beta)-2].\end{aligned} \tag{42}$$

Substituting for γ from Eq. (12c) and solving for r_s, we obtain

$$r_s=6.02\beta^2[(2+\beta)\ln(1+2/\beta)-2]^{-1}. \tag{43}$$

Since it is not possible to invert this relation and find β explicitly as a function of r_s, we have computed the latter as a function of β and have plotted the results in Fig. 2. From the curve thus obtained, one can read off β for any desired value of r_s. The significance of the upper portion of the curve, where β takes on values greater than unity, may well be questioned. The average electron spacing already becomes equal to a half-wavelength at about $k/k_0=0.82$. It is not clear whether

[20] Reference 9, Eq. (6.8).

[21] This function has been calculated from Eq. (8), and does not include the effect of exchange, which has been found in the preceding section to reduce the dispersion coefficient by the relatively minor amount of about 10% (for $r_s=2$). Since the effect of exchange on the dispersion relation as a whole has not yet been worked out, we are forced to neglect it. This is, however, not a serious handicap in the present section, since the goal here is to illustrate how, once the correct relation is known, it can be used to determine the cutoff. For the present purposes it is of no great consequence how this dispersion relation is obtained. One can even use the experimental dependence of ω on k, whenever this has been measured to sufficient accuracy. See, for example, reference 25 below.

[22] The behavior near cutoff has been obtained from Eq. (51) below. It is interesting to note that the eigenloss curve becomes tangent to the continuum at the point of contact.

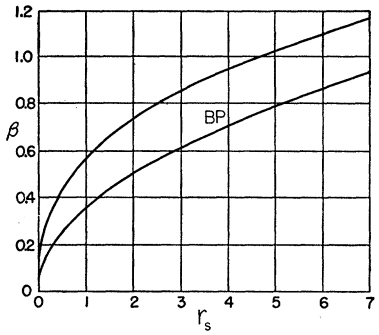

FIG. 2. The cutoff momentum (in units of the Fermi momentum) as function of r_s, the unit-sphere radius (in Bohr radii). The curve labelled "BP" is determined from Pines' expression, Eq. (41).

or not this is a relevant comparison. More conclusively, the large values of β correspond in turn to large values of r_s, or very low electron densities. For these densities the "condensation" of the electrons into a body-centered cubic lattice can be expected to set in. There will be strong electron-electron positional correlations in the ground state of the system[23] and the simple Fermi sea description, which is at the basis of the present work, will no longer be applicable.

On the other hand, in the passage to the high-density limit, Eq. (43) can be expected to become quite reliable. As can be seen from Fig. 2, for small r_s the cutoff ratio becomes very much larger than the Bohm-Pines cutoff parameter, which is also plotted for comparison. Since

$$r_s \sim 3.01\beta^2 \ln^{-1}\beta^{-1}, \tag{44}$$

the ratio of the cutoff parameters is asymptotically equal to $(2.67 \ln\beta^{-1})^{\frac{1}{2}}$ and becomes infinite as $r_s \to 0$. The ratio is already considerably greater than unity in the range of the naturally occurring electron densities. This removes a discrepancy which was encountered in the first comparison[24] of the experimental results of Watanabe with the Bohm-Pines theory. The latter gave for the maximum angle of scattering in aluminum $\beta_{BP}(E_0/E)^{\frac{1}{2}}=11.0$ milliradians, where E is the energy of bombardment (25 kev in Watanabe's experiment). But according to Fig. 2, in place of $\beta_{BP}=0.507$ one should use $\beta=0.74$. This increase of 46% raises the cutoff angle to 16.0 milliradians.[25] Watanabe reports that the eigenloss fades into the background at 15–18 milliradians.

