

## CHAPTER II

### FRÖHLICH METHOD OF COHESION CALCULATION



#### 2.1 The Cellular Method

The method which has been most successful for calculating the metallic binding is that of Wigner and Seitz<sup>10,13</sup>. This method was first applied to metallic sodium, the second member in the alkali series. In these metals one valence electron per atom moves in the field of atomic cores which are closed shells.

The Wigner - Seitz method has been applied only to metals having the face -centered and body - centered cubic structures. In lattices with these structures we can fill up the whole of space with polyhedra, one surrounding each atom in the following way. For the face - centered structure we draw planes bisecting the lines which join each atom to its nearest neighbours. We thus obtain a dodecahedron surrounding each atom (Fig. 2.1 a)<sup>16</sup>; for the body - centered structure we bisect the lines joining an atom to its nearest and next nearest neighbours, a truncated octahedron (Fig. 2.1 b)<sup>16</sup> is obtained. We call these 'atomic polyhedra' .

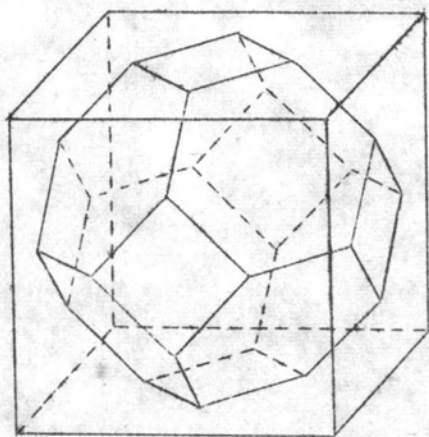


Fig. (2.1.1a)

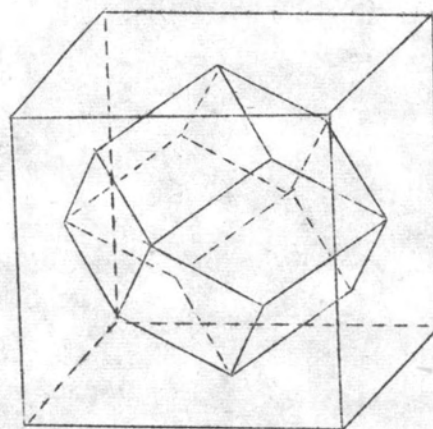


Fig. (2.1.1b)

Fig. 2.1 : The atomic polyhedra for (a) the face - centered cubic lattice, and (b) the body - centered cubic lattice.

The potential energy of the lattices may be divided up into<sup>16</sup> :

- 1) the interaction between the charges in one polyhedron,
  - 2) the interaction of the polyhedra with each other.
- Since each polyhedron is electrically neutral and because its symmetrical structures is not very far from that of a sphere, we should expect the second term to be small. The interaction energy of the polyhedra with one another may

thus be treated as a small correction , and we have only to calculate the energy of the charges within an isolated polyhedron. The field is taken to be spherically symmetrical within each of the polyhedra, and the potential energy of an electron is denoted by  $V(r)$ .

In an alkali atom, a single valence electron moves in the field of a core, i.e. of a nucleus surrounded by a number of electrons forming a closed shell. If  $Ze$  is the charge on the nucleus, the number of electrons constituting the core is  $Z - 1$  . Therefore, the valence electron moves in the field of a positively charged sphere carrying a charge  $+e$ . A theorem in electrostatics states that the field of such a sphere is the same as it would be if the charge were concentrated at the center. Therefore at large distances from the nucleus., the field in which the valence electron moves is the same as that of a hydrogen atom.

