

Lecture note- 5

Physical Chemistry CHE 503

QUANTUM CHEMISTRY

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Quantum Chemistry – I

5.1 Introduction:

A statistical interpretation of the electron wave function was proposed by Max Born in 1926. This interpretation has been widely adopted since it has many advantages. According to this view, the electron is still considered as a particle and the value of ψ^2 at any point is taken to represent the probability of finding the electron at the point at any instant. It should be noted that consideration of the electron as a particle necessitate this statistical interpretation, for although a particle can only be in one position at a given instant, the Heisenberg uncertainty principle tells us that this position can never be precisely known. So, what we can do is only to state probability of the electron being found at a given point in space. Thus ψ^2 is interpreted as giving a direct measure of this probability. Consequently, the greater the wave amplitude, the greater is the probability of finding the electron at the point at a given instant or if a time interval is considered, the longer on an average is the total time the electron spends at that point.

5.2 Interpretation of Schrödinger Wave Equation:

The Schrödinger equation can have several solutions, not all of which correspond to any physical or chemical reality. Such solutions or wave functions are, therefore not acceptable. The acceptable wave functions must satisfy the following conditions:

1. The wave function ψ is single valued, i.e., for each value of variables x, y, z there is one value of ψ . Suppose one of the variables is an angle θ then, single-valuedness of ψ requires that

$$\psi(\theta) = \psi(\theta + 2n\pi) \text{ where } n \text{ is an integer.}$$

2. The wave function ψ and its first derivative with respect to its variables must be continuous, i.e., there must not be sudden change in ψ when its variables are changed.

Satisfying these conditions, Schrödinger equation yields significant solutions for certain definite values of total energy E . These values are called eigen values.

5.3 Eigen values and Eigen Functions:

In unit 4 we have deduced the relation

$$\frac{\partial^2 f(x)}{\partial x^2} = \frac{-4\pi^2}{\lambda^2} f(x) \dots\dots\dots(5.1)$$

In connection with the problems of standing waves in a stretched string, it is apparent that the solution $f(x)$ of equation (5.1) can have significance only for certain definite values of wavelength λ . These are the wavelengths corresponding to normal modes of vibration of the string. The values are referred to as eigen values. The corresponding functions $f(x)$ which are the solutions of equation (5.1) are called eigen functions or wave functions must satisfy certain conditions which in the case of stretched string are not difficult to understand. In the

first place, $f(x)$ must be zero at each end of the string, since the system is fixed at these points and the vibration amplitude will be zero. In the second place, $f(x)$ must be single valued and finite between the limits of x represented by the two ends of the string. That means, at each point the vibrating string amplitude has a definite value at any given instant.

Just as the amplitude function, $f(x)$ in eqn. (5.1) has significance only for certain definite values of λ , so the functions ψ are satisfactory solutions of the wave equation only for certain values, the eigen values, of total energy, E . For an atom these eigen values are equivalent of discrete set of energy values postulated by Bohr's theory. The occurrence of definite energy levels of the atom is thus a direct consequence of wave mechanical treatment. The corresponding values of the function ψ are called as wave functions or eigen functions of the Schrödinger equation. Like $f(x)$, the eigen functions, ψ of this equation must also satisfy certain conditions; that is they must be single valued, finite and continuous throughout of the whole of the configuration space of the system under consideration, that is for all possible values of the coordinates x , y and z including infinity.

5.4 Operators:

An operator is a mathematical instruction or procedure be carried out on a function. It is written in the form,

(operator) (function) = (another function)

The function on which the operator is carried out is called an operand. The left hand side of the above equation does not mean that the function is multiplied with the operator. Evidently, an operator written alone has no meaning.

A few examples of operator are given below:

(a) $\frac{d}{dx}(x^5) = 5x^4$. Here, $\frac{d}{dx}$ which stands for differentiation with respect to x is the operator. x^5 is the operand and $5x^4$ is the result of the operation.

(b) $\int x^2 dx = \frac{x^3}{3} + C$. Here $\int x^2 dx$ which stands for the integration with respect to x is the operator, x^2 is the operand and $\frac{x^3}{3} + c$ is the result of the operation.

In case the symbol used for the operator is not self explanatory, a suitable letter or some symbol for the operator is used with the symbol \wedge over it.

(c) Find the expression for the following operators

(i) $(\frac{d}{dx} + x)^2$

(ii) $(\frac{d}{dx} - x)(\frac{d}{dx} + x)$

Solution: let $\psi(x)$ be the operand.

$$(\frac{d}{dx} + x)^2 \psi(x) = (\frac{d}{dx} + x) \left(\frac{d}{dx} + x \right) \psi(x)$$

$$\begin{aligned}
&= \left(\frac{d}{dx} + x \right) \left(\frac{d\psi}{dx} + x\psi \right) \\
&= \frac{d^2\psi}{dx^2} + 2x \frac{d\psi}{dx} + x^2\psi + \psi \\
&= \left(\frac{d^2}{dx^2} + 2x \frac{d}{dx} + x^2 + 1 \right) \psi \quad \left(\text{as } \frac{dx}{dx} = 1 \right)
\end{aligned}$$

Removing ψ from both sides of this equation we get

$$\left(\frac{d}{dx} + x \right)^2 = \frac{d^2}{dx^2} + 2x \frac{d}{dx} + x^2 + 1$$

$$\begin{aligned}
\text{(ii)} & \left(\frac{d}{dx} - x \right) \left(\frac{d}{dx} + x \right) \psi(x) \\
&= \left(\frac{d}{dx} - x \right) \left(\frac{d\psi}{dx} + x\psi \right) \\
&= \frac{d^2\psi}{dx^2} + \frac{d}{dx} (x\psi) - x \frac{d\psi}{dx} - x^2\psi \\
&= \frac{d^2\psi}{dx^2} + \left(x \frac{d\psi}{dx} + \psi \frac{dx}{dx} \right) - x \frac{d\psi}{dx} - x^2\psi \\
&= \frac{d^2\psi}{dx^2} + x - x^2\psi \\
&= \left(\frac{d^2}{dx^2} + 1 - x^2 \right) \psi
\end{aligned}$$

Removing ψ from both side of the equation, we get

$$\left(\frac{d}{dx} - x \right) \left(\frac{d}{dx} + x \right) = \frac{d^2}{dx^2} + 1 - x^2.$$

5.4.1 Algebra of Operators:

The operators follow certain rules similar to algebra. A few of those are given below:

(a) addition and subtraction of operators:

if \hat{A} and \hat{B} are two different operators. And f is operand, then

$$(\hat{A} + \hat{B}) f = \hat{A}f + \hat{B}f \quad \dots\dots\dots(5.2)$$

$$(b) \text{ similarly } (\hat{A} - \hat{B})f = \hat{A}f - \hat{B}f \quad \dots\dots\dots(5.3)$$

5.4.2 Multiplication of Operators:

If \hat{A} and \hat{B} are two different operators and f is the operand then $\hat{A}\hat{B}f$ means that first f is operated by operator \hat{B} to get the result, say f' , and then f' is operated by \hat{A} to get the final result, say f'' . i.e. $\hat{A}\hat{B}f$ means that $\hat{B}f = f'$ and then $\hat{A}f' = f''$, so that we can write

$$\hat{A}\hat{B}f = f'' \quad \dots\dots\dots (5.4)$$

It should be clear to you, that the order using the operator is from right to left, as written in the above equation. If the same operation is to be done a number of times in succession, it is written by the power of the operator. For example $\hat{A}\hat{A}f$ is written as \hat{A}^2f

That means $\hat{A}\hat{A}f = \hat{A}^2f$ (5.5)

It may be noted that usually $\hat{A}\hat{B}f \neq \hat{B}\hat{A}f$

5.4.3 Linear Operators:

An operator \hat{A} is said to linear if the two functions f and g are related as $\hat{A}(f+g) = \hat{A}f + \hat{A}g$ (5.6)

i.e., the operator on the sum of the two functions gives the same result as the sum of the two results obtained by carrying out the same operation on the two functions separately. For example $\frac{d}{dx}$, $\frac{d^2}{dx^2}$ etc. are linear operators, whereas “taking the square, square root” etc. are non linear.

