

The Theoretical Constitution of Metallic Lithium

FREDERICK SEITZ, *Palmer Physical Laboratory, Princeton University*

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On the basis of previous theoretical developments concerning the nature of cohesion in metals which were applied to sodium, a treatment of metallic lithium is presented. As before, the system of Fock equations are solved by an indirect procedure as a start. These solutions differ appreciably from those for sodium in several important respects and account for a greater percentage of the observed binding energy than in the latter case. The modification of the exchange energy of the electrons arising from these dif-

ferences is computed. Finally, the work of Wigner on correlation energies of metal electrons is applied directly to obtain a final binding energy of 34 kg.cal. as compared with the observed value of 38.9. The lattice constant is found to agree with the observed one to within about three percent. Some general remarks concerning the applicability of the present development to solids other than metals are made.

INTRODUCTION

IN previous work¹ a basis for an investigation of the constitution of metals was laid and applied to sodium. In this work a completely self-consistent solution of Fock's equation for the lattice was found and this result was then employed in finding an additional approximation to the problem of minimizing the total energy.² The final results of this work yielded a binding energy of 22.3 kg.cal. per mole, to be compared with the observed value of 26.9 kg.cal.

The solution to Fock's equation was undertaken under the guiding principles afforded by the free electron picture of metals, and it was found that the results yielded 4.7 kg.cal. Since

this discrepancy was many times larger than the computational errors could allow it was concluded that the simple Slater determinant was inadequate to handle the complexity of the problem and an effort was made to find a more general solution based upon the one-electron one.

An attempt in this direction was presented in II of the previously mentioned papers and this met with partial success. Upon this basis, however, Wigner¹ was able to establish a much more rigorous method and succeeded in solving a set of equations which were the counterpart of the Fock equations in an extended minimal problem, namely, that of minimizing the energy integral by use of a function of the form

$$\Psi = \begin{vmatrix} \psi_1(x_1; y_1 \cdots y_n) \cdots \psi_1(x_n; y_1 \cdots y_n) & \psi_1(y_1) \cdots \psi_1(y_n) \\ \vdots & \vdots \\ \psi_n(x_1; y_1 \cdots y_n) \cdots \psi_n(x_n; y_1 \cdots y_n) & \psi_n(y_1) \cdots \psi_n(y_n) \end{vmatrix}, \quad (1)$$

in which the variables x and y refer to the three position coordinates of electrons of upward and downward spin, respectively, $\psi_\nu(y_i)$ are the one-electron solutions of Fock's equations and $\psi_\nu(x, y_1 \cdots y_n)$ are functions of the variable x and parameters $y_1 \cdots y_n$. The last set of functions are to be determined in such a way as to minimize

¹ Wigner and Seitz, *Phys. Rev.* **43**, 804 (1933); **46**, 509 (1934) (I and II). Wigner, *Phys. Rev.* **46**, 1002 (1934). This work is closely connected with the following papers of J. C. Slater, *Phys. Rev.* **45**, 794 (1934); *Rev. Mod. Phys.* **6**, 209 (1934).

² A complete account of the equations of Hartree, Fock and Dirac and their interconnection has been given by L. Brillouin, *Actualités Scientifiques et Industrielles*, Nos. 71, 159, 160.

the energy. The final energy value obtained was 22.3 kg.cal. for the observed lattice-constant of 4.23A. The remaining discrepancy is regarded as arising principally from a conservative computation of the gain given by (1).

After assuming an ion-core field the work on sodium was considerably lightened by the fact that the solutions of Hartree's equations for the lattice were almost exactly of the form

$$\psi_\kappa = (1/V^{1/2})e^{i\kappa \cdot \mathbf{r}}, \quad (2)$$

where \mathbf{r} is the position vector of the particle, κ is a lattice vector in the inverse-lattice space and V is the total volume of the crystal. This had as

its first important consequence the fact that the solutions of Hartree's equations were practically identical with those of Fock² so that the best one-electron solution was obtained with an ease not met in any atomic problem involving more than one electron. In the second place, this gave a definite analytic form to the ψ (y)'s in (1) and allowed an analytic solution of the problem outlined in the previous paragraph. Since (2) are the wave functions for perfectly free electrons, it is to be expected that this simplicity will not generally be met with even in simple metals, for the probability distribution function of each electron will usually be greater inside the unit cell surrounding each ion than on its boundary.

In order to investigate the possibility of applying the scheme employed for sodium to more general cases, the corresponding solution for lithium was undertaken from a similar viewpoint, and these results are presented in the following sections. This work begins with the development of an effective ion core field which reproduces the atomic energy values and follows with a solution of Hartree's equations using this field. The connection between Hartree's and Fock's equations is not as well defined as in the case of sodium but it is found that the energies determined by both are practically identical. In the present paper the work of Wigner on the correlation hole is applied without additional modification.

§1. THE EFFECTIVE ION-CORE FIELD

The problem of determining a coulomb field $V(r)$ which when placed in an equation of the simple Schroedinger type

$$(\hbar^2/2\mu)\Delta\psi + (V(r) - E)\psi = 0 \quad (3)$$

will yield eigenvalues that are identical with the term values of a single electron series and yet be physically plausible, may not be expected to possess even an approximate solution in any but the simplest of practical cases. The correctness of this assertion follows from consideration of the extensive work of Hartree when viewed in the light of Fock's equations. For the best one-electron solution of any atomic problem is given by the system of equations

$$((\hbar^2/2\mu)\Delta_j + \sum_{i \neq j} V_i(x_j) + \mathbf{A}_j - E_j)\psi_j = 0, \quad (4)$$

in which i and j range over all electrons of the atom, $V_i(x_j)$ is the coulomb potential arising from the i th electron wave function when regarded as an electron charge distribution, and \mathbf{A} , is a linear integral "exchange" operator of the form

$$\mathbf{A}_j\psi_j(x_j) = \sum_{i \neq j} e^2 \int (1/|x_j - x_i|)(j|\rho|i)\psi_j(x_i)d\tau_i, \quad (5)$$

in which $(j|\rho|i)$ is the ij th matrix component of the density matrix

$$(j|\rho|i) = \sum_k \psi_k^*(x_j)\psi_k(x_i). \quad (5a)$$

That \mathbf{A}_j is not completely negligible is shown by the fact that in the case of a single valence electron, Hartree's energy parameters E_j do not agree exactly with the term values of the one-electron states. Because of the form of the exchange operator it is not to be expected that it can be replaced by a central field term, but it may be hoped that in the case of one-electron outside closed shells, its effect on the terms E_j may be roughly approximated by such a field. In the case of Na this was found to be the case, for the Prokofjew field employed in reference 1 gave very good results from the standpoint of energy levels, all of the values agreeing with the observed ones to within one percent.

If this were true for Na, it might be expected that similar results would be true for Li so an attempt was made to find such a field. Prokofjew³ employed the Wentzel-Kramers-Brillouin approximation in his work, but I found that the field obtained by this method is not a very definitely determined one since all terms in a given series cannot be fitted with equal accuracy in the manner prescribed by Prokofjew. As a result the following device was used.