The potential energy function  $V(r)$  , which gives the work that must be done to bring up the valence electron from infinity to a distance  $r$  from the nucleus, is equal to  $-e^2/r$  for large distances. The energy that the valence electron may have is determined by Schrödinger's equation,

$$\nabla^2 \psi + \frac{2m}{\hbar^2} (E - V) \psi = 0 \quad (2.1)$$

Solution of Schrödinger's equation may be obtained in spherical coordinates in the form



$$\psi = \Psi(r) Y_{\ell m}(\theta, \phi),$$

and  $\Psi(r)$  satisfies the equation

$$\frac{d^2\Psi}{dr^2} + \frac{2}{r} \frac{d\Psi}{dr} + \frac{2m}{\hbar^2} \left[ E - V(r) - \frac{\ell(\ell+1)}{r^2} \right] \Psi = 0. \quad (2.2)$$

If  $\ell = 0$ , the solution is spherically symmetrical

$$\frac{d^2\Psi}{dr^2} + \frac{2}{r} \frac{d\Psi}{dr} + \frac{2m}{\hbar^2} (E - V(r)) \Psi = 0$$

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By using atomic units, the above equation reduces to

$$\frac{d^2\Psi}{dr^2} + \frac{2}{r} \frac{d\Psi}{dr} + (E - V(r)) \Psi = 0 \quad (2.3)$$

Now the wave function  $\Psi$  for the lowest state is periodic within the period of the lattice; further, it is symmetric about any nucleus. Hence, on the boundary of any atomic polyhedron, the condition<sup>10</sup>

$$\frac{\partial \Psi}{\partial n} = 0 \quad (2.4a)$$

must be satisfied; where  $\frac{\partial}{\partial n}$  denoting differentiation normal to the bounding plane. Since the polyhedron is approximately sphere with equal volume<sup>10</sup>, we call such a sphere 'atomic sphere'. The condition (2.4a) over the surface of the atomic sphere with radius  $r_s$ , volume  $\frac{4}{3} \pi r_s^3$  can be rewritten as

$$\left. \left( \frac{\partial \Psi}{\partial r} \right) \right|_{r=r_s} = 0 \quad (2.4)$$

To obtain the wave function within this sphere, we have to solve the Schrödinger equation (2.3) with the lowest state energy  $E(r_s)$  subjects to the boundary condition (2.4).

## 2.2 Application of the Cellular Method in Calculating the Cohesive Energy

Following Fröhlich<sup>9</sup>, the Schrödinger equation was solved with the boundary condition (2.4). Then two values of  $r$  was obtained for any given  $E$ , but the minimum energy yielded only one value of  $r$ , denoted by  $r_0$ . Then we have

$$\frac{d^2 \psi}{dr^2} = 0 \quad \text{at } r = r_0, \quad (2.5)$$

along with (2.4),

$$E(r_0) = V(r_0) \quad (2.6)$$

Since

$$V(r) = -\frac{2}{r},$$

we get

$$E(r_0) = -\frac{2}{r_0} \quad (2.7)$$

At  $r = r_0$ , the wave function which corresponds to the energy  $E(r_0)$  and satisfies (2.4) and (2.5) is constant. Thus for region lying near  $r = r_0$

$$\Psi(r) = 1 + \phi(r) \quad ; \quad \phi(r) \ll 1 \quad (2.8)$$

and

$$\phi(r_0) = 0 \quad (2.9)$$

The equation for  $\phi(r)$  which is valid only near  $r = r_0$  is obtained by substituting (2.8) into (2.3) and then neglecting the second order term,

$$\frac{d^2\phi}{dr^2} + \frac{2}{r} \frac{d\phi}{dr} + \left(\frac{2}{r} - \frac{2}{r_0}\right) \phi = 0$$

The solution satisfying (2.5) and (2.9) is

$$\phi(r) = \frac{(r - r_0)^3}{3rr_0},$$

which gives

$$\Psi = 1 + \frac{(r - r_0)^3}{3rr_0} \quad (2.10)$$

This solution holds for  $\frac{(r - r_0)^3}{3rr_0} \ll 1$  and for values of  $r$  which are greater than the ion radius.

In order to extend the energy from  $E_n$  to an arbitrary energy  $E$  when the solution  $\Psi_n$  has already

been obtained for the energy  $E_n$ , we set

$$E = E_n + \epsilon, \quad (2.11)$$

and the corresponding wave function

$$\Psi = \Psi_n(r) f(r), \quad (2.12)$$

where  $f(r)$  is to be determined. Substituting (2.12) into (2.3), the equation for  $f(r)$  is obtained

$$\frac{d^2 f}{dr^2} + \frac{2\phi'}{\phi} \frac{df}{dr} + \epsilon f = 0, \quad (2.13)$$

$$\phi = r\Psi_n, \quad \phi' = \frac{d\phi}{dr}.$$

This equation can be solved in two different ways:

Case I We consider function  $\Psi_0$  instead of  $\Psi_n$  for small values of  $\epsilon$ . Since  $\Psi_0$  is nearly flat in the most part of the atomic sphere<sup>17</sup>, its derivative is zero.

