

## On the Constitution of Metallic Sodium

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(Received March 18, 1933)

Previous developments in the theory of metals may be divided clearly into two parts: that based principally upon the hypothesis of free electrons and dealing with conductivity properties, and that based upon calculations of valence forces and dealing with the chemical properties. In the present article an intermediate point of view is adopted and the free-electron picture is employed in an investigation of chemical properties of metallic sodium. The assumption is made that in the metal the  $K$  and  $L$  shells of an atom are not altered from their form in the free atom. The properties of the wave functions of the electrons are discussed qualitatively, first of all, and it is concluded that the binding en-

ergy will be positive even when the Pauli principle is taken account of. This is followed by a quantitative investigation of the energy to be associated with the lowest state. First of all it is shown to what extent the present picture takes account of the interactions of electrons with both parallel and antiparallel spins, and to what extent remaining effects may be neglected. Next a Schroedinger equation is solved in order to determine the lowest energy level for various values of the lattice constant. To this a correction is made to account for the Pauli principle and from the result the lattice constant, binding energy and compressibility are calculated with favorable results.

### I.

THE investigations which have been carried out so far on the constitution of metals by quantum mechanics may be divided into two classes, the work on conductivity and related phenomena, carried out chiefly by Bloch, Peierls, Nordheim and Brillouin<sup>1</sup> are mainly based on the hypothesis of free electrons<sup>2</sup> and are concerned with the interaction between the electronic motion and the vibrations of the lattice, which is responsible for the electric resistance. The works of the other class<sup>3</sup> are mainly concerned with the chemical properties and crystal structure of the metals and are based on calculations of valence forces. They encounter great mathematical difficulties because the application of the usual methods to calculate valence forces becomes more and more difficult as the number of atoms increases.

The present work intends to take an intermediate point of view by applying the free electron picture but aiming at a calculation of chem-

ical properties of metallic sodium such as lattice constant, heat of vaporization, compressibility, etc. The method of calculation is the same one as that proposed by Hund for molecules<sup>4</sup> and more recently applied by Lenz and Jensen<sup>5</sup> to ionic lattices, and by Lennard-Jones and H. J. Woods<sup>6</sup> to two dimensional metallic lattices. The electrons are assumed to move freely in a potential field and their interaction is supposed to be contained to a large extent in this field, much as in Hartree's method of the self-consistent field which is actually the field adopted in the calculations of Lenz (not in ours). The initial assumptions which one makes about the statistical connections of positions of different electrons are necessarily rather rough in this picture and should be improved afterwards.

### II.

We assume first that the electrons in the  $K$  and  $L$  shells are not affected by the metallic bond and their wave functions the same as in the

<sup>1</sup> Cf. the comprehensive treatment by L. Brillouin, *Die Quantenstatistik*. Berlin, 1932.

<sup>2</sup> Cf. W. Pauli, *Zeits. f. Physik* **41**, 81 (1927); A. Sommerfeld, *Zeits. f. Physik* **47**, 1 (1928).

<sup>3</sup> J. C. Slater, *Phys. Rev.* **35**, 509 (1930); E. A. Hylleraas, *Zeits. f. Physik* **63**, 771 (1930); and especially H. S. Taylor, H. Eyring, A. Sherman, *J. Chem. Phys.* **1**, 68 (1933).

<sup>4</sup> F. Hund, *Zeits. f. Physik* **40**, 742 (1927) and applications of this point of view to crystals, *Zeits. f. Physik* **74**, 1 (1932).

<sup>5</sup> W. Lenz, *Zeits. f. Physik* **77**, 713 (1932); H. Jensen, *Zeits. f. Physik* **77**, 722 (1932).