5.4.4 Vector Operators:

Operators are not necessarily limited to operate on function of one variable. The differential operator $\frac{d}{dx}$ can operate on function $f(x, y, z)$. An important group of operators are the vector operators. A vector operator ∇ (‘del’) is defined in Cartesian coordinates as:

$$\nabla = i\frac{\partial}{\partial x} + j\frac{\partial}{\partial y} + k\frac{\partial}{\partial z} \quad \text{.....(5.7)}$$

Here i, j, k are unit vectors along the $x, y,$ and z axes. Operating on a scalar function ϕ , operator generates a vector called the gradient of ϕ .

$$\nabla\phi = i\frac{\partial\phi}{\partial x} + j\frac{\partial\phi}{\partial y} + k\frac{\partial\phi}{\partial z} \quad \text{.....(5.8)}$$

5.4.5 Laplacian operators:

Laplacian operators is a very common operator used in quantum mechanics. It is represented by ∇^2 (del squared). Mathematically this is defined as,

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

Schrödinger wave equation can be represented in term of Laplacian operators as,

$$\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2} + \frac{8\pi^2 m(E-V)}{\hbar^2}\psi = 0$$

$$\nabla^2\psi + \frac{8\pi^2 m(E-V)}{\hbar^2}\psi = 0 \quad \text{.....(5.9)}$$

5.4.6 Hamiltonian Operators:

Schrödinger wave equation in terms of Laplacian operators is written as:

$$\nabla^2\psi = -\frac{8\pi^2 m(E-V)}{\hbar^2}\psi$$

$$\nabla^2\psi = -\frac{8\pi^2 m}{\hbar^2}(E\psi - V\psi)$$

$$\text{or } \frac{-\hbar^2}{8\pi^2 m} \nabla^2 \psi + V\psi = E\psi$$

$$\text{or } \left(\frac{-\hbar^2}{8\pi^2 m} + V \right) \psi = E\psi \quad \dots\dots\dots 5.10$$

This equation means that the operation $\left(\frac{-\hbar^2}{8\pi^2 m} \nabla^2 + V \right)$ carried out on the function ψ , is equal to the total energy multiplied by the function ψ . The operator $\left(\frac{-\hbar^2}{8\pi^2 m} \nabla^2 + V \right)$ is called Hamiltonian operator and is represented by \hat{H} , so,

$$\hat{H} = \frac{-\hbar^2}{8\pi^2 m} \nabla^2 + V$$

equation (5.10), thus can be written as

$$\hat{H}\psi = E\psi$$

This is another form of the Schrödinger wave equation.

5.5 Mathematical Consideration of Schrödinger Wave Equation:

5.5.1 Normalisation

Till now you have studied that Schrödinger wave equation is a homogeneous differential equation whose solution gives a value of ψ , but when ψ is multiplied by a constant factor it would give the same differential equation. It is, therefore, necessary to find some conditions which will indicate which constant factor is to be used.

As the electron must be found somewhere, one can say that the probability of finding an electron in the whole of space considered in a particular problem is unity. This may mathematically be written as

$$\int |\psi|^2 dx = 1 \quad \dots\dots\dots (5.11)$$

Where dx is the volume of the whole space. This integral determines by what constant ψ must be multiplied for the solution of a particular problem. This constant is known as the **normalization** constant. An eigen function which has to be completely evaluated in this manner is said to be **normalised**

The amplitude in the wave function is determined by using the normalization condition. For ψ to represent a wave packet (i.e., a group of waves), the above condition for normalisation condition should be satisfied. The numerical coefficient in ψ , the amplitude factor should be independent of time.

5.5.2 Orthogonality:

Suppose we have two wave functions ψ_p and ψ_q correspond to two values of the energy E_p and E_q . If these two functions are separate solutions of the Schrödinger's equation, then $\int \psi_p \psi_q dx = 0$ and the wave function ψ_p, ψ_q are said to **orthogonal**. This property will be proved for one-dimension only.

Now let us consider two Schrödinger equations which are written in one dimension only (for the motion of a particle in straight line).

$$\frac{d^2 \psi_p}{dx^2} + \frac{8\pi^2 m}{h^2} (E_p - V_p) \psi_p = 0 \quad \dots\dots\dots(5.12)$$

$$\frac{d^2 \psi_q}{dx^2} + \frac{8\pi^2 m}{h^2} (E_q - V_q) \psi_q = 0 \quad \dots\dots\dots(5.13)$$

Multiplying equation (5.12) by ψ_q and equation (5.13) by ψ_p and on subtracting we get

$$\frac{d}{dx} \left(\psi_q \frac{d\psi_p}{dx} - \psi_p \frac{d\psi_q}{dx} \right) + \frac{8\pi^2 m}{h^2} (E_p - E_q - V_p + V_q) \psi_p \psi_q = 0 \quad \dots\dots\dots(5.14)$$

Integrating equation (5.14) with respect to x over the whole of place from $-\infty$ to $+\infty$ and since ψ and V are zero at infinity the first term vanishes and the second term becomes

$$\frac{8\pi^2 m}{h^2} (E_p - E_q) \int_{-\infty}^{+\infty} \psi_p \psi_q dx = 0 \quad \dots\dots\dots 5.15$$

As $E_p \neq E_q$

$$\text{Hence } \int_{-\infty}^{+\infty} \psi_p \psi_q dx = 0 \quad \dots\dots\dots(5.16)$$

It is possible to make a linear combination of orthogonal functions.