Therefore (2.13) reduces to

$$\frac{d^2 f}{dr^2} + \frac{2}{r} \frac{df}{dr} + \epsilon f = 0. \quad (2.13a)$$

The solution is

$$f = \frac{A \sin \beta r}{r} + \frac{C \cos \beta r}{r},$$



where

$$\beta = \sqrt{\epsilon}$$

We can put  $C = 0$  since it can be proved that it is a small quantity<sup>9</sup>. Thus

$$f = \frac{A \sin \beta r}{r}$$

for small  $\epsilon$  and using (2.11), (2.12)

$$f = \frac{\sin \beta r}{\beta r} \quad (2.14)$$

According to (2.10), (2.14) and (2.12), the wave function in case I is

$$\Psi_I(r) = \left[ 1 + \frac{(r - r_0)^3}{3rr_0} \right] \frac{\sin \beta r}{\beta r} \quad (2.15)$$

Expanding  $\sin \beta r$  in a series,

$$\Psi_I(r) = 1 + \frac{(r - r_0)^3}{3rr_0} - \frac{\epsilon r^2}{6}, \quad (2.16)$$

and making use of (2.4), we get

$$\epsilon(r_s) = \frac{(r_s - r_0)^2}{r_s^2 r_0} \left[ 2 + \frac{r_0}{r_s} \right] \quad (2.17)$$

Therefore from (2.11), (2.17) and (2.7), the lowest state energy which corresponds to the wave function  $\Psi_I(r)$  is



$$E_I(r_s) = -\frac{2}{r_0} + \frac{(r_s - r_0)^2}{r_s^2 r_0} \left[ 2 + \frac{r_0}{r_s} \right],$$

$$E_I(r_s) = -\frac{2}{r_s} - \frac{r_s^2 - r_0^2}{r_s^3}. \quad (2.18)$$

Case II As hinted by Fröhlich<sup>9</sup>, we can consider small values of  $\epsilon$  and therefore (2.13) can be rewritten in the form

$$\frac{d^2 f}{dr^2} + \frac{2\phi'}{\phi} \frac{df}{dr} + \epsilon(f - 1) + \epsilon = 0.$$

Since  $\epsilon(f - 1)$  is a small quantity of the second order, it thus can be neglected.

The above equation, then reduces to

$$\frac{d^2 f}{dr^2} + \frac{2\phi'}{\phi} \frac{df}{dr} + \epsilon = 0.$$

Letting

$$y = \frac{df}{dr},$$

we get

$$\frac{dy}{dr} + \frac{2\phi' y}{\phi} = -\epsilon.$$

The solution is

$$y = e^{-\int_0^v \frac{2\phi'}{\phi} du} \int_0^v e^{\int_0^u \frac{2\phi'}{\phi} dw} (-\epsilon) du ,$$

$$y = -\frac{\epsilon}{\phi^2(v)} \int_0^v \phi^2(u) du ,$$

or

$$f = \int_0^r -\frac{\epsilon}{\phi^2(v)} \left[ \int_0^v \phi^2(u) du \right] dv + C .$$

By using the condition that as  $\epsilon$  approaches zero, the function  $f(r)$  should have a value approaching one. Hence

$$f = 1 - \epsilon \int_0^r \frac{1}{\phi^2(v)} \int_0^v \phi^2(u) du dv . \quad (2.19)$$