<sup>6</sup> J. E. Lennard-Jones and H. J. Woods, *Proc. Roy. Soc.* **A120**, 727 (1928).

free state. This is justified since the corresponding wave functions practically vanish in half the interatomic distance. For the valence electron, however, such an assumption is quite out of the way, since the maximum of the corresponding wave function is (quite necessarily, as we shall see) just about half way between two atoms. Contrary to the conditions which exist in the free state, however, the wave function must not drop to zero after the maximum but can continue periodically through the whole crystal. It will therefore be much smoother than the wave function of the free atom, and the kinetic energy of the corresponding state will consequently be much smaller than that of the electron in the free atom. The potential energy, on the other hand, will be negatively larger in the lattice than in the free state because outside of the above-mentioned maximum the wave will not be under the influence of the nucleus considered originally, but under that of the next nucleus of the lattice, which is nearer. The electron with the wave function just described will have a larger negative energy than that in the free atom and we consider this to be the essence of the metallic state.

Of course, the wave function which one obtains by continuing the atomic wave function periodically in the lattice is not the real wave function of the free electron in the lattice, but the energy of the latter will be even smaller than that of the former. We shall try to find an approximation to the real wave function by actually solving a differential equation.

It must be added that not all the free electrons can be in the state given above, because of the Pauli principle. This reduces the magnitude of the metallic bond, because the electrons must have an additional kinetic energy, which is known as the zero-point energy of a Fermi gas. One sees easily, however, that this additional energy is smaller than the reduction of the kinetic energy which was obtained by continuing the wave function periodically through the whole lattice, so that there certainly remains a positive amount for the metallic bond.

### III.

First, we shall calculate the energy of the free electron in the lowest state. We shall do this by

numerically solving a Schrodinger equation. It will not be necessary to solve it for the entire lattice, because it will have the same symmetry as the crystal and hence will merely repeat itself a great number of times. Because of this symmetry, the derivative of the wave function at every crystallographic symmetry plane will be zero perpendicular to this plane. This will be used as a boundary condition. The crystallographic symmetry planes which we shall use in this way bisect perpendicularly the lines connecting the second nearest atoms. If we draw lines connecting the nearest atoms and consider the planes bisecting these perpendicularly, we have every atom surrounded by a truncated octahedron (Fig. 1).

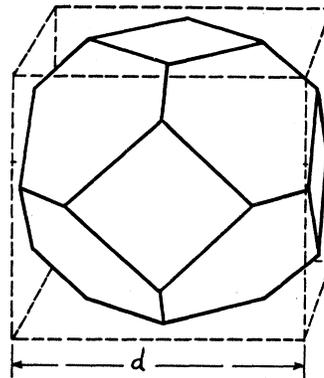


FIG. 1.

The middle points of the planes of the latter possess such symmetry ( $S_6$ ) that the derivative of the wave function must vanish at these points in every direction. It will be quite a good approximation to replace the polyhedron of Fig. 1 by a sphere of equal volume, and to take as boundary conditions that the derivative of the wave function vanishes at the boundary of this sphere.

The determination of the potential function to be used inside this sphere is more difficult. It would be quite out of the way to use Hartree's method as the density of electrons in the greatest part of the domain is very small. This fundamental difference between metallic and ionic lattices was already pointed out by Lenz.<sup>5</sup> If we assume that two electrons are never around the same ion, every ion may be supposed to be surrounded by a spherical electron cloud which will

exactly<sup>7</sup> cancel its potential outside of the sphere. Hence it seems to be the best simple assumption to take the potential as that of the ion inside the sphere mentioned above. The knowledge of this potential will allow us to set down the differential equation for the free electron which will be solved with the boundary condition that the derivative vanish at the boundaries of a sphere. The solution will be obviously spherically symmetric about each atom, which is of course not true for the actual wave function of the free electron but is a consequence of our approximations. It is not very far from the truth, however, since the wave function will actually have the highest crystallographic symmetry ( $0^h$ ) which is not very far from spherical symmetry, for to every direction there are not less than 47 other equivalent directions.

