CHARACTERISTIC FUNCTIONS AND ENERGY OF A LITHIUM CRYSTAL

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ABSTRACT

An expression for the energy of a lithium crystal is derived which involves an unknown parameter. The best value of the energy is obtained by making the energy of the crystal a minimum with respect to this parameter according to the Ritz approximation method. The characteristic functions involved are similar to those which Bloch derived. They differ from Bloch's in that a function containing the above mentioned unknown parameter takes the place of the atomic functions which he used.

The value of the binding energy which is obtained for the lithium crystal is -.85 elec.-volts. The lattice constant is found to be 3.07 Angstroms, and a calculation of the compressibility gives 10×10^{-12} ergs/cm^3. The energy is 50% too low, the lattice constant 12% too low and the compressibility 13% too high.

Characteristic Functions and Energy of a Lithium Crystal

The first electron theory of metals which involved quantum mechanics was that of Sommerfeld[1] which he published in 1928. The theories preceding Sommerfeld's theory were mainly due to Drude[2] and Lorentz[3] and were based on classical mechanics. However, Sommerfeld's theory was still to a great extent a theory of free electrons. He applied the new quantum statistics of Fermi and Dirac but he did not attempt to solve the problem of the characteristic functions and energy of an electron in the periodic potential of a crystal lattice.

The first attempt toward taking into consideration of the fields of force surrounding the atoms in a crystal was due to Dr. Houston[4] who worked on the scattering of the electrons by the crystal lattice. In order to calculate the scattering Dr. Houston made use of the wave properties of the electrons but did not actually solve for their characteristic functions.

The first detailed investigation of the wave properties of the electrons making use of the Schroedinger theory was made by Bloch[5] in 1928. The underlying assumptions of his work were

a. Each electron moves in a periodic field of force

due to all of the atoms in the crystal lattice.

b. The mutual interaction of the electrons may be neglected.

c. The boundary conditions may be taken care of by imposing the condition on the wave functions that they be periodic in the directions of the edges of the crystal with periods K_1, K_2, and K_3.

The numbers K_1, K_2, and K_3 are taken large and may be thought of as being the actual dimensions of the crystal whose properties are being investigated.

Schroedinger's equation for this model has the form

$$\nabla^2\phi + \frac{8\pi^2\mu}{h^2}(E - V) = 0. \qquad 1$$

V is the electrostatic potential of the grating and must be a periodic function. If we introduce the vector

$$\bar{r}_{\lambda\mu\nu} = \lambda\bar{a} + \mu\bar{b} + \nu\bar{c} \qquad \lambda,\mu,\nu = \text{whole num.}$$

where $\bar{a}$, $\bar{b}$, and $\bar{c}$ are the fundamental vectors of the lattice, then V must satisfy the equation

$$V(\bar{r}) = V(\bar{r} + \bar{r}_{\lambda\mu\nu}).$$

Bloch shows that the solution of (1) which satisfies the boundary condition of periodicity already mentioned is

$$\phi_{lmn} = e^{2\pi i\left(\frac{lx}{K_1} + \frac{my}{K_2} + \frac{nz}{K_3}\right)} u_{lmn}(xyz) \qquad (2)$$

The function $u_{lmn}(xyz)$ must be periodic with the periods $\bar{a}$, $\bar{b}$, $\bar{c}$. For the free electron model u_{lmn} is a constant and lmn are proportional to the components of momentum of the electron. In the general case it is difficult to obtain the form of $u_{lmn}(xyz)$ and, therefore, approximate solutions of (1) are used. If $u_{lmn}(xyz)$ is not a constant, then lmn are related, though no longer proportional, to the components of momentum of the electron. Each electron in the crystal is distinguished by a different set of numbers lmn which are the quantum numbers of that electron. However, $u_{lmn}(xyz)$ may also depend on other quantum numbers as well.

To get a more useful form of the function ϕ_{lmn} Bloch treated the problem as a purturbation of the model for which each electron is bound to its own atom. The zero order approximation which he obtained for the charactic functions is

$$\phi_{lmn} = \sum_{\lambda\mu\nu} e^{2\pi i\left(\frac{l\lambda}{G_1} + \frac{m\mu}{G_2} + \frac{n\nu}{G_3}\right)} u_{\lambda\mu\nu} \qquad (3)$$

The numbers G_1, G_2, G_3 are the numbers of atoms in the fundamental crystal in the directions $\bar{a}$, $\bar{b}$, $\bar{c}$, respec-

tively. Thus

$$K_1 = G_1 a, \quad K_2 = G_2 b, \quad K_3 = G_3 c.$$

The notation $u_{\lambda\mu\nu}$ indicates that u is a function of the distance measured from the ion situated aththe point λ, μ, ν, The summation over λ, μ, ν is extended to all the ions of the fundamental crystal lattice.

The quantum numbers l, m, and n must take on a range of values such that each function ϕ_{lmn} will correspond to one and only one set of numbers l, m, n, and such that all the possible functions ϕ_{lmn} will be accounted for. In addition, since l, m, n are related to the momentum of the electron, the range of values chosen must be the lowest possible. Let l, m, and n be the coordinates of a point in space, then the points corresponding to the possible values of l, m, and n will fill a certain region. The region thus defined is the primary zone.

The primary zone for the simple cubic lattice is a rectangular parallelopiped defined by

$$-G_1/2 < l < G_1/2, \quad -G_2/2 < m < G_2/2, \quad -G_3/2 < n < G_3/2.$$

For more complicated types of crystals a method due to Brillouin [6] must be used to determine the limits on l,

m, and n.

A method of determining the primary zone which is applicable to crystals which are describable in terms of three mutually perpendicular fundamental vectors is as follows

Let the numbers λ, μ, ν take on fractional as well as integral values so that every point occupied by an ion in the lattice can be specified in terms of the three fundamental vectors $\bar{a}$, $\bar{b}$, $\bar{c}$. In order to make the treatment specific let us confine ourselves to the body centered lattice which will be of particular interest later, then (3) may be rewritten in the form,

$$\phi_{lmn} = \sum_{\substack{\frac{G_1}{2}\ \frac{G_2}{2}\ \frac{G_3}{2} \\ -\frac{G_1}{2}\ -\frac{G_2}{2}\ -\frac{G_3}{2}}} \left\{ e^{2\pi i\left(\frac{l\lambda}{G_1} + \frac{m\mu}{G_2} + \frac{n\nu}{G_3}\right)} u_{\lambda\mu\nu} + e^{2\pi i\left(\frac{(\lambda+1/2)l}{G_1} + \frac{(\mu+1/2)m}{G_2} + \frac{(\nu+1/2)n}{G_3}\right)} u_{\lambda+1/2,\ \mu+1/2,\ \nu+1/2} \right\} \qquad (4)$$

l, m, n integral

To find the limits on l, m, n, we must set

$$\phi_{lmn} = \phi_{l+l,\ m+m,\ n+n} \qquad (5)$$

and determine the values of l , m , n which satisfy this equation. In order for (5) to be satisfied both of the following equations must be satisfied simul-

taneously.

$$\frac{l'\lambda}{G_1} + \frac{m'\mu}{G_2} + \frac{n'\nu}{G_3} = \text{integer}$$

$$\frac{l'}{G_1}(\lambda+\tfrac{1}{2}) + \frac{m'}{G_2}(\mu+\tfrac{1}{2}) + \frac{n'}{G_3}(\nu+\tfrac{1}{2}) = \text{integer} \qquad (6)$$

In order that the first equation of (6) be true for all values of λ, μ, ν we must have l'/G_1, m'/G_2, n'/G_3 equal to integers. The second equation will then be true provided

$$\frac{l'}{G_1} + \frac{m'}{G_2} + \frac{n'}{G_3} = \text{even integer.} \qquad (7)$$

Let $x = l'/G_1$, $y = m'/G_2$, $z = n'/G_3$. Then, to construct the primary zone, first locate the nearest points x, y, z which give the same ϕ function as the origin. In this case the points for which this is true are,

$\pm 2,\ 0,\ 0$	$\pm 1,\ \pm 1,\ 0$
$0,\ \pm 2,\ 0$	$\pm 1,\ \pm 0,\ \pm 1$
$0,\ 0,\ \pm 2$	$0,\ \pm 1,\ \pm 1$.

Next construct the planes which are normal to each of the lines connecting the origin to the above points and which bisect these lines. These planes enclose the primary zone. This is true because a shift in the values of l, m, n sufficient to carry a point on one side of

the primary zone thus constructed to the opposite side leaves the function ϕ unchanged. For the body centered cube the primary zone is the dodecahedron of volume 2 built upon the unit cube.

Slater[7] by a method slightly different from that of Bloch has built up characteristic functions for the electrons in a crystal lattice which he has used for the calculation of the energy, compressibility and lattice constant of the alkali crystals. He also has shown that Bloch's functions are a close approximation to the true functions for a compressed crystal and that some functions developed by Heisenberg are a good approximation for the extended lattice.

Dr. Epstein[8] using Slater's form of the secular equations for the first order perturbation of a system of identical atoms has built up a theory which is able to account for the basic facts of magnetism. His expression for the individual terms of the energy is similiar to Bloch's but to get the total energy he sums this expression differently from the way Bloch does.

Derivation of the Expression for the Energy of a Lithium Crystal

Dr. Houston[9] has shown that a wave function for the

crystal as a whole can be constructed out of the Bloch type functions which will approach the exact solution of the ground state provided that a function is chosen which makes the energy a minimum according to the Ritz perturbation method.

The model which he considers is essentially the same as that of Bloch, namely, a crystal which consists of centers of positive charge arranged in the form of the known crystal lattice of the metal to be treated. Each center is surrounded by a spherically symmetrical field, which, in the application of the method to be discussed later, is approximated by a Coulomb field. The remaining electrons then move in the field of these nuclei and are subject to their own mutual repulsions. The magnetic interaction of the spins are neglected.

The Schroedinger equation which describes this model is

$$\sum_{i=1}^{N} \nabla_i^2 \psi + \frac{8\pi^2\mu}{h^2}\left\{E - \sum_{i=1}^{N}\sum_{\lambda\mu\nu} U_{i,\lambda\mu\nu} - \tfrac{1}{2}\sum_{i\neq k}^{N}\frac{e^2}{r_{ik}}\right\}\psi = 0 \qquad (8)$$

where N is the number of electrons in the fundamental crystal. U has the same significance as the potential already discussed in connection with the functions of Bloch.

If the interaction term $\sum_{i,k}\frac{e^2}{r_{ik}}$ is neglected then (8)

becomes a sum of equations of the type of (1) and therefore is seperable. The solutions of the separate parts will be the Bloch type functions already discussed, i. e.,

$$\phi_{p,lmn} = C_{p,lmn} \sum_{\lambda\mu\nu} e^{2\pi i\left(\frac{l\lambda}{G_1} + \frac{m\mu}{G_2} + \frac{n\nu}{G_3}\right)} u_{p,\lambda\mu\nu} \qquad (9)$$

The only difference between this equation and equation (3) is that a normalizing constant, $C_{p,lmn}$, is included and that the dependence on other quantum numbers l, m, n is specifically shown by the subscript p.