From (2.12), (2.10) and (2.19), the wave function in case II is

$$\Psi_{II}(r) = \left[ 1 + \frac{(r-r_0)^3}{3rr_0} \right] \left[ 1 - \epsilon \int_0^r \frac{1}{\phi^2(v)} \int_0^v \phi^2(u) du dv \right] , \quad (2.20a)$$

or

$$\Psi_{II}(r) = 1 + \frac{(r-r_0)^3}{3rr_0} - \epsilon \int_0^r \frac{1}{\phi^2(v)} \int_0^v \phi^2(u) du dv , \quad (2.20)$$

when the second order term is neglected. The wave function  $\Psi_{II}(r)$  subjects to the condition (2.4) yields

$$\epsilon_{II}(r_s) = \frac{(r_s - r_0)^2}{r_s^2 r_0} \left[ 2 + \frac{r_0}{r_s} \right] \frac{r_s}{3} \frac{\phi^2(r_s)}{\int_0^{r_s} \phi^2(r) dr} \quad (2.21)$$

This leads to (2.17) except for the factor  $\frac{r_s}{3} \phi^2(r_s) /$

$\int_0^{r_s} \phi^2(r) dr$  which is the  $\gamma$  - term in the expression

for  $\alpha$ , the effective mass of electron in metals. This has been derived by Bardeen<sup>18</sup> in his paper on the improved calculation of the energies for Li and Na .

From (2.11) and (2.7) , we have

$$E_{II}(r_s) = -\frac{2}{r_0} + \epsilon_{II}(r_s) ,$$

with  $\epsilon_{II}(r_s)$  defined by (2.21) .

The values of  $E_I(r_s)$  and  $E_{II}(r_s)$  can be calculated if  $r_0$  is known. In order to obtain  $r_0$  , the Schrödinger equation for free atom must be solved in the region of  $r = r_0$  . Letting  $-E$  be the ionization energy  $I$  , we get from (2.11)

$$\epsilon(\infty) = \frac{2}{r_0} - I \quad (2.22)$$

For free atom if  $r$  is greater than the ion radius, substituting  $E = -I$  and  $V(r) = -\frac{2}{r}$  into (2.3) , we get

$$\frac{d^2 \Psi}{dr^2} + \frac{2}{r} \frac{d\Psi}{dr} + \left( \frac{2}{r} - I \right) \Psi = 0 \quad . \quad (2.23)$$

Putting

$$I = \omega^2 \quad . \quad (2.24)$$

Let us now write

$$\Psi = y/r \quad . \quad (2.25)$$

Equation (2.23) becomes

$$\frac{d^2 y}{dr^2} + \left( \frac{2}{r} - \omega^2 \right) y = 0 \quad , \quad (2.26)$$

or it can be rewritten as

$$\left[ \frac{d^2}{dr^2} + \frac{2}{r} - \omega^2 + \frac{\frac{1}{4} - \left(\frac{1}{2}\right)^2}{r^2} \right] y = 0 \quad . \quad (2.26a)$$

Letting

$$z = 2\omega r \quad ,$$

we obtain the following equation

$$\frac{d^2 y}{dz^2} + \left[ -\frac{1}{4} + \frac{1}{\omega z} + \frac{\frac{1}{4} - \left(\frac{1}{2}\right)^2}{z^2} \right] y = 0 \quad , \quad (2.26b)$$

which is in the standard form of the Confluent Hypergeometric equation<sup>19</sup>

$$\frac{d^2 y}{dz^2} + \left[ -\frac{1}{4} + \frac{k}{z} + \frac{\left(\frac{1}{4} - m^2\right)}{z^2} \right] y = 0 \quad . \quad (2.26c)$$



The solution is known as Whittaker's function and its asymptotic expansion is given by the formula<sup>19</sup>

$$y_{k,m}(z) = e^{-z/2} z^k \left[ 1 + \sum_{n=1}^{\infty} \frac{[m^2 - (k - \frac{1}{2})^2] [m^2 - (k - \frac{3}{2})^2] \dots [m^2 - (k - n + \frac{1}{2})^2]}{n! z^n} \right],$$

for large values of  $|z|$  when  $|\arg z| \leq \pi - \alpha < \pi$ . Hence we obtain

$$y_{\frac{1}{\omega}, \frac{1}{2}}(z) = e^{-z/2} z^{\frac{1}{\omega}} \left[ 1 + \sum_{n=1}^{\infty} \frac{[\frac{1}{4} - (\frac{1}{\omega} - \frac{1}{2})^2] [\frac{1}{4} - (\frac{1}{\omega} - \frac{3}{2})^2] \dots [\frac{1}{4} - (\frac{1}{\omega} - n + \frac{1}{2})^2]}{n! z^n} \right] \quad (2.27)$$

as the solution of the equation (2.26b).