The peculiar high-density behavior of the cutoff expressed by Eq. (44) is unexpected and bears closer examination. In particular, we want to study in detail the manner in which $\hbar\omega$ approaches and merges with the continuum of one-electron excitation energies.[26] This is facilitated by a simplification which the high-density limit introduces into the Bohm-Pines dispersion relation, By steps similar to those yielding Eq. (42), Eq. (8) can be integrated and put into the form

$$1=\left(\frac{3}{64\gamma^2z^2}\right)\left[\frac{(u-z)^2-1}{2z}\ln\left(\frac{u-z-1}{u-z+1}\right)+\frac{(u+z)^2-1}{2z}\ln\left(\frac{u+z+1}{u+z-1}\right)-2\right]. \tag{44a}$$

Here we are using Lindhard's[27] variables $z=k/2k_0$ and $u=\omega/kv_0$. Thus, u is the ratio of the plasma phase velocity to the Fermi velocity. At high electron densities, z is restricted to very small values. Expanding the quantity inside the brackets in powers of z and keeping only the first nonvanishing term yields $2u\ln[(u+1)/(u-1)]-4$. Hence the plasmon energy, $\hbar\omega$, depends on the wave number only through the combination $4\gamma z=2\gamma k/k_0$. This dimensionless variable measures the top of the one-electron continuum in units of $\hbar\omega_p$. In terms of it we have $\omega/\omega_p=u(2\gamma k/k_0)$. Equation (44a) reduces, with the above high-density approximation, to

$$2\gamma k/k_0=\left[\frac{3u}{2}\ln\left(\frac{u+1}{u-1}\right)-3\right]^{\frac{1}{2}}. \tag{44b}$$

From this simplified dispersion relation, it is possible to obtain the plot of ω/ω_p as a function $2\gamma k/k_0$ shown in Fig. 3. The cutoff determined by Eq. (44) occurs at a very large value of $2\gamma k/k_0$, for the high-density case. But for values greater than two, the plasmon energy lies very close to the top of the continuum (shown by the straight line in Fig. 3). Thus the tangential portion of the eigenloss curve already noted in reference 22 in reference to Fig. 1 now accounts for most of the interval of variation of k/k_0. [It should be mentioned that the

[23] See, for example, J. S. Plaskett, Phil. Mag. **45**, 1255 (1954).

[24] See reference 6, p. 117 and reference 9, p. 493.

[25] As mentioned above (reference 21), this calculation neglects exchange, which may be expected to lower the cutoff. On the other hand, the large dispersion coefficient found experimentally by Watanabe seems to indicate that the positive-ion lattice has an effect on the dispersion relation which more than compensates for that of exchange. If one uses Watanabe's experimental $(k/k_0)^2$ and $(k/k_0)^4$ coefficients one finds a cutoff ratio of 0.70 and a cutoff angle of 15.1 milliradians. *Note added in proof.*—G. Meyer, [Z. Physik **148**, 61 (1957)], has recently also completed an experimental investigation of the 15-ev eigenloss in aluminum. With his incident energy of 30 kev the cutoff should be expected at 14.6 milliradians. This is consistent with his measurements which exhibit the (somewhat broadened) eigenloss at 11.1 milliradians, but show only the broad excitation to the continuum at 14.9 milliradians. Meyer himself claims to calculate 11 milliradians by using the mean separation of the electrons as a cutoff criterion. As explained above, this criterion has no sound basis and is actually incorrect for values of r_s less than three, for which it yields too large a cutoff angle. In the present case it would give 16.2 milliradians, so that we are forced to the conclusion that Meyer's calculated cutoff angle must be numerically in error. Of further interest is the value of the dispersion coefficient which can be inferred from Meyer's Fig. 5. We find 0.53 ± 0.10, which is significantly less than Watanabe's value and agrees with the theoretical value including exchange (see Table I).

[26] The author wishes to thank Professor K. A. Brueckner for interesting discussion on this point.

[27] Equation (44a) can also be obtained from Lindhard's equation (37) (reference 16) by setting his expression for the dielectric constant equal to zero.

approximations made in deriving Eq. (44b) are not valid in the vicinity of the cutoff.] In this tangential region the stability of the plasma oscillations with respect to damping might well be questioned. A small perturbation might shift the plasmon energy down into the one-electron continuum. More conclusively, as shown at the end of Sec. V, such plasma oscillations are not excited by inelastic scattering of fast electrons. An expression for the fractional contribution of plasmon excitation to the sum rule is derived there and plotted as the lower curve in Fig. 3. It will be noted that this has already dropped by a factor of about two at $2\gamma k/k_0=2$, or $k/k_0=\gamma^{-1}$. This value of k/k_0 is twice that given by Eq. (40), and can be taken as the effective "cutoff" at high density. The eigenloss intensity relative to the lower-lying continuum is considerably less than one-half at this point, since the sum rule weights the intensities according to their excitation energies. Thus it must be concluded that the cutoff determined by Eq. (44) is of a rather artificial nature at high density. The actual eigenloss scattering intensity undergoes a gradual "cutoff" at momentum values given by a factor of the order of $r_s^{\frac{1}{2}}$ times the Fermi momentum.

