BARD-J 38-0003

The large temperature coefficient of thermal reaction between 302 and 348° cannot be attributed to the reaction CH_3+H_2 since this has, as will be shown, a much smaller coefficient. The dark deposit on the reaction walls is evidence of the production of polymethylenic polymerization products. Evans and Lee[17] on studies of the electrolysis of methyl mercuric bromide and Shukla and Walker[18] in electrolysis of fatty acids and their salts postulate methane production by the second of the above processes.

Activation energies of the reactions

If the logarithm of the rates of methane production from Table V be plotted against $1/T$ in the range 160–300° a straight line is obtained whose slope is 8.1 kcal. per mole. As is evident from the expression

$$d[CH_4]/dt=2k_2[CH_3][H_2]$$

this value is a summation of the effect of temperature on the stationary state concentration of methyl radicals and the activation energy E_M of the process $CH_3+H_2=CH_4+H$.

A plot of ethane production, in presence or absence of hydrogen, against $1/T$ gives a single straight line over the entire temperature range the slope of which indicates an activation energy of 1.5 kcal. per mole. As suggested previously, this energy requirement may be attributable to the reaction between free methyl and mercury dimethyl. In such case the effect of temperature on the recombination of methyl radicals whether bimolecularly, or at the wall, must be very small indeed and E_M would be 8.1 kcal. per mole. This latter value would be reduced, if the value of E_2 for ethane formation were to be attributed to an activation energy of the recombination process, by the whole amount, 1.5 kcal., in case of a wall recombination, or by 0.75 kcal. for a bimolecular association in the gas phase. These alternatives would set the value for E_M between 6.6 and 8.1 kcal. with the greater weight attaching to the upper figure.

The experimental figures of Hartel and Polanyi[14] led them to a value $E_M=8$ kcal., although a series at 10 mm hydrogen pressure gave a value of ~6 kcal. In a parallel investigation by Taylor and Rosenblum[19] on the photolysis of acetone in presence of hydrogen the value for E_M deduced on the basis of bimolecular recombination with negligible activation energy is 8.7 kcal., rising to 11 kcal. if the recombination process were unimolecular at the wall. Upon these bases therefore we must conclude that the most trustworthy value now available for the activation energy, E_M, is 9 ± 2 kcal.

[17] Evans and Lee, J. Am. Chem. Soc. **56**, 654 (1934).
[18] Shukla and Walker, Trans. Faraday Soc. **27**, 35 (1931).
[19] H. S. Taylor and C. Rosenblum, J. Chem. Phys. **6**, 119 (1938).

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An Improved Calculation of the Energies of Metallic Li and Na

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The method of calculation used in the present work is a modification of that used by Wigner and Seitz in their original calculations of the energies of metallic Li and Na. The main difference lies in an improved method for the calculation of the Fermi energy. In each polyhedral cell, the wave function of an electron is taken to be of the form $\psi_k=[u_0(r)+i(\mathbf{k}\cdot\mathbf{x})(v_1(r)-u_0(r))]\exp[i\mathbf{k}\cdot\mathbf{x}]$, where $u_0(r)$ and $v_1(r)$ are radial s and p functions, respectively, which depend only on the distance from the ion in the center of the cell. Both functions are determined explicitly from the differential equations, and the energy of the electron is expressed in terms of the boundary values of the wave function. Values of the Fermi energy, and of the total energy of each metal, are tabulated as a function of the lattice spacing. Calculated values of the lattice constants, heats of sublimation, and compressibilities are in fair agreement with experiment.

THE most accurate method for the calculation of metallic binding which has yet been suggested is that of Wigner and Seitz.[1] The method is especially suitable for the monovalent metals, and was first applied to the calculation of the binding energy and lattice constant of sodium. A rough value was also given for the compressibility. Lithium was considered in a later paper by Seitz.[2] His calculation of the energy did not extend to values of the lattice constant smaller than the observed, so that it was not possible to obtain the compressibility. The main object of the present work is to determine the energies of Li and Na and their dependence on volume with sufficient accuracy to obtain the compressibilities and their variation with pressure. A comparison of the results with recent experimental values of Bridgman, which extend to pressures of the order of 45,000 kg/cm², will be given in the following paper.[3]

The two main factors which determine the binding energy of a metal are the energy of an electron in its lowest state and the Fermi energy. Only two electrons can occupy the lowest state; the Fermi energy represents the average additional energy of electrons in higher states of the filled band. We will first give the general theory of the method used for the calculation of the electronic wave functions and energies, and then give the detailed numerical calculations of the binding energies.

