

Quantum mechanics is a branch of science which deals with the study of various theoretical and mathematical relationships between energy and matter. Now-a-days all branches of sciences cannot develop without the knowledge of quantum mechanics.

The development of quantum mechanics began in the early 20th century, when scientists started studying atomic and molecular phenomena and discovered that Newtonian/classical mechanics and wave theory of light did not explain the results of their experiments. Classical mechanics based on Newton's law of motion and Maxwell's wave theory was able to explain phenomenon related to large objects. However, it fails when applied to small particles such as electrons, atoms, molecules, etc. (microscopic particles). For example, according to classical mechanics, it should be possible to determine simultaneously the position and velocity (or momentum) of a moving particle, but this is contracted by Heisenberg uncertainty principle. Similarly classical mechanics assumes that the energy is emitted or absorbed continuously whereas the Planck's quantum theory postulates that energy is not absorbed or emitted continuously, but discontinuously, in the form of packets of energy called photon or quanta. Further the concept of quantum numbers was introduced arbitrarily to explain the atomic spectra. A few phenomenon for which the classical mechanics fails to give the satisfactory explanation are: black body radiation, photoelectric effect, heat capacities of solids and atomic and molecular spectra.

⇒ In view of the failure of classical mechanics to explain the phenomenon associated with microparticles (electrons, atoms, molecules), a new mechanics has been put forward to explain these phenomenon. One of these is called the *Matrix Mechanics* put forwarded by Heisenberg in 1925. It is purely mathematical and does not assume any atomic model. The other is called the *Wave Mechanics* put forwarded by Schrodinger in 1926. It is based on the de Broglie concept of dual character of matter and thus takes into account the particle as well as wave nature of material particles. However, it has been shown that both the mechanics are essentially equivalent so far as the basic physical concepts are concerned. Wave mechanics being comparatively simpler and more useful in application to chemistry, and will be discussed here. It is also called *Particle Mechanics* or *Quantum Mechanics* because it deals with the problems that arise when particles such a electrons, atoms, nuclei, molecules etc. are subjected to force. Thus quantum mechanics taken into consideration of de Broglie concept of dual nature of mater and Planck's quantum theory and is able to explain the phenomenon related to small particles. Some of the important applications of quantum mechanics are:

- (i) It enables scientists to calculate energy levels and other properties of atoms and molecules.
- (ii) It helps to understand the periodic variations in properties like ionization potential, electronaffinity, atomic size etc.
- (iii) It helps to understand the nature of chemical bonding in molecules.
- (iv) The energy levels, bond lengths and bond angles can be calculated quite accurately for many molecules. The increasing power of computers has made these calculations more and more accurate.

- (v) Quantum mechanical principles together with symmetry idea of molecules can help to predict that whether a molecule has dipole moment or not.
- (vi) Quantum mechanics also provides the basis for understanding the results of spectroscopic measurements. Spectroscopy is useful for the identification of molecules and determination of their concentration and is especially important in physical chemistry because it yields information about molecules properties. Microwave and infrared spectroscopy yield information about bond length and bond angles. IR and Raman spectroscopy yield information about vibrational frequencies of the molecules. UV-visible spectroscopy provides information on dissociation energies, bond energies and electronic excited states.
- (vii) It also connects properties of individual atoms, molecules with the thermodynamics properties of bulk matter through statistical mechanics or chemical statistics or quantum statistics using information obtained from spectroscopic method.

A comparison of classical mechanics and quantum mechanics is listed below.

Classical Mechanics	Quantum Mechanics
(i) It deals with the study of macroscopic objects, e.g. planets, stars etc.	(i) It deal with the study of microparticles, e.g., electrons, atom, molecule etc.
(ii) It is based as Newton's law of motion.	(ii) It is based on Schnodineger wave equation.
(iii) It is based on only on the particle nature of the object.	(iii) It is based on the dual nature of the object.
(iv) It puts no limitation in the accuracy for measuring any observable	(iv) It has certain limitations on the measurement of observable.
(v) In classical mechanics everything can be measured with 100% accuracy.	(v) In quantum mechanics, we cannot measure everything with 100% accuracy.
(vi) Two obserables can be measured simultaneously e.g. position and momentum.	(vi) Two observable cannot be measured simultaneously.
(vii) According to classical mechanics energy is absorbed or emitted in a continuous fashion.	(vii) In quantum mechanics, energy is no longer a continuous function.
(viii) Classical mechanics is a complete definite theory in the sense that the computational procedure do not introduce any statistical uncertainties into the system.	(viii) It is not a complete definite statistical theory. No result is definite rather most probable.

Classical Mechanics	Quantum Mechanics
(ix) Th classical mechanics cannot be generally extended down to atom realm (state)	(ix) It can be used to calculate properties of gross system where classical mechanics is valid, through the efforts involved may be greater than those on the classical basis. This idea is known referred as "correspondence principle"
(x) Normally large units are used for measurement, e.g. km, kg etc.	(x) Usually small units are used e.g. Å, nm, mm, cm.
(xi) Classical mechanics fails to explain the energy-matter relationship	(xi) Quantum mechanics successful explains these relationship.
(xii) Classical mechanics deals with matter without considering the atomic or molecular structure.	(xii) Quantum mechanics can utilize the data of classical mechanics, and give an insight into reaction mechanics.
(xiii) Classical mechanics cannot deal with advanced scientific problems.	(xiii) It is the science of future and discusses many problems of both physical and medical sciences.

However, both types of mechanics use same energy units, e.g. joule, caloric etc. Like quantum mechanics, classical mechanics can explain some atomic and molecular structures using classical equation, e.g. Bohr's theory.

2.13 THE SCHRODINGER WAVE EQUATION

In 1926 Erwin Schrodinger, an Austrian Physicist developed the wave mechanical model of the atom. This model takes into account the wave and particle nature of the electron. In his model, he visualized the atom as a positively charged nucleus surrounded by a standing electron wave which extends round the nucleus.

(Schrodinger proposed that if the electron has wave-like nature, it would obey the same equation of motion as all other known types of wave obey. On the basis of this simple idea, he derived an equation which describes the wave motion of an electron wave along any of the three axes viz. x, y and z axis and is called Schrodinger Wave Equation.) This equation cannot be proved or derived. Rather, it may be taken as the starting point for a discussion of modern quantum theory. It is possible, however, to make an argument for the Schrodinger equation in the following way.

Let us consider a particle P moving with uniform angular velocity ω rad s^{-1} in a circular path of radius A, which is executing simple harmonic motion. We measure time from the instant when P passes O and then after a time t second, we

imagine P to have described an angle $\theta = \omega t$ radians. The variation of displacement with time can be represented by a simple harmonic wave as shown in Fig. 2.9.

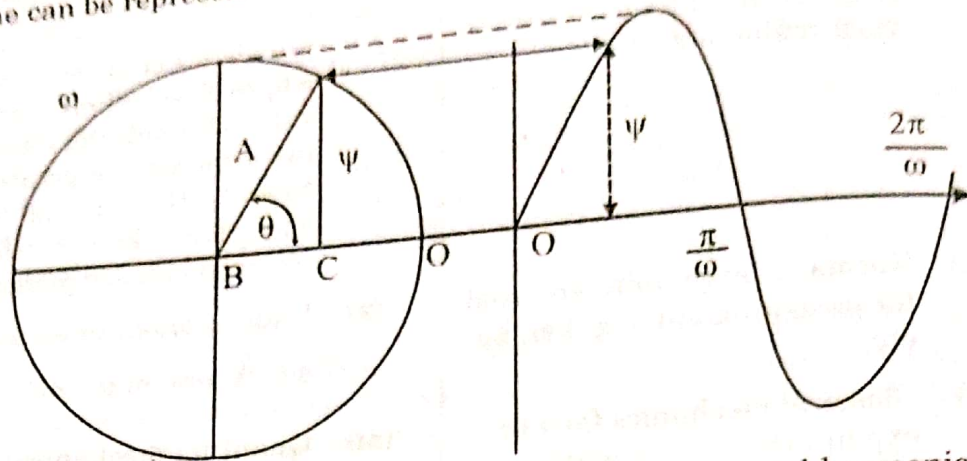


Fig. 2.9 The representation of simple harmonic motion and harmonic wave

A simple harmonic wave may be produced in a medium by a body executing simple harmonic motion. By considering the right angled triangle PBC, we can write

$$\frac{PC}{PB} = \frac{\Psi}{A} = \sin \theta$$

$$\Psi = A \sin \theta = A \sin \omega t \quad (\because \theta = \omega t)$$

2.35

Where Ψ (pronounced a psi) represents the vertical displacement of the harmonic wave. We can plot this displacement against time as on the right hand side of Fig. 2.9

The angle velocity, $\omega = 2\pi\nu$

Where ν is the frequency

$$\Psi = A \sin 2\pi\nu t \quad (2.36)$$

In order to consider the nature of progressive waves, we are more interested in the distance variation of displacement. For this purpose we need the fundamental distance — time relationship.

$$x = vt$$

(2.37)

Where x is distance covered in time t at speed v .

Combining Equation (2.35) and Equation (2.36), we have

$$\Psi = A \sin \frac{2\pi\nu x}{v} \quad (\because t = x/v) \quad (2.38)$$

and wave is shown in Fig. 2.10

$$\begin{aligned} t &= \frac{\theta}{\omega} \\ \theta &= 2\pi \\ \text{or } t &= \frac{2\pi}{\omega} \\ \nu &= \frac{1}{t} \\ \nu &= \frac{\omega}{2\pi} \\ \omega &= 2\pi\nu \end{aligned}$$

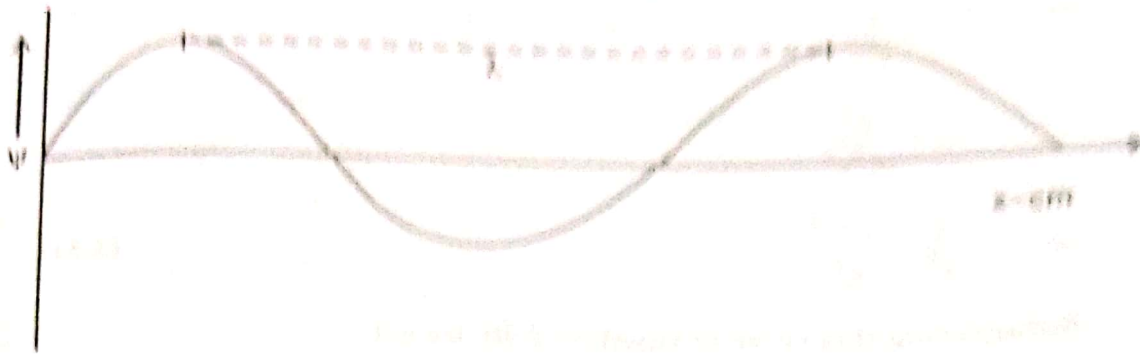


Fig. 2.10 The concept of progressive wave with wavelength λ .

Besides the frequency ν , we now have another property by which we can characterize the wave \rightarrow its wavelength λ , which is the distance traveled during a complete cycle.

$$\nu = \frac{v}{\lambda} \quad (\because v = \nu\lambda)$$

So, we have

$$\Psi = \Lambda \sin \frac{2\pi x}{\lambda} \tag{2.39}$$

On differentiating Equation (2.39) with respect to x , we get

$$\begin{aligned} \frac{d\Psi}{dx} &= \left(\Lambda \cos \frac{2\pi x}{\lambda} \right) \left(\frac{2\pi}{\lambda} \right) \\ &= \frac{2\pi}{\lambda} \Lambda \cos \frac{2\pi x}{\lambda} \end{aligned}$$

Differentiating again, we get

$$\begin{aligned} \frac{d^2\Psi}{dx^2} &= \frac{2\pi\Lambda}{\lambda} \left(-\sin \frac{2\pi x}{\lambda} \right) \left(\frac{2\pi}{\lambda} \right) \\ &= \frac{-4\pi^2}{\lambda} \left(\Lambda \sin \frac{2\pi x}{\lambda} \right) \\ &= \frac{-4\pi^2}{\lambda} \Psi \quad \left(\because \Psi = \Lambda \sin \frac{2\pi x}{\lambda} \right) \end{aligned}$$

or
$$\frac{d^2\Psi}{dx^2} + \frac{4\pi^2}{\lambda^2} \Psi = 0 \tag{2.40}$$

This is the classical wave equation describing the wave motion of any particle along x -axis. Since the electron is proved to have a wave character, let us assume that the same behavior is shown by electron waves. To apply this equation to a particle, λ must be replaced by the momentum of the particle using de-Broglie's relationship i.e.,

$$\lambda = \frac{h}{mv}$$

$$\lambda = \frac{h^2}{m^2 v^2}$$

$$\text{or } \frac{1}{\lambda^2} = \frac{m^2 v^2}{h^2} \quad (2.41)$$

Substituting this value in equation 2.40, we get

$$\frac{d^2 \Psi}{dx^2} + \frac{4\pi^2 m^2 v^2}{h^2} \Psi = 0 \quad (2.42)$$

In order to express this equation in terms of energy, we make use of the fact that total energy (E) is the sum of kinetic energy and potential energy (Bohr's theory).