Setting

$$m = \frac{1}{\omega},$$

from (2.27) substituting  $z = 2\omega r$  and taking into account only the first three terms, the third term being omitted in Fröhlich's calculation, we get

$$y_{\frac{1}{\omega}, \frac{1}{2}}(2\omega r) = e^{-\omega r} (2\omega r)^m \left[ 1 - \frac{m(m-1)}{2\omega r} + \frac{m(m-1)^2(m-2)}{2(2\omega r)^2} \right].$$

Therefore from (2.25) the wave function for free atom is

$$\psi = 2\omega e^{-\omega r} (2\omega r)^{m-1} \left[ 1 - \frac{m(m-1)}{2\omega r} + \frac{m(m-1)^2(m-2)}{2(2\omega r)^2} \right]. \quad (2.28)$$

Then at  $r = r_0$ , we equate the value of  $\Psi$  and  $\frac{d\Psi}{dr}$  of the wave function in (2.15) and in (2.28) or more simply by matching the logarithmic derivatives between the two functions. That is

$$\frac{d}{dr} \ln \Psi_I(r) = \frac{d}{dr} \ln \Psi(r), \text{ at } r = r_0. \quad (2.29)$$

Substituting (2.15) into the left side of (2.29), we thus have

$$\begin{aligned} \frac{d}{dr} \ln \Psi_I(r) &= \frac{d}{dr} \ln \left[ \left( 1 + \frac{(r-r_0)^3}{3rr_0} \right) \frac{\sin \beta r}{\beta r} \right], \\ &= \frac{d}{dr} \left[ \ln \left( 1 + \frac{(r-r_0)^3}{3rr_0} \right) + \ln \sin \beta r - \ln \beta r \right], \\ &= \beta \cot \beta r_0 - \frac{1}{r_0}, \text{ at } r = r_0. \quad (2.30) \end{aligned}$$

After the replacement of  $\Psi(r)$  from (2.28), the right side of (2.29) becomes

$$\begin{aligned} \frac{d}{dr} \ln \Psi(r) &= \frac{d}{dr} \ln \left[ 2\omega e^{-\omega r} (2\omega r)^{m-1} \left( 1 - \frac{m(m-1)}{2\omega r} + \frac{m(m-1)^2(m-2)}{8\omega^2 r^2} \right) \right], \\ &= \frac{d}{dr} (\ln 2\omega + \ln e^{-\omega r} + \ln (2\omega r)^{m-1} \\ &\quad + \ln \left( 1 - \frac{m(m-1)}{2\omega r} + \frac{m(m-1)^2(m-2)}{8\omega^2 r^2} \right)), \end{aligned}$$

$$= -\omega + \frac{m-1}{r_0} + \frac{1}{1 - \frac{m(m-1)}{2\omega r_0} + \frac{m(m-1)^2(m-2)}{8\omega^2 r_0^2}} \left[ \frac{m(m-1)}{2\omega r_0^2} - \frac{m(m-1)^2(m-2)}{4\omega^2 r_0^3} \right]$$

$$\text{at } r = r_0. \quad (2.31)$$

Due to (2.29), (2.30) and (2.31), we get

$$\beta \cot \beta r_0 \left[ 1 - \frac{m(m-1)}{2\omega r_0} + \frac{m(m-1)^2(m-2)}{4\omega^2 r_0^3} \right] = -\omega + \frac{m(m+1)}{2r_0} - \frac{m(m-1)^2(m+2)}{8\omega r_0^2} + \frac{m(m-1)^2(m-2)^2}{8\omega^2 r_0^3}$$