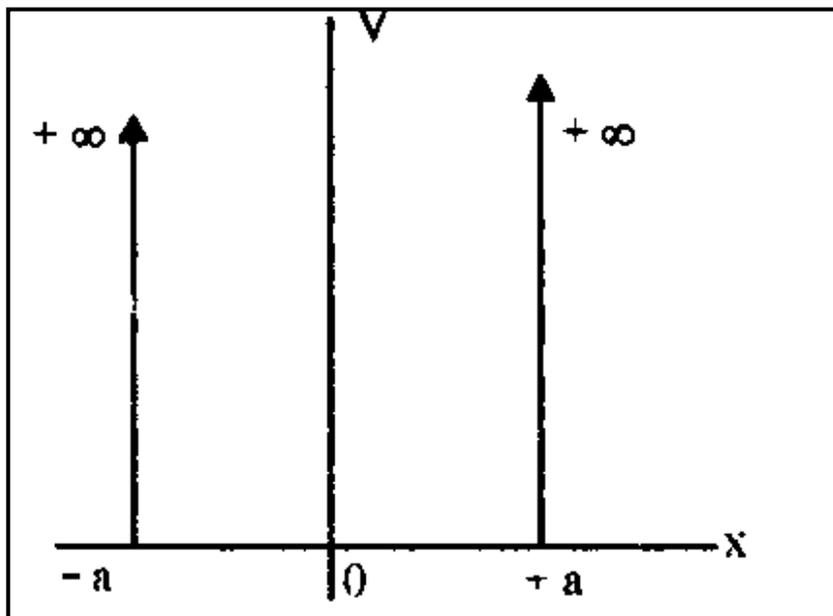
5.5.3 Degeneracy:

You have already proved that for every wave function ψ , there must be a corresponding energy value E , i.e., for every eigenfunction there will be one eigen value. That means each energy state must have a wave function which will be the characteristics of the system. If two different ψ 's have the same value of energy then these two states of different ψ 's are called degenerate state.

5.6 Solution of the Schrödinger Wave Equation for Some Simple Systems:

5.6.1 Particle in One-dimensional box:

We shall consider some model systems for which the Schrödinger wave equation can be solved exactly. First we will discuss one-dimensional particle whose potential energy is everywhere same is free particle. convenient choice is $V=0$. A system in which



exactly. First we will discuss one-dimensional particle whose potential energy is everywhere same is free particle. convenient choice is $V=0$. A system in which

potential energy is zero within a closed region and infinite ($V=\infty$) everywhere else is known as a potential box. Fig.5.1

Fig 5.1 Particle in a box

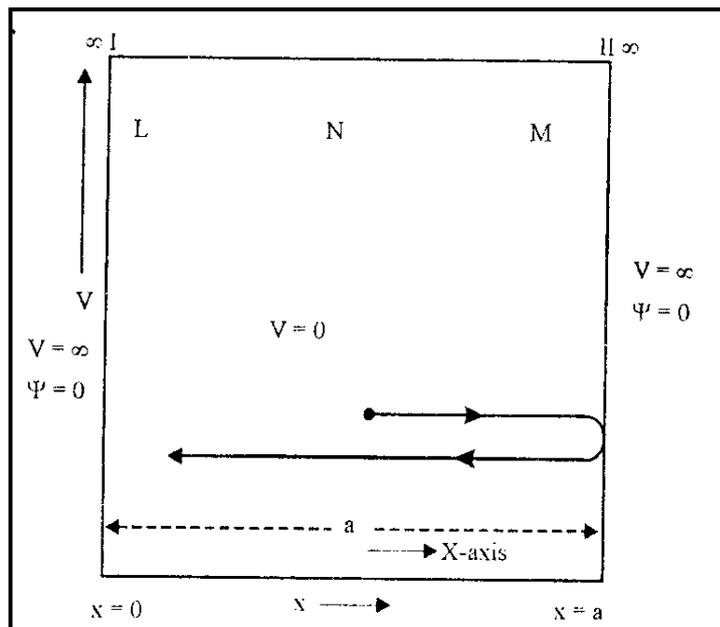


Fig. 5.2 Wave mechanical treatment of a particle in one-dimensional box

Now consider a particle of mass m confined to move in a one-dimensional box of length a having infinitely high walls Fig.5.2.

It is simplest problem related to a particle in a microscopic system (say, electron in the atom) involves the calculation of the wave function and energy of the particle (electron) constrained to move in with in a certain distance in a given direction forward and backward.

Let us consider a particle (electron) in one dimensional box as shown in Fig.5.2. The particle is restricted to move along X -axis, forward or backward. Suppose that the particle does not lose energy when it collides against the wall of the box, so its energy remain

constant. This box can then be represented by a potential box of width with potential walls of infinite (∞) height at $x=0$ and $x=a$. So potential energy (V) of the particle becomes infinity ($V=\infty$) on the side L ($x=0$) and M ($x=a$) of the box and is constant inside the box. For the sake of simplicity, it is assumed that the potential energy of the particle is zero everywhere inside the box, that is,

$$V = 0$$

However, outside the box the potential energy is infinity, i.e., $V=\infty$ at $x < 0$ (i.e., negative side of X-axis) and at $x > a$. Therefore, the wave function ψ and probability of finding the particle (i.e., ψ^2) must be zero when $x < 0$, $x=0$ and $x \geq a$. In other words, the particle is confined in the box and cannot escape the box, i.e., the particle does not exist outside the box. Now the Schrödinger's wave equation with respect to space is:

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} + \frac{8\pi^2 m}{h^2} (E - V)\psi = 0 \quad \dots\dots\dots(5.17)$$

For a particle moving in x - direction, this equation becomes

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{8\pi^2 m}{h^2} (E - V)\psi = 0 \quad \dots\dots\dots (5.18)$$

Now we know within the box, $V= 0$. Therefore we have

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{8\pi^2 m}{h^2} E\psi = 0$$

Or $\frac{\partial^2 \psi}{\partial x^2} = -\frac{8\pi^2 m}{h^2} E\psi \quad \dots\dots\dots(5.19)$

As π , m , E and λ are constant, the equation (5.19) can be written as

$$\frac{\partial^2 \psi}{\partial x^2} = -k^2 \psi \quad \dots\dots\dots(5.20)$$

Where $\frac{8\pi^2 m}{h^2} E = k^2$

Equation (5.20) is an ordinary second order differential equation which has the solution of the form

$$\psi = A\sin(kx) + B\cos(kx) \quad \dots\dots\dots(5.21)$$

Where A and B are constants

Equation (5.21) represents all the solutions of equation (5.20) which are mathematically satisfactory. However, these solutions (wave functions) do not necessarily satisfy our boundary conditions, and we should now examine equation (5.21) in view of these requirements. Differentiating equation (5.21) with respect to x , we get

$$\frac{\partial^2 \psi}{\partial x^2} = -k^2(A\sin kx + B\cos kx) \quad \dots\dots\dots(5.22)$$

The Schrödinger wave equation is satisfied if $\psi = 0$ everywhere outside the box, which means that the particle cannot be found outside the box, i.e., It is confined within the box. This implies that ψ must be zero at the walls of the box, i.e., at $x = 0$ and $x = a$. Since ψ has to be a continuous function of x , it leads to the conclusion that in equation (5.21) B must be zero. Thus the solution of equation (5.20) is of the form

$$\psi = A \sin kx \quad \dots\dots\dots(5.23)$$

Since $\psi = 0$ at $x = 0$ and at $x = a$,

hence $A \sin ka = 0$,

$$\sin ka = n\pi$$

$$\text{Hence, } ka = \frac{n\pi}{a} \quad \dots\dots\dots(5.24)$$

where $n = (1, 2, 3, \dots)$ is the quantum number. Putting the value of k from equation (5.24) in equation (5.23), we get

$$\psi = A \sin\left(\frac{n\pi x}{a}\right) \quad \dots\dots\dots(5.25)$$

The probability of finding the particle within the box in a small length segment dx is $\psi^2 dx$. Since the particle must be within the box, therefore,

$$\int_0^a \psi^2 dx = 1$$

$$\text{or } \int_0^a A^2 \sin^2 \frac{n\pi x}{a} dx = 1$$

The solution of the integral gives A as $\left(\frac{2}{a}\right)^{1/2}$ so,

$$\psi = \left(\frac{2}{a}\right)^{1/2} \sin \frac{n\pi x}{a}$$

5.6.2 Energy of the Particle:

From equation (5.21), (5.24), and (5.25) we can calculate the energy of the particle.