The justification of the assumption that two electrons are never around the same ion arises from two sources. Consider first the statistical connections between the positions of two electrons in an ideal Fermi gas. The complete wave function will be a determinant

$$\Psi(1, 2, \dots, n) = \frac{1}{(n!)^{\frac{1}{2}}} \begin{vmatrix} \psi_1(1) & \psi_2(1) & \dots & \psi_n(1) \\ \psi_1(2) & \psi_2(2) & \dots & \psi_n(2) \\ \vdots & \vdots & \ddots & \vdots \\ \psi_1(n) & \psi_2(n) & \dots & \psi_n(n) \end{vmatrix} \quad (1)$$

where the numbers in parentheses represent the Cartesian and spin coordinates of the corresponding electrons and the  $\psi$  are the wave functions of the different states.<sup>8</sup> In order to obtain the statistical relations between the positions of two electrons we have to square (1) and integrate it over the coordinates of all electrons except those considered, which will be taken as 1 and 2. Because of the orthogonality relations of the  $\psi_\kappa$  the result will be, apart from a constant,

$$\sum_{\kappa=1}^n \sum_{\lambda=1}^n [|\psi_\kappa(1)|^2 |\psi_\lambda(2)|^2 - \psi_\kappa(1)\psi_\lambda(1)^* \psi_\kappa(2)^* \psi_\lambda(2)]. \quad (2)$$

This still contains the spin coordinates  $s_1$  and  $s_2$  of 1 and 2 and reads more explicitly, if the edge of the cubic-shaped crystal is  $L$ ,

$$\sum_{\nu_1 \nu_2 \nu_3} \sum_{\mu_1 \mu_2 \mu_3} [ |e^{2\pi i(\nu_1 x_1 + \nu_2 y_1 + \nu_3 z_1)/L}|^2 |e^{2\pi i(\mu_1 x_2 + \mu_2 y_2 + \mu_3 z_2)/L}|^2 \delta_{s_1 \sigma_1} \delta_{s_2 \sigma_2} - e^{2\pi i[(\nu_1 - \mu_1)(x_1 - x_2) + (\nu_2 - \mu_2)(y_1 - y_2) + (\nu_3 - \mu_3)(z_1 - z_2)]/L} \delta_{s_1 \sigma_1} \delta_{s_1 \sigma_2} \delta_{s_2 \sigma_2} \delta_{s_2 \sigma_1} ]. \quad (2a)$$

There are really two questions to discuss: the statistical connection between electrons with antiparallel spin ( $\sigma_1 = -\sigma_2$ ) and between those with parallel spin ( $\sigma_1 = \sigma_2$ ). For a pair of the first kind the second term of (2a) vanishes so that they are statistically independent. For two electrons with parallel spin, on the other hand, we have to evaluate the sum of (2a) after having omitted the spin factors. We shall denote the distance of the two electrons by  $r$ , and may assume that the line joining them lies in the  $X$  direction, since the

probability will not depend on the direction. With these conditions, (2a) becomes

$$\sum_{\nu_1 \nu_2 \nu_3} \sum_{\mu_1 \mu_2 \mu_3} (1 - e^{2\pi i(\nu_1 - \mu_1)r/L}). \quad (3)$$

Here the summation over  $\nu_2, \nu_3, \mu_2, \mu_3$  can be carried out at once. The limitation on the  $\nu_1, \nu_2, \nu_3$  and  $\mu_1, \mu_2, \mu_3$  being

$$\nu_1^2 + \nu_2^2 + \nu_3^2 \leq \nu^2; \quad \mu_1^2 + \mu_2^2 + \mu_3^2 \leq \nu^2$$

$$\nu = (3n/8\pi)^{\frac{1}{3}} \quad (4)$$

it gives

$$P(r) = \sum_{\nu_1=-\nu}^{\nu} \sum_{\mu_1=-\nu}^{\nu} \pi^2(\nu^2 - \nu_1^2)(\nu^2 - \mu_1^2)(1 - e^{2\pi i(\nu_1 - \mu_1)r/L}). \quad (5)$$

Now the summation over  $\nu_1$  and  $\mu_1$ , after dividing by  $\pi^2 \nu^2 (4\nu^2 - 1)^2 / 9$  gives for the probability of the electrons with parallel spin being a distance  $r$  apart

<sup>7</sup> There is nothing like exchange forces in our picture.

