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Theory of the Work Function
II. The Surface Double Layer

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An expression for the work function of a monovalent metal, previously obtained by E. Wigner and the author, included a term which represents the energy required to move an electron through an electrostatic double layer at the surface of the metal. In order to determine the moment of this double layer, it is necessary to make an explicit calculation of the electronic charge density at the surface of the metal, which is attempted in the present paper. In the model taken for this calculation, the density of positive electricity is assumed constant on the negative side of the YZ plane, and is zero in the positive half-space. The electrons are so distributed as to neutralize the positive charge density in the interior, and the metal as a whole is neutral. An approximate self-consistent solution of the Fock equations gives the charge density at the surface. An attempt is made to go beyond these equations, so as to include the effect of correlation (or polarization) forces on the double layer. The density of positive electricity assumed is the same as that which would exist in Na if the ions were treated as a continuous charge distribution. The final values obtained are 2.35 and 2.0 ev for the work function, and 0.4 and 1.0 ev for the moment of the double layer, where the first values in each are obtained when the correlation forces are included, and the second when these forces are omitted in the calculation. A comparison of these values with the experimental values of the work function of Na is given. It is concluded that the surface barrier is due primarily to exchange and polarization forces, and that ordinary electrostatic forces play a minor role.

1. INTRODUCTION

THE theory of the work functions of monovalent metals has been discussed in a recent paper[1] by E. Wigner and the author. This work was incomplete in two respects. In the first place, the free-electron values were used for the Fermi, Coulomb, exchange and correlation energies of the metal. This defect could be removed by making explicit calculations of these energies for the different metals. Such calculations have been carried out, at least in part, for Na,[2, 3] Li,[4, 5] and Cu.[6, 7] Secondly, the electrostatic double layer at the surface of the metal was left undetermined.

The main object of the present work is to show how the double layer is determined and to make a rough calculation of the moment of the double layer at the surface of an ideal metal. The charge distribution at the surface is calculated by the method of the self-consistent field based on the Fock equations. This calculation may be of some interest, not only in the present connection, but also because it yields some information about the potential barrier at the surface of the metal.

In the previous paper, the work function was obtained by first calculating the energy $E(n_i, n_e)$

* Society of Fellows. The major part of this work was completed while the author was a Fellow in Mathematics at Princeton University.

[1] E. Wigner and J. Bardeen, Phys. Rev. **48**, 84 (1935).
[2] E. Wigner and F. Seitz, Phys. Rev. **43**, 804 (1933); **46**, 509 (1934).
[3] J. C. Slater, Phys. Rev. **45**, 794 (1934).
[4] F. Seitz, Phys. Rev. **47**, 400 (1935).
[5] J. Millman, Phys. Rev. **47**, 286 (1935).
[6] H. M. Krutter, Phys. Rev. **48**, 664 (1935).
[7] K. Fuchs, Proc. Roy. Soc. **A151**, 585 (1935).

of a metal containing n_i ions and n_e electrons. This calculation required but a slight modification of the method used by Wigner and Seitz[8] for calculating the energy of an uncharged metal. The work function, φ, was then easily obtained, as

$$\varphi = -(\partial E(n_i, n_e)/\partial n_e)_{n_i=n_e}. \quad (1)$$

It was shown that the work function consists of two parts, the "binding energy" of the electron, and the energy required to move the electron through an electrostatic double layer at the surface of the metal. The first part may be calculated without reference to the surface, and this has been carried out in (I). In order to determine the moment of the double layer, it is necessary to make an explicit calculation of the charge density at the surface.

As our model for the present calculation, we suppose that the metal occupies the half-space on the negative side of the Y-Z plane. The density of positive electricity is constant for $x<0$ and is zero for $x>0$. This same model has been treated by Frenkel[9] from the standpoint of the Thomas-Fermi theory. We here determine the charge distribution at the surface from an approximate solution of the Fock equations. Our calculation also gives the work function of the model from a somewhat different viewpoint than that used in (I). The density of electrons assumed is approximately the same as the density of free electrons in Na, and a comparison is made of the work functions of our model and that of Na. An attempt is made to include the correlation (or polarization) forces which are neglected in the Slater-Fock approximation of one-electron wave functions.

2. Definitions

The work function may be defined (cf. I) as the difference in energy between a lattice with an equal number of ions and electrons, and the lattice with the same number of ions, but with one electron removed. It is assumed in both cases that the lowest electronic states are completely filled, so that the electron is removed from the highest energy state of the neutral metal. Since the work function may be different for different crystallographic planes, it is necessary to specify the position of the electron after its removal from the lattice. It is supposed that the electron is removed to a point in the neighborhood of a surface plane of the crystal, the distance from this plane being small compared with the dimensions of the plane, but large in comparison with atomic dimensions. The potential differences between the outer neighborhoods of differently oriented crystal surfaces will be equal to the differences of the work functions of these surfaces.

The moment of the electric double layer on the surface may be defined as the difference in potential between a point outside the surface and a point in the interior. This definition will serve for our free-electron model. As the potential in the interior of an actual metal is not constant in the interior, but is periodic, it is necessary to specify further the position of the interior point relative to the lattice. The position of this point is somewhat arbitrary, but once chosen, it fixes the otherwise arbitrary constant in the energy parameters of the wave equations for the different electrons which are valid in the interior of the metal. It will be sufficiently accurate to specify the position of the interior point with respect to the approximate model of Wigner and Seitz in which the actual metal is replaced by a set of close-packed spheres (the s spheres).[2] In each sphere, the potential will be a function only of the distance from the center of the sphere. As our interior point we shall take, as in (I), a point on the surface of the s sphere. This definition is most convenient, as it gives a zero moment if the electron-distribution in the s spheres of the surface ions is the same as that in the s spheres of the interior ions. The double layers are due to the fact that the actual distribution may extend outside the limits of the s spheres of the surface ions, and may have greater or smaller densities in the interior of these spheres.

