SEPTEMBER 15, 1934 PHYSICAL REVIEW VOLUME 46

On the Constitution of Metallic Sodium. II

E. WIGNER AND F. SEITZ, *Palmer Physical Laboratory, Princeton University*

(Received June 18, 1934)

The present work represents an extension to a previous development by the same authors, on the theory of metallic sodium. In the first part of this paper a completely self-consistent solution of Fock's equations for the sodium lattice is carried through indirectly, this being the approximation in which one-electron functions are employed. The question of the correlations between electrons with parallel spin is investigated quantitatively and the Fermi "zero-point energy" is calculated using the proper effective field. The results show that the electrons behave almost exactly as if they were entirely free, the binding energy being 9 kg cal and the lattice constant 4.86A, as compared with the observed values 26.9 kg cal and 4.23A. To complete the picture, the correlations between electrons with anti-parallel spins are investigated in the latter part, since these are not included in the Fock picture. A general discussion of this question is presented and a quantitative treatment of its effect is made which yields a new binding energy of 23.2 kg cal and a lattice constant of 4.75A. The source of the remaining discrepancy is discussed.

I. THE POTENTIAL INSIDE THE LATTICE

1.

In a previous paper by the same authors a method of calculating the binding properties of metals was developed[1] and applied to sodium. The procedure employed was essentially one of solving the Fock system of equations[2] for the valence electrons (i.e., the system of equations to which the Schrödinger equation reduces when one electron functions are assumed). This solution did not proceed from a formal investigation of Fock's differential equations, but was developed indirectly under the guiding principles of the picture afforded by the free electron theory.

To begin with, the lattice was subdivided into polyhedrons of equal size and form, which we shall call s-polyhedrons, each of which surrounds one ion lying in its center, and is bounded by the planes which bisect, perpendicularly, the lines connecting the corresponding ion with its 14 neighbors (the alkali metals form body centered lattices). Since these polyhedrons closely resemble spheres, they may be replaced by spheres of equal volume for many purposes and these we shall designate as s-spheres, their radius being $r_s=(3v_0/4\pi)^{\frac{1}{3}}$, where v_0 is the atomic volume.

Concerning the nature of the electronic states of the lattice, we know that there will be bands of allowed levels, no more than two electrons occupying each level because of the restrictions imposed by the Pauli principle, and that the lowest state in the lowest band will possess the symmetry of the lattice. From this it follows that its normal derivative will vanish on the boundaries of the s-polyhedrons and to obtain its wave function, it is only necessary to solve the Schrödinger equation within one polyhedron, by using a suitable effective field and this boundary condition. Approximate wave functions of other electrons may be obtained from this by multiplying it with factors of the form

$$e^{2\pi i(\nu_1 x+\nu_2 y+\nu_3 z)/L}, \tag{1}$$

where ν_1, ν_2, ν_3 are positive or negative integers and L is the length of the crystal-edge, corresponding to free electrons with nonvanishing eigenvalues of momentum.

In order to find the effective potential field inside of an s-polyhedron, we first replace them by s-spheres, correcting later for the small error arising from this. For an electron at a given point the field consists of three parts: first, the potential arising from the ion at the center of the s-sphere, second, the potential of the other ions; and third, the potential arising from the other free electrons. Instead of making a direct calculation of each of these in the order given it is found far more advantageous to begin with an investigation of the third for it happens that simplifying assumptions concerning the nature of this interaction may be fully justified at a later stage and allow a simple treatment of the first two.

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[1] E. Wigner and F. Seitz, Phys. Rev. **43**, 804 (1933).

[2] J. C. Slater, Phys. Rev. **35**, 210 (1930); V. Fock, Zeits. f. Physik **61**, 126 (1930).

The potential of the electron under consideration arising from the other electrons is equal to that arising from a continuous electron fluid of density which is e times the probability of having an electron at the corresponding point of the lattice. If we assume that all wave functions arise from one by multiplication with a factor of the form (1), the probability distribution will be the same for each. Moreover, since it will be spherically symmetric within each sphere the effective field of each ion will be neutralized outside of the sphere in which it is contained, and the only field which remains to be taken into account for our chosen electron is that arising from the charge within the s-sphere which contains it. Since this will give rise to a spherically symmetric field and a spherically-symmetric wave function, the assumption of spherical symmetry is completely self-consistent. The error introduced by replacing the s-polyhedrons by spheres is calculated in appendices 1 and 2 and turns out to be negligibly small.

In the previous work only the field arising from the ion in each s-sphere was taken into account and it was assumed that correlations were such that other electrons did not penetrate the given sphere. Under this assumption, the wave function turned out to be practically constant for more than 90 percent of the volume of the sphere (cf. Fig. 1), a fact which allows us to take the other electrons into account very simply and correct for the inaccuracies involved. For if we now introduce the assumption that all of the electrons have the distribution given by ψ_{000} of Fig. 1 (with factors (1)), it is found that this set of one-electron functions forms a practically self-consistent solution of Fock's equations for the lattice.

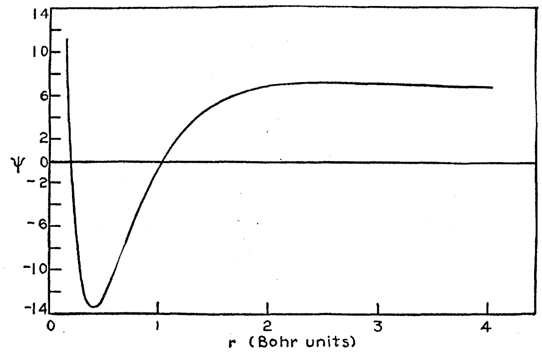

FIG. 1. Metallic wave function for lowest electronic state. The corresponding energy is -0.6 Rydberg units and the proper boundary condition is satisfied at 4.04 Bohr units.

The potential $V(x, y, z)$ which enters into the wave equation of an electron in Fock's system is not the ordinary average of the potentials of the other particles for all configurations, but the average of the potentials with each configuration taken with the weight it has under the assumption that the considered electron is in the point x, y, z. We have seen Eq. (6) that there is a hole in the otherwise uniform electron fluid around every electron because the probability of two electrons having parallel spin being very near is very small. We shall call this the Fermi hole. Its effect is such as to make the potential more negative than it would otherwise be. Since its shape is practically independent of the position of the electron, the change of the potential arising from it is constant and it alters the energy but not the wave function. The previous work merely gave an estimate of this change and we shall give a more accurate calculation here.

Because the wave functions of electrons of higher energy are given by multiplying ψ_{000} by (1) only in the case of free electrons (i.e., when ψ_{000} is constant), we have investigated this very important point in more detail (cf. Section II), and have found that the energy differences between the different states is the same as that obtained when the electrons are free. The wave functions are not simply ψ_{000} multiplied by (1), however, but each is multiplied in addition by a factor which is nearly constant within a sphere one Bohr unit in radius but becomes exponential outside.

In all of the work sketched in the previous paragraphs we have been able to restrict ourselves to the one electron picture, that is, the wave function for all of the electrons may be assumed to be a determinant of single electron functions. This leads to correlations between electrons of parallel spin of the type expressed by the Fermi holes and to none whatever between electrons of antiparallel spin. There are such correlations, however, arising from the mutual repulsion terms, but they lie beyond the scope of Fock's equations. We shall call these holes "correlation holes" and the corresponding energy "correlation energy," and shall attempt to handle them in Section III.

2.

Under the assumption of a uniform charge distribution the potential within the s-sphere at the distance r from the ion is

$$V(r)+(3e^2/2r_s)-(e^2r^2/2r_s^3), \tag{2}$$

where the first term arises from the ion, and the other two from the electron fluid inside the s-polyhedron. In reference 1 the wave equation for the potential $V(r)$ alone—which was taken from Prokofjew's work[3]—was solved and the corresponding characteristic value determined. The correction for the fact that this is not exactly the energy of the corresponding wave function is taken care of in Appendix 1. The second term in (2) is independent of r, leaving the wave function unchanged, and gives a positive contribution

$$E_{11}=3e^2/4r_s \tag{3}$$

to the energy. A factor $\frac{1}{2}$ enters, since the interactions between electrons have to be counted only once.