<sup>8</sup> This consideration is contained implicitly in the work of Uhlenbeck and Gropper for the case of only slightly degenerated gases, Phys. Rev. 40, 1029 (1932). We are interested in the case of complete degeneracy, however.

$$4\pi r^2 P(r) = 4\pi r^2 \left\{ 1 - \left( \frac{3 \cos(\pi r/L) \sin(2\pi \nu r/L) - 2\nu \sin(\pi r/L) \cos(2\pi \nu r/L)}{2\nu(4\nu^2 - 1) \sin^3(\pi r/L)} \right)^2 \right\}$$

$$= 4\pi^2 r^2 \left\{ 1 - \left( 3 \frac{\sin(r/d') - (r/d') \cos(r/d')}{(r/d')^3} \right)^2 \right\}. \tag{6}$$

Here  $d' = v_0^{1/3}/3^{1/3}\pi^{2/3}$  and  $v_0 = L^3/n$  is the atomic volume. The function  $P(r)$  is sketched in Fig. 2, it vanishes for  $r=0$  and approaches 1 as  $r$  becomes large compared with the lattice constant. It attains its half-value for  $r = 1.79 d'$  or  $0.460 d$  for a body-centered lattice with a cube edge  $d$ . The radius of the sphere described above is about the same, namely  $(\frac{3}{8}\pi)^{1/3}d = 0.492 d$ . So we see that two electrons with parallel spin will be very rarely at the same ion, simply in consequence of the exclusion principle. This will be also true for a Fermi gas subject to a periodic potential, as the potential does not materially alter this argument.

It remains to investigate the case of antiparallel spins somewhat more closely. As it is not possible that three electrons have antiparallel spins, the probability of three electrons being at the same ion will be very small anyway. For two electrons with antiparallel spins and without interaction, however, there is no statistical connection of the positions. If one should take the interaction into account, it would turn out, however, that there is a connection of such a kind that they are but rarely in the neighborhood of each other. This is already indicated in the well-known solution of Hylleraas<sup>9</sup> for He and in the similar solution of Bethe<sup>10</sup> for the negative hydrogen ion. These solutions also show that the connection is of such an order of magnitude that the choice of potential function, which corresponds

to our rather rough picture of the metallic bond, is justified to some extent. It must be admitted, however, that the lower limit of the energies of the free electrons, which we calculate in this way, will certainly give too large a binding energy for the lattice, as all of the electrons will not be at different ions with certainty, and also because the terms of Hylleraas and Bethe just discussed will increase the kinetic energy above the value which we obtain by our boundary conditions. We shall not take up this question in more detail this time as it is deeply connected with the interaction problem of the electron and the justification of the notions of the free and bound electrons and we hope to return to it at another time.

IV.

The calculation of the wave function inside the proper spheres of the ions is very simple in principle. The potential function of Prokofjew<sup>11</sup> was used for the purpose. This was obtained by Prokofjew following a method of Kramers<sup>12</sup> in which one employs experimental values of the terms of Na. The differential equation for the radial function  $R = r\psi(r)$  is

$$-(\hbar^2/8\pi^2m)(\partial^2R/\partial r^2) + V(r)R = ER(r) \tag{7}$$

and in units of the Bohr radius of  $H$ , the quantity  $Q(\rho) = -a_0\rho^2V/e^2$ , is approximated for various intervals by parabolas, as follows:

$\rho = 0.00$ to $0.01$	$Q = 11\rho$
0.01 0.15	$= -26.4 \rho^2 + 11.53 \rho - 0.00264$
0.15 1.00	$= -2.84 \rho^2 + 4.46 \rho + 0.5275$
1.00 1.55	$= +1.508 \rho^2 - 4.236 \rho + 4.876$
1.55 3.30	$= 0.1196\rho^2 + 0.2072\rho + 1.319$
3.30 6.74	$= 0.0005\rho^2 + 0.9933\rho + 0.0222$
6.74 $\infty$	$= \rho$

The boundary condition  $\partial\psi/\partial r = 0$  requires that at the boundary  $R$  should satisfy

$$\partial R/\partial r = R/r. \tag{8}$$

<sup>9</sup> E. A. Hylleraas, Zeits. f. Physik 48, 469 (1928).

<sup>10</sup> H. Bethe, Zeits. f. Physik 57, 815 (1929).

<sup>11</sup> W. Prokofjew, Zeits. f. Physik 58, 255 (1929). (Note: Prokofjew's table of  $Q(\rho)$  (p. 258) contains obvious errors

in two places, one in decimal point and one in sign. These were easily detected by the continuity conditions. The form given here is corrected.)

