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A Collective Description of Electron Interactions: IV. Electron Interaction in Metals

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The effects of the Coulomb interaction between free electrons in an electron gas are considered for a variety of phenomena. The analysis is based on the collective description, which describes the long-range correlations in electronic positions (due to the Coulomb force) in terms of the collective oscillations of the system as a whole. It is shown that an independent electron model should provide a good description of the electrons in a metal in many cases of interest. The ground state energy of the free electron gas is determined, and an estimate of the correlation energy is obtained, with results in good agreement with those of Wigner. The exchange energy is shown to be greatly reduced by the long-range correlations, so that its effect on the level density and the specific heat is comparatively slight, leading to an electronic specific heat for Na which is approximately 80 percent of the free-electron value. The possible ferromagnetism of a free-electron gas is investigated, and it is found that the long-range Coulomb correlations are such that a free-electron gas will never become ferromagnetic (no matter how low the density). The excitation of the collective oscillations by a fast charged particle is studied, and the semiclassical results obtained by Bohm and Pines are verified by a quantum-mechanical calculation. The results are applied to the experiments of Ruthermann and Lang on the scattering of electrons by thin metallic films and to experiments on the stopping power of light metals for fast charged particles, with resulting good agreement between theory and experiment.

I.

IN the preceding paper,[1] a quantum-mechanical collective description of the electrons in a dense-electron gas has been developed. In this paper we wish to apply this collective description to the motion of the conduction electrons in metals. In so doing, we shall assume that the effect of the positive ions in the metal may be represented by a smeared out uniform background of positive charge. This assumption should be quite a good one for the alkali metals (in which the electronic wave functions are almost plane waves), and we may expect it to apply generally for any metallic phenomenon in which the periodicity of the lattice plays no important role. In assuming a uniform positive charge, we are also neglecting the ionic charge density fluctuations and so cannot consider the interaction of the electrons with the lattice vibrations. Actually, a collective description of the ionic motion is also possible and offers a promising approach to the treatment of problems in which the electron-lattice interaction plays an important role.[2,3]

We also assume that the only interactions of importance for the conduction electrons in a metal are those with the other conduction electrons. If this is not true, as might be the case if, for instance, the exchange interaction with the core electrons is large, then the collective description may well become inapplicable. For the validity of the collective description requires that the mean collision time for electron collisions which tend to disrupt the collective motion should be large compared to the period of a collective oscillation. This follows from the fact that the effect of these disruptive collisions is to cause damping of the collective oscillation, and the criterion,

$$\tau_{\text{coll}} \gg 2\pi/\omega_p, \tag{1}$$

is just the criterion that such damping be small.[4] If (1) is not valid then the damping is large, and the whole concept of collective oscillation loses its significance in a description of electron interaction.

The criterion (1) will be satisfied for a free-electron gas, since as was shown in Paper III, the only collisions which act to disrupt organized motion are via the short-range screened Coulomb force, and for an almost degenerate Fermi gas these lead to a collision time considerably larger than $2\pi/\omega_p$. This will also be the case for the collisions between the electrons and the lattice vibrations in metals, since the mean free time between such collisions is $\gtrsim 10^{-12}$ sec, which is long compared to the period of a collective oscillation. Whether the criterion (1) is satisfied for other disruptive effects requires detailed investigation for the metal in consideration, and we shall not enter on such questions here.

We first apply the collective description to a consideration of the widespread success of the independent electron model for the motion of electrons in metals. In this model, the motion of a given electron is assumed, in first approximation, to be independent of the motion of all the other electrons. The effect of the other electrons on this electron is then represented by a smeared-out potential, which can be determined by using the self-consistent field methods of Hartree and Fock. In this one-electron approximation, the correlations in the position and energy of the electrons due to their Coulomb interactions are treated as small perturbations, and often entirely neglected. It is rather puzzling that such an independent electron model should have been so successful qualitatively, and in many cases, quantitatively, since the Coulomb inter-

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[1] D. Bohm and D. Pines, preceding paper [Phys. Rev. 92, 609 (1953)]. This paper will hereafter be referred to as Paper III. The earlier papers in this series, hereafter referred to as I and II, respectively, are D. Bohm and D. Pines, Phys. Rev. 82, 625 (1951) and D. Pines and D. Bohm, Phys. Rev. 85, 338 (1952).

[2] D. Bohm and T. Staver, Phys. Rev. 84, 836 (1951).

[3] T. Staver, Ph.D. thesis, Princeton University, 1952 (unpublished).

[4] D. Bohm and E. P. Gross, Phys. Rev. 75, 1864 (1949).

action is a long-range interaction and might be expected to affect profoundly the electron motion in metals. In fact, as we have seen, it does bring about long-range correlations in the electron positions and so leads to organized oscillation of the electron system as a whole, a phenomenon which cannot be described in terms of an independent electron model.

The introduction of the collective description enables us to investigate in some detail just what physical phenomena are associated with the long-range aspects of the Coulomb force. We may sum up the mathematical results obtained in Paper III by writing down our Hamiltonian in the collective description. If we use Eqs. (59), (60), and (61) of III, we find

$$H=H_{\text{part}}+H_{\text{coll}}+H_{\text{s.r.}}, \tag{2}$$

where

$$H_{\text{part}}=\sum_i \frac{P_i^2}{2m}\left(1-\frac{n'}{3n}\right)-2\pi ne^2\sum_{k<k_c}\frac{1}{k^2}, \tag{3}$$

$$H_{\text{coll}}=\sum_{k<k_c}(\hbar\omega/2)(A_k{}^*A_k+A_kA_k{}^*), \tag{4}$$

$$H_{\text{s.r.}}=2\pi e^2\sum_{\substack{i\neq j\\ k>k_c}}\frac{\exp[i\mathbf{k}\cdot(\mathbf{X}_i-\mathbf{X}_j)]}{k^2}. \tag{5}$$

We also have a set of subsidiary conditions on our electronic wave functions which are [Eq. (65), III]

$$\sum_i \frac{\omega^2}{\omega^2-(\mathbf{k}\cdot\mathbf{P}_i/m-\hbar k^2/2m)^2}\exp(i\mathbf{k}\cdot\mathbf{X}_i)\Psi=0. \tag{6}$$

The above Hamiltonian and subsidiary conditions are accurate to order

$$\alpha=(\mathbf{k}\cdot\mathbf{P}_i/m\omega)^2{}_{\text{Av}} \tag{7}$$

or $(n'/3n)$ with respect to the electronic kinetic energy and the zero-point energy of the collective oscillations. As we shall see, this constitutes quite an accurate approximation. We have also neglected $H_{\text{r.p.}}$ [Eq. (73), III] since as pointed out in III, it will produce negligible effects when compared with $H_{\text{s.r.}}$, and this latter term itself is small.

We see from (2)–(5) that the long-range part of the Coulomb interactions has been effectively redescribed in terms of the collective oscillations of the system as a whole. The frequency of these oscillations is, from [Eq. (67), III],

$$\omega=\omega_p\left(1+\frac{k^2}{2nm^2}\sum_i\frac{P_i^2}{\omega^2{}_p}+\frac{\hbar^2k^4}{8m^2\omega_p{}^2}\right). \tag{8}$$

It may easily be seen that the energy of a quantum of collective oscillation is so high (being greater than the energy of an electron at the top of the Fermi distribution) that these will not be excited in metals at ordinary temperatures, and hence may not be expected to play an important role in our description of a metal under ordinary conditions. (We discuss the excitation of these oscillations by an external fast charged particle in Sec. V.)