In order that a product of the functions $\phi_{p,lmn}$ be a solution of (8) it is necessary that they satisfy the boundary conditions (which can be seen by inspection to be the case), that they form an orthogonal set and that they make the energy matrix diagonal.

We may prove that they are orthogonal to eachother as follows

$$\int \phi^*_{p',l'm'n'} \phi_{p,lmn}\, dv =$$

$$\sum_{\lambda'\mu'\nu'} \sum_{\lambda\mu\nu} e^{2\pi i\left\{\frac{l\lambda - l'\lambda'}{G_1} + \frac{m\mu - m'\mu'}{G_2} + \frac{n\nu - n'\nu'}{G_3}\right\}} \int u^*_{p',\lambda'\mu'\nu'} u_{p,\lambda\mu\nu}\, dv$$

$$= \sum_{\lambda'\mu'\nu'} \sum_{\lambda\mu\nu} e^{2\pi i\left\{\frac{l(\lambda-\lambda')}{G_1} + \frac{m(\mu-\mu')}{G_2} + \frac{n(\nu-\nu')}{G_3}\right\}}$$

$$\times e^{2\pi i\left\{\frac{(l-l')\lambda'}{G_1} + \frac{(m-m')\mu'}{G_2} + \frac{(n-n')\nu'}{G_3}\right\}} \int u^*_{p,\substack{\lambda+r\\ \mu+s\\ \nu+t}} u_{p,\lambda\mu\nu}\, d\nu \qquad (10)$$

In the last part of (10) the substitutions, $r = \lambda' - \lambda$, $s = \mu' - \mu$, $t = \nu' - \nu$, have been made. Since the integration does not depend on the positions of the atoms λ', μ', ν', and λ, μ, ν but only on their separation, we may rewrite (10) thus

$$\int \phi^*_{p',l'm'n'} \phi_{p,lmn}\, d\nu = \sum_{\lambda'\mu'\nu'} e^{2\pi i\left\{\frac{(l-l')\lambda'}{G_1} + \frac{(m-m')\mu'}{G_2} + \frac{(n-n')\nu'}{G_3}\right\}}$$

$$\times \sum_{rst} e^{-2\pi i\left\{\frac{rl}{G_1} + \frac{sm}{G_2} + \frac{tn}{G_3}\right\}} \int u^*_{p',rst} u_{p,000}\, d\nu \qquad (11)$$

The first sum is independent of the second and is the sum of the roots of unity. It is, therefore, equal to zero unless

$$l = l', \quad m = m', \quad n = n'.$$

Hence

$$\int \phi^*_{p';l'm'n'} \phi_{p,lmn}\, d\upsilon = N\delta_{ll'}\delta_{mm'}\delta_{nn'} \sum_{rst} e^{-2\pi i\left(\frac{rl}{G_1}+\frac{sm}{G_2}+\frac{tn}{G_3}\right)} \int u^*_{p';rst}\, u_{p,\alpha\beta\gamma}\, d\upsilon \qquad (12)$$

The functions $\phi_{p,lmn}$ thus form an orthogonal set if the functions $\phi_{p,lmn}$ are orthogonal for different values of p.

The elements of the energy matrix for the ϕ functions are given by

$$H^{o}_{p';l'm'n';p,lmn} = -\int \phi^*_{p';l'm'n'} \left\{ \frac{h^2}{8\pi^2\mu} \nabla^2 - \sum_{\alpha\beta\gamma} U_{\alpha\beta\gamma} \right\} \phi_{p,lmn}\, d\upsilon$$

$$= -\sum_{\lambda'\mu'\nu'} \sum_{\lambda\mu\nu} e^{2\pi i \left\{ \frac{l\lambda - l'\lambda'}{G_1} + \frac{m\mu - m'\mu'}{G_2} + \frac{n\nu - n'\nu'}{G_3} \right\}} \int u^2_{\lambda'\mu'\nu'} \left\{ \frac{h^2\nabla^2}{8\pi^2\mu} - \sum_{\alpha\beta\gamma} U_{\alpha\beta\gamma} \right\} d\upsilon \qquad (13)$$

Since the potential function $\sum_{\alpha\beta\gamma} U_{\alpha\beta\gamma}$ is summed over all atoms of the crystal, it looks the same from any atom and, therefore, the last integral of (13) is only a function of the distance of the $\lambda'\mu'\nu'$ point from the $\lambda\mu\nu$ point. Consequently we can rewrite (13) in the form

$$H^{o}_{p';l'm'n';plmn} = \delta_{ll'}\delta_{mm'}\delta_{nn'} \sum_{rst} e^{-2\pi i\left(\frac{rl}{G_1}+\frac{sm}{G_2}+\frac{tn}{G_3}\right)} \times \int u^*_{p';rst} \left\{ \frac{h^2}{8\pi^2\mu} \nabla^2 - \sum_{\alpha\beta\gamma} U_{\alpha\beta\gamma} \right\} u_{o\beta\delta}\, d\upsilon \qquad (14)$$

where as before $r = \lambda' - \lambda$, etc.

If now the functions u are so determined that (14) is zero for $p' \neq p$, then the functions ϕ will be a solution of the differential equation. The u function for the ground state may be determined by the Ritz perturbation method.

The solution of the differential equation (8) when the interaction is neglected is best written in the form of a determinant. This method of writing the solution of a separable equation is due to Slater. Thus

$$\psi(a_1 \cdots a_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi(a_1 x_1)\, \phi(a_1 x_2) & \cdots & \phi(a_1 x_N) \\ \phi(a_2 x_1)\, \phi(a_2 x_2) & \cdots & \phi(a_2 x_N) \\ \cdots & \cdots & \cdots \\ \cdots & \cdots & \cdots \\ \cdots & \cdots & \cdots \\ \phi(a_N x_1)\, \phi(a_N x_2) & \cdots & \phi(a_N x_N) \end{vmatrix} \qquad (15)$$

The letter a is written in place of all of the quantum numbers p, l, m, m and σ which enter into the function. σ is the spin quantum number which must be taken into account because of Pauli's exclusion principle.

It has been shown that (15) is the solution of (8) when the interaction terms are neglected. To prove that it is also a solution when these interaction terms are taken into consideration we must be able to show that the non-diagonal terms of the energy matrix H are zero where H is the energy operator corresponding to the entire differential equation (8). These non-diagonal terms are

$$H_{a_1'\cdots a_N' a_1\cdots a_N} = \int \psi^*(a_1'\cdots a_N') H \psi(a_1\cdots a_N)\, dv_1 \cdots dv_N \qquad (16)$$

Because of (14) all of the non-diagonal terms of (16) vanish except the parts which depend upon the interaction terms of H. If we represent the interaction terms by $I_{a_1'\cdots a_N' a_1\cdots a_N}$ we have

$$I_{a_1'\cdots a_N' a_1\cdots a_N} = \sum_{i=k} \int \psi^*(a_1'\cdots a_N') \frac{e^2}{r_{ik}} \psi(a_1'\cdots a_N)\, dv_1 \cdots dv_N \qquad (17)$$

Since it has been proved that the ϕ functions are orthogonal, the interaction terms will vanish if more than two of the a',s are different from the a,s. Two cases then must be discussed. First, the case where only one a' is different from the corresponding a and second, where two are different.

a. $a_k' \neq a_k$. All other primed states equal to un-

primed states. In $I_{a_1' \ldots a_k' a_l \ldots a_N}$ there will appear, for each $i \neq k$, N! terms of the type

$$\frac{1}{N!}\iint \phi^*_{a_k'}(x_1)\phi^*_{a_i}(x_2)\frac{e^2}{r_{12}}\phi_{a_k}(x_1)\phi_{a_i}(x_2)dv_1 dv_2$$

If the spin of a_i is equal to that of a_k, then there will also appear for each $i \neq k$ N! terms of the type

$$-\frac{1}{N!}\iint \phi^*_{a_k'}(x_1)\phi^*_{a_i}(x_2)\frac{e^2}{r_{12}}\phi_{a_k}(x_2)\phi_{a_i}(x_1)dv_1 dv_2$$

But if the spins of a_i and a_k are different, then no terms of the last type will appear. Therefore

$$I_{a_1' \ldots a_k' a_l \ldots a_N}$$

$$= \sum_{i(\neq k)} \iint \phi^*_{a_k'}(x_1)\phi^*_{a_i}(x_2)\frac{e^2}{r_{12}}\phi_{a_k}(x_1)\phi_{a_i}(x_2)dv_1 dv_2$$

$$- \sum_{\substack{i(\neq k) \\ \| \text{ spin}}} \iint \phi^*_{a_k'}(x_1)\phi^*_{a_i}(x_2)\frac{e^2}{r_{12}}\phi_{a_k}(x_2)\phi_{a_i}(x_1)dv_1 dv_2 \qquad (18)$$

Let us discuss one term of the type under the summation signs in (18). If we substitute for the ϕ functions their expressions from (9) we obtain

$$\iint \phi^*_{a_k'}(x_1)\phi^*_{a_i}(x_2)\frac{e^2}{r_{12}}\phi_{a_k}(x_1)\phi_{a_i}(x_2)dv_1 dv_2$$

$$= \sum_{\substack{\lambda_i \mu_i \nu_i' \\ \lambda_i \mu_i \nu_i \\ \lambda_k' \mu_k' \nu_k' \\ \lambda_k \mu_k \nu_k}} |C_i^2| C_k^* C_k \, e^{-2\pi i\left(\frac{l_i \lambda_i'}{G_1} + \frac{m_i \mu_i'}{G_2} + \frac{n_i \nu_i'}{G_3}\right)}$$

$$e^{-2\pi i\left(\frac{l_k' \lambda_k'}{G_1} + \frac{m_k' \mu_k'}{G_2} + \frac{n_k' \nu_k'}{G_3}\right)} e^{2\pi i\left(\frac{l_i \lambda_i}{G_1} + \frac{m_i \mu_i}{G_2} + \frac{n_i \nu_i}{G_3}\right)} e^{2\pi i\left(\frac{l_k \lambda_k}{G_1} + \frac{m_k \nu_k}{G_2} + \frac{n_k \nu_k}{G_3}\right)}$$

$$\iint U^*_{\lambda_k' \mu_k' \nu_k'}(x_1) U^*_{\lambda_i' \mu_i' \nu_i'}(x_2) \frac{e^2}{r_{12}} U_{\lambda_k \mu_k \nu_k}(x_1) U_{\lambda_i \mu_i \nu_i}(x_2) \, dv_1 \, dv_2 \tag{19}$$