<sup>12</sup> H. A. Kramers, Zeits. f. Physik 39, 828 (1926).

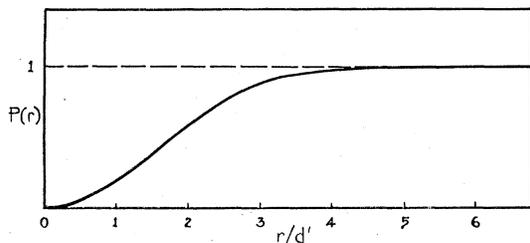


FIG. 2.

Instead of finding the energy value  $E$  for different radii of the sphere, the radii corresponding to different energy values were determined. Thus an arbitrary energy value  $E$  was taken and the corresponding wave function was obtained from (7) using the method of finite differences employed by Prokofjew. The calculation was started at  $r=0$ , however, so that every calculated wave function could be used. For  $r=0$  the radial function  $R$  vanishes and the solution up to  $r=0.025$  was calculated by means of a power series in  $r$ . After this the method of finite differences was employed, first with differences of 0.005 and then with larger ones when allowable. The largest difference employed was 0.32 ( $r > 4.6$ ). The wave function had practically no dependence on  $E$  in the neighborhood of the origin so that it was not always necessary to repeat this part of the calculation. As a check, the energy of the electron in the free atom was also determined, the calculated value lies between 0.3820 and 0.3800 Rydberg

units, while the experimental value is 0.3778. In Fig. 3, the wave function of the free atom and the wave function for  $E=0.500$  are plotted. The numerical tables will be published at another time.

After having the wave function, it was easy to determine the radius of the sphere, for which the boundary condition (8) is satisfied by drawing the tangents to  $R$  from the origin. The figure shows, that the boundary conditions are satisfied for two different radii, so that every numerical integration yields two points of the  $E(r)$  curve, which gives the energy of the most strongly bound free electron as a function of the lattice constant  $d = (8\pi/3)^{1/2}r$ . In Fig. 4 the  $E(r)$  curve is given (lower line), the unit of energy being the ionization energy of  $H$ . For very large  $r$  it approaches the ionization energy of atomic Na, possesses a minimum around  $r=3$ , and rises again for smaller values of  $r$ . This latter behavior is due to the fact that a further compression of the lattice would push the valence electron inside the closed  $L$  shell, which of course requires energy. The lattice, unlike a similar  $H$  lattice,<sup>13</sup> would be stable, therefore, even without taking into account Fermi statistics.

The calculation of a wave function took about two afternoons, and five wave functions were calculated on the whole, giving the ten points of

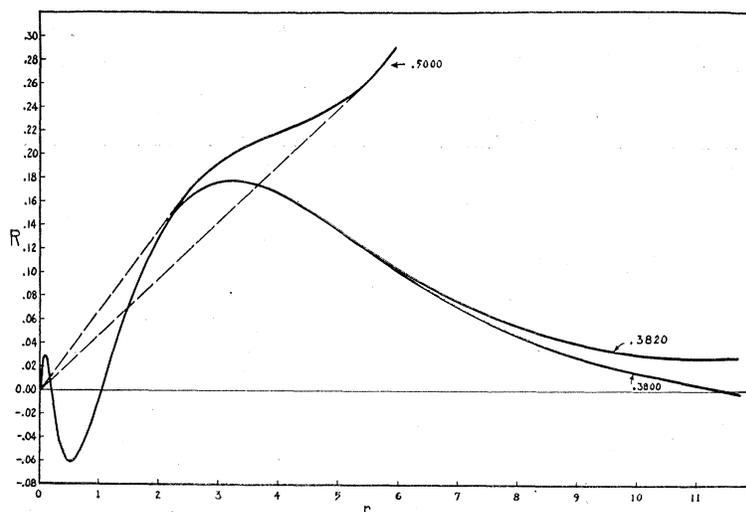


FIG. 3.

<sup>13</sup> Cf. E. A. Hylleraas, reference 3.