The remainder of our Hamiltonian corresponds to a collection of individual electrons interacting via a comparatively weak short-range force $H_{\text{s.r.}}$. These electrons differ from the usual "free" electrons in that they possess a slightly larger effective mass,

$$m^*=(m/[1-(n'/3n)]), \tag{9}$$

and their wave functions are subject to a set of n' restrictions, as given by the subsidiary conditions (6). However, in the limit of small $n'/3n$, we may expect that both of these changes are unimportant qualitatively (and in some cases quantitatively). Furthermore, since the effective electron-electron interaction is so greatly reduced in our collective description, we should expect that it is quite a good approximation to neglect it for many applications. Thus we are led directly to the independent electron model for a metal.

The use of the collective description not only enables us to understand qualitatively the general success of the independent electron model, but it also enables us to clear up a number of quantitative difficulties arising from the application of this model to problems in which the electron-electron interaction is taken into account. We consider these questions in Sec. III.

II.

In this section we calculate, on the basis of the collective description, the ground-state energy for our free-electron gas. In so doing, we shall determine the maximum collective oscillation wave vector k_c (and hence the number of collective degrees of freedom n'), by minimizing the resultant energy with respect to this hitherto arbitrary parameter. We then apply our results to a consideration of the correlation energy correction to the calculation of the cohesive energies of the alkali metals.

Our wave equation for the ground state is

$$H\psi_0=\epsilon_0\psi_0, \tag{10}$$

where ψ_0 and ϵ_0 are the ground-state eigenfunction and energy, respectively. We will also have a set of subsidiary conditions on our wave function,

$$\sum_i\frac{\omega^2\exp(i\mathbf{k}\cdot\mathbf{X}_i)}{\omega^2-(\mathbf{k}\cdot\mathbf{P}_i-\hbar k^2/2m)^2}\psi_0=0\quad(k<k_c) \tag{11}$$

but, as was emphasized in III, for the ground state the exact eigenfunction ψ_0 which satisfies (10) will automatically satisfy (11). Thus, we may concentrate on obtaining the best possible solution of our eigenvalue equation (10). In doing so, we may expect that an approximate ψ_0 will not satisfy the subsidiary conditions, but that any errors we make in determining the energy of the lowest state will not be increased by our failure to satisfy this subsidiary condition, since an

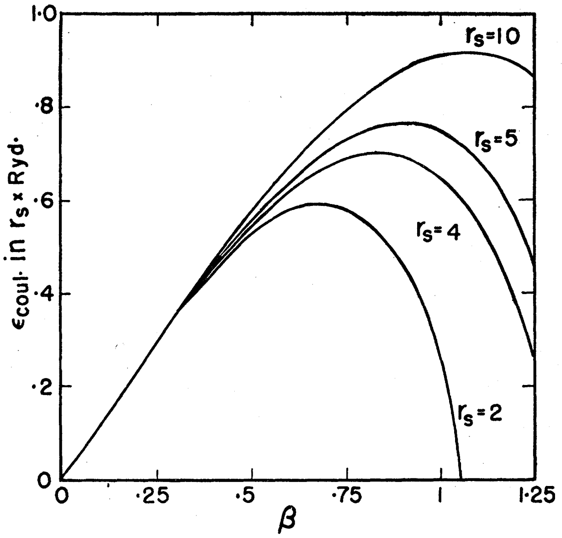

FIG. 1. ϵ_{Coul} *vs* β for several values of r_s.

exact solution satisfies it and leads to the lowest possible energy state.

We may obtain an approximate solution for ψ_0 by treating the comparatively weak short-range electron-electron interaction term $H_{\mathrm{s.r.}}$ as a small perturbation in our expression for H, Eq. (2). In this case, we have as a first approximation,

$$\psi_0 = \psi_0^{\mathrm{osc}} \chi_0, \tag{12}$$

where ψ_0^{osc} represents a product of simple harmonic oscillator lowest-state wave functions, one for each collective oscillation wave-vector up to $k = k_c$, and χ_0 is the usual Slater determinant made up of the free-electron wave functions appropriate to the ground state of our system. The foregoing treatment may then be improved by taking into account the short-range correlations in electronic positions brought about by $H_{\mathrm{s.r.}}$. We return to this question later.

In using the wave function (12), we are describing to a high degree of approximation the long-range correlations in electronic positions brought about by the Coulomb interactions. The great virtue of the collective description is that these quite complex correlations may be simply described in terms of the collective oscillations of the electron gas, and for the ground state of our system, are for the most part contained in ψ_0^{osc}. We note that if we attempted to express (12) in terms of our original "bare" electron coordinates $(\mathbf{x}_i \mathbf{p}_i)$, in a manner similar to that used in obtaining Eq. (23, III), we find that ψ_0 would be a complicated many-electron wave function, which would bear no simple resemblance to a determinant composed of single particle wave-functions and would not easily lend itself to a computation of the system energy.

Before evaluating the lowest-state energy ϵ_0, we find it convenient to re-express our Hamiltonian (2) by introducing the dimensionless parameter β, where

$$\beta = k_c / k_0. \tag{13}$$

We obtain

$$\begin{aligned} H = \sum_i P_i^2/2m(1-\beta^3/6) - (ne^2/\pi)\beta k_0 \\ + \tfrac{1}{2} \sum_{k<\beta k_0} \hbar\omega (A_k^* A_k + A_k A_k^*) \\ + 2\pi e^2 \sum_{\substack{i \neq j \\ k > \beta k_0}} \frac{\exp[i\mathbf{k}\cdot(\mathbf{X}_i - \mathbf{X}_j)]}{k^2}. \end{aligned} \tag{14}$$

If we now evaluate ϵ_0 using (14) and ψ_0 as given in (12), we find that the ground-state energy per electron is given by

$$\epsilon_0' = (\epsilon_0/n) = \epsilon_F + \epsilon_{\mathrm{Coul}} + \epsilon_{\mathrm{exch}}, \tag{15}$$

where

$$\epsilon_F = E_F(1-\beta^3/6) = \tfrac{3}{10}(\hbar^2 k_0^2/m)(1-\beta^3/6), \tag{16}$$

$$\epsilon_{\mathrm{Coul}} = -(e^2/\pi)\beta k_0 + (n'/n)\left\langle \frac{\hbar\omega}{2} \right\rangle_{\mathrm{Av}}, \tag{17}$$

$$\epsilon_{\mathrm{exch}} = -2\pi e^2 \sum_{\substack{k,\,k' < k_0 \\ |\mathbf{k}-\mathbf{k}'| > \beta k_0}} \frac{1}{|\mathbf{k}-\mathbf{k}'|^2}. \tag{18}$$

In Eq. (15), ϵ_F represents the average Fermi energy, differing from the usual expression in that our electrons have the effective mass m^*. ϵ_{Coul} represents the difference in energy (per electron) between the zero-point energy of the collective oscillations $(n'/n)(\langle \hbar\omega \rangle_{\mathrm{Av}}/2)$ and the usual self-energy of the charge distribution the oscillations here describe $-e^2/\pi \beta k_0$. It may be regarded as arising from the reduction in the long-range density fluctuations of the electron gas, as described, for instance, by Eq. (77, III). $\langle \omega \rangle_{\mathrm{Av}}$ is the average frequency of collective oscillation, obtained by averaging our dispersion relation over all $k < k_c$. One finds, from (68, III) that

$$\langle \omega \rangle_{\mathrm{Av}} = \omega_p (1 + 3\alpha[1 + (3/10)\beta^2]). \tag{19}$$

In Fig. 1 we give a plot of ϵ_{Coul} (in units of $r_s \times$ rydbergs) *vs* β for several values of

$$r_s = r_0/a_0 = (3n/4\pi)^{\frac{1}{3}}(me^2/\hbar^2), \tag{20}$$

the interelectron spacing measured in units of the Bohr radius.