In order to take into account the last term, the Schrödinger perturbation theory may be applied and this yields

$$E_{12}=\tfrac{1}{2}\left(-\frac{e^2}{2r_s^3}\int\psi^2r^2dv+\frac{e^4}{4r_s^6}\sum_{\kappa}{}'\frac{(\int\psi\psi_\kappa r^2dv)^2}{E-E_\kappa}\right) \tag{4}$$

up to the second approximation where ψ and E are the solutions of the wave equation with the potential $V(r)$ alone, which we know from reference 1. The factor $\frac{1}{2}$ arises for the same reason given before. To determine the first part of (4) we have numerically evaluated the integral over ψ^2r^2 for three different values of the lattice constant, i.e., r_s and the corresponding energy. The results are tabulated in Table I, the energy being given in Rydberg units, r_s in Bohr units, and the integral in squares of Bohr units. For the actual lattice constant $r_s=4$, the integral has the same value that it would have if ψ were a constant. The last column gives the ratio f of the numerically calculated integral to that calculated with a constant ψ for the other cases.

TABLE I.

E	r_s	$\int\psi^2r^2dv$	f
−0.60	4.05	9.90	0.994
−0.55	4.74	12.95	0.962
−0.50	5.48	16.50	0.916

In the second part of (4) the denominator may be replaced by a mean value $E-E_k$ and the summation in the numerator gives $\int\psi^2r^4dv-(\int\psi^2r^2dv)^2$ in the usual way.[4] By taking ψ to be constant for this small term one obtains

$$-\frac{1}{E_k-E}\cdot(e^4/r_s^2)\cdot\left(\frac{3}{56}-\frac{9}{200}\right)=-0.005e^2/r_s. \tag{5}$$

The mean value of E_k has been estimated to be +0.3 Rydberg units. The effect of the perturbing terms in (2) on the wave functions can safely be said to be extremely small because of the smallness of (5), and their total contribution to the energy is

$$E_{12}=(-0.15f-0.005)e^2/r_s. \tag{6}$$

The fact that we must deal with the s-polyhedron instead of s-sphere is taken into account in Appendix 2.

3.

In the preceding section we have calculated using the ordinary average potential. We know, however, that in order to calculate the potential of an electron at a certain point we should average over the configuration of the other electrons with the weights which they would have if the electron under consideration were at the given point. It was shown in reference 1 that if there is an electron at a given point the probability of another electron being at a distance r from it is

$$\tfrac{1}{2}\frac{e}{v_0}\left[1-9\left(\frac{\sin(r/d')-(r/d')\cos(r/d')}{(r/d')^3}\right)^2\right]. \tag{7}$$

The factor $\frac{1}{2}$ expresses the fact that only the distribution of charge with parallel spin is affected, v_0 is the atomic volume and $d'=(v_0/3\pi^2)^{\frac{1}{3}}$. (7) was derived under the assumption that ψ_{000} is constant and that the higher ones are obtained from it by multiplication with (1). Both assumptions will be shown to be practically correct

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[3] W. Prokofjew, Zeits. f. Physik **58**, 255 (1929).

[4] A. Unsöld, Zeits. f. Physik **43**, 563 (1927).

insofar as energies are concerned. The total amount of charge removed because of the hole expressed by (7) is exactly e and may be viewed as being concentrated in the electron at the center of the hole. To this approximation it has been assumed that all of this hole is in the parallel charge distribution—an assumption not exactly correct, however.

The decrease in the potential energy of the electron at the center of the hole is

$$\frac{9}{2}\frac{e^2}{v_0}\int_0^\infty \frac{1}{r}\left(\frac{\sin(r/d')-(r/d')\cos(r/d')}{(r/d')^3}\right)^2 4\pi r^2 dr=\frac{3^{4/3}e^2}{2\pi^{1/3}v_0^{1/3}}=\frac{3^{5/3}}{2^{5/3}\pi^{2/3}}\frac{e^2}{r_s}=0.916\frac{e^2}{r_s}. \tag{8}$$

Since this energy[5] does not depend on the position of the electron, it is to be carried forward at once as an energy with a factor $\frac{1}{2}$, in order that the interactions between pairs of electrons is taken into account only once. We have, therefore,

$$E_2=-0.458e^2/r_s. \tag{9}$$

If the wave function were not entirely flat in the lowest state, (7) should be more rigorously multiplied by $v_0\psi_{000}$. The integral (8) will hardly be affected by this, however, because the regions in which ψ_{000} changes appreciably are small compared to the distance in which (7) has appreciable variation and the mean value of (8) for different positions of the electron will differ from the calculated value by even a smaller percentage.

The sum $E_{11}+E_{12}+E_2$ from the viewpoint of Fock's equation, gives the effect arising from the fact that the potential at any point is not exactly $V(r)$ (where r is the distance from the nearest ion), as it would be if the hole in the electron fluid of the other electrons extended exactly over the s-sphere. It really surrounds (cf. Fig. 2) the electron under consideration spherically in such a way that part (A) of the s-sphere is left uncovered. On the other hand, it extends over regions (C) outside the s-sphere. Now E_2 represents the effect of the entire hole ($B+C$), while $E_{11}+E_{12}$ represents the effect of the lack of hole in the regions A and B. The fact that we made all calculations under the assumption that the electron density is constant, will not greatly affect our final result, since in the largest region, B, it does not matter which density we use, as long as we use the same density in both cases. An error will be introduced only by using an improper density in A and C—but here ψ_{000} is very nearly constant.

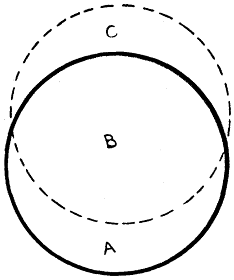

FIG. 2. Schematic diagram of prominent regions in the unit cell.

II. THE FERMI ENERGY

4.

Our next task is the calculation of the zero-point energy of the free electrons. First of all, an error in reference 1 should be corrected, for it was stated there that the zero-point energy is actually smaller than it would be for free electrons. It was observed that $\psi^0_{\nu_1\nu_2\nu_3}=\psi_{000}\exp\left[2\pi i(\nu_1x+\nu_2y+\nu_3z)/L\right]$ possessed the proper transformation properties for a state with the quantum numbers ν_1, ν_2, ν_3 (the "components of momentum" being[6] $2\pi\hbar\nu_1/L$, $2\pi\hbar\nu_2/L$, $2\pi\hbar\nu_3/L$). Moreover its mean energy was higher than that of ψ_{000} by the amount $2\pi^2\hbar^2(\nu_1^2+\nu_2^2+\nu_3^2)$ which is just the Fermi cor-

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[5] This formula was first found by F. Bloch, Zeits. f. Physik **57**, 545 (1929).

[6] $\hbar$ in this paper is Dirac's h, namely, Planck's constant divided by 2π. We would like to correct another error of reference 1 here. The subtraction of 2500 cal. from the binding energy at the end of Section IV is incorrect. The fact that the binding energy of the inner shells decreases with increasing binding of the valence electrons does not appear in the Prokofjew picture because the potential energy of the valence electron is taken to be ρV instead of $\frac{1}{2}\rho V$, so that it is not necessary to consider the change of the potential acting on the other particles.

rection for an entirely free electron. As the real $\psi_{\nu_1\nu_2\nu_3}$ is the solution of a minimum problem, it was concluded that its energy is even lower than that of $\psi^0_{\nu_1\nu_2\nu_3}$.

This argument is not correct, however, since $\psi_{\nu_1\nu_2\nu_3}$ has the lowest energy of only those states which are orthogonal to the states of the K and L shells. This is correct for ψ_{000} but not for $\psi^0_{\nu_1\nu_2\nu_3}$ and the real $\psi_{\nu_1\nu_2\nu_3}$ should be calculated just as ψ_{000} was—by solving a differential equation.