Let

$$\begin{aligned} \lambda_i' &= \lambda_i + r, & \mu_i' &= \mu_i + s, & \nu_i' &= \nu_i + t \\ \lambda_k' &= \lambda_i + R, & \mu_k' &= \mu_i + S, & \nu_k' &= \nu_i + T \\ \lambda_k &= \lambda_i + \rho, & \mu_k &= \mu_i + \sigma, & \nu_k &= \nu_i + \tau. \end{aligned} \tag{20}$$

then

$$\iint \phi^*_{a_k'}(x_1) \phi^*_{a_i}(x_2) \frac{-e^2}{r_{12}} \phi_{a_k}(x_1) \phi_{a_i}(x_2) \, dv_1 \, dv_2$$

$$= \sum_{\substack{\lambda_i \mu_i \nu_i \\ r\, s\, t \\ R\, S\, T \\ \rho\, \sigma\, \tau}} e^{-2\pi i\left\{\frac{\lambda_i(l_k' - l_k)}{G_1} + \frac{\mu_i(m_k' - m_k)}{G_2} + \frac{\nu_i(n_k' - n_k)}{G_3}\right\}}$$

$$e^{-2\pi i\left(\frac{l_i r}{G_1} + \frac{m_i s}{G_2} + \frac{n_i t}{G_3}\right)} e^{-2\pi i\left(\frac{l_k' R}{G_1} + \frac{m_k' S}{G_2} + \frac{n_k T}{G_3}\right)}$$

$$e^{2\pi i\left(\frac{l_k\rho}{G_1}+\frac{m_k\sigma}{G_2}+\frac{n_k\tau}{G_3}\right)}\,|G_i|^2 C_k^* C_k$$

$$\iint U^*_{RST}(x_1)U^*_{rst}(x_2)\frac{e^2}{r_{12}}u_{pqr}(x_1)u_{000}(x_2)\,dv_1\,dv_2 \qquad (21)$$

It can be seen that the sum of $\lambda_i\mu_i\nu_i$ involves only the term

$$e^{-2\pi i\left\{\frac{\lambda_i(l_k'-l_k)}{G_1}+\frac{\mu_i(m_k'-m_k)}{G_2}+\frac{\nu_i(n_k'-n_k)}{G_3}\right\}}$$

and since this is a root of unity, the result of the first sum in (21) is zero unless

$$l_k' = l_k,\ m_k' = m_k,\ n_k' = n_k.$$

Therefore there are no non-diagonial terms for which only one of the $a_1'\ldots a_N'$ differs from the corresponding number of the $a_1\ldots a_N$.

b. $a_i' \neq a_i$, $a_k' \neq a_k$. All other primed states equal the corresponding unprimed states. Since in this case we have the a_i fixed as well as the a_k, the result is the same as (18) with the sum over i removed and the first a_i under each integral sign replaced by a_i'.

Thus

$$I_{a_1'\ldots a_N' a_1 \ldots a_N} = \iint \phi^*_{a_k'}(x)\phi^*_{a_i'}(x_2)\frac{e^2}{r_{12}}\phi_{a_k}(x_1)\phi_{a_i}(x_2)\,dv_1\,dv_2$$

$$- \iint \phi^*_{a_k'}(x_1)\phi^*_{a_i'}(x_2)\frac{e^2}{r_{12}}\phi_{a_k}(x_2)\phi_{a_i}(x_1)\,dv_1\,dv_2 \qquad (22)$$

The first integral of (22) is zero unless the spin of the a_i' = spin of a_i and spin of a_k' = spin of a_k. The second integral is zero unless spin of a_k' = spin of a_i and spin of a_k' = spin of a_i.

Again substituting for the ϕ functions from (9) and making the substitutions of (20), we obtain in place of (22) the equation

$$I_{a_1'\ldots a_N' a_1 \ldots a_N} = \sum_{\substack{\lambda_i \mu_i \nu_i \\ R S T \\ \rho \sigma \tau}} C^*_{k'} C_k C^*_{i'} C_i$$

$$e^{-2\pi i\left\{\frac{\lambda_i(\lambda_k' + \lambda_i' - \lambda_k - \lambda_i)}{G_1} + \frac{\mu_i(m_k' + m_k' - m_i - m_i)}{G_2} + \frac{\nu_i(n_k' + n_k' - n_i - n_i)}{G_3}\right\}}$$

$$e^{-2\pi i\left(\frac{\lambda_i r}{G_1} + \frac{m_i s}{G_2} + \frac{n_i t}{G_3}\right)} e^{-2\pi i\left(\frac{\lambda_k' R}{G_1} + \frac{m_k' S}{G_2} + \frac{n_k' T}{G_3}\right)} e^{2\pi i\left(\frac{\lambda_k \rho}{G_1} + \frac{m_k \sigma}{G_2} + \frac{n_k \tau}{G_3}\right)}$$

$$\iint u^*_{RST}(x_1)u^*_{rst}(x_2)\frac{e^2}{r_{12}}u_{\rho\sigma\tau}(x_1)u_{000}(x_2)\,dv_1\,dv_2$$

$$- \iint u^*_{RST}(x_1)u^*_{rst}(x_2)\frac{e^2}{r_{12}}u_{\rho\sigma\tau}(x_2)u_{000}(x_1)\,dv_1\,dv_2 \qquad (22a)$$

Again the sum over $\lambda_i \mu_i \nu_i$ involves only the exponential, so that

$$\ell_k' + \ell_i' = \ell_k + \ell_i, \quad m_k' + m_i' = m_k + m_i, \quad n_k' + n_i' = n_k + n_i \qquad (23)$$

Since the diagonal term energy increases with an increase in ℓ, m, n, it will be possible to satisfy this condition only by considering terms with a higher diagonal energy. Hence the correction to the energy will be of the second order in these non-diagonal terms and will be such as to lower the calculated energy. This effect will be neglected here although its magnitude cannot be properly said to be negligible.

Dr. Houston therefore concludes that (15) is a good approximate solution of (8) for the ground state provided the functions $\phi_{p,\ell mn}(x)$ are made orthogonal to the filled states, and then so chosen that the energy is a minimum.

In that which follows the above theory will be used to calculate the energy and lattice constant of the lithium crystal. It is not possible to carry out the necessary integrations for a general crystal since the explicit expression for $u_{p,\lambda\mu\nu}$ is needed. It is for this reason that the calculations are restricted to lithium.

If the crystal lattice of lithium were very large the u function would simply be the 2s function of the isolated lithium atom. It would therefore seem reasonable to take as a first trial function, one that is similiar to this 2s function of lithium. Slater's[10] approximation to this function is

$$u = C_2 r e^{-r/\alpha} \tag{23a}$$

Equation (23a), however, is not orthogonal to the 1s state of lithium. Slater's approximation to the 1s state is $C_1 e^{-r/\beta}$ where β has the value .185Å and $C_1 = 1/\sqrt{\pi\beta^3}$. In order to get a trial function that is orthogonal to the 1s state let us assume

$$u = a_1 C_1 e^{-r/\beta} + a_2 C_2 r e^{-r/\alpha} \tag{24}$$

Then

$$\int (a_1 C_1 e^{-r/\beta} + a_2 C_2 r e^{-r/\alpha}) C_1 e^{-r/\beta} \, d\tau = 0 \tag{25}$$

Therefore

$$a_1 = -\frac{24}{\sqrt{3}} \frac{\sqrt{\alpha^3\beta^5}}{(\alpha+\beta)^4} a_2 = -Aa_2 \tag{26}$$

In order that $\int u^2 d\tau = 1$, we must have

$$a^2 = \frac{1}{\sqrt{1 - A^2}} . \tag{27}$$

This gives the required form for u and in order that it give a good approximation to the correct u, α must be fixed at the value which makes the energy of the lattice a minimum.

This form for u makes equation (12) zero also because the integral of a 1s function on one atom times a 2s function on another atom is negligible for lithium.

The energy of the electrons in the field of the nuclei and of each other is given by the diagonal term of the matrix of the energy operator introduced in equation (16). That is

$$H_{a_1'\ldots a_N a_1\ldots a_N} = \int \psi^*(a_1'\ldots a_N')H\psi(a_1\ldots a_N)dv_1\ldots dv_N \tag{28}$$

To this must be added the energy NP_g of interaction of the ions of the grating. Thus the total energy of the crystal is

$$E = 2\sum_{i=1}^{N/2}|c_i|^2 \sum_{\lambda'\mu'\nu'} e^{2\pi i\left\{\frac{l_i(\lambda-\lambda')}{G_1}+\frac{m_i(\mu-\mu')}{G_2}\right.}$$

$$\left.+\frac{n_i(\nu-\nu')}{G_3}\right\}\int u_{\lambda'\mu'\nu'}H^0u_{\lambda\mu\nu}dv + 2\sum_{i,k=1}^{N/2}|c_i|^2|c_k|^2$$

$$\times \sum_{\substack{\lambda\mu\nu \\ \lambda'\mu'\nu' \\ \alpha\beta\gamma \\ \alpha'\beta'\gamma'}} e^{2\pi i\left\{\frac{l_i(\lambda-\lambda')}{G_1}+\frac{m_i(\mu-\mu')}{G_2}+\frac{n_i(\nu-\nu')}{G_3}\right\}}$$

$$e^{2\pi i\left\{\frac{l_k(\alpha-\alpha')}{G_1}+\frac{m_k(\beta-\beta')}{G_2}+\frac{n_k(\gamma-\gamma')}{G_3}\right\}} \iint \{2u_{\lambda'\mu'\nu'}(1)u_{\alpha'\beta'\gamma'}(2)$$

$$- u_{\lambda'\mu'\nu'}(2)u_{\alpha'\beta'\gamma'}(1)\left\{\frac{e^2}{2r_{12}}u_{\lambda\mu\nu}(1)u_{\alpha\beta\gamma}(2)dv_1 dv_2 + NP_g \qquad (29)\right.$$

The upper limit, N/2, is obtained for the sums over i and k, on the assumption that only half of the possible states are filled but that each filled state contains two electrons corresponding to positive and negative spins. This also accounts for the factor of 2 which appears in two places in (29) The factor of (2) is not placed in front of the exchange integral because there are only half as many of these terms as of the others.