For a coulomb field of the form Ze^2/r , the W.K.B. approximation gives energy values that are determined by an equation of the Balmer type, namely $E = hcZ^2R/n^2$ in which R is the Rydberg constant in wave numbers per cm, n is an integer, and E the energy in ergs. Since only that portion of r for which

$$\left(E - \frac{Ze^2}{r} + \frac{\hbar^2(l + \frac{1}{2})^2}{2\mu r^2}\right)^{\frac{1}{2}} \quad (6)$$

³ Prokofjew, Zeits. f. Physik 58, 255 (1929).

is real is of importance in using the W.K.B. approximation, where l is the modern angular momentum quantum number and μ the reduced electron mass, the effective field was taken to be of the form e^2/r from ∞ to the value r_m given by the smallest allowable root of (6) for the series of smallest l in which the terms are hydrogen-like. The value of 3.24 Bohr units was taken to be a safe estimate of this quantity, r_m , and will be employed in all of the following work. The problem reduces itself to that of determining a $V(r)$ within this radius which shall join the function e^2/r continuously and with continuous first derivative at this point, be of the form $3e^2/r$ near the nucleus, and reproduce the energy spectrum of the s , p and d series. Other series will automatically be given because of the choice of e^2/r outside of $3.24a_h$.

Now the form of the wave functions for regions beyond r_m may be found for each of the observed energy values because the boundary condition at infinity entirely determines the form of the function in any region excluding the sphere of radius r_m . Hence the ratio $\psi'(r_m)/\psi(r_m)$ may be determined by use of an asymptotic series, for example. This was done for five of the lowest energy values of the Li spectrum and the results for $R'r/R$ at r_m , where $R=r\psi$, are shown in Table I. $V(r)$ is to be chosen so that the functions

TABLE I. Values of $R'r/R$ at r_m .

Term	Energy (Ryd. units)	rR'/R (calc.)	Original V	Final V
2s	0.3963	-0.1331	-0.06931	-0.122
3s	0.1484	-1.646	-1.538	-1.642
4s	0.07723	-2.255	-2.126	-2.2570
2p	0.2605	0.2422	2.192	0.2428
3d	0.1111	1.92	1.91	1.92

derived using it satisfy the proper boundary conditions at the origin and have the same ratio of rR'/R at r_m for the given energies. An initial field V_I was selected on the basis of reasonableness and its solution yielded the ratio shown in the fourth column of Table I. $Z_p=rV_I$ is given in Table II in which Rydberg units are employed. From knowledge of the change of wave functions, it was concluded that V was to be made more negative in the neighborhood of the nucleus to bring the s ratios into agreement and more positive in the neighborhood of the boundary,

TABLE II. Values of rV_I and rV_{II} .

r	rV_I	rV_{II}	r	rV_I	rV_{II}
0.00	6.000	6.000	0.84	2.528	2.490
0.04	5.512	5.481	1.00	2.384	2.392
0.08	5.294	5.236	1.16	2.284	2.322
0.12	5.078	4.998	1.32	2.214	2.262
0.20	4.652	4.540	1.64	2.122	2.172
0.28	4.232	4.102	1.96	2.066	2.100
0.36	3.810	3.672	2.28	2.034	2.038
0.44	3.408	3.274	2.60	2.012	2.012
0.52	3.118	2.994	2.92	2.004	2.004
0.68	2.748	2.660	3.24	2.000	2.000

r_m , to improve the p ratios. The correction adopted was of the form

$$-0.4(1.2-r)^2 - 0.05(0.8-r)(2.5-r)^2 \quad 0 \leq r \leq 1.2,$$

$$-0.05(0.8-r)(2.5-r)^2, \quad 1.2 \leq r \leq 2.5.$$

This brought about the agreement shown in the last column of Table I and yields the second column of Table II.

The full significance of the procedure employed here is probably best shown by Fig. 1 in which curves A correspond to the ratio $R'r/R$ at $r_m=3.24$ plotted against the energy parameter for the system of functions in which the proper boundary condition is satisfied at infinity and the field $-e^2/r$ is employed. This system is a highly singular one, of course, since $R(r_m, E)$ will have an infinite number of roots in the range between -1 and 0 on the Rydberg scale of units. Only two branches of this curve are shown. Curves B_I and B_{II} represent plots of the same ratio derived

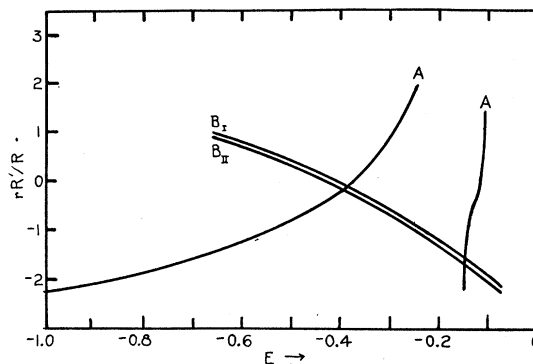


FIG. 1. Plot showing the ratio rR'/R for $r_m=3.24$ as a function of energy. The curve A corresponds to solutions satisfying the proper boundary conditions at infinity, while curves B_I and B_{II} correspond to solutions which satisfy the proper condition at the origin for the initial and final fields, respectively. The abscissas are in Rydberg units and the ordinates in Bohr units.

for the system of functions which satisfy the proper conditions at the origin and for which V_I and V_{II} have been employed. The points at which either B_I and B_{II} cross the system A yield the eigenvalues of the corresponding fields. Our endeavor has been to make these points be identical with the observed term values and the degree of success is illustrated by the fact that on the scale of this plot the curve B_{II} completely overlaps the curve C drawn through the intercepts of A and the observed term values.

Similar considerations for the Prokofjew field for Na show that the corresponding B curve is not nearly so good a fit of the corresponding curve C and that it would be difficult to find a better field.⁴

§2. SOLUTION OF HARTREE'S EQUATIONS

The procedure to be employed in solving Hartree's equations for the lattice will be very similar to that used in the case of Na. On the basis of an approximate Hamiltonian H_i^0 which is the same for each electron, and possesses the proper symmetry properties for the lattice set of "starting functions" are determined by numerical integration of the Schroedinger equation arising from H_i^0 . Using these solutions, a Hamiltonian H_i^H may be written down which contains the interaction terms of the i th electron with each ion in the lattice and the Hartree field of interaction between the i th electron and all others, assuming that their charge distribution is determined by the solutions of H_i^0 . This field will be the same for all electrons since it is the potential arising from all electrons minus that arising from the electron under consideration and the ratio of the latter to the form will generally be of the order $1/N$, where N is the total number of electrons, that is a very large number. Regarding $H_i^H - H_i^0$ as a perturbation on H_i^0 , we may apply the perturbation scheme of Schroedinger or of Brillouin-Wigner⁵ and if

this perturbation does not appreciably alter the wave functions the solution will be self-consistent in the Hartree sense. Since the perturbation is symmetric (i.e., possesses the same symmetry group as the unperturbed problem) we know at once that no states in the lowest band will enter in the new functions and but one from each of the higher bands, namely that which belongs to the same representation as the unperturbed function.

