CHAPTER IV

APPLICATIONS OF THE BOHR-SOMMERFELD QUANTIZATION RULE

4.1 Solution of the Radial Wave Equation

For a particle of mass m moving in a central field $V(r)$ which is a function of the radial coordinate only, the Schrödinger equation is

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V(r)\right]u = Eu \qquad (4.1.1)$$

where u and E are the wave function and the energy eigenvalue respectively.

By inserting the wave function u in the form

$$u(r,\theta,\phi) = R(r)\,Y_{l,m}(\theta,\phi) \qquad (4.1.2)$$

into eq.(4.1.1), we obtain the radial wave equation

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) + \frac{2m}{\hbar^2}\left[E - V(r) - \frac{\hbar^2}{2m}\frac{l(l+1)}{r^2}\right]R = 0 \quad . \qquad (4.1.3)$$

And by letting $U(r) = rR(r)$, eq.(4.1.3) becomes

$$\frac{d^2U}{dr^2} + \frac{2m}{\hbar^2}\left[E - V(r) - \frac{\hbar^2}{2m}\frac{l(l+1)}{r^2}\right]U = 0 \qquad (4.1.4)$$

which has the same form as eq.(2.1.17), but the boundary conditions now are specified at the values 0 and $+\infty$ of the independent variable r instead of at $-\infty$ and $+\infty$ as in the one-dimensional case. To bring the conditions in line with those of the one-dimensional problem, the transformation which first suggested by Langer (1937) is introduced here :

$$r = e^{s} \quad , \quad U(r) = e^{\frac{1}{2}s}\phi(s) \quad . \qquad (4.1.5)$$

This transformation maps the points $r = 0, +\infty$ to $s = -\infty, +\infty$ respectively. It is a straightforward matter to verify that

$$\frac{d^2U}{dr^2} = e^{-3s/2}\left[\frac{d^2\phi}{ds^2} - \frac{1}{4}\phi\right] \qquad (4.1.6)$$

hence eq.(4.1.4) becomes

$$\frac{d^2\phi}{ds^2} + \frac{2m}{\hbar^2}\left[\left\{E - V(e^{s})\right\}e^{2s} - \frac{\hbar^2}{2m}(\ell+\frac{1}{2})^2\right]\phi = 0 \qquad . (4.1.7)$$

The boundary coditions for $\phi(s)$ can be considered from the transformation given in eq.(4.1.5), it is found that

$$\phi(s) = e^{\frac{1}{2}s}R(e^{s})$$

which tends to zero as $s \longrightarrow \pm\infty$. (4.1.8)

Eqs.(4.1.7) and (4.1.8) correspond exactly to the one-dimensional case, and therefore the Bohr-Sommerfeld quantization rule can be applied to this system. The radial quantization condition from eq.(2.3.4)

$$\oint p_r\, dr = (n_r + \tfrac{1}{2})h \quad , n_r = 0, 1, 2, \ldots (4.1.9)$$

can be modified to

$$\oint p_r\, dr = (n - \ell - \tfrac{1}{2})h \qquad (4.1.10)$$

since we know from eq.(2.3.6) that the principal quantum number

$$n = n_\theta + n_r + n_\phi + 1 \qquad (4.1.11)$$

and from page 305 of Goldstein(1959) the angular momentum (or orbital) quantum number ℓ can be related to n_θ and n_ϕ as

$$\ell = n_\theta + n_\phi \qquad (4.1.12)$$

and n_r is then inserted into eq.(4.1.9).

From eqs.(4.1.7) and (4.1.10) we have

$$2\int_{S_1}^{S_2}\left[2m\left\{E - V(e^s)\right\}e^{2s} - \hbar^2(\ell+\tfrac{1}{2})^2\right]^{1/2} ds = (n-\ell-\tfrac{1}{2})h \qquad (4.1.13)$$

where S_1 and S_2 are the limits of the region in which the quantity in the brackets is positive.

