CHAPTER II

THE BOHR-SOMMERFELD QUANTIZATION RULE

2.1 Old Quantum Theory Approach

Bohr(1913) was able to explain the monochromatic spectral line emitted from atoms, at least in hydrogen, by assuming that the atom was capable of existing only in certain definite stationary states, each of a definite energy. He purposed that radiation was not emitted continuously as the electromagnetic field from a rotating or vibrating particle would do and that the atom would stay in one energy level until it made a suddenly jump to a second lower level with emission of a photon. He assumed that electrons and other atomic particles obayed classical mechanics but that there were addition conditions, imposed on them, which limited the allowed classical motion to a discrete set called stationary states. The simplest method of formulating these quantum conditions was suggested by Sommerfeld(1928), and the quantum conditions are often known by Sommerfeld's name.

The Sommerfeld quantum conditions can be stated most simply by examining a motion in one dimension. The system he first considered was the "harmonic oscillator", a point mass m bounding elastically to its rest position and moving to either side of the central position only in a direction $x = q$ or its reverse. It then experiences a restoring force but no damping resistance. Letting ν be the frequency of the oscillator, the vibrating phenomena is expressed by

$$x = q = a \sin 2\pi \nu t \qquad (2.1.1)$$

where a is a constant and t stands for time.

In this case the momentum p becomes equal to $m\dot{q}$, i.e.,

$$p = 2\pi \nu m a \cos 2\pi \nu t \qquad (2.1.2)$$

By eliminating t from eq. (2.1.1) and eq. (2.1.2), an ellipse in the p-q plane has the equation

$$\frac{q^2}{a^2} + \frac{p^2}{b^2} = 1 \qquad (2.1.3)$$

in which the minor axis is defined by
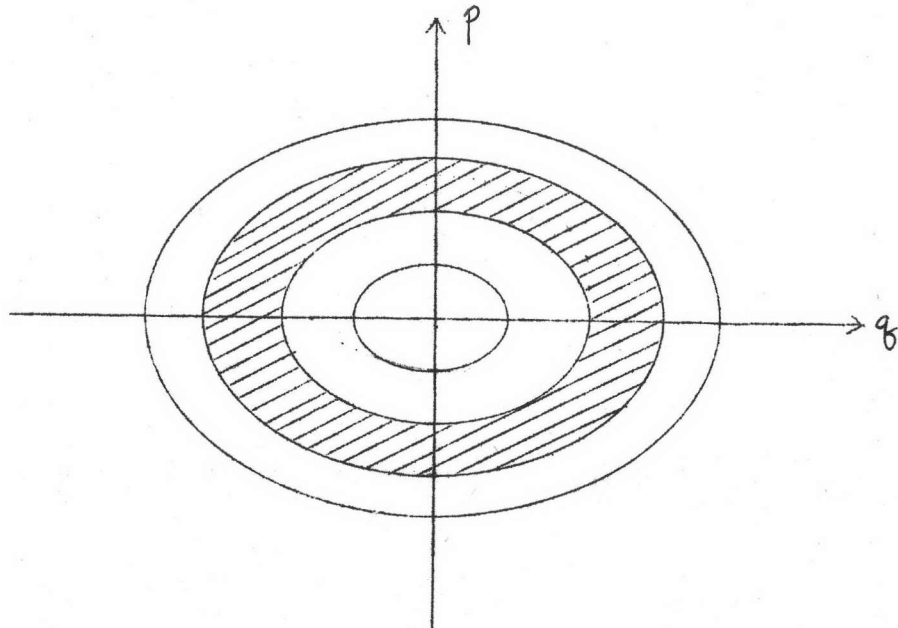
$$b = 2\pi \nu m a \qquad (2.1.4)$$

Fig.2.1 Phase plane of the harmonic oscillator

The area of the ellipse

$$ab\pi = 2\pi^2 \nu m a^2 \qquad (2.1.5)$$

is defined as "phase area" which is an area drawn on q-p rectangular coordinates. This quantity is equal to $\frac{W}{\nu}$, where W denotes the energy of the system, which remains constant during the vibration, i.e.,

$$ab\pi = W/\nu \qquad (2.1.6)$$

Eq.(2.1.6) can be verified by calculating W at time $t=0$, the potential is zero and the kinetic energy is

$$\frac{m}{2}\dot{q}^2 = \frac{m}{2}a^2(2\pi\nu)^2 = W, \qquad (2.1.7)$$

and hence eq.(2.1.6) can be found.