The expression for H^o may be written

$$H^o = -\frac{h^2}{8\pi^2\mu}\nabla^2 + U_{\lambda\mu\nu} + \sum_{\substack{rst \\ \neq\lambda\mu\nu}} U_{rst} \qquad (30)$$

and this operating on $u_{\lambda\mu\nu}$ gives

$$H^o u_{\lambda\mu\nu} = \left\{E_1 + \sum_{\substack{rst \\ \neq\lambda\mu\nu}} U_{rst}\right\} u_{\lambda\mu\nu} \qquad (31)$$

Substitution of this into (29) along with

$$\lambda' - \lambda = R,\ \mu' - \mu = S,\ \nu' - \nu = T$$
$$\alpha - \lambda = r,\ \beta - \mu = s,\ \gamma - \nu = t \qquad (32)$$
$$\alpha' - \lambda = r',\ \beta' - \mu = s',\ \gamma' - \nu = t'$$

leads to

$$E = NE_1 + 2N \sum_{i=1}^{N/2} \sum_{RST} e^{2\pi i \left(\frac{Rl_i}{G_1} + \frac{Sm_i}{G_2} + \frac{Tn_i}{G_3} \right)} |C_i|^2$$
$$\times \int u_{RST} \sum_{\substack{rst \\ \neq 000}} u_{rst} u_{000}\, dv \ + N \sum_{i=1}^{N/2} \sum_{k=1}^{N/2} |C|^2 |C|^2$$

$$\times \sum_{\substack{RST \\ rst \\ r's't'}} e^{2\pi i \left\{ \frac{Rl_i}{G_1} + \frac{Sm_i}{G_2} + \frac{Tn_i}{G_3} + \frac{(r-r')l_k}{G_1} + \frac{(s-s')m_k}{G_2} + \frac{(t-t')n_k}{G_3} \right\}}$$
$$\times \iint \left\{ 2u^*_{RST}(1) u^*_{r's't'}(2) - u^*_{RST}(2) u^*_{r's't'}(1) \right\} \frac{e^2}{r_{12}} u_{000}(1) u_{rst}(2)\, dv_1\, dv_2$$
$$+ \ N P_g \qquad (33)$$

It is necessary to carry through a separate discussion for the two parts of the electron interaction terms above. We will get the biggest terms of the first part of the triple sum over RST, rst, and $r's't'$, by setting $r' = r$, $s' = s$, $t' = t$. The biggest contribution to the second part of this triple sum will be obtained by setting $R = r$, $S = s$, $T = t$ and $r' = s' = t' = 0$. Then (33) becomes

$$E = NE_1 + N\sum_{i=1}^{N/2}|C_i|^2\sum_{RST} e^{2\pi i\left(\frac{Rl_i}{G_1}+\frac{Sm_i}{G_2}+\frac{Tn_i}{G_3}\right)}$$

$$\left\{2\int u_{RST}\sum_{\substack{rst\\ \neq 000}} U_{rst}\,u_{000}\,dv + \sum_{k=1}^{N/2}|C_k|^2\sum_{rst}\iint 2\,u^*_{RST}(1)\right.$$

$$\left.\times u^*_{rst}(2)\frac{e^2}{r_{12}}u_{000}(1)u_{rst}(2)\,dv_1dv_2\right\} + N\sum_{i=1}^{N/2}|C_i|^2\sum_{k=1}^{N/2}|C_k|^2$$

$$\sum_{RST} e^{2\pi i\left\{\frac{R(l_i+l_k)}{G_1}+\frac{S(m_i+m_k)}{G_2}+\frac{T(n_i+n_k)}{G_3}\right\}}\iint u^*_{RST}(2)u_{000}(1)\frac{e^2}{r_{12}}$$

$$u_{000}(1)u_{rst}(2)\,dv_1dv_2 + NP_g \qquad (34)$$

The double integrals of (33) decrease with increasing rst and r′s′t′ roughly in the same way that the normalizing constants C_i and C_k decrease with increasing i and k. Therefore in order to partially account for the approximations made in the first part of the electron interaction which eliminated the sum over r′s′t′, set

$$\sum_{k=1}^{N/2}|C_k|^2 = 1/2$$

and to account for the elimination of two sums in the

second part, set

$$C_i = \frac{1}{N} \text{ and } C_k = \frac{1}{N}. \text{ Then}$$

$$E = NE_1 + N\sum_{i=1}^{N/2} |C_i|^2 \sum_{RST} e^{2\pi i\left(\frac{Rl_i}{G_1} + \frac{Sm_i}{G_2} + \frac{Tn_i}{G_3}\right)} B_{RST}$$

$$-N\sum_{i,k=1}^{N/2} \frac{1}{N^2} \sum_{RST} e^{2\pi i\left(\frac{R(l_i+l_k)}{G_1} + \frac{S(m_i+m_k)}{G_2} + \frac{T(n_i+n_k)}{G_3}\right)} I_{RST} \quad (35)$$

where

$$B_{RST} = 2V_{RST} + K_{RST} \quad (36)$$

and

$$V_{RST} = \sum_{\substack{rst \\ \neq 000}} \int u^*_{RST}\, U_{rst}\, u_{000}\, dv$$

$$K_{RST} = \sum_{rst} \iint u^*_{RST}(1)\, u^*_{rst}(2) \frac{e^2}{r_{12}} u_{000}(1)\, u_{rst}(2)\, dv_1\, dv_2 \quad (37)$$

$$I_{RST} = \iint u^*_{RST}(2)\, u^*_{000}(1) \frac{e^2}{r_{12}} u_{000}(1)\, u_{RST}(2)\, dv_1\, dv_2$$

If we assume that functions for the K shell do not overlap, then we may write for the expression for P_g

$$P_g = \frac{1}{2} \sum_{RST} \frac{e^2}{d_{RST}} = \frac{1}{2} \frac{e^2}{d} \sum_{RST} \frac{1}{\sqrt{R^2+S^2+T^2}} \quad (38)$$

where d_{RST} is the distance between the atom at 000 and

the atom at RST. Thus all the terms in (35) except NE_1 may be written as a sum over RST. The terms in this sum get smaller as RST gets larger and for RST very large the negative and positive parts cancel each other. That is, when two atoms are far apart the distance between each atom and its electron is negligible in comparison to the distance between the two atoms, and the positive nuclear charge and the negative charge of the electron are practically at the same point. Therefore, if the sum over RST is carried out far enough the remaining terms are negligible. For purposes of computation here, the sums will be taken over only the first fourteen neighboring atoms.

To this order of approximation, if we represent them by NE_2, the terms in (35) involving B_{RST} may be written in the following form

$$NE_2 = N \sum_{i=1}^{N/2} |C_i|^2 \left\{ B_{000} + 8B_{\frac{1}{2}\frac{1}{2}\frac{1}{2}} \cos\frac{\pi \ell_i}{G_1} \cos\frac{\pi m_i}{G_2} \cos\frac{\pi n_i}{G_3} + 2B_{100} \left(\cos\frac{2\pi\, i}{G_1} + \cos\frac{2\pi m_i}{G_2} + \cos\frac{2\pi n_i}{G_3} \right) \right\} \qquad (39)$$

This is possible because,

$$B_{-RST} = B_{RST} = B_{-R-ST} = B_{-R-S-T}, \text{ etc.}$$

By definition

$$\frac{1}{|C_i|^2} = \sum_{\lambda'\mu'\nu'} \sum_{\lambda\mu\nu} e^{2\pi i\left\{\frac{l_i(\lambda-\lambda')}{G_1} + \frac{m_i(\mu-\mu')}{G_2} + \frac{n_i(\nu-\nu')}{G_3}\right\}} \times \iiint u^*_{\lambda'\mu'\nu'} u_{\lambda\mu\nu}\, dv$$

$$= N \sum_{RST} e^{-2\pi i\left(\frac{Rl_i}{G_1} + \frac{Sm_i}{G_2} + \frac{Tn_i}{G_3}\right)} \iiint u_{RST}\, u_{000}\, dv \qquad (40)$$

Let $a = \int u_{\frac{1}{2}\frac{1}{2}\frac{1}{2}} u_{000}\, dv$ and $b = \int u_{100}\, u_{000} dv$,

then

$$\frac{1}{|C_i|^2} = N\left\{1 + 8a\cos\frac{\pi l_i}{G_1}\cos\frac{\pi m_i}{G_2}\cos\frac{\pi n_i}{G_3} + 2b\left(\cos\frac{2\pi l_i}{G_1} + \cos\frac{2\pi m_i}{G_2} + \cos\frac{2\pi n_i}{G_3}\right)\right\} \qquad (41)$$

Therefore,

$$NE_2 = \sum_{i=1}^{N/2} \frac{B_{000} + 8B_{\frac{1}{2}\frac{1}{2}\frac{1}{2}}\cos\frac{\pi l_i}{G_1}\cos\frac{\pi m_i}{G_2}\cos\frac{\pi n_i}{G_3}}{1+8a\cos\frac{\pi l_i}{G_1}\cos\frac{\pi m_i}{G_2}\cos\frac{\pi n_i}{G_3} + 2b\left(\cos\frac{2\pi l_i}{G_1} + \cos\frac{2\pi m_i}{G_2} + \cos\frac{2\pi n_i}{G_3}\right)}$$

$$+ \frac{2B_{100}\left(\cos\frac{2\pi l_i}{G_1} + \cos\frac{2\pi m_i}{G_2} + \cos\frac{2\pi n_i}{G_3}\right)}{1+8a\cos\frac{\pi l_i}{G_1}\cos\frac{\pi m_i}{G_2}\cos\frac{\pi n_i}{G_3} + 2b\left(\cos\frac{2\pi l_i}{G_1} + \cos\frac{2\pi m_i}{G_2} + \cos\frac{2\pi n_i}{G_3}\right)} \qquad (42)$$

If we assume that $B_{100}/B_{\frac{1}{2}\frac{1}{2}\frac{1}{2}}$ is approximately equal to b/a* then

*See page 51.

$$NE_2 = \frac{NB_{1/2\,1/2\,1/2}}{2a} + (B_{000} - \frac{B_{1/2\,1/2\,1/2}}{a})SN \qquad (43)$$

where

$$S = \frac{1}{N}\sum_{i=1}^{N/2} \frac{1}{1+8a\cos\frac{\pi l_i}{G_1}\cos\frac{\pi m_i}{G_2}\cos\frac{\pi n_i}{G_3}+2b(\cos\frac{2\pi l_i}{G_1}+\cos\frac{2\pi m_i}{G_2}+\cos\frac{2\pi n_i}{G_3})} \qquad (44)$$

Let NE_3 equal the terms of (35) involving I_{RST} then

$$E_3 = \frac{1}{N^2}\sum_{i,k=1}^{N/2} \Big\{ I_{000} + 8I_{1/2\,1/2\,1/2}\cos\frac{\pi}{G_1}(l_i+l_k)\cos\frac{\pi}{G_2}(m_i+m_k)$$

$$\cos\frac{\pi}{G_3}(n_i+n_k) + 2I_{100}\Big\{\cos\frac{2\pi}{G_1}(l_i+l_k) + \ldots\Big\} \qquad (45)$$

In the appendix it is shown that the approximate value of E_3 is

$$E_3 = 1/4\ I_{000} + \frac{128}{\pi^6}\ I_{1/2\,1/2\,1/2} \qquad (46)$$

The complete expression for the energy becomes

$$E = NE_1 + \frac{NB_{1/2\,1/2\,1/2}}{2a} + (B_{000} - \frac{B_{1/2\,1/2\,1/2}}{a})SN + \frac{N}{4}\ I_{000}$$

$$+ \frac{128}{\pi^6}\ NI_{1/2\,1/2\,1/2} + NP_g \qquad (47)$$

Analytical Expressions for the Functions Appearing in E

The derivation of the formulas which are listed here have been placed in an Appendix which will be found at the end of the thesis.