Electronic Wave Functions and Energies

The wave function of an electron in its lowest state is determined as follows. By passing planes perpendicular to and bisecting the lines joining near neighbors, the whole space of the crystal is broken up into a set of regular polyhedra, one surrounding each ion. It is a good approximation

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[1] E. Wigner and F. Seitz, **43**, 804 (1933); **46**, 509 (1934); E. Wigner, Phys. Rev. **46**, 1002 (1934). A survey of this work, together with references to applications of the method to other problems may be found in Mott and Jones, *Theory of the Properties of Metals and Alloys* (Oxford, 1936), Chapters II and IV.
[2] F. Seitz, Phys. Rev. **47**, 400 (1935).
[3] A discussion of an approximate method for the calculation of the energies of the alkali metals, due to Fröhlich, is also given in this paper.

to take for the potential in each polyhedron that of the ion in the center of the polyhedron.[4] Since the wave function of an electron in its lowest state has the symmetry of the lattice, its normal derivative must vanish on the surface of the polyhedron. Wigner and Seitz replace the polyhedron by a sphere of equal volume (s sphere), and satisfy the boundary condition on the surface of this sphere. The wave function is then the radial solution of the Schrödinger equation:

$$-(\hbar^2/2\mu)\Delta\psi_0+V(r)\psi_0=E_0\psi_0, \tag{1}$$

subject to the boundary condition

$$(d\psi_0/dr)_{r=r_s}=0, \tag{2}$$

where r_s is the radius of the s sphere. In Eq. (2), $V(r)$ is the potential of a free (positive) ion, and E_0 is the energy of the electron in its lowest state.

The wave function of an electron in a higher state is of the form

$$\psi_k=u_k(x)\exp[i\mathbf{k}\cdot\mathbf{x}], \tag{3}$$

where $u_k(\mathbf{x})$ has the translational period of the lattice. The equation for u_k, obtained by substituting the above in the Schrödinger equation, is:

$$-(\hbar^2/2\mu)(\Delta u_k+2i\mathbf{k}\cdot\operatorname{grad}u_k)+Vu_k=(E_k-\hbar^2k^2/2\mu)u_k, \tag{4}$$

which differs from the equation for u_0 (the wave function of an electron in its lowest state) in the presence of the cross term, $-i(\hbar^2/\mu)\mathbf{k}\cdot\operatorname{grad}u_k$. This term will be small if u_0 is fairly flat throughout most of the volume (free electron case). In any case, it will be small for small k. We may treat this term as a perturbation, and obtain the energy, E_k, to the second order in k, by means of the ordinary Schrödinger perturbation theory.[5] To this order, the energy may be written:

$$E_k=E_0+\alpha\hbar^2k^2/2\mu \tag{5}$$

since the linear term in k is zero. For perfectly free electrons, $\alpha=1$. In general, α may be either greater or smaller than unity.

It is our purpose to determine the value of α. We attempt to solve (4) by a series starting with u_0:

$$u_k=u_0+u_1+u_2+\cdots, \tag{6}$$

where
$$-(\hbar^2/2\mu)\Delta u_0+Vu_0=E_0u_0, \tag{7}$$

$$-(\hbar^2/2\mu)\Delta u_1+Vu_1=E_0u_1+i(\hbar^2/\mu)\mathbf{k}\cdot\operatorname{grad}u_0. \tag{8}$$

We consider only the first-order correction to the wave function, and thus determine the energy to the second order in k. The function u_1 is odd, and, since it is periodic, it will change sign as we pass from one polyhedron into the next. The wave function will therefore be very small on the surface of the polyhedron. It is a good approximation to again replace the polyhedron by a sphere, and to require that u_1 vanish on the surface of the sphere.