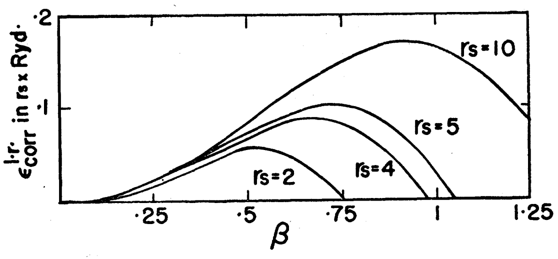

FIG. 2. $\epsilon_{\mathrm{corr}}^{\mathrm{l.r.}} (= -\epsilon_0' + E_F + E_{\mathrm{exch}})$ *vs* β for several values of r_s.

ϵ_{exch} is the exchange energy arising from $H_{\text{s.r.}}$, the short-range electron interaction energy. The sums over $\mathbf{k}$ and $\mathbf{k}'$ in (18) are to be carried out for all electrons of parallel spin in the Fermi distribution (i.e., $k<k_0$, $k'<k_0$) such that $|\mathbf{k}'-\mathbf{k}|>\beta k_0$. This latter restriction arises from the short-range character of the interaction, as expressed by the restriction of k values in (5) to $k>\beta k_0$. We evaluate ϵ_{exch} in Appendix I, and there show that

$$\epsilon_{\text{exch}}=-(0.916/r_s)(1-(4/3)\beta+\beta^2/2-\beta^4/48) \text{ ry}. \qquad (21)$$

The results of our calculation of the ground-state energy are given in Figs. 2 and 3. In Fig. 2 we plot ϵ_0' (actually $\epsilon_{\text{corr}}^{\text{l.r.}}=\epsilon_0'-E_{\text{exch}}-E_F$ [see Eq. (24)] as a function of β for various values of r_s. From this we may easily obtain $\beta_{\min}$, that value of β for which the ground-state energy is a minimum. In Fig. 3 we plot $\beta_{\min}$ as a function of r_s.

On the basis of these calculations we see that for the electronic densities encountered in metals (r_s roughly between 2 and 5), $\beta_{\min}$ runs between 0.5 and 0.75. We may now verify the validity of our perturbation theory expansions in powers of α and $(n'/3n)$. In terms of β these are given by

$$\alpha\cong\beta^2/2r_s, \qquad (22)$$

and

$$n'/3n=\beta^3/6. \qquad (23)$$

We find from (22), and Fig. 4, that $\alpha\sim 1/16$ for $r_s=2$ and $\alpha\sim 1/20$ for $r_s=5$, so that expansions in powers of α should be quite accurate. Similarly, we find $(n'/3n)$ is (1/48) for $r_s=2$ and $\sim$(1/17) for $r_s=5$, so that it constitutes an equally valid expansion parameter.

The preceding results are conveniently analyzed by the introduction of the concept of the correlation energy of the free-electron gas. This energy may be defined as the difference between the energy calculated by means of suitable many-electron wave functions and the energy calculated in the Hartree-Fock one-electron approximation. The latter energy is[5]

$$E=E_F+E_{\text{exch}}, \qquad (24)$$

where

$$E_F=\tfrac{3}{5}(\hbar^2k_0^2/2m)=(2.21/r_s^2) \text{ ry}. \qquad (25)$$

and

$$E_{\text{exch}}=-(0.916/r_s) \text{ ry}. \qquad (26)$$

TABLE I. Correlation energy in the free-electron gas model for the alkali metals.
Units: Rows (c), (d), and (e), $r_s\times$ry;
Rows (f) and (g), kcal/mole.

Metal	Li	Na	K	Rb	Cs
(a) r_s	3.22	3.96	4.87	5.18	5.57
(b) $\beta_{\min}$	0.63	0.68	0.73	0.75	0.77
(c) $\epsilon_{\text{corr}}^{\text{l.r.}}$	−0.076	−0.086	−0.100	−0.106	−0.112
(d) $\epsilon_{\text{corr}}^{\text{s.r.}}$	−0.164	−0.183	−0.206	−0.213	−0.221
(e) ϵ_{corr}	−0.240	−0.269	−0.308	−0.319	−0.333
(f) $\epsilon_{\text{corr}}\frac{\text{kcal}}{\text{mole}}$	23.3	21.1	19.5	19.1	18.6
(g) ϵ_{corr}(Wigner)	21.7	19.7	17.9	17.4	16.8

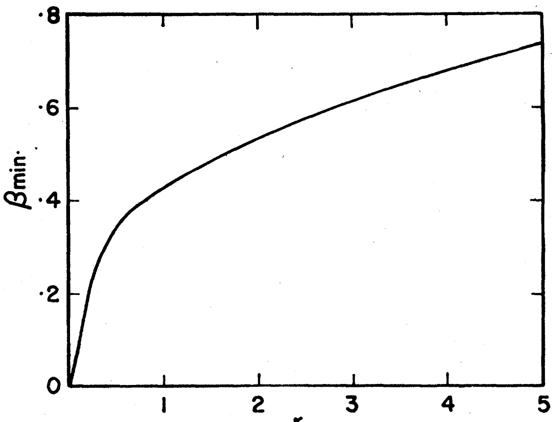

FIG. 3. $\beta_{\min}$ *vs* r_s.

The correlation energy for the free-electron gas was first calculated by Wigner,[6] who used a perturbation theory method in which the wave function of the electron of a given spin was assumed to depend on the positions of all the electrons of opposite spin. Wigner extended the results of his calculation, which was only valid for very high electronic densities ($r_s\lesssim 1$), to lower densities in such a way as to approach the correct value of the correlation energy for very low densities ($r_s\gg 1$). He obtained the result,

$$E_{\text{corr}}=-0.576/(r_s+5.1) \text{ ry}, \qquad (27)$$

which he estimated to be accurate to within 20 percent.

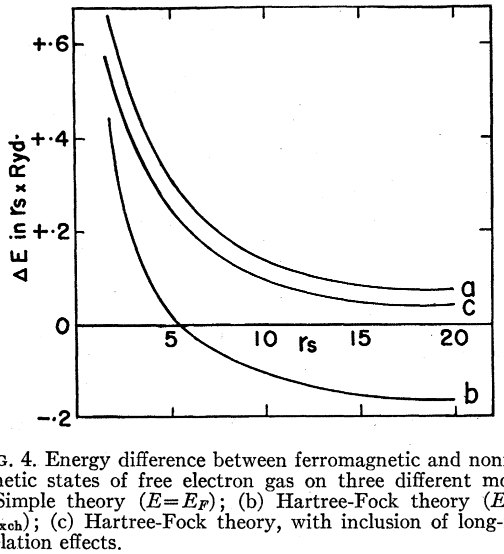

FIG. 4. Energy difference between ferromagnetic and nonferromagnetic states of free electron gas on three different models: (a) Simple theory ($E=E_F$); (b) Hartree-Fock theory ($E=E_F+E_{\text{exch}}$); (c) Hartree-Fock theory, with inclusion of long-range correlation effects.

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[5] F. Seitz, *The Modern Theory of Solids* (McGraw-Hill Book Company, Inc., New York, 1940), p. 341.