The constants

$$d = \text{grating constant}$$

$$\lambda = \frac{d}{\alpha}$$

and the functions

$$-\mathrm{Ei}(-X) = \int_x^\infty \frac{e^{-t}}{t}\,dt$$

$$F_o(1,\lambda) = \frac{8}{15}\left(1 + \frac{5}{\lambda} + \frac{20}{\lambda^2} + \frac{45}{\lambda^3} + \frac{45}{\lambda^4}\right)$$

appear in a number of places below.

$$a = \frac{e^{-\frac{\sqrt{3}}{2}\lambda}}{80(1-A^3)}(\lambda^4+5.7735\lambda^3+26.667\lambda^2+69.282\lambda+80) \quad (48)$$

$$b = \frac{e^{-\lambda}}{45(1-A^3)}(\lambda^4 + 5\lambda^3 + 20\lambda^2 + 45\lambda + 45) \quad (49)$$

$$V_{000} = -\frac{e^2}{d}\left\{15.2374-\frac{2e^{-\sqrt{3}\lambda}}{(1-A^2)}\left(\lambda^3+2\sqrt{3}\lambda+6\lambda+\frac{8\sqrt{3}}{3}\right)\right.$$

$$\left.-\frac{2e^{-2\lambda}}{(1-A^2)}\left(\lambda^3 + 3\lambda^2 + \frac{9}{2}\lambda + 3\right)\right\} \quad (50)$$

$$K_{000} = \frac{e^2}{d}\left\{15.2374 + .5\lambda/(1-A^2) - .137\lambda/(1-A^2)^2 - \frac{8e^{-\sqrt{3}\lambda}}{3(1-A^2)^2}\right.$$

$$(1.0045\times10^{-3}\lambda^7 + .01218\lambda^6 + .08437\lambda^5 + .4060\lambda^4$$

$$+1.395\lambda^3 + 3.309\lambda^2 + 4.910\lambda + 3.464)$$

$$-\frac{e^{-2\lambda}}{(1-A^2)^2}(2.381\times10^{-3}\lambda^7 + .025\lambda^6 + .15\lambda^5 + .625\lambda^4$$

$$\left.+1.860\lambda^3 + 3.820\lambda^2 + 4.910\lambda + 3)\right\} \qquad (51)$$

$$V_{\frac{1}{2}\frac{1}{2}\frac{1}{2}} = -\frac{e^2}{d(1-A^2)}\left\{2.876a + \lambda a/2 - \lambda^5/160\ e^{-\sqrt{3}\lambda/2} - 2a/\sqrt{3}\right.$$

$$\left[6(-E_i(-1.1547\sqrt{3}\lambda/2)) + 3(-E_i(-1.633\sqrt{3}\lambda/2))\right.$$

$$\left.+(-E_i(-\sqrt{3}\lambda)) + 3(-E_i(2.0696\sqrt{3}\lambda/2))\right] - \frac{\sqrt{3}}{3}e^{-2.1547\frac{\sqrt{3}}{2}\lambda}$$

$$((2.1547)^2 3\lambda^2/4 + 3\sqrt{3}(2.1547)\lambda + \lambda^2/4 + 18)$$

$$-\frac{\sqrt{3}}{6}e^{-2.633\frac{\sqrt{3}}{2}\lambda}\left((2.633)^2\frac{3}{4}\lambda^2 + 3\sqrt{3}(2.633)\lambda + \frac{\lambda^2}{4} + 18\right)$$

$$-\frac{\sqrt{3}}{18}e^{-\frac{3\sqrt{3}}{2}\lambda}(27/4\lambda^2 + 9\sqrt{3}\lambda + \lambda^2/4 + 18)$$

$$\left.-\frac{\sqrt{3}}{6}e^{-1.5348\sqrt{3}\lambda}\left((3.0696)^2\frac{3}{4}\lambda^2 + 3\sqrt{3}(3.0696)\lambda + \frac{\lambda^2}{4} + 18\right)\right\} \qquad (52)$$

$$K_{\frac{1}{2}\frac{1}{2}\frac{1}{2}} = -V_{\frac{1}{2}\frac{1}{2}\frac{1}{2}} + \frac{e^2\sqrt{3}e^{-\frac{\sqrt{3}}{2}\lambda}}{24(1-A^2)^2 d}(\lambda^4 + 4.6189\lambda^3 - 5.75\lambda^2 + 57.3273\lambda$$

$$- 59.563) + \frac{e^2\sqrt{3}e^{-\frac{3\sqrt{3}}{2}\lambda}}{64(1-A^2)^2 d}(\lambda^4+11.547\lambda^3+58.333\lambda^2$$

$$+148.83\lambda+158.83) - \frac{e^2 a\, e^{-\frac{\sqrt{11}}{2}\lambda}}{64(1-A^2)^2 d}(.07428\lambda^6+.9406\lambda^5$$

$$+6.181\lambda^4+34.05\lambda^3+56.72\lambda^2+65.295\lambda+39.375)$$

$$- \frac{e^2 a\, e^{-\frac{3\sqrt{3}}{2}\lambda}}{64(1-A^2)^2 d}(1.0984\lambda^6+8.8781\lambda^5+41.01\lambda^4+131.5\lambda^3$$

$$+ 139.2\lambda^2 + 102.30\lambda + 39.375) - \frac{e^2 a\, e^{-\frac{\sqrt{19}}{2}\lambda}}{96(1-A^2)^2}$$

$$(.38275\lambda^6+3.6880\lambda^5+20.31\lambda^4+77.64\ ^3+97.97\lambda^2$$

$$+85.814\lambda+39.375) - \frac{e^2\, e^{-\frac{\sqrt{3}}{2}\lambda}}{96(1-A^2)\, d}(\frac{3\sqrt{3}}{8}\lambda^3+3\ ^2+\frac{9\sqrt{3}}{2}\lambda+9)$$

(53)

$$I_{000} = \left\{\frac{.5\lambda}{(1-A^2)} - \frac{.137\lambda}{(1-A^2)^2}\right\}\frac{e^2}{d} \qquad (54)$$

$$I_{½½½} = \frac{e^2}{\alpha}\left\{\frac{2}{\sqrt{3}\lambda} - \frac{e^{-\sqrt{3}\lambda}}{6\lambda}(1.005\text{x}10^{-3}\lambda^7+.01218\lambda^6+.08437\lambda^5\right.$$

$$\left.+4060\lambda^4+1.395\lambda^3+3.309\lambda^2+4.910\lambda+3.464)\right\} \quad (55)$$

$$S = \frac{\left\{1 - \frac{3\pi^4}{8}\alpha'\beta' + (\frac{3\alpha}{5}+\frac{27\pi^4\beta'^2}{176})(\frac{3\pi^2}{4})^{2/3}+\frac{9\pi^2}{28}(\alpha'^2 - \beta')(\frac{3\pi^2}{4})^{1/3}\right\}}{1 + 8a + 6b}$$

(56)

$$\alpha' = \frac{4(a+b)}{1+8a+6b}, \quad \beta' = \frac{a+4b}{3(1+8a+6b)} \tag{57}$$

$$E_1 = \frac{3.877(1+A^2\rho(5\rho-4))}{3^2(1-A^2)} - e^2\frac{(1+2A^2/3(\rho-2))}{2(1-A^2)} \tag{58}$$

$$\rho = \frac{\alpha}{\beta}$$

$$\frac{P_g}{N} = 15.2374\frac{e^2}{d} \tag{59}$$

Calculation of the Energy of a Lithium Crystal

The total energy of the lattice, when expressed in the above form, is a function of both α and d. For a fixed d, the best value of the energy is its minimum value, considered as a function of α.

The energy, thus obtained, is a function of d only. It also should have a minimum for a value of d equal to the lattice constant, and this final minimum value for the energy should be the total energy of the atom in the crystal.

The following table gives the calculated values of the energy as a function of α and d. The minimum value of the energy for the atom in the crystal is seen to be -5.24 elec.-volts. The minimum energy for the isolated atom is -4.39 elec.-volts, which was

obtained from the graph of equation (58). Therefore the energy of the lattice binding is

- . 85 elec.-volts per atom.

This is to be compared with the observed value of about - 1.89 elec.-volts per atom.

α \ d	2.922	3.018	3.120	3.225
.9125	-4.51			
.9430	-5.23	-4.53		
.9740	-5.14	-5.24	-4.55	
1.0060		-5.13	-5.24	-4.56
1.0400			-5.13	-5.23
1.0750				-5.11

TABLE. Dependence of E on α and d, showing position of minimum.

The observed value of the binding energy was obtained by adding the heats of fusion and of vaporization to the heat required to bring the crystal from the zero point to the boiling point and substracting from this 3kT/2 for the energy of the gas.

The grating constant of

3.07 Angstroms

is to be compared with the observed value of 3.50 Å.

A calculation of the compressibility on the basis of the above data gives

$$10\times10^{-12} \text{ ergs/cm}^3.$$

The observed value is 8.9×10^{-12} ergs/cm^3. The compressibility was obtained by fitting a parabola to the curve connecting the energy and d. Let the parabola be

$$(E - E_o) = \frac{c}{2}(x - d)^2$$

and substitute into this E_o = -5.24 elec.-volts, E = -5,23 elec.-volts, d = 3.07 Å and x = 3.225 Å, then

$$c = \frac{2\times.01}{(.155)^2} \text{elec.-volts } (\text{Å})^2$$

$$= 1.3\times10^4 \text{ ergs/cm}^2.$$

The definition of compressibility is

$$\beta = \frac{1}{V}\frac{\partial V}{\partial p}$$

but $p = \frac{\partial E}{\partial V}$. Therefore, since $V = x^3/2$, (vol. occupied by one atom)

$$\beta = \frac{9d}{2c} = \frac{9\times3.07\times10^{-8}}{2\times1.31\times10^4} \text{ ergs/cm}^3 = 10\times10^{-12} \text{ergs/cm}^3.$$

The energy obtained above is too high. This can be accounted for in the following ways:

a. The Ritz approximation method should always give an energy that is too large since it gives the correct answer only when that form of the characteristic function is found which makes the energy lower than all other possible forms.

b. The contribution of the non-diagonal terms, which have been neglected, would also lower the energy.

c. It is manifestly incorrect to use only s-functions and to leave out the p-functions entirely. This is clearly indicated by the recent work of O'Brien and Skinner[11] on soft x-rays.