We conclude this section with a discussion of the variation of the intensity of the eigenloss beam as a function of scattering angle, in the vicinity of the cutoff. An incident electron, passing through a metal foil in which there is present a plasma oscillation of the type treated in Sec. III, experiences the interaction

$$-e\varphi(\mathbf{x},t)=-e\varphi_0 e^{i(\mathbf{k}\cdot\mathbf{x}-\omega t)}-e\varphi_0 e^{-i(\mathbf{k}\cdot\mathbf{x}-\omega t)}.$$

The second term can cause the incident electron to lose

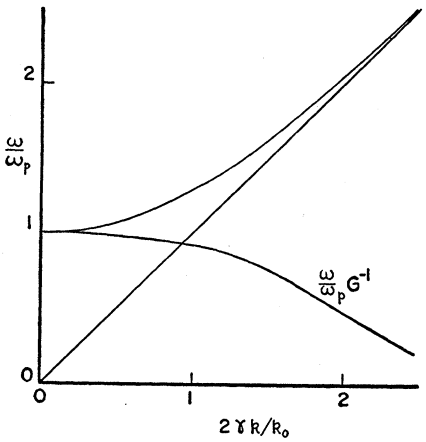

FIG. 3. Dispersion relation and angular dependence of eigenloss intensity for high electron density. The upper curve gives the ratio of the plasma frequency, ω, to the classical frequency, ω_p, as a function of 2γ times momentum (in units of the Fermi momentum). γ is the ratio of the Fermi energy to $\hbar\omega_p$ and equals $1.061\, r_s^{-\frac{1}{2}}$, where r_s is the unit-sphere radius (in Bohr radii). The straight line represents the energy (in units of $\hbar\omega_p$) at the top of the continuum of one-electron excitations. Note how the plasma excitation energy approaches the continuum asymptotically. The lower curve gives the fractional contribution of plasma excitation to the sum rule limit.

energy. The squared matrix element for this process is $e^2\varphi_0^2$, and corresponds to the excitation of the plasma oscillator from the νth to the $(\nu+1)$th state, where ν is the quantum number of excitation, determined in Sec. III above. From Eq. (33) we can eliminate φ_0^2 in terms of ν, to obtain for the squared matrix element an expression proportional to ν. This simple linear dependence on the excitation quantum number is characteristic of the harmonic oscillator. Although the present method is only able to handle the case of large ν, corresponding to the classical limit, we can treat also the small ν case by applying Bohr's *correspondence principle*. A quantum-mechanical approach, (such as that of reference 1), will yield the same linear dependence on ν and according to the *correspondence principle* must in addition agree with the present result for large ν. The proportionality constant is thereby determined, and one is able to write down the squared matrix element for absorption of energy by the plasma, or in other words, plasmon creation. An important special case is plasmon creation in the ground state. By dividing $e^2\varphi_0^2$ by ν, (or, actually, $\nu+1$ but the difference is inappreciable for large ν), we obtain the following squared matrix element:

$$|H_{\mathbf{k}}'|^2=G^{-1}2\pi e^2\hbar\omega_p/Vk^2. \tag{45}$$

G is the function defined in Sec. III [following Eq. (33)]. For small k, $G\approx 1$, and Eq. (45) becomes identical to Eq. (5) of reference 1. Equation (8) derived there for the angular dependence of the intensity of the eigenloss beam consequently still holds for small angles, but is reduced at larger angles by the factor G^{-1}.