[6] E. P. Wigner Phys. Rev. **46**, 1002 (1934).

We shall regard the correlation energy, when calculated in the collective description, as split into two parts, representing long-range and short-range effects. The long-range correlation energy is associated with the long-range correlations in the electronic positions which are essentially described by our introduction of the collective degrees of freedom. This is therefore given by the difference between the ground-state energy we calculated above and the expression (24). The short-range correlation energy then arises from the modification in electronic wave functions brought about by $H_{\text{s.r.}}$, an effect we consider below.

The long-range correlation energy is thus from (24) and (15),

$$\epsilon_{\text{corr}}{}^{\text{l.r.}} = -(\beta^3/6)E_F + \epsilon_{\text{Coul}} + [\epsilon_{\text{exch}} - E_{\text{exch}}]. \tag{28}$$

The first two terms in (28) are both negative and represent the energy gain arising from the long-range Coulombic correlations we have considered above. The third term is positive, and represents the difference between the effect of the exclusion principle in a gas of *interacting* electrons and in a gas of *free* electrons. In Table I we give the calculated values of $\epsilon_{\text{corr}}{}^{\text{l.r.}}$ for electron gases of the same density as those found in alkali metals.

We may understand the origin of the terms contributing to $\epsilon_{\text{corr}}{}^{\text{l.r.}}$ in the following way. In the collective description we consider *ab initio* the correlations brought about by the Coulomb interactions. We find that the electrons tend to stay out of one another's way, and that in fact these long-range Coulomb correlations are such that the effective electron interaction is given by $H_{\text{s.r.}}$. The energy gain from such Coulombic correlations is $\epsilon_{\text{Coul}} - (\beta^3/6)E_F$. We then put in the exclusion principle in the usual way and find an additional energy gain coming from the "accidental" correlations due to the exclusion principle in our gas of *interacting electrons*, which is ϵ_{exch}. On the other hand, E_{exch} represents the exchange energy for a gas of *free electrons*, in which Coulombic effects are otherwise neglected. The use of this term represents an overestimate of the role of the exclusion principle, since the long-range Coulomb forces tend to keep the electrons apart, and would do so even if the electrons had integral spin. In consequence the exclusion principle should properly play no role in such long-range correlations, and we see that this is properly accounted for by our correction to the exchange energy $(\epsilon_{\text{exch}} - E_{\text{exch}})$. Other effects associated with the different role of the exclusion principle in a gas of interacting electrons are considered in the following section.

The short-range electron-electron interaction term, $H_{\text{s.r.}}$ may be consistently treated as a perturbation in the Hamiltonian (2), since it is of such a short-range and weak strength that it does not affect the individual electronic motion appreciably. The short-range correlation energy may then be calculated according to perturbation-theoretic techniques. When this is done one finds that the short-range correlation energy is associated almost entirely with correlations between electrons of antiparallel spin, and it is this latter energy which we list in Table I. The details of this calculation, together with a more extensive investigation of correlation phenomena, will be published in the near future.

We have summarized the results of our correlation-energy calculations in Table I, where we give those values corresponding to the electron densities encountered in the alkali metals. It may be seen that our results are in quite close agreement with those of Wigner, an agreement which is well within the accuracy of the two methods. The major source of error in our calculation lies in our perturbation theoretic estimate of the effects of $H_{\text{s.r.}}$, and a rough estimate indicates that the use of perturbation theory, together with certain other approximations, may be responsible for errors of as much as 20 percent in $\epsilon_{\text{corr}}{}^{\text{s.r.}}$. Our expansion parameters α and $(n'/3n)$ are both quite small, so that the errors introduced by our neglect of higher-order terms in these parameters will be less than 10 percent of $\epsilon_{\text{corr}}{}^{\text{l.r.}}$. An order of magnitude estimate of the exchange energy associated with $H_{\text{r.p.}}$ (a term we neglected in comparison to $H_{\text{s.r.}}$) shows that this is less than $(0.01/r_s)$ ry for Na, so that the neglect of this term is justified within the accuracy of the present treatment. If we combine the above estimates, we are led to estimate the over-all accuracy of our calculated correlation energy as approximately 15 percent.

III.

In this section we consider briefly the result of including electron-electron interactions in a description of certain metallic phenomena. In general, the most simple form of the theory of metals, in which the electron-electron interactions are entirely neglected, has led to qualitative, and in many cases, quantitative agreement with experiment. If the electron-electron interactions are then included in the one-electron picture, the corrections to the simple theory arise from the exchange energy contributions to the phenomenon under consideration. These corrections, far from improving the agreement with experiment, tend to worsen it, both qualitatively and quantitatively. Wigner[7] suggested that correlations brought about by the Coulomb interactions may counteract the difficulties arising from these exchange contributions. We here wish to show that the long-range correlations we have considered in the collective description have just this property.

In the one-electron approximation, the exchange energy contribution to the Coulomb interaction energy of two electrons of wave vectors k_1 and k_2 is

$$W_{1,2} = -4\pi e^2/|\mathbf{k}_1 - \mathbf{k}_2|^2. \tag{29}$$

For a given electron, the total energy of interaction

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[7] E. P. Wigner, Trans. Faraday Soc. 34, 678 (1938).

with all the other electrons is then

$$W_i=\sum_{j\neq i} W_{i,j}=-\frac{e^2k_0}{2\pi}\left(2+\frac{k_0^2-k^2}{k_0k}\ln\frac{k+k_0}{k-k_0}\right), \quad (30)$$

if we assume the electrons form a completely degenerate gas. As a consequence of (30) the *E versus k* curve for a given electron becomes very steep as k approaches k_0, so that the density-in-energy of electron levels at low temperatures will be greatly reduced. Bardeen[8] and Wohlfarth[9] calculated the modification in the specific heat of a free-electron gas due to the inclusion of the exchange energy (30) and found that at low temperatures the specific heat should vary as $T/\ln T$. This result is in contradiction with the experimental results, which show a linear dependence on T—a result that follows from theory if exchange effects are entirely ignored. This large reduction in the density of electron energy levels might also be expected to affect profoundly other metallic phenomena which are sensitive to its magnitude, such as paramagnetism, conductivity, and the optical properties of metals; such an effect on these phenomena has also not been found experimentally.

The origin of these difficulties lies in the long-range of the Coulomb interaction which leads to a very large exchange energy for electrons of nearly equal momentum; this, in turn, is responsible for the undesirable behavior of (30). If we have, instead, an effective short-range, screened Coulomb interaction between the electrons, these large exchange energy contributions are greatly reduced, and the energy term corresponding to (30) takes a more satisfactory form.

Actually, a screened Coulomb interaction between electrons was proposed empirically by Landsberg,[10] who found it necessary to introduce such an effective interaction in order to obtain agreement between theory and experiment for the width of the tail of the soft x-ray emission spectrum of sodium. Wohlfarth[9] then showed that the effect of the exchange energy on the specific heat of the electron gas is greatly reduced, provided the electron-electron interaction potential is empirically taken as $(e^2/r_{ij})\exp[-(r_{ij}/\lambda)]$, with a screening radius λ of the order of 10^{-8} cm, the value introduced by Landsberg.