Wigner and Seitz find u_1 by the usual perturbation theory, i.e., they expand u_1 in terms of the characteristic functions of the unperturbed equation (7).[6] The solution may be obtained in a much simpler way, if we note that a particular solution of (8) is:

$$u_1=-i(\mathbf{k}\cdot\mathbf{x})u_0(r), \tag{9}$$

as may be verified by direct substitution. To the particular solution, we must add a solution, $i(\mathbf{k}\cdot\mathbf{x})v_1(r)$, of the homogeneous equation in order to satisfy the boundary condition. Thus we take

$$u_1=i(\mathbf{k}\cdot\mathbf{x})v(r)=i(\mathbf{k}\cdot\mathbf{x})[v_1(r)-u_0(r)] \tag{10}$$

and require that

$$v_1(r)=u_0(r) \quad \text{at} \quad r=r_s. \tag{11}$$

There is one solution of the homogeneous equation which is finite at the origin; Eq. (11) determines the scale factor of this solution. Let

[4] It might be better to take instead the potential $V(r)+(3e^2/2r_s)-(e^2r^2/2r_s^3)$. The last two terms represent the potential due to the space charge of the valence electrons in the polyhedron. In order to get the proper value for the interaction energy of the electrons, it would then be necessary to subtract approximately $1.2e^2/r_s$ from the expression for W_s given in Eq. (29). The final value for the total energy would probably be little changed.

[5] An alternative method for the calculation of the energy of electrons in excited states has been given by J. C. Slater, Phys. Rev. 45, 794 (1934). Slater applied the method to Na; it has been applied to Li by J. Millman, Phys. Rev. 47, 286 (1935). The entire wave function, $U_k(\mathbf{x})\exp[i\mathbf{k}\cdot\mathbf{x}]$ is expanded in a series of spherical harmonics in each polyhedron, and the boundary conditions are fitted at a number of points on the surface of the polyhedron. The disadvantage of this method lies in the fact that it is necessary to expand the factor $\exp[i\mathbf{k}\cdot\mathbf{x}]$. This may introduce an error even though the potential is flat (cf. W. Shockley, Phys. Rev. 52, 866 (1937)). The method we have used is, of course, most satisfactory when the wave functions are nearly the same as those of free electrons, which is the usual case for the alkali metals.

[6] See especially F. Seitz, reference 2.

To this order, the energy may be written:

$$E_k = E_0 + \alpha\hbar^2k^2/2\mu \tag{5}$$

since the linear term in k is zero. For perfectly free electrons, $\alpha = 1$. In general, α may be either greater or smaller than unity.

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We consider only the first-order correction to the wave function, and thus determine the energy to the second order in k. The function u_1 is odd, and, since it is periodic, it will change sign as we pass from one polyhedron into the next. The wave function will therefore be very small on the surface of the polyhedron. It is a good approximation to again replace the polyhedron by a sphere, and to require that u_1 vanish on the surface of the sphere.

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$$u_1 = i(\mathbf{k}\cdot\mathbf{x})v(r) = i(\mathbf{k}\cdot\mathbf{x})[v_1(r) - u_0(r)] \tag{10}$$

and require that

$$v_1(r) = u_0(r) \quad \text{at} \quad r = r_s. \tag{11}$$

There is one solution of the homogeneous equation which is finite at the origin; Eq. (11) determines the scale factor of this solution. Let us set

$$u_0(r) = R(r)/r, \qquad v_1(r) = P(r)/r^2. \tag{12}$$

The equations for $R(r)$ and $P(r)$ are then:

$$d^2R/dr^2 + (2\mu/\hbar^2)(E_0 - V)R = 0, \tag{13}$$

$$d^2P/dr^2 - (2/r^2)P + (2\mu/\hbar^2)(E_0 - V)P = 0. \tag{14}$$

The first is the radial equation for the s function, the second is the radial equation for the p function. These equations must be integrated (in general numerically) to find R and P.