The Hamiltonian H_i^0 is taken to be of the form

$$-\frac{\hbar^2}{2\mu}\Delta_i + \sum_{\alpha\beta\gamma}^* V_{\alpha\beta\gamma} = -\frac{\hbar^2}{2\mu}\Delta_i + V^*, \quad (7)$$

in which $V_{\alpha\beta\gamma}$ represents the potential arising from the ion situated at the position $\alpha\tau_1 + \beta\tau_2 + \gamma\tau_3$ where α, β, γ are integers, τ_1, τ_2, τ_3 are the primitive translations of the group, and \sum^* indicates that the sum is to be carried out in such a way that $V_{\alpha\beta\gamma}$ is regarded as being zero outside of the rhombic dodecahedron surrounding the α, β, γ -th ion. In other words the potential at a given point is to be taken as that arising from the ion in the polyhedron within which the point is situated, so that it will generally be a function with discontinuous derivative. That (7) is a good starting operator arises from the fact that it regards the ion-ion interaction as just balancing the interaction of the given electron with all other electrons and ions outside of the polyhedron, in which the electron is, and the interaction of outer electrons with the ion in this polyhedron which would be true if the other electrons formed a constant charge distribution outside of the polyhedron containing the given electron. The results for Na show that this is a rough description of affairs for all simple metals.

Using H_0 and the fact that all wave functions are to be of the form $\eta_\kappa e^{i\kappa \cdot \mathbf{r}}$ in which η_κ is invariant under the translation-group and κ is a lattice vector in the inverse-lattice space, the Schroedinger equation for η_κ may be written

$$-(\hbar^2/2\mu)\Delta\eta_\kappa - (\hbar^2/\mu)i\kappa \cdot \nabla\eta_\kappa + V^*\eta_\kappa = E_\kappa'\eta_\kappa, \quad (8)$$

where $E_\kappa' = E_\kappa - (\hbar^2/2\mu)\kappa^2$ may be regarded as being the energy of η_κ . If the operator $-(\hbar^2/\mu)i\kappa \cdot \nabla$ be viewed as a perturbation then as in reference 1 we have, using the Schroedinger perturbation theory

⁴ As yet unpublished work of Dr. E. Gorin has shown that there is no satisfactory field for K, but that each series may be approximated to within several percent by means of separate fields. I wish to thank Dr. Gorin for the privilege of making this statement.

⁵ Brillouin, *J. de physique* **1** (III), 373 (1932). Wigner, *Bull. Hung. Acad.* (to appear shortly). Brillouin first presented the perturbation scheme and Wigner later showed that various stages of approximation yield mean values of the Hamiltonian operator.

$$E_{\kappa'} = E_0 - \sum_{\lambda} \frac{|\int \eta_{\lambda} (\hbar^2/\mu) \kappa \cdot \nabla \eta_0|^2}{E_{\lambda} - E_0}, \quad (9)$$

$$\eta_{\kappa} = \eta_0 + i \sum_{\lambda} \frac{\hbar^2}{\mu} \frac{\int \eta_{\lambda} \kappa \cdot \nabla \eta_0}{E_{\lambda} - E_0} \eta_{\lambda}, \quad (9a)$$

where λ runs over all solutions of the unperturbed problem. If we consider any η to be expressed by a sum \sum^* over each of the polyhedrons, it was previously shown that the polyhedron may be replaced by a sphere of equal volume for purposes of determining energies. The lowest η_0 is then that function for which the boundary condition $\psi' \equiv \eta' = 0$ is satisfied at the surface of the sphere, while the only η_{λ} 's which need be considered are those p functions which satisfy the relation $\eta_{\lambda} = 0$ at the boundary of the sphere. For the observed lattice constant of Li, namely, 3.46Å, the radius r_s of the equivalent sphere is $3.21a_h$. The energy- r_s curves are shown in Fig. 2.

If we employ the Hartree system of units for which the Bohr radius is the unit of length, e^2/a_h is the unit of energy and both \hbar and the electron mass are 1, the values of the integrals $\int \eta_{\lambda} \partial \eta_0 / \partial x = \alpha_{\lambda}$ are given in Table III for the

TABLE III. Values of integrals $\int \eta_{\lambda} \partial \eta_0 / \partial x = \alpha_{\lambda}$.

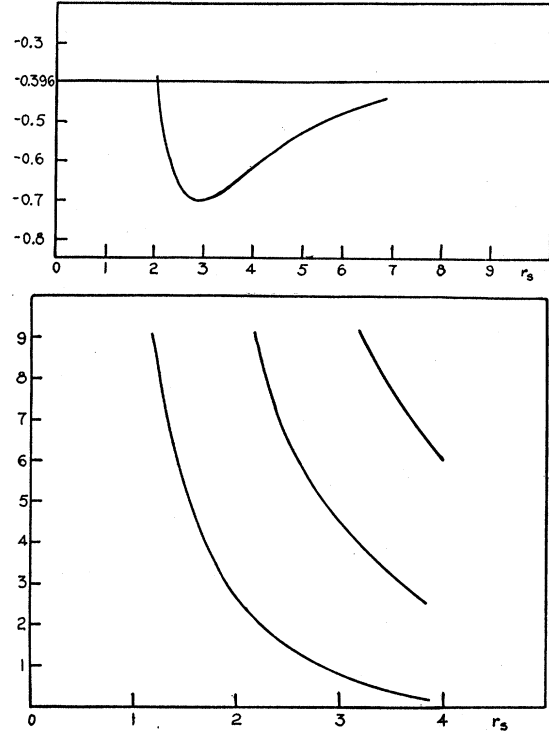
	r_1	3.21	3.33	3.62	3.88
I	$E - E_0$	0.64	0.60	0.50	0.43
	α_{λ}	0.2402	0.2214	0.1720	0.1407
II	$E - E_0$	2.27	2.10	1.79	1.54
	α_{λ}	0.2718	0.2565	0.2317	0.2142
III	$E - E_0$	4.84	4.55	3.93	3.47
	α_{λ}	0.2045	0.1822	0.1568	0.1513

three lowest-energy p functions going with four values of r_s . The values of $E_{\lambda} - E_0$ are listed simultaneously in terms of Hartree's energy unit. The Roman numerals refer to each of the three sets of p functions of Fig. 2. Using these integrals and the same system of units, the sum in (9) reduces to the form $\beta \kappa^2 / 2$ for which β takes the values given in Table IV. In the perturbation scheme

TABLE IV. Values of β .

r_s	3.21	3.33	3.62	3.88
β	0.266	0.245	0.194	0.168

of Brillouin-Wigner the second approximation for the energy has a form much the same as (9),



FIGS. 2a and 2b show the energy- r_s curves for s and p function, respectively. The ordinates are in Rydberg units and the abscissas in Bohr units.