The exact definition of the moment of the double layer is of importance in our connection when we compare the work function and double layer of our free-electron model with the corresponding quantities of the sodium crystal. We shall find that the work functions may be directly compared, but that, as a consequence of

[8] Cf. reference 2. A general review has been given by J. C. Slater, Rev. Mod. Phys. **6**, 209 (1934).

[9] J. Frenkel, Zeits. f. Physik **51**, 232 (1928). This paper also gives a discussion of the surface double layer.

the above definitions, the moment of the double layer of the 110-face of the sodium crystal is about 0.25 ev less than that of the free-electron model.

3. Magnitude of the Double Layers

Before proceeding with the calculation, it might be well to say a few words about the expected order of magnitude of the moment of the double layers. The most direct evidence was given in (I). It was found that the theoretical values of the work functions of the alkalies checked the experimental values very closely, even though the double layer was omitted entirely. This suggests that the double layers of these elements are probably small (less than half a volt).

Since the potential in the interior of a metal is constant (or, more accurately, periodic), the differences in the work functions of different surface planes of the same crystal are equal to the differences in the moments of the corresponding double layers. These differences, experimentally, are of the order of $\frac{1}{2}$ to 1 volt.[10] One might expect that the moments themselves are of this same order of magnitude.

On the other hand, experiments show that the value of the work function depends to a large extent on the condition of the surface.[11] Adsorbed gas or deposits of foreign material may alter the work function considerably. Ives and Olpin[12] and J. J. Brady[13] have shown that a monatomic layer of alkali atoms deposited on a metal may reduce its work function by as much as 50–75 percent. These data indicate that the work function of a surface is really determined by the top few layers of atoms, and not by the metal as a whole. The large changes in the work function due to different surface conditions, must, of course, be due to corresponding changes in the surface double layer. A knowledge of the charge distribution at the surface is thus really necessary for the determination of the work function. One may expect, however, that the distribution for pure metals will be such that the double layer is small.

4. The Free-Electron Model

The density of positive electricity has the constant value $e\rho_+$ in the half-space on the negative side of the YZ plane and is zero elsewhere. If the density of electrons is $\rho_-(x)$, the electrostatic potential, V, will be given by the solution of

$$d^2V/dx^2=-4\pi e\rho(x);\ \rho(x)=\begin{cases}\rho_+-\rho_-(x) & x<0,\\ -\rho_-(x) & x>0.\end{cases} \tag{2}$$

If the charge distribution is known, this equation may be solved for V. The boundary conditions are, if the metal is uncharged:

$$\begin{aligned} &V=0,\quad dV/dx=0 \quad \text{as} \quad x\to\infty, && \text{(a)}\\ &dV/dx=0 \quad \text{as} \quad x\to-\infty. && \text{(b)}\end{aligned} \tag{3}$$

Condition (3b) requires that[14]

$$\lim_{x\to-\infty}\int_x^\infty \rho(x)dx=0. \tag{4}$$

The constant value of the potential in the interior,[15] V^0, is, by definition, the moment of the surface double layer.

5. The Fock Equations

Our calculation of the charge density at the surface is based on the Slater-Fock[16] approximation of one-electron wave functions. An attempt is made, however, to correct for the correlation (or polarization) forces which are neglected in this approximation (cf. section 8). If there are n electrons which occupy $n/2$ doubly degenerate states, the Fock equations have the form:

$$(-(\hbar^2/2\mu)\Delta_j-eV(\mathbf{r}_j)-A_j)\psi_j(\mathbf{r}_j)=E_j\psi_j(\mathbf{r}_j), \tag{5}$$

where $V(\mathbf{r}_j)$ is the Coulomb potential of the combined positive and negative charges. If

$$\rho(\mathbf{r},\mathbf{r}_j)=\sum_i\psi_i^*(\mathbf{r})\psi_i(\mathbf{r}_j) \tag{6}$$

[10] N. E. Farnsworth and B. A. Rose, Proc. Nat. Acad. Sci. **19**, 777 (1933); B. A. Rose, Phys. Rev. **44**, 585 (1933); N. Underwood, Phys. Rev. **47**, 502 (1935).

[11] See, for example, A. L. Hughes and L. A. DuBridge, *Photoelectric Phenomena* (McGraw-Hill, 1932), p. 72.

[12] H. E. Ives and A. R. Olpin, Phys. Rev. **34**, 117 (1929).

[13] J. J. Brady, Phys. Rev. **41**, 613 (1932).

[14] If the metal has a surface charge, the integral of Eq. (4) is no longer zero. In this case, condition (3a) is replaced by $dV/dx=4\pi\sigma$ as $x\to\infty$, where σ is the surface density of charge.

[15] The superscript zero will be used throughout to indicate values which apply in the interior.

[16] J. C. Slater, Phys. Rev. **34**, 1293 (1929); **35**, 210 (1930). V. Fock, Zeits. f. Physik **61**, 126 (1930). An excellent review has been given by L. Brillouin, *Les Champs "self-consistents" de Hartree et de Fock*, Actualités scientifiques (Herman, Paris, No. 159, 1934).

is the Dirac density matrix, the exchange operator A_j is defined by

$$A_j\psi_j(\mathbf{r}_j)=-\frac{e^2}{2}\int\frac{\rho(\mathbf{r},\mathbf{r}_j)\psi_j(\mathbf{r}_j)d\mathbf{r}}{|\mathbf{r}-\mathbf{r}_j|}, \tag{7}$$

The sum in (6) is over all orbital wave functions, the spin factors being omitted. The factor $\frac{1}{2}$ appears in (7) because the exchange operator is effective only for electrons of parallel spin, while the wave functions of all electrons are summed in $\rho(\mathbf{r},\mathbf{r}_j)$. The density of electrons is $\rho_-(\mathbf{r})=\rho(\mathbf{r},\mathbf{r})$.