Since $S = \log r$, we can reexpress the above condition in term of r as

$$2\int_{r_1}^{r_2}\left[2m\left\{E - V(r)\right\} - \frac{\hbar^2}{r^2}(\ell+\tfrac{1}{2})^2\right]^{1/2} dr = (n-\ell-\tfrac{1}{2})h . \qquad (4.1.14)$$

By employing a transformation given in eq.(3.3.30), we can write eq.(4.1.14) in the atomic unit as

$$\frac{2}{\pi\sqrt{2}}\int_{\rho_1}^{\rho_2}\left[Q(\rho) - P_{n\ell}(\rho)\right]^{1/2}\frac{d\rho}{\rho} = n-\ell-\tfrac{1}{2} . \qquad (4.1.15)$$

where ρ_1 and ρ_2 are two classical turning points.

We may recall that

$$Q(\rho) = \alpha\rho^2 + \beta\rho + \gamma \qquad (4.1.16)$$

and

$$P_{n\ell}(\rho) = \tfrac{1}{2}\epsilon_{n\ell}\rho^2 + \tfrac{1}{2}(\ell+\tfrac{1}{2})^2 . \qquad (4.1.17)$$

4.2 Asymptotic Survey

Our aim now is to construct the effective potential of an alkali atom. Since the alkali atom has a single valence electron and a nucleus with compact core electrons, the methods outlined in the previous sections can be used directly. We start by considering its characteristic asymptotic regions, near the nucleus and far away from the core, and then considering the region between them.

4.2.1 Potential near the Nucleus

At the region near the nucleus, the potential energy should be a pure coulomb field due only to the nuclear charges Ze ,i.e.,

$$V(r) = -\frac{Ze^2}{r} \quad \text{or} \quad Q(\rho) = Z\rho \quad . \qquad (4.2.1)$$

The potentialfield should hold upto some radial distance r_Z at which the contributions to the potential due to the core electrons begin to be dominant.

4.2.2 Potential outside the Ion Core

At the region far away from the core, the valence electron "sees" only the net charge e since all of the core electrons with total negative charges, $-(Z-1)e$, reduce the positive nuclear charges Ze. Therefore the potential energy

$$V(r) = -\frac{e^2}{r} \quad \text{or} \quad Q(\rho) = \rho \qquad (4.2.2)$$

should hold down to some radial distance r_0.

We shall also assume that there exists additional contribution due to the polarization of the core (Kittel, 1971, refers as the polarizability). This polarization potential is proportional to $-1/r^4$ so that the corresponding additional term of $Q(\rho)$ is proportional to $1/\rho^2$. The $Q(\rho)$ with polarization can be expressed as

$$Q(\rho) = \rho + \delta/\rho^2 \qquad (4.2.3)$$

where δ is a parameter to be determined.

4.2.3 Potential between the Two Regions

The potential energy between those two asymptotic regions can be determined by assuming $Q(\rho)$ to be a parabolic function of ρ ,

$$Q(\rho) = \alpha\rho^2 + \beta\rho + \gamma \qquad (4.2.4)$$

where α , β , and γ are parameters to be determined.

4.3 The Procedure

4.3.1 Outside the Ion Core

At the region outside the core, the integral

$$J = \oint \sqrt{A + \frac{2B}{\rho} + \frac{C}{\rho^2} + \frac{D_1}{\rho^3} + \frac{D}{\rho^4}}\; d\rho \qquad (4.3.1)$$

must be encountered in both cases as mentioned in the previous section. A, B, C, D_1, and D in eq.(4.3.1) are all constants.