$$\text{Since } k = \frac{n\pi}{a}$$

$$\text{Hence } k^2 = \frac{n^2 \pi^2}{a^2}$$

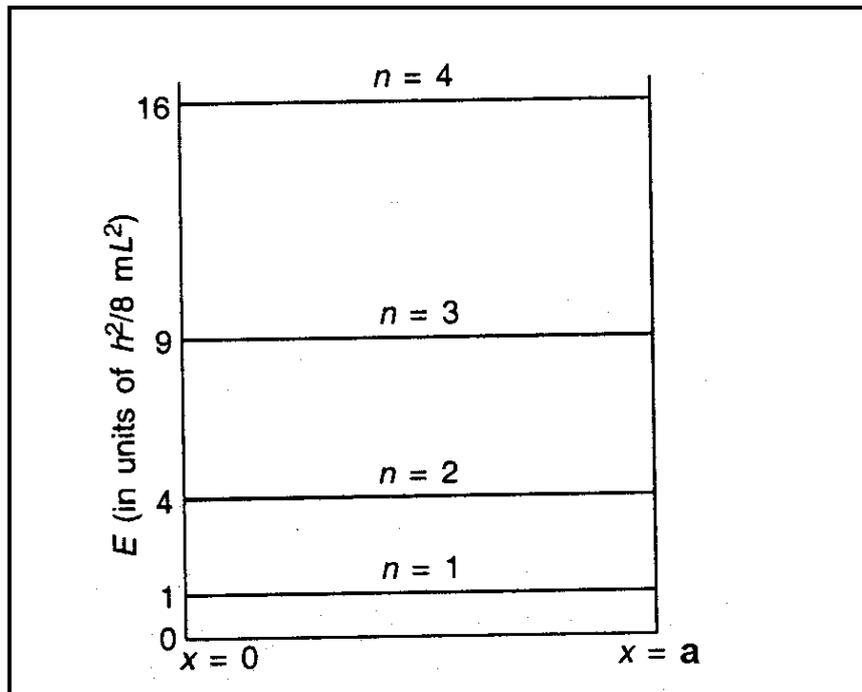
Also from equation (5.20),

$$k^2 = \frac{8\pi^2 mE}{h^2} = \frac{n^2 \pi^2}{a^2}$$

Or $E = E_n = \frac{n^2 h^2}{8ma^2}$ where $n = 1,2,3$ (5.26)

This is the expression for energy of the particle in one-dimensional box. Since the energy depends upon the quantum number n , which can have any integral value. The energy levels of the particle in the box are quantized. The equation (5.26) gives permissible value of energy corresponding to $n = 1, n = 2, n = 3, n = 4, \dots$ etc. E_n stands for energy of the particle in n^{th} level. Hence symbol E_n is used in the place of E . As already said that n is

called number, assume integral is clear that particle



quantum can only value. It the may have

Fig 5.3 Energy levels in a particle

only certain discrete values of E . These are eigen values of E . The value of E can not be zero, because in that case, $\psi = \sin 0 = 0$, everywhere in the box. However, this is impossible, therefore, $n = 0$ is not possible. Hence it is clear from the above discussion that the concept of energy quantization is inherent in the wave mechanics.

5.6.3 Calculation of Normalisation Factor A:

The mathematical operation for calculating the value of A in equation (5.25) is called normalization. The process is given below.

$\psi = A \sin \left(\frac{n\pi x}{a} \right)$ (5.27)

You know the probability that the particle with in the space x and $x + dx$ for one dimensional box is given by $\psi^2 dx$. As a consequence of this assumption, we can write

$$\int_{-\infty}^{\infty} \psi^2 dx = 1$$

Applying the condition that the probability of finding the particle with in a box, i.e., between $x = 0$ and $x = a$, is unity the above equation becomes

$$\int_0^a \psi^2 dx = 1$$

As we have already discussed above that $\psi = A \sin kx$

Then $\int_0^a A^2 \sin^2 kx dx = 1$

Hence $A^2 \int_0^a \sin^2 kx dx = 1$

As you know:

$$\sin^2 kx = \frac{1}{2}(1 - \cos 2kx)$$

So, $\frac{A^2}{2} \int_0^a (1 - \cos 2kx) dx = 1$

or $\frac{A^2}{2} [\int_0^a dx - \int_0^a \cos 2kx dx] = 1$

or $\frac{A^2}{2} \{ [x]_0^a - \frac{1}{2k} [\sin 2kx]_0^a \} = 1$

or $\frac{A^2}{2} \left[a - \frac{1}{2k} (\sin 2ka - \sin 0) \right] = 1$

or $\frac{A^2}{2} \left[a - \frac{1}{2k} \sin 2ka \right] = 1$ (as $\sin 0 = 0$)

as we know $k = \frac{n\pi}{a}$

or $ka = n\pi$

Hence $\frac{A^2}{2} \left[a - \frac{1}{2k} \sin 2n\pi \right] = 1$

since $\sin 2n\pi = 0$

we get $\frac{A^2}{2} a = 1$

or $A = \sqrt{\frac{2}{a}}$

So, solution of Schrödinger's wave equation for a particle in one dimensional box can be written as

$$\psi = \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi x}{a}\right) \dots\dots\dots(5.28)$$

As $k = \frac{n\pi}{a}$

And $k = \sqrt{\frac{8\pi^2 mE}{h^2}}$

$$\frac{n\pi}{a} = \sqrt{\frac{8\pi^2 mE}{h^2}}$$

So $\psi_n = \sqrt{\frac{2}{a}} \sin\left(\sqrt{\frac{8\pi^2 mE}{h^2}} \cdot x\right)$

The wave function ψ_n is said to be normalized and normalization factor is $\sqrt{2/a}$. The above equation is normalized wave function or normalized solution of Schrödinger wave equation for particle one dimensional box.

5.7 Some Consequences of Energy Equation:

5.7.1 Energy Levels:

You have just studied that the energy of the particle is: $E_n = \frac{n^2 h^2}{8\alpha^2 m}$ where n is an integer, called quantum number and has the value $n=1, 2, 3, \dots$. It can never be zero or fractional. This means that the particle will have only discrete values for energy.

The above discussion means, the energy of the particle is quantized in the box and cannot change in a continuous manner. These permissible acceptable or discrete values of E depend upon n which are independent of x . These values are called eigen values. So, a free particle, like electron, can have all values of energy but when it is confined with a certain range of space, the energy values (i.e., energy levels) become quantized. The greater the localization, the higher is the energy.