Since  $m = \frac{1}{\omega}$ , the final equation of  $r_0$  becomes

$$r_0^3 \frac{(1+\omega)}{2\omega^3} r_0^2 + \frac{(1-\omega)^2(1+2\omega)r_0}{8\omega^6} - \frac{(1-\omega)^2(1-2\omega)^2}{8\omega^8} + x \cot x \left[ \frac{r_0^2}{\omega} - \frac{(1-\omega)r_0}{2\omega^4} + \frac{(1-\omega)^2(1-2\omega)}{8\omega^7} \right] = 0, \quad (2.32)$$

where

$$x = \sqrt{2r_0 - \omega^2 r_0^2}$$

Repeating the same method, Fröhlich's  $r_0$  equation can be put into the form

$$r_0^2 - \frac{(1+\omega)r_0}{2\omega^3} + \frac{(1-\omega)^2}{2\omega^5} + \left[ \frac{r_0}{\omega} - \frac{1-\omega}{2\omega^4} \right] x \cot x = 0. \quad (2.33)$$

In this way, the equation of  $r_0$  can be again obtained when using  $\Psi_{II}(r)$  from (2.20) instead of  $\Psi_I(r)$  from (2.15) in matching with the free atom wave function at  $r = r_0$ . This has, however, not been solved yet. This problem has a little more difficulty to calculate.

However, the values of  $r_0$  displayed in table 2.1 are solutions of (2.32) and (2.33) respectively.

	Li	Na	K	Rb	Cs
Ionization Potential	0.397	0.378	0.319	0.308	0.287
$r_0$ (equation (2.32))	3.030	3.261	4.175	4.389	4.831
$r_0$ (equation (2.33))	3.005	3.238	4.158	4.374	4.819

Table 2.1 The values of  $r_0$  of the alkali series

In order to obtain the total energy, the average kinetic energy per free electron or Fermi energy  $E_F$  must be added to the lowest state energy  $E_I(r_s)$  in (2.18) on the assumption that the corresponding wave function is nearly flat just as for free electrons.

Therefore

$$E_F = \frac{2.21}{r_s^2}$$



Neglecting the correction terms, the total energy is given by

$$U(r_s) = -\frac{2}{r_s} - \frac{r_s^2 - r_0^2}{r_s^3} + \frac{2.21}{r_s^2} \quad (2.34)$$

The equilibrium atomic radius  $\rho$ , which corresponds to the minimum of  $U(r_s)$ , can be calculated by the following relation

$$\frac{\partial U}{\partial r_s} = \frac{3(r_s^2 - r_0^2)}{r_s^4} - \frac{4.42}{r_s^3} = 0, \quad \text{at } r_s = \rho$$

We get

$$\rho = 0.737 + (r_0^2 + 0.543)^{\frac{1}{2}} \quad (2.35)$$

The cohesive energy per atom denoted by  $S$  is

$$S = -U(\rho) - I \quad (2.36)$$

$$S = \frac{2}{\rho} - \frac{0.737}{\rho^2} - I \quad (2.36a)$$

As referring in section 1.1, the atomic units are used throughout of the calculation. The energy unit is Rydberg and the unit of length is Bohr unit. To obtain  $\rho$  in C.G.S. units, we multiply by  $0.528 \times 10^{-8}$ ,  $S$  in kcal./mole can be obtained by multiplying with 313.630. The values of  $\rho$  and  $S$  are shown for comparison in table 2.2.

The theoretical values of the cohesive energy for alkali metals are not satisfactory when compared with the experimental results. This is due to the fact that the procedure is rather crude. A better procedure for calculating the total energy is to use a determinantal wave function form which causes the wave function to be antisymmetric. Then the exchange energy<sup>17,20</sup>  $E_{xe}$  between parallel spins can be accounted for, i.e., given by (A.24) (see Appendix A)

$$E_{xe} = - \frac{0.916}{r_s} \text{ ryd.} \quad (2.37)$$

Another energy correction term is the Coulomb self potential energy<sup>17</sup>  $E_s$  of the charge distribution of electron within a cell. This term can be expressed as (see Appendix A)

$$E_s = \frac{1.2}{r_s} \text{ ryd.} \quad (2.38)$$

The expression for the average energy  $U(r_s)$  per electron can be obtained by adding (2.37) and (2.38) to (2.34)

$$U(r_s) = E_I(r_s) + \frac{2.21}{r_s^2} - \frac{0.916}{r_s} + \frac{1.2}{r_s} ,$$