The integral in eq.(4.3.1) was integrated in the complex plane by Sommerfeld (1928). The result of integration for $A<0$, $C<0$ and $D_1 = 0$ can be expressed as (see Appendix A)

$$J = 2\pi \left\{ \frac{B}{\sqrt{-A}} - \sqrt{-C} + \frac{1}{4C\sqrt{-C}} \left(\frac{3DB^2}{C} - A \right) \right\} . \qquad (4.3.2)$$

From eqs.(4.1.16) and (4.3.1) we have

$$n - l - \frac{1}{2} = \sqrt{2} \left\{ \frac{B}{\sqrt{-A}} - \sqrt{-C} + \frac{1}{4C\sqrt{-C}} \left(\frac{3DB^2}{C} - A \right) \right\} . \qquad (4.3.3)$$

In general,

$$A = \alpha - \frac{1}{2}\epsilon_{nl} , \quad B = \frac{\beta}{2} , \quad C = \gamma - \frac{1}{2}(l+\frac{1}{2})^2 , \quad D = \delta \qquad . \quad (4.3.4)$$

For our integral, we have $\alpha = \gamma = 0$, $\beta = 1$ and $D = \delta$ which is zero if we exclude the polarization.

The experimental energy, ϵ_{nl} , of f states - the outer states - and the corresponding quantum numbers, n and l , are inserted in eq.(4.3.3). The parameter D can be determined by adjusting it until the right hand side of eq.(4.3.3) equals to the left hand side. All parameters which have to be determined - A , B , C , and D - are now known. The lower turning point can then be found by setting the quantity in the **integrand** equal to zero. Thus the lower turning point, ρ_{min} , is determined by the equation

$$A\rho^2 + 2B\rho + C + \frac{D}{\rho^2} = 0 \qquad . \quad (4.3.5)$$

For the simpler case when $D = 0$, ρ_{min} is given by the formula

$$\rho_{min} = \frac{-B + \sqrt{B^2 - AC}}{A} \quad . \qquad (4.3.6)$$

Now we have

$$Q_0(\rho) = \begin{cases} \rho \\ \rho + \delta/\rho^2 \quad \text{(including polarization)} \end{cases} , \quad \rho_{10} < \rho < \infty \qquad (4.3.7)$$

ρ_{10} may be chosen from ρ_{min}'s from any f states.

4.3.2 The Matching

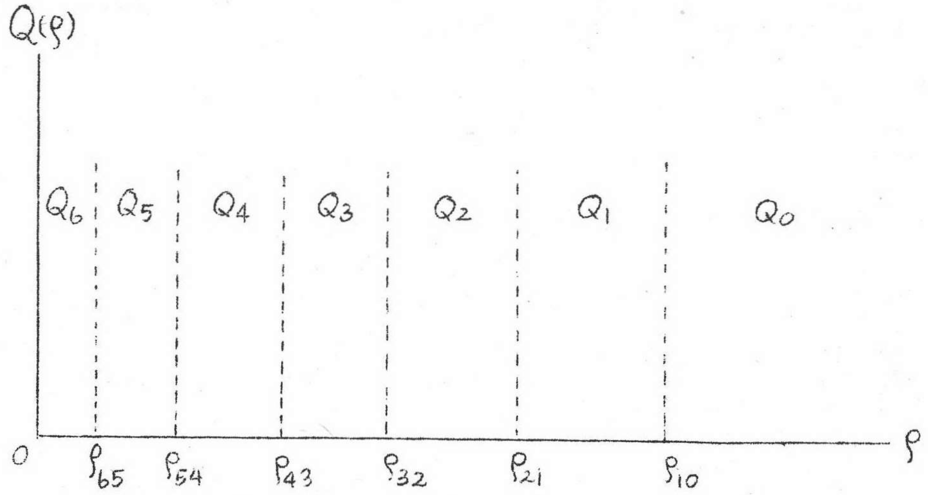

Fig.4.1 Diagram for constructing $Q(\rho)$

For the inside region, two continuity conditions are introduced in order to match the new $Q_1(\rho)$ of the inside region with the created one, $Q_0(\rho)$. At any matching point ρ_{10} the values of these two functions and their derivatives must be equal, i.e.,

$$Q_0(\rho_{10}) = Q_1(\rho_{10}) \quad , \qquad (4.3.8)$$

and $$Q_0'(\rho_{10}) = Q_1'(\rho_{10}) , \qquad (4.3.9)$$

where primes denote the derivatives.