with the exception that $E_{\kappa'}$ replaces E_0 in the denominator of each term in the sum, so that one obtains an implicit equation for $E_{\kappa'}$. Since $E_{\kappa'}$ is a function of κ^2 , we may obtain a power series for $E_{\kappa'}$ from this by means of a successive approximation method in which the solution obtained by placing $E_{\kappa'} = E_0$ in the denominator is regarded as the first-order solution. The next approximation is obtained by placing this in the denominator and expanding the fraction in terms of κ^2 , etc. This series is of the form

$$E_{\kappa'} = E_0 - \frac{1}{2} \lambda_1 \kappa^2 + \frac{1}{4} \lambda_2 \kappa^4 - \frac{1}{8} \lambda_3 \kappa^6,$$

in which λ_1 is just β of the Schroedinger approximation and

$$\lambda_2 = \lambda_1 \left(\sum_{\lambda} \frac{2\alpha_{\lambda}^2}{(E_{\lambda} - E_0)^2} \right),$$

$$\lambda_3 = \lambda_2 \sum_{\lambda} \frac{2\alpha_{\lambda}}{(E_{\lambda} - E_0)^2} + \lambda_1^2 \sum_{\lambda} \frac{2\alpha_{\lambda}}{(E_{\lambda} - E_0)^3}.$$

The values of λ_2 and λ_3 for the values of r_s previously listed are given in Table V. The value

TABLE V. Values of λ_2 , λ_3 and k .

r_s	λ_2	λ_3	k
3.21	0.0829	0.0745	0.5978
3.33	0.0747	0.0509	0.5754
3.62	0.0482	0.0319	0.5301
3.88	0.0423	0.0251	0.4946

$\sqrt{\kappa^2} = k$ corresponding to the uppermost electrons of the filled band of levels is given by $k = (9\pi/4)^{1/2}/r_s$ and from the last column of Table V it is seen that the term in k^6 is practically negligible. The term in k^4 corresponds to part of the fourth order approximation of the Schrodinger scheme so that its order of magnitude is an indication of the error made in employing the second order approximation of either perturbation scheme. The mean energy per electron of the function $\psi_\kappa = \eta_\kappa e^{i\kappa \cdot r}$ will be $\bar{E}_\kappa = \bar{E}_\kappa' + \frac{1}{2}\kappa^2$ in Hartree units or

$$\bar{E}_\kappa = E_0 + \frac{3}{10}(1 - \lambda_1)k^2 + \frac{3}{28}\lambda_2 k^4 - \frac{1}{24}\lambda_3 k^6. \quad (10)$$

The corresponding energy for perfectly free electrons in a potential trough of depth E_0 is $E_0 + 3k^2/10$. The ratio of (10) to this, excluding E_0 in both cases, is given in Table VI along with the ratio $1 - \beta$ for the Schrodinger perturbation scheme. As expected from the minimum-value viewpoint, the Brillouin-Wigner scheme yields a higher energy than the Schrodinger scheme in the same approximation although they differ by only about a percent. In the last column of Table VI, the equivalent Fermi energy of the former scheme is listed in terms of kg.cal. per mole.

In the second appendix of II, reference 1, it was shown that the electrostatic energy of a body-centered lattice of positive charges e surrounded by a uniform distribution of negative charge such that there are e units per s polyhedron, was practically the same as the energy

 TABLE VI. $(1 - \beta)$ and the ratio of $E_0 + 3k^2/10$ to \bar{E}_κ for the Brillouin-Wigner scheme.

r_s	$1 - \beta$	Brillouin-Wigner	Difference	Energy (kg. cal.)
3.21	0.734	0.744	0.010	48.8
3.33	0.755	0.763	0.008	46.5
3.62	0.806	0.810	0.004	42.0
3.88	0.832	0.835	0.003	37.8

of a uniformly charged sphere with a point charge e at its center, so that the classical energy per electron of the lattice, when the actual distribution is present, will be that of the actual charge distribution in the s sphere. As a result of this, we shall assume that the proper Hartree field to employ in writing down H_i^H of the first paragraph of this section, is just $H_i^0 + \sum_{\alpha\beta\gamma}^* V_{e, \alpha\beta\gamma}$, where $V_{e, \alpha\beta\gamma}$ is the Hartree potential arising from the electron charge distribution within the $\alpha\beta\gamma$ th s polyhedron. $V_{e, \alpha\beta\gamma}$ will be a slowly varying positive function of position within a given polyhedron just as in the case of sodium, so that $\sum_{\alpha\beta\gamma}^* V_{e, \alpha\beta\gamma}$ will be slowly varying throughout the lattice. Hence the integrals $\int \psi_\kappa^* (\sum_{\alpha\beta\gamma}^* V_{e, \alpha\beta\gamma}) \psi_\lambda$ will be small in all cases except when $\kappa = \lambda$ because of orthogonality, and the eigenfunctions of H_i^H will be practically identical with those of H_i^0 . This is clearly seen if $\sum_{\alpha\beta\gamma}^* V_{e, \alpha\beta\gamma}$ is regarded as a perturbation on H_i^0 as in reference 1, II.

Thus the eigenfunctions of H_i^0 are the solutions of Hartree's equations for the lattice and we may now proceed with an investigation of Fock's equations.

§3. THE SOLUTION OF FOCK'S EQUATIONS FOR THE LATTICE

For the case of perfectly free electrons, Fock's Eqs. (4) are reducible to the Schrodinger form since exponential functions are⁶ eigenfunctions of the operator \mathbf{A} , so that Fock's and Hartree's equations are identical. In the present case this will not be precisely true, but we may easily determine the order of magnitude of the difference in the mean energies of the total Hamiltonian of the crystal obtained from an anti-symmetric combination of each set of solutions.

We have found that the eigenfunctions of H_i^0 were approximately of the form

$$\psi_n = \sum_{\alpha\beta\gamma}^* (f_0(r_{\alpha\beta\gamma}) + i\kappa \cdot \mathbf{r}_{\alpha\beta\gamma} f_1(r_{\alpha\beta\gamma})) e^{i\kappa \cdot \mathbf{r}}, \quad (11)$$

where $r_{\alpha\beta\gamma}$ is the radial distance in the $\alpha\beta\gamma$ th s polyhedron, f_0 is an s function normalized within an s polyhedron, and f_1 is $r_{\alpha\beta\gamma}$ times a

⁶ L. Brillouin, J. de physique 5, 413 (1934).

sum of the radial part of p functions. More explicitly, if we normalize the radial p functions $f_\lambda(r)$ so that

$$\int_{\vartheta_0} f_\lambda^2 r^2 dr = 3/4\pi, \quad \text{or}$$

$$\int_{\vartheta_0} [(\kappa \cdot \mathbf{r})^2 / r^2] f_\lambda^2 r^2 dr \sin \theta d\theta d\varphi = \kappa^2,$$

where ϑ_0 is the volume of an s -sphere, (11) is of the form

$$\psi_\kappa = e^{i\kappa \cdot \mathbf{r}} \sum_{\alpha\beta\gamma}^* (f_0 + i \cdot \kappa \cdot \mathbf{r}_{\alpha\beta\gamma} \sum_\lambda \gamma_\lambda f_\lambda / r_{\alpha\beta\gamma}) \quad (11a)$$

with

$$\gamma_\lambda = (\hbar^2 / \mu) \int_{\vartheta_0} \eta_\kappa (\partial / \partial x_\kappa) \eta_0 d\tau / (E_\lambda - E_0) = \alpha_\lambda / (E_\lambda - E_0), \quad (11b)$$

$$\text{so that} \quad f_1 = \sum_\lambda \gamma_\lambda f_\lambda / r_{\alpha\beta\gamma}. \quad (11c)$$