In the collective description, the exchange energy contribution to the Coulomb interaction energy of two electrons of wave vectors k_1 and k_2 arises from $H_{\text{s.r.}}$, and is given by

$$\begin{aligned} W_{1,2}&=-4\pi e^2/|\mathbf{k}_1-\mathbf{k}_2|^2, && (|\mathbf{k}_1-\mathbf{k}_2|>k_c);\\ W_{1,2}&=0, && (|\mathbf{k}_1-\mathbf{k}_2|<k_c). \end{aligned} \quad (31)$$

In Appendix I, we show that for a given electron of wave vector **k**, the total energy of interaction with all the other electrons is

$$W_i=-\frac{e^2k_0}{2\pi}\left\{1+\frac{k_0^2-k^2}{kk_0}\ln\left(\frac{k+k_0}{\beta k_0}\right)+\frac{3k^2-k_0^2}{2kk_0}-2\beta+\frac{\beta^2k_0}{2k}\right\}, \quad (32a)$$

when $(k_0-k_c)<k<k_0$, and

$$W_i=-\frac{e^2k_0}{2\pi}\left\{2+\frac{k_0^2-k^2}{kk_0}\ln\left(\frac{k+k_0}{k_0-k}\right)-4\beta\right\}, \quad (32b)$$

when $k<(k_0-k_c)$. It may easily be verified that the *E versus k* curve given by (32) no longer displays singular behavior as k approaches k_0.

With the aid of (32), we may now obtain an estimate of the exchange-energy contributions to the electronic specific heat in metals. We are limited in the accuracy of our estimate, because in considering the specific heat we should properly take into account the effect of our subsidiary conditions (6) on the excited states of the electron gas. As was pointed out in Paper III, this effect is in the direction of reducing the effective number of degrees of freedom of the electron gas from $3n$ to $3n-n'$. Since, as we have seen, $(n'/3n)\ll 1$ for electrons in metals, we might expect that the neglect of the subsidiary conditions should be a reasonably good approximation, and it is this approximation we adopt in what follows.

We may obtain the influence of the exchange energy on the specific heat of the electron gas by considering its effect on the density of levels at the top of the Fermi distribution. Lidiard[11] has shown by the use of a variational Fermi-Dirac distribution function, that provided the free energy may be sensibly expanded in powers of (KT/E_0) near $T=0$ according to the method of Sommerfeld and Bethe,[12] the specific heat per electron may be written as

$$C_e=\frac{\pi^2K^2T}{3n}\left(\frac{dn}{d\epsilon}\right)_{\epsilon=E_0}, \quad (33)$$

where $(dn/d\epsilon)_{\epsilon=E_0}$ is the density of electronic levels at the top of the Fermi distribution, and K is Boltzmann's constant. We may write

$$\frac{dn}{n}=\frac{k^2}{\pi^2}\frac{3\pi^2}{k_0^3}dk=\frac{3k^2}{k_0^3}\frac{d\epsilon}{(d\epsilon/dk)}, \quad (34)$$

so that

$$C_e=\frac{\pi^2K^2T}{k_0}\frac{1}{(\partial\epsilon/\partial k)_{k=k_0}}. \quad (35)$$

Now, from (32) we find that near the top of the Fermi

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[8] J. Bardeen, Phys. Rev. **50**, 1098 (1936).

[9] E. P. Wohlfarth, Phil. Mag. **41**, 534 (1950).

[10] P. T. Landsberg, Proc. Phys. Soc. (London) **A162**, 49 (1949).

[11] A. B. Lidiard, Phil. Mag. **42**, 1325 (1951) and private communication. We should like to thank Dr. Lidiard for communicating his results to us.

[12] A. Sommerfeld and H. Bethe, *Handbuch der Physik* (J. Springer, Berlin, 1934), Vol. 24, p. 12.

distribution ($k>k_c$),

$$\epsilon=\frac{\hbar^2k_0^2}{2m}-\frac{e^2k_0}{2\pi}\left\{1+\frac{k_0^2-k^2}{kk_0}\ln\left(\frac{k+k_0}{\beta k_0}\right)+\frac{3(k^2-k_0^2)}{2kk_0}-2\beta+\frac{\beta^2k_0}{2k}\right\},\tag{36}$$

and hence

$$C_e=\frac{\pi^2K^2T}{2E_0}\frac{1}{1+\dfrac{me^2}{2\pi\hbar^2k_0}\left[2\ln\left(\dfrac{2}{\beta}\right)+\dfrac{\beta^2}{2}-2\right]}.\tag{37}$$

Thus the ratio of the above electronic specific heat to the usual electronic specific heat $C_0=(\pi^2K^2T/2E_0)$ is

$$\frac{C_e}{C_0}=\left[1+\frac{r_s}{12}\left\{2\ln\frac{2}{\beta}+\frac{\beta^2}{2}-2\right\}\right]^{-1}.\tag{38}$$

For Na, for which $r_s=4$ and $\beta=0.65$, we find

$$C_e/C_0=1/1.22=0.82.\tag{39}$$

Thus the effect of taking the exchange energy into account is to reduce the electronic specific heat to about 80 percent of its free electron value for Na. We note from (38) that our calculated reduction in the density of energy levels at the top of the Fermi distribution is now comparatively small, so that the influence of the exchange effects on other metallic phenomena may be expected to be correspondingly small. The experimental accuracy in the determination of electronic specific heats does not at present appear to be sufficiently great to check the validity of the above formulas.

There is probably a slight further reduction in the electronic specific heat arising from the effect of the subsidiary conditions in reducing the number of individual electronic degrees of freedom. In addition, we may expect the short-range correlations produced by $H_{\text{s.r.}}$ to affect the density of energy levels and the electronic specific heats. This effect will be considered in a later paper.

We may also use our results on the long-range correlation energy to investigate the possible ferromagnetism of a free electron gas. If the energy of an electron in the gas in the nonmagnetic state is given by the expression (24)

$$E=+E_F+E_{\text{exch}}=2.21/r_s^2-0.916/r_s,$$

then it is clear that for sufficiently large r_s, the electron gas should become ferromagnetic. For the cost in kinetic energy which results from lining the spins up (an increase in k_0 to $k_0\sqrt[3]{2}$) will eventually be more than compensated by the gain in the exchange energy. Thus the energy for the magnetic state is given by

$$E=3.52/r_s^2-1.156/r_s,$$

and one finds that electron gases for which $r_s>5.47$ should be ferromagnetic. This is not the case (e.g., Cs), and the reason that it is not lies in the Coulomb correlation energy, as Wigner[7] has pointed out. We will now show that the long-range correlation energy is actually sufficient to prevent the free-electron gas from becoming ferromagnetic.

Qualitatively it is easy to understand why this is so. We have seen that the Coulomb interaction keeps the electrons sufficiently far apart so that the exchange-energy attraction which acts to line up the electron spins is greatly reduced, even for $r_s\sim4$. Then as we go to higher r_s and lower electronic density, the screening cloud around each electron due to long-range correlations becomes even more efficient (corresponding to a higher value of β), so that the exchange energy is, in fact, further reduced, rather than having its relative strength increase. In Fig. 4 we give r_s times the energy difference between the ferromagnetic and nonferromagnetic states using our energy expression (15). This result has been obtained by calculating ϵ_0' as a function of β for both the nonmagnetic and ferromagnetic states, and choosing an optimum value of β (for which ϵ_0' is a minimum) in each case. For comparison we have plotted this energy difference as calculated using the simple theory, $E=E_F$, and using the Hartree-Fock approximation, $E=E_F+E_{\text{exch}}$. A result similar to this has been obtained by Wigner[7] on the basis of a somewhat different model for the free-electron gas.