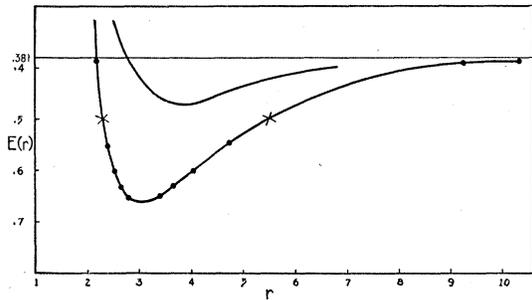


FIG. 4.

the figure. The points of the wave function of Fig. 4 are marked by a cross.

Another point which should be mentioned is that concerning the change in energy of the inner shells. The change is not due chiefly to the change of the boundary conditions as discussed above for the valence electron. This, of course, does increase the binding energy of these electrons, but only by a very small amount. A greater change arises from the increase in the probability of the valence electron being inside the *L*-electrons, because of the material change of the normalization factor. This decreases the binding energy of the inner electrons and hence lowers the heat of vaporization. A calculation of this effect has been made and shows that the decrease in binding energy is 0.008 Rydberg units per atom, or 2500 small calories per mole. This was obtained by evaluating the change of the potential of the inner electrons in the field due to the valence electron for the free and bound atom. The inner charge distribution was taken to be that given by Hartree.\*

V.

The last question we have to investigate is concerned with the additional energy of the other free electrons due to the Fermi distribution. This energy was calculated by the simple Fermi formula and it gives a mean additional energy for every electron

$$\frac{3h^2}{10m} \left(\frac{3}{8\pi}\right)^{\frac{2}{3}} \frac{1}{V_0^{\frac{2}{3}}} = \frac{9h^2}{80\pi m} \left(\frac{3}{2\pi}\right)^{\frac{2}{3}} \frac{1}{r^2} \quad (9)$$

or  $(9\pi/10)(3/2\pi)^{\frac{2}{3}}r^{-2}$  if the energy is measured in Rydberg units and *r* in Bohr units. As a matter of fact, this formula is valid only for free electrons

\* Hartree, Proc. Camb. Phil. Soc. 24, 111 (1927).

and it certainly gives too large a value for bound electrons. The fact that the energy differences for bound electrons are smaller than for free electrons was shown first by Bloch.<sup>14</sup> It also follows from the following argument. Let the wave function of the electron with the lowest energy be  $\psi_{000}(x, y, z)$ , which is invariant with respect to an addition of an identity period to the coordinates. This invariance is not possessed by the wave functions of the other free electrons, and that with the quantum numbers  $\nu_1, \nu_2, \nu_3$ , will be multiplied by  $e^{2\pi i\nu_1 d/L}$ ,  $e^{2\pi i\nu_2 d/L}$  and by  $e^{2\pi i\nu_3 d/L}$  if *x*, *y*, or *z* are increased by *d*, respectively. Now  $\psi_{000}$  gives the lowest possible energy of all wave functions, which are orthogonal to the wave functions of the *L* and *K* shells. For the wave function with the quantum numbers  $\nu_1, \nu_2, \nu_3$  this is true if we compare it only with functions which have the same symmetry character, i.e., are multiplied by the same factors if one replaces *x*, *y* or *z* by *x*+*d*, *y*+*d* or *z*+*d*, respectively. There is, however, the function

$$\psi_{\nu_1\nu_2\nu_3} = e^{2\pi i(\nu_1x+\nu_2y+\nu_3z)/L}\psi_{000}(x, y, z), \quad (10)$$

which has all the required properties and the energy of which differs from that of  $\psi_{000}$  only by  $(h^2/2mL^2)(\nu_1^2+\nu_2^2+\nu_3^2)$ , the Fermi energy for free electrons. This is easily seen upon calculating  $(\psi_{\nu_1\nu_2\nu_3}, H\psi_{\nu_1\nu_2\nu_3})$  for (10) and remembering that  $\psi_{000}$  may be assumed to be real. The energy of the real wave function with the quantum numbers  $\nu_1, \nu_2, \nu_3$  is certainly less than that of (10) and so the average additional energy for the free electrons in higher states is also certainly less than (9). Nevertheless (9) was adopted in the subsequent calculation and the corresponding expression added to the energy of the lowest electron *E*(*r*). The result is given in Fig. 4 (upper line). It is probably true that the fact that (9) gives a too high value largely compensates the error which was made by the assumption of the free electrons, as discussed in Section III.