In the following, we shall use instead of the exchange operator, an exchange potential defined by:[17]

$$A_j(\mathbf{r}_j)=-\frac{e^2}{2}\int\frac{\rho(\mathbf{r},\mathbf{r}_j)\psi_j(\mathbf{r})d\mathbf{r}}{|\mathbf{r}-\mathbf{r}_j|\psi_j(\mathbf{r}_j)}. \tag{8}$$

This exchange potential thus depends on the wave function, and will be different for different wave functions. The advantages of using the exchange potential rather than the exchange operator are two. First, the potential is easier to visualize physically. As Slater and Krutter[17] point out, the field acting on the electron is actually to be identified with the sum of the Coulomb and exchange potentials, rather than the Coulomb potential alone. There is a hole cut out of the charge distribution about each electron due to the fact that the probability of two electrons of parallel spin being close together is small. The total charge cut out by the hole is exactly e. The exchange potential is essentially the potential resulting from the hole.[18] The second reason is more practical. We want to find a self-consistent solution of these equations, and this must be obtained by numerical calculations. The exchange integrals are very difficult to evaluate directly. The procedure adopted was to approximate the actual set of wave functions by a set of analytic functions for which some of the required integrations could be performed. It was found that the exchange potentials were much less sensitive to the actual form of the wave functions than the exchange integrals.

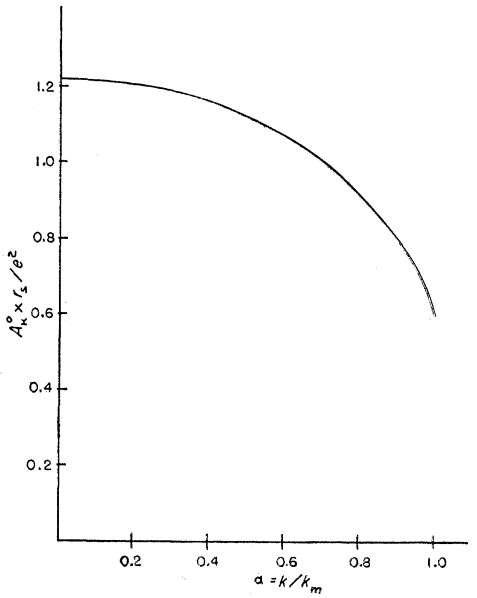

FIG. 1. Exchange potential in interior as a function of the velocity of the electron.

6. WAVE FUNCTIONS IN THE INTERIOR

We shall replace the actual infinity of wave functions for the free-electron model by a finite number by introducing periodic boundary conditions (period L) in the Y and Z directions, and a fixed boundary at $x=-L$. The wave functions in the interior[15] will be the plane waves

$$\psi_k{}^0(x,y,z)=2^{\frac{1}{2}}L^{-\frac{3}{2}}\sin(k_1x+\gamma)e^{i(k_2y+_3kz)}. \tag{9}$$

The allowed values of k_2 and k_3 are $2\pi\nu_2/L$ and $2\pi\nu_3/L$ where ν_2 and ν_3 are integral. The allowed values of k_1 are $2\pi\nu_1/L$ where the values of ν_1 lie close to the half-integers ($\frac{1}{2}$, 1, $\frac{3}{2}$, $\cdots$). We suppose that there are n electrons in the volume L^3 and that all states are doubly occupied from $\nu=0$ to $\nu=\nu_m$, where $\nu=(\nu_1{}^2+\nu_2{}^2+\nu_3{}^2)^{\frac{1}{2}}$ and $\nu_m=(3n/8\pi)^{\frac{1}{3}}$. The radius of the sphere (s sphere) whose volume is equal to the average volume occupied per electron is:

$$r_s=(3/4\pi n)^{\frac{1}{3}}L=1.92(2\pi\nu_m/L)=1.92k_m. \tag{10}$$

[17] Cf. reference 8, and J. C. Slater and H. M. Krutter, Phys. Rev. **47**, 559 (1935).

[18] It should be emphasized that this interpretation cannot be made in all cases. The exchange potential defined in this manner may be complex or may have infinite values. In our case, the potential is real and finite. The probability of an electron in the jth state being in the volume element $d\mathbf{r}$, and a second electron being in the volume $d\mathbf{r}_1$ is the *real* part of:

$$\Sigma_i(\psi_i{}^*(\mathbf{r}_1)\psi_i(\mathbf{r}_1)\psi_j{}^*(\mathbf{r})\psi_j(\mathbf{r})-\psi_i{}^*(\mathbf{r}_1)\psi_i(\mathbf{r})\psi_j{}^*(\mathbf{r})\psi_j(\mathbf{r}_1))d\mathbf{r}d\mathbf{r}_1.$$

The second term represents the "hole."

We shall find it convenient to use r_s as a parameter which gives, indirectly, the density of the electrons.

The exchange potential in the interior is constant. The exchange operator acting on a wave function of the form (9) has the effect of multiplying the wave function by a constant. This constant, which has been evaluated by Dirac,[19] depends on the ratio $\alpha=k/k_m$ of the momentum of the given electron to the maximum momentum of the Fermi distribution. The value of the exchange potential in the interior is:

$$A_k{}^0=e^2k_mf(\alpha)/2\pi=0.306e^2f(\alpha)/r_s,$$

where

$$f(\alpha)=2+(1/\alpha)(1-\alpha^2)\log((1+\alpha)/|1-\alpha|). \quad (11)$$

A plot of $A_k{}^0$ as a function of α is given in Fig. 1.

The equation for $\psi_k{}^0$ is:

$$(-(\hbar^2/2\mu)\Delta-eV^0-A_k{}^0)\psi_k{}^0=E_k\psi_k{}^0, \quad (12)$$

so that $$E_k=(\hbar^2/2\mu)k^2-eV^0-A_k{}^0. \quad (13)$$

It may be noted here that, to the approximation of the Fock equations, the energy required to remove the kth electron from the metal is $-E_k$. The work function, φ, is the minimum value of $-E_k$, or

$$\varphi=-(\hbar^2/2\mu)k_m{}^2+eV^0+A_{k_m}{}^0. \quad (14)$$

This agrees, except for the correlation energy which we have so far neglected, with the results of (I).