It is interesting to compare the above results for lithium with those which Slater[12] obtained for sodium. Slater obtains a value for the energy of sodium which is 50% too large. The value obtained here for lithium is 50% too small. Slater's lattice constant is roughly 30% too small, whereas the lattice constant calculated here is 12% too small. And finally, Slater says that his compressibility is 2 or 3 times too small if he considers only adjacent pairs and is "much too great" when the next set of atoms is considered. The compressibility calculated here is about 13% too large.

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APPENDIX

Evaluation of S

Let $\frac{\pi l_i}{G_1} = x$, $\frac{\pi m_i}{G_2} = y$ and $\frac{\pi n_i}{G_3} = z$. In the cube which represents half the octahedron over which l_i, m_i and n_i vary, we must have $-\frac{G_1}{2} < l_i < \frac{G_1}{2}$, $-\frac{G_2}{2} < m_i < -\frac{G_2}{2}$ and $\frac{-G_3}{2} < n_i < \frac{G_3}{2}$ or $\frac{-\pi}{2} < x < \frac{\pi}{2}$, $\frac{-\pi}{2} < y < \frac{\pi}{2}$ and $\frac{-\pi}{2} < z < \frac{\pi}{2}$.

This cube has a volume equal to π^3 and contains N/2 points. Therefore, to each point there is a volume $2\pi^3/N$. If we approximate the sum over the N/2 states of lowest energy by an integral over a sphere of volume π^3, then the radius of this sphere must be given by

$$\frac{4\pi R^3}{3} = \pi^3 \text{ or } R = \left(\frac{3\pi^2}{4}\right)^{1/3}$$

and equation (44) becomes

$$S = \frac{1}{2\pi^3}\int_0^R \frac{4\pi r^2 dr}{1+8a\cos x\cos y\cos z+2(\cos 2x+\cos 2y+\cos 2z)} \qquad (60)$$

Expand the cosines in terms of their arguments, then

$$S = \frac{2}{\pi^2}\int_0^R \frac{r^2 dr}{(1+8a+6b)-4(a+b)r^2+\frac{a+4b}{3}r^4+\frac{4(a-b)}{3}(x^2y^2+y^2z^2+z^2x^2)} \tag{61}$$

Since $(a-b) < a$ or b, the last term in the denominator is negligible. Hence

$$S = \frac{2}{M\pi^2}\int_0^R \frac{r^2 dr}{1-\alpha' r^2+\beta' r^4} \tag{62}$$

where the substitutions

$$M = 1 + 8a + 6b$$

$$\alpha' = \frac{4(a+b)}{M}$$

$$\beta' = \frac{a+4b}{3M}$$

have been made.

In the region for which the minimum energy occurs, $\alpha' \sim .5$ and $\beta' \sim .1$. The maximum value of $\alpha' r^2 - \beta' r^4$ which occurs for $r^2 \sim 2.5$ is of the order of .6. Therefore the denominator of (62) may be raised to the minus one power leading to

$$S = \frac{2}{M\pi^2}\int_0^R r^2\left\{1+\alpha' r^2-\beta' r^4+\alpha'^2 r^4-2\alpha'\beta' r^6+\beta'^2 r^8\right\} dr \tag{63}$$

The result of integrating (63) is equation (56).

Evaluation of E_3

Making the substitutions $x_1 = \pi \ell_i / G_1$, etc. in equation (45) and replacing the sum over i and k by integrations, leads to

$$E_3 = \frac{1}{N^2}\left(\frac{N}{2\pi s}\right)^2 \int_{-\pi/2}^{\pi/2} \cdots \int_{-\pi/2}^{\pi/2} \Big\{ I_{000} + 8 I_{\frac{1}{2}\frac{1}{2}\frac{1}{2}} \cos(x_1 + x_2)\cos(y_1 + y_2)$$

$$\cos(z_1 + z_2) + 2 I_{00} \Big[\cos 2(x_1 + x_2) + \cos 2(y_1 + y_2) + \cos 2(z_1 + z_2) \Big] \Big\}$$

$$dx_1\, dy_1\, dz_1\, dx_2\, dy_2\, dz_2 \qquad (64)$$

The result of this integration is contained in equation (46).

Evaluation of E_1

$$E_1 = -\frac{h^2}{8\pi^2 \mu} \int u \nabla^2 u \, dv - e^2 \int \frac{u^2}{r}\, dv \qquad (65)$$

Substituting the expression for u from (24), together with

$$\nabla^2 u = \frac{1}{\sqrt{1-A^2}} \left\{ -AC_1 \left(\frac{1}{\beta^2} - \frac{2}{r\beta}\right) e^{-r/\beta} + C_2 \left(\frac{2}{r} - \frac{4}{\alpha} + \frac{r}{\alpha^2}\right) e^{-r/\alpha} \right\}$$

into (65), and carrying out the indicated integration,

we obtain equation (58).

Evaluation of Equations (48) to (55)

By working out some of the integrals below using the complete form for u contained in equation (24), it was found that the results were approximately the same as would have been obtained if only the 2s part, namely

$$u = C_2 r e^{-r/\alpha} \tag{66}$$

had been used, provided the factor $1/(1-A^2)$ was suitably inserted. For this reason the integrals have been carried through using only (66) and have then been corrected to take care of $1/(1-A^2)$.

1. $$a = \int u_{\frac{1}{2}\frac{1}{2}\frac{1}{2}} u_{000}\, dv \tag{67}$$

$$= \frac{1}{3\pi\alpha^5}\int r_{\frac{1}{2}\frac{1}{2}\frac{1}{2}} r_{000}\, e^{-\frac{r_{\frac{1}{2}\frac{1}{2}\frac{1}{2}}+r_{000}}{\alpha}}\, dv$$

Let

$$r_{\frac{1}{2}\frac{1}{2}\frac{1}{2}} = k(u + v)$$

$$r_{000} = k(u - v)$$

where $2k = (\sqrt{3}/2)d$, then

$$dv = 2\pi k^3(u^2 - v^2)\,du\,dv$$

and

$$a = \frac{1}{3\pi\alpha^5}\frac{2\pi}{32}\frac{9\sqrt{3}}{32}d^5\int_{-1}^{1}\int_{1}^{\infty}(u^2 - v^2)^2 e^{-\frac{\sqrt{3}\lambda u}{2}}\,dudv$$

$$= \frac{e^{-\frac{\sqrt{3}\lambda}{2}}}{80}\left(\lambda^4 + \frac{10}{\sqrt{3}}\lambda^3 + \frac{80}{3}\lambda^2 + \frac{120}{\sqrt{3}}\lambda + 80\right) \qquad (68)$$

This is the same as (48) when multiplied by $1/(1-A^2)$

2. Since the integral for b is the same function of the points 100 and 000 that a is of ½½½ and 000, we may get the expression for (49) by substituting λ for $\sqrt{3}\lambda/2$ in (48).

3.
$$V_{000} = -8e^2\int\frac{u_{000}^2}{r_{½½½}}dv - 6e^2\int\frac{u_{000}^2}{r_{100}}dv \qquad (69)$$

Both integrals of (69) are of the same type.

Let us work out the second integral and then the first may be obtained by substituting $\sqrt{3}\lambda/2$ for λ and $\sqrt{3}d/2$ for d.

$$\int\frac{u_{000}^2}{r_{100}}dv = \frac{\pi d^4}{4x6\pi\alpha^5}\int_{-1}^{1}\int_{1}^{\infty}(u + v)^3 e^{-\lambda(u+v)}\,dudv$$

$$= \frac{1}{d} - \frac{e^{-2\lambda}}{3d}\left(\lambda^3 + 3\lambda^2 + \frac{9}{2}\lambda + \frac{3}{4}\right) \qquad (70)$$

Thus

$$V_{000} = -\frac{15.2374e^2}{d}\,\frac{2e^2}{(1-A^2)d}\left\{e^{-\sqrt{3}\lambda}\left(\lambda^3+2\sqrt{3}\lambda^2+6\lambda+\frac{8\sqrt{3}}{3}\right)\right.$$

$$+\frac{e^{-2\lambda}}{(1-A^2)}(\lambda^3 + 3\lambda^2 + \frac{9}{2}\lambda + 3) \qquad (71)$$

4.
$$V_{\frac{1}{2}\frac{1}{2}\frac{1}{2}} = -e^2\int \frac{u_{\frac{1}{2}\frac{1}{2}\frac{1}{2}}u_{000}}{r_{\frac{1}{2}\frac{1}{2}\frac{1}{2}}}dv - 6e^2\int \frac{u_{\frac{1}{2}\frac{1}{2}\frac{1}{2}}u_{000}}{r_{100}}dv$$
$$- 3e^2\int \frac{u_{\frac{1}{2}\frac{1}{2}\frac{1}{2}}u_{000}}{r_{\frac{1}{2}-\frac{1}{2}-\frac{1}{2}}}dv - e^2\int \frac{u_{\frac{1}{2}\frac{1}{2}\frac{1}{2}}u_{000}}{r_{-\frac{1}{2}\frac{1}{2}-\frac{1}{2}}}dv$$
$$- 3e^2\int \frac{u_{\frac{1}{2}\frac{1}{2}\frac{1}{2}}u_{000}}{r_{-100}}dv \qquad (72)$$

The first integral of (72) is readily calculated as follows:

$$\int \frac{u_{\frac{1}{2}\frac{1}{2}\frac{1}{2}}u_{000}}{r_{\frac{1}{2}\frac{1}{2}\frac{1}{2}}}dv = \frac{2\pi}{3\pi\alpha^5}\times\frac{9}{16}\frac{d^4}{16}\int_{-1}^{1}\int_{1}^{\infty}(u-v)(u^2-v^2)e^{-\frac{\sqrt{3}\lambda u}{2}}du$$
$$= \frac{\lambda e^{-\frac{\sqrt{3}\lambda}{2}}}{18d}(\frac{3\sqrt{3}}{8}\lambda^3+3\lambda^2+\frac{9\sqrt{3}}{2}\lambda+9) \qquad (73)$$

The other four integrals involve distances from three points and are therefore more difficult to handle. The method of integrating these integrals was suggested by Dr. H. Bateman. All are of the following type

$$I_1 = \frac{e^2}{3\pi\alpha^5}\int \frac{r_1 r_2}{r_3}e^{-\frac{r_1+r_2}{\alpha}}dv \qquad (74)$$

r_1, r_2 and r_3 are the distances from three different

points to the element of integration dv. Since r_3 appears in the denominator only, this is the potential at the 3 point of the distribution of charge whose density is

$$\rho = \frac{e^2}{3\pi\alpha^5} r_1 r_2 e^{-\frac{r_1+r_2}{\alpha}} \qquad (75)$$

Therefore I_1 must satisfy Poisson's equation

$$\frac{\partial^2 I_1}{\partial x_3^2} + \frac{\partial^2 I_1}{\partial y_3^2} + \frac{\partial^2 I_1}{\partial z_3^2} + \frac{4\pi e^2}{3\pi\alpha^5} e^{-\frac{R_1+R_2}{\alpha}} R_1 R_2 = 0 \qquad (76)$$

where x_3, y_3 and z_3 are the coordinates of the 3 point and R_1 and R_2 are the distances from the 3 point to the 1 point and the 2 point respectively.