By changing W we get the phase orbit as a family of similar ellipse since the ratio $\frac{b}{a}$ has the constant value $2\pi\nu m$. "A selection is made in order that each ellipse zone has the same area h, the Planck's constant." Then h is the area of the first ellipse; the second ellipse has thus the area $2h$, the nth the area nh. If W_n is the energy of the oscillator describing the nth ellipse, then according to eq.(2.1.6)

$$W_n = nh\nu \qquad (2.1.8)$$

All points lying on one of our ellipse, therefore, represent the stationary states of the oscillator. Eq.(2.1.8) shows that in these orbits the energy is an integer multiple of the elementary quantumof energy ϵ, i.e.,

$$\epsilon = h\nu \quad , \quad W_n = n\epsilon . \qquad (2.1.9)$$

When the energy of the oscillator changes and when its graph point passes over to a smaller ellipse it emits energy, but when its graph point passes over to a larger ellipse it absorbs energy. The

emission and absorption occur in multiple of the energy quantum ϵ .

It can be concluded (for the oscillator and for every mechanical system of one degree of freedom) that " The graph point of the system in the phase plane is restricted to certain "quantized" phase orbits (which characterize certain quanta). Between each orbit and its successor there is an elementary region of area h . The nth orbit (if closed) has an area nh . Expressed as a formula this is the phase integral

$$J = \oint p\,dq = nh .$$ (2.1.10)

The integral is to be taken along the nth orbit.

For the rotator, a point mass m rotating about a fixed center uniformly in a circle of radius a , the natural coordinate of position is the angle ϕ . By setting $q = \phi$ the kinetic energy becomes

$$E_{kin} = \frac{m}{2} a^2 \dot{q}^2 .$$ (2.1.11)

Since a is constant during the motion, the potential is constant, i.e.,

$$E_{pot} = constant .$$

The momentum coordinate in this case, the angular momentum, can be written by employing the relation $P_k = \dfrac{\partial E_k}{\partial \dot{q}_k}$ as

$$P = m a^2 \dot{q}$$ (2.1.12)

which is also constant.

The phase orbit of the rotation is a sraight line parallel to the q axis (Fig.2.2). In the direction of the phase plane
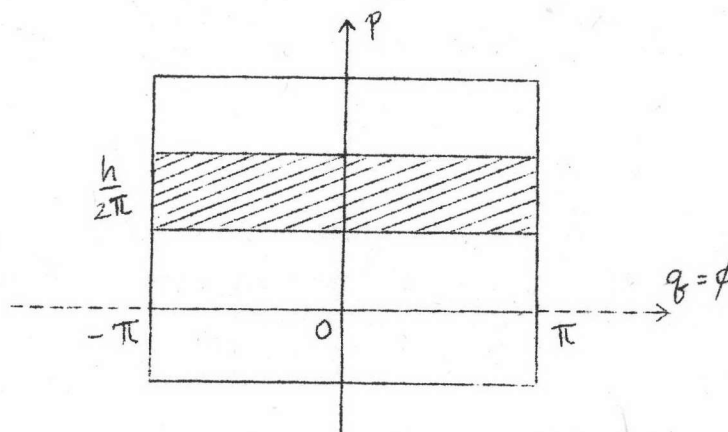

Fig.2.2 Phase plane of the rotator

has only the length 2π and so we may cut it along the lines $q = \pm\pi$ and join the edges so as to form a cylinder. The surface area between the nth and the $(n-1)^{th}$ phase orbit being a rectangular on the base 2π is equal to $2\pi(p_n - p_{n-1})$.

By setting the surface equal to h, the phase integral (for this case, the surface between the nth and the zeroth phase orbit representing by the q axis) is given again by

$$J = \int p\,dq = 2\pi p_n = nh . \qquad (2.1.13)$$

Thus it has been from eq.(2.1.13) that " The rotator is to be quantized not only in **energy** but also in angular momentum ". In this case the angular momentum p must be an integer multiple of $\hbar = h/2\pi$. On the other hand, the kinetic energy can be obtained from eqs.(2.1.11) and (2.1.12) and can be written as

$$E_{kin} = nh\nu/2 \qquad (2.1.14)$$

by setting the rotation frequency equal to $\dot{q}/2\pi$. We see that the energy is not an integer multiple but a half integer multiple of $h\nu$.

For the case of f degrees of freedom, the phase integral for one dimensional case, eq.(2.1.10), was postulated by Sommerfeld to be an integer multiple of h ;i.e., the phaseintegral for the kth degree of freedom can be expressed as

$$\int p_k dq_k = n_k h \qquad (2.1.15)$$

where $n_k = 1,2,3,\ldots\ldots$.