To estimate the reduction in plasmon production as the angle is increased, we can make a series expansion similar to that leading to Eq. (9) in Sec. II. Working to order k^4, we find

$$G=\left\langle\frac{\omega_p^3(\omega-\mathbf{k}\cdot\mathbf{v}_i)}{[(\omega-\mathbf{k}\cdot\mathbf{v}_i)^2-\hbar^2k^4/4m^2]^2}\right\rangle$$
$$=(\omega_p/\omega)^3+2(\omega_p/\omega)^5\omega_p^{-2}k^2\langle v^2\rangle$$
$$+3\omega_p^{-4}k^4\langle v^4\rangle+\hbar^2k^4/2m^2\omega_p^2+\cdots. \tag{46}$$

Substituting from Eq. (11) and taking the inverse yields

$$G^{-1}=1-\frac{6}{5}\gamma^2(k/k_0)^2+\left(\frac{18}{35}\gamma^4-\frac{1}{2}\gamma^2\right)(k/k_0)^4+\cdots. \tag{47}$$

The function represented by the first three terms has been plotted as a dashed line in Fig. 4, for the case of $r_s=2$. As k/k_0 is increased this approximation becomes inaccurate and G^{-1} decreases more rapidly than the first three terms of Eq. (47) would indicate. In the vicinity of the cutoff G^{-1} drops rapidly to zero. The asymptotic behavior at the cutoff is conveniently found from the top line of Eq. (46) by factoring the

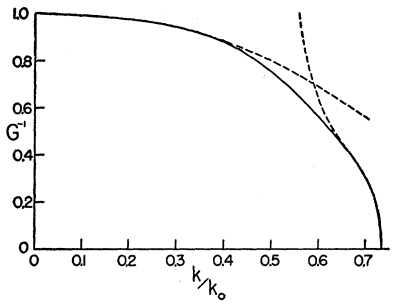

FIG. 4. Eigenloss-intensity reduction factor as function of plasmon momentum (in units of the Fermi momentum) for $r_s=2$. The dashed lines represent approximate expressions. Note the rapid decrease in scattering intensity in the vicinity of the cutoff $k/k_0=0.73$.

denominator and by making the replacements $\mathbf{k}\cdot\mathbf{v}_i\rightarrow kv_0$ and $\omega\rightarrow kv_0+\hbar k^2/2m$ in the nonsingular parts of G. Introducing $y=\beta-k/k_0$ for the distance from the cutoff, we have asymptotically

$$G\sim(m\omega_p{}^3/2\hbar k^2)\langle(\omega-\mathbf{k}\cdot\mathbf{v}_i-\hbar k^2/2m)^{-2}\rangle$$
$$\sim(m\hbar^3\omega_p{}^3/2\hbar^2k^2)\langle[\hbar\omega-2E_0(k/k_0)u_i-E_0(k/k_0)^2]^{-2}\rangle$$
$$\sim16^{-1}\gamma^{-3}\beta^{-4}\langle(1+f(y)-u_i)^{-2}\rangle. \quad (48)$$

Here we have replaced $(k_0/2k)[\hbar\omega/E_0-2(k/k_0)-(k/k_0)^2]$ by $f(y)$. This function is a measure of the amount by which the eigenloss lies above the continuum. The definition of u_i has been given earlier in this section. Near the cutoff the dominant contribution to G comes from electrons near the surface of the Fermi sea, with $u\sim1$. Therefore it is desirable to introduce the new variable $u'=1-u$. The average in Eq. (48) can now be expressed as the integral

$$\langle\,\rangle=N^{-1}\frac{V}{8\pi^3}2\int d^3\mathbf{k}=\frac{k_0{}^3}{4\pi^3n}\int_{-1}^{+1}du\,\pi(1-u^2)$$
$$=\frac{3}{2}\int_0^2 du'\,u'(1-u'/2).$$

In the present case, the upper limit can be left indefinite, and the second factor in the integrand neglected. Thus we obtain the asymptotic equivalences

$$\langle[1+f(y)-u_i]^{-2}\rangle\sim\frac{3}{2}\int_0\frac{u'du'}{(u'+f)^2}\sim\tfrac{3}{2}\ln(f^{-1}).$$

The behavior of the reduction factor in the vicinity of the cutoff is therefore given by

$$G^{-1}\sim32\gamma^3\beta^4/3\ln(f^{-1}). \quad (49)$$

The numerical coefficient in Eq. (49) is of the order of unity, so that small values of G^{-1} occur only very near the cutoff. The function $f(y)$ can be determined by explicitly carrying out the summation over velocities which is indicated in the dispersion relation, Eq. (8). Substituting $u=1+z+f$ and $z=k/2k_0$ into Eq. (44a), we find

$$\frac{3}{16\gamma^2}\left(\frac{k}{k_0}\right)^{-3}\left\{\left[2\left(f+\frac{k}{k_0}\right)+\left(f+\frac{k}{k_0}\right)^2\right]\ln\left(\frac{2+f+k/k_0}{f+k/k_0}\right)\right.$$
$$\left.-2k/k_0-(2f+f^2)\ln(1+2/f)\right\}=1. \quad (50)$$