Total Energy = Kinetic Energy + Potential

$$E = \frac{1}{2} mv^2 + V$$

$$\text{or } \frac{1}{2} mv^2 = E - V$$

$$mv^2 = 2(E - V)$$

$$v^2 = \frac{2(E - V)}{m}$$

Substituting this value of v^2 in equation 2.42, we get

$$\frac{d^2 \Psi}{dx^2} + \frac{8\pi^2 m}{h^2} (E - V) \Psi = 0 \quad (2.43)$$

This is the wave equation when the particle is moving in one dimensional system, i.e., the wave is moving in one direction x. For electrons which can have their wave motion along any of the three, axes, x, y, z, we can similarly write the wave equation as

$$\frac{\partial^2 \Psi}{\partial x^2} + \frac{\partial^2 \Psi}{\partial y^2} + \frac{\partial^2 \Psi}{\partial z^2} + \frac{8\pi^2 m}{h^2} (E - V) \Psi = 0 \quad (2.44)$$

or simply

$$\nabla^2 \Psi + \frac{8\pi^2 m}{h^2} (E - V) \Psi = 0 \quad (2.45)$$

where ∇^2 (de squared) is known as the *Laplacian operator*.

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

Equation 2.43, 2.44 and 2.45 are different forms of the Schrodinger wave equation.

Equation 2.45 can be written in another way as

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

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

Multiply this equation by $\frac{h^2}{8\pi^2 m}$

$$\frac{h^2}{8\pi^2 m} \nabla^2 \Psi = -E\Psi + V\Psi$$

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

$$\text{or } E\Psi = \left(-\frac{h^2}{8\pi^2 m} \nabla^2 + V \right) \Psi$$

$$\text{or } H\Psi = E\Psi$$

(2.46)

where $H = -\frac{h^2}{8\pi^2 m} \nabla^2 + V$, and is known as Hamiltonian operator. It represents a certain way of expressing the total energy of a system and E is the numerical value of that energy.

Applications of Schrodinger Wave Equation

Important applications of the equation are:

- (i) This equation is used to calculate the energy and wave function of a particle such as electron in a one-dimensional box.
- (ii) This equation is used to calculate the energy and wave function of particle in a three dimensional box.
- (iii) This equation introduces the concept of degeneracy in atomic orbitals.
- (iv) This equation has been used to derive an expression for an electron in H-atom.
- (v) This equation has been used to derive various quantum numbers which represent the postal address of an electron in an atom.
- (vi) This equation has been used to calculate the energy of π -electrons in conjugated systems like benzene.
- (vii) This is also used to calculate the resonance energy of molecules.

2.14 THE INTERPRETATION OF WAVE FUNCTION (Ψ)

The wave function Ψ is a sort of an *amplitude function*. In the case of a light wave, the intensity of a light at any point is proportional to the square of the amplitude of wave at that point. In terms of light quanta or photon $h\nu$, the more intense the light at any place, the more photons are falling on that place. This fact can be expressed in another way by saying that the greater the value of amplitude of a light wave in any region the greater is the probability of a photon being within that region.

Ψ being a mathematical function has no physical meaning by itself. Max Born suggested in 1927 that the product Ψ^2 does have physical meaning, since it gives the probability of finding the particle (or the product of the wave function Ψ and its complex conjugate Ψ^* is a probability density). The probability of finding the electron in space is not given by Ψ only, even though Ψ is considered to be a complete function which has a real value and always zero or positive. The complex conjugate of Ψ is obtained by changing i to $-i$ everywhere in Ψ . If the behaviour of the electron is represented by a wave equation, we can equate the square of the function with either (a) the electron density and (b) the probability that the electron will be found in a given volume element, we thus get a physical significance for the function $\Psi(x, y, z)$ in that

$$\Psi^2 \cdot dx \cdot dy \cdot dz (= \Psi^2 dv)$$

measures the probability that the electron will be found in the volume element dv surrounding the point whose coordinates are (x, y, z) .

The other interpretation $\Psi^2 dv$ represents the electron density in the volume element dv cannot be justified so vigorously as the probability interpretation, but it has proved to be very useful in practice. But difficulties arise when applied to single electron system.

The probability density at some point multiplied by a differential is the probability that a particle will be found there. For example, if a particle can move along the x -axis and has a wave function $\Psi(x)$, then

$$\text{the probability density, } f(x) = \Psi^*(x) \Psi(x).$$

The probability that the particle is between x and $x + dx$ is

$$f(x)dx = \Psi^*(x) \cdot \Psi(x) \cdot dx$$

The probability that it is between x_1 and x_2 is

$$\int_{x_1}^{x_2} \Psi^*(x) \cdot \Psi(x) dx$$

The probability that the particle is between $x = -\infty$ and $+\infty$ is of course, unity

$$\int_{-\infty}^{+\infty} \Psi^*(x) \cdot \Psi(x) dx = 1$$

When the integral of the wave function times its complex conjugate over the entire space available is equal to unity, the wave function is said to be *normalized*.

In calculating probability densities, the wave function is multiplied by its complex conjugate so that the probability density is always real and positive. The function Ψ as a matter of fact may involve an imaginary part i.e. Ψ may be a complex quantity.

$$\text{Let } \Psi = a + ib$$

where a is real quantity and b is an imaginary part.

Then its complex conjugate

$$\Psi^* = a - ib$$

where i (iota) is an imaginary part.

These two values of Ψ and Ψ^*

$$\therefore i^2 = -1$$

$$i = \sqrt{-1}$$

may be imaginary, in order to get a real quantity we multiply them

$$\Psi\Psi^* = (a + ib)(a - ib) = a^2 - (ib)^2$$

$$= a^2 + b^2$$

$$\text{or } |\Psi|^2 = a^2 + b^2$$

$$\text{or } \Psi^2 = a^2 + b^2$$

Strictly speaking that Ψ^2 should be the square of the absolute value of the wave function i.e. $|\Psi|^2$. However most of the wave functions in atomic or molecular structural problems contain real terms only, and so Ψ^2 may be employed.

✓ "The quantity Ψ^2 tells us where the particle/electron is likely to be (not where it is)."

A wave function not only contains the information about where a particle may be located, but it contains all the information that can be learned about the system this is represented by the wave function. Other physical quantities can be obtained from wave function.

Since $\Psi\Psi^*$ is a probability density, a wave function must have certain general properties.

or

The physical interpretation of the wave function as a probability amplitude implies that it must obey certain mathematical conditions.

Following are the mathematical requirements which must be met by physically acceptable wave functions.

1. The wave function must be *normalized*, the integral of $\Psi\Psi^*$ over all the space is unity, since the particle must exist somewhere in that interval if it is to exist at all.

$$\int_{-\infty}^{+\infty} \Psi\Psi^*(x) dx = 1$$

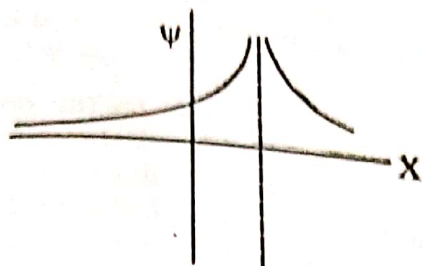
$$\text{or} \quad \int_{-\infty}^{+\infty} \Psi(x)\Psi^*(x) dx = 1$$

2. $\Psi(x)$ and $\frac{d\Psi(x)}{dx}$ must be everywhere *single-valued*. It must be single-valued because the probability of finding the electron at any point must have only one value. If the Ψ were double-valued, there would be two probabilities for the same position which would be physically meaningless.
3. $\Psi(x)$ and $\frac{d\Psi(x)}{dx}$ must be *everywhere finite*. It cannot be infinite at any point, for then the electron would be fixed at exactly that point which would be *inconsistent* with its wave properties or Ψ cannot become infinite since that would correspond to certainty of particle being at some definite points.
4. $\Psi(x)$ and $\frac{d\Psi(x)}{dx}$ must be everywhere *continuous*. The reason for that is that certain properties (e.g. momentum) are calculated by taking the derivatives of the wave function. If the wave function is discontinuous at some point. Its first derivative is infinite at this point. But values of physical properties cannot be infinite, so the wave function cannot be discontinuous. Moreover the requirement of continuity is helpful in the selection of physically reasonable solutions for the wave equation.

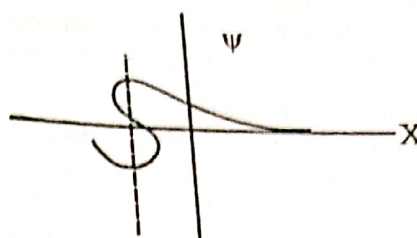
Because of these limitations only certain solutions of Schrodinger equation are of physical interest.

A discontinuous Ψ cannot correspond to a physically acceptable situation, because it leads to finite derivative infinite.

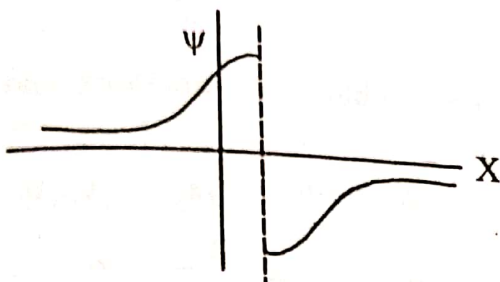
The wave function Ψ gives information on the outcome of a measurement of any property, not just position, e.g. momentum, energy and angular momentum. Ψ is not to be thought of as a physical wave. Instead Ψ is an abstract mathematical entity that gives information about the state of a system. Everything that can be known about the system in a given state is contained in the state function Ψ . Instead of saying "the state described by the function Ψ " we can just as well say "the state Ψ ." The information given by Ψ is the probabilities of the possible outcomes of measurements of the systems, physical properties.



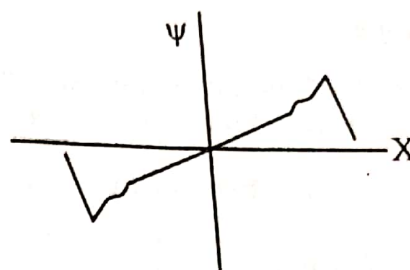
(a) This function becomes infinite at certain value of x



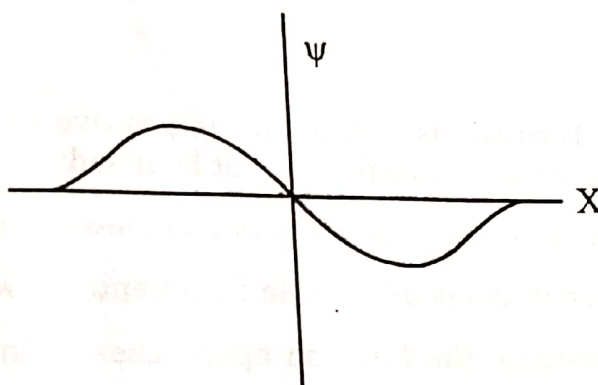
(b) This function is not single valued at every position over the allowed range of x



(c) This function is not everywhere continuous



(d) This function has discontinuous derivative at each cusp.



(d) This meets all the requirements and hence is acceptable.

Fig.2.11. Example of the wave functions that do and do not meet requirement, for physically acceptable solutions.

2.15 STATIONARY STATES

In quantum mechanics, the state of a system is specified by the wave function $\Psi(x, y, z, t)$ which is a function of both the space coordinate and the time coordinate. This function contains all the information necessary for our purpose and is not directly measurable, in contrast to classical concepts. If the probability density function $\Psi\Psi^*$ does not change with time, then such states are known as stationary.
This is in the stationary states.

$$|\Psi(x,y,z,t)|^2 = |\Psi(x,y,z)|^2$$

The stationary state in the quantum mechanics is the counterpart of the state of standing wave in classical mechanics. When a particle is described by such a wave function its energy has a definite value.

Since most of the physical properties of a system depend on the probability density, we could specify the state of the system by $\Psi(x, y, z)$ which depends only on the space coordinates. The wave equation which is independent of the time coordinate, represents the stationary state of the system and will also be known as Schrodinger time-independent equation. This equation contains two unknowns, (i) the allowed energy, E and (ii) the allowed wave function, Ψ . In order to solve the Schrodinger equation for a problem, it is necessary to introduce certain boundary conditions for a well-behaved function.

Example 2.5

Which of the following expressions are acceptable wave functions, and which are not? For those which are not, state why?

- (i) $\Psi = x^2 + 1$, where x can be any value
- (ii) $\Psi = \pm \sqrt{x}$, $x \geq 0$
- (iii) $\Psi = \frac{1}{\sqrt{2}} \sin \frac{x}{2}$, $-\frac{\pi}{2} \leq x \leq \frac{\pi}{2}$
- (iv) $\Psi = \frac{1}{4-x}$, $0 \leq x \leq 10$
- (v) $\Psi = \frac{1}{4-x}$, $0 \leq x \leq 3$

Solution

- (i) Not acceptable, because as x approaches positive or negative infinity, the function also approaches infinity. It is not bounded.
- (ii) Not acceptable because the function is not single-valued.
- (iii) Acceptable because it meets all criteria for acceptable wave functions.
- (iv) Not acceptable, because the function approaches infinity for $x = 4$, which is part of the range.
- (v) Acceptable, because the function meets all criteria for acceptable wave functions, within the stated range of variable x .

2.16 SOLUTION OF SCHRODINGER WAVE EQUATION TO PARTICLE IN A BOX

This is simplest application of Schrodinger wave equation (SWE) to the translational motion of a particle (electron, atom or molecule) in space. The results obtained can explain as to why the energies are quantized, i.e. can have only discrete values unlike the classical mechanics according to which energies associated with the motion of a particle can vary continuously, i.e., can have any value. Such a model, usually called 'the particle in a box' model serves as the simplest case for the treatment of bound electrons in atoms and molecules.

Suppose that we have a particle of mass m confined in a one-dimensional box of length L . For simplicity, we assume that the potential energy of the particle is zero

inside the box; it has only kinetic energy. At each end of the box there is an infinite potential wall so that there is no probability of finding the particle outside the box. The model is shown in the figure 2.12.