Eq.(2.1.15) is always written as a closed path integral

$$\oint p_k dq_k = n_k h \qquad (2.1.16)$$

2.2 The WKB Approach

There exists a method for the approximate treatment of the Schrödinger equation which shows the connection between the Bohr-Sommerfeld quantization rule and the Schrödinger equation. The method is made on an expansion of the wave function in powers of $\hbar$. It is called the Wentzel-Kramers-Brillouin (WKB) approximation (Wentzel, Kramers, Brillouin, 1926).

A solution $u(x)$ of the one-dimensional time independent Schrödinger equation which describes a motion of a particle of mass m in a potential $V(x)$ and having an eigenvalue E ,i.e.,

$$\frac{d^2u}{dx^2} + \frac{2m}{\hbar^2}\left[E - V(x)\right]u = 0 \quad , \qquad (2.2.1)$$

can be written in the form

$$u(x) = A e^{iS(x)/\hbar} \qquad (2.2.2)$$

where $S(x)$ is to be determined.

Eq.(2.2.1) may be one of the forms :

$$\frac{d^2u}{dx^2} + k^2 u = 0 \qquad k^2 > 0 \qquad (2.2.3)$$

$$\frac{d^2u}{dx^2} - \kappa^2 u = 0 \qquad k^2 > 0 \qquad (2.2.4)$$

where $\quad k(x) = \dfrac{1}{\hbar}\left\{2m\left[E - V(x)\right]\right\}^{1/2} \qquad$ when $V(x) < E \quad (2.2.5)$

$$k(x) = \frac{1}{\hbar}\left\{2m\left[V(x) - E\right]\right\}^{1/2} \qquad \text{when } V(x) > E \quad (2.2.6)$$

Substituting $u(x)$ into eq.(2.2.3) gives

$$i\hbar S'' - S'^2 + \hbar^2 k^2 = 0 \qquad (2.2.7)$$

where primes denote differentiation with respect to x .

We expand S in powers of $\hbar$

$$S = S_0 + \hbar S_1 + \dots \dots \qquad (2.2.8)$$

when inserting S into eq.(2.2.7) by equating equal powers of $\hbar$ we have

$$-S_0' + 2m(E - V) = 0 \qquad (2.2.9)$$

and $\qquad\qquad i S_0'' - 2 S_0' S_1 = 0 \qquad$ etc. $\qquad (2.2.10)$

Integration of these equations we get

$$S_0(x) = \pm \hbar \int^x k(x') dx'$$ (2.2.11)

$$S_1(x) = \frac{i}{2} \ln k(x)$$ (2.2.12)

where x' is a dummy variable.

We thus obtain from eqs.(2.2.2),(2.2.11),and (2.2.12)

$$u(x) = A k^{-1/2} \exp(\pm i \int^x k\, dx)$$, $V < E$.(2.2.13)

Similarly, the approximate solution of eq.(2.2.4) is

$$u(x) = B k^{-1/2} \exp(\pm \int^x K\, dx)$$, $V > E$.(2.2.14)

After determining the asymptotic nature of the solutions and considering the two solutions at a linear turning point, we get two asymptotic connection formulas (as shown in Schiff,1955 or Mathews and Venkatesan, 1976) :

$$\frac{1}{2} K^{-1/2} e^{-\xi_2} \longrightarrow k^{-1/2} \cos(\xi_1 - \frac{\pi}{4}) ,$$ (2.2.15)

$$\sin\eta\, K^{-1/2} e^{\xi_2} \longrightarrow k^{-1/2} \cos(\xi_1 - \frac{\pi}{4} + \eta)$$ (2.2.16)