Let us express (76) in terms of the ellipsoidal coordinates of 3 with respect to 1 and 2 defined by

$$\theta = \frac{R_1 + R_2}{2k}, \mu = \frac{R_1 - R_2}{2k} \qquad (78)$$

2k being the distance between the 1 point and the 2 point. The result of this transformation is

$$\frac{\partial}{\partial\theta}\left\{(\theta^2-1)\frac{\partial I_1}{\partial\theta}\right\} + \frac{\partial}{\partial\mu}\left\{(1-\mu^2)\frac{\partial I_1}{\partial\mu}\right\} + \beta(\theta^2-\mu^2)^2 e^{-\lambda\theta} = 0 \qquad (79)$$

where $\beta = 4e^2k^4/(3\alpha^5)$ and $\lambda = 2k/\alpha$.

Assume $I_1 = \sum_{n=0}^{\infty} A_n(\theta) P_n(\mu)$ where $P_n(\mu)$ are

Legendre polynomials and $A_n(\theta)$ are functions to be determined so that (79) is satisfied.

Since A_n will be a function of λ also, it will be convient to show this by writing it $A_n(\theta,\lambda)$. After substituting this assumed form for I_1 in (79), we obtain as the new form of the equation

$$\sum_n P_n(\mu)\left[\frac{d}{d\theta}\left\{(\theta^2-1)\frac{dA_n}{d\theta}\right\} - n(n+1)A_n(\theta)\right] + \beta(\theta^2-\mu^2)^2 e^{-\lambda\theta} = 0 \qquad (80)$$

But the last part of this equation can be expanded in a series of Legendre polynomials, thus

$$\beta(\theta^2-\mu^2)^2 = \beta\left[8/35\ P_4(\mu) + (4/7 - 4/3\theta^2)P_2(\mu) + (\theta^4 - 2/3\theta^2 + 1/5)P_0(\mu)\right]$$

$$= \sum_n a_n P_n(\mu)$$

so that (80) can be rewritten

$$\sum_n P_n(\mu)\left[\frac{d}{d\theta}\left\{(\theta^2-1)\frac{dA_n}{d\theta}\right\} - n(n+1)A_n(\theta,\lambda) + a_n\right] = 0 \qquad (81)$$

If (81) is to be true, then

$$\frac{d}{d\theta}\left\{(\theta^2-1)\frac{dA_0}{d\theta}\right\} + \beta(\theta^4 - 2/3\theta^2 + 1/5)e^{-\lambda\theta} = 0$$

$$\frac{d}{d\theta}\left\{(\theta^2-1)\frac{dA_2}{d\theta}\right\} - 6A + \beta(4/7 - 4/3\theta^2)e^{-\lambda\theta} = 0$$

$$\frac{d}{d\theta}\left\{(\theta^2-1)\frac{dA_4}{d\theta}\right\}-20A_4+\beta\frac{8}{35}e^{-\lambda\theta} = 0 \qquad (82)$$

It is not obvious from the above analysis that the remaining functions $A_n(\theta,\lambda)$ are zero, but nevertheless it can be shown that this is the case.

The equations (82) are inhomogeneous Legendre differential equations and are most easily solved by making use of the appropriate Green's function which is

$$\begin{aligned} g(\theta,x) &= Q_n(\theta)P_n(x) \qquad 1\leq x\leq\theta \\ &= Q_n(x)P_n(\theta) \qquad \theta\leq x\leq\infty. \end{aligned} \qquad (83)$$

Hence

$$A_0(\theta,\lambda) = \beta\left\{Q_0(\theta)\int_1^\theta(x^4-\frac{2}{3}x^2+\frac{1}{5})e^{-\lambda x}dx+\int_\theta^\infty Q_0(x)(x^4-\frac{2}{3}x^2+\frac{1}{5})e^{-\lambda x}dx\right\}$$

$$A_2(\theta,\lambda) = \beta\left\{Q_2(\theta)\int_1^\theta P_2(x)(\frac{4}{7}-\frac{4}{3}x^2)e^{-\lambda x}dx+P_2(\theta)\int_\theta^\infty Q_2(x)(\frac{4}{7}-\frac{4}{3}x^2)e^{-\lambda x}dx\right\}$$

$$A_4(\theta,\lambda) = \beta\left\{Q_4(\theta)\int_1^\theta P_4(x)\ \frac{8}{35}e^{-\lambda x}\ dx + P_4(\theta)\int_\theta^\infty Q_4(x)\ \frac{8}{35}e^{-\lambda x}\ dx\right\} \qquad (84)$$

$A_2(\theta,\lambda)$ and $A_4(\theta,\lambda)$ are much smaller than $A_0(\theta,\lambda)$. Furthermore, they not only enter into $V_{½½½}$ but also into $K_{½½½}$. The small error made in neglecting them here is partially eliminated by leaving them out of $K_{½½½}$ also. For this reason only the solution for $A_0(\theta,\lambda)$ will be worked out here.

The first integral of $A_o(\theta,\lambda)$ gives

$$\int_1^{\theta} (x^4 - \tfrac{2}{3}x^2 + \tfrac{1}{5}) e^{-\lambda x} dx = \frac{e^{-\lambda}}{\lambda} F_o(1,\lambda) - \frac{e^{-\lambda\theta}}{\lambda} F_o(\theta,\lambda) \qquad (85)$$

Let the second integral in $A_o(\theta,\lambda)$ be represented by $R_o(\theta,\lambda)$. Integration of it by parts gives

$$R_o(\theta,\lambda) = \frac{e^{-\lambda\theta}}{\lambda} F_o(\theta,\lambda) Q_o(\theta) - \frac{1}{\lambda}\int_{\theta}^{\infty} \frac{F_o(x,\lambda)}{x^2 - 1} e^{-\lambda x} d\theta \qquad (86)$$

$$F_o(\theta,\lambda) = \theta^4 + \frac{4\theta^3}{\lambda} + \theta^2\left(\frac{12}{\lambda^2} - \frac{2}{3}\right) + \frac{\theta}{\lambda}\left(\frac{24}{\lambda^2} - \frac{4}{3}\right) + \frac{24}{\lambda^4} - \frac{4}{3\lambda^2} + \frac{1}{5} \qquad (87)$$

$$= \theta^4 + c_3\theta^3 + c_2\theta^2 + c_1\theta + c_o$$

Performing the division under the integral sign of (86) and integrating the part which is a simple integral, we get

$$R_o(\theta,\lambda) = \frac{e^{-\lambda\theta}}{\lambda} F_o(\theta,\lambda) Q_o(\theta) - \frac{e^{-\lambda\theta}}{\lambda^2}\left(\theta^2 + \frac{6\theta}{\lambda} + \frac{1}{3} + \frac{18}{\lambda^2}\right)$$

$$- \frac{1}{\lambda}\int_{\theta}^{\infty} \frac{(c_1 + c_3)x + c_o + c_2 + 1}{x^2 - 1} e^{-\lambda x} dx \qquad (88)$$

Breaking up the last integral by means of partial fractions, leads to

$$\int_{\theta}^{\infty} \frac{(c_1 + c_3)x + c_o + c_2 + 1}{x^2 - 1} e^{-\lambda x} dx = \frac{1}{2} F_o(1,\lambda) e^{-\lambda} \int_{\lambda(\theta-1)}^{\infty} \frac{e^{-x}}{x} dx$$

$$- \frac{1}{2} F_o(1,-\lambda) e^{\lambda} \int_{\lambda(\theta+1)}^{\infty} \frac{e^{-x}}{x} dx$$

$$= \tfrac{1}{2}F_o(1,\lambda)e^{-\lambda}\left\{-E_i\left[-\lambda(\theta-1)\right]\right\} - \tfrac{1}{2}F_o(1,-\lambda)e^{\lambda}\left\{-E_i\left[-\lambda(\theta+1)\right]\right\} \tag{89}$$

Therefore the resulting expression for $R_o(\theta,\lambda)$ is

$$R_o(\theta,\lambda) = \frac{e^{-\lambda\theta}}{\lambda}F_o(\theta,\lambda)Q_o(\theta) - \frac{e^{-\lambda\theta}}{\lambda^2}\left(\theta^2 + \frac{6\theta}{\lambda} + \frac{1}{3} + \frac{18}{\lambda^2}\right)$$
$$+ \tfrac{1}{2}F_o(1,\lambda)e^{-\lambda}\left\{-E_i\left[-\lambda(\theta-1)\right]\right\}$$
$$- \tfrac{1}{2}F_o(1,-\lambda)e^{\lambda}\left\{-E_i\left[-\lambda(\theta+1)\right]\right\} \tag{90}$$

and that for $A_o(\theta,\lambda)$ is

$$A_o(\theta,\lambda) = \beta\left\{\frac{e^{-\lambda}}{\lambda}F_o(1,\lambda)\left[Q_o(\theta) + \tfrac{1}{2}E_i\left(-\lambda(\theta-1)\right)\right]\right.$$
$$\left. -\frac{e^{\lambda}}{2\lambda}F_o(1,-\lambda)Ei\left[-\lambda(\theta+1)\right] - \frac{e^{-\lambda\theta}}{\lambda^2}\left(\theta^2+\frac{6\theta}{\lambda}+\tfrac{1}{3}+\tfrac{18}{\lambda^2}\right)\right\} \tag{91}$$

The integrals in $V_{\frac{1}{2}\frac{1}{2}\frac{1}{2}}$ are obtained from $A_o(\theta,\lambda)$ by substituting for λ, $\sqrt{3}\lambda/2$, and for θ the values

$$\theta = \frac{\sqrt{\alpha^2+\beta^2+\gamma^2}' + \sqrt{(\alpha-1/2)^2+(\beta-1/2)^2+(\gamma-1/2)^2}'}{\sqrt{3}/2}$$

Using (73) and (91) and inserting $1/(1-A^2)$, we obtain equation (52).