Making approximations suitable for small y reduces this [by means of Eq. (42)] to

$$f\ln(f^{-1})=(2+\beta)^{-1}[2+8\gamma^2\beta^2(4+\beta)/3]y. \quad (51)$$

Since it is not possible to solve this simple relationship explicitly for f as a function of y and then substitute into Eq. (49), we have instead solved for f from Eq. (49) and substituted into Eq. (51), thereby obtaining y as a function of G^{-1}. For the particular case of $r_s=2$ the resulting equation has also been plotted in Fig. 4, again as a dashed line. The solid line has been drawn to join on smoothly to the two dashed lines in their regions of validity, and represents the inferred behavior of the reduction factor for all values of k/k_0. The error involved in drawing this interpolation curve could be avoided by explicitly carrying out the integration implicit in the definition of G. This can be accomplished in terms of elementary functions, but the labor involved does not seem warranted at present. The above approximate results are sufficient to establish that the angular dependence derived in reference 1 is substantially correct, except near the cutoff, where the intensity of the eigenloss beam drops abruptly. This conclusion does not apply to the case of high density, however, which requires special study and is discussed at the end of the next section.

V. PREDOMINANCE OF COLLECTIVE EXCITATION

As emphasized in reference 1, a fast electron passing through a metal foil can lose energy by either of the two alternatives of collective or one-electron excitation. Having studied collective excitation in the preceding sections we now want to conclude our discussion with a quantitative treatment of the alternative mechanism of one-electron excitation. This is facilitated by a sum rule which was encountered in Sec. III of reference 1 (where it was noted that the differential stopping power was independent of the interaction between electrons), but which seems to have first been recognized by Nozières and Pines.[10,14] In the notation of reference 1, their sum rule requires

$$\sum_n f_{n0}{}^{\mathbf{k}}=N, \quad (52)$$

where

$$f_{n0}{}^{\mathbf{k}}=(2m\omega_{n0}/\hbar k^2)\,|\,V(\rho_{\mathbf{k}})_{n0}\,|^2. \quad (53)$$

The matrix element is taken between the ground state and the nth excited state, and the sum is over all excited states. As they state, the proof is quite straight-

forward. It is most easily carried out by considering

$$\sum_n (f_{n0}{}^{\mathbf{k}}+f_{n0}{}^{-\mathbf{k}}) = -(2m/\hbar^2k^2)\langle[[H,V\rho_{\mathbf{k}}],V\rho_{-\mathbf{k}}]\rangle_0 = 2N. \quad (54)$$

Equation (52) then follows, since there is no preferred direction in the ground state and the individual sums for $+\mathbf{k}$ and $-\mathbf{k}$ are equal. Equation (54) is a generalization of the Nozières-Pines sum rule to excited states where this equality of individual sums no longer holds.

Designating the one-plasmon state of momentum $\hbar\mathbf{k}$ by $n=1$, let us now evaluate the oscillator strength $f_{10}{}^{\mathbf{k}}$. From Eq. (45) and the definition of H' in terms of $\rho_{\mathbf{k}}$[28] we find

$$|(\rho_{\mathbf{k}})_{10}|^2 = (k^2\hbar\omega_p/8\pi e^2V)G^{-1},$$

giving

$$f_{10}{}^{\mathbf{k}} = (\omega/\omega_p)G^{-1}N. \quad (55)$$

ω_{10} has been replaced by ω, the frequency of a plasma vibration of wave number k. Both ω/ω_p and G^{-1} approach unity as $k\to 0$. Thus in this limit the sum rule is exhausted by the collective excitation alone. by substituting from Eqs. (11) and (47) into Eq. (55) we can determine for any particular value of k the fraction of the sum-rule limit accounted for by the plasmon state. The sum rule itself then gives the fraction of the total contributed by one-electron excitation:

$$\sum_{n\neq 1} f_{n0}{}^{\mathbf{k}}/N = 1-(\omega/\omega_p)G^{-1} = (192/175)\gamma^4(k/k_0)^4+\cdots. \quad (56)$$