Prokofjew (1929) employed eq.(4.3.3) with $D = 0$, eqs.(4.3.8) and (4.3.9) to determine the unknown parameters α_1, β_1, and γ_1 for $Q_1(\rho)$. The same procedure was recently repeated by Dumrongsak (1976), and the same result was obtained.

Neither eq.(4.1.15) nor eq.(4.3.8) are reliable in our works because the function $Q_0(\rho)$ for $\rho_{10} < \rho < \infty$ has been determined. In constructing the effective potential in the inner interval, we have used the quantization condition

$$n-\ell-\frac{1}{2} = \frac{\sqrt{2}}{\pi}\left[\int_{\rho_{min}}^{\rho_{10}}\left\{Q_1(\rho)-P_{n\ell}(\rho)\right\}^{1/2}\frac{d\rho}{\rho} + \int_{\rho_{10}}^{\rho_{max}}\left\{Q_0(\rho)-P_{n\ell}(\rho)\right\}^{1/2}\frac{d\rho}{\rho}\right] \qquad (4.3.10a)$$

for the inner states, d states, instead of

$$n-\ell-\frac{1}{2} = \frac{\sqrt{2}}{\pi}\int_{\rho_{min}}^{\rho_{max}}\left\{Q_1(\rho)-P_{n\ell}(\rho)\right\}^{1/2}\frac{d\rho}{\rho} \qquad (4.3.10b)$$

used by Prokofjew.

In general, the quantization condition

$$n-\ell-\frac{1}{2} = \frac{\sqrt{2}}{\pi}\left[\int_{\rho_{min}}^{\rho_{21}}\left\{Q_2(\rho)-P_{n\ell}(\rho)\right\}^{1/2}\frac{d\rho}{\rho} + \int_{\rho_{21}}^{\rho_{10}}\left\{Q_1(\rho)-P_{n\ell}(\rho)\right\}^{1/2}\frac{d\rho}{\rho} + \int_{\rho_{10}}^{\rho_{max}}\left\{Q_0(\rho)-P_{n\ell}(\rho)\right\}^{1/2}\frac{d\rho}{\rho}\right] \qquad (4.3.11)$$

is expressed in summation of three integrals. $Q_2(\rho)$ is the inner unknown function matching with the known one, $Q_1(\rho)$, at ρ_{21}.

We cannot use the integration formula given in eq.(4.3.2) to perform our integrals in eq.(4.3.10a). Instead we must use the integration formula for finite limits (one of them is neither ρ_{max} nor ρ_{min})

$$\int \sqrt{\mathcal{X}(\rho)}\,\frac{d\rho}{\rho} = \sqrt{\mathcal{X}(\rho)} - \frac{B}{2\sqrt{-A}}\sin^{-1}\left(\frac{2A\rho+B}{\rho}\right) - \sqrt{-C}\,\sin^{-1}\left(\frac{B\rho+2C}{\rho\Delta}\right) \qquad (4.3.12)$$

given by Gradshteyn and Ryzhik (1965).

The function $\mathcal{X}(\rho)$ and Δ in eq.(4.3.12) are defined as

$$\mathcal{X}(\rho) = A\rho^2+B\rho+C \quad , \quad \Delta = (B^2-4AC)^{1/2} \quad . \qquad (4.3.13)$$

The two turning points are now

$$\rho_{\substack{min \\ max}} = \frac{-B\pm\Delta}{2A} \qquad (4.3.14)$$

and B for the $Q_0(\rho)$ should be "1" instead of "1/2".