We now want to find the mean value of the energy using the wave function:

$$\psi_k = [u_0(r) + i(\mathbf{k}\cdot\mathbf{x})v(r)]\exp[i(\mathbf{k}\cdot\mathbf{x})]. \tag{15}$$

We have

$$E_k = \int_{\text{cell}} \psi_k^*[-(\hbar^2/2\mu)\Delta + V]\psi_k d\tau. \tag{16}$$

The integration is over one polyhedral cell. The wave function is normalized so that

$$\int_{\text{cell}} \psi_k^*\psi_k d\tau = 1. \tag{17}$$

Substituting (15) into (16), and making use of the Schrödinger equation and the normalization condition, we find that we may express E_k, to the order k^2, in the form (5), with

$$\alpha = 1 + \int u_0[v(r) + (\mathbf{k}\cdot\mathbf{x})^2(kr)^{-2}(dv/dr)]d\tau. \tag{18}$$

After integration over the angular coordinates, we obtain:

$$\alpha = 1 + 4\pi\int_0^{r_s} u_0(r)[v(r) + (r/3)(dv/dr)]r^2dr. \tag{19}$$

Integrating by parts, we may express α in the form:

$$\alpha = 1 - (8\pi/3)\int_0^{r_s} v(r)(du_0/dr)r^2dr. \tag{20}$$

The integration may be carried out as follows.[7] Let us put (cf. Eqs. (10) and (12))

$$v(r) = P/r^2 - R/r \tag{21}$$

and
$$u_0(r) = R/r.$$

With these substitutions:

$$\alpha = 1 - (8\pi/3)\int_0^{r_s} (P - rR)(dR/dr - R/r)dr. \tag{22}$$

Now

$$\int_0^{r_s} rR(dR/dr)dr = (rR^2)_{r=r_s} - \int_0^{r_s} (R^2 - rR(dR/dr))dr,$$

so that, to the approximation we are considering,

$$(8\pi/3)\int_0^{r_s} rR(dR/dr)dr = (4\pi/3)r_s^3[u_0(r_s)]^2 - \tfrac{1}{3}.$$

Thus

$$\alpha = (4\pi/3)r_s^3[u_0(r_s)]^2 - (8\pi/3)\int_0^{r_s} P(dR/dr - R/r)dr. \tag{23}$$

This result may be expressed in the following form, after a further integration by parts:

$$\alpha = (4\pi/3)\left\{r_s^3[u_0(r_s)]^2 - P(r_s)u_0(r_s) + \int_0^{r_s} [R(dP/dr) - P(dR/dr) + 2PR/r]dr\right\}. \tag{24}$$

From the differential equations which are satisfied by P and R, we have:

$$R(d^2P/dr^2) - P(d^2R/dr^2) = 2PR/r^2,$$

which may be transformed to

$$\frac{d}{dr}\left\{rR\frac{dP}{dr} - rP\frac{dR}{dr}\right\} = R\frac{dP}{dr} - P\frac{dR}{dr} + \frac{2PR}{r^2} \tag{25}$$

The integration in Eq. (23) can therefore be carried out in terms of the boundary values of the wave functions. Making use of the boundary condition (11), we have, finally,

$$\alpha = \gamma[(r/P)(dP/dr) - 1]_{r=r_s}, \tag{26}$$

where $\gamma = (4\pi/3)r_s^3[u_0(r_s)]^2$ is the ratio of the square of the wave function at the boundary of the s sphere to its mean value.

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ge of this method lies in the fact that it is necessary to pand the factor $\exp[i\mathbf{k}\cdot\mathbf{x}]$. This may introduce an error en though the potential is flat (cf. W. Shockley, Phys. ev. 52, 866 (1937)). The method we have used is, of urse, most satisfactory when the wave functions are arly the same as those of free electrons, which is the ual case for the alkali metals.

[6] See especially F. Seitz, reference 2.

[7] The possibility of carrying out the integration in Eq. (20) in terms of the boundary values of the wave function was pointed out to the author by C. W. Ufford.

Equation (26) provides a very simple method for the calculation of the Fermi energy. But a single integration of the differential equation (14) is required for each value of the lattice constant.

Numerical Calculation of the Energies of Li and Na

According to Wigner and Seitz,[1] the energy of a monovalent metal may be expressed in the following form:

$$W=E_0+F+W_e+W_I. \tag{27}$$

This is the negative of the energy per atom required to break up the metal into positive ions and free electrons, and thus is the sum of the atomic heat of sublimation and the ionization potential. The first two terms represent the value of E_k averaged over all the occupied states; E_0 is the energy of an electron in its lowest state, and F is the additional energy required by the Pauli principle. The next term, W_e, is a small correction to the interaction energy of the electrons (not taken adequately into account in the first two terms) which will be discussed at more length later on. The last term, W_I, is the very small nonelectrostatic interaction energy of the ions (the overlap and van der Waals energies) which we will neglect in the present work.