Table VII gives the γ 's corresponding to the

TABLE VII. Values of γ corresponding to the α 's of Table III.

r_s	3.21	3.33	3.62	3.88
I	0.375	0.369	0.344	0.313
II	0.120	0.123	0.130	0.140
III	0.042	0.040	0.040	0.044

α 's of Table III. In order to proceed further with the present discussion we shall assume that f_0 and f_1 are constants. Aside from the fact that both of these functions are slowly varying, this

will not affect any conclusions concerning relative orders of magnitude of effects. Under this assumption (11) reduces to

$$\psi_\kappa = \sum_{\alpha\beta\gamma}^* (1 + i\gamma_\kappa \cdot \mathbf{r}_{\alpha\beta\gamma}) / \vartheta_0^{\frac{1}{2}}, \quad (12)$$

$$\text{where} \quad \gamma^2 = 5 \left(\sum_\lambda \gamma_\lambda^2 \right) / r_s^2. \quad (13)$$

The normalizing constant for (12) is then $1/A$ where

$$A^2 = N(1 + \kappa^2 \gamma^2), \quad (13a)$$

N being the total number of electrons in the metal. In the following work, integrations over the entire crystal may be replaced by integrations over the s -sphere if the factor N in (13a) is neglected.

The term containing the operator \mathbf{A}_κ in Fock's equations for ψ_κ may, as is well known, be replaced by the summation

$$-\sum'_\nu g_\nu(x) \psi_\nu(x), \quad (14)$$

where ν is summed over all values except κ and

$$g_\nu(x) = [\int \psi_\nu^*(y) \psi_\kappa(y) d\tau_y] / |y-x|, \quad (15)$$

where y and x each refer to three coordinate variables and $d\tau_y$ is the corresponding volume element. For the functions (12), if we let

$$\psi_\nu = \sum_{\alpha\beta\gamma}^* (1 + i\gamma_\nu \cdot \mathbf{r}_{\alpha\beta\gamma}) / \vartheta_0^{\frac{1}{2}},$$

any term of (14) may be written

$$(1 + i\gamma_\nu \cdot \mathbf{x}) e^{i\nu \cdot \mathbf{x}} \int [(1 + i\gamma_\kappa \cdot \mathbf{y})(1 - i\gamma_\nu \cdot \mathbf{y}) / |y-x|^2] e^{i(\kappa-\nu) \cdot \mathbf{y}} d\tau_y.$$

Or if we make the transformation $z = y - x$ this is identically

$$(1 + i\gamma_\kappa \cdot \mathbf{x}) e^{i\kappa \cdot \mathbf{x}} \int [(1 + i\gamma_\kappa \cdot \mathbf{z})(1 - i\gamma_\nu \cdot \mathbf{z}) e^{i(\kappa-\nu) \cdot \mathbf{z}} / |z|] d\tau_z \quad (16)$$

to within terms of the second order in γ_ν and γ_κ . The integral in (16) is a constant, however, and may be added directly to the energy parameter. Hence to within terms of the second order in the foregoing quantities, Hartree's and Fock's equations are identical for functions of the type (12). The energy terms of this order of magnitude which arise in the so-called "exchange integrals," will be found to be negligibly small.

§4. THE ENERGY RESULTING FROM THE SOLUTIONS OF FOCK'S EQUATIONS

We may now proceed with a computation of the mean value of the proper Hamiltonian for the metal based upon the previous one-electron solutions. This Hamiltonian will be of the form

$$H = \sum_i \frac{\hbar^2}{2\mu} \Delta_i + \frac{1}{2} \sum'_{i,j} \frac{e^2}{r_{ij}} + \frac{1}{2} \sum'_{\alpha,\beta} \frac{e^2}{r_{\alpha\beta}} + \sum_{i\alpha} V_{\alpha i}, \quad (17)$$

using the notation of §1 where $V_{\alpha i}$ is the potential of the i th electron in the field of the α th nucleus. The simple form of the third term arises from the fact that the nuclei are separated enough so that the closed shells do not overlap. It was shown in II, reference 1, that the mean values of the first and last two operators combine with the coulomb integrals of the second in such a manner that the result is simply the sum of the energy parameters of (8) plus N times the self-potential of the charge distribution within an s -sphere. From (9), this distribution, is simply the mean value over occupied states of

$$e(f_s^2 + (\kappa \cdot \mathbf{r})^2 f_1^2(r))(1 - \kappa^2 \gamma' + \kappa^4 \gamma'^2), \quad (18)$$

where $\gamma' = \sum_{\lambda} \gamma_{\lambda}^2$. The last factor is simply the normalizing constant. This mean value is

$$e \left(1 - \gamma' \frac{3}{5} k^2 + \gamma'^2 \frac{3}{7} k^4 \right) f_s^2 + \left(\frac{k^2}{5} - \gamma' \frac{k^4}{7} \right) (\sum_{\kappa} \alpha_{\kappa} f_{\kappa})^2, \quad (19)$$

which is illustrated in Fig. 3 for $r_s = 3.21$. If we designate by χ the part of this which deviates from the constant mean value e/ϑ_0 , that is, let (19) be replaced by $e/\vartheta_0 + \chi$, the self-energy, may be written

$$\frac{6}{10} \frac{e^2}{r_s} + \int \chi \left(\frac{3}{2} \frac{e^2}{2r_s} - \frac{e^2 r^2}{2r_s^3} \right) r^2 dr, \quad (20)$$

in which the self-energy of χ has been neglected. The integral in (20) has been evaluated for four values of the lattice constant and in each case the results were $0.001e^2/a_h$ (0.6 kg.cal.).

It now remains to compute the total exchange energy of the electrons. In the previous work this was done by determining the so-called Fermi-hole which is a function describing the probability that another electron will be at a distance r from a given electron and then evaluating the decrease in interaction energy of electrons resulting from this correlation. This decrease is just the exchange

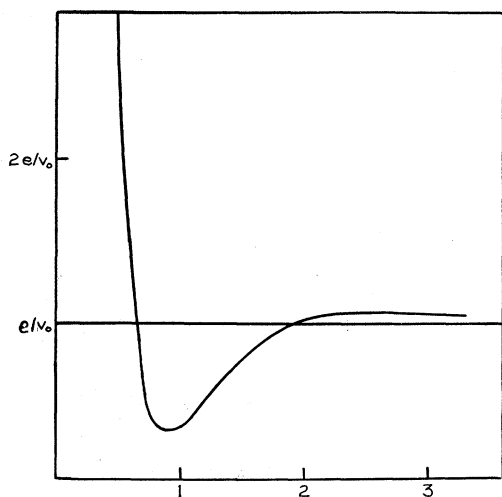


FIG. 3. Plot of mean charge distribution within a given s -sphere. The abscissas are in Bohr units.

