

CHAPTER III



KUHN'S METHOD IN COHESIVE ENERGY CALCULATION

3.1 Imai¹¹'s WKB Improvement Wave Function

The WKB approach is an approximate method used for solving quantum mechanical problems. However it breaks down at the turning points at which the wave function becomes infinite. An important improvement of the WKB - Langer²⁵ method was developed by Imai. The advantage of the Imai's formula is that it provides for a good representation of the wave function near the turning point, where the conventional WKB - Langer method failed. This method is concerned with the asymptotic solution of the second-order differential equation :

$$\frac{d^2\phi}{dx^2} + k^2P(x)\phi = 0, \text{ for } k \rightarrow \infty. \quad (3.1)$$

The solution in the vicinity of the turning point can be obtained in the following manner.

Letting

$$z = \int P^{\frac{1}{2}} dx, \quad \phi = P^{-\frac{1}{4}} \psi. \quad (3.2)$$

Equation (3.1) becomes

$$\frac{d^2\psi}{dz^2} + \left(k^2 - P^{-\frac{1}{4}} \frac{d^2 P^{\frac{1}{4}}}{dz^2} \right) \psi = 0 ,$$

or

$$\frac{d^2\psi}{dz^2} + (k^2 - Q) \psi = 0 , \quad (3.3)$$

where

$$Q = P^{-\frac{1}{4}} \frac{d^2 P^{\frac{1}{4}}}{dz^2} = P^{-\frac{3}{4}} \frac{d^2 (P^{\frac{1}{4}})}{dx^2} . \quad (3.4)$$

Q is finite everywhere except in the immediate neighbourhood of the turning points. In asymptotical limit, (3.3) reduces to

$$\frac{d^2\psi}{dz^2} + k^2\psi = 0 . \quad (3.5)$$

The solutions of equation (3.5) are of the form

$$\psi \sim Ae^{ikz} + Be^{-ikz} \quad \text{or} \quad A'e^{k|z|} + B'e^{-k|z|}$$

according to the sign of $P(x)$. If the turning point is taken at $x = 0$ and $P(x)$ is assumed to be represented by a power series about this point

$$P(x) = \sum_{m=1}^{\infty} a_m x^m , \quad (3.6)$$

we obtain

$$\frac{1}{P^2} = \frac{1}{a_1^2} \frac{1}{x^2} \left[1 + \frac{1}{2} \frac{a_2 x}{a_1} + \frac{1}{2} \frac{a_3 x^2}{a_1} + \frac{1}{2} \frac{a_4 x^3}{a_1} - \frac{1}{8} \frac{a_2^2 x^2}{a_1^2} - \frac{1}{4} \frac{a_2 a_3 x^3}{a_1^2} + \frac{1}{16} \frac{a_2^3 x^3}{a_1^3} \right] .$$

Now from (3.2), we get

$$z = \frac{2}{3} a_1^{\frac{1}{2}} x^{\frac{3}{2}} \left[1 + \frac{3}{10} \frac{a_2 x}{a_1} + \frac{3}{14} \frac{a_3 x^2}{a_1} + \frac{1}{6} \frac{a_4 x^3}{a_1} - \frac{3}{56} \frac{a_2^2 x^2}{a_1^2} - \frac{1}{12} \frac{a_2 a_3 x^3}{a_1^2} + \frac{1}{48} \frac{a_2^3 x^3}{a_1^3} \right] \quad (3.7)$$

Equation (3.4) can be rewritten in the form

$$Q = -\frac{5}{16} P^{-3} \left[\left(\frac{dP}{dx} \right)^2 - \frac{4P}{5} \frac{d^2 P}{dx^2} \right],$$

with $P(x)$ defined in (3.6). Therefore in terms of x , Q is given by

$$Q = -\frac{5}{16 a_1^3 x^3} \left[a_1^2 - \frac{3}{5} a_1 a_2 x - \frac{9}{5} a_1 a_3 x^2 - \frac{23}{5} a_1 a_4 x^3 + \frac{6}{5} a_2^2 x^2 + \frac{34}{5} a_2 a_3 x^3 - \frac{14}{5} \frac{a_2^3 x^3}{a_1} \right],$$

or

$$Q = -\frac{5}{36} z^{-2} \left[1 + \frac{48}{175} (3a_2^2 - 5a_1 a_3) a_1^{-4} \left(\frac{3}{2} a_1 z \right)^{\frac{4}{3}} - \frac{64}{375} (14a_2^3 - 35a_1 a_2 a_3 + 25a_1^2 a_4) a_1^{-6} \left(\frac{3}{2} a_1 z \right)^2 + \dots \right] \quad (3.8)$$