The Schrodinger wave equation in one dimension is given by

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

Inside the box $V = 0$

Therefore,

$$\frac{d^2\Psi}{dx^2} + \frac{8\pi^2m}{h^2} E \Psi = 0 \quad (2.47)$$

$$\text{Let } \lambda^2 = \frac{8\pi^2m}{h^2} E \quad (2.48)$$

Where λ is a constant, and is independent of x .

$$\frac{d^2\Psi}{dx^2} + \lambda^2 \Psi = 0 \quad (2.49)$$

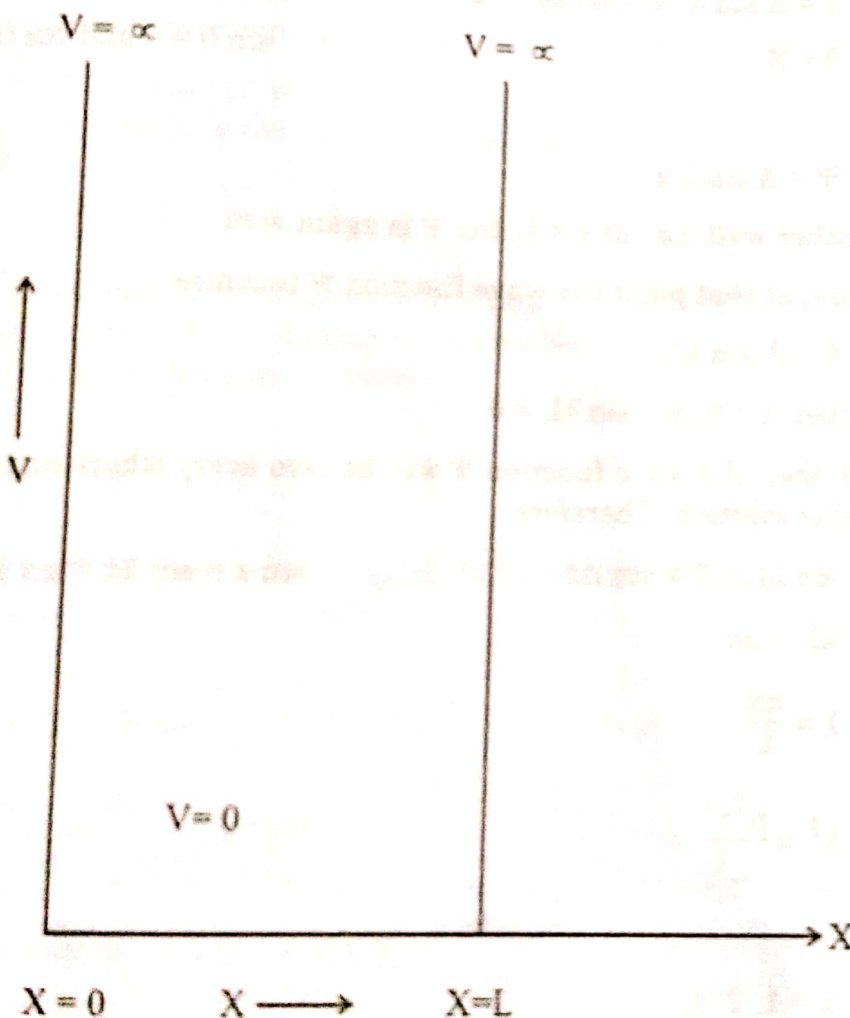


Fig. 2.12 One dimensional box with infinite potential barriers

Equation 2.41 is a second order differential equation. The general solution of the equation is

$$\Psi = A \sin \lambda x + B \cos \lambda x \quad (2.50)$$

Where A and B are two arbitrary constants. The values of these constants can be determined by applying the boundary conditions. One of the boundary conditions on our wave function is that they wave function must be a continuous function of the x . Since the wave function Ψ is zero outside the box, there should be no sudden changes in the values of Ψ at the walls of the box. Therefore, Ψ must be zero at $x = 0$ and $x = L$.

$$\Psi = 0$$

$$\Psi = A \sin \lambda x + B \cos \lambda x$$

$$\Psi = 0$$

$$x < 0$$

$$0 \leq x \leq L$$

$$L < x$$

Moreover, the wave function is normalizable because it is nonzero only in the finite interval $0 \leq x \leq L$ and it is finite every where within the interval.

Now apply the boundary conditions.

- (i) When $x = 0$, then equation 2.50 becomes

$$0 = A \sin \lambda \cdot 0 + B \cos \lambda \cdot 0$$

$$0 = B$$

$$(\because \sin 0 = 0 \text{ and } \cos 0 = 1)$$

Thus

$$\Psi = A \sin \lambda x$$

$$(2.51)$$

- (ii) At the other wall, i.e., at $x = L$, the Ψ is again zero.

Therefore, at that point the wave function Ψ becomes

$$0 = A \sin \lambda L$$

$$(2.52)$$

Now either $A = 0$ or $\sin \lambda L = 0$

If $A = 0$, then the wave function Ψ will be zero every where and this is not an acceptable solution. Therefore

$$\sin \lambda L = 0 = \sin n\pi$$

$$(\sin \pi = \sin 2\pi = \sin 3\pi = 0)$$

$$\lambda L = n\pi$$

or $\lambda = \frac{n\pi}{L}$

$$\lambda^2 = \frac{n^2 \pi^2}{L^2}$$

$$(2.53)$$

Where

$$n = 1, 2, 3, \dots$$

Comparing this value of λ^3 with the value given by equation 2.48,

$$\frac{8n^2 m}{h^2} E = \frac{n^2 \pi^2}{L^2}$$

$$E = \frac{n^2 h^2}{8mL^2} \quad (2.54)$$

Where E is the energy for n th level. A particle moving between two points on a line can have only the energies given by this equation for integer values of n , i.e., the energy is quantized. No such discrete energy levels are expected on the basis of classical mechanics.

A particle in a box cannot have zero energy because the lowest energy $\frac{h^2}{8mL^2}$ is obtained by substituting $n = 1$ in equation 2.54, and this energy is known as *zero point energy*.

$$E_{\text{zero point}} = \frac{h^2}{8mL^2} \quad (2.55)$$

This shows that the particle inside the box is not at rest. Therefore the position of the particle cannot be precisely known. Although $n = 0$ satisfies the boundary conditions, the corresponding wave function is zero everywhere.

Each of the energy values E has a corresponding wave function Ψ that is obtained by substituting the value of λ into Equation (2.51)

$$\Psi = A \sin \frac{n\pi}{L} x \quad (2.56)$$

The next step is to determine A . Since the particle must remain inside the box, the total probability of finding the particle between $x = 0$ and $x = L$ must be unity. This *normalization* process gives

$$\int_0^L \Psi^2 dx = 1$$

Where $\Psi^2 dx$ represents the probability of finding the particle between x and $x + dx$. We write

$$\int_0^L \left(A \sin \frac{n\pi x}{L} \right)^2 dx = 1$$

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

But $\sin^2 \theta = 1/2 (1 - \cos 2\theta)$

So $\frac{A^2}{2} \int_0^L \left(1 - \cos \frac{2n\pi x}{L} \right) dx = 1$

$$\text{or } \frac{A^2}{2} \left(\int_0^L dx - \int_0^L \cos \frac{2n\pi x}{L} x \cdot dx \right) = 1$$

$$\text{or } \frac{A^2}{2} \left(x - \frac{L}{2n\pi} \sin \frac{2n\pi}{L} x \right)_0^L = 1 \quad \left(\because \int \cos ax \cdot dx = \frac{1}{a} \sin ax \right)$$

$$\text{or } \frac{A^2}{2} \left(L - \frac{L}{2n\pi} \sin 2n\pi \right) = 1$$

Where n is an integer, the second term in the bracket contains the sine of angles that are integral multiples of 2 radians. Hence the above expression becomes

$$(\because \sin n\pi = 0)$$

$$\frac{A^2}{2} [L - 0] = 1$$

$$A = \sqrt{2/L}$$

Thus the normalized wave function of a particle in a one-dimensional box is given by

$$\Psi = \sqrt{\frac{2}{L}} \sin \frac{n\pi x}{L} \quad (2.57)$$

The probability of finding the particle at a particular value of x is given by

$$\Psi^2 = \frac{2}{L} \sin^2 \frac{n\pi}{L} x \quad (2.58)$$

Plots of the allowed energy levels as well as Ψ and Ψ^2 are shown in Figure 2.13.

Some important results are mentioned below.

1. The (kinetic) energy of the particle is quantized according to Equation 2.55. Only certain energies are allowed for a particle in a one-dimensional box of length L .
2. The lowest energy level is not zero but is equal to $\frac{h^2}{8mL^2}$. This zero point energy can be accounted for by the Heisenberg uncertainty principle. If the particle could possess zero energy, its velocity would also be zero, consequently, there would be no uncertainty in determining its momentum i.e., $\Delta p = 0$. But with $\Delta p = 0$, the equation of law indicates that Δx would be infinite, so the particle could not be located within the box which is against the principle.
3. Depending on the value of n , the wave behavior of the particle is described by Equation 2.57, but the probability is given by Ψ^2 , which is always positive. For $n = 1$, the maximum probability is at $x = \frac{L}{2}$, for $n = 2$, the maximum occurs at $x = \frac{L}{4}$ and $x = \frac{3L}{4}$. In the latter cases the probability is zero at $x = \frac{L}{2}$.

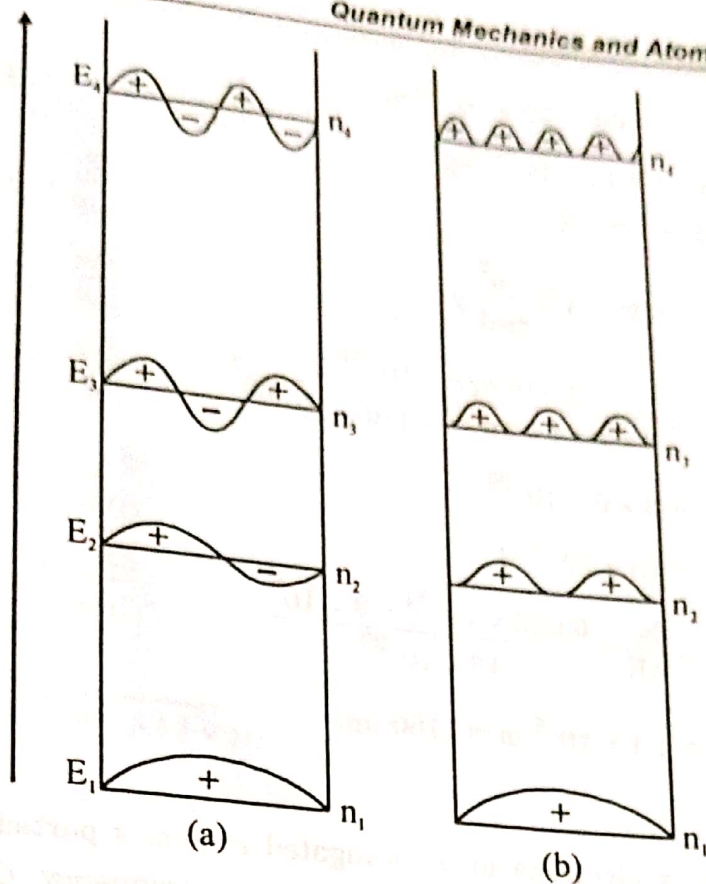


Fig. 2.13 Plots of (a) Ψ and (b) Ψ^2 for the first four energy levels in a one-dimensional box

The point at which Ψ (and hence Ψ^2 is zero is called *node*. Generally the no. of nodes increases with energy. In classical mechanics the probability of finding the particle is the same along the box, irrespective of its energy.

4. As we go higher energy levels with more nodes, the maxima and minima of probability curves come closer together and the variations in probability along the box ultimately becomes undetectable. For high quantum numbers, we approach the classical results of uniform probability density. This is in agreement with the *Bohr correspondence principle*. According to this principle, the quantum mechanical prediction or results approach the predictions of classical mechanics as the quantum numbers describing the system become very large.

Example 2.6

What is the wavelength of light absorbed when an electron in a linear molecule 10\AA long makes a transition for the energy level, $n = 1$ to the level $n = 2$.

Solution

$$E_n = \frac{n^2 h^2}{8mL^2}$$

Example 2.9

Butadiene molecule shows longest wave length of absorption at 210 nm. Find the length of the molecule.

Solution

In case of butadiene the longest wave length of absorption corresponds to the promotion of π electrons from $n = 2$ to $n = 3$.

$$\Delta E = E_3 - E_2 = \frac{5h^2}{8mL^2}$$

$$h\nu = \frac{5h^2}{8mL^2}$$

$$\nu = \frac{5h}{8mL^2}$$

$$\lambda = \frac{8mL^2 \cdot c}{5h} \quad \left(\therefore \lambda = \frac{c}{\nu} \right)$$

$$L^2 = \frac{5\lambda h}{8mc} = \frac{5 \times 210 \times 10^{-9} \times 6.626 \times 10^{-34}}{8 \times 9.11 \times 10^{-31} \times 3 \times 10^8}$$

$$L = 5.65 \times 10^{-10} \text{ m} = 0.565 \text{ nm}$$

Application of the Particle in -a Box Model

The problem of particle in a one-dimensional box is not merely an exercise in mathematics, it can serve as a good model for the calculation of approximate energies in the atomic and molecular systems, besides accounting for the effect of quantization.