7. Method of Calculation

The exchange potential decreases in magnitude as one approaches the surface, and goes to zero as $x\rightarrow\infty$. It is independent of y and z. The Fock equation (cf. Eq. (5)) thus has the form:

$$(-(\hbar^2/2\mu)\Delta-eV(x)-A_k(x))\psi_k(r)=E_k\psi_k(r) \quad (15)$$

with $V(x)$ given by (2) and (3) and E_k by (13).

Since the potential is independent of y and z, the wave functions must be of the form:

$$\psi_k(x,y,z)=\varphi(k,x)e^{i(k_2y+k_3z)}. \quad (16)$$

The equation for $\varphi(k,x)$ is

$$(-(\hbar^2/2\mu)(d^2/dx^2)-eV(x)-A_k(x))\varphi(k,x) =(E_k-(\hbar^2/2\mu)(k_2{}^2+k_3{}^2))\varphi(k,x) \quad (17)$$

and the asymptotic form of $\varphi(k,x)$ in the interior is:

$$\varphi^0(k,x)=2^{\frac{1}{2}}L^{-\frac{3}{2}}\sin(k_1x+\gamma). \quad (18)$$

The phase, γ, may depend on k_2 and k_3 as well as k_1.

In order to obtain an accurate solution of Fock's equations, one takes a set of starting wave functions, and then computes the Coulomb and exchange potentials from these. The next approximation to the correct wave functions is obtained by solving Fock's equations using these potentials. This procedure is repeated until a self-consistent set of wave functions is obtained, i.e., a set such that the Coulomb and exchange potentials computed from these wave functions are the same as the potentials used in deriving the wave functions. Because of the numerical difficulties involved in evaluating the exchange integrals, it was not found feasible to carry out this process in full.

Instead, the exchange potentials were chosen at the beginning and held fixed throughout. A self-consistent solution was then obtained for the electrostatic part of the problem. In the final stage, the Coulomb potential calculated from the final wave functions was equal to the potential used in determining these wave functions. The exchange potentials were determined from an approximate set of wave functions which will be described in the next section. As the charge distribution corresponding to these approximate wave functions is fairly close to the calculated charge distribution, one may expect that the exchange potentials as determined from the two sets of wave functions are also very nearly the same. The Fermi hole is very large near the surface, and so should not be sensitive to the exact form of the wave functions at the surface.

8. Calculation of Exchange Potentials

As one approaches the surface of the metal, the Fermi hole will increase in volume in such a way that a total charge e is always cut out by the hole. The shape of the hole will depend not only on the speed of the electron, but also on its direction. The dependence on direction is rather small, and is unimportant for our purpose. The exchange potential of an electron whose motion is perpendicular to the surface will drop a little more

[19] P. A. M. Dirac, Proc. Camb. Phil. Soc. **26**, 376 (1930).

slowly than the potential of an electron of the same energy whose motion is parallel to the surface, but the drop will start sooner, so that the potentials of the two electrons will be about equal half-way down the slope. We shall, in our work, neglect this dependence on direction.

It is very difficult to evaluate the exchange potentials for wave functions other than the plane waves discussed above. It is possible, however, to get some idea of the behavior of the exchange potentials by calculating $A_k(x)$ for the wave functions of a somewhat simplified model. We shall suppose that the electrons move in a constant negative potential, W, for $x<a$ and that the potential is zero for $x>a$. The position of the barrier, a, and the height of the barrier, W, are adjusted in such a way that the wave functions and charge distribution of this simplified model correspond most closely with the wave functions of the free-electron model. The integrals are so complicated, even for this simple model, that it is difficult to evaluate them except at the potential wall, $x=a$.

Instead of using x as a coordinate, we shall use $\xi=x-a$, so that the barrier is at $\xi=0$. The wave functions are then of the form (16) with

$$\varphi(k,\xi)=\begin{cases}2^{\frac{1}{2}}L^{-\frac{3}{2}}\cdot(1/p)(-(p^2-k^2)^{\frac{1}{2}}\sin k\xi \\ \qquad\qquad +k\cos k\xi) & \xi<0, \\ 2^{\frac{1}{2}}L^{-\frac{3}{2}}(k/p)e^{-(p_2-k_2)^{\frac{1}{2}}\xi} & \xi>0,\end{cases} \tag{19}$$

where
$$p^2=-2\mu W/\hbar^2. \tag{20}$$

The integrals we must evaluate are those of Eq. (7).

$$A_k(\xi)\psi_k(\mathbf{r})=\frac{e^2}{2}\sum_l\int\frac{\psi_l^*(\mathbf{r}_1)\psi_l(\mathbf{r})\psi_k(\mathbf{r}_1)d\mathbf{r}_1}{|\mathbf{r}-\mathbf{r}_1|}. \tag{21}$$