Substituting (3.8) into (3.3), we get

$$\frac{d^2 \psi}{dx^2} + \left[k^2 + \frac{5z^{-2}}{36} + \frac{5z^{-2}}{36} \left(\frac{48}{175} (3a_2^2 - 5a_1 a_3) a_1^{-4} \left(\frac{3}{2} a_1 z \right)^{\frac{4}{3}} \right) + \frac{5z^{-2}}{36} \left(\frac{64}{375} (14a_2^3 - 35a_1 a_2 a_3 + 25a_1^2 a_4) a_1^{-6} \left(\frac{3}{2} a_1 z \right)^2 \right) \right] \psi = 0.$$

This can be rearranged into a more simpler form

$$\frac{d^2\psi}{dz^2} + \left(\kappa^2 + \frac{5z^{-2}}{36} + \lambda(3z)^{-2/3} \right) \psi = 0, \quad (3.9)$$

where

$$\kappa^2 = k^2 - \frac{4}{75}(14a_2^3 - 35a_1a_2a_3 + 25a_1^2a_4)a_1^{-4}, \quad (3.9a)$$

and

$$\lambda = \frac{12}{35}(3a_2^2 - 5a_1a_3)(2a_1^2)^{-4/3}. \quad (3.9b)$$

Equation (3.9) can be solved asymptotically in two cases.

Case I As z approaches zero, the term z^{-2} is dominant. Therefore (3.9) reduces to

$$\frac{d^2\psi}{dz^2} + \left(\frac{5z^{-2}}{36} \right) \psi = 0. \quad (3.10)$$

Then the solution is assumed to be

$$\psi = z^m (a_0 + a_1z + a_2z^2 + \dots + a_nz^n).$$

Substituting this into (3.10), the solution is given by

$$\psi = a_0 z^{\frac{1}{6}}, \quad (3.11)$$

where a_0 is a constant.

Case II As z has the value approaching infinity, the term z^{-2} vanishes.

Hence (3.9) becomes

$$\frac{d^2\Psi}{dz^2} + (\kappa^2 + \lambda(3z)^{-2/3})\Psi = 0 \quad ,$$

$$\frac{d^2\Psi}{dz^2} + \left(\frac{(3z)^{2/3} + \lambda\kappa^{-2}}{\kappa^{-2}(3z)^{2/3}} \right)\Psi = 0 \quad .$$

Now, changing the variable from z to ξ by letting

$$\xi = (3z)^{2/3} + \lambda\kappa^{-2} \quad , \quad (3.12)$$

the equation for Ψ can be rewritten as

$$4(3z)^{-2/3} \frac{d^2\Psi}{d\xi^2} - 2(3z)^{-4/3} \frac{d\Psi}{d\xi} + \xi(3z)^{-2/3} \kappa^2\Psi = 0 \quad ,$$

or

$$\frac{d^2\Psi}{d\xi^2} - \frac{1}{2}(3z)^{-2/3} \frac{d\Psi}{d\xi} + \frac{1}{4}\xi \kappa^2\Psi = 0 \quad . \quad (3.13)$$

For large z , the term $(3z)^{-2/3}$ is approximately zero.

Equation (3.13) is given in the form of Airy differential equation²⁶ except for the opposite sign of the second term in

$$\frac{d^2\Psi}{d\xi^2} + \frac{1}{4}\xi\kappa^2\Psi = 0 \quad , \quad (3.14)$$

or in a simplified form

$$\frac{d^2 \Psi}{dX^2} + X\Psi = 0, \quad (3.15)$$

where

$$X = \left(\frac{\kappa}{4}\right)^{\frac{2}{3}} \xi$$

Since the differential equation for Airy function $Ai(X)$ is

$$\frac{d^2 \Psi}{dX^2} - X\Psi = 0,$$

the solution to (3.15) is the Airy function with negative argument $Ai(-X)$.