At any rate, it can be assumed from the transformation property of $\psi_{\nu_1\nu_2\nu_3}$ that it has the form

$$\psi_{\nu_1\nu_2\nu_3}=\chi_{\nu_1\nu_2\nu_3}\exp\left[2\pi i(\nu_1x+\nu_2y+\nu_3z)/L\right], \tag{10}$$

where $\chi_{\nu_1\nu_2\nu_3}$ has the translational periods of the lattice. By inserting (10) into the Schrödinger equation, one obtains

$$\begin{gathered}H\chi_{\nu_1\nu_2\nu_3}+\frac{2\pi i\hbar^2}{mL}\left(\nu_1\frac{\partial}{\partial x}+\nu_2\frac{\partial}{\partial y}+\nu_3\frac{\partial}{\partial z}\right)\chi_{\nu_1\nu_2\nu_3}=F_{\nu_1\nu_2\nu_3}\chi_{\nu_1\nu_2\nu_3},\\ E_{\nu_1\nu_2\nu_3}=F_{\nu_1\nu_2\nu_3}+(2\pi^2\hbar^2/mL^2)(\nu_1^2+\nu_2^2+\nu_3^2).\end{gathered} \tag{11}$$

If we neglect the second term on the left side to begin with, the equation is identical with the equation for ψ_{000}, which we shall denote by ψ_0 in this section, the other solutions of (11) with $\nu_1=\nu_2=\nu_3=0$ being designated by ψ_κ. To this approximation $E_{\nu_1\nu_2\nu_3}=E_{000}+2\pi^2\hbar^2/mL^2(\nu_1^2+\nu_2^2+\nu_3^2)$ which is just the result of reference 1.

We shall take into account the second term of (11) by the Rayleigh-Schrödinger perturbation method. The first approximation gives zero, since $\int\psi_0\partial\psi_0/\partial x$ vanishes, and the second approximation will be proportional to the ν's. From considerations of the s-polyhedron, the boundary conditions were found to be such that the value and derivative of the wave functions should be equal in the two points at which a line perpendicular to the boundary plane cuts the boundary. We know furthermore from group theory that all solutions ψ_κ of the unperturbed problem are either even or odd functions of x, y, z. Now if we calculate the second approximation for the energy, we need integrals of the type $\int\psi_0\partial\psi_\kappa/\partial x$, and since ψ_0 is an even function of the coordinates, ψ_κ must be even in y, z and odd in x, or the integral vanishes. Therefore, all three perturbing terms in (11) will give non-vanishing matrix elements only with different ψ_κ. The second approximation for the energy is, therefore

$$F_{\nu_1\nu_2\nu_3}=\frac{4\pi^2\hbar^4}{m^2L^2}(\nu_1^2+\nu_2^2+\nu_3^2)\sum_\kappa{}'\frac{|\int\psi_\kappa\,\partial\psi_0/\partial x|^2}{E_0-E_\kappa}, \tag{12}$$

since the integral with the y and z-derivatives can be replaced by integrals with x derivatives, E_κ is the energy of the state ψ_κ. The sum in (12) contains one positive term (arising from the $2p$ level) and all other terms are negative. Since the value of the positive term is very sensitive to the actual shape of the wave function ψ_0, we tried to transform (12) in a form more suitable for the calculation in the following way.

If ψ_0 and ψ_κ were the characteristic functions of an atom, (12) could be evaluated by the Thomas-Kuhn sum rule and would give just the negative Fermi correction, so that the sum of the first and second approximation would be zero. In the present case of periodic boundary conditions, however, the partial integrations cannot be performed in the same way. We obtain from the Schrödinger equation for ψ_κ by multiplication with $x\psi_0$ and subtracting the corresponding equation for ψ_0 multiplied by $x\psi_\kappa$

$$(E_\kappa-E_0)\int x\psi_0\psi_\kappa=-\frac{\hbar^2}{2m}\int\left[x\psi_0\Delta\psi_\kappa-\psi_\kappa\Delta(x\psi_0)\right]-\frac{\hbar^2}{m}\int\psi_\kappa\frac{\partial\psi_0}{\partial x}. \tag{13}$$

The first term can be transformed by Green's theorem into a surface integral and we have

$$\int\psi_\kappa\frac{\partial\psi_0}{\partial x}dv=\frac{m(E_0-E_\kappa)}{\hbar^2}\int x\psi_\kappa\psi_0dv-\tfrac{1}{2}\int\left(x\psi_0\frac{\partial\psi_\kappa}{\partial n}-\psi_\kappa\frac{\partial(x\psi_0)}{\partial n}\right)df, \tag{14}$$

where $\partial/\partial n$ denotes the normal derivative. For the usual boundary conditions, the last term in (14) would vanish. After replacing *one* of the integrals in (12) by the expression (14), the summation over κ can be carried out in the first term by the completeness-relation[7] and yields

$$(4\pi^2\hbar^2/mL^2)(\nu_1^2+\nu_2^2+\nu_3^2)\int x\psi_0(\partial\psi_0/\partial x)dv. \tag{15}$$

Since ψ_0 is a function of r alone, we have

$$\int x\psi_0\frac{\partial\psi_0}{\partial x}dv=\frac{2\pi}{3}\int_0^{r_s} r^3\frac{\partial\psi_0{}^2}{\partial r}dv=\tfrac{1}{2}v_0\psi_0(r_s)^2-\tfrac{1}{2}.$$

The $-\frac{1}{2}$ gives the negative Fermi correction and cancels the first approximation. The first term, however, gives an expression very similar to the Fermi correction, namely

$$\frac{2\pi^2\hbar^2}{mL^2}(\nu_1^2+\nu_2^2+\nu_3^2)v_0\psi_0(r_s)^2, \tag{16}$$

the difference being that the value of ψ_{000} at the boundary enters instead of the mean value.

The second term of (14), inserted into (12), gives

$$-\frac{2\pi^2\hbar^4}{m^2L^2}(\nu_1^2+\nu_2^2+\nu_3^2)\sum_{\kappa}{}'\frac{\int(\psi_\kappa\,\partial\psi_0/\partial x)dv}{E_0-E_\kappa}\int x\psi_0\frac{\partial\psi_\kappa}{\partial n}df, \tag{17}$$

since all odd ψ_κ vanish at the boundary. To this sum the $2p$ state does not contribute anything more, because its wave function is practically zero outside $r=3$. Similarly we found upon direct computation, that the integral $\int\psi_\kappa\partial\psi_0/\partial x d\vartheta$ vanishes "accidentally" for $r_s=4$ for the next higher odd state. The energy of the next is of the order of magnitude +5 Rydberg units and we have replaced E_κ in the denominators of (17) by a mean value E_κ of this magnitude. Now $\int\psi_\kappa\partial\psi_0/\partial x d\vartheta$ is the expansion coefficient of ψ_κ in the series for $\partial\psi_0/\partial x$ so that the summation can be carried out in the numerator and gives $\int x\psi_0(\partial/\partial n)(\partial\psi_0/\partial x)df$. Since ψ_0 is a function of r alone, (17) can further be transformed into

$$-\frac{2\pi^2\hbar^4}{m^2L^2}(\nu_1^2+\nu_2^2+\nu_3^2)\frac{4\pi}{3}r_s{}^3\psi_0(r_s)\frac{\partial^2\psi_0(r_s)}{\partial r^2}. \tag{18}$$

Here $\partial^2\psi_0/\partial r^2$ can be calculated from Schrödinger's equation and we obtain for the entire zero-point energy the sum of (16) and (18)

$$E_{\nu_1\nu_2\nu_3}-E_{000}=(2\pi^2\hbar^2/mL^2)(\nu_1^2+\nu_2^2+\nu_3^2)v_0\psi_0(r_s)^2[1+2(E_0-V(r_s)/(E_0-\bar{E}_k)]. \tag{19}$$

This equation shows that the ratio of the actual zero-point energy of the electrons to the zero point energy of free electrons is

$$v_0\psi_0(r_s)^2[1+2(E_0-V(r_s)/(E_0-\bar{E}_k)] \tag{19a}$$

can be larger than 1. It approaches zero for very large r_s but increases greatly with decreasing r_s when the pressing of the valence electrons into the inner shells becomes appreciable. The second term of (19) is negligible, and several values of the first are given in the table below:

r_s	3.67	4.05	4.74	5.48
$v_0\psi_0(r_s)^2$	1.08	0.99	0.89	0.76

Once again, it is found that ψ_{000} behaves at $r=4$ as if it were constant. Moreover it is remarkable that the second term in (19a) increases the Fermi energy over the classical value by a very small amount, if the potential is taken as arising entirely from the ion, and it decreases it somewhat below that value if ψ_0 is supposed to be

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[7] This is exactly London's reasoning (Zeits. f. Physik **39**, 322 (1926)) with the only difference that the partial integration must be carried through more carefully than in his case.

the solution of a Schrödinger equation with the potential (2).