Firstly, the model can be used to estimate the quantization effects in energy of gaseous molecules having low molecular weights at any low temperature. Secondly, the model provides basis for calculating approximate energy levels of electrons in atoms and molecules where the bound electrons may be assumed to move in "boxes" of length 1 — 10 Å. The minimum energy gap between two levels is then of the order of 10^{-18} to 10^{-20} J, which is greater than the thermal energy (kT) at ordinary temperatures. Hence, the quantization of electronic energy may be observed in atoms and molecules. Such calculations also provide satisfactory interpretation of electronic spectra of atoms and molecules. An electron in an atom or molecule can jump from a lower energy level to a higher level by absorption of light of suitable wavelength (λ) or it can jump from higher to lower level by emission of light. The wavelength of light emitted or absorbed is related to the energy gap between two levels.

$$\Delta E = \frac{hc}{\lambda} \quad (c \text{ is the velocity of light})$$

The model is suitable for explaining the electronic spectra (uv-visible) of conjugated organic molecules. Spectral data for polyenes agree fairly with the calculated values. Such linear molecules are treated as one-dimensional boxes in which the π electrons move from one end of conjugated chain to the other end.

2.17 EIGENFUNCTIONS AND EIGENVALUES

The time independent Schrodinger wave equation is usually written in the compact form

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

It belongs to the class of equations called *eigenvalue equations*. The word "eigenvalue" is a partial translation of the German word 'Eigenwert'. A full translation is "characteristic value". An eigenvalue equation has on one side an operator operating on a function, and on the other side a constant called the *eigenvalue* multiplying, the same function, which is called the *eigenfunction*. In the above equation \hat{H} represents the Hamiltonian operator, E the eigenvalue and Ψ the eigenfunction.

$$(\text{operator}) (\text{function}) = (\text{constant factor}) \times (\text{same function})$$

When a operator operates on a function and the same function is reproduced with same numerical value, then the function is called an eigenfunction and numerical value is called its eigenvalue. An equation that contains both eigenfunction and eigenvalue is called an *eigen equation*.

The SWE is the eigenvalue equation for Hamiltonian operator. The coordinate wavefunction is the eigenfunction of the Hamiltonian operator, and is often called energy eigenfunction. The eigenvalue of the Hamiltonian operator E , is the value of energy, and is called the *energy eigenvalue*. Solving an equation means finding not only the set of eigenfunctions that satisfy the equation, but also the eigenvalue that belongs to each eigenfunction. Two common cases occur. The first case is that the eigenvalue can take an any value within same range of values (a continuous spectrum of eigenvalues). The second case is that there is a discrete set of eigenvalues with the values between the members of the set not permitted (a discrete spectrum of eigenvalues). The occurrence of a discrete spectrum of eigenvalues corresponds to quantization.

In addition to satisfying the SWE, a wave function must satisfies other conditions. Since it represents a wave, we assume that it has following properties, which are generally shared by waves.

- (i) The wave function is single-valued
- (ii) The wave function is continuous, and
- (iii) The wave function is finite

These properties will lead to boundary conditions that have important consequences.

Example 2.10
Which of the following operator/function combinations would yield eigenvalue equations? What are eigenvalues of the eigenfunctions?

(i) $\frac{d}{dx}(\sin x)$

(ii) $\frac{d}{dx}(\cos x)$

(iii) $\frac{d}{dx}(e^{ax})$

(iv) $\frac{d}{dx}(e^x)$

(v) $\frac{d^2}{dx^2}\left(\cos \frac{x}{4}\right)$

(vi) $\frac{d}{dx}(e^{-4x})$

(vii) $\frac{d}{dx}(e^{-4x^2})$

(viii) $\frac{d^2}{dx^2}(\sin 4x)$

(xi) $\frac{d^n}{dx^n}(e^{ax})$

(x) $\frac{d}{dx}(5x^3)$

Solution

(i) $\frac{d}{dx}(\sin x) = \cos x$

This is not an eigenequation as function $\sin x$ is not generated.

(ii) $\frac{d}{dx}(\cos x) = -\sin x$

This is not an eigenequation as function $\cos x$ is not generated.

(iii) $\frac{d}{dx}(e^{ax}) = a \cdot e^{ax}$

This is an eigen equation with an eigenvalue of a .

(iv) $\frac{d}{dx}(e^x) = 1 \cdot e^x$

This is eigen equation with an eigenvalue of 1.

(v) $\frac{d^2}{dx^2}\left(\cos \frac{x}{4}\right) = -\frac{1}{16} \cos \frac{x}{4}$

This is an eigenvalue equation with an eigenvalue of $-1/16$.

(vi) $\frac{d}{dx}(e^{-4x}) = -4(e^{-4x})$

This is an eigenvalue equation with an eigenvalue of -4 .

(vii) $\frac{d}{dx}(e^{-4x^2}) = -8x(e^{-4x^2})$

This is not an eigenvalue equation because although the original function is reproduced, it is not multiplied by a constant, it is multiplied by another function $-8x$.

$$(viii) \quad \frac{d^2}{dx^2} (\sin 4x) = \frac{d}{dx} (4 \cos 4x) = -16 \sin 4x$$

This is an eigenvalue equation with an eigenvalue of -16 .

$$(ix) \quad \frac{d^n}{dx^n} (e^{\alpha x}) = \alpha^n e^{\alpha x}$$

This is an eigenvalue equation with an eigenvalue of α^n .

$$(x) \quad \frac{d}{dx} (5x^3) = 3 \cdot 5 \cdot x^2 = 15x^2$$

This is not an eigenvalue equation as the function is not reproduced.

2.18 NORMALISATION OF WAVE FUNCTIONS

According to Born the probability of finding a particle is represented by $\Psi\Psi^*$ $dx dy dz$ in a volume element $dxdydz$. If the probability for a particle having wave function Ψ were evaluated over the entire space in which the particle exists, then the probability should be equal to 1 or 100%. Mathematically it can be stated as

$$\int_{-\infty}^{+\infty} \Psi\Psi^* dxdydz = 1$$

$$\text{or} \quad \int_{-\infty}^{+\infty} \Psi\Psi^* d\tau = 1 \quad (2.59)$$

(where $d\tau = dxdydz$ is small volume element).

Where the integral of the wave function times its complex conjugate over the entire space available is equal to unity, then the wave function is said to be normalised and this condition is known as normalisation of wave function. The limits $-\infty$ and $+\infty$ are conventionally used to represent "all space" although the entire space of a system may not actually extend to infinity in both directions. The integral must be equal to unity since the particle must exist somewhere in that interval if it is to exist at all. For one dimension the above equation can be written as

$$\int_{-\infty}^{+\infty} \Psi\Psi^*(x) dx = 1 \quad (2.60)$$

The SWE is a homogenous differential equation whose solution gives a value for Ψ . Very often Ψ is not a normalised wave function. But it can be shown that multiplication of a wave function Ψ by any constant A is also a solution to the wave equation.

Let us assume that a wave function for a system exists and is $\Psi(x) = \sin(\pi x/2)$ where x is the only variable. If the region of interest is from $x = 0$, to $x = 1$, then

normalisation of wave function is carried out as below.

According to equation (2.59) the function must be multiplied by some constant so that

$$\int_0^1 \Psi \Psi^* dx = 1$$

Note that the limits are 0 to 1, not $-\alpha$ to $+\alpha$ and that $d\tau$ is simply dx for this one-dimensional example. Let us assume that Ψ is multiplied by some constant A .

$$\Psi \longrightarrow A\Psi$$

Substituting for Ψ into integral, we get

$$\int_0^1 (A\Psi) (A\Psi)^* dx = \int_0^1 AA^* \left(\sin \frac{\pi x}{2} \right) \left(\sin \frac{\pi x}{2} \right)^* dx$$

Since A is a constant, it can be pulled out of the integral, and since this function is a real function, the $*$ has no effect on the function.

Therefore, we get

$$\int_0^1 AA^* \left(\sin \frac{\pi x}{2} \right) \left(\sin \frac{\pi x}{2} \right)^* dx = A^2 \int_0^1 \sin^2 \frac{\pi x}{2} dx$$

Normalization requires that this expression equal 1:

$$A^2 \int_0^1 \sin^2 \frac{\pi x}{2} dx = 1$$

The integral in this expression has a known form and it can be solved and the definite interval from limits 0 to 1 can be evaluated.

$$\int \sin^2 bx dx = \frac{x}{2} - \frac{1}{4b} \sin 2bx$$

In this case $b = \pi/2$, evaluating the integral between limits,

$$A^2 \left[\frac{x}{2} - \frac{2}{4\pi} \sin^2 \frac{2\pi x}{2} \right]_0^1 = 1$$

$$A^2 \left[\frac{x}{2} - \frac{1}{2\pi} \sin^2 \pi x \right]_0^1 = 1$$

$$A^2 \left(\frac{1}{2} \right) = 1$$

$$A = \sqrt{2}$$

Hence the correctly normalized wave function is therefore

$$\Psi_{(x)} = \sqrt{2} \left(\sin \frac{\pi x}{2} \right)$$

2.19 ORTHOGONALITY OF WAVE FUNCTION

There may be many acceptable solutions to SWE $\hat{H}\Psi = E\Psi$ for a particular system. Each wave function has a corresponding energy value E . For any two wave functions Ψ_n and Ψ_m corresponding to the energy values E_n and E_m , the following condition must be fulfilled.

$$\int_{-\infty}^{+\infty} \Psi_n \Psi_m \, d\tau = 0 \quad (2.61)$$

Such a condition is called condition of Orthogonality of wave functions: the two functions Ψ_n and Ψ_m are said to be orthogonal to each other. Equation (2.61) is a general property of the wave functions. Wave functions that are solution of a given SWE are usually orthonormal to one another. They are independent of one another and the integral of their product over the whole space is zero. They are not degenerate wave functions (having same energy) and are exact solution of the wave equation.

The normalization and orthogonality conditions may be combined as follows

$$\int_{-\infty}^{+\infty} \Psi_n^* \Psi_m \, d\tau = 1, \quad \text{if } n = m$$

$$\int_{-\infty}^{+\infty} \Psi_n^* \Psi_m \, d\tau = 0, \quad \text{if } n \neq m$$

These relations can be combined by writing

$$\int_{-\infty}^{+\infty} \Psi_n^* \Psi_n \, d\tau = \delta_{nm}$$

$$\text{or} \quad \int_{-\infty}^{+\infty} \Psi_n \Psi_m^* \, d\tau = \delta_{nm} \quad (2.62)$$

where δ_{nm} is called *Kronecker delta*, which is defined by

$$\delta_{nm} = \begin{cases} 0 & \text{for } n \neq m \\ 1 & \text{for } n = m \end{cases} \quad (2.63)$$

wave functions that satisfy equation (2.63) are said to be *orthonormal*.

An exception to the Orthogonality rule occurs when two or more wave functions correspond to the same energy level. Such levels are said to be degenerate levels. Wave functions for degenerate levels are not always orthogonal to one another. However, they are orthogonal to all other wave functions, that are solutions of the same wave equation.

Example 2.11

Show that the wave functions in the following equation are orthogonal for any pair of different values of n

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

Solution

Orthogonality is a mathematical property of an eigen function. For particle in a one-dimensional box, let $n = l, m$, the two different integers. Limits are changed since the particle is confined below $0 < x < a$

$$\begin{aligned} \int_0^a \Psi_l \Psi_m dx &= \int_0^a \sqrt{\frac{2}{a}} \sin\left(\frac{l\pi x}{a}\right) \sin\left(\frac{m\pi x}{a}\right) \sqrt{\frac{2}{a}} dx \\ &= \frac{2}{a} \int_0^a \sin\left(\frac{l\pi x}{a}\right) \sin\left(\frac{m\pi x}{a}\right) dx \end{aligned}$$

Using the trigonometric relation

$$\sin \alpha \sin \beta = \frac{1}{2} [\cos(\alpha - \beta) - \cos(\alpha + \beta)]$$

$$\begin{aligned} \int_0^a \Psi_l \Psi_m dx &= \frac{2}{a} \times \frac{1}{2} \int_0^a \left[\cos\left(\frac{l\pi x}{a} - \frac{m\pi x}{a}\right) - \cos\left(\frac{l\pi x}{a} + \frac{m\pi x}{a}\right) \right] dx \\ &= \frac{1}{a} \int_0^a \left[\cos(l - m) \frac{\pi x}{a} - \cos(l + m) \frac{\pi x}{a} \right] dx \\ &= \frac{1}{a} \frac{a}{(l - m)\pi} \times \sin\left[(l - m) \frac{\pi x}{a}\right]_0^a - \frac{1}{a} \times \frac{a}{(l + m)\pi} \left[\sin(l + m) \frac{\pi x}{a} \right]_0^a \\ &= \frac{1}{\pi} \left[\frac{\sin(l - m) \pi x}{l - m} - \frac{\sin(l + m) \pi x}{l + m} \right]_0^a \\ &= \frac{1}{\pi} \left[\frac{\sin(l - m)\pi}{l - m} - \frac{\sin(l + m)\pi}{l + m} \right] \\ &= 0 \end{aligned}$$

Since the difference and the sum of the two quantum numbers l and m must be integers, the sinus of the angles are all zero and have the integral is zero.

$$\therefore \int \cos lx \cdot dx = \frac{1}{l} \sin lx$$

This integral is used in the derivation of above relationship.

This result may also be obtained by graphing the functions. Fig.21.5 the two functions and their product. The integral is the area enclosed by the integrand. Figure shows that the area is zero.