From (3.15), we obtain

$$\Psi(x) = \text{constant} \cdot Ai(-X), \quad (3.16)$$

where $Ai(-X)$ defined by²⁶

$$Ai(-X) = \frac{1}{\pi} \int_0^{\infty} \cos\left(\frac{1}{3}u^3 - uX\right) du.$$

This Airy function can be represented in terms of Bessel function of order $\frac{1}{3}$. That is

$$Ai(-X) = \frac{1}{3} X^{\frac{1}{2}} \left[J_{\frac{1}{3}}\left(\frac{2}{3}X^{\frac{3}{2}}\right) + J_{-\frac{1}{3}}\left(\frac{2}{3}X^{\frac{3}{2}}\right) \right],$$

or

$$\text{Ai}(-\xi) = \frac{1}{3} \left(\frac{\kappa}{2}\right)^{\frac{1}{3}} \xi^{\frac{1}{2}} \left[J_{\frac{1}{3}}\left(\frac{1}{3}\kappa\xi^{\frac{3}{2}}\right) + J_{-\frac{1}{3}}\left(\frac{1}{3}\kappa\xi^{\frac{3}{2}}\right) \right] \quad (3.17)$$

Finally from (3.2), (3.11), (3.16) and (3.17), the solution to (3.1) in the neighbourhood of the turning point, $x = 0$, is obtained as

$$\phi = \text{constant} \cdot z^{\frac{1}{6}} \xi^{\frac{1}{2}} P^{-\frac{1}{4}} \left[J_{\frac{1}{3}}\left(\frac{1}{3}\kappa\xi^{\frac{3}{2}}\right) + J_{-\frac{1}{3}}\left(\frac{1}{3}\kappa\xi^{\frac{3}{2}}\right) \right]$$

By writing

$$\zeta = \frac{1}{3}\kappa\xi^{\frac{3}{2}}$$

we have

$$\phi = \text{constant} \cdot z^{\frac{1}{6}} \xi^{\frac{1}{2}} P^{-\frac{1}{4}} \left(J_{\frac{1}{3}}(\zeta) + J_{-\frac{1}{3}}(\zeta) \right) \quad (3.18)$$

3.2 The WKB Justification of Quantum Defect Method

Kuhn¹² found with Imai's procedure (section 3.1) that the differential equation (3.1) had a more general solution, i.e.,

$$\phi = z^{\frac{1}{6}} \xi^{\frac{1}{2}} P^{-\frac{1}{4}} \left(\cos\left(\frac{\pi}{3} + \eta_1\right) J_{\frac{1}{3}}(\zeta) + \cos\left(\frac{\pi}{3} - \eta_1\right) J_{-\frac{1}{3}}(\zeta) \right), \quad (3.19)$$

in the neighbourhood of the turning point x_1 instead of in the neighbourhood of the origin as considered by

Imai's. Here the amplitude factor has been omitted and η_1 is an arbitrary constant. The definition of each parameter is the same as section 3.1 except for $P(x)$ which is the series expanded about x_1 and for z from (3.2) with an explicit limit. That is

$$P(x) = \sum_{m=1}^{\infty} a_m (x - x_1)^m, \quad (3.20a)$$

$$z = \int_{x_1}^x [P(x)]^{\frac{1}{2}} dx. \quad (3.20b)$$

The asymptotic behavior⁸ of (3.19) when k is so large that $k^2 > \kappa^2$ (κ is defined by (3.9a)) can (at large distances from the turning points) be given by

$$\phi \sim P^{-\frac{1}{4}} \cos(kz - \frac{\pi}{4} + \eta_1) \quad \text{for } P > 0, \quad (3.21a)$$

$$\phi \sim P^{-\frac{1}{4}} e^{i\pi/4} (2 \sin \eta_1 e^{|kz|} + e^{-|kz| - i\eta_1}) \quad \text{for } P < 0. \quad (3.21b)$$