The summation over l is over all occupied states, and may be replaced by an equivalent integration over a sphere S of radius $k_m=(2\pi/L)(3n/8\pi)^{\frac{1}{3}}$. ($n$ is the number of electrons in the volume L^3.) It is shown in the appendix that if we replace ψ_k by (16) and then integrate over y_1, and z_1, that we have:

$$A_k(\xi)\varphi(k,\xi)=\frac{e^2L^3}{4\pi^2}\int d\xi_1\int_S\varphi(l,\xi_1)\varphi(l,\xi)\times\varphi(k,\xi_1)(e^{-\lambda|\xi-\xi_1|}/\lambda)dl_1dl_2dl_3, \tag{22}$$

where
$$\lambda^2=(l_2-k_2)^2+(l_3-k_3)^2.$$

The integration over l_2 and l_3 is difficult to carry out in general unless $k_2=k_3=0$, or, in other words, unless the electron is moving in a direction perpendicular to the surface. Since the exchange potential of an electron depends mainly on its velocity, one may obtain a good approximation for arbitrary k_2, k_3 by first carrying out the integration with k_2 and k_3 set equal to zero, and then replacing k_1, by $(k_1^2+k_2^2+k_3^2)^{\frac{1}{2}}$ in the final result. If $k_2=k_3=0$, the integral (22) reduces to:

$$A_k(\xi)\varphi(k,\xi)=\frac{e^2L^3}{2\pi}\int_{-\infty}^{+\infty}d\xi_1\int_{-k_m}^{k_m}dl_1\int_0^{(k_m^2-l_1^2)^{\frac{1}{2}}}\times d\lambda e^{-\lambda|\xi-\xi_1|}\varphi(l_1,\xi_1)\varphi(l_1,\xi)\varphi(k_1,\xi). \tag{23}$$

The integration over λ may be also carried out, but before doing this it is best to substitute the expressions (21) for $\varphi(l_1,\xi)$ and then integrate over ξ_1. The integration over λ may then be carried out at $\xi=0$. If one then divides by the value of $\varphi(k,\xi)$ at $\xi=0$, one obtains the following integral for $A_k(0)$.

$$A_k(0)=\frac{e^2}{\pi p^2}\int_{k_m}^{k_m}\begin{Bmatrix}k\\l\end{Bmatrix}\left[\tfrac{1}{2}(BC+kl)\times\log\left((k_m^2+l^2-2kl)/(k-l)^2\right)+(lB-kC)\tan^{-1}\left(D/(k-l)\right)\right]+k^2\log\left((B+C+D)/(B+C)\right)\Big\}dl \tag{24}$$

where $B=(p^2-k^2)^{\frac{1}{2}}$, $C=(p^2-l^2)^{\frac{1}{2}}$, $D=(k_m^2-k^2)^{\frac{1}{2}}$. The last integration may be carried out if $p=\infty$, i.e., if the barrier at $\xi=0$ is infinite. In this case

$$A_k(0)=(e^2k_m/\pi)\left[\tfrac{3}{4}-1/4\alpha^2+(1/8\alpha^3)\times(1+2\alpha^2-3\alpha^4)\log\left((1+\alpha)/|1-\alpha|\right)\right], \tag{25}$$

where $\alpha=k_1/k_m$. It can be shown that this last equation is rigorously correct for electrons of *arbitrary* direction if $\alpha=(k_1^2+k_2^2+k_3^2)^{\frac{1}{2}}/k_m$.

Fig. 2 gives the variation of the exchange potential with α for $p=\infty$ and for $p=1.15k_m$. The latter were obtained by numerical integration. The wave functions for $p=1.15k_m$ correspond most closely with the computed wave functions of the free-electron model.

These data enable one to get a reasonably good picture of the way in which the exchange poten-

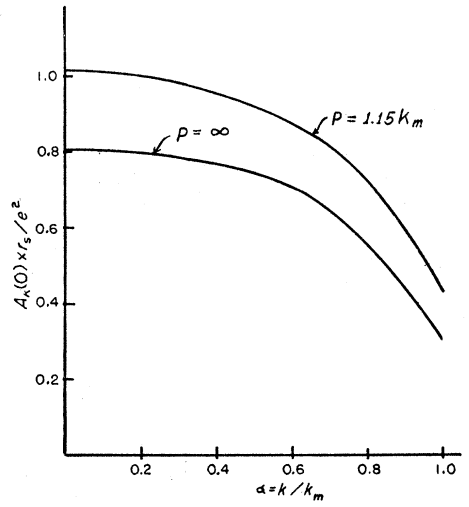

FIG. 2. Exchange potentials at the barrier for $p=1.15k_m$ and $p=\infty$.

tials vary near the surface of the metal. The exchange potentials for wave functions of the type we are considering depend mainly on the charge distribution, and not on the exact form of the wave functions at the surface. The Fermi hole is so large that any local irregularities are ironed out when one integrates over the hole to obtain the potential.

The position of the barrier is at $\xi=0$ or at $x=a$. The value of a is fixed for any value of p by the requirement that the metal be neutral, i.e., the requirement of Eq. (4). It may be shown by straightforward calculation that this gives:

$$a=(3/2k_m^3)[\pi k_m^2/4 - (k_m^2-p^2/2)\sin^{-1}(k_m/p)-\tfrac{1}{2}(p^2-k_m^2)]. \quad (26)$$

If $p=\infty$, $a=3\pi/8k_m=0.61r_s$. Similarly if $p=1.15k_m$, $a=0.11r_s$.

If the positions of the barriers are fixed in this manner, the exchange potentials are rather insensitive to the value of p. The values of the exchange potentials have been computed for $p=\infty$ at a point a distance $0.5r_s$ behind the barrier, or at $x=0.11r_s$. These values, obtained by numerical integration, agreed to within one percent with those computed at the same point for $p=1.15k_m$.

In the actual calculation, the positions of the barriers were taken at points slightly different from those given above. The wave functions corresponded more closely with those of the free-electron model with the barriers placed at $a=0.58r_s$ and at $a=0.08r_s$ for $p=\infty$ and for $p=1.15k_m$, respectively, instead of at points a distance $0.03r_s$ further out. The difference, however, is very slight, and hardly enough to affect the results appreciably.