The above results are subject to corrections arising from the effect of the subsidiary conditions (6) on our lowest-state wave function, since the lowest-state wave function is no longer nondegenerate and hence will no longer satisfy the subsidiary conditions automatically. However this should not alter our results appreciably, since the relative number of subsidiary conditions is small even for very low densities ($n'/3n\sim15$ percent for $r_s\sim10$), and since the subsidiary conditions involve only long-wavelength density fluctuations ($k<k_c$) while the exchange energy depends primarily on short-wavelength density fluctuations ($k>k_c$). Further corrections, which are in the direction of making ferromagnetism even less likely, will come from the short-range correlation energy. This follows from the fact that our energy $\epsilon_{\text{corr}}^{\text{s.r.}}$ will be absent in the magnetized state. We have not included these corrections here, because in the region of possible ferromagnetism ($r_s>5.47$), our perturbation theoretic estimates are beginning to become unreliable.

IV.

In the preceding sections we have considered the low-lying states of electrons in metals in the collective description. We have seen that at ordinary temperatures we should not expect the collective oscillations to be excited, since $\hbar\omega_p$ lies several electron volts higher than E_F for all metals, so that no electron in the metal will have sufficient energy to excite a collective oscillation. (Temperature excitation is clearly out of the question.) Thus, the only way that collective oscillations can be excited in a metal is by bombardment of the metal with charged particles of sufficient energy to excite the oscillations. In this section, we will apply our canonical transformation to the investigation of the interaction of a charged particle with the electron gas.

This problem was treated classically in II by the density fluctuation method. There it was shown that a fast charged particle would excite collective oscillation, and the results for this excitation, together with some semiclassical arguments, were applied to the experiments of Ruthemann[13] and Lang[14] on the scattering of kilovolt electrons by thin metallic films. By so doing, excellent agreement was obtained between theory and experiment. The density fluctuation method has also been applied to a determination of the contribution of the conduction electrons in a metal to its stopping power for a fast charged particle.[15] In this section, we shall obtain the appropriate quantum-mechanical results and verify the validity of the results obtained by the semiclassical application of the density fluctuation method.[16]

Let us consider a charged particle of mass M, charge Ze, position and momentum $(\mathbf{r}_0, \mathbf{P}_0)$. We can describe its motion and interaction with our electron gas by adding the following terms to the original Hamiltonian of Paper III, Eq. (43, III):

$$\frac{P_0^2}{2M}+-4\pi Ze^2\sum_{ik}\frac{e^{i\mathbf{k}\cdot(\mathbf{x}_i-\mathbf{r}_0)}}{k^2}. \tag{40}$$

The effect of the canonical transformation to the collective description on these terms may then be obtained by using Eq. (51, III) and applying the random phase approximation and the dispersion relation [Eq. (57, III)] to the resulting terms. We find that the above terms then become

$$\begin{aligned}H_{\text{add}}=&-4\pi Ze^2\sum_{ik>k_c}\frac{\exp[i\mathbf{k}\cdot(\mathbf{X}_i-\mathbf{r}_0)]}{k^2}\\&-Ze\sum_{k<k_c}\left(\frac{2\pi\hbar\omega}{k^2}\right)^{\frac{1}{2}}(A_{-k}+A_k^*)e^{-i\mathbf{k}\cdot\mathbf{r}_0}+\frac{P_0^2}{2m}\\&-4\pi Ze^2\sum_{ik<k_c}\frac{\exp[i\mathbf{k}\cdot(\mathbf{X}_i-\mathbf{r}_0)]}{k^2}.\end{aligned} \tag{41}$$

The first term in H_{add} describes a short-range screened Coulomb interaction between the charged particle and the individual electrons in our electron gas. This interaction is of the same form as that found for the interaction between the individual electrons $H_{\text{s.r.}}$ [Eq. (5)]. The second term describes the interaction between the charged particle and the collective oscillations of the system and may lead to the excitation of collective oscillations by the particle. The last term in H_{add} will be the only term affected by the subsidiary conditions on our system wave function. We see that when (6) is applied, this term reduces to

$$-4\pi Ze^2\sum_{ik<k_c}\frac{(\mathbf{k}\cdot\mathbf{P}_i/m)-(\hbar k^2/2m)^2}{\omega^2-(\mathbf{k}\cdot\mathbf{P}_i/m-\hbar k^2/2m)^2}\times\exp[i\mathbf{k}\cdot(\mathbf{X}_i-\mathbf{r}_0)], \tag{42}$$

which may be neglected in the approximation of small $(\mathbf{k}\cdot\mathbf{P}_i/m\omega)$.

Thus, we see that the use of our canonical transformation to the collective description provides us with a simple, natural splitup of the interaction between a charged particle and the electron gas into two parts: a short-range interaction with the individual electrons, and the interaction with the collective oscillations of the system as a whole (which has its origin in the long-range electron-electron and electron-particle interactions). This splitup is analogous to the splitup of the density fluctuations into individual particle and collective components, which was carried out in II.

Let us now consider the interaction between the charged particle and the collective oscillations. For this purpose, it is convenient to introduce the canonical collective variables, P_k and Q_k, defined by

$$\begin{aligned}Q_k&=(\hbar/2\omega)^{\frac{1}{2}}(A_k-A_k^*),\\P_k&=i(\hbar\omega/2)^{\frac{1}{2}}(A_k^*+A_{-k}).\end{aligned} \tag{43}$$

In terms of these variables, the collective interaction term in (4) becomes

$$iZe\sum_{k<k_c}(4\pi/k^2)^{\frac{1}{2}}P_ke^{-i\mathbf{k}\cdot\mathbf{r}_0}, \tag{44}$$

and

$$H_{\text{coll.}}=\tfrac{1}{2}\sum_{k<k_c}(P_k^2+\omega^2Q_k^2).$$

The equations of motion of our charged particle and the collective field are then given by

$$M\ddot{\mathbf{r}}_0=\mathbf{P}_0=-Ze\sum_{k<k_c}(4\pi)^{\frac{1}{2}}\boldsymbol{\varepsilon}_kP_ke^{-i\mathbf{k}\cdot\mathbf{r}_0} \tag{45}$$

and

$$\ddot{P}_k+\omega^2P_k=+Zei\omega^2(4\pi/k^2)^{\frac{1}{2}}e^{+i\mathbf{k}\cdot\mathbf{r}_0}. \tag{46}$$

Equation (46) describes forced harmonic oscillation of the collective fields and is directly analogous to Eq. (47) of II. Because of the similarity between these equations, and because the latter equation was analyzed in some detail in II, we will merely quote the results of our solutions for (46) here.

We can obtain a straightforward solution of (46) provided the velocity of the charged particle $\mathbf{V}_0=\mathbf{P}_0/M$ may be taken as constant. (This will be a good approxi-

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[13] G. Ruthemann, Ann. Phys. 2, 113 (1948).

[14] W. Lang, Optik 3, 233 (1948).

[15] D. Pines, Phys. Rev. 85, 931 (1952). For earlier work on this subject, see references 18–21.

[16] D. Gabor [Phil. Mag. (to be published)], has obtained results in substantial agreement with ours by the use of a somewhat different method. We should like to thank Dr. Gabor for communicating his results to us prior to publication.

mation as long as the change in velocity of the charged particle during the period of oscillation is small compared to V_0, which will be true for all applications of interest to us here.) Then if $\mathbf{k}\cdot\mathbf{V}_0$ is not equal to ω, Eq. (46) has the steady-state solution

$$P_k=\left(\frac{4\pi}{k^2}\right)^{\frac{1}{2}}\frac{Zei\omega^2}{\omega^2-(\mathbf{k}\cdot\mathbf{V}_0)^2}e^{i\mathbf{k}\cdot\mathbf{r}_0}. \tag{47}$$

This solution corresponds to the particle moving through the electron gas accompanied by a co-moving cloud of collective oscillation. This co-moving cloud leads only to a somewhat larger effective mass for the charged particle, which may be calculated by substituting (47) into (44).