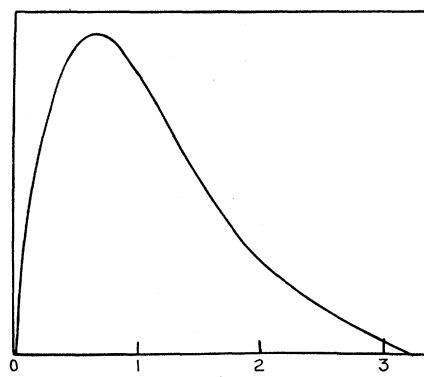


FIG. 4. Relative scale plot of the radial function f_1 . The abscissas are in Bohr units.

energy and in the Fock approximation arises only for electrons of parallel spin. Explicitly, the energy is

$$\frac{e^2}{2} \sum_{\mu} \sum_{\nu} \int \frac{\psi_{\mu}^*(x_1) \psi_{\nu}^*(x_2) \psi_{\mu}(x_2) \psi_{\nu}(x_1)}{|x_1 - x_2|} d\tau_1 d\tau_2, \quad (21)$$

in which ν and μ are to be summed over all occupied states of parallel spin. The factor $\frac{1}{2}$ enters in order that interactions are not counted doubly. If the order of summation and integration is interchanged the mean value of the summed numerator, when regarded as a function of $x_1 - x_2$ is just the Fermi-hole.

In the case of the approximate eigenfunctions $e^{i\nu \cdot \mathbf{r}}$ this function depended only upon $|x_1 - x_2|$ so that the "exchange potential"

$$\int \psi_{\mu}^*(x_1) \psi_{\nu}^*(x_2) \psi_{\mu}(x_2) \psi_{\nu}(x_1) / |x_1 - x_2| d\tau_{x_1 - x_2}$$

of a given electron did not depend upon its position in the lattice. This statement is clearly identical with the previous one that the operator \mathbf{A} , in (4) is constant for exponential functions.

In the case of lithium, the functions ψ_{ν} are of the form (11) so that the shape of the Fermi-hole and the exchange energy will differ from that of sodium. Any direct calculation of this change is made very difficult in comparison with the calculations of the coulomb energy because of the fact that the integral in (21) may not be split into integrals over single s -polyhedrons in any simple manner. For purposes of simplifying this computation, we shall assume a modified form of the function (11), namely, that in which both f_0 and f_1 are taken to be constants. The first function is very nearly constant, just as in the case of sodium, so that the error arising from this source will not be appreciable. The second has the form shown in Fig. 4, and though not constant, it varies smoothly and is small in comparison with f_0 . An estimate of the error made in adopting this last assumption will be obtained from the magnitude of the energy terms arising from f_1 for it will be clear that these cannot undergo any great change if the actual f_1 is replaced by a constant.

We start, then, with functions

$$\psi_{\nu} = (e^{i\nu \cdot \mathbf{r}} / \vartheta_0^{\frac{1}{2}}) (1 - i\vartheta_0^{\frac{1}{2}} \sum_{\alpha} \nu \cdot \mathbf{r}_{\alpha} f_1(r_{\alpha})), \quad (22)$$

for which the normalizing constant is

$$\int_{\nu} |\psi_{\nu}|^2 d\tau = N(1 + \nu^2 \gamma) = N\gamma_{\nu}'. \quad (22a)$$

The numerator of (21) is

$$\begin{aligned} e^{i(\nu - \mu) \cdot (\mathbf{r}_1 - \mathbf{r}_2)} (1 / \vartheta_0^2 N^2 \gamma_{\mu}' \gamma_{\nu}') [1 + i\vartheta_0^{\frac{1}{2}} \sum_{\alpha} (\nu - \mu) \cdot \mathbf{r}_{\alpha} f_1(r_{1\alpha}) + i\vartheta_0^{\frac{1}{2}} \sum_{\beta} (\mu - \nu) \cdot \mathbf{r}_{2\beta} f_1(r_{2\beta}) \\ + i(\sum_{\alpha} (\mu - \nu) \cdot \mathbf{r}_{1\alpha} f_1(r_{1\alpha})) (\sum_{\beta} (\mu - \nu) \cdot \mathbf{r}_{2\beta} f_1(r_{2\beta})) + \vartheta_0 \sum_{\alpha} (\nu \cdot \mathbf{r}_{1\alpha}) (\mu \cdot \mathbf{r}_{1\alpha}) f_1^2(r_{1\alpha}) \\ + \vartheta_0 \sum_{\beta} (\mu \cdot \mathbf{r}_{2\beta}) (\nu \cdot \mathbf{r}_{2\beta}) f_1^2(r_{2\beta})] \end{aligned} \quad (23)$$

in which terms involving the components of μ and ν to higher than the second power have been dropped. That this is allowable will be seen from the results below by comparing the order of magnitude of the effects arising from the term in the first power with those from the second.

If we now set $\mathbf{r}_{2\beta} = \mathbf{r}_{1\alpha} + \xi - \tau_{\alpha\beta}$ where ξ is to be regarded as being defined over the entire range of the crystal, and $\tau_{\alpha\beta}$ is the lattice vector connecting the α th and β th polyhedron, we obtain upon integrating over r_1 with $f_1 = z \equiv (15\gamma/4\pi r_0^3)^{\frac{1}{2}}$

$$\begin{aligned}
 e^{i(\nu-\mu)\cdot\xi}(1/\vartheta_0^2 N^2 \gamma_\mu' \gamma_\nu') & \left[N\vartheta_0 + i\vartheta_0^3 z \sum^* \int (\mu-\nu)\cdot(\xi-\tau_{\alpha\beta}) d\tau_1 + N\vartheta_0(\mu-\nu)^2 \gamma \right. \\
 & + \vartheta_0 z^2 \sum_\alpha^* \int (\mu-\nu)\cdot\mathbf{r}_{1\alpha}(\mu-\nu)\cdot(\xi-\tau_{\alpha\beta}) d\tau_1 + 2N\vartheta_0 \nu\cdot\mu\gamma + \vartheta_0 z^2 \sum_\alpha^* \int \mu\cdot\mathbf{r}_{1\alpha} \nu\cdot(\xi-\tau_{\alpha\beta}) d\tau_1 \\
 & \left. + \vartheta_0 z^2 \sum_\alpha^* \int \nu\cdot\mathbf{r}_{1\alpha} \mu\cdot(\xi-\tau_{\alpha\beta}) d\tau_1 + \vartheta_0 z^2 \sum_\alpha^* \int \mu\cdot(\xi-\tau_{\alpha\beta}) \nu\cdot(\xi-\tau_{\alpha\beta}) d\tau_1 \right]. \quad (24)
 \end{aligned}$$

The integrals \int^* are defined in such a way as to take the continuous nature of ξ into account. That is, in integrating r_1 over the range contained in a single polyhedron the discontinuous range associated with functions of r_2 must be kept clearly in mind. This may be done without difficulty if each integral \int^* is regarded as being a sum of integral such that each one corresponds to a range of r_1 for which $r_1 + \xi$ lies within a fixed polyhedron. It is clear that the integrals of r_1 over different polyhedra are equal, so that we may restrict the discussion to just one and drop the N in the denominator of (24).