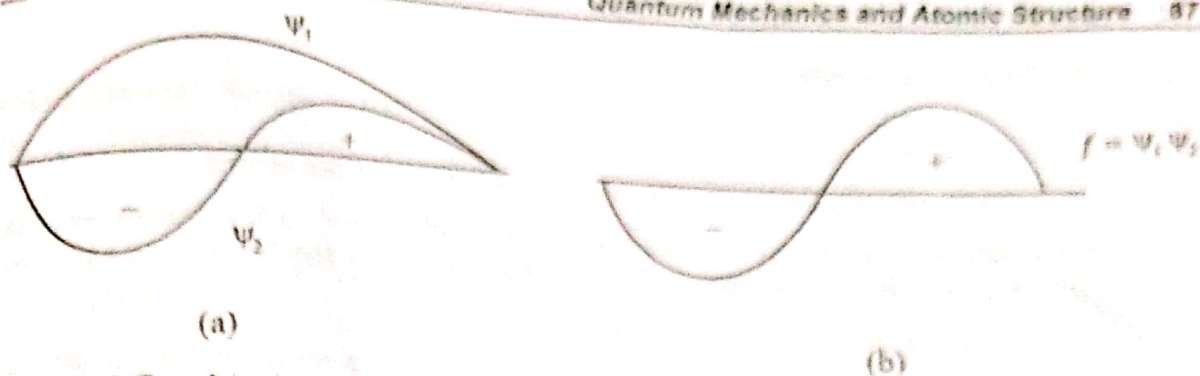


Fig. 21.5 Graphical method for verifying orthogonality of a pair of functions. (a) the first two functions of a particle in a box (b) Product of the two functions. The integral is the area under the curve in (b). Since the positive and negative parts cancel each other, the total area under the curve is zero.

2.20 OBSERVABLE AND OPERATORS

When studying the state of a system, one typically makes various measurements of its properties, such as mass, volume, position, momentum and energy. Each individual property is called an observable. An observable is any property of the system which could be measured. Since quantum mechanics postulates that the state of a system is given by a wave function, how does one determine the value of various observable (say, position or momentum, or energy) from wave functions.

The next postulates of quantum mechanics states that in order to determine the value of an observable you have to perform some mathematical operation on a wave function. This operation is represented by an *operator*.

☞ "An operator represents a mathematical rule that transforms one function into another or one vector into another".

or

☞ "An operator is an instruction to carry out certain operations".

or

"An operator is a symbol or sign that tells us to do something of what follows the symbol".

Consider some examples

(i) In the differential equation $\frac{d}{dx} \sin x = \cos x$. The operator is $\frac{d}{dx}$. If differentials the function on its right.

(ii) In the equation

$$y = \ln x$$

The \ln operator takes the natural logarithm of x , transforming into y .

(iii) In the equation

$$y = x f(x)$$

The operator x stands for the rule: multiple by x the function to the right of x . The result is a new function called .

(iv) In the matrix equation

$$\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \begin{pmatrix} 1 \\ i \end{pmatrix} = \begin{pmatrix} i \\ 1 \end{pmatrix}$$

The matrix operator transforms one vector into another vector.

Evidently an operator is a set of instructions embodied in the definition of the operator and the operations can always be written in the form of an equation

$$(\text{operator}) (\text{function}) = (\text{another function}) \quad (2.64)$$

The function on which the operation is carried out is often called an *operand*. The left hand side of Eq.(2.64) does not mean that the function is multiplied by the operator. In a sense an operator therefore does not have any meaning when it stands alone. For example $\sqrt{\quad}$ is an operator which is itself does not mean anything, but if a quantity or number put under it, it transforms that quantity into its square root, another quantity. An operator, unless it is otherwise obvious, is hereafter written with a symbol (^) overhead. Thus an operator A is symbolised by \hat{A} . Operators are extremely important in quantum mechanics because they provide the means for calculating possible measured values of observable properties of the system. It is the postulate of quantum mechanics that for any observable in classical mechanics, there is a linear quantum mechanical operator. It is further postulated that the possible measured values are the eigen values obtained from SWE. The physical significance of the eigen values of any physical quantity is, that they are the possible results of measurements of physical quantity.

Algebra of Operators

Although operators do not have any physical meaning, they can be added, subtracted, multiplied, and have some other properties.

Addition and Subtraction

The addition or subtraction of operators yields new operators, the sum or the difference of operators being defined by

$$(\hat{A} \pm \hat{B}) f(x) = \hat{A} f(x) \pm \hat{B} f(x)$$

For example, let \hat{A} be \log_e and \hat{B} be $\frac{d}{dx}$, and $f(x)$ be x ; then

$$\begin{aligned} (\hat{A} \pm \hat{B}) f(x) &= \left(\log_e \pm \frac{d}{dx} \right) x^2 = \log_e x^2 \pm \frac{d}{dx} (x^2) \\ &= 2 \log_e x \pm 2x = \hat{A} f(x) \pm \hat{B} f(x) \end{aligned}$$

Multiplication

Multiplication of two operators means operation by the two operators one after the other, the order of operation being from right to left; for example, $\hat{A}\hat{B} f(x)$

means that the function $f(x)$ is first operated on by \hat{B} to yield a new function $g(x)$ which is then operated on by \hat{A} to yield the final function $h(x)$,

$$\hat{A}\hat{B} f(x) = \hat{A}[\hat{B} f(x)] = \hat{A} g(x) = h(x)$$

For example, let \hat{A} be $4x^2$, \hat{B} be $\frac{d}{dx}$, and $f(x) = ax^3$, then

$$\hat{A}\hat{B} f(x) = 4x^2 \cdot \frac{d}{dx} (ax^3) = 4x^2 \cdot (3ax^2) = 12ax^4$$

The square of an operator means that the same operator is applied successively twice, i.e. $\hat{A}^2 f(x) = \hat{A}\hat{A} f(x)$. For example,

$$\text{let } \hat{A} = \frac{d}{dx} \text{ and } f(x) = \sin x, \text{ then } \hat{A}^2 f(x) = \left(\frac{d}{dx}\right)^2 \sin x$$

$$\text{or } \frac{d^2}{dx^2} (\sin x) = \frac{d}{dx} \left[\frac{d}{dx} (\sin x) \right] = \frac{d}{dx} (\cos x) = -\sin x$$

Commutative Property

When a series of operation are performed on a function successively the result depends on the sequence in which the operation are performed; in other words, in operator algebra it is not necessary that $\hat{A}\hat{B} f(x) = \hat{B}\hat{A} f(x)$. For example, let \hat{A} denote $\frac{d}{dx}$, \hat{B} stand for $3x^2$, and the function $f(x)$ be $\sin x$; then,

$$\begin{aligned} \hat{A}\hat{B} f(x) &= \frac{d}{dx} [3x^2, (\sin x)] = \frac{d}{dx} (3x^2 \sin x) \\ &= 6x \sin x + 3x^2 \cos x \end{aligned}$$

$$\text{and } \hat{B}\hat{A} f(x) = 3x^2 \cdot \frac{d}{dx} (\sin x) = 3x^2 \cdot \cos x = 3x^2 \cos x$$

If two operators are such that the result of their successive applications is the same irrespective of the order of operations then the two operators are said to be *commutative*. In the above example, the two operators are non commutative. Now

let \hat{A} stand for $3 +$, \hat{B} for 4 , and $f(x)$ be ax ; then,

$$\hat{A}\hat{B} f(x) = 3 + 4 + (ax) = 3 + (4 + ax) = 7 + ax$$

$$\hat{B}\hat{A} f(x) = 4 + 3 + (ax) = 4 + (3 + ax) = 7 + ax$$

Thus, \hat{A} and \hat{B} commute

Linear Operator

An operator is said to be linear if its application on the sum of two functions gives the result which is equal to the sum of the operation on the two functions separately, i.e., if,

$$\hat{A} [f(x) + g(x)] = \hat{A} f(x) + \hat{A} g(x)$$

$$\text{or } \hat{A}[Cf(x)] = C \cdot \hat{A} f(x), \text{ where } C \text{ is constant}$$

Examples

(i) $\frac{d}{dx}$ is a linear operator because $\frac{d}{dx} (ax^m + bx^n) = \frac{d}{dx} (ax^m) + \frac{d}{dx} (bx^n)$

(ii) $\sqrt{\quad}$, square root, is not a linear operator because

$$\sqrt{f(x) + g(x)} \neq \sqrt{f(x)} + \sqrt{g(x)}$$

Commutator Operator

For any two operator \hat{A} and \hat{B} , the difference $\hat{A} \hat{B} - \hat{B} \hat{A}$, which is simply denoted by $\hat{A} \hat{B} - \hat{B} \hat{A}$ or $[A, B]$ is called "commutator operator".

If \hat{A} and \hat{B} commute then $[A, B] = 0$, where 0 is called the zero operator which means multiplying a function with zero.

In the earlier example, where, $\hat{A} = \frac{d}{dx}$, $\hat{B} = 3x^2$ and $f(x) = \sin x$, the commutator is obtained as follows

$$\begin{aligned} [A, B] f(x) &= [\hat{A} \hat{B} - \hat{B} \hat{A}] f(x) \\ &= (6x \sin x + 3x^2 \cos x) - 3x^2 \cos x \\ &= 6x \sin x = 6x f(x) \end{aligned}$$

$$\text{or } [A, B] = 6x$$

The Operator ∇ and ∇^2

So far we have given the examples of simple one-dimensional operators viz. $\frac{d}{dx}$, $4x$, etc., which operate on functions of a single variable like $f(x)$ or $f(x) + g(x)$. But there may be two-or three-dimensional operators which operate on function or more than one variable, i.e., $f(x, y, z)$. Thus, the operator $\frac{\partial}{\partial x} + \frac{\partial}{\partial y} + \frac{\partial}{\partial z}$ when applied to a function f , where f stands for $f(x, y, z)$, gives the results,

$$\left(\frac{\partial}{\partial x} + \frac{\partial}{\partial y} + \frac{\partial}{\partial z} \right) f = \frac{\partial f}{\partial x} + \frac{\partial f}{\partial y} + \frac{\partial f}{\partial z}$$

A very important differential operator, known as "del" or ∇ -operator, or a vector operator, is defined as,

$$\nabla = \vec{i} \frac{d}{dx} + \vec{j} \frac{d}{dy} + \vec{k} \frac{d}{dz}$$

where \hat{i} , \hat{j} and \hat{k} are unit vectors along the x , y and z axes. This is a vector operator in the sense that when applied to a scalar function it transforms it into its gradient which is a vector.

The rules for converting a classical function to corresponding quantum mechanical operator are as follows.

1. Quantum mechanical operator corresponding to each Cartesian coordinate is the same as its classical value, for example,

$$\hat{x} = x, \hat{y} = y \text{ etc.} \quad (2.65)$$

2. Each Cartesian component of linear momentum is replaced by the operator.

$$\hat{p}_x = \frac{h}{2\pi i} \cdot \frac{\delta}{\delta x} = -\frac{i\hbar}{2\pi} \frac{\delta}{\delta x} \quad (2.66)$$

Similarly,

$$\hat{p}_y = \frac{h}{2\pi i} \cdot \frac{\delta}{\delta y} \text{ and } \hat{p}_z = \frac{h}{2\pi i} \cdot \frac{\delta}{\delta z}$$

where $i = \sqrt{-1}$. The quantity $\frac{1}{i}$ is equal to $-i$, because $i(-1) = 1$.

On the basis of these rules, operator for other quantities can be determined.

Thus the operator for energy is the Hamiltonian (\hat{H}) angular momentum is \hat{L} . These can be expressed in terms of equations (2.65, 2.66). As we know that the total energy of a conservative system in classical mechanics is represented by H and its value is equal to the kinetic energy (T) and the potential energy (V), i.e.

$$H = T + V$$

The corresponding Hamiltonian operator

$$\hat{H} = \hat{T} + \hat{V} \quad (2.67)$$

Thus the eigenvalue equation for the energy may be written as

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

Some common quantum-mechanical operators as derived from their classical expressions are shown in Table 2.1

Actually the rules given here relatively the operators to classical observable are only one of the many possible ways of constructing a set of rules. We call a given set of rules a particular representation (here the coordinates representation) of quantum mechanics. The other representation is the momentum representation.

Table 2.1 Common Quantum Mechanical Operators as Derived from their Classical Expressions

Classical Variable	Quantum Mechanical Operator	Operation
Position x	\hat{x} (similarly for the y- and z-direction)	x (multiplication)
Linear momentum p_x (x-direction)	\hat{p}_x (similarly for the y- and z-direction)	$\frac{h}{2\pi i} \left(\frac{\partial}{\partial x} \right)$
Angular momentum L_z (rotation about the z-axis)	\hat{L}_z	$\frac{h}{2\pi i} \left(\frac{\partial}{\partial \phi} \right)$
Kinetic energy T	\hat{T}	$-\frac{h^2}{8\pi^2 m} \nabla^2$
Potential energy $V(x, y, z)$	$\hat{V}(x, y, z)$	$V(x, y, z)$ (multiplication)
Total energy H (Hamiltonian)	$\hat{H} = \hat{T} + \hat{V}$	$-\frac{h^2}{8\pi^2 m} \nabla^2 + \hat{V}$

Example 2.12

Show that if all the eigen functions of two operators \hat{A} and \hat{B} are the same functions, \hat{A} and \hat{B} commute with each other. The eigen values of \hat{A} and \hat{B} are represented by a_i and b_i eigenfunctions are Ψ_i , so that

$$\hat{A} \Psi_i = a_i \Psi_i$$

and $\hat{B} \Psi_i = b_i \Psi_i$

Solution

The eigen functions of the operators $\hat{A}\hat{B}$ are obtained as follows:

$$\hat{A}\hat{B}\Psi_i = \hat{A}(\hat{B}\Psi_i) = \hat{A}b_i\Psi_i = b_i\hat{A}\Psi_i = b_i a_i \Psi_i$$

Similarly

$$\hat{B}\hat{A}\Psi_i = \hat{B}(\hat{A}\Psi_i) = \hat{B}a_i\Psi_i = a_i\hat{B}\Psi_i = a_i b_i \Psi_i$$

since $a_i b_i = b_i a_i$,

or \hat{A} and \hat{B} commute with each other.