$$5.\quad K_{\frac{1}{2}\frac{1}{2}\frac{1}{2}} = 2e^2\iint \frac{u_{\frac{1}{2}\frac{1}{2}\frac{1}{2}}(1)u_{000}(1)u_{000}^{2}(2)}{r_{12}}dv_1\,dv_2$$

$$+ 6e^2 \iint \frac{u_{\frac{1}{2}\frac{1}{2}\frac{1}{2}}(1)u_{000}(1)u^2_{100}(2)}{r_{12}} dv_1 dv_2$$

$$+ 3e^2 \iint \frac{u_{\frac{1}{2}\frac{1}{2}\frac{1}{2}}(1)u_{000}(1)u^2_{\frac{1}{2}-\frac{1}{2}-\frac{1}{2}}(2)}{r_{12}} dv_1 dv_2$$

$$+ e^2 \iint \frac{u_{\frac{1}{2}\frac{1}{2}\frac{1}{2}}(1)u_{000}(1)u^2_{-\frac{1}{2}-\frac{1}{2}-\frac{1}{2}}(2)}{r_{12}} dv_1 dv_2$$

$$+ 3e^2 \iint \frac{u_{\frac{1}{2}\frac{1}{2}\frac{1}{2}}(1)u_{000}(1)u^2_{-100}(2)}{r_{12}} dv_1 dv_2 \qquad (92)$$

The integration, in each of the above integrals, over electron (2) is the same as that carried through on page 40 resulting in equation (70). If we let $r_{\alpha\beta\gamma}$ be the distance from the point $\alpha\beta\gamma$ to the volume of integration dv_1 then

$$\int \frac{u^2_{\alpha\beta\gamma}(2)}{r_{12}} dv_2 = \frac{1}{r_{\alpha\beta\gamma}} - \frac{e^{-\frac{2r_{\alpha\beta\gamma}}{\alpha}}}{3\alpha^3}\left(r^2_{\alpha\beta\gamma} + 3\alpha r_{\alpha\beta\gamma} + \frac{9}{2}\alpha^2 + \frac{3\alpha^3}{r_{\alpha\beta\gamma}}\right) \qquad (93)$$

The first integral of $K_{\frac{1}{2}\frac{1}{2}\frac{1}{2}}$ can be evaluated explicitly

$$e^2 \iint \frac{u_{\frac{1}{2}\frac{1}{2}\frac{1}{2}}(1)u_{000}(1)u^2_{000}(2)}{r_{12}} dv_1 dv_2 = \frac{e^2}{3\pi\alpha^5} \int r_{\frac{1}{2}\frac{1}{2}\frac{1}{2}} r_{000}$$

$$e^{-\frac{r_{\frac{1}{2}\frac{1}{2}\frac{1}{2}} + r_{000}}{\alpha}} \left\{ \frac{1}{r_{000}} - \frac{e^{-\frac{2r_{000}}{\alpha}}}{3\alpha^3}\left(r^2_{000} + 3\alpha r_{000} + \frac{9\alpha^2}{2} + \frac{3\alpha^3}{r_{000}}\right)\right\} dv$$

$$= \frac{2\pi e^2}{3\pi\alpha^5}\left(\frac{\sqrt{3}}{4}d\right)^5 \int_{-1}^{1}\int_{1}^{\infty} (u^2-v^2)^2 e^{-\frac{\sqrt{3}\lambda}{2}} \left\{ \frac{1}{\sqrt{3}d/4(u-v)} - \frac{e^{-\frac{\sqrt{3}\lambda/2(u-v)}}{2}}{3\alpha^3} \right.$$

$$\left. \left[\frac{3}{16}d^2(u-v)^2 + 3\alpha\frac{\sqrt{3}}{4}d(u-v) + \frac{9\alpha^2}{2} + \frac{3\alpha^3}{\sqrt{3}d/4(u-v)} \right] \right\} du\,dv$$

$$= \frac{e^2 3\sqrt{3}}{d\ 144} e^{-\frac{\sqrt{3}\lambda}{2}} (\lambda^4 + \frac{8}{\sqrt{3}}\lambda^3 - \frac{17.25}{3}\lambda^2 + \frac{297.872}{3\sqrt{3}}\lambda - \frac{33.504}{9}x16)$$

$$+ \frac{e^2}{d}\cdot\frac{\sqrt{3}}{128} e^{-\frac{3\sqrt{3}\lambda}{2}} (\lambda^4 + 11.547\lambda^3 + 58.333\lambda^2 + 148.83\lambda + 158.83)$$

(94)

The remaining integrals of $K_{½½½}$ are all of the same type, namely

$$e^2 \iint \frac{U_{½½½}(1)\,U_{000}(1)\,U^2_{\alpha\beta\gamma}(2)}{r_{12}} dv_1\,dv_2 = I_2$$

$$= \frac{e^2}{3\pi\alpha^5} \int r_{½½½}\,r_{000}\, e^{-\frac{r_{½½½}+r_{000}}{\alpha}} \left\{ \frac{1}{r_{\alpha\beta\gamma}} - \frac{e^{-\frac{2r_{\alpha\beta\gamma}}{\alpha}}}{3\alpha^3} \right.$$

$$\left. (r^2_{\alpha\beta\gamma} + 3r_{\alpha\beta\gamma}\alpha + \frac{9\alpha^2}{2} + \frac{3\alpha^3}{r_{\alpha\beta\gamma}}) \right\} dv. \qquad (95)$$

The first term of this integral is I_1. Let I_3 be the rest of the integral. It was necessary to approximate I_3 in someway and the method used was as follows. Replace

$$r_{½½½}\,r_{000}\, e^{-\frac{r_{½½½}+r_{000}}{\alpha}} dv \quad \text{by} \quad c\,r^2_{¼¼¼}\, e^{-\frac{2r_{¼¼¼}}{\alpha}} dv$$

and determine c so that the integrals of the two ex-

pressions are equal.

$$c\int r_{1/4\,1/4\,1/4}^{2}\, e^{-\frac{2r_{1/4\,1/4\,1/4}}{\alpha}}\, dv = \int r_{1/2\,1/2\,1/2}\, r_{000}\, e^{-\frac{r_{1/2\,1/2\,1/2}+r_{000}}{\alpha}}\, dv$$

The integral on the left is just the normalizing integral and therefore equals $3\pi\alpha^5$. The integral on the right is equal to $3\pi\alpha^5 a$. (See equation 67). This makes $c = a$ and hence

$$I_3 = -\frac{e^2}{3\pi\alpha^5}\,\frac{a}{3\alpha^3}\int r_{1/4\,1/4\,1/4}^{2}\, e^{-\frac{2}{\alpha}(r_{1/4\,1/4\,1/4}+r_{\alpha\beta\gamma})}\,(r_{\alpha\beta\gamma}^{2}+3\alpha r_{\alpha\beta\gamma}+\frac{9}{2}\alpha^2 + \frac{3\alpha^3}{r})dv \qquad (96)$$

Using ellipsoidal coordinates with

$$r_{1/4\,1/4\,1/4} = k(u+v)$$

and

$$r_{\alpha\beta\gamma} = k(u-v)$$

this becomes

$$I_3 = \frac{-ae^2}{9\pi\alpha^5}2\pi k^5\int_{-1}^{1}\int_{1}^{\infty}(u+v)^2 e^{-\frac{4ku}{\alpha}}\left\{(u-v)^2k^2+3\alpha k(u-v) + \frac{9}{2}\alpha^2+\frac{3\alpha^3}{k(u-v)}\right\}(u^2-v^2)\,du\,dv$$

$$= -\frac{ae^2e^{-2\lambda'}}{288}\left(\frac{8}{35}\lambda'^6+\frac{12}{5}\lambda'^5+\frac{72}{5}\lambda'^4+60\lambda'^3+\frac{165}{2}\lambda'^2+\frac{315}{4}\lambda'+\frac{315}{8}\right) \qquad (97)$$

where, in this integral, $\lambda' = d'/\alpha$ and d' equals the

distance from the ¼¼¼ point to the point 000. There are then in K½½½ 6 integrals of the form I_3 for which

$$\lambda' = \frac{\sqrt{11}}{4},$$

4 for which

$$\lambda' = \frac{3\sqrt{3}}{4},$$

and 3 for which

$$\lambda' = \frac{\sqrt{19}}{4}.$$

Collecting together then into K½½½ the various integrals thus worked out, and inserting $1/(1-A^2)$ where needed, we obtain equation (53).

6.
$$K_{000} = \frac{e^2}{3\pi\alpha^5}\int r_{000}^2\, e^{-\frac{2r_{000}}{\alpha}}\left\{\frac{1}{r_{000}} - \frac{e^{\frac{-2r_{000}}{\alpha}}}{3\alpha^3}\left(r_{000}^2 + 3\alpha r_{000} + \frac{9}{2}\alpha^2 + \frac{3\alpha^3}{r_{000}}\right)\right\}dv + \frac{8e^2}{3\pi\alpha^5}\int r_{000}^2\, e^{-\frac{2r_{000}}{\alpha}}$$
$$\left\{\frac{1}{r_{½½½}} - \frac{e^{\frac{-2r_{½½½}}{\alpha}}}{3\alpha^3}\left(r_{½½½}^2 + 3\alpha r_{½½½} + \frac{9}{2}\alpha^2 + \frac{3\alpha^3}{r_{½½½}}\right)\right\}dv$$
$$+ \frac{6e^2}{3\pi\alpha^5}\int r_{000}^2\, e^{-\frac{2r_{000}}{\alpha}}\left\{\frac{1}{r_{100}} - \frac{e^{\frac{-2r_{100}}{\alpha}}}{3\alpha^3}\left(r_{100}^2\right.\right.$$
$$\left.\left. + 3\alpha r_{100} + \frac{9}{2}\alpha^2 + \frac{3\alpha^3}{r_{100}}\right)\right\}dv \qquad (98)$$

The first integral above is also I_{000} and the second is also $I_{½½½}$, if the factor of (8) is omitted.

The first integral is integrable without change of variables. It leads to I_{000} without difficulty.

The first term in each of the two last integrals has already been worked out. The result is contained in (70), page 40) The remaining term is of the same form as I_3, page 49, equations (96) and (97). Thus

$$-\frac{e^2}{3\pi\alpha^5}\int \frac{e^{-\frac{2(r_{000}+r_{100})}{\alpha}}}{3\alpha^3}\, r_{000}^2\left(r_{100}^2+3\alpha r_{100}+\frac{9}{2}\alpha^2+\frac{3\alpha^3}{r_{100}}\right)dv$$

$$=-\frac{e^2e^{-2\lambda}}{288\alpha}\left(\frac{8}{35}\lambda^6+\frac{12}{5}\lambda^5+\frac{72}{5}\lambda^4+60\lambda^3+\frac{165}{2}\lambda^2+\frac{315}{4}\lambda+\frac{315}{8}\right) \quad (99)$$

Using then equations (70) and (99) and I_{000}, we get equation (51) when $1/(1-A^2)$ is inserted properly.

Comparison of $B_{\chi\chi\chi}/B_{000}$ with a/b

The minimum of the energy occurs for $\lambda = 3.1$. In the neighborhood of this value of λ

$$B_{\chi\chi\chi}/B_{000} = 1.26$$

and

$$a/b = 1.16.$$

The percent difference in these two figures is 8%.

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