Equation (2.2) can be rewritten as

$$\frac{d^2 \psi}{dr^2} + \frac{2}{r} \frac{d\psi}{dr} + \left[E - V(r) - \frac{\ell(\ell + 1)}{r^2} \right] \psi = 0. \quad (3.22)$$

Substituting $\phi^{(\ell)}(r) = r\psi(r)$ into the above equation, (3.22) becomes

$$\frac{d^2\phi^{(\ell)}}{dr^2} + \left[E - V(r) - \frac{\ell(\ell+1)}{r^2} \right] \phi^{(\ell)} = 0 \quad (3.23)$$

By applying the following substitution

$$\theta = -Er, \quad \gamma^2 = (-E)^{\frac{1}{2}}, \quad (3.24)$$

(3.23) is transformed to

$$\frac{d^2\phi^{(\ell)}}{d\theta^2} + \frac{1}{\gamma^2} \left[-1 - V(\theta) - \frac{\ell(\ell+1)\gamma^2}{\theta^2} \right] \phi^{(\ell)} = 0, \quad (3.25)$$

where $V(\theta) = -\frac{2}{\theta}$. By introducing new parameters

$$\theta = e^x, \quad \phi^{(\ell)}(x) = e^{x/2} u(x) \quad (3.26)$$

into (3.25), we obtain

$$\frac{d^2u}{dx^2} + \frac{1}{\gamma^2} \left[-e^{2x} - e^{2x} V(e^x) - \left(\ell + \frac{1}{2}\right)^2 \gamma^2 \right] u = 0 \quad (3.27)$$

Equation (3.27) can be solved if the potential $V(e^x)$ is known. In this procedure the potential is assumed to be hydrogenic in the region $(x \gg X)$ outside the atomic core. X is expected to lie between the two turning points of (3.25) or (3.27). Therefore $V(e^x)$ can be put to equal to $-2e^{-x}$. Equation (3.27) with hydrogenic potential is in the form of (3.1) and $k^2 P_h(x)$ is given by

$$k^2 P_h(x) = \gamma^{-2} \left[-e^{2x} + 2e^x - \left(\ell + \frac{1}{2}\right)^2 \gamma^2 \right]. \quad (3.28)$$

The 'h' specifies the hydrogenic form of potential used in $P(x)$. The two turning points can be obtained by setting $P_h(x)$ equal to zero. Thus we have

$$x = \ln \left[1 \pm \left(1 - \gamma^2 \left(\ell + \frac{1}{2} \right)^2 \right) \right], \quad (3.29)$$

The plus and minus signs refer to the inner and the outer turning points x_1 , x_2 respectively. The inner turning point, corresponding to small values of r or x , always occurs close to the nucleus where $V(e^x)$ is non-hydrogenic, or at least does not correspond to a singly charged ion. However, the outer turning point occurs in the hydrogenic region²⁷. From the known value of x_2 ; z , κ , λ and ξ can be obtained. This leads to the approximate wave function in this region with unknown phase constant η_2 .

Now at the origin $r = 0$ or corresponding to $x = -\infty$, we have the boundary condition that the wave function $\Phi^{(\ell)}(x)$ of any energy is zero. This implies that from (3.21b), $\sin \eta_1$ must be zero otherwise the term containing $e^{|kz|}$ will blow up. Therefore η_1 is zero or multiples of π ⁸. To obtain η_2 , we expand the wave function about the two turning points and match them to those of (3.21a) and (3.21b).

We get

$$\eta_2 = (m + \frac{1}{2})\pi - k \int_{x_1}^{x_2} [P(x)]^{\frac{1}{2}} dx, \quad (3.30)$$

m is any integer includes zero and $P(x)$ is equal to the square bracket in (3.27). The integral in the right hand side cannot be integrated unless $V(r)$ is known. To avoid this difficulty, the quantum defect δ is introduced. Defining

$$\pi\delta = k \int_{x_1}^{x_2} [P(x)]^{\frac{1}{2}} dx - k \int_{x_1'}^{x_2} [P_h(x)]^{\frac{1}{2}} dx, \quad (3.31)$$

where

$$k [P(x)]^{\frac{1}{2}} dx = \left[E - V(r) - \frac{(\ell + \frac{1}{2})^2}{r^2} \right]^{\frac{1}{2}} dr, \quad (3.32)$$

and x_1' is the inner turning point of the hydrogenic form of square bracket in (3.28).