2.21 COMPLEX NUMBERS

A complex number is one which contains $\sqrt{-1}$ or i as it is usually symbolized. Thus $A + iB$ is a complex number. We speak of the real (A) and the imaginary (B) part of a complex number. If

$$C = A + iB \quad (i)$$

then the complex conjugate of C , called C^* , is defined by replacing i wherever it appears of $-i$. Thus

$$C^* = A - iB \quad (ii)$$

The magnitude or absolute value of a complex number is defined as

$$|C| \equiv (CC^*)^{1/2} = (A^2 + B^2)^{1/2} \quad (iii)$$

Note that the magnitude of a complex number is always real. Two complex numbers are equal only if both their real and imaginary parts are equal. Addition and subtraction follow the same rules as for vectors. That is the real and imaginary parts are added independently. Thus if $Z_1 = x_1 + iy_1$ and $Z_2 = x_2 + iy_2$, then

$$Z_1 + Z_2 = (x_1 + x_2) + i(y_1 + y_2) \quad (iv)$$

An equation which will often be used in dealing with complex numbers is Euler's Formula.

$$e^{i\alpha} = \cos\alpha + i\sin\alpha \quad (2.68)$$

An equation of the above type (Euler's Formula) can be derived by expanding each of the quantities $e^{i\alpha}$, $\cos\alpha$ and $\sin\alpha$ in a Maclaurin series. By equating the power series expansions it can easily be shown that equation (v) leads to an identity.

2.22 PARTICLE IN A THREE-DIMENSIONAL BOX

We have seen that a particle moving freely in a one-dimensional box (potential energy $v = 0$) serves as a very convenient model for several types of atomic and molecular systems. Calculations, though approximate, agree fairly well with observed results. Electronic motions in atoms and molecules, are, however, three-dimensional and a three-dimensional box model should be more appropriate. Though

electron motions in atoms and molecules are complicated due to some other factors, let us see how far results of quantum-mechanical treatment of a single particle moving in a three-dimensional box are of interest.

Let us consider a particle of mass "m" moving in a three-dimensional rectangular box having sides a, b, and c along x, y and z-axis as shown in Fig.2.16. The potential energy of the particle moving inside the box will be zero. The remainder of space outside the box will have infinite potential energy. The potential energy at the boundaries of the rigid walls will also be zero in order to avoid discontinuity of the wave function, i.e.

$$V(x, y, z) = 0,$$

for $0 < x < a$, $0 < y < b$ and $0 < z < c$

$$V(x, y, z) = \infty \text{ elsewhere}$$

The Schrodinger wave equation for such a particle moving within the box is given by

$$\frac{\partial^2 \Psi}{\partial x^2} + \frac{\partial^2 \Psi}{\partial y^2} + \frac{\partial^2 \Psi}{\partial z^2} + \frac{8\pi^2 m}{h^2} E \Psi = 0 \quad (2.69)$$

$$\text{or} \quad \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) \Psi + \frac{8\pi^2 m}{h^2} E \Psi = 0$$

$$\text{or} \quad \nabla^2 \Psi + \frac{8\pi^2 m}{h^2} E \Psi = 0 \quad (2.70)$$

This is second-order particle differential equation where the wave function Ψ is a function of coordinates (x, y, z) and ∇^2 (del square) is a Laplacian operator. It is initially assumed that the wave function $\Psi(x, y, z)$ is a product of these function, each depending on just one coordinate, i.e.,

$$\Psi(x, y, z) = X_{(x)} Y_{(y)} Z_{(z)} \quad (2.71)$$

Since $\frac{\partial^2}{\partial x^2}$ has no effect on $Y_{(y)}$ and $Z_{(z)}$ and similarly $\frac{\partial^2}{\partial y^2}$ has no effect on $X_{(x)}$ and $Z_{(z)}$ etc. the differential equations for each wave function may be written as

$$\frac{\partial^2 \Psi}{\partial x^2} = YZ \frac{d^2 X}{dx^2} \quad (a)$$

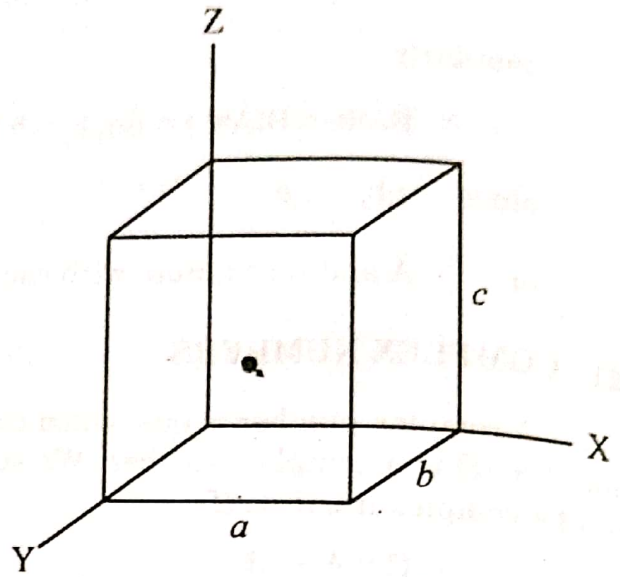


Fig.2.16 Particle in a three-dimensional box

$$\frac{\partial^2 \psi}{\partial x^2} = XZ \frac{d^2 X}{dx^2}$$

and $\frac{\partial^2 \psi}{\partial y^2} = XY \frac{d^2 Y}{dy^2}$ (b)

(c)

Substituting the values from (a), (b) and (c), into equation (2.69), we get

$$YZ \frac{d^2 X}{dx^2} + XZ \frac{d^2 Y}{dy^2} + XY \frac{d^2 Z}{dz^2} + \frac{8\pi^2 m}{h^2} EXYZ = 0$$

or $YZ \frac{d^2 X}{dx^2} + XZ \frac{d^2 Y}{dy^2} + XY \frac{d^2 Z}{dz^2} = -\frac{8\pi^2 m}{h^2} EXYZ$

Divide the above equation by XYZ, we get

$$\frac{1}{X} \frac{d^2 X}{dx^2} + \frac{1}{Y} \frac{d^2 Y}{dy^2} + \frac{1}{Z} \frac{d^2 Z}{dz^2} = -\frac{8\pi^2 m}{h^2} E \quad (2.72)$$

It is apparent that each term on the L.H.S. of equation (2.72) is a function of

only one variable and sum of these terms is equal to a constant quantity $\left(-\frac{8\pi^2 m E}{h^2}\right)$. For example, if x is varied and y and z are held constant, then second and third terms will be zero. Since the sum of these terms is a constant quantity, such a situation can exist only if the first term is equal to a constant quantity. Let this quantity or constant be $\left(-\frac{8\pi^2 m}{h^2} E_X\right)$. Similarly, the second and third terms must also be constant. This converts the partial differential equation (2.72) into these ordinary differential equations.

$$\frac{1}{X} \cdot \frac{d^2 X}{dx^2} = -\frac{8\pi^2 m}{h^2} E_X \quad (2.73(a))$$

$$\frac{1}{Y} \cdot \frac{d^2 Y}{dy^2} = -\frac{8\pi^2 m}{h^2} E_Y \quad (2.73(b))$$

$$\frac{1}{Z} \cdot \frac{d^2 Z}{dz^2} = -\frac{8\pi^2 m}{h^2} E_Z \quad (2.73(c))$$

Equation (2.73 a, b, and c) can be rearranged to give

$$\frac{d^2 X}{dx^2} + \frac{8\pi^2 m}{h^2} E_X X = 0 \quad (2.74(a))$$

$$\frac{d^2 Y}{dy^2} + \frac{8\pi^2 m}{h^2} E_Y Y = 0 \quad (2.74(b))$$

(2.74(c))

$$\frac{d^2Z}{dz^2} + \frac{8\pi^2m}{h^2} E_z Z = 0$$

It is clear from these equations that

(2.75)

$$E = E_x + E_y + E_z$$

Each of the equations (2.74a-c) is the same as the equation for one-dimensional box. Therefore, the solution of these equations may be written as

$$X = \sqrt{\frac{2}{a}} \sin\left(\frac{n_x \pi x}{a}\right) \quad (2.76-a)$$

$$Y = \sqrt{\frac{2}{b}} \sin\left(\frac{n_y \pi y}{b}\right) \quad (2.76-b)$$

$$Z = \sqrt{\frac{2}{c}} \sin\left(\frac{n_z \pi z}{c}\right) \quad (2.76-c)$$

and
$$E_x = \frac{n_x^2 h^2}{8ma^2} \quad (2.76-a)$$

$$E_y = \frac{n_y^2 h^2}{8mb^2} \quad (2.77-b)$$

$$E_z = \frac{n_z^2 h^2}{8mc^2} \quad (2.77-c)$$

where n_x , n_y and n_z are integers, excluding zero. Thus, there is a quantum for each coordinate. The total kinetic energy of particle from equations (2.77 a-c) is given by

$$E = \frac{n_x^2 h^2}{8ma^2} + \frac{n_y^2 h^2}{8mb^2} + \frac{n_z^2 h^2}{8mc^2}$$

$$E = \frac{h^2}{8m} \left(\frac{n_x^2}{a^2} + \frac{n_y^2}{b^2} + \frac{n_z^2}{c^2} \right) \quad (2.78)$$

The complete wave function for the particle is given by

$$\Psi = X_{(x)}, Y_{(y)}, Z_{(z)}$$

$$\Psi = \sqrt{\frac{2}{a}} \sin\left(\frac{n_x \pi x}{a}\right) \cdot \sqrt{\frac{2}{b}} \sin\left(\frac{n_y \pi y}{b}\right) \cdot \sqrt{\frac{2}{c}} \sin\left(\frac{n_z \pi z}{c}\right)$$

$$\Psi = \sqrt{\frac{8}{abc}} \sin\left(\frac{n_x \pi x}{a}\right) \cdot \sin\left(\frac{n_y \pi y}{b}\right) \cdot \sin\left(\frac{n_z \pi z}{c}\right)$$

or
$$\Psi = \sqrt{\frac{8}{v}} \cdot \sin\left(\frac{n_x \pi x}{a}\right) \cdot \sin\left(\frac{n_y \pi y}{b}\right) \cdot \sin\left(\frac{n_z \pi z}{c}\right)$$

$$\text{or } \Psi = \sqrt{\frac{8}{v}} \cdot \sin\left(\frac{n_x \pi x}{a}\right) \cdot \left(\frac{n_y \pi y}{b}\right) \cdot \sin\left(\frac{n_z \pi z}{c}\right) \quad (2.79)$$

The lowest (ground state) energy (E_1) corresponds to $n_x = n_y = n_z = 1$. This is also known as zero point energy. The properties of the wave functions will be same as that in one-dimensional box problem, except for nodes (in the latter) and degeneracy (in the former). Here the factor $\sqrt{\frac{8}{v}}$ is the normalization of factor or constant.

The results of particle in a three-dimensional box are of interest mainly with regard to the following points:

- (i) Unlike the classical predictions, the probability of finding the particle is not constant, but is a function of x , y and z -coordinates.
- (ii) The probability of finding the particle in a particular portion of the box depends upon the energy of the particle.
- (iii) Only certain energy levels, related to n are allowed, others are not allowed. The lowest kinetic energy is given when $n_x = n_y = n_z = 1$

$$E_{111} = \frac{3h^2}{8ma^2}$$

Example 2.13

Determine the lowest kinetic energy of a particle in a three-dimensional box of dimensions 0.1×10^{-15} m, 1.5×10^{-15} m and 2.0×10^{-15} m.

Solution

$$E = \frac{h^2}{8m} \left(\frac{n_x^2}{a^2} + \frac{n_y^2}{b^2} + \frac{n_z^2}{c^2} \right)$$

In lowest state, $n_x = n_y = n_z = 1$

$$\begin{aligned} E &= \frac{(6.626 \times 10^{-34})^2}{8 \times 9.11 \times 10^{-31}} \left[\frac{1}{(0.1 \times 10^{-15})^2} + \frac{1}{(1.5 \times 10^{-15})^2} + \frac{1}{(2.0 \times 10^{-15})^2} \right] \\ &= \frac{(6.626 \times 10^{-34})^2}{8 \times 9.11 \times 10^{-31}} \times \frac{1}{10^{-30}} \left[\frac{1}{(0.1)^2} + \frac{1}{(1.5)^2} + \frac{1}{(2.0)^2} \right] \\ &= 6.067 \times 10^{-8} \text{ J} \end{aligned}$$

2.23 DEGENERACY

In the case of particle in a one-dimensional box, the state of the particle could be specified by specifying energy of the system. All of the energies and eigen functions are different. For the general 3-D particle in a box, because the total energy depends on not only the quantum numbers n_x , n_y and n_z but also the individual dimensions of the box, a , b , and c , one can imagine that in some cases the quantum

numbers and the lengths might be such that different sets of quantum numbers (n_x , n_y and n_z) would yield the same energy of the two different wave functions.