It is interesting to note that, to order $(k/k_0)^2$, the falloff in eigenloss intensity is just that required to compensate for the rise in ω/ω_p and avoid exceeding the sum-rule limit. To this order, the collective excitation continues to exhause the sum rule—failing to do so first in order $(k/k_0)^4$. The first term of Eq. (56) is an accurate representation of the one-electron contribution only for relatively small k/k_0. It yields about 10% at the cutoff, for $r_s=2$, while the actual one-electron fraction must increase much more rapidly in the neighborhood of this value of k/k_0 and becomes unity when it is attained.

For the case of high electron density the one-electron excitation contribution to the sum-rule limit has a considerably different momentum dependence, and assumes almost the entire value of the sum already for momentum values much smaller than the cutoff momentum, as determined from Eq. (44). The eigenloss therefore undergoes an effective cutoff in the region of these much smaller momentum values. The fading out of the eigenloss intensity can be studied in detail by making the high-density approximation of neglecting the $-\hbar^2k^4/4m^2$ term in the expression for the reduction factor and by carrying out an integration similar to that in Eq. (42). Using the variables already introduced in the preceding section for treating the dispersion relation at high density, one finds

$$G\approx\left\langle\frac{\omega_p{}^3}{(\omega-\mathbf{k}\cdot\mathbf{v}_i)^3}\right\rangle = \frac{3}{4(2\gamma k/k_0)^3}\left[\frac{2u}{u^2-1}-\ln\left(\frac{u+1}{u-1}\right)\right]. \quad (57)$$

From this equation and Eq. (44b) the fractional plasma contribution to the sum rule, $(\omega/\omega_p)G^{-1}$, has been computed as a function of the dimensionless variable $2\gamma k/k_0$ and plotted as the lower curve in Fig. 3. The plasma contribution drops below 50% at a momentum value approximately equal to $r_s^{\frac{1}{2}}$ times the Fermi momentum.

VI. SUMMARY

Although the work in this paper has been carried out outside the framework of the Bohm-Pines theory, we feel that the latter provides the only complete treatment of all the properties of metals connected with the Coulomb interactions of the electrons (cohesive energy, specific heat, etc., as well as plasma oscillations). We have not employed in the present work the theory of Bohm and Pines simply in the interest of simplicity, and are confident that the results obtained can also be deduced from their more general theory. In addition we have been motivated to treat the plasma oscillations without the introduction of collective coordinates so as to avoid some of the uncertainties associated with the subsidiary conditions. We do not regard the latter as serious difficulties and feel that the Bohm-Pines theory is valid in its essentials. The relatively small cutoff wavelength found in Sec. IV does, however, focus attention on the question of the subsidiary conditions. With these larger values of β the plasma oscillations account for an appreciable fraction of the total number of degrees of freedom in most metals. It would also seem that the range of the residual screened Coulomb potential must be shorter than determined by Pines, since it is intimately related to the cutoff wavelength.

It should be emphasized that all of the results obtained in Secs. III, IV, and V are subject to corrections due to electron exchange and to the positive-ion lattice. The first type has been estimated in Sec. II in connection with the dispersion relation and has been found to be relatively minor. The second type can, on the other hand, radically affect the nature of the plasma oscillations. These cannot only be shifted in frequency but in some cases be severely damped. This latter is easily understood on the basis of Fig. 1, which indicates the ideal case where the lifetime of a plasmon would be infinitely long. This is because, for momenta smaller than the cutoff value, the plasmon energy is cleanly separated from the lower lying continuum of one-

[28] See reference 1, p. 557.

electron transition energies.[29] This ceases to be the case when the lattice sufficiently modulates the electron wave functions that it furnishes to the electrons to an appreciable extent multiples of the reciprocal lattice vectors. By virtue of this additional momentum conveyed by the lattice, the one-electron transition energies are no longer limited to small values but instead form a continuum which extends up to and beyond the plasmon energy. As a consequence the plasma excitation will show up in the electron energy-loss experiments as a broad eigenloss which may in some cases lose its identity and merge with the background of the one-electron continuum. In these cases both collective and one-electron transitions are involved and a point of view which took only one aspect of the phenomenon into account would be inadequate. A quantitative treatment of some actual cases of this type would be quite desirable, but must remain a subject for future study.