According to (3.32), $-\frac{2}{r}$ the hydrogen-like potential is inserted for $V(r)$. The second integral in (3.31) then becomes

$$k \int_{x_1'}^{x_2} [P_h(x)]^{\frac{1}{2}} dx = \int_{r_1}^r \left[E + \frac{2}{r} - \frac{(\ell + \frac{1}{2})^2}{r^2} \right]^{\frac{1}{2}} dr, \quad (3.33)$$

r_1 and r_2 correspond to x_1 and x_2 in (3.24) and (3.26). Equation (3.33) can be rewritten as

$$k \int_{x_1}^{x_2} [P_h(x)]^{\frac{1}{2}} dx = \int_{r_1}^{r_2} \left[Er^2 + 2r - \left(\ell + \frac{1}{2} \right)^2 \right]^{\frac{1}{2}} \frac{dr}{r}.$$

We apply the formula

$$\int_a^b \sqrt{H(r)} \frac{dr}{r} = \left[\sqrt{H(r)} - \frac{B}{2\sqrt{-A}} \sin^{-1} \left(\frac{2Ar+B}{\sqrt{B^2-4AC}} \right) - \sqrt{-C} \sin^{-1} \left(\frac{Br+2C}{r\sqrt{B^2-4AC}} \right) \right]_a^b, \quad (3.34)$$

when $A < 0$ and $C < 0$ ²⁸. If a and b are the two roots of $H(r) = Ar^2 + Br + C$, the above formulas reduces to

$$\int_a^b \sqrt{H(r)} \frac{dr}{r} = \left(\frac{B}{2\sqrt{-A}} - \sqrt{-C} \right) \pi.$$

Thus we have

$$\int_{r_1}^{r_2} \left[Er^2 + 2r - \left(\ell + \frac{1}{2} \right)^2 \right]^{\frac{1}{2}} \frac{dr}{r} = \gamma^{-1} \pi - \ell \pi - \frac{1}{2} \pi,$$

or

$$k \int_{x_1'}^{x_2} [P_h(x)]^{\frac{1}{2}} dx = \gamma^{-1}\pi - \ell\pi - \frac{1}{2}\pi .$$

From (3.30) and (3.31), we get

$$\pi\delta = (m + \frac{1}{2})\pi - \eta_2 - (\gamma^{-1}\pi - (\ell + \frac{1}{2})\pi) ,$$

$$\eta_2 = n\pi - \delta\pi - \gamma^{-1}\pi , \quad (3.35)$$

in which the arbitrary integer $n = m + \ell + 1$ is greater than ℓ . Since the wave function must approach zero as r or $x \rightarrow +\infty$, we get $\eta_2 = 0$. Therefore (3.35) becomes

$$E = -(n - \delta)^{-2} , \quad (3.36)$$

which is just Rydberg's law differing from that of hydrogen only in the quantity of the quantum defect.

On the other hand, η_2 can be evaluated by (3.35) if δ is known from the spectroscopic data for any value of energy. Thus the wave function in hydrogenic region can be obtained in an explicit form.

3.3 WKB Approach in Conjunction with Quantum Defect in Cohesive Energy Calculation

For evaluating the cohesive energy, (3.27) and (3.1) were compared. The resultant wave function is (3.19) with parameters defined by (3.9a), (3.9b), (3.12), (3.20a) and (3.20b). The wave function is

$$u(x) = z^{\frac{1}{6}} \xi^{\frac{1}{2}} P_h^{-\frac{1}{4}} \left(\cos\left(\frac{\pi}{3} + \eta_2\right) J_{\frac{1}{3}}(\zeta) + \cos\left(\frac{\pi}{3} - \eta_2\right) J_{-\frac{1}{3}}(\zeta) \right). \quad (3.37)$$