The more physically interesting case occurs when $\mathbf{k}\cdot\mathbf{V}_0=\omega$. In this case the steady-state solution (47) is no longer appropriate, and the correct solution corresponds to resonant excitation of the collective oscillation. This oscillation, which was discussed in some detail in II, will take the form of a wake of collective oscillation trailing behind the particle, a phenomenon which resembles closely the Čerenkov radiation produced by fast electrons in passing through dielectric materials. We calculate the energy loss per unit length to the collective oscillations by obtaining the force due to the wake at the position of the particle, under the boundary condition that the energy loss occurs behind the charged particle. We find

$$\left(\frac{dT}{dX}\right)_{\text{coll}}=\frac{2\pi nZ^2e^4}{MV_0^2}\left\{\ln\left[\frac{\beta^2k_0^2(V_0^2-\langle V^2\rangle_{\text{Av}})}{\omega_p^2}\right]+\frac{\langle V^2\rangle_{\text{Av}}}{V_0^2}\beta^2k_0^2(V_0^2-\langle V^2\rangle_{\text{Av}})\right\}, \tag{48}$$

where $\langle V^2\rangle_{\text{Av}}$ is the mean-square velocity of the electrons in the metal, and we have used $k_c=\beta k_0$. This result differs slightly in two respects from that obtained in II [Eq. (59a, II)]. The logarithmic term is slightly altered because in obtaining (48) we have chosen as the maximum value of the collective oscillation wave vector perpendicular to V_0 a more accurate value than that used in II, *viz.* $[\beta^2k_0^2(1-\langle V^2\rangle_{\text{Av}}/V_0^2)-\omega_p^2/V_0^2]^{\frac{1}{2}}$. The appearance of the second term in the brackets (multiplying $2\pi nZ^2e^4/MV_0^2$) is due to the fact that in (48) we have ω^2 as a factor on the right-hand side of the equation, as compared to the factor ω_p^2 appearing in the similar position in the analogous equation of II. Both of these differences become negligible in the limit of $V_0^2\gg\langle V^2\rangle_{\text{Av}}$.

As pointed out in II, our picture of collective oscillations of the electrons in a metal and the excitation of collective oscillations by a fast charged particle finds experimental confirmation in the experiments of Ruthemann[12] and Lang[13] on the scattering of kilovolt electrons by thin metallic films. They found that for Be and Al the electrons lose energy in integral multiples of a well-defined basic quantum. Theoretically we should expect this quantum to be very nearly $\hbar\omega_p$, since as we saw in II, the long-wavelength quanta play a major role in the stopping power if V_0 is considerably greater the mean velocity of the metallic electrons, as is the case in these experiments. The experimental values of this quantum of energy loss are 14.7 ev for Al and 19.0 ev for Be, and these agree very well with our calculated $\hbar\omega_p$ (under the assumption that all the valence electrons are free) of 15.9 ev for Al and 18.8 ev for Be.

We may also calculate the mean free path for the emission of a quantum of collective oscillation. In the limit of $V_0^2\gg\langle V^2\rangle_{\text{Av}}$, this is

$$\lambda=\frac{\hbar\omega_p}{(dT/dx)_{\text{coll}}}=\frac{\hbar\omega_pMV_0^2}{4\pi nZ^2e^4\ln(\beta k_0V_0/\omega_p)}. \tag{49}$$

From the data given by Lang on the thickness of his Al films, one may obtain an experimental estimate for λ. This turns out to be somewhat less than 185A. The theoretical value of λ is, from (49), ~160A (for the 7.6-kev electrons used by Lang) and is in good agreement with the above experimental estimate.

Lang and Ruthemann did not find a similar set of discrete energy losses in Ag, Cu, and Ni. This is probably due to the fact that the valence electrons in these metals are not sufficiently free (in the sense of Sec. IV) to take part in undamped collective motion. In the cases of Cu and Ag there is some evidence for a large exchange interaction with the core electrons, which is probably responsible for the damping of the collective oscillation.[17] Experiments have not yet been performed on the alkali metals, where we should expect to find collective oscillation and the appearance of discrete energy losses.

The interaction between the charged particle and the individual electrons in our electron gas, which is described by the term

$$-4\pi Ze^2\sum_{ik>k_c}(1/k^2)\exp[i\mathbf{k}\cdot(\mathbf{X}_i-\mathbf{r}_0)],$$

in our Hamiltonian (41), provides an alternate mechanism for the energy loss of the particle in traversing the gas. This term is not appreciably affected by our subsidiary condition (6), since the latter involves only long-wavelength density fluctuations ($k<k_c$). Thus the energy loss per unit length due to these individual electron collisions may be obtained by the usual methods of collision theory and is, in the nonrelativistic limit,

$$\left(\frac{dT}{dx}\right)_{\text{i.p.}}=\frac{4\pi nZ^2e^4}{MV_0^2}\ln\left(\frac{1}{b\beta k_0}\right) \tag{50}$$

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[17] See reference 5. Recently P. Wolff [Bull. Am. Phys. Soc. 28, No. 2, 35 (1953)] has used the Hartree approximation to investigate the effect of the binding of the electrons in the lattice on collective oscillation. He finds that this may account for the single line of rather considerable width found in these metals.

for collisions involving impact parameters greater than b. The appropriate choice of a minimum impact parameter depends on the details of the collision considered (through Z, M, and V_0), but in general the energy loss to the individual electrons is roughly comparable to that given up to the collective oscillations. The total energy loss per unit path length of the charged particle is the sum of (48) and (50) and is

$$\frac{dT}{dx}=\frac{4\pi nZ^2e^4}{MV_0^2}\left\{\left(\ln\frac{V_0}{\omega_p b}\left[1-\frac{\langle V^2\rangle_{\mathrm{Av}}}{V_0^2}\right]^{\frac{1}{2}}\right)+\frac{\beta^2k_0^2\langle V^2\rangle_{\mathrm{Av}}}{2\omega_p^2}\left(1-\frac{\langle V^2\rangle_{\mathrm{Av}}}{V_0^2}\right)\right\}. \tag{51}$$

We see that, in the limit of $V_0^2\gg\langle V^2\rangle_{\mathrm{Av}}$, this expression essentially is independent of our choice of screening parameter β.

It is of some interest to compare our description of the energy loss of a charged particle traversing a free-electron gas with those due to Kramers[18] and Bohr.[19] Both Kramers and Bohr take into account the effects of electron-electron interaction in determining this energy loss, and although their methods are rather different from ours, as we shall see their results are essentially equivalent to (51). Kramers[18] used a macroscopic description in which the electrons were treated as a continuum characterized by an effective dielectric constant. His method of treating the polarization effects associated with electron interaction is closely related to that used by Fermi in treating the analogous polarization effects for very fast particles interacting with bound electrons (the "density effect"). Bohr[19] has given a very interesting microscopic description of the collisions between the charged particle and the individual electrons (both free and bound) in which the influence of the electron-electron interactions is taken into account explicitly. Bohr has shown that the energy loss of a fast charged particle to a system of bound electrons may be considered to take place in two different modes. One mode corresponds to the Čerenkov radiation, which may be regarded as corresponding to the organized behavior of the system brought about by the electron-electron interaction. The other essentially corresponds to the interaction of the particle with the individual electrons, and displays no collective aspect. This microscopic separation of the mechanisms of energy loss of the charged particle to the bound electrons is directly analogous to that we have given above for the free-electron gas. We might add that, as is the case with the Čerenkov radiation for bound electrons, the energy given up by the particle to the collective oscillations does not constitute an additional source of energy loss from a microscopic viewpoint; for a collective oscillation is due to the cumulative contributions arising from the displacement of the individual electrons by the charged particle and represents the organized motion associated with these displacements.