The results of this integration will be a continuous function of ξ and the variables ν and μ . If we average over the latter two the result will be simply the Fermi-hole for a given electron.

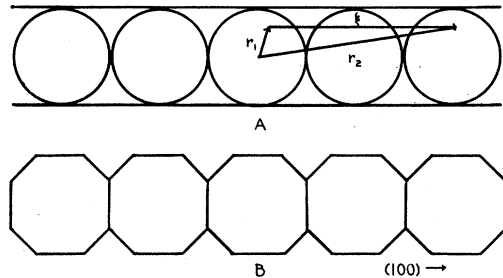
It is not convenient to carry out the integration over r_1 for all orientations of ξ because of the complexity of the integrand and we shall restrict the discussion to the case in which ξ lies in the (100) direction. This will not alter the results arising from the constant term in the parenthesis of (24), since this gives rise to a spherically symmetric function of ξ , which was just the Fermi-hole in the case of sodium. Since there are fully forty-eight equivalent directions for a crystal having body-centered symmetry, the function arising from the remaining terms will be nearly spherically symmetric so that this restriction is not of major significance.

If we expand the normalizing constant $1/\gamma_\mu' \gamma_\nu'$ to second order terms in μ and ν and combine this with the parenthesis an important reduction is effected and the result is

$$\begin{aligned}
 e^{i(\nu-\mu)\cdot\xi}(1/\vartheta_0) & \left[1 + i\vartheta_0^3 z \int^* (\mu-\nu)\cdot(\xi-\tau_\alpha) d\tau_1 + z^2 \int^* \mu\cdot\mathbf{r}_1 \mu(\xi-\tau_\alpha) d\tau_1 \right. \\
 & \left. + z^2 \int^* \nu\cdot\mathbf{r}_1 \nu\cdot(\xi-\tau_\alpha) d\tau_1 + z^2 \int^* \mu\cdot(\xi-\tau_\alpha) \nu\cdot(\xi-\tau_\alpha) d\tau_1 \right].
 \end{aligned}$$

In performing the integration over r_1 , we shall replace the s -polyhedron by the equivalent sphere of radius r_s in the usual manner. Because of this, the vector ξ if fixed in direction will always lie within the cylinder generated by moving this sphere in the given direction. Since spheres do not form space-filling solids, we must adopt some reasonable arrangement of these within this cylinder corresponding to the different polyhedra. There are several reasonable configurations, but that which we shall adopt will be chosen in such a manner as to compensate in part the assumption that ξ lies in the (100) direction. We shall use the arrangement of Fig. 5 in which the spheres are placed tangentially on the axis of the cylinder. This is to be compared with Fig. 5b in which the actual polyhedron boundaries are shown on the corresponding scale for a plane normal to the (001) axis. There are several

points to be noted in this comparison. First, the distance between sphere-centers does not correspond to the distance between polyhedron-centers, and this partly compensates the fact that neighboring polyhedra are farthest apart in the (100) direction. Second, since ξ lies in the (100) direction each of the integrands will be



FIGS. 5a and 5b. A comparison of the relative positions of s -spheres and polyhedrons for a cut in the (100) direction of the crystal, orthogonal to the (010) direction.

the same function of $(\xi - \tau_{\alpha\beta})$ for polyhedra lying in the same vertical plane. Because of this, we shall take the integrand to be axially symmetric in the region of the cylinder outside of two neighboring spheres and assume that a node plane passes through the point of tangency. The volume outside of spheres is not equal to that contained in spheres, the ratio being 1:2, but this is not of great consequence. There are then three important regions of integration to be considered:

- I. The region of \mathbf{r}_1 for which $\mathbf{r}_1 + \xi$ is in the same sphere as when $\mathbf{r}_1 = 0$.
- II. The region for which $\mathbf{r}_1 + \xi$ lies in an adjacent sphere.
- III. The region for which $\mathbf{r}_1 + \xi$ lies outside of spheres.

Only in the case for which $\xi = nr_s$ with n an integer is the contribution from II and III zero. The correction to the Fermi-hole resulting from this integration is shown in Fig. 6 along with the Fermi-hole for free electrons. The exchange energy as a function of r_s is

$$-0.458e^2/r_s - 1.05\gamma^{\frac{1}{2}}e^2/r_s^4 + 1.40\gamma e^2/r_s^5 - 2.49\gamma e^2/r_s^5.$$

The energy arising from each of these terms is given in Table VIII along with the sum. The

TABLE VIII. Energies arising from each term in the expression for the exchange energy.

r_s	1	2	3	4	Sum
3.21	-88.5	-1.2	0.1	-0.3	-89.9
3.33	-85.3	-1.0	0.1	-0.3	-86.5
3.62	-78.4	-0.7	0.0	-0.2	-79.3
3.88	-73.2	-0.5	0.0	-0.1	-73.8

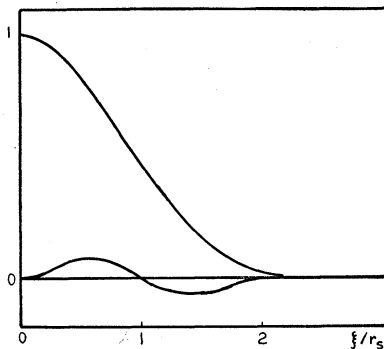


FIG. 6. The large curve is the Fermi-hole function for free electrons and the small curve represents the relative scale correction to this. Abscissas are in units of r_s .

energies are in kg.cal. As might have been expected, the energy arising from the linear term in ν of the parenthesis of (25) is larger than that arising from the quadratic terms by a factor of about 5. On the whole, however, the exchange energy is not greatly affected in spite of the presence of this linear term and we may conclude that f_1 in (11) causes a change in the shape of the Fermi-hole of such a type as to leave the energy almost unaltered.

We may now sum up the results of this investigation of the solution of Fock's equations with Table IX in which the mean value of the proper

TABLE IX. Mean values of the proper Hamiltonian.

r_s	3.21	3.33	3.62	3.88
Energy (kg. cal.)	13.9	14.5	14.0	12.6

Hamiltonian when taken with an antisymmetric combination of the solutions is listed. The minimum value of the energy occurs for $r_s = 3.38$ corresponding to a lattice constant of 3.65A.

§5. CONCERNING ADDITIONAL CORRELATIONS

As was pointed out in reference 1, II, the principal weakness of the Slater-Fock approximation lies in the fact that it does not give rise to correlations between electrons of antiparallel spin, that is, there is no analog of the Fermi-hole for electrons of antiparallel spin. That such a hole is of major importance from the standpoint of binding energy was a viewpoint adopted from the start and it was concluded that practically all of the discrepancy between the observed binding energy and that given by the solution to Fock's equations arises from this source. The process of introducing more general correlations is simply one of selecting a more general complete wave function than the Slater determinant, as discussed in the introduction, for the case in which the solutions to Fock's equations were practically of the form $e^{i\mathbf{k}\cdot\mathbf{r}}$, it was found possible to present another approximation which forms a natural sequel to the Fock approximation.