By defining

$$\begin{aligned} g_\gamma(x) &= z^{\frac{1}{6}} \xi^{\frac{1}{2}} P_h^{-\frac{1}{4}} J_{\frac{1}{3}}(\zeta), \\ h_\gamma(x) &= z^{\frac{1}{6}} \xi^{\frac{1}{2}} P_h^{-\frac{1}{4}} J_{-\frac{1}{3}}(\zeta), \end{aligned} \quad (3.38)$$

(3.37) becomes

$$u(x) = \cos\left(\frac{1}{3} - \delta - \gamma^{-1}\right) \pi g_\gamma(x) + \cos\left(\frac{1}{3} + \delta + \gamma^{-1}\right) \pi h_\gamma(x). \quad (3.39)$$

Since the wave function have to satisfy the condition (2.4) at the boundary of the atomic sphere, we get

$$\frac{d\phi}{d\theta} = \frac{\phi}{\theta} \quad \text{at } \theta = \theta_s .$$

This condition can be written as

$$u'(x_s) - \frac{1}{2}u(x_s) = 0 \quad . \quad (3.40)$$

Substituting (3.39) into (3.40) , we obtain

$$\delta = \frac{1}{\pi} \tan^{-1} \left[\frac{1}{\sqrt{3}} \frac{F_Y(x_s) + 1}{F_Y(x_s) - 1} \right] - \frac{1}{Y} , \quad (3.41)$$

where $F_Y(x)$ defined by

$$F_Y(x) = - \frac{h'_Y(x) - \frac{1}{2} h_Y(x)}{g'_Y(x) - \frac{1}{2} g_Y(x)} \quad . \quad (3.42)$$

The calculation of the ground state energy is very difficult if all the expressions involve in (3.41) are used without making any approximation. One way of approaching this problem is Fröhlich's method which states that the minimum energy E_{om} when $\ell = 0$ is related to r_{sm} by

$$E_{om} = - \frac{2}{r_{sm}} \quad \text{or} \quad \theta_{sm} = 2 , \quad (3.43)$$

which can be represented by a new variable x as

$$x_{sm} = \ln 2 \quad . \quad (3.44)$$

To obtain the minimum energy we expand the function $h_\gamma(x)$, $g_\gamma(x)$ and ${}_3F_\gamma(x)$ in terms of $(x - x_2)$. The expression for $J_{\frac{1}{3}}(\frac{1}{3}\kappa\xi^2)$ and $J_{-\frac{1}{3}}(\frac{1}{3}\kappa\xi^2)$ are²⁸

$$J_{\frac{1}{3}}(\zeta) = \frac{3\sqrt{\frac{\zeta}{2}}}{\Gamma(4/3)} \sum_{k=0}^{\infty} (-1)^k \frac{(\zeta\sqrt{3})^{2k}}{2^{2k} k! 1.4.7\dots(3k+1)},$$

$$J_{-\frac{1}{3}}(\zeta) = \frac{3\sqrt{\frac{2}{\zeta}}}{\Gamma(2/3)} \left[1 + \sum_{k=1}^{\infty} (-1)^k \frac{(\zeta\sqrt{3})^{2k}}{2^{2k} k! 2.5.8\dots(3k-1)} \right].$$

Substituting x_{sm} for x to give $F(x_{sm})$ as a function of the energy parameter in the form

$$F_{E_{om}}(x_{sm}) = \left(\frac{3}{2}\right)^{2/3} \frac{\Gamma(4/3)}{\Gamma(2/3)} (-E_{om})^{1/3} \left(\frac{4}{5} - \frac{5,583}{98,000} E_{om} + \frac{21,918,107}{6,585,600,000} E_{om}^2 + \dots \right), \quad (3.45)$$

in which $-\gamma^2$ is replaced by E_{om} .

The quantum defect in (3.41) can be represented by an interpolation formula⁸

$$\delta = a + b(1/n^2) + c(1/n^2)^2 + d(1/n^2)^3, \quad (3.46)$$

here $1/n^2$ stands for $-E_{om}$. The coefficients a , b , c and d ⁸ for each element of the alkalis are all presented in table 3.1. In calculating the minimum energy, we use

Element	a	b	c	d
Li	0.399503	0.029352	0.00270	-0.00052
Na	1.347980	0.06173	0.01223	-0.0026
K	2.180112	0.13779	0.0600	-0.0190
Rb	3.13130	0.17873	0.1096	-0.0435
Cs	4.04822	0.2548	0.1353	-0.0638

Table 3.1 The interpolation coefficients for quantum defect.