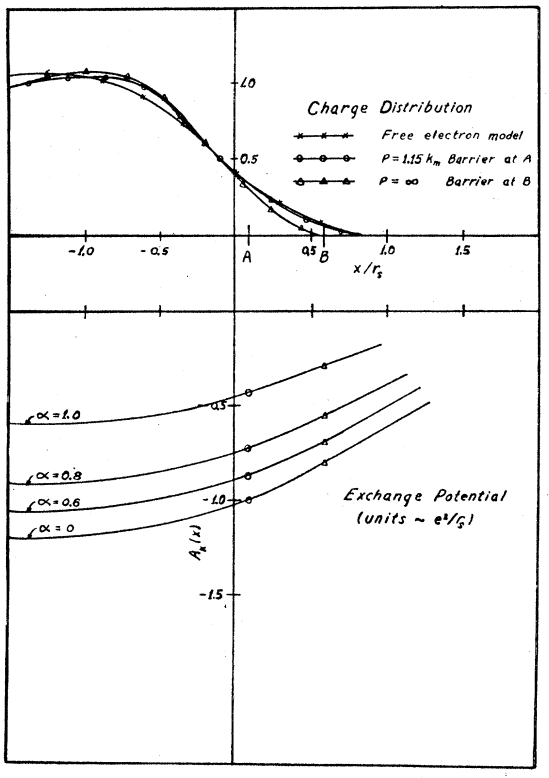

FIG. 3. Charge distributions for approximate wave functions and exchange potentials adopted.

Fig. 3 shows the charge distributions for $p=\infty$ and $p=1.15k_m$ as well as the charge distribution for the free-electron model which will be discussed at more length later on. The charge distributions match fairly well, so that it may be expected that the exchange potentials will also agree.

The exchange potentials which have been adopted are also shown in Fig. 3. These were obtained by drawing smooth curves through the known points at $x=0.08r_s$ and at $0.58r_s$ in such a way that they are asymptotic to the known values of the exchange potentials in the interior, and to zero for large positive values of x. The circles represent the values of the exchange potentials for $p=1.15k_m$ as taken from the curve of Fig. 2. The triangles represent the corresponding values for $p=\infty$. One would, of course, expect

that the circles are closer to the actual exchange potentials than the triangles, but the latter are probably not far off. This method for obtaining the exchange potentials is, of course, very rough, but it was not thought advisable to attempt a more accurate calculation at the present time.

Before discussing the solution obtained, we shall, in the next section, discuss the modification introduced by the correlation or polarization forces which we have so far neglected.

9. The Correlation Energy

Because of electrostatic repulsion, electrons tend to keep as far away from each other as possible. In the Slater-Fock approximation, electrons of parallel spin keep apart because of the exchange effect. There is, however, no allowance for the interaction of electrons of one spin with those of opposite spin except that resulting from the integrated charge distribution. The correlation energy of a metal is the energy gain in the binding energy of a metal which results from the use of a more general wave function than the Slater determinant of one-electron wave functions. Wigner[20] computed this energy for free electrons by using a wave function which allowed for a statistical correlation of the positions of the electrons of one spin with those of opposite spin. The direct contribution of the correlation hole to the work function, computed in (I), is

$$e^2 f(r_s) - e^2 r_s f'(r_s)/3, \qquad (27)$$

where $r_s f(r_s)$ is the correlation function of Wigner.[20]

The correlation hole will also influence the charge distribution at the surface, and therefore the double layer. This latter effect seems to be very difficult to take rigorously into account, because to do so it would be necessary to abandon the one-electron wave functions we have used so far. One would expect, however, that the influence on the charge distribution could be approximately taken into account by an appropriate modification of the potential curves for the one-electron wave functions. This modification would be such as to lower the potential in the interior of the metal. At large distances from the surface, the combined potential of the exchange and correlation forces should go over into the image potential, $-e^2/4x$.

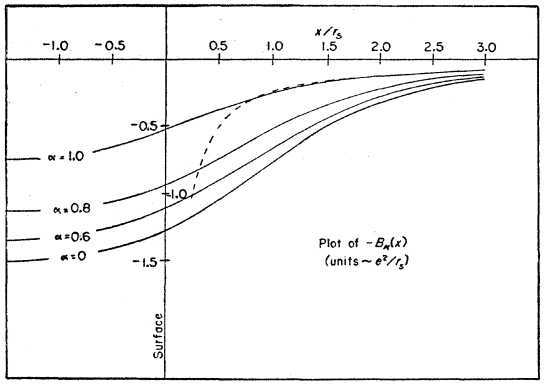

FIG. 4. Combined exchange and correlation potentials ($r_s=4$ Bohr units).

The amount the potential is lowered in the interior will depend on the velocity of the electron, and will be smaller for electrons of high velocity than for those of lower velocity. In the following work we shall make the crude approximation that the correlation potential varies in the same way with velocity and position as the exchange potential in the interior and at small distances from the surface of the metal, and that at large distances from the surface the combined correlation and exchange potential approaches the image potential asymptotically.[21] In other words, we shall replace $A_k(x)$ in Eq. (17) by a potential $B_k(x)$ where

$$B_k(x) = (1+c)A_k(x) \qquad (28)$$

except for large x, and we assume that when x is large, $B_k(x) \sim e^2/4x$. We shall take for c the ratio of the correlation to the exchange energy of the free-electrons. If $r_s=4$ Bohr units, $c=0.24$.

Fig. 4 gives the potentials $B_k(x)$ for several values of x which were obtained from the exchange potentials, $A_k(x)$, of Fig. 3 by the method described above. These curves apply for $r_s=4$ Bohr units.[22]

[20] E. Wigner, Phys. Rev. **46**, 1002 (1934). The correlation function is represented by the lower curve of Fig. 7.

[21] J. C. Slater has suggested a treatment along these lines. Cf. reference 8.

[22] The curves for the smaller values of α should probably approach the image potential more rapidly than I have indicated. This modification would make little difference in the present connection, but should be borne in mind if these curves are put to some other use. The author is indebted to Professor Slater for this remark.