It is found that

$$\sin^{-1}\left(\frac{2A\rho+B}{\Delta}\right)\Bigg|_{\rho_{min}}^{\rho_{max}} = -\pi \quad , \qquad (4.3.15)$$

$$\sin^{-1}\left(\frac{B\rho+2C}{\rho\Delta}\right)\Bigg|_{\rho_{min}}^{\rho_{max}} = \pi \quad , \qquad (4.3.16)$$

and

$$\sqrt{\mathcal{X}(\rho)}\,\Bigg|_{\rho_{min}}^{\rho_{max}} = 0 \quad . \qquad (4.3.17)$$

After substituting the limits of integration into eq.(4.3.10a)and using all of the facts given above, eq.(4.3.10a) becomes

$$n-\ell-\frac{1}{2} = \frac{\sqrt{2}}{\pi}\left[\left\{G_1-H_1(\rho_{10})\right\}+\left\{H_0(\rho_{10})+G_0\right\}\right] \qquad (4.3.18)$$

where
$$G_0 = \left[\frac{B_0}{2\sqrt{-A_0}} - \sqrt{-C_0}\right] \sin^{-1}(1) \qquad (4.3.19)$$

which is independent of ρ ,

$$H_0(\rho) = \frac{B_0}{2\sqrt{-A_0}} \sin^{-1}\left(\frac{2A_0\rho_{10} + B_0}{\Delta}\right) + \sqrt{-C_0}\sin^{-1}\left(\frac{B_0\rho_{10} + 2C_0}{\rho_{10}\Delta}\right), \qquad (4.3.20)$$

and the subscript "O" denotes the corresponding $Q_0(\rho)$ used.
The two matching conditions in eqs.(4.3.8) and (4.3.9) for $D = 0$ can be reexpressed in general forms at any point ρ_i as

$$\alpha_{m+1}\rho_i^2 + \beta_{m+1}\rho_i + \gamma_{m+1} = \alpha_m\rho_i^2 + \beta_m\rho_i + \gamma_m$$

and
$$2\alpha_{m+1}\rho_i + \beta_{m+1} = 2\alpha_m\rho_i + \beta_m$$

which lead to

$$\left.\begin{aligned} \beta_{m+1} &= 2(\alpha_m - \alpha_{m+1})\rho_i + \beta_m \\ \gamma_{m+1} &= (\alpha_{m+1} - \alpha_m)\rho_i^2 + \gamma_m \end{aligned}\right\} \qquad . \quad (4.3.21)$$

β_{m+1} and γ_{m+1} can then be obtained from any assumed α_{m+1} since α_m , β_m and γ_m here are known parameters.
The processes to solve eqs.(4.3.18) and (4.3.21) simultaneously are:

1) β_1 and γ_1 can be obtained by assuming a value for α_1 and substituting it into eq.(4.3.21)
2) Substitute the parameters - $\epsilon_{n\ell}$, n and ℓ - into eq.(4.3.18)
3) If the right hand side of eq.(4.3.18) is not equal to the left hand side, the value of α_1 appearing on the right hand side of eq.(4.3.21) must be a new assumed value.

When the parameters - α_1 , β_1 and γ_1 - have been determined, the corresponding ρ_{min} for $Q_1(\rho)$ can be obtained from eq.(4.3.14). We now have

$$Q_1(\rho) = \alpha_1\rho^2+\beta_1\rho+\gamma_1 \quad , \quad \rho_{21}<\rho<\rho_{10} \qquad (4.3.22)$$

where ρ_{21} may be chosen from any ρ_{min}'s of d states in the same manner as ρ_{10} . We found that there exists three integrals appearing in the quantization condition for Li which must be integrated while there exists only two integrals required for Na, since $Q_2(\rho)$ still exists for Li. For Li we have

$$Q_2(\rho) = \alpha_2\rho^2+\beta_2\rho+\gamma_2 \quad , \quad \rho_{32}<\rho<\rho_{21} \qquad (4.3.23)$$

It is noted that the matching conditions (4.3.21) hold only when $D = \delta = 0$. Whenever $D \neq 0$, the two matching conditions are

$$\left.\begin{aligned} \alpha_1\rho_{10}^2+\beta_1\rho_{10}+\gamma_1 &= \rho_{10}+\delta/\rho_{10}^2 \quad , \\ \text{and} \qquad 2\alpha_1\rho_{10}+\beta_1 &= 1-2\delta/\rho_{10}^3 \quad . \end{aligned}\right\} \qquad (4.3.24)$$