5.7.2 Zero Point Energy:

In any atom which is taken as a type of potential well or potential box, there are several discrete energy levels corresponding to $n=1, 2, 3, \dots$,

when (a) $n=1, E_1 = \frac{h^2}{8ma^2}$

(b) $n=2, E_2 = \frac{4h^2}{8ma^2}$

so, $E_2 - E_1 = \frac{3h^2}{8ma^2}$

(c) $n=3, E_3 = \frac{9h^2}{8ma^2}$

so, $E_3 - E_2 = \frac{5h^2}{8ma^2}$. and so on.

So, It is clear that energy difference between successive energy levels is not constant.

It is clear from above discussion that minimum value of n is, one, hence, energy corresponding to $n=1$ will be minimum and is given by $E_{\min} = \frac{h^2}{8ma^2}$

Hence when the particle is present in the potential box, the energy of the lowest level ($n=1$) is called zero point energy.

It is the characteristics of the systems executing to-and fro motion (vibration) that the energy of their lowest allowed state is greater than zero, i.e., a zero point energy exists.

It shows that:

- (i) The energy of harmonic oscillator is quantised contrary to the classical view, and the result emerges from the solution of Schrödinger equation.
- (ii) The energies are determined by the parameter n which is called “vibrational quantum number” of the oscillator
- (iii) The lowest value of energy (when $n = 0$) is $\frac{1}{2}h\nu$. “This is the zero point energy” (in classical view it is zero).
- (iv) As n increases by unity, the energy increases by $h\nu$ so the energy levels are equally spaced as shown in Fig.(5.4)

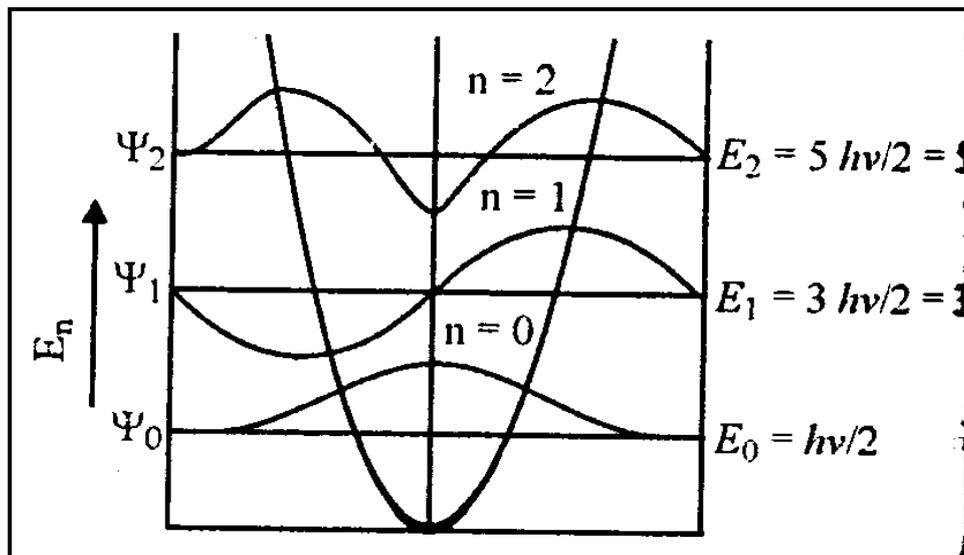


Fig.5.4 Plots of the wave function ψ and probability ψ^2 against x

5.8 Physical significance of ψ and ψ^2 :

The plots of wave function (ψ) and probabilities (ψ^2) against x in Fig.5.4 reveals several interesting features of quantum mechanical harmonic oscillator:

- (i) The wave functions are either symmetric (even) or unsymmetrical (odd) with respect to $x = 0$. We have seen that the exponential part of the wave function, is necessarily symmetric because of the quantity x^2 , the polonomial part will be symmetric for x^0, x^2, x^4, \dots and ant symmetric for x, x^3, x^5, \dots
- (ii) The functions ψ^2 are never negative and hence necessarily symmetric.
- (iii) In the ground state ($n = 0$) there are no nodes; and each successive state has one additional node.
- (iv) The presence of nodes indicates the points of zero probability.
- (v) Still more curious is the fact that ψ and ψ^2 are non zero even for large values of x , i.e. beyond the classical turning point, i.e., the particle can penetrate the potential barrier.
- (vi) The ψ^2 plot reveals the fact that the particle in the ground state has the maximum probability of being found at the central position ($x = 0$) while in the excited states the probability increases towards the classical turning points.

Example: An electron is confined in one dimensional box of length 1\AA . Calculate its ground state energy in electron volts (eV).

Solution: Ground state, $n=1$

$$\begin{aligned}
 E &= \frac{n^2 h^2}{8ma^2} \\
 &= \frac{1^2 (6.626 \times 10^{-34} \text{ Js})^2}{8(9.109 \times 10^{-31} \text{ Kg})^2 (1.603 \times 10^{-19} \text{ J/eV})} \\
 &= 37.6 \text{ eV}
 \end{aligned}$$

5.9 Linear Harmonic Oscillator:

The quantum mechanical treatment of the simple harmonic oscillator is required for the clear cut understanding of molecular vibrations.

A point mass undergoing simple harmonic oscillations in one dimension, due to attraction by a force proportional to the displacement from the equilibration position, constitutes a linear harmonic oscillator. Before the quantum mechanical treatment is considered the classical treatment of the linear harmonic oscillator is attempted to provide a background.

As you know in a simple harmonic oscillator, the force tending to restore the particle to its equilibrium position is always directed towards equilibrium position, and is directly proportional to the displacement (x) from it.

Thus,

$$F = -kx \quad \dots\dots\dots(5.29)$$

Where k = force constant
 x =displacement

The minus sign shows that restoring force is working in the opposite direction to the displacement.

If m is the mass of the particle, then

$$\begin{aligned} F &= \text{mass} \times \text{acceleration} \\ &= m \times \left(\frac{d^2x}{dt^2} \right) \end{aligned} \quad \dots\dots\dots(5.30)$$

From equation (5.29) and (5.30),

$$m \times \left(\frac{d^2x}{dt^2} \right) = -kx \quad \dots\dots\dots(5.31)$$

as the displacement (x) is harmonic, it can be written as,

$$x = A \sin 2\pi \nu t \quad \dots\dots\dots(5.32)$$

Where A = amplitude of vibration

ν = frequency of oscillation

Double differentiating equation (5.32) with respect to t ,

$$\frac{d^2x}{dt^2} = -4\pi^2 \nu^2 A \sin 2\pi \nu t \quad \dots\dots\dots(5.33)$$

From equation (5.31) and (5.33)

$$m (-4\pi^2 \nu^2 A \sin 2\pi \nu t) = -kx \quad \dots\dots\dots(5.34)$$

putting the value of x from equation (5.32) in equation (5.34), we get

$$4\pi^2 \nu^2 A \sin 2\pi \nu t = k A \sin 2\pi \nu t$$

so $k = 4\pi^2 m \nu^2$

hence:

$$\nu = \frac{1}{2\pi} \sqrt{\frac{k}{m}} \quad \dots\dots\dots(5.35)$$

Equation (5.35) gives the frequency of the linear harmonic oscillator.