5.

If one plots the Fermi energy against $(\nu_1^2+\nu_2^2+\nu_3^2)^{\frac{1}{2}}$ Eq. (19) should give the curvature of the plot at the zero point. It would not be right, however, to assume that it is correct for all ν. As a matter of fact we know from the work of F. Bloch[8] that for higher ν it may depend upon the ratios $\nu_1 : \nu_2 : \nu_3$ and from the work of P. M. Morse, R. Peierls[9] and especially L. Brillouin[10] that it is not a continuous function of the ν's everywhere but has discontinuities corresponding to wave-lengths for which the Bragg-Laue conditions of x-ray reflections are fulfilled.

According to Brillouin this discontinuity in the space of the ν's is on the rhombdodecahedron $\nu_1 \pm \nu_2 = \pm L/d$, $\nu_1 \pm \nu_3 = \pm L/d$, $\nu_2 \pm \nu_3 = \pm L/d$ where d is the lattice constant in the space of the ν's. In order to obtain an idea of the size of these discontinuities, we have taken three points of this rhombdodecahedron, corresponding to the three directions (100), (110), (111) and tried to obtain the two energy values for each of them, the transformation properties of the corresponding waves being determined for the symmetry elements of the space group.

It was an easy matter to find a function which had the proper transformation properties within the s-polyhedron but it seemed difficult for us to satisfy the continuity conditions at the boundary. The procedure finally adopted possesses no rigorous justification, but it was decided most reasonable to select wave functions which were continuous only at the midpoint of the fourteen boundary planes, with linear combinations of s, p, d, f and g functions. For the point $\nu_1 = \nu_2 = L/2d$, $\nu_3 = 0$ ((110) direction) it was sufficient to take a linear combination of the s; d and g functions for the lowest function at the discontinuity and a p function for the upper. For the (111) direction the lower was represented by a linear combination of p and d functions and the upper by a combination of s, f and g while for the (100) direction the lower part was a linear combination of p and d functions and the upper was a d function. The results for the observed lattice constants are shown in Fig. 3 in which the abscissa is $(\nu_1^2+\nu_2^2+\nu_3^2)^{\frac{1}{2}} d/L$ and the energy is in Rydberg units. The parabola corresponds to free electrons; the heavy section representing the extent to which electrons would occupy the levels, and the other three curves correspond to the designated direction $\nu_1 : \nu_2 : \nu_3$. In accord with the remarks in previous paragraphs that the electrons behave almost as if free, the discontinuities are not very pronounced. The calculations leading to Fig. 3 do not justify an accuracy greater than 0.05 Rydberg units for absolute values of energy, although the energy differences at the discontinuities are probably more accurate.

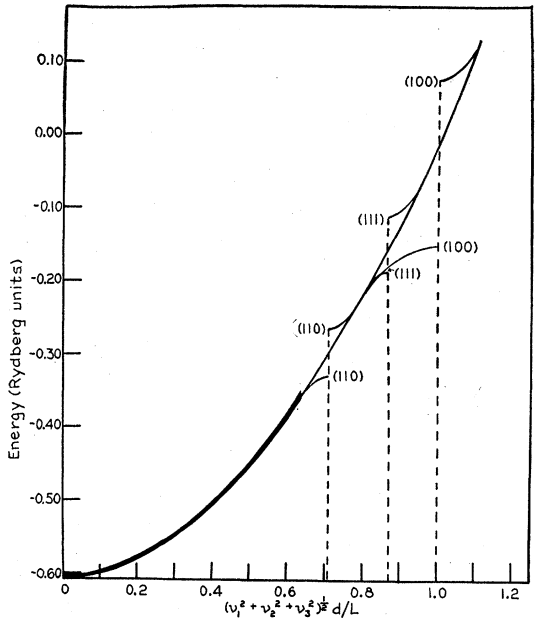

FIG. 3. Graph showing the energy as a function of $(\nu_1^2+\nu_2^2+\nu_3^2)^{\frac{1}{2}} d/L$ for wave functions of electrons 'moving' in three prominent crystallographic directions.

In a recent paper which has appeared while this manuscript was in preparation, Slater[11] has investigated this phase of the problem from a viewpoint similar to that presented here. He has made a formal solution satisfying the proper boundary conditions at the centers of the eight hexagonal faces of the s-polyhedron, which

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[8] F. Bloch, Zeits. f. Physik **52**, 555 (1928).

[9] P. M. Morse, Phys. Rev. **35**, 1310 (1930); R. Peierls, Ann. d. Physik **4**, 121 (1930).

[10] L. Brillouin, Die Quantenstatistik, Berlin 1931, p. 281–316.

[11] J. C. Slater, Phys. Rev. **45**, 794 (1934). Cf. also H. Jones, N. F. Mott, H. W. B. Skinner, Phys. Rev. **45**, 379 (1934).

requires a general function with eight arbitrary parameters that he chose to be a linear combination of one s, three p, three d and one f function each with arbitrary coefficients. This yields a secular equation of the eighth order which he solves in a degenerate case, namely, when the wave is traveling in a direction orthogonal to one of the coordinate axes. For the case of the (110) direction, which he considers in detail, the results agree, essentially, with those we have obtained and bear out our conclusions completely regarding the accuracy with which the free electron picture represents facts.

6.

The unsatisfactory feature of the previous paragraph is that the wave functions employed are not continuous so that they do not possess an energy-value in a strict sense. It is evident, however, as Slater points out, that a continuous wave function would be obtained by superposing an infinite number of wave functions with different angular factors, which is also possible in the case of a constant potential, though it would be a rather awkward procedure, since we know the wave functions accurately. This would correspond to a development of $e^{2\pi i\nu x/L}$ into a series

$$e^{2\pi i\nu x/L}=f_0(r)+P_1(\theta,\,\varphi)f_1(r)+P_2(\theta,\,\varphi)f_2(r), \quad (20)$$

where the P_l are the spherical harmonics and the f_l depend only on the distance from the center of the s-polyhedron and are essentially Bessel-functions. If we determine (20) in each s-polyhedron, the resulting functions will join each other continuously, since they all represent the same function $e^{2\pi i\nu x/L}$. For the energy value of 0.15 Rydberg units which in the case of free electrons corresponds to $\nu d/L=\frac{1}{2}$, the quantities rf_l'/f_l are given at the surface of the s-sphere in the first line of the table below:

	s	p	d	f
l	0	1	2	3
Free electron	-0.9666	0.049	1.647	2.7
Electron in lattice	-1.00	0.044	1.674	2.8

The last line gives the same quantities for the Prokofjew-field of Na for the distance $r_s=4$ and the energy value -0.45 Rydberg units, which lies 0.15 above the energy value -0.60 of the electron with the lowest energy. The first two numbers were obtained by graphical integration, and the others are those for a simple Coulomb field, since the field of the Na ion does not give different values from those of a simple Coulomb field for d, f and higher terms. It is seen that the deviation of the two sets of numbers in the table are very small. Hence, if one adds the s, p, d, etc., solutions of the Prokofjew field with such coefficients that the value of each function at $r=r_s$ is equal to the value of the corresponding function f_l in (20) for the same radius, one obtains a function within the s-polyhedron which will join similar functions in the other s-polyhedra continuously and even with practically continuous first derivatives. This shows that the energy of the waves for $(\nu_1^2+\nu_2^2+\nu_3^2)^{\frac{1}{2}}d/L=\frac{1}{2}$ is higher than that of the wave $\nu_1=\nu_2=\nu_3=0$ by the same amount (0.15 Rydberg units) in both cases. The same is true for all ν's which characterize states occupied by electrons.