where $\xi_1 = \int_{x_i}^x k\, dx$, $\xi_2 = \int_x^{x_i} K\, dx$ for a typical linear turning point shown in Fig.2.3 and η is the phase difference which can be appreciably different from zero or an integer multiple of π. The arrow in eq.(2.2.15) implies that the asymptotic solution in region 2 appearing on the left goes into the asymptotic solution
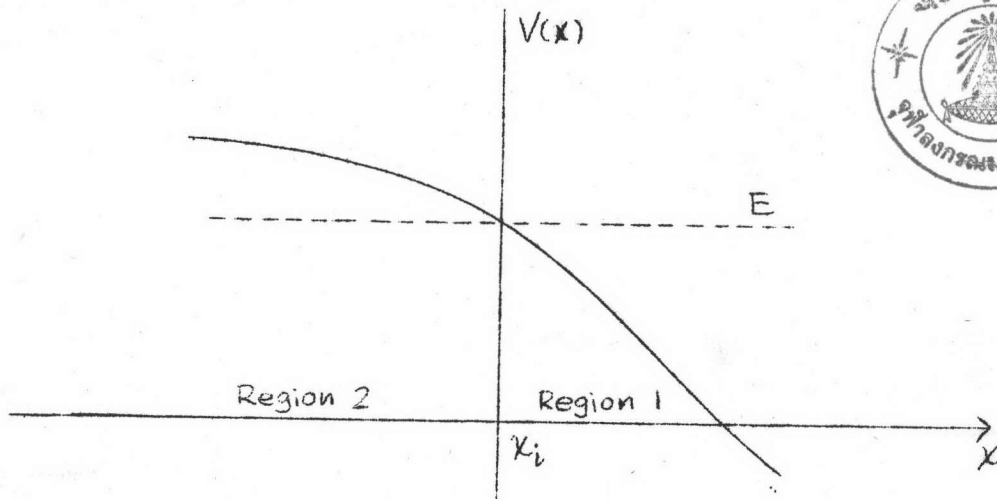
Fig.2.3 A typical linear turning point, where $V(x) = E$ at $x = x_i$; in region 1 , $E > V(x)$, and in region 2 , $E < V(x)$.

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in region 1 appearing on the right but that the converse is not necessarily true. Similarly, the arrow in eq.(2.2.16) shows the asymptotic solution in region 2 for the reverse connection.

The Bohr-Sommerfeld quantization rule can be derived from the two WKB connection formulas as follows :
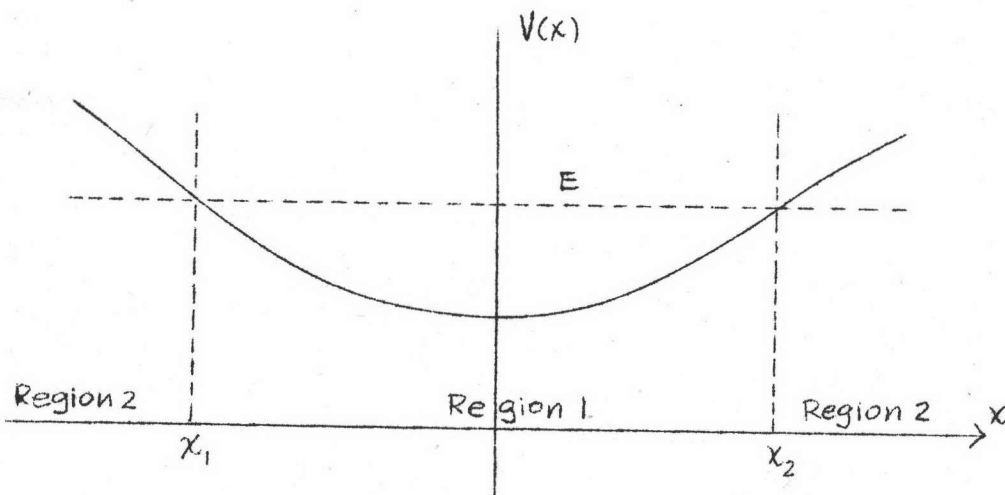

Fig.2.4 One dimensional potential well

We consider the problem of finding the energy levels of a particle moving in the one-dimensional potential well shown in Fig.2.4 . For any assumed energy levels E , there are supposed to be just two turning points of the classical motion such that $V(x_1) = V(x_2) = E$. The region $x < x_1$ and $x > x_2$ are type 2 regions in which we know that u decreases away from the turning points (this be required in the boundary conditions at $x = \pm \infty$). We therefore need only the decreasing exponential WKB solutions in these regions.

The connection formula , eq.(2.2.15), can be applied at the turning point x_1 . The region 1 is in the range $x_1 < x < x_2$, so that the solution to the right of the turning point is

$$k^{-1/2} \cos \left(\int_{x_1}^{x} k \, dx - \pi/4 \right) \qquad (2.2.17)$$

apart from an arbitrary multiplying constant.