The same process to find α_1 must be carried out except the integral

$$\int_{\rho_{10}}^{\rho_{max}}\left\{Q_0(\rho)-P_{n\ell}(\rho)\right\}^{1/2}\frac{d\rho}{\rho} = \int_{\rho_{10}}^{\rho_{max}}\left\{-\frac{1}{2}\epsilon_{n\ell}\rho^2+\rho-\frac{1}{2}(\ell+\frac{1}{2})^2+\frac{\delta}{\rho^2}\right\}^{1/2}\frac{d\rho}{\rho} \qquad (4.3.25)$$

must be integrated numerically by Simpson's integration formula (see Appendix B) since no explicit analytical formula for finite-limit integration as above is available.

4.3.3 Region near the Nucleus

The potential at the region near the nucleus is $-\frac{Ze^2}{r}$

or
$$Q_6(\rho) = Z\rho \quad , \quad 0 < \rho < \rho_{min} \text{ of 1s state.} \qquad (4.3.26)$$

The maximum point for this potential should be the ρ_{min} of the 1s state since its associated wave function is the one nearest to the nucleus. The ρ_{min} may be determined from eq.(4.3.14) after obtaining α_5, β_5 and γ_5 for $Q_5(\rho)$ of the 1s state from eqs.(4.3.18) and (4.3.21). The eq.(4.3.21) is still available for the reverse matching because of the commutation of the indices $m+1$ and m.

We also have

$$Q_5(\rho) = \alpha_5\rho^2 + \beta_5\rho + \gamma_5 \quad , \quad \rho_{65} < \rho < \rho_{max} \qquad (4.3.27)$$

where ρ_{min} of the 1s state is replaced by ρ_{65}.

For the Na atom the same procedure, as that was employed by Prokofjew, is used to create $Q_4(\rho)$ for p states :

He let $Q_4(\rho)$ of the 2p state join smoothly with $Q_5(\rho)$ of the 1s state and then found out ρ_{min} of $Q_4(\rho)$ of the 2p state. ρ_{min} of the 2p state was chosen to be the maximum possible point for $Q_5(\rho)$. Each $Q_4(\rho)$ of the other np states was also allowed to match with that of (n-1)s states, and then the averaged $Q_4(\rho)$ for the p states was determined.

The potential $Q_4(\rho)$ is given by

$$Q_4(\rho) = \alpha_4\rho^2 + \beta_4\rho + \gamma_4 \quad , \quad \rho_{54} < \rho < \rho_{43} \qquad (4.3.28)$$

where ρ_{max} in eq.(4.3.27) was replaced by ρ_{54} and ρ_{max} of $Q_4(\rho)$ was written as ρ_{43}.

It is noted that the matching of $Q_4(\rho)$ of the p states with $Q_5(\rho)$ of the s states is not possible in the case of Li but the $Q_2(\rho)$ of the p states can match with the $Q_1(\rho)$ of the d states.

4.3.4 Constructed Parts without Data

All experimental data have now been used. However, we still have $Q(\rho)$ for the region $\rho_{43} < \rho < \rho_{21}$ in the case of Na or i.e. the region between ρ_{min} of the p states and ρ_{max} of the s states in the case of Li to be determined.

In the case of Na, two functions

$$Q_3(\rho) = \alpha_3\rho^2 + \beta_3\rho + \gamma_3 \quad , \quad \rho_{43} < \rho < \rho_{32} \tag{4.3.29}$$

and

$$Q_2(\rho) = \alpha_2\rho^2 + \beta_2\rho + \gamma_2 \quad , \quad \rho_{32} < \rho < \rho_{21} \tag{4.3.30}$$

are created to join $Q_4(\rho)$ with $Q_1(\rho)$ continuously, and these two equations must satisfy the matching conditions in eq.(4.3.21). ρ_{32} in both equations is an arbitrary point which is chosen to make the potential able to reproduce energy levels in agreement with the experimental data.