VI.

The upper curve in Fig. 4 gives at once all quantities we desire to calculate. The position of the minimum gives the radius of the sphere for which the energy is the smallest and

<sup>14</sup> F. Bloch, Zeits. f. Physik.

when multiplied by  $(8\pi/3)^{1/3}$  it should give the lattice constant for the absolute zero point. Similarly the depth of the minimum below the line of the energy for the free atom should give, after subtracting the correction for the energy gained by the inner shells (2.5 kilo cal.) the energy difference between the gas and the solid state (i.e., the heat of vaporization per atom) in Rydberg units at the absolute zero point. Finally the curvature at the minimum  $r_m$  is in a simple connection with the compressibility: the energy change for a linear compression in the ratio  $\alpha$  per volume  $v_0$  is  $v_0\kappa(3\alpha)^2/2$ , where  $\kappa$  is the compressibility, and, on the other hand, it is  $\frac{1}{2}r_m^2\alpha^2 d^2E(r_m)/dr^2$  when calculated from the figure. This gives

$$\kappa = (1/9)(r_m^2/V_0)(d^2E(r_m)/dr^2). \quad (11)$$

The quantity  $d^2E/dr^2$  was calculated as if the lower curve were linear at  $r_m$  and all the curvature arose from (9), which is approximately true according to the figure. The final values obtained for the three quantities  $d$ ,  $\lambda$  and  $\kappa$  are  $d=4.2\text{\AA}$ ,  $\lambda=25.6$  kilo cal./mol,  $\kappa=1.6\times 10^{-11}$  c.g.s. The depth of the minimum of the lower curve below the energy of the free atom is 88.5 kilo cal.; and the depth at the point where the upper curve has its minimum is 70.4. The Fermi correction at this point is 42.3 kilo cal. In order to have a fair comparison with experiment, the experimental values for these quantities must be extrapolated to the absolute zero point. It must be remembered, however, that we did not treat the motion of the nuclei by quantum me-

chanics and in consequence, the extrapolation should be done in such a way as to neglect the quantum effects. This was done by taking the values for room temperature and correcting them linearly. The three values for room temperatures are<sup>15</sup>:  $d=4.30\text{\AA}$ ;  $\lambda=26.00$  kilo cal./mol;  $\kappa=1.67\times 10^{-11}$  c.g.s. The coefficient of thermal expansion is  $62\times 10^{-6}$ ;<sup>16</sup> the corrected value of  $\lambda$  is determined by adding the difference in heat content of solid and gas ( $(6-3)$  cal./deg. $\times 300$  deg.=900 cal.) to the room temperature value of  $\lambda$ ; and the value of  $\kappa$  at 0°K was obtained by extrapolating values given along with the above. The final values are:  $d=4.23\text{\AA}$ ,  $\lambda=26.9$  kilo cal./mol;  $\kappa\sim 1.0\times 10^{-11}$  c.g.s. The theoretical values compare favorably with these, partly, without doubt, as a consequence of compensating errors.

The work on sodium is being extended with particular reference to a more exact determination of the distribution of energy levels in the neighborhood of the lowest one. Moreover, the corresponding calculations on Li, K, Rb, by using Hartree's and Hargreaves' fields,<sup>17</sup> are being undertaken by one of us.

<sup>15</sup>  $d$ : P. P. Ewald, Hand. d. Phys. XXIV, 331.

$\lambda$ : J. Sherman, Chem. Rev. 11, 93 (1932).

$\kappa$ : Landolt Bornstein, Erster Ergaenzungsband 5 auf., 25. Int. Crit. Tables III, 47.

<sup>16</sup> Int. Crit. Tables II, 461.

<sup>17</sup> We wish to offer our thanks, at this time, to Professor J. C. Slater and hence to Dr. Hartree, for the use of the unpublished tables of K<sup>+</sup>.