An interesting situation arises if the box is cubical i.e., $a = b = c$, then the wave functions and energies are represented as:

$$\Psi_{(x,y,z)} = \sqrt{\frac{8}{a^3}} \sin\left(\frac{n_x \pi x}{a}\right) \sin\left(\frac{n_y \pi y}{a}\right) \sin\left(\frac{n_z \pi z}{a}\right) \quad (2.80)$$

$$E = \frac{h^2}{8ma^2} (n_x^2 + n_y^2 + n_z^2) \quad (2.81)$$

The energy depends on a set of constants and the sum of the squares quantum numbers. If a set of three quantum numbers adds up to the same total as another set of three quantum numbers, or if the quantum numbers themselves exchange values, the energies would be exactly the same even though the wave functions are different. This condition is called *degeneracy*. Different, linearly independent wave functions that have the same energy are called *degenerate*. A specific level of degeneracy is indicated by the number of different wave functions that have the exact same energy. If these are two, the energy level is two-fold (doubly) degenerate; if there are three different wave functions, it is three-fold (triply) degenerate and so on.

Let

n_x	n_y	n_z	
1	2	1	$E_{121} = 6 \cdot \frac{h^2}{8ma^2}$
2	1	1	$E_{211} = 6 \cdot \frac{h^2}{8ma^2}$
1	1	2	$E_{112} = 6 \cdot \frac{h^2}{8ma^2}$

E_{121} , E_{211} and E_{112} have same energy, even through each energy observable corresponds to a different wave function. This value of energy is three-fold degenerate. There are three different wave functions that have the same energy. Degenerate wave functions may have different eigen values of other observable.

This example of degeneracy is a consequence of a wave function in three dimensional space where each dimension is independent but equivalent. This might be considered degeneracy by symmetry. One can also find examples of accidental degeneracy. For example, a cubical box has wave functions with the sets of quantum numbers (3, 3, 3) and (5, 1, 1) and energies are

$$E_{333} = \frac{h^2}{8ma^2} (9 + 9 + 9) = 27 \cdot \frac{h^2}{8ma^2}$$

$$E_{511} = \frac{h^2}{8ma^2} (25 + 1 + 1) = 27 \cdot \frac{h^2}{8ma^2}$$

This is an example of accidental degeneracy. The corresponding wave functions have no common quantum number, but their energy eigenvalues are exactly the same. If we recognize that E_{151} and E_{115} also have the same energy, the level of degeneracy in this example becomes four-fold. The number of different quantum states belonging to the same energy level is known as *degree of degeneracy*. Degeneracy depends upon the symmetry of the atoms and molecules. If symmetry increases, its degeneracy also increases and vice versa. A diagram of the energy levels of the 3-D particle in a box is shown in Fig.2.17. For a particle in three-dimensional box, this degree of degeneracy can be removed by a slight distortion of the system, or by using a box of different dimensions.

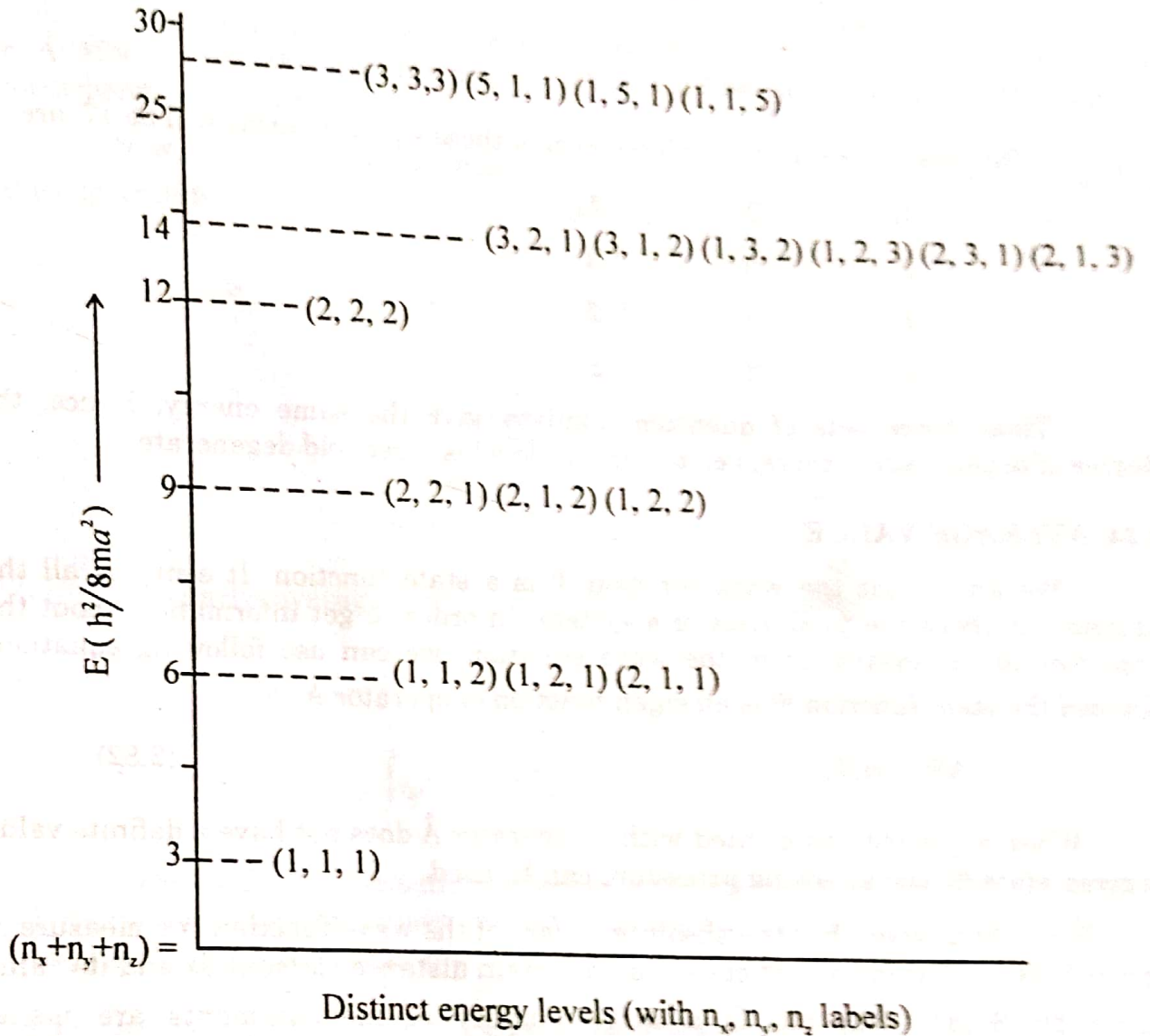


Fig.2.17 The energy levels of a 3-D particle in a cubical box

Example 2.14

Determine the degree of degeneracy of the energy level $\frac{17h^2}{8ma^2}$ of a particle in a cubical box.

Solution

Energy of a particle in a box with three equal dimensions is given by

$$E = \frac{h^2}{8ma^2} (n_x^2 + n_y^2 + n_z^2)$$

$$E = \frac{17h^2}{8ma^2}$$

$$\therefore n_x^2 + n_y^2 + n_z^2 = 17$$

The possible ways, in which the sum of these squared terms will be 17, are

n_x	n_y	n_z
2	2	3
2	3	2
3	2	2

Thus, three sets of quantum numbers give the same energy. Hence, the degree of degeneracy is three, i.e., the energy level is three fold degenerate.

2.24 AVERAGE VALUE

We know that the wave function Ψ is a state function. It contains all the information about the properties of a system. In order to get information about the properties of the system from the wave equation, we can use following equations provided the state function Ψ is an eigen function of operator \hat{A}

$$\hat{A}\Psi_i = a_i\Psi_i \quad (2.82)$$

When a quantity associated with an operator \hat{A} does not have a definite value in a given state Ψ , the following procedure can be used.

It has been seen that the absolute square of the wave function is a measure of the probability of finding a particle within a certain distance element dx and its value is given by $\Psi^*(x) \cdot \Psi(x) dx$. If a large number of measurements are made, corresponding to different position of the particles, then the average value of the positions will be the mean of the sum (integral) of probabilities of all the positions. This average value is also known as the expectation value. Mathematically, it is represented by the symbol, $\langle x \rangle$. Thus, the average value of position of a particle

$$\langle x \rangle = \int \Psi^* x \hat{\Psi} dx$$

In general, the expectation value or average value of a physical property A, for a system whose state function is Ψ , given by

$$\langle A \rangle = \int_{-\infty}^{+\infty} \Psi^* \hat{A} \Psi \, d\tau \quad (2.83)$$

where \hat{A} is the operator corresponding to the physical property. This formula holds only if the wave function is normalised. Otherwise, the following formula is used

$$\langle A \rangle = \frac{\int_{-\infty}^{+\infty} \Psi^* \hat{A} \Psi \, d\tau}{\int_{-\infty}^{+\infty} \Psi^* \Psi \, d\tau} \quad (2.84)$$

However, if Ψ is an eigenfunction satisfying Equation (2.82) we shall find $\langle A \rangle = a$, i.e., the average value $\langle A \rangle$ will be equal to the eigenvalue 'a' corresponding to every observation.

Now, the average momentum $\langle p_x \rangle$ of a particle described by a function Ψ is the expectation value of the momentum operator. In one-dimension, this becomes.

$$\begin{aligned} \langle p_x \rangle &= \int_{-\infty}^{+\infty} \Psi^*(x) \hat{p}_x \Psi(x) \, dx \\ &= \int_{-\infty}^{+\infty} \Psi^*(x) \frac{h}{2\pi i} \cdot \frac{d}{dx} \Psi(x) \, dx \\ &= \frac{h}{2\pi i} \int_{-\infty}^{+\infty} \Psi^*(x) \frac{d}{dx} \Psi(x) \, dx \end{aligned}$$

Similarly, average energy of a particle can be written as

$$\begin{aligned} \langle E \rangle &= \int_{-\infty}^{+\infty} \Psi^* \hat{H} \Psi \, d\tau \\ &= \int \Psi^* \left(-\frac{h^2}{8\pi^2 m} \nabla^2 + V \right) \Psi \, d\tau \end{aligned}$$

The study of expectation values is very important, because all the conclusions of quantum theory, representing various physical properties, can be deduced by selecting appropriate operators.

2.25 POSTULATES OF QUANTUM MECHANICS

A number of postulates of quantum mechanics have been introduced as they have been needed.

1. The state of a quantum mechanical system is fully described by a wave function $\Psi(x, y, z, t)$ or $\Psi(r, t)$ that is the function of the coordinates of particle and time. It contains all the information known about the system.

2. The wave function $\Psi(x, t)$ and its first and second derivatives $\frac{\partial \Psi(x, t)}{\partial x}$ and $\frac{\partial^2 \Psi(x, t)}{\partial x^2}$ must be continuous finite, and single valued for all values of x .
3. Every physical property (observable) A of a system can be characterised in quantum mechanics by a linear operator \hat{A} or Hermitian operator \hat{A} . This operator satisfies the following condition for any pair of functions Ψ_1 and Ψ_2 which describes physical states of system.

$$\int \Psi_1^* \hat{A} \Psi_2 dx = \int \Psi_2 (\hat{A} \Psi_1)^* dx$$

4. The only possible values which a measurement of the property A can yield are the eigen values α_i of the equation.

$$\hat{A} \Psi_i = \alpha_i \Psi_i$$

where \hat{A} is the operator corresponding with the observable.

5. Average value of the property A associated with the operator \hat{A} is given by

$$\langle A \rangle = \int_{-\infty}^{+\infty} \Psi^* \hat{A} \Psi d\tau$$

where Ψ is the normalized wave function for the state.

$$\text{or } \langle A \rangle = \frac{\int_{-\infty}^{+\infty} \Psi^* \hat{A} \Psi d\tau}{\int_{-\infty}^{+\infty} \Psi^* \Psi d\tau}$$

where Ψ is the system, state function.

6. The wave function of a system changes with time according to time-dependent Schrodinger wave equation.

$$-\frac{ih}{2\pi} \frac{\partial \Psi(x, y, z, t)}{\partial t} = \hat{H} \Psi(x, y, z, t)$$

These postulates cannot be proved or derived, we can treat these postulates in the same light as the acceptance of Newton's second law of motion. This classical law is accepted without proof on the strength of its agreement with experimental results. Thus the entire justification of postulatory basis of Quantum Mechanics lies ultimately in the agreement of theoretical results with experimental ones.

2.32 THE RIGID ROTATOR

By a rigid rotator we mean, a two or more particle system, in which the distance between the particles is assumed to remain fixed during rotation and cannot vary with time. The theory of such a rigid rotator is useful in dealing with the rotational spectra of diatomic molecules. If the masses of the electrons and the vibration of the nuclei are ignored, a diatomic molecule may be compared to a rigid rotator.