APPENDIX I. EXCHANGE CORRECTION TO DISPERSION COEFFICIENT

We follow the procedure outlined in the text and linearize the integral exchange operator which appears as the first mathematical expression following Eqs. (12a–c). Assuming the $A_j^{(\pm)}$ to be real and calculating only to lowest order in k, we find that the matrix element of this perturbing operator for the transition between the unperturbed state φ_i and the state $\varphi_i e^{\pm i\mathbf{k}\cdot\mathbf{x}}$ is

$$-(2\pi e^2/V)\sum_j A_j/|\mathbf{k}_i-\mathbf{k}_j|^2.$$

Therefore in place of the matrix element for the Hartree field alone, $-e\varphi_0$, which appears in Eq. (5) and is given in Eq. (7), we should have

$$(4\pi e^2/k^2V)\sum_j(1-f_{ij})A_j,$$

where

$$f_{ij}=k^2/2|\mathbf{k}_i-\mathbf{k}_j|^2. \tag{13}$$

[29] Throughout this work we have ignored the damping of the plasma oscillations by two-electron excitation—via short-range collisions. Although this becomes appreciable at the short wavelengths, according to the estimate of Nozières and Pines [reference 10, Eq. (28)], it varies smoothly with wavelength and is unlikely to obscure the much more abrupt cutoff discussed in the present work, which is due to one-electron excitation. (In this equation the quantities τ_1 and ω_p should evidently be replaced by their reciprocals). In any case, the cutoff determined here is the maximum possible.

If we further introduce

$$F_i=[(\omega-\mathbf{k}\cdot\mathbf{v}_i)^2-\hbar^2k^4/4m^2]^{\frac{1}{2}}, \tag{14}$$

$$a_i=F_iA_i, \tag{15}$$

$$L_{ij}=N^{-1}F_i^{-1}F_j^{-1}, \tag{16}$$

$$L_{ij}'=-L_{ij}f_{ij}, \tag{17}$$

$$\lambda=\omega_p^{-2}, \tag{18}$$

we obtain from Eq. (5) the homogeneous linear equations

$$\sum_j(L_{ij}+L_{ij}')a_j=\lambda a_i. \tag{19}$$

A set of a_i's which satisfy these equations can be considered an "eigenvector" of the linear self-adjoint operator $L_{ij}+L_{ij}'$, associated with the eigenvalue λ. Purely for the purpose of solving the formal mathematical problem posed by Eq. (19) ω and $\mathbf{k}$ can be considered as given, and, in searching for an eigensolution, λ can be considered to vary. This is permissible since the electron charge appears only in λ and nowhere else in Eq. (19). The procedure thus amounts to finding what strength of interaction will sustain a plasma oscillation of a specified frequency and wavelength. Once the relationship is established, it can be used to find the plasma frequency as a function of wave number, for the naturally occurring value of the electron charge.

Since we are interested here only in solving Eq. (19) for small k, we can use perturbation theory to evaluate the shift in λ caused by the perturbation L_{ij}'. The "zero-order eigenvector" is given, to sufficient accuracy, by $a_i=N^{-\frac{1}{2}}$, so the perturbation in λ is

$$\Delta\lambda=\sum_{i,j}a_iL_{ij}'a_j=N^{-1}\sum_{i,j}L_{ij}'\approx-\frac{k^2}{2\omega^2N^2}\sum_{i,j}\frac{1}{|\mathbf{k}_i-\mathbf{k}_j|^2}. \tag{20}$$

It is not necessary to evaluate here this double sum over the Fermi sea, since it is essentially identical to the well-known expression for the exchange energy per electron,[12]

$$E_{\text{ex}}=-\frac{2\pi ne^2}{N^2}\sum_{i,j}\frac{1}{|\mathbf{k}_i-\mathbf{k}_j|^2}. \tag{21}$$

Thus we find

$$\Delta\omega_p^2=-\lambda^{-2}\Delta\lambda=-\omega_p^4\Delta\lambda\approx-E_{\text{ex}}k^2/m, \tag{22}$$

which, in conjunction with Eq. (9), yields

$$\omega_p^2=\omega^2-k^2\langle v^2\rangle-E_{\text{ex}}k^2/m. \tag{23}$$