The same connection formula can also be applied at x_2 by reversing the direction of the x axis; the arrow in eq.(2.2.15) still means that we go from a region 2 solution to a region 1 solution, but now the latter is to the left of the turning point and the former is to the right. We now redefine $\xi_1 = \int_{x}^{x_2} k \, dx$, $\xi_2 = \int_{x_2}^{x} k \, dx$. In such a case, eq.(2.2.15) can be used without any modification. The solution to the left of the turning point is then

$$k^{-1/2} \cos \left(\int_{x}^{x_2} k \, dx - \pi/4 \right) \qquad (2.2.18)$$

which can be written as

$$k^{-1/2} \cos \left(\int_{x_1}^{x} k \, dx - \frac{\pi}{4} - \eta \right), \quad \eta = \int_{x_1}^{x_2} k \, dx - \frac{\pi}{2}. \quad (2.2.19)$$

The two solutions, eq.(2.2.17) and eq.(2.2.19), have to join together smoothly somewhere in the interior of region 1. This evidently requires that η be zero or a positive integer multiple of π, since $\int_{x_1}^{x_2} k \, dx$ is necessarily positive. Thus we have an equation

$$\int_{x_1}^{x_2} k \, dx = (n + \tfrac{1}{2}) \pi, \quad n = 0, 1, 2, \ldots \quad (2.2.20)$$

to determine the eigenvalues. Eq.(2.2.20) is to be used for values of n upto the point at which E becomes so large that one or both of the turning points disappears.

By substituting k from eq.(2.2.5) into eq.(2.2.20) we get an equation for the Bohr-Sommerfeld quantization rule of the old quantum theory

$$2 \int_{x_1}^{x_2} \left\{ 2m \left[E - V(x) \right] \right\}^{1/2} dx = (n + \tfrac{1}{2}) h \quad .(2.2.21)$$

The left hand side of eq.(2.2.21) is the integral around a complete circle of the motion (from x_1 to x_2 and back to x_1) of the momentum $\left[2m(E-V) \right]^{1/2}$. The right hand side is the quantum value of the phase integral, with half-integer rather than integer quantum numbers. The quantization condition is similar to that derived in the old quantum theory, the difference is only in the quantity $h/2$. These two quantization expressions are nearly the same

for $n \rightarrow \infty$ which corresponds to the classical limit. In practice, the results obtained from the WKB approximation, however, are found to be quite good even for low quantum numbers.

2.3 The Generalized Bohr-Sommerfeld Quantization Rule

The problem we encounter now is the question when does one use an integral or a half-integral multiple of h in the Bohr-Sommerfeld quantization rule. Resolution of this problem has been attempted since the WKB approximation was suggested. Kramers (1926) showed that the quantization conditions for separable systems are consequences of quantum mechanics in the limit of Planck's constant tends to zero. For a more general case, Brillouin (1926) applied the Schrödinger equation to both separable and non-separable systems in order to derive the quantum conditions, however, the results were incorrect because they yielded only integer quantum numbers. Keller (1958) developed this idea and get the quantization conditions which could be applied correctly to both types of systems. His quantization conditions are expressed as

$$\oint \sum_k p_k \, dq_k = h \left[n + \frac{m}{4} \right] \qquad (2.3.1)$$

where k is the running number from 1 to N,

N is the number of independent coordinates,

and m is a number determined from the amplitude of the wave function $u(x) = A e^{iS(x)/\hbar}$.

Maslov(1972) then generalized the ideas of Keller. His work has been reviewed recently by Percival (..to be published in Advanced Chemical Physics). Maslov gave the following quantization rule for the separable case

$$\oint p_k dq_k = (n + \frac{\alpha_k}{4})h \quad , \quad n = 0,1,2,.. \quad (2.3.2)$$

where α_k is the topological Maslov index which has the value "2" for librations and "0" for rotations. We refer to this as the generalized Bohr-Sommerfeld quantization rule.

We see that the right hand side of eq.(2.3.2) is $\alpha_k/4$ greater than that of eq.(2.1.16), the Sommerfeld's postulate for a system of f degrees of freedom. The difference does not,however, imply that the Bohr-Sommerfeld quantization, $\oint p dq = nh$,is useless since it can still be applied to a whole system or a separable coordinate which has a periodicity of time.

To see this we now consider a system described by the spherical coordinates :

Since r and θ are libration variables and ϕ is a rotation variable, we have

$$J_\theta \equiv \oint p_\theta d\theta = (n_\theta + \frac{1}{2})h \quad , \quad n_\theta = 0,1,2,.... \quad (2.3.3)$$

$$J_r \equiv \oint p_r dr = (n_r + \frac{1}{2})h \quad , \quad n_r = 0,1,2,.... \quad (2.3.4)$$

$$J_\phi \equiv \oint p_\phi d\phi = n_\phi h \quad , \quad n_\phi = 0,1,2,.... \quad (2.3.5)$$

giving

$$J = J_\theta + J_r + J_\phi = (n_\theta + n_r + n_\phi + 1)h \quad ,$$

namely that the total phase integral J is quantized in integral multiple of h, "beginning at 1". Thus the Bohr-Sommerfeld quantization rule is still true and can always be applied to any system.