(a) Potential Energy (V) of the Linear Harmonic Oscillator:

Suppose the spring represents a chemical bond. The work done in stretching the spring increases the potential energy of the system. If the potential energy for the equilibrium length of the spring (or chemical bond) is assumed to be zero, that the other length is given by

$$V = \int_0^x (-F) dx$$

But $F = -kx$

Hence $V = \int_0^x kx dx$

$$= k \int_0^x x dx$$

$$= \frac{1}{2}k x^2 \quad \dots\dots\dots(5.36)$$

Here x = distortion from the equilibrium length. The plot of potential energy of a particle executing linear harmonic oscillation against displacement from the equilibrium position is shown in fig. 5.3

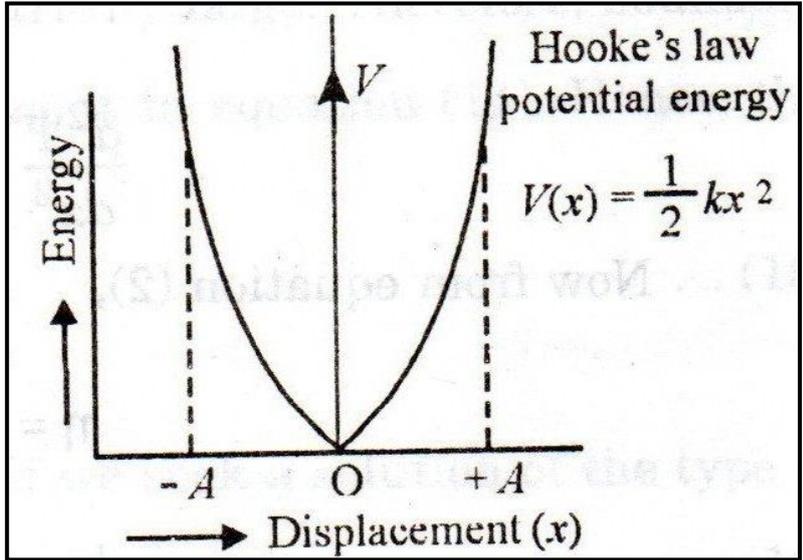


Fig.5.5 Potential energy diagram for a linear harmonic oscillator:

The Schrödinger wave equation in one dimension is given by,

$$\frac{d^2\psi}{dx^2} + \frac{8\pi^2m}{h^2}(E - V) = 0 \quad \dots\dots\dots(5.37)$$

The potential energy of a linear harmonic oscillator (i.e., simple harmonic oscillator executing motion in one dimension) is

$$V = \frac{1}{2}k x^2 \quad (k = \text{force constant})$$

So,
$$\frac{d^2\psi}{dx^2} + \frac{8\pi^2m}{h^2} (E - \frac{1}{2}k x^2)\psi = 0 \quad \dots\dots\dots(5.38)$$

If we change over to two new independent dimensionless variables η and α which are defined as,

$$\eta = \left(\frac{2\pi}{h}\sqrt{km}\right)^{1/2} x$$

but $k = 4\pi^2mv^2$

hence
$$\eta = \left(\frac{2\pi}{h}\sqrt{4\pi^2mv^2m}\right)^{1/2} x$$

$$= \left(\frac{4\pi^2mv}{h}\right)^{1/2} x \quad \dots\dots\dots(5.39)$$

And
$$\alpha = \frac{4E\pi}{h} \sqrt{\frac{m}{k}}$$

$$\begin{aligned}
&= \frac{4E\pi}{h} \sqrt{\frac{m}{4\pi^2 mv^2}} && \text{(as } k = 4\pi^2 mv^2 \text{)} \\
&= \frac{4E\pi}{h} \left(\frac{1}{2\pi v}\right) \\
\alpha &= \frac{2E}{hv} && \dots\dots\dots(5.40)
\end{aligned}$$

From equation (5.39),

$$\begin{aligned}
\eta^2 &= \frac{4\pi^2 mv}{h} x^2 \\
\text{Hence } x^2 &= \frac{\eta^2 h}{4\pi^2 mv} && \dots\dots\dots(5.41)
\end{aligned}$$

From equation (5.40),

$$E = \frac{h\nu\alpha}{2} \dots\dots\dots(5.42)$$

$$\begin{aligned}
\text{Now } \frac{d^2\psi}{dx^2} &= \frac{d}{dx} \left(\frac{d\psi}{dx} \right) \\
&= \frac{d}{dx} \frac{d\psi}{d\eta} \cdot \frac{d\eta}{dx} \\
&= \frac{d}{d\eta} \frac{d\psi}{dx} \frac{d\eta}{dx} \\
&= \frac{d}{d\eta} \left(\frac{d\psi}{d\eta} \cdot \frac{d\eta}{dx} \right) \frac{d\eta}{dx}
\end{aligned}$$

$$\text{So } \frac{d^2\psi}{dx^2} = \frac{d^2\psi}{d\eta^2} \left(\frac{d\eta}{dx}\right)^2 \dots\dots\dots(5.43)$$

From equation (5.39),

$$\begin{aligned}
\eta &= \left(\frac{4\pi^2 mv}{h}\right)^{1/2} x \\
\frac{d\eta}{dx} &= \left(\frac{4\pi^2 mv}{h}\right)^{1/2}
\end{aligned}$$

On squaring both sides, we get

$$\left(\frac{d\eta}{dx}\right)^2 = \frac{4\pi^2 mv}{h} \dots\dots\dots(5.44)$$

Substituting this value in equation (5.43),

$$\frac{d^2\psi}{dx^2} = \frac{d^2\psi}{d\eta^2} \left(\frac{4\pi^2 mv}{h}\right) \dots\dots\dots(5.45)$$

from (5.38), (5.40), (5.41) and (5.45)

$$\left(\frac{4\pi^2 mv}{h}\right) \frac{d^2\psi}{d\eta^2} + \frac{8\pi^2 m}{h^2} \left[\frac{h\nu\alpha}{2} - \left(\frac{1}{2} 4\pi^2 mv^2\right) \left(\frac{\eta^2 h}{4\pi^2 mv}\right)\right] \psi = 0$$

Dividing both side by $\frac{4\pi^2 mv}{h}$, we get,

$$\frac{d^2\psi}{d\eta^2} + \frac{2}{hv} \left[\frac{h\nu\alpha}{2} - \frac{1}{2} v h \eta^2\right] \psi = 0$$

or $\frac{d^2\psi}{d\eta^2} + (\alpha - \eta^2)\psi = 0$ (5.46)

or $\frac{d^2\psi}{d\eta^2} - (\eta^2 - \alpha)\psi = 0$ (5.47)

or $\frac{\frac{d^2\psi}{d\eta^2}}{(\eta^2 - \alpha)\psi} = 1$ (5.48)

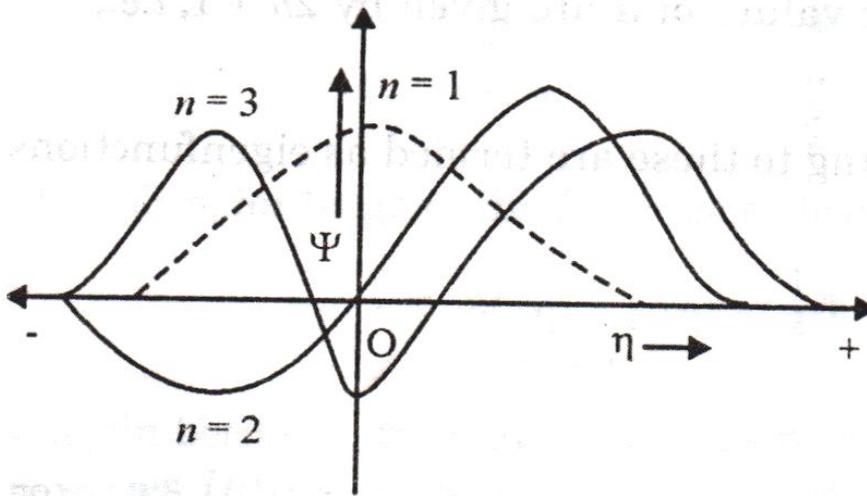


Fig 5.6 Characteristic wave functions of the linear harmonic oscillator.