10. The Self-Consistent Solution

Two solutions of Eqs. (17) have been obtained, one using the exchange potentials of Fig. 3, and the second using $B_k(x)$ of Fig. 4. The first solution was very rough, and served only to indicate the order of magnitude of the moment of the double layer. The Coulomb potential of the second was self-consistent to within $\pm 0.01e^2/r_s$. The density of electrons in both cases was taken to be approximately equal to the density of free-electrons in Na, assuming one free-electron per atom, the actual value corresponding to $r_s=4$.

The solutions were obtained in the following manner. One first assumes a charge distribution for the electrons, and then calculates the Coulomb potential, $V(x)$, by integration of Eq. (2). Eq. (17) is then integrated numerically from large positive values of x into the interior, where $\varphi(k, x)$ must join smoothly with the solution in the interior, $\sin(k_1x+\gamma)$. This requirement determines the amplitude of the wave function, and also the phase, γ, of the plane wave in the interior. The integration is carried out for a sufficient number of values of k_1, k_2, k_3, so that one may integrate over the occupied states and obtain the charge distribution. If this calculated distribution checks the assumed distribution, the problem is solved. If not, a new distribution is assumed, and the wave functions and charge distribution are redetermined. This process is repeated until a self-consistent solution is obtained. The exchange potentials $A_k(x)$ (or $B_k(x)$) are held fixed throughout.

In order to determine an accurate self-consistent solution of Fock's equations, the exchange potentials should also be redetermined from the calculated wave functions, but this involves a difficult numerical integration and has not been carried out.

In the pure Fock case, the exchange potentials $A_k(x)$, are used, and the work function, φ, is

$$\varphi = -(\hbar^2/2\mu)k_m^2 + eV^0 + A_{km}^0. \qquad (29)$$

Rough calculations that have been carried out indicate that the moment of the double layer, eV^0, is about one volt for $r_s=4$. The maximum value of the Fermi energy, $\hbar^2k_m^2/2\mu$, is 3.15 ev. The exchange energy of the electron of maximum velocity is $0.61\ e^2/r_s=4.1$ ev. Thus if we neglect the correlation energy entirely, the work function will be about two volts. If we include the direct contribution of the correlation energy (cf. section 8) the work function is about three volts.

It is not altogether reasonable to include the direct contribution of the correlation energy if we omit it in the calculation of the surface double layer (V^0) because the work function is rather insensitive to the exchange potential employed. Our neglect of the correlation energy has been partly compensated by a large V^0. If we had omitted the exchange energy, we would still obtain a positive (though probably small) value for the work function with a very large V^0 (~ 4 volts).

The solution obtained when the potentials $B_k(x)$ of Fig. 4 were used is illustrated in Fig. 5. The potential curves shown include the Coulomb potential, $V(x)$. The moment of the double layer, V^0, is $0.06e^2/r_s$, or about 0.4 volt. The value of

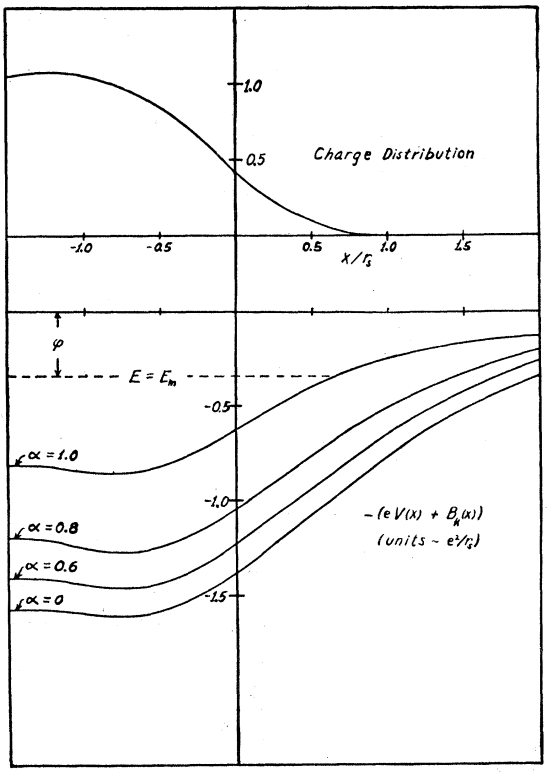

FIG. 5. Self-consistent charge distribution and potentials for the free-electron model ($r_s=4$ Bohr units). The potential curves shown include the exchange and correlation potentials of Fig. 4 and the Coulomb potential of the charge distribution.

the work function is then 2.35 volts, if we include the direct contribution of the correlation energy (1.0 ev).

11. Comparison with Sodium

It has been shown by Wigner and Seitz[2] and by Slater[3] that the wave functions of the conducting electrons of the sodium crystal are, except in the immediate vicinity of the ions, very nearly the same as those of perfectly free electrons. The density of electrons is practically uniform throughout the crystal. The Fermi energy is within one or two percent of the classical free-electron value, $3\hbar^2k_m^2/10\mu$. The exchange potentials are very nearly constant in space, and are close to the free-electron values in magnitude. One would thus expect that the free-electron model which has been discussed in the preceding sections would bear a close relationship with the sodium crystal.

Since the exchange potentials are constant in the interior of the lattice, the Fock equations are identical with the Hartree equations. The exchange terms affect the energies of the electrons, but not the wave functions. If we omit the exchange terms, the potential field in which the electrons move is the combined potential of the ions and the Coulomb potential of the electrons. Wigner and Seitz replace the actual (body-centered) lattice by a set of close packed spheres. They found that if the zero of potential is taken on the surface of an s sphere, the energy of the lowest state is $E_0=-0.23$ ev. The actual potential on the surface of an s sphere, relative to a point outside one of the faces of the crystal, will differ from zero by the moment of the double layer of this face.

The work function, φ, is (cf. (I)):

$$\varphi_{\mathrm{Na}}=-E_0+eD+A_{k_m}{}^0+C-\hbar^2k_m^2/2\mu, \quad (30)$$

where we have written C for the contribution from the correlation energy, and eD for the moment of the double layer. The only difference between (30) and the corresponding formula for the free-electron model is that $-E_0+eD$ replaces eV^0 of the latter.