(3.41) with δ formulated by (3.46) and to the right side an integer q is added. Thus we have

$$\frac{1}{\pi} \tan^{-1} \left[\frac{1}{\sqrt{3}} \frac{F_{\gamma_{om}}(x_{sm}) + 1}{F_{\gamma_{om}}(x_{sm}) - 1} \right] - \frac{1}{\gamma_{om}} + q - a - b\left(\frac{1}{n}\right) - c\left(\frac{1}{n}\right)^2 - d\left(\frac{1}{n}\right)^3 = 0 \quad (3.47)$$

The integer q is set to be 2, 3, 4, 5 and 6 for Li, Na, K, Rb and Cs respectively in order to keep both sides the same order of magnitude. This does not affect the results since it is equivalent to the argument of the tangential function. The numerical calculation of E_{om} from (3.47) is performed on HP - 97 calculator with the executed program namely 'calculus and roots of $f(x)$ ' as a main program and the program of the left side of (3.47) as a subprogram.

elements	E_{om} (ryd.)	r_{sm} (B.U.)
Li	-0.704	2.841
Na	-0.668	2.996
K	-0.534	3.745
Rb	-0.516	3.877
Cs	-0.474	4.223

Table 3.2 The minimum energy and radius of the alkalis.

From (2.18) the ground state energy due to Fröhlich⁹ may be represented as

$$E_o = \frac{c}{r_s^3} - \frac{3}{r_s}, \quad (3.48)$$

in which the minimum value is $-\frac{2}{r_{sm}}$. This leads to

$$c = r_{sm}^2. \quad (3.49)$$

Equation (3.48) with (3.49) can be written in the form

$$E_o = \frac{r_{sm}^2}{r_s^3} - \frac{3}{r_s}. \quad (3.50)$$

To obtain the total energy E_T , the Fermi energy must be included. By using the same reason as that used in

section (2.2) , the Fermi energy for free electron is added. We have

$$E_T = \frac{r_{sm}^2}{r_s^3} - \frac{3}{r_s} + \frac{2.21}{r_s^2} \quad (3.51)$$

At equilibrium , E_T must satisfy the condition

$$\frac{dE_T}{dr_s} = 0 \quad ,$$

which gives

$$3r_s^2 - 4.42 r_s - 3r_{sm}^2 = 0 \quad (3.52)$$

Substituting the values of r_s into (3.51) yield the total energy. With the aid of (2.36) the cohesive energy is now known.

The total energy with the correction terms given by (2.37) , (2.38) and (2.41) is

$$E_T = \frac{r_{sm}^2}{r_s^3} - \frac{3}{r_s} + \frac{2.21}{r_s^2} - \frac{0.916}{r_s} + \frac{1.2}{r_s} + 0.031 \log r_s - 0.115. \quad (3.53)$$

Repeating the same procedure, the equation for r_s is

$$0.031 r_s^3 + 2.716 r_s^2 - 4.42 r_s - 3 r_{sm}^2 = 0 \quad (3.54)$$

The values of the cohesive energy S and the atomic radius r_s in two cases are compared in the table (3.2).

	Li	Na	K	Rb	Cs
Ionization energy ²⁹ I	0.396	0.378	0.319	0.307	0.286
Neglecting the correction terms					
S (kcal/mole)	38.008	29.795	26.564	27.124	26.013
r_s (B.U.)	3.617	3.822	4.553	4.683	5.023
Including the correction terms					
S (kcal/mole)	44.849	37.270	36.962	37.949	37.636
r_s (B.U.)	3.804	3.955	4.684	4.813	5.150
Experimental S (kcal/mole)	36.5	26	22.6	18.9	18.8

Table 3.3 The comparison of the cohesive energy and the atomic radius of the alkalis when neglecting the correction terms and including such those terms