Equation (5.45) (5.46) and (5.47) are the different forms of the wave equation for the linear harmonic oscillator.

5.10 Eigen Function:

Consider the equation:

$$\frac{d^2\psi}{d\eta^2} - (\eta^2 - \alpha)\psi = 0 \quad \text{.....(5.49)}$$

Suppose ψ should be finite, continuous and single valued at $\eta = 0$, the proper solution of the equation (equation-5.49) can be shown to be as follows:

When $\alpha = 1$, $\psi = \frac{1}{2} e^{-\eta^2/2}$

When $\alpha = 3$, $\psi = 2\eta e^{-\eta^2/2}$

When $\alpha = 5$, $\psi = (4\eta^2 - 2)e^{-\eta^2/2}$ and so on....

From the above discussion it follows that, the proper value of α is given by

$2\eta + 1$ i.e

$\alpha = 2n + 1$

Also we know $\alpha = \frac{2E}{\hbar\nu}$

So,

so $\frac{2E}{\hbar\nu} = 2n + 1$

or $E = (n + \frac{1}{2})\hbar\nu$ (5.50)

Equation (5.50) gives the quantum states of linear harmonic oscillator.

For each value of α we get a different wave functions ψ_n . Each ψ_n contains polynomial $H_n(\eta)$ generally called Hermite polynomial in either even or odd power of η remembering that for normalization, the condition is

$$\int_{-\infty}^{+\infty} |\psi_n|^2 d\eta = 1 \quad (n = 0, 1, 2, \dots)$$

The general formula for ψ_n is found to be

$$\psi_n = \left(\frac{4\pi m\nu}{h}\right)^{\frac{1}{4}} (2^n n!)^{-\frac{1}{2}} H_n(\eta) \exp(-\frac{\eta^2}{2})$$
(5.51)

Table 5.1 Hermite polynomials

n	$H_n(\eta)$	α	E_n
0	1	1	$\hbar\nu/2$
1	2η	3	$3\hbar\nu/2$
2	$4\eta^2 - 2$	5	$5\hbar\nu/2$
3	$8\eta^3 - 12\eta$	7	$7\hbar\nu/2$
4	$16\eta^4 - 48\eta^2 + 12$	9	$9\hbar\nu/2$
5	$32\eta^5 - 160\eta^3 + 120\eta$	11	$11\hbar\nu/2$

The characteristics wave function corresponding to $n=1,2,3,\dots$, for the linear harmonic oscillator are shown in fig 5.7.

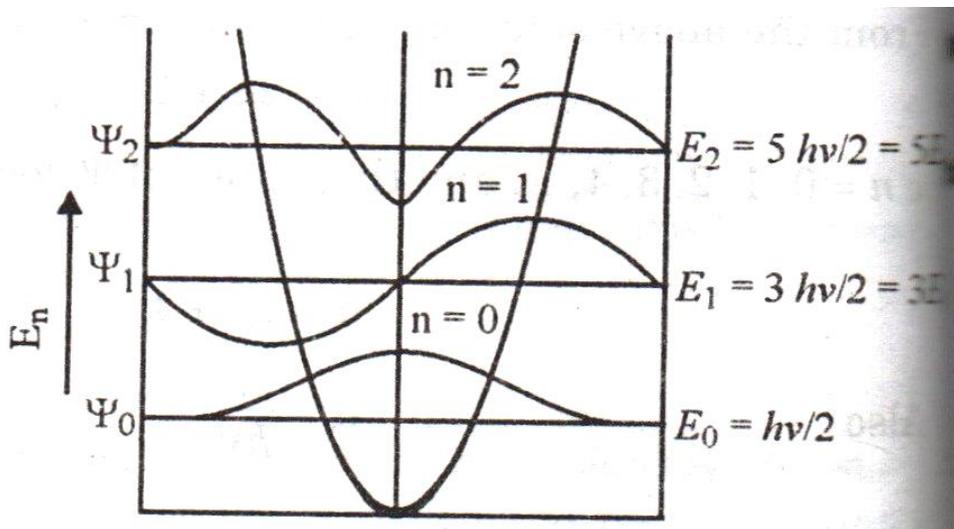


Fig 5.7 Various energy levels

The curve shown in fig 5.7 shows that for small values of η the wave function becomes zero. This means that wave packet behaves very much like a particle with fizzy cages and associated wave packet is found only in the immediate neighborhood of the particle. The various energy levels are sketched in fig 5.7. these curves shows that the wave functions are alternately symmetrical and unsymmetrical about the origin.

5.11 The Rigid Rotor (or Rotator):

5.11.1 Introduction:

The rotational motion is of great interest in atomic and molecular problems. It crops up whenever we have to deal with motion of a particle under the influence of central field of force, for example, the motion of an electron around the nucleus of an atom.

For a single particle executing such a motion, the Schrödinger equation can be solved exactly. Now we shall describe first the rotational motion of a particle in a plane (particle in a ring) and then some other problems. We shall use the results for the case of a rotating diatomic molecule.

5.11.2 Rotational Energy of Rigid Rotator:

A diatomic molecule rotating about an axis perpendicular to the inter-nuclear axis and passing through the centre of gravity of the molecule, forms an example of a rigid rotor, it is being assumed that the inter-nuclear distance does not change during rotation. The kinetic energy (K.E) of the molecule is given by

$$\text{K. E.} \equiv T = \frac{1}{2} I \omega^2 = \frac{L^2}{2I} \quad \dots\dots\dots 5.52$$

Where ω is the angular velocity and I is the moment of inertia of the rotating molecule. The angular momentum $L = I\omega$. If no force act on the rotor, we can put the potential energy $V = 0$. Hence, the Hamiltonian is expressed as

$$H = T + V = L^2/2I \quad \dots\dots\dots 5.53$$

The equation for L^2 in spherical coordinates (r, θ and ϕ) is given by

$$L^2 = -\hbar^2 \left[\frac{1}{\sin\theta} \frac{\partial}{\partial\theta} \left(\sin\theta \frac{\partial}{\partial\theta} \right) + \frac{1}{\sin^2\theta} \frac{\partial^2}{\partial\phi^2} \right] \quad \dots\dots\dots 5.54$$