If the numbers of the first line were smaller than those of the second, the Fermi energy would be smaller for free electrons than in the actual lattice. A more detailed numerical consideration shows that this is actually the case, though only to a very small extent. The situation seems to be opposite, however, if one takes into account the perturbation given in (3). The difference does not amount to more than 1 or 2 percent in either case, however, and we shall employ the numbers corresponding to free electrons in the following.

Of course the coincidence of the two sets of numbers arises simply from the fact that the electrons in our picture behave very nearly like free electrons. We know that the optical properties of metals can also be explained very well on this assumption,[12] so it possesses additional backing.

When all the energy terms calculated in section 1 are added, one obtains the lower curve of Fig. 4 for the energy of the bottom of the Fermi distribution as a function of the lattice constant, which is represented by the radius of the s-sphere. The upper curve contains the Fermi energy and gives the total energy of the electrons in the Fock picture. It yields a lattice constant of 4.76A and a binding energy of 9.0 cal.

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[12] C. Zener, Nature **132**, 968 (1933); R. de L. Kronig, Nature **133**, 211 (1934).

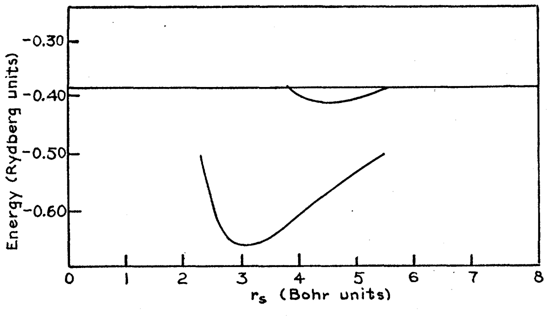

FIG. 4. Energies as functions of r_s. The lower curve is the energy of the lowest electronic state while the upper curve represents the energy of the entire lattice computed on the basis of the one-electron picture.

III. Correlations Between Electrons with Antiparallel Spin

7.

In proceeding with a generalization of the foregoing sections to include electron correlations more general than those allowed by the one electron picture, we no longer have at hand guiding principles that are as definite as those which we had there. Since the energy is to be minimized, the extensions to be made rest principally upon the possibility of forming a hole around every electron in the charge distribution of the other electrons. This possibility is, of course, given by the multi-dimensionality of the wave function, which allows a different probability distribution of the other electrons for different positions of the one considered. Since such a hole is already present in the charge distribution of the electrons with parallel spin, we have principally to consider the possibility of a similar hole in the distribution of the electrons with antiparallel spin. These holes are not included in the one electron picture (cf. reference 3), but we know them to exist in atomic eigenfunctions from the works of Bethe[13] and Hylleraas.[14] They seem to play an even more important rôle in metals than in free atoms.[15]

The wave function employed in the previous sections for $2n$ electrons, may be written under neglect of the spin part, as[16]

$$\Psi(x_1\cdots x_n, y_1\cdots y_n)=(1/n!)\begin{vmatrix}\psi_1(x_1) & \cdots & \psi_1(x_n)\\ \vdots & & \vdots\\ \psi_n(x_1) & \cdots & \psi_n(x_n)\end{vmatrix}\cdot\begin{vmatrix}\psi_1(y_1) & \cdots & \psi_1(y_n)\\ \vdots & & \vdots\\ \psi_n(y_1) & \cdots & \psi_n(y_n)\end{vmatrix}. \qquad (21)$$

Here x_k represents the three Cartesian coordinates of the kth electron with upward spin and the y refer in a similar way to the electrons with downward spin. The functions $\psi_1, \cdots, \psi_n$, previously designated by $\psi_{\nu_1\nu_2\nu_3}$ are the n lowest energy wave functions for an electron in the field of all the ions and the other electrons, regarded as a charge distribution. The task of the previous section, which we believe to be solved to a sufficient degree of accuracy, was to calculate the functions ψ and the energy of the total Ψ of (21) as functions of the lattice constant.

A natural suggestion for the generalization of (21) is to include the coordinates of all electrons of antiparallel spin in $\psi_\nu(x_k)$ as parameters. This function will then be a different function of x_k for different values of $y_1, \cdots, y_n$, and will have a minimum around every value of the set. We shall consider the effect on the function ψ_ν and the energies if we replace the continuous charge distribution of the electrons by point charges at $y_1\cdots y_n$. This replacement will alter the field acting on the electron x and we shall use a perturbation method to calculate its consequences.

We shall set

$$\Psi(x_1,\cdots,x_n;y_1,\cdots,y_n)=(1/n!)\begin{vmatrix}\psi_1(y_1,\cdots,y_n;x_1) & \cdots & \psi_1(y_1,\cdots,y_n;x_n)\\ \vdots & & \vdots\\ \psi_n(y_1,\cdots,y_n;x_n) & \cdots & \psi_n(y_1,\cdots,y_n;x_n)\end{vmatrix}\cdot\begin{vmatrix}\psi_1(y_1) & \cdots & \psi_1(y_n)\\ \vdots & & \vdots\\ \psi_n(y_1) & \cdots & \psi_n(y_n)\end{vmatrix} \qquad (22)$$

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[13] H. Bethe, Zeits. f. Physik **57**, 815 (1929).

[14] E. A. Hylleraas, Zeits. f. Physik **48**, 469 (1928).

[15] We are much indebted to Professor Slater for the remark that possibly the disagreement between experiment and his theory for the order and distance of atomic terms due to the same configuration, also arises from the fact that the correlation energy is greater for singlets than for higher multiplets.

[16] M. Delbrück, Proc. Roy. Soc. (London) **A129**, 686 (1930).

and denote by

$$\Psi_0(x_1,\cdots,x_n;y_1,\cdots,y_n)=\psi_1(y_1,\cdots,y_n;x_1)\cdots\psi_n(y_1,\cdots,y_n;x_n)\cdot|y|, \tag{22a}$$

the part of (22) which is not yet antisymmetrized in the x's, where $|y|$ is the second determinant in (22). When no ambiguity arises, we shall designate $\psi_\nu(y_1\cdots y_n, x)$ by $\psi_\nu(x)$, in which it is to be understood that both x and ν correspond to sets of three numbers. In addition, it will be assumed that both $\psi_\nu(y_1\cdots y_n, x)$ and its complex conjugate appear in the first determinant of (22) when this function is not real, that the same is true regarding $\psi_\nu(y)$ in $|y|$, and that the $\psi_\nu(y_1\cdots y_n, x)$ as functions of x are solutions of a characteristic value problem so that

$$\int\psi_\nu(y_1,\cdots,y_n;x)^*\psi_{\nu'}(y_1,\cdots,y_n;x)dx=\delta_{\nu\nu'} \tag{23}$$

for all values of y.

It is well known that the total energy of Ψ can be written in the form [17]

$$\int\int\Psi^*(K_x+K_y+V_0+V)\Psi_0 dxdy,$$

where K_x and K_y are the operators for the kinetic energy of the electrons of upward and downward spin respectively, V_0 is the old potential function calculated from the viewpoint in which the electrons are regarded as smeared out over the entire crystal, and V is the potential function required to account for the change incurred by viewing the y-electrons to be point charges with regard to their interaction with the x-electrons. The first three terms are those dealt with in the previous work and yield the wave function (21), while the last is a perturbing term and will yield a perturbation energy. If we retain the old wave functions in the neighborhood of the ions and replace them by a more general solution of (22) in regions where they behave like $e^{2\pi i\nu x/L}$, the expectation value of V_0 will be left unchanged since the electron density is changed nowhere, and in addition, it may be seen that (7) remains essentially true. The sum of the energy correction E and the Fermi energy F will be given, therefore, by the integral

$$E+F=\int\int\Psi^*(K_x+K_y+V)\Psi_0 \tag{24}$$

taken over the part of the configuration space in which the wave function is changed and which we shall assume to be the entire space.[18] It is to be noted that for an entirely flat wave function the expectation value of V, namely

$$\int\int V|y|^2dxdy \tag{25}$$

is zero. We shall proceed with a calculation of the energy correction E.

8.