Strictly speaking, these results are valid only in the case of exponential eigenfunctions, but at the present time they will be taken over directly for the case of Li. The results on exchange energies indicate that the error introduced will probably not lie outside the computational error

of the work of Wigner so that until some future time when the entire work of correlation energies is gone over from a more rigorous standpoint, this will be considered adequate.

Using the work of Wigner directly, we obtain the results of Table X in which the upper row

TABLE X.

r_s	3.21	3.33	3.62	3.88	Obs.
Corr. energy (kg. cal.)	19.8	19.2	18.4	17.9	
Total	33.7	33.7	32.4	30.5	38.9

gives the correlation energies and the lower the final binding energies as functions of r_s . The final lattice constant is found to be 3.53A corresponding to $r_s = 3.27$ for which the binding energy is 33.8 kg.cal. The observed lattice constant of 3.46A corresponds to $r_s = 3.21$. The sources of these experimental values are the same as those used for sodium.

The fact that the results of the present work are in better accord with experimental results as far as the lattice constant is concerned, I believe to rest upon the increased accuracy of the computation for lattice constants other than the observed one. In the case of sodium most attention was paid to the computations for this value of r_s . For example, this was particularly true in the determination of the Fermi-energy. I hope that time permits a renewed investigation of this point in the near future.

§6. GENERAL REMARKS CONCERNING THE SOLUTIONS OF FOCK'S EQUATIONS FOR SOLIDS

There are several features of the preceding development that will be valid for crystals other than the monovalent metals lithium and sodium if slightly altered. It may be of interest to point these out at this time.

In the first place, the Hamiltonian (17) contains the explicit assumption that the full effect of closed shells and ions on the valence electrons may be included in the resultant field arising from the superposition of central fields which satisfy the conditions described in §1. This assumption is generally too stringent, for as discussed in the same section, these conditions may be satisfied only in the simplest cases. If the closed-shell electrons are not greatly affected by the precise form of the valence-electron functions, as Hartree's work shows to be the case for

very many atoms, this ion-core field may be replaced by one of the Hartree type in which the classical potential of the core charge is employed. Then when Fock's equations have been solved for this field, the interaction energy of valence and core electrons may be treated as an additive constant to the binding energy. Such a procedure would be highly practicable in those cases in which the Hartree fields are known and probably represents the best approach to the theoretical solution of most solids for some time to come.

Next, in dealing with ion-ion interaction, it was assumed in the present case that the overlapping of closed shells was sufficiently small so that the interaction was purely classical and, as a consequence, the same as that arising from point centers. This is clearly the simplest possible case. The next degree of complexity of interaction is that in which overlapping occurs to such an extent that the interchange forces between neighboring ions are small but not negligible; that is, the magnitude of the interchange interaction energies is not negligible but the core eigenfunctions will not be altered enough to change the Hartree field arising from them. For most of the solids formed of atoms in the short periods of the periodic chart as well as the alkali and alkaline earth metals this will be the case, and the exchange interaction energy may be computed on the basis of the usual Heitler-London approximation for which a good deal of work has already been done.⁷ In those cases in which the closed-shell electrons are considerably affected by ion-ion interaction, as may occur with certainty in the long series in which "unstable" closed shells are present in the free atom, the closed-shell electrons must be treated on an equal footing with the valence electrons. It is just in these cases that the clear-cut concept of valency breaks down from the chemist's viewpoint as well as that of the atomic spectroscopist. It is needless to say that although the formal procedure of solution may be well defined in such

⁷ Heitler and London, *Zeits. f. Physik* **44**, 455 (1927); A. Unsöld, *Zeits. f. Physik* **43**, 563 (1927); L. Pauling, *Zeits. f. Krist.* **67**, 377 (1928); N. Bruck, *Zeits. f. Physik* **51**, 707 (1928); M. Born and J. Mayer, *Zeits. f. Physik* **75**, 1 (1932); J. Mayer and L. Helmholtz, *Zeits. f. Physik* **75**, 19 (1932); W. Bleick and J. Mayer, *J. Chem. Phys.* **2**, 252 (1934).

cases, the practical difficulty will be as great as it is in the case of Hartree's work. It is at this point that questions of ferromagnetism arise and quantitative treatment of this topic will probably be approached only after surmounting the difficulties outlined here, for the works of Heisenberg, and Bloch⁸ give convincing indications that the source of ferromagnetism lies in strong ion-ion interaction rather than in the mere presence of free electrons of the type met with in lithium and sodium.

Next, in proceeding with the solution of Fock's equations for all electrons not in "fixed" closed shells we have assumed at start that the one-electron wave functions are of such a form that they extend throughout the entire crystal, or more exactly, that $|\psi|^2$ possesses the symmetry of the lattice in the space-group sense. This had as an extremely important consequence, from the practical computational standpoint, the fact that Fock's equation for each wave function is practically identical with all others because the effect on a given electron of an electron in the same state is negligible in comparison with the effect of all other electrons. As discussed in §2, the ratio of effects is $1 : N$, N being the total number of unit cells in the crystal. This rests directly upon the presence of translational symmetry, characteristic of the solid state in general, and is a primary point in which the Fock approximation for solids is simpler than for complex atoms or molecules. The importance of this lies not only in the fact that we need deal with but

one equation of the form (4) in which $\sum_{i \neq j} V_i(x_j)$ and \mathbf{A}_j are practically the same for all electrons, but that the different solutions are automatically orthogonal without introducing normalization parameters, or rather that these parameters may be taken to be zero.

As a final point, the neglect of magnetic interaction of electrons may be open to discussion. The general computational theory of atomic spectra shows that these forces are usually large only for tightly bound electrons that play an important role in the production of x-ray spectra and may be neglected for valence electrons. This neglect is unquestionably safe in the case of light atoms as the work of Hylleraas on He, Guillemin and Zener, Slater, and Wilson on lithium, and James and Coolidge on H_2 shows⁹ to be the case.

In the present work it has been assumed that the so-called Brillouin discontinuities in the energy surface are not important. This was found to be true in sodium¹ and will probably be true in other alkali metals. In cases in which there are two or more valence electrons per atom, this neglect will not be permissible since electrons will occupy states outside of the first zone. At the present time the author is carrying on an investigation of these discontinuities from the standpoint of the representations of space-groups which it is hoped may clear up some uncertain points in connection with their existence.

⁸ See Van Vleck, *The Theory of Electric and Magnetic Susceptibilities*, Oxford Press, Chapter XII.

⁹ E. A. Hylleraas, *Zeits. f. Physik* **57**, 815 (1929); V. Guillemin and C. Zener, *Zeits. f. Physik* **61**, 199 (1930); J. C. Slater, *Phys. Rev.* **36**, 57 (1930); E. B. Wilson, *J. Chem. Phys.* **1**, 210 (1933); H. M. James and A. S. Coolidge, *J. Chem. Phys.* **1**, 825 (1933).