The Schrödinger equation $\hat{H}\psi = E\psi$ may be written as

$$\frac{1}{2I} \left[-\hbar^2 \left\{ \frac{1}{\sin\theta} \frac{\partial}{\partial\theta} \left(\sin\theta \frac{\partial\psi}{\partial\theta} \right) + \frac{1}{\sin^2\theta} \frac{\partial^2\psi}{\partial\phi^2} \right\} \right] = E\psi \quad \dots\dots\dots 5.55$$

Equation 5.55 may be written as

$$\frac{1}{\sin\theta} \frac{\partial}{\partial\theta} \left(\sin\theta \frac{\partial\psi}{\partial\theta} \right) + \frac{1}{\sin^2\theta} \frac{\partial^2\psi}{\partial\phi^2} + \frac{8\pi^2 I}{\hbar^2} E\psi = 0 \quad \dots\dots\dots 5.56$$

Equation 5.56 contains two angular variables θ and ϕ . It can be solved by the method of separation of variables, i.e., we look for a solution of the form

$$\psi(\theta, \phi) = (T\theta)(F\phi) \quad \dots\dots\dots 5.57$$

Substituting equation (5.57) in equation (5.56), we get.

$$\frac{\sin\theta}{T} \frac{\partial}{\partial\theta} \left(\sin\theta \frac{\partial T}{\partial\theta} \right) + \frac{8\pi^2 IE}{\hbar^2} \sin^2\theta = -\frac{1}{F} \frac{\partial^2 F}{\partial\phi^2} \quad \dots\dots\dots 5.58$$

We can put both sides of equation 5.58 equal to a constant say, m^2 , and obtain two differential equations each in one variable. These equations are given by

$$\frac{\partial^2 F}{\partial\phi^2} + m^2(F) = 0 \quad \dots\dots\dots 5.59$$

And

$$\frac{1}{\sin\theta} \frac{\partial}{\partial\theta} \left(\sin\theta \frac{\partial T}{\partial\theta} \right) + \left(\beta - \frac{m^2}{\sin^2\theta} \right) (T) = 0 \quad \dots\dots\dots 5.60$$

where $\beta = \frac{8\pi^2 IE}{\hbar^2}$

Equation (5.59) has the solution

$$(F\phi) = N \exp(\pm im\phi) \quad \dots\dots\dots 5.61$$

Where $i = \sqrt{-1}$ and N is normalization constant

This wave function is acceptable provided m is an integer. This condition arises because (F) must be single valued.

Therefore $(F\phi) = F(\phi + 2\pi)$

Hence, it follows that

$$\exp(2\pi mi) = 1$$

Since $e^x = \cos x + i \sin x$ (from Euler's relation)

$$\therefore \cos 2\pi m + i \sin 2\pi m = 1$$

This can be true only when if $m=0, \pm 1, \pm 2 \dots\dots\dots$ etc. Let us normalize the wave function $F(\phi)$ to determine the normalization constant N.

$$\int_0^{2\pi} F^* F d\phi = 1 \quad (0 \leq \phi \leq 2\pi)$$

$$\text{or } N^2 \int_0^{2\pi} e^{im\phi} \times e^{-im\phi} d\phi = 1$$

$$\text{or } N^2 \int_0^{2\pi} d\phi = 1$$

$$\text{or } N^2 (2\pi) = 1$$

So that $N = (2\pi)^{-1/2}$

Hence, the normalized wave function becomes

$$F_{\pm m}(\phi) = (2\pi)^{-1/2} \exp(\pm im\phi); m = 0, 1, 2, 3, \dots$$

Here we are not trying to obtain a complete solution of equation (5.60) but will merely state that if $\beta = \ell(\ell + 1)$ where ℓ is **rotational quantum number**, then this equation becomes a standard mathematical equation whose solutions are known to be associated Legendre polynomials $P_{\ell}^{|m|}(\cos \theta)$ where ℓ is either zero or a positive integer and $\ell > |m|$.

The normalized solutions are given by

$$T(\theta) = T_{\ell, \pm m}(\theta) = \left[\frac{2\ell+1}{2} \times \frac{(\ell-|m|)!}{(\ell+|m|)!} \right]^{1/2} P_{\ell}^{|m|}(\cos \theta)$$

The energy eigen values of rigid rotor are obtained as follows:

$$\beta = 8\pi^2 IE/h^2 = \ell(\ell + 1)$$

Hence, $E = \frac{\ell(\ell+1)h^2}{8\pi^2 I}$ where $\ell = 0, 1, 2, \dots$

Normally we use the symbol J rather than ℓ for the rotational quantum number, so the rotational energy levels are given by the equation

$$E_J = \frac{J(J+1)h^2}{8\pi^2 I} \quad \text{where } J = 0, 1, 2, \dots$$

This is the equation for rotational energy levels.

5.12 Physical significance of the Wave Function:

The only dependent variable in the Schrödinger wave equation is the wave amplitude of the wave function, ψ and it depends on the coordinate of the particle. In some cases, it may turn out to be a complex function of the form, $\psi = u + iv$, where u and v are the functions of the coordinates and $i = \sqrt{-1}$. The complex conjugate of ψ is $\psi^* = u - iv$. Their product $\psi\psi^* = u^2 + v^2$, and if ψ is real, $\psi\psi^*$ is identical with ψ^2 . Neither ψ nor ψ^* has any physical significance but $\psi\psi^*$ (or ψ^2 , when real) has. In dealing with all forms of wave motion, such as light waves, sound waves, electrical field or matter waves the square of the wave amplitude at any point is interpreted as the intensity of the effect at that point. So, the value of ψ^2 (ψ^2 can be used instead of $\psi\psi^*$, Since the most of the wave functions in atom or molecular structure problems contain real term only) at any point around the nucleus gives a measure of the electronic charge density at the point. This interpretation was originally suggested by Schrödinger. According to this view, the electron is to be regarded as smeared out forming a cloud of electricity, the density of which varies from point to point around the nucleus.

5.13 Conclusion:

Certain conclusions derived from the results described above bring the quantum mechanical harmonic oscillator into sharp contrast with the classical oscillator. In the first place, the energy of the former is quantized as in the case of particle in a box, and the energy levels are given by a vibrational quantum number. The energy of the classical harmonic oscillator on the other hand, is continuous. The occurrence of the vibrational energy levels is responsible for the vibrational spectra of molecules which the classical treatment could not explain.

The lowest energy (the zero point energy) of a quantum mechanical harmonic oscillator is $\frac{1}{2} h\nu$, while that of classical harmonic oscillator is zero (no zero point energy). This means that molecular vibrations around equilibrium bond distances will never stop, not even at absolute zero of temperature. This behavior is again similar to that of a particle in a box having infinite walls. In fact, the existence of zero point energy is characteristic of any quantum mechanical system executing to and fro motion.

Wave function (ψ and ψ^2) reveal still more interesting features. Probability calculations so that in the ground state, the most probable position of quantum harmonic oscillator is at the equilibrium point, while for a classical harmonic oscillator it lies at the maximum displacement points. The distinction gradually disappears as the quantum number increases i.e., in the excited states, when the points of maximum probability even for the former shift more and more towards the classical turning points, reaching these in the limiting case. This again is similar to the case of particle in a box.

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