A somewhat different method of treating this problem, which is in some respects similar to that used in the collective description, is due to Kronig and Korringa.[20] They have given a treatment by the methods of classical hydrodynamics in which the effects of electron-electron interactions are described in part in terms of an artificially introduced internal friction of the conduction electron fluid. Kronig[21] has suggested that this theory bears a relationship to that of Kramers which is similar to that obtaining between hydrodynamics and a kinetic theory of fluids.

For the free electron gas, both Kramers and Bohr find, in the nonrelativistic limit,

$$\frac{dT}{dx}=\frac{4\pi nZ^2e^4}{MV_0^2}\ln\left(\frac{V_0}{\omega_p{}^b}\right). \tag{42}$$

Our expression (41) differs from (42) due to the fact that we have taken into account the dependence of the frequency of organized oscillation on the electron kinetic energy. This correction is rather small and may be neglected in the limit of high particle velocity $V_0^2\gg\langle V^2\rangle_{\mathrm{Av}}$.

The total stopping power of a metal for a fast charged particle is the sum of that due to the conduction electrons and to the core electrons. Thus, in order to obtain experimental verification of our expression (41) as applied to the conduction electrons, we must consider metals in which the number of core and valence electrons is roughly comparable, e.g., Li and Be. Bohr has used the expression (42) together with the appropriate theoretical expression for the core electrons to obtain a theoretical average excitation potential of 45 ev for Li and 60 ev for Be. (The corresponding excitation potentials using (41) are 44 ev and 57 ev, respectively.) These values are in good agreement with the experimental values of Bakker and Segrè, who found excitation potentials of 34 ev for Li and 60 ev for Be, when one considers the fact that an experimental uncertainty of ~10 percent in the stopping power for Li corresponds to an uncertainty in the Li excitation potential of ~50 percent.[19]

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[20] R. Kronig and J. Korringa, Physica **10**, 406 (1943).

[21] R. Kronig, Physica **15**, 667 (1949).

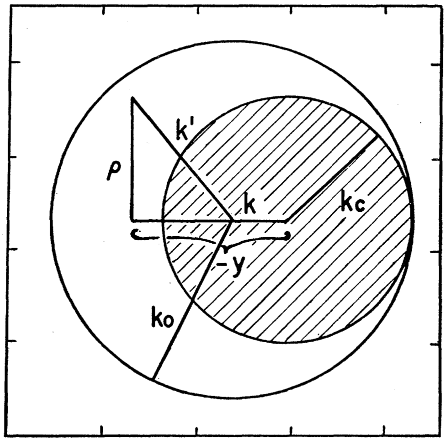

FIG. 5. Allowed regions for $\mathbf{k}'$ integration.

APPENDIX I

In this appendix we wish to evaluate ϵ_{exch} which may be written, according to (18), as

$$\epsilon_{\text{exch}} = -2\pi e^2 \sum_{\substack{k,\,k'<k_0 \\ |\mathbf{k}'-\mathbf{k}|>k_c}} \frac{1}{|\mathbf{k}'-\mathbf{k}|^2}, \tag{A1}$$

where the sum is to be carried out for all electrons of parallel spin in the Fermi distribution, such that $|\mathbf{k}'-\mathbf{k}|>k_c$, this latter restriction arising from the short-range character of the interaction $H_{\text{s.r.}}$. Let us first obtain the exchange energy of interaction with all the other electrons for a given electron of wave vector k. This is, on changing our sum over $\mathbf{k}'$ to an integral,

$$W_i = -\frac{4\pi e^2}{(2\pi)^3}\int d\mathbf{k}' \frac{1}{|\mathbf{k}'-\mathbf{k}|^2}, \tag{A2}$$

where the integration must be carried out in such a way as to exclude the shaded portion of the k_0 sphere (corresponding to $|\mathbf{k}'-\mathbf{k}|<k_c$) as illustrated in Fig. 5.

It is convenient to introduce for our $\mathbf{k}'$ coordinate system, cylindrical coordinates (ρ, y, φ) centered at k, as shown in Fig. 5, for we then find that

$$(\mathbf{k}'-\mathbf{k})^2 = \rho^2 + y^2. \tag{A3}$$

The requirement that $|\mathbf{k}'-\mathbf{k}|$ be greater than k_c then leads to the following regions of integration for our $\mathbf{k}'$ integration:

$k>k_0-k_c$

$$\int d\mathbf{k}' = \int_{-(k+k_0)}^{-k_c} dy \int_0^{[k_0^2-(y+k)^2]^{\frac{1}{2}}} \rho d\rho \int_0^{2\pi} d\varphi + \int_{-k_c}^{[k_0^2-k_c^2-k^2]/2k} dy \int_{[k_c^2-y^2]^{\frac{1}{2}}}^{[k_0^2-(y+k)^2]^{\frac{1}{2}}} \rho d\rho \int_0^{2\pi} d\varphi,$$

$k<k_0-k_c$

$$\int d\mathbf{k}' = \int_{-(k+k_0)}^{-k_c} dy \int_0^{[k_0^2-(y+k)^2]^{\frac{1}{2}}} \rho d\rho \int_0^{2\pi} d\varphi + \int_{-k_c}^{k_c} dy \int_{[k_c^2-y^2]^{\frac{1}{2}}}^{[k_0^2-(y+k)^2]^{\frac{1}{2}}} \rho d\rho \int_0^{2\pi} d\varphi + \int_{k_c}^{k_0-k} dy \int_0^{[k_0^2-(y+k)^2]^{\frac{1}{2}}} \rho d\rho \int_0^{2\pi} d\varphi.$$

The integrations for W_i are quite straightforward and yield for $k_0-k_c<k<k_0$

$$W_i = -\frac{e^2k_0}{2\pi}\left\{1+\frac{k_0^2-k^2}{kk_0}\ln\left(\frac{k+k_0}{\beta k_0}\right) + \frac{3k^2-k_0^2}{2kk_0} - 2\beta + \frac{\beta^2 k_0}{2k}\right\},$$

$k<(k_0-k_c)$

$$W_i = -\frac{e^2k_0}{2\pi}\left\{2+\frac{k_0^2-k^2}{kk_0}\ln\left(\frac{k+k_0}{k_0-k}\right) - 4\beta\right\}.$$

We may then evaluate ϵ_{exch} by summing over all $\mathbf{k}$ within the Fermi distribution (and dividing by two so that no interactions are counted twice). We find

$$\epsilon_{\text{exch}} = \tfrac{1}{2}\sum_k W_i = \frac{1}{(2\pi)^3}\int d\mathbf{k} W_i = -\frac{3e^2k_0 n}{4\pi}\left\{1-\frac{4}{3}\beta+\frac{\beta^2}{2}+\frac{\beta^4}{48}\right\},$$

where $\beta = k_c/k_0$. The exchange energy per electron may then be written as

$$\epsilon_{\text{exch}}' = -\frac{0.916}{r_s}\left\{1-\frac{4}{3}\beta+\frac{\beta^2}{2}-\frac{\beta^4}{48}\right\}\text{ry}.$$