To begin with, we shall transform the three terms of (24) to a more suitable form. In calculating the expectation value of $\hbar^2/2m\cdot\Delta_x$, we can use (23) to carry out the integration over all of the remaining x's and obtain

$$\int\int\Psi^*K_x\Psi_0 dxdy=-\frac{\hbar^2}{2m}\frac{1}{n!}\sum_\nu\int\int\psi^*\times\Delta_x\psi_0|y|^2dxdy. \tag{26}$$

If the same is done for $-\hbar^2/2m\cdot\Delta_y$, the terms arising from the second derivative of the determinant are

$$(4\pi^2\hbar^2/2m)\sum\nu^2. \tag{27a}$$

Those terms containing the derivatives of the $\psi_\nu(y_1\cdots y_n, x_\nu)$ and of the determinant may be integrated over all of the x's except x_ν and lead to expressions of the form

$$\int\int y_\nu(x_\nu)^*|y|\frac{\partial\psi_\nu(x_\nu)}{\partial y_\kappa}\frac{\partial}{\partial y_\kappa}|y|dx_\nu dy.$$

If this is added to the similar term containing the derivative of ψ_ν^* it follows from (23) that the sum will vanish upon integration over x_ν. Finally, those terms which contain the second derivative of Ψ_0 are of two types, namely,

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[17] Cf. e.g. E. Wigner, Gruppentheorie und ihre Anwendung. Braunschweig 1931. p. 323.

[18] The difference of the two volumes is negligible.

$$-(\hbar^2/2m)(1/n!)\sum_\nu\int\int\psi_\nu(x_\nu)^*\Delta y_\kappa\psi_\nu(x_\nu)|y|^2dx_\nu dy \tag{27b}$$

and

$$-(\hbar^2/2m)(1/n!)\sum_{\nu\neq\mu}\int\int[\psi_\nu(x_\nu)^*\psi_\mu(x_\mu)^*-\psi_\nu(x_\mu)^*\psi_\mu(x_\nu)^*]\cdot\mathrm{grad}_{y_k}\psi_\nu(x_\nu)\ \mathrm{grad}_{y_k}\psi_\mu(x_\mu)|y|^2dx_\nu dx_\mu dy.$$

If $\psi_\nu\neq\psi_\mu^*$ we can add to the latter the term in which ψ_ν^* replaces ψ_ν and the sum will vanish upon integration over x. Hence the only terms resulting from the first term in the bracket are

$$-\hbar(^2/2m)(1/n!)\sum_\nu\int\left|\int\psi_\nu(x_\nu)^*\ \mathrm{grad}_{y_k}\ \psi_\nu(x_\nu)dx_\nu\right|^2|y|^2dy \tag{27c}$$

and those from the second are such as to yield

$$-(\hbar^2/2m)(1/n!)\sum_{\mu\neq\nu}\int\left|\int\psi_\mu(x)^*\ \mathrm{grad}_{y_k}\ \psi_\nu(x)dx\right|^2|y|^2dy. \tag{27d}$$

If $\mu=\nu$ in (27d), we obtain (27c), so that the sum of (26), (27a, b, c, d) and

$$(1/n!)\sum_\nu\int\int|\psi_\nu(y_1,\cdots,y_n;x)|^2V(y_1,\cdots,y_n;x)dx|y|^2dy$$

leads to

$$\frac{1}{n!}\sum\int\int\psi_\nu(x)^*\left[V(y_1,\cdots,y_n;x)-\frac{\hbar^2}{2m}\left(\Delta_x+\Delta_{y_1}+\cdots+\Delta_{y_n}+\frac{4\pi^2\nu^2}{L^2}\right)\right]\cdot\psi_\nu(x)dx|y|^2dy$$
$$-(\hbar^2/2m)(1/n!)\sum_\kappa\sum_{\mu,\nu}\int\left|\int\psi_\nu(x)\ \mathrm{grad}_{y_k}\ \psi_\nu^*(x)dx\right|^2|y|^2dx=E \tag{28}$$

for the change in energy since

$$F=(\hbar^2/2m)2\sum_\nu(4\pi^2\nu^2/L^2)$$

is the Fermi energy. The summations over μ and ν are to be extended over all occupied states. In the following it will appear from the form given $\psi_\nu(y_1\cdots y_n,x)$ (i.e., see (29)) that the last expression in (28), which could only lower the energy, vanishes.

We shall proceed under the assumption that $\psi_\nu(y_1\cdots y_n,x)$ has the form

$$\psi_\nu(y_1,\cdots,y_n;x)=e^{2\pi i\nu.x/L}\chi_\nu(x-y_1,\cdots,x-y_n), \tag{29}$$

in which χ_ν to the approximation considered here, is a constant plus a sum of functions, each of which depends on one argument $x-y_k$. When substituted in (28) this yields

$$E=\sum_\nu\int\int\chi_\nu^*[V(y_1,\cdots,y_n;x)-(\hbar^2/2m)(2\Delta_x+(4\pi i/L)\nu\cdot\mathrm{grad}_x)]\psi_\nu\cdot|y|^2dxdy. \tag{30}$$

In order to minimize this χ_ν must satisfy the equation

$$-(\hbar^2/2m)\Delta\chi_\nu-(2\pi i\hbar^2/mL)\nu\cdot\mathrm{grad}\ \chi_\nu+V(y_1,\cdots,y_n;x)\chi_\nu=\epsilon_\nu\chi_0(y_1,\cdots y_n;x). \tag{31}$$

Eq. (31) is much the same as (11), the principal difference being that the relative mass $\frac{1}{2}m$ appears instead of m.

9.

The characteristic values ϵ_ν of (31) will depend on the position $y_1\cdots y_n$ of the electrons with downward spin, and we must average this characteristic value using $|y|^2$ as a weight-function to obtain a final value. It is possible to perform this general calculation to a sufficient degree of accuracy using a modification of the usual Rayleigh-Schrödinger perturbation process, since it does not converge in its usual form, but this involves a rather lengthy computation, so we shall content ourselves here with an estimate of the solution to (31) and present the more general solution at a later time.

It is evident that if the y's are to be most favorable for a large negative value of the correction energy we shall want the regions in which no y occurs to be as large as possible. In these regions $\chi_\nu(y_1\cdots y_n, x)$ will have large maxima and the electron x will have the greatest probability of being as far as possible from the electrons of opposite spin. A secondary effect resulting from this will be an alteration of the original Fermi distribution $|y|^2$, and, as a consequence, (8), but we shall not take this into account in the present calculation.[19]

The most disadvantageous configurations for the y's, that is those giving the smallest $-\epsilon_\nu(y\cdots y_n)$, are the close-packed lattices, while the most advantageous is one in which all of the y electrons are at one corner-point of the lattice. This latter is practically impossible for the Fermi distribution, however, while the former possess the greatest probability. A graphical integration of (8), however, shows that the mean distance of the nearest electron with parallel spin to a given electron is $1.1r_s$ in contrast with the nearest distance of $2.3r_s$ for close-packed configurations. For this reason it seems reasonable to us, as far as energy is concerned, to make use of a "mean configuration" of the electrons with downward spin in which pairs of electrons form a body-centered lattice. In this the nearest electron will be much closer than it should be but there are no clusters of more than two electrons present, which compensates the fact that the pairs are at the most disadvantageous position.

The energy $\epsilon_\nu(y_1\cdots y_n)$ of this mean configuration can be calculated very simply by the method employed in reference 1; the radius of the sphere surrounding every electron is $(4)^{\frac{1}{3}}r_s$ and the potential energy within the sphere is

$$V=2e^2/r+e^2r^2/r_1^3-3.6e^2/r_1, \qquad (32)$$

in which the last term has been introduced in order to satisfy (25). We shall designate $\chi_\nu(y_1, \cdots, y_n, x)$ by $\chi_\nu(x, y, z)$ when the configuration of the $y_1, \cdots, y_n$ introduced here is implied.