One might at first be tempted to identify eV^0 with eD. Some care must be taken, however, as the definitions of the moments in the two cases are slightly different. Thus eD will be zero if the distribution of electrons in the surface s spheres is the same as that in the inner s spheres, while eV^0 will be zero if the distribution is constant for $x<0$ and zero for $x>0$. For the same distribution of electrons, eD will be somewhat smaller than eV^0. The difference can be computed for any face of the crystal, and it amounts to approximately 0.25 ev for the 110-face. Values for other faces are slightly larger.

Thus $-E_0+eD$ for the 110-face should be about the same as eV^0, while the corresponding values for other faces should be a little less. This, of course, rests on the assumption that the electronic charge distribution at the surface of the sodium crystal is approximately equal to that of the free-electron model. Calculations that have been attempted for the 110-face indicate that this assumption is justified.

Table I summarizes the results that have been obtained for the free-electron model, together with the rather uncertain experimental values of the work function of sodium. The agreement is very satisfactory, considering the approximate nature of the theory. The moment listed for sodium was obtained by reducing the value for the free-electron model (0.4 volt) by 0.25 volt.

Table I. *Comparison of theoretical values of the work function of the free-electron model with experimental values for sodium.*

	Free-Electron Model, Correlation Forces Omitted	Free-Electron Model, Correlation Forces Included	Sodium (exp.)
Moment of double layer	1.0	0.4	(0.15)
Work function	2.0	2.35	2.46* 2.25†

* A. R. Olpin, see reference 11, p. 75.
† Z. Berkes, Math. Phys. Lapok **41**, 131 (1934).

12. Conclusions

The following are the main results obtained from the present investigation of the free-electron model:

(1) The barrier at the surface is due largely to exchange and polarization forces, rather than to ordinary electrostatic forces.

(2) There is no single potential barrier which is satisfactory for electrons of all velocities. Each electron has, so to speak, its own barrier.

(3) The moment of the double layer at the surface is relatively small, in agreement with the conclusions reached in reference I. This, of course, means that the ordinary electrostatic potential in the interior is small.

(4) Approximate agreement is obtained between the work function of the free-electron model and the experimental values of the work function of sodium.

The writer wishes to express his gratitude to Professor E. Wigner, under whose direction this work was carried out, and to Professor J. H. Van Vleck, Professor J. C. Slater, and Dr. F. Seitz for interesting discussions.

Appendix

Evaluation of the integral:

$$I=\int\int \frac{e^{i[(k_2-l_2)(y-y_1)+(k_3-l_3)(z-z_1)}}{((\xi-\xi_1)^2+(y-y_1)^2+(z-z_1)^2)^{\frac{1}{2}}}dy_1dz_1.$$

This integral is not absolutely convergent, and in evaluating it one must be careful to introduce polar coordinates, θ, ρ in place of y_1 and z_1 and then integrate first over θ. If one chooses the origin of θ properly, the integral takes the form:

$$I=\int_0^\infty \rho d\rho \int_{-\pi}^{\pi} \frac{e^{i\lambda\rho\cos\theta}}{((\xi-\xi_1)^2+\rho^2)^{\frac{1}{2}}}d\theta$$

with $\lambda^2=(k_2-l_2)^2+(k_3-l_3)^2$. The integration over θ gives Bessel's function $J_0(\lambda\rho)$. We thus have:

$$I=2\pi\int_0^\infty \frac{\rho J_0(\lambda\rho)d\rho}{((\xi-\xi_1)^2+\rho^2)^{\frac{1}{2}}}=(2\pi/\lambda)e^{-\lambda|\xi-\xi_1|}.$$

Eq. (22) follows immediately.

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The Variation of Young's Modulus with Magnetization and Temperature in Nickel

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The relation between Young's modulus, magnetization, and temperature in annealed polycrystalline nickel, 99.7 percent pure, is determined for values of J between zero and saturation, and for values of T between 23.5°C and 400°C. The percent increase in Young's modulus is proportional to J^2 between zero and about 0.4 saturation, at all temperatures below 311°C. The total increase in the modulus from the demagnetized to the saturated state is 6.7 percent at 23°, reaches a maximum of 18.7 percent at 185°, and decreases to zero at the Curie point. The results indicate that the theory of this phenomenon offered by Akulov is probably essentially correct but requires modification. The method employed for the measurement of Young's modulus yields at the same time a measure of the coefficient of internal friction of the material. The internal friction decreases with increasing magnetization at all temperatures below the Curie point. In the demagnetized material it reaches a maximum value at the same temperature as does the change in elastic modulus. Its value at magnetic saturation is the same order of magnitude as that of a nonferromagnetic substance.

THE domain theory of ferromagnetism, first suggested by Webster in connection with magnetostriction and since developed by Heisenberg, Akulov and others, is noteworthy for its success in correlating different ferromagnetic phenomena in both single and polycrystalline materials. For example, Akulov[1] has shown that the change of Young's modulus with magnetization in a polycrystalline substance can be described solely in terms of the initial susceptibility and one magnetostrictive constant of a single crystal. The present paper is a report of an experimental investigation of the relation between Young's modulus and magnetization in annealed polycrystalline nickel at various temperatures below the Curie point. The results are compared with the formulae of Akulov's theory.

[1] Akulov, Zeits. f. Physik **85**, 661 (1933).

Experimental Method

The research consists in ascertaining the value of the Young's modulus, E, corresponding to an intensity of magnetization, J, and a temperature, T, for values of J lying between zero and technical saturation, and values of T ranging from 20°C to 400°C. Accordingly the experimental method must permit the simultaneous measurement of E, J, and T. To this end a preliminary determination is made of the relation between J, T and the normal magnetic induction, B, so that in the subsequent procedure a knowledge of B and T suffices to fix the value of J.