In order to obtain E_0, it is necessary to find the radial solution of Eq. (1) (or, equivalently, of Eq. (13)), subject to the boundary condition (2). The solutions, $\psi_0(r, E_0)$ which are finite at the origin, depend on two variables, the radial distance r and the energy parameter, E_0. The actual value of E_0 for a given value of r_s is that for which $(d\psi_0/dr)_{r=r_s}=0$. It was desired to find E_0 for a fairly wide range of values of r_s near the energy minimum. In this region, E_0 does not vary rapidly, so that it was possible to obtain accurate values of $\psi_0(r, E_0)$ covering the desired range by integrating Eq. (1) numerically, using but three different values of E_0 for each metal. The values chosen for Li were -0.63, -0.65, and -0.67 Ry, and for Na -0.60, -0.62, and -0.64 Ry. The derivative, $d\psi_0/dr$, for each of these solutions, was obtained by numerical methods. The energy, $E_0(r_s)$, for a given value of r_s, was then obtained by finding, by quadratic interpolation between the three different energies, the value of E_0 for which $(d\psi_0/dr)_{r=r_s}=0$.[8] The same ion-core fields used by Wigner and Seitz were also used in the present calculation.[9] The results are given in Tables I and II for Li and Na, respectively.

Neglecting terms in k^4 and higher order, the Fermi energy is:

$$F=3\alpha\hbar^2k_0^2/10\mu=2.21\alpha/r_s^2 \text{ Ry}, \tag{28}$$

where k_0 is the magnitude of k for the highest occupied state of the Fermi distribution. We have determined α from Eq. (26) after finding $P(r, E_0)$ by numerical integration of Eq. (14). The energies chosen were again -0.63, -0.65, and

Tables I and II. *r_s is the radius of a sphere of atomic volume; E_0 is the energy of an electron in its lowest state; γ is the ratio of the square of the wave function at the boundary of the s sphere to its mean value; α is the effective number of free electrons per atom; F is the Fermi energy $=2.21\alpha/r_s^2$; and W is the total energy per atom. Atomic units (reference 12) have been used.*

Energy of lithium

r_s	$-E_0$	γ	α	F	$-W$
2.36	0.5727	1.179	0.2034	0.0807	0.4501
2.52	.6219	1.165	.3282	.1142	.4717
2.68	.6509	1.151	.4322	.1330	.4869
2.84	.6646	1.134	.5171	.1417	.4964
3.00	.6682	1.114	.5843	.1435	.5022
3.16	.6653	1.094	.6391	.1414	.5048
3.32	.6582	1.072	.6839	.1371	.5049
3.48	.6484	1.050	.7211	.1317	.5031

Energy of sodium

r_s	$-E_0$	γ	α	F	$-W$
3.16	0.6619	1.1294	1.1392	0.2521	0.3907
3.32	.6552	1.1033	1.1165	.2238	.4152
3.48	.6458	1.0779	1.1016	.2010	.4312
3.64	.6346	1.0531	1.089	.1816	.4417
3.80	.6225	1.0287	1.079	.1651	.4482
3.96	.6099	1.0047	1.069	.1507	.4520
4.12	.5972	.9793	1.059	.1379	.4537
4.28	.5846	.9549	1.050	.1266	.4540
4.44	.5722	.9305	1.041	.1166	.4530

[8] An alternative procedure would be to find the values of r_s for which $(d\psi/dr)_{r=r_s}=0$ for each of the three energy values. This would yield six values of $E_0(r_s)$, there being two values of r_s for each energy. One could then interpolate between these values to obtain E_0 for intermediate values of r_s. This procedure is not as satisfactory as the one adopted, because, in the region of interest, interpolation between the different energies for a fixed value of r_s is more accurate than interpolation between different values of r_s for fixed E_0.

[9] The Prokofjew field was used for Na; the semi-empirical field of Seitz was used for Li.