In order to determine the χ_0 associated with the lowest energy, we shall regard V in (31) as a perturbation, for which the unperturbed problem is

$$-(\hbar^2/m)\Delta\xi(x, y, z)=\eta\xi(x, y, z). \qquad (33)$$

Each of the solutions of this possess an "azimuthal quantum number" l, these for $l=0$ and $l=1$ being of the form $r\xi_{0\kappa}=\int m\omega_\kappa r$, and $r\xi_{1\kappa}=\partial/\partial x \sin\omega_\kappa r$, etc., where the ω_κ are to be determined from the relation $\tan\omega_\kappa r_1=\omega_\kappa r_1$ arising from the boundary conditions. The normalized solutions for $l=0$, are, to a sufficient degree of accuracy

$$\xi_{00}=(3/4\pi r_1^3)^{\frac{1}{2}}; \quad \xi_{01}=\frac{1.024}{(2\pi r_1)^{\frac{1}{2}}}\frac{\sin 1.43\pi r/r_1}{r} \qquad (34)$$

$$\xi_{0\kappa}=(1/2\pi r_1)^{\frac{1}{2}}\frac{\sin(2\kappa+1)\pi r/2r_1}{r}=(1/2\pi r_1)^{\frac{1}{2}}\frac{\sin\omega_1 r}{r}$$

for which the corresponding unperturbed energies are

$$\eta_{00}=0, \qquad n_{0\kappa}=\hbar^2\omega_\kappa^2/m. \qquad (34a)$$

The matrix elements $V_{0\kappa}$ of V may be obtained as follows. We have

$$V_{0\kappa}=\int\xi_{00}V\xi_{0\kappa}dV$$
$$=-(3/4\pi r_1^3)^{\frac{1}{2}}(1/\omega_1^2)\int V\Delta\xi_{0\kappa}dV, \qquad (35)$$

in which the Laplacian may be made to operate on the V by use of partial integration. From Poisson's equation ΔV is $-8\pi e^2(\delta(r)-\frac{3}{4}\pi r_1^3)$ in which the last term gives rise to a vanishing contribution since it, like ξ_{00}, is constant and the

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[19] It cannot be taken into account without also replacing the effect of electrons with parallel spin on each other by point charges in a similar way to that carried through here for the electrons with antiparallel spin. If this is not done, the two kinds of electrons will push each other into different parts of the crystal, thus invalidating the assumption under which we have calculated their mean effect.

integral over it vanishes in (35). The first term yields

$$V_{0\kappa}=(24)^{\frac{1}{2}}e^2/\omega_\kappa r_1^2 \tag{36}$$

so that the solution of (31) for $\nu=0$ is

$$\chi_{00}=(3/4\pi r_1^3)^{\frac{1}{2}}-\sum_\kappa{}' \frac{V_{0\kappa}}{\hbar^2\omega_\kappa^2/m+V_{\kappa\kappa}}\xi_{0\kappa} \tag{37}$$

and the corresponding energy is[20]

$$1/(16.2+3.07r_s)+0.005. \tag{38}$$

Although this is given in atomic units, the correction is true for only half of the electrons and must be taken in Rydberg units. The solution (37) has also been obtained by use of numerical integration and is illustrated in Fig. 5.

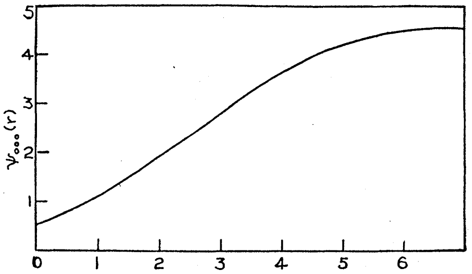

FIG. 5. Wave function corresponding to a solution of (30) with $\nu=0$ and $r_s=4$.

The wave function of an electron has only about 30 percent of its mean value in the region where two other electrons are situated and only 50 percent in the region where there is an electron with antiparallel spin.

For ν other than 0, we shall have greater energy gains because the Fermi distribution will be narrower as a result of the presence of the field arising from the $y_1\cdots y_n$ electrons than it would be without this field. In this case we can take the second term of (35) into account as a perturbation, the calculation being very similar to that employed in Section 4. The first approximation is zero, while the second, namely

$$(4\pi^2\hbar^4/m^2L^2)\nu^2\sum|\int(\partial\Psi_{00}/\partial x)\chi_\kappa|^2/-E_\kappa \tag{39}$$

is evidently negative, and would vanish if χ_{00} were entirely flat. Because of the selection rules, it is sufficient to take wave functions with $l=1$ for χ_κ, which are simply derivatives of the functions (34) to a first approximation, while χ_{00} must be taken from (37). The sum (39) may be conveniently compared with the Fermi energy of free electrons and a simple calculation shows that it is 4 percent of this quantity.

If this result and (38) are subtracted from the upper curve in Fig. 4, one obtains Fig. 6 which yields $r_s=4.40$ or a lattice constant of 4.75A, and a heat of sublimation of 23.2 kg. cal. The experimental values are 4.23A and 26.9 kg. cal., respectively. For the observed lattice constant the calculated energy is 18.6 cal. It may be mentioned at this point that the preceding calculation of the correlation energy is valid only in the neighborhood of $r_s=4$.

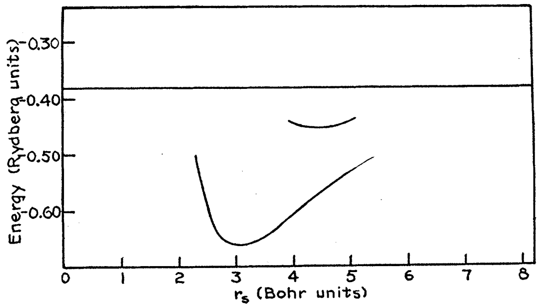

FIG. 6. The upper curve replaces that of Fig. 4 and contains the results arising from the correction to the one-electron picture.

It is to be noted that the actual χ_ν will not have, in general, forms such as those we have calculated here. For irregular configurations of the electrons with downward spin they will be rather complicated linear combinations of these functions, possessing energies that are nearly the same, however. Each function ψ_ν going with an energy ϵ_ν will have a maximum in that region in which the potential has a trough allowing such a characteristic value and will be small everywhere else as a result of interference of the superposed waves.[21] This does not affect the actual wave function (22), for all of the electrons, however, since this is a determinant of the ψ_ν and does not change upon taking such a linear combination.

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[20] The V_{kk} must be calculated graphically. We obtained $V_{11}=2.4\,e^2/r_1$.

[21] Cf. the discussion of a very similar problem by F. Hund, Zeits. f. Physik **40**, 742 (1927).

10.

It is hardly necessary to mention that the calculation of the last section must be regarded only as an attempt to find the correct wave function for the electrons in the metal, and we are well aware that we could guess its form only roughly. We should like to mention that the deviation of the wave function from the determinantal form (21) using plane de Broglie waves is much more pronounced here than in the one electron picture (cf. Fig. 5) in which the plane waves were a surprisingly good representation. They still form a reasonably good approximation to the true state of affairs, however, and for this reason we believe that the fact that (22) is not symmetric under interchange of x and y is not of extremely great importance. The function (22) still possesses this property if we consider the differences of the ψ_ν from the de Broglie waves as small quantities and neglect the second order terms.

The remaining discrepancy of 3.7 kg. cal. we believe to arise from two sources. First it is not evident that the Prokofjew field is completely suitable for calculations of this kind and, in fact, it is surprising that the atomic levels are as good as we have found them to be. Rigorously the exchange terms between the valence electrons and the closed shells cannot be transformed into the form of potentials because they are represented by more general operators, and there is a possibility that the effect of these is not described accurately enough for the states occurring in the crystal by an effective potential field. This important point is being more accurately investigated in connection with a treatment of Li to appear shortly and it is hoped that more light may be thrown upon it.

On the other hand, it is also possible that the actual wave function is not represented to a sufficient degree of accuracy by a wave function of the form (2). It does not seem to be easy to use wave functions of a greater generality, however.