$$U(r_s) = E_I(r_s) + \frac{2.21}{r_s^2} + \frac{0.284}{r_s} \quad (2.39)$$

Although the exchange and self-potential energy has been included, the cohesive energy is still too weak since this energy term  $U(r_s)$  does not account for the correlation energy. This correlation energy term is responsible for the Coulomb correlation between the electrons with antiparallel spins. We do not wish to go into full details since it is a very difficult problem. A possible method for handling this problem is to use the perturbation theory which is valid only at high densities ( $r_s \ll 1$  B.U.). The essential terms in the Hamiltonian for a free electron gas are

$$-\frac{\hbar^2}{2m} \sum_{i=1}^N \nabla_i^2 + \frac{1}{2} \sum_{i \neq j}^N \sum_{j}^N \frac{e^2}{r_{ij}} .$$

The second term is treated as perturbing term. The calculations must include the higher-order perturbation correction. In order to get the correlation energy  $w$  at metallic densities, the interpolation between high densities and low densities of electron must be utilized.

This was earliest done by Wigner<sup>21,22</sup> (see Appendix B) and gave

$$w = -\frac{0.88}{r_s + 7.8} \text{ ryd.} \quad (2.40)$$

Another formula<sup>17,23,24</sup> (see Appendix B)

$$w = 0.031 \log r_s - 0.115 \text{ ryd.} \quad (2.41)$$

obtained by Bohm and Pines<sup>23,24</sup> with the use of the concept of the plasma oscillations. This is valid in the region of the real metallic density.

The final expression for the average energy per electron of an alkali metal should be

$$U(r_s) = E_I(r_s) + \frac{2.21}{r_s^2} + \frac{0.284}{r_s} + w(r_s),$$

where  $w(r_s)$  is given either by (2.40) or (2.41). In our calculation, the expression (2.41) for  $w(r_s)$  is used. We thus have

$$\begin{aligned} U(r_s) &= -\frac{3}{r_s} + \frac{r_0^2}{r_s^3} + \frac{2.21}{r_s^2} + \frac{0.284}{r_s} + 0.031 \log r - 0.115, \\ &= -\frac{2.716}{r_s} + \frac{2.21}{r_s^2} + \frac{r_0^2}{r_s^3} + 0.031 \log r_s - 0.115. \end{aligned}$$

(2.42)

Repeating the procedure for obtaining (2.35), the cubic equation for  $r_s = \rho$  is

$$0.031 \rho^3 + 2.716 \rho^2 - 4.42 \rho - 3r_0^2 = 0. \quad (2.43)$$

The values of  $\rho$  can be calculated by using the program executed in the calculator model HP-97, and then substituted into (2.42). Using (2.36), we then get the cohesive energy. These values are all tabulated in table 2.2.



	Li	Na	K	Rb	Cs
Ionization potential (obs.)	0.397	0.378	0.319	0.308	0.287
$r_0$ (A)					
Theoretical					
Fröhlich(equation(2.33))	1.587	1.710	2.195	2.309	2.544
Equation (2.32)	1.600	1.722	2.204	2.317	2.551
$\rho$ (A)					
Theoretical					
Fröhlich(equation(2.35))	2.023	2.143	2.619	2.731	2.963
Equation (2.43)	2.106	2.224	2.694	2.804	3.031
(with $r_0$ obtained from(2.32))					
Experimental <sup>9</sup>	1.69	2.10	2.61	2.82	3.01
S (kcal./mole)					
Theoretical					
Fröhlich(equation(2.36a))	23.472	21.985	17.020	16.021	14.420
Equation(2.36)(Including the correction terms in $U(\rho)$ )	30.332	29.979	28.307	27.904	27.337
Experimental <sup>8</sup>	36.5	26	22.6	18.9	18.8
$U(\rho)$ (ryd.)					
Theoretical					
Fröhlich(equation(2.34))	-0.472	-0.448	-0.373	-0.359	-0.333
Equation(2.42)	-0.494	-0.474	-0.409	-0.397	-0.374

Table 2.2 The comparison of the calculated atomic radius and the cohesive energy with the experimental values ; the average energy per electron .