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Neglecting terms in k^4 and higher order, the Fermi energy is:

$$F=3\alpha\hbar^2k_0^2/10\mu=2.21\alpha/r_s^2 \text{ Ry}, \quad (28)$$

where k_0 is the magnitude of k for the highest occupied state of the Fermi distribution. We have determined α from Eq. (26) after finding $P(r, E_0)$ by numerical integration of Eq. (14). The energies chosen were again -0.63, -0.65, and -0.67 Ry for Li and -0.60, -0.62, and -0.64 Ry for Na. From these solutions, values of rdP/Pdr were obtained by numerical methods. Interpolation between these gave the corresponding values for the actual energy, E_0, going with a particular value of r_s. To obtain α, values of $\gamma=(4\pi/3)r_s^3[\psi_0(r_s)]^2$ are also required; these were obtained by numerical integration. Values of γ and α are listed in Tables I and II for Li and Na, respectively. Values of the Fermi energy F, as obtained from Eq. (28), are also given in these tables. It seems to be very difficult to estimate the magnitude of terms in k^4 and higher order in the Fermi energy. They are probably much more important for Li than for Na.

TABLES I AND II. *r_s is the radius of a sphere of atomic volume; E_0 is the energy of an electron in its lowest state; γ is the ratio of the square of the wave function at the boundary of the s sphere to its mean value; α is the effective number of free electrons per atom; F is the Fermi energy $=2.21\alpha/r_s^2$; and W is the total energy per atom. Atomic units (reference 12) have been used.*

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[9] The Prokofjew field was used for Na; the semi-empirical field of Seitz was used for Li.

[10] Cf. Mott and Jones, reference 1, p. 137.

The rapid decrease of the values of α for Li with decreasing r_s in the neighborhood of the normal lattice constant has already been noted by Seitz[2] and by Millman.[5] The decrease continues throughout the range we have considered. The Fermi energy itself decreases below $r_s=3$. Since the Fermi energy does not change rapidly, the normal lattice constant is determined mainly by the minimum of E_0. The Fermi energy of Na is but slightly larger than the free electron value.

If there were never more than one electron in each polyhedral cell, the energy per atom would be E_0+F. To this we must add the correction term, W_c, resulting from the correlations between the positions of the electrons.[10] This correction term is really the sum of three terms: (1) Electrostatic interaction energy of a given electron with other electrons in the same polyhedral cell, assuming no correlation between the positions of the electrons, $(0.6e^2/r_s)$; (2) Exchange energy resulting from the "Fermi hole" between electrons of parallel spin $(-0.458e^2/r_s)$; (3) Energy gain resulting from correlations between the positions of electrons of one spin with those of opposite spin $(\sim -0.58/(r_s+5.1)$ Ry). The values given in parentheses are the free electron values which we will use in the present work.[11] Thus, in atomic units,[12]

$$W_c=[0.284/r_s-0.58/(r_s+5.1)] \text{ Ry}. \quad (29)$$

The total energy per atom (experimentally, the ionization potential plus the atomic heat of sublimation) is

$$W=E_0+F+W_c.$$

Values of W for different values of r_s are also given in Tables I and II.

TABLE III.

	Lattice Constant	Heat of Sublimation (Kcal./mole)	Compressibility
Li (exp.)	3.46A	39[1]	7.4[2]
Li (calc.)	3.49A	34	8.4
Na (exp.)	4.25A	26[1]	12.3[2]
Na (calc.)	4.53A	23	12.0

[1] Bichowsky and Rossini, *Thermochemistry of Chemical Substances*, (Reinhold, 1936).
[2] From Bridgman's data (cf. following paper).

A comparison of the theoretical and experimental values of the lattice constants, heats of sublimation, and compressibilities of Li and Na is given in Table III. The theoretical values for Li are very nearly the same as those obtained by Seitz.[2] The lattice constant of Na is smaller than that obtained by Wigner and Seitz (4.75A) and is in better agreement with experiment. The smaller lattice constant is due to the fact that our values for the Fermi energy do not increase as fast with decreasing r_s as do those used by the above authors. Our calculations permit fairly accurate determinations of the compressibilities, which previously had only been roughly estimated. The variation of compressibility with pressure is discussed in the following paper.

[11] Seitz (reference 2) has shown that, even for Li, the free electron values are close to the actual values.

[12] Unit of length is the Bohr radius, 0.528×10^{-8} cm; the Rydberg unit of energy is equal to the ionization potential of hydrogen (13.5 ev).