APPENDIX 1

It is possible to continue the wave function with the same spherically symmetric potential over the whole volume of the s-polyhedron. If one assumes this ψ to be valid in all the s-polyhedrons of the lattice, the resulting wave function will be continuous everywhere, but the derivatives will be discontinuous at the boundary planes. The energy, therefore, is not the characteristic value of the differential equation, but must be calculated as the sum of kinetic and potential energy. The correction for the potential energy will be given in Appendix 2, while the correction for the kinetic energy is

$$(\hbar^2/2m)\left\{\int_{V_1}(\text{grad }\psi)^2 d\vartheta-\int_{V_2}(\text{grad }\psi)^2 d\vartheta\right\}, \tag{1}$$

where V_1 is the region of the s-sphere outside of the s-polyhedron and V_2 is the equally large volume of the s-polyhedron outside of the s-sphere. In the neighborhood of the s-sphere, we can set

$$\frac{\hbar^2}{2m}\text{grad }\psi=\frac{\hbar^2}{2m}\frac{d^2\psi(r_s)}{dr^2}(r-r_s)=(V(r_s)-E)\psi(r_s)(r-r_s), \tag{2}$$

so that (1) becomes

$$(2m/\hbar^2)(V(r_s)-E)^2\psi(r_s)^2\left\{\int_{V_1}(r-r_s)^2dv-\int_{V_2}(r-r_s)^2dv\right\}. \tag{3}$$

Now the mean value of $r-r_0$ is certainly smaller than $r_0/20$, V_1 is smaller than $v_0/10$, and $\psi(r_s)^2v_0\sim 1$, so that the first part of (3) is

$$(2mr_s^2/\hbar^2)(V(r_s)-E)^2/4000=0.0004 \text{ Rydberg units.}$$

In addition to this, the second term of (3) essentially cancels the first, so that the total correction really is negligible.

APPENDIX 2

It is necessary to calculate the potential energy of a body-centered lattice of positive point charges in a fluid of negative charge of density $\rho=\psi^2$ and then to compare this energy with the electrostatic energy of the s-sphere.

To begin with, we can draw s'-spheres around each positive charge which are smaller than the s-spheres and just touch one another. Outside of these s'-spheres we may assume the density to be uniform and of magnitude ρ. Relative to the regions of space outside of the lattice, the energy of the s'-spheres is as large as if the negative charge had a constant density within the sphere. This is because the potential outside a sphere arising from a spherically symmetric charge distribution is independent of the radial distribution inside of the sphere.

The total electrostatic energy of the lattice may now be divided into two parts: first, the energy E_1 of a body-centered lattice of positive charges $v_s\rho=e$ with a uniform negative charge-density and second the difference, E_2, of the inner energy of an s'-sphere with the actual s'-sphere on the one hand and an s'-sphere with uniform charge distribution on the other. Since the density is actually ρ outside of the s'-sphere, the second energy is equal to the difference in energy of the actual s-sphere and one with constant negative distribution ρ. This second part is

$$E_2=E_t-(3^{5/3}\pi^{1/3}/5)(\rho^2v_0^2/d)=E_t-3.6557\rho^2v_0^2/2d,$$

where E_t is the energy of the actual s-sphere, that is, the energy employed in the text, and $-3.6557\rho^2v_0^2/2d$ is the energy of an s-sphere with uniform charge distribution.

If E_1 were $-3.6557\rho^2v_0^2/4d$ our calculation would be exactly correct. Since it is actually $-3.6391\rho^2v_0^2/4d$, as will be shown at once, the total energy is smaller than that used in the text by the amount

$$0.0166\rho^2v_0^2/2d=0.004e^2/r_s,$$

which for $r_s=4$ is only 0.62 kg. cal.

The calculation of E_1 is a problem of electrostatics, we have used essentially the procedure of Appell-Madelung. Since the proper energy of the positive point charge, which must be obtained, is infinite, we must assume positive charges of finite size concentrated into small cubes with edges 2δ.

The Fourier expansion of the density is, then,

$$\sum_{\kappa,\,\lambda,\,\mu=-\infty}^{\infty} a_{\kappa\lambda\mu}\exp\left[2\pi i(\kappa x+\lambda y+\mu z)/d\right]$$

with

$$a_{\kappa\lambda\mu}\begin{cases}2\rho v_0\sin\alpha\kappa\sin\alpha\lambda\sin\alpha\mu/d^3\alpha^3\kappa\lambda\mu,\\ 0\end{cases}$$

where $\alpha=2\pi\delta/d$ and the first line is valid for $\kappa+\lambda+\mu$ even and the second for this odd in addition to the case $\kappa=\lambda=\mu=0$.

The total energy per atom of the lattice is

$$E_{11}=\sum d^5|a_{\kappa\lambda\mu}|^2/4\pi(\kappa^2+\lambda^2+\mu^2).$$

The density distribution of the positively charged cube may be written in the form of the Fourier integral

$$\int\int\int_{-\infty}^{\infty} a(\kappa\lambda\mu)\exp\left[2\pi i(\kappa x+\lambda y+\mu z)/d\right]d\kappa d\lambda d\mu$$

with

$$a(\kappa\lambda\mu)=\rho v_s\sin\alpha\kappa\sin\alpha\lambda\sin\alpha\mu/d^3\alpha^3\kappa\lambda\mu$$

and the corresponding energy is

$$E_{12}=(d^5/2\pi)\int\int\int_{-\infty}^{\infty}|a(\kappa\lambda\mu)|^2/(\kappa^2+\lambda^2+\mu^2)d\kappa d\lambda d\mu.$$

The energy E_1 is now simply $E_{11}-E_{12}$. If we put $\delta=0$ both E_{11} and E_{12} diverge, but if we take the difference before passing to the limit and then set $\delta=0$, we obtain

$$E_1=\lim_{N\to\infty}\lim_{\delta\to 0}\sum_{\kappa,\lambda,\mu=-N}^{N}\frac{d^5}{4\pi}\frac{|a_{\kappa\lambda}|^2}{\kappa^2+\lambda^2+\mu^2}-\frac{d^5}{2\pi}\int\int\int_{(-N-\frac{1}{2})}^{(N+\frac{1}{2})}\frac{|a(\kappa\lambda\mu)|^2}{\kappa^2+\lambda^2+\mu^2}d\kappa d\lambda d\mu$$

$$=\lim_{N\to\infty}\frac{\rho^2 v_0^2}{\pi d}\left\{\sum_{-N}^{N}\frac{1}{\kappa^2+\lambda^2+\mu^2}-\tfrac{1}{2}\int\int\int_{(-N-\frac{1}{2})}^{(N+\frac{1}{2})}\frac{d\kappa d\lambda d\mu}{\kappa^2+\lambda^2+\mu^2}\right\}.$$

In $\sum'$, the values for which $\kappa+\lambda+\mu$ is odd and the case $\kappa=\lambda=\mu=0$ are to be omitted.

The summation and integration over μ were carried out directly and yield

$$E_1=\frac{\rho^2 v_s^2}{2d}\left\{\sum_{\kappa+\lambda\ \mathrm{odd}}\left(\frac{1}{\kappa^2+\lambda^2}\right)^{\frac{1}{2}}\mathrm{tgh}\,\frac{\pi}{2}(\kappa^2+\lambda^2)^{\frac{1}{2}}+\sum_{\kappa+\lambda\ \mathrm{even}}\left(\frac{1}{\kappa^2+\lambda^2}\right)^{\frac{1}{2}}\mathrm{ctgh}\,\frac{\pi}{2}(\kappa^2+\lambda^2)^{\frac{1}{2}}-\int\int\frac{d\kappa d\lambda}{(\kappa^2+\lambda^2)^{\frac{1}{2}}}\right\},$$

which was then calculated directly. The tgh and ctgh may be replaced by 1 when either κ or λ is greater than 3. For κ or λ greater than 9, the bracketed difference is $1/24(\kappa^2+\lambda^2)^{\frac{3}{2}}$ with sufficient accuracy, and the integration over κ and λ was carried out in this region. The terms for which $\kappa\leqq 3$, $\lambda\leqq 3$ yielded -3.57221, while the second sum gave

$$E_1=-3.6391\rho^2 v_0^2/2d.$$

The van der Waals attraction of the ions is -0.12 cal. per mol.

Note added in proof. In Fig. 3 the upper point of the (110) discontinuity, given by a pure *p* function, lies at -0.33 Rydberg units in place of the value shown. The lower is at -0.34. Although the first lies below the parabola, this is undoubtedly of no real significance.