1. Classical Treatment of Rigid Rotator

Let us consider a two-particle rigid rotator like a diatomic molecule with masses m_1 and m_2 and separated by fixed distance "r". Assume that the centre of gravity of the system is fixed at the origin of our coordinate. Let the distance of m_1 from the centre of gravity be r_1 and distance m_2 be r_2 , then

$$m_1 r_1 = m_2 r_2 \quad (2.126)$$

$$\text{or } r_1 + r_2 = r \quad (2.127)$$

From Eq. (2.125) and (2.126)

$$\begin{aligned} m_1 r_1 &= m_2 r_2 \\ &= m_2 (r - r_1) \quad (\because r_1 + r_2 = r) \\ &= m_2 r - m_2 r_1 \end{aligned}$$

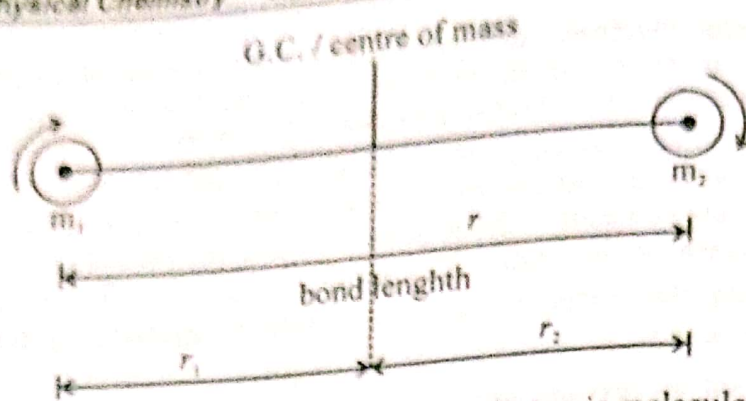


Fig. 2.23 Rigid rotator model for a diatomic molecule.

$$\text{or } m_1 r_1 + m_2 r_1 = m_2 r$$

$$r_1 (m_1 + m_2) = m_2 r$$

$$r_1 = \frac{m_2 r}{m_1 + m_2}$$

Similarly,

$$r_2 = \frac{m_1 r}{m_1 + m_2}$$

The moment of inertia (I) of the rotating body, about the C.G. is

$$I = m_1 r_1^2 + m_2 r_2^2 \quad (2.127)$$

$$\left(I = \sum_{i=1}^n m_i r_i^2 \right)$$

Substituting the values of r_1 and r_2 in 2.127, we get

$$\begin{aligned} I &= m_1 \left(\frac{m_2 r}{m_1 + m_2} \right)^2 + m_2 \left(\frac{m_1 r}{m_1 + m_2} \right)^2 \\ &= m_1 \left(\frac{m_2}{m_1 + m_2} \right)^2 r^2 + m_2 \left(\frac{m_1}{m_1 + m_2} \right)^2 r^2 \end{aligned}$$

Taking $m_1 m_2$ as common.

$$= m_1 m_2 \left[\frac{m_2 + m_1}{(m_1 + m_2)^2} \right] r^2$$

$$= m_1 m_2 \left[\frac{1}{m_1 + m_2} \right] r^2$$

$$= \left[\frac{m_1 m_2}{m_1 + m_2} \right] r^2$$

$$I = \mu r^2 \quad (2.128)$$

$$\mu = \frac{m_1 m_2}{m_1 + m_2} = \text{reduced mass}$$

(Reduced mass: When masses of two particles are converted into a single mass, then it is called reduced mass, because in quantum mechanics, it is easy to handle one particle system as compared to two particles.)

Since the distance between the two particles is fixed, the P.E. is treated as zero. Therefore, the rigid rotator has only K.E. The K.E. of rotation, (T) is given by

$$T = \frac{1}{2} m_1 v_1^2 + \frac{1}{2} m_2 v_2^2$$

where v_1 and v_2 are the linear velocities of masses m_1 and m_2 respectively. Then, in terms of angular velocity, we can write

$$\begin{aligned} T &= \frac{1}{2} m_1 \omega^2 r_1^2 + \frac{1}{2} m_2 \omega^2 r_2^2 \\ &= \frac{1}{2} \omega^2 (m_1 r_1^2 + m_2 r_2^2) \\ &= \frac{1}{2} \omega^2 I \end{aligned} \quad (2.129)$$

where ω (omega) is the angular velocity and I is the moment of inertia about an axis passing through the centre of the gravity and normal to the line through the masses.

Since the angular momentum L , is related to the moment of Inertia, I through the relation

$$L = \omega I \quad (2.130)$$

Therefore,

$$T = \frac{L^2}{2I} = \frac{L^2}{2\mu r^2} \quad (2.131)$$

$$\therefore T = \frac{1}{2} \omega^2 I = \frac{1}{2} \frac{\omega^2 I^2}{I} = \frac{L^2}{2I}$$

Quantum Mechanical Treatment of Rigid Rotator

Now, let us consider the two particle rigid rotator from quantum-mechanical stand point.

N.B. The molecule is called rigid rotator because it is not compressed in any situation, because we are dealing with an ideal system.

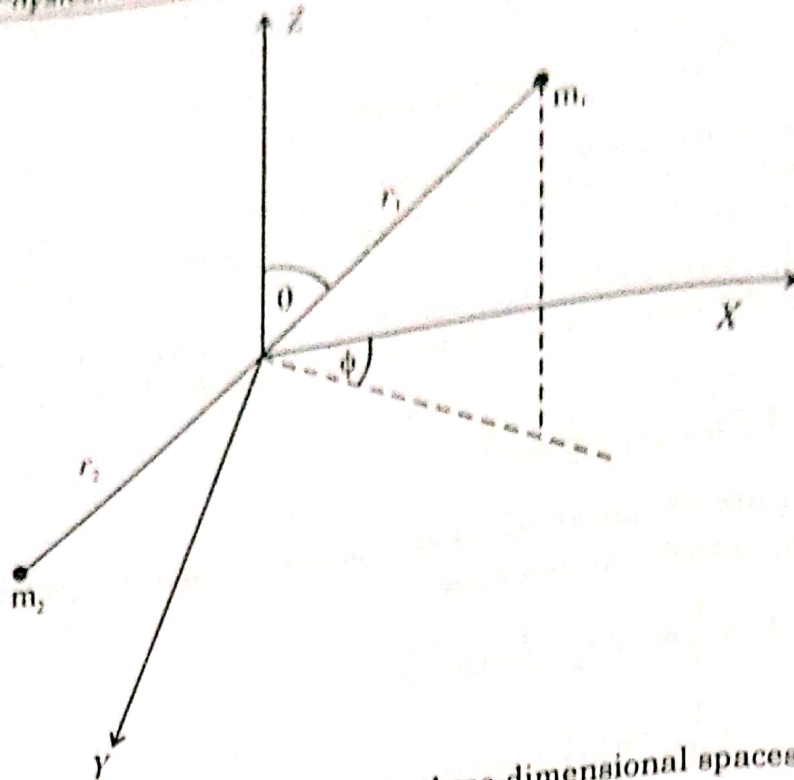


Fig.2.24 The rigid rotator in three-dimensional spaces

It will be recalled that the three-dimensional Schrodinger wave equation for a single particle is

$$\nabla^2 \Psi + \frac{8\pi^2 m}{h^2} (E - V) \Psi = 0$$

The potential energy of the rigid rotator will be constant and this constant value may be conveniently taken as zero. Applying above equation to the rigid rotator and putting $V = 0$

$$\nabla^2 \Psi + \frac{8\pi^2 \mu}{h^2} E \Psi = 0 \quad (2.132)$$

The Laplacian operator was given in terms of spherical polar coordinates.

$$\nabla^2 = \frac{1}{r^2} \cdot \frac{\partial}{\partial r} \left(r^2 \cdot \frac{\partial}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \cdot \frac{\partial}{\partial \theta} \sin \theta \cdot \frac{\partial}{\partial \theta} + \frac{1}{r^2 \sin^2 \theta} \cdot \frac{\partial^2}{\partial \phi^2}$$

For the rigid rotator, r has constant value. Since r is constant, factors involving $\partial/\partial r$ will be zero.

$$\therefore \nabla^2 = \frac{1}{r^2 \sin \theta} \cdot \frac{\partial}{\partial r} \left(\sin \theta \cdot \frac{\partial}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \cdot \frac{\partial^2}{\partial \phi^2}$$

Substitute this value in equation (2.132), we get

$$\frac{1}{r^2 \sin \theta} \cdot \frac{\partial}{\partial \theta} \left(\sin \theta \cdot \frac{\partial^2 \Psi}{\partial \theta^2} \right) + \frac{1}{r^2 \sin^2 \theta} \cdot \frac{\partial^2 \Psi}{\partial \phi^2} + \frac{8\pi^2 \mu E}{h^2 r^2} \Psi = 0 \quad (2.133)$$

Multiplying both sides by r^2 . We get

$$\frac{1}{\sin\theta} \cdot \frac{\partial}{\partial\theta} \left(\sin\theta \cdot \frac{\partial\Psi}{\partial\theta} \right) + \frac{1}{\sin^2\theta} \cdot \frac{\partial^2\Psi}{\partial\phi^2} + \frac{8\pi^2 I}{h^2} E\Psi = 0 \quad (2.134)$$

Equation (2.134) contains two angular variable θ and ϕ . It is solved once again by the method of separation of variables. It is assumed that Ψ is a product of two functions, each of which is a function of only one of the variables. It is assumed therefore, that

$$\Psi(\theta, \phi) = Y(\theta) \cdot Z(\phi) \quad (2.135)$$

which means that Ψ (which is a function of θ and ϕ) is equal to the product of two functions "Y" and "Z" where "Y" is a function only of θ and "Z" is a function only of ϕ . Equation (2.135) may be written more simply as

$$\Psi = YZ \quad (2.135)$$

Since the function Z is independent of θ , differentiation of equation (2.135) w.r.t. θ yields

$$\frac{\partial\Psi}{\partial\theta} = Z \cdot \frac{dY}{d\theta} \quad (2.136)$$

Similarly, differentiation w.r.t. ϕ gives

$$\frac{\partial\Psi}{\partial\phi} = Y \frac{dZ}{d\phi}$$

and further differentiation w.r.t. ϕ yields,

$$\frac{\partial^2\Psi}{\partial\phi^2} = Y \cdot \frac{d^2Z}{d\phi^2} \quad (2.137)$$

Substituting from Eq. (2.136) and (2.137) into (2.134) gives

$$\frac{Z}{\sin\theta} \frac{d}{d\theta} \left(\sin\theta \frac{dY}{d\theta} \right) + \frac{Y}{\sin^2\theta} \cdot \frac{d^2Z}{d\phi^2} + \frac{8\pi^2 I E}{h^2} YZ = 0$$

Multiplying by $\sin^2\theta/YZ$

$$\frac{\sin\theta}{Y} \cdot \frac{d}{d\theta} \left(\sin\theta \cdot \frac{dY}{d\theta} \right) + \frac{1}{Z} \cdot \frac{d^2Z}{d\phi^2} + \frac{8\pi^2 I E}{h^2} \cdot \sin^2\theta = 0 \quad (2.138)$$

$$\text{or} \quad \frac{\sin\theta}{Y} \cdot \frac{d}{d\theta} \left(\sin\theta \cdot \frac{dY}{d\theta} \right) + \frac{8\pi^2 I E}{h^2} \cdot \sin^2\theta = -\frac{1}{Z} \cdot \frac{d^2Z}{d\phi^2} \quad (2.139)$$

Each side of equation (2.139) contains only one variable. The L.H.S. has only terms in the variable θ and the R.H.S. has only a term in the variable ϕ . As the equation must hold for all values of θ and ϕ , each side of the equation must be a constant. Representing this constant value by m^2 allows each side of equation (2.139) to be written

$$-\frac{1}{Z} \cdot \frac{d^2 Z}{d\phi^2} = m^2$$

$$\text{or } \frac{1}{Z} \cdot \frac{d^2 Z}{d\phi^2} + m^2 = 0$$

(2.140)

$$\text{or } \frac{d^2 Z}{d\phi^2} + m^2 Z = 0$$

$$\text{and } \frac{\sin \theta}{Y} \cdot \frac{d}{d\theta} \left(\sin \theta \cdot \frac{dY}{d\theta} \right) + \frac{8\pi^2 I E}{h^2} \cdot \sin^2 \theta = m^2$$

$$\text{or } \frac{\sin \theta}{Y} \cdot \frac{d}{d\theta} \left(\sin \theta \cdot \frac{dY}{d\theta} \right) + \beta \sin^2 \theta = m^2$$

$$\text{Putting } \beta = \frac{8\pi^2 I E}{h^2}$$

$$\text{or } \frac{\sin \theta}{Y} \cdot \frac{d}{d\theta} \left(\sin \theta \cdot \frac{dY}{d\theta} \right) + \beta \sin^2 \theta - m^2 = 0$$

Multiply by $Y/\sin^2 \theta$

$$\frac{1}{\sin \theta} \cdot \frac{d}{d\theta} \left(\sin \theta \cdot \frac{dY}{d\theta} \right) + \left(\beta - \frac{m^2}{\sin^2 \theta} \right) Y = 0$$

Carrying out the differentiation indicated in the first term and remembering that $(\sin \theta) \left(\frac{dY}{d\theta} \right)$ must be differentiated as a product.

$$\frac{1}{\sin \theta} \cdot \sin \theta \cdot \frac{d^2 Y}{d\theta^2} + \cos \theta \cdot \frac{dY}{d\theta} + \left(\beta - \frac{m^2}{\sin^2 \theta} \right) Y = 0$$

The variable in the equation is now changed by putting.

$$z = \cos \theta$$

$$z^2 = \cos^2 \theta$$

$$\sin^2 \theta + \cos^2 \theta = 1$$

$$\sin^2 \theta = 1 - \cos^2 \theta = 1 - z^2$$

$$\therefore \frac{1}{\sin \theta} \cdot \frac{d}{d\theta} \left(\sin \theta \cdot \frac{dY}{d\theta} \right) + \left(\beta - \frac{m^2}{1 - z^2} \right) Y = 0$$

$$\text{or } \frac{1}{\sin \theta} \cdot \frac{d}{d\theta} \left(\sin \theta \cdot (-\sin \theta) \frac{dY}{d\theta} \right) + \left(\beta - \frac{m^2}{(1 - z^2)} \right) Y = 0$$

$$\text{or } \frac{1}{\sin \theta} \cdot \frac{d}{d\theta} \left(-\sin^2 \theta \cdot \frac{dY}{d\theta} \right) + \left(\beta - \frac{m^2}{1 - z^2} \right) Y = 0$$

$$\text{or } \frac{1}{\sin \theta} \left[-2 \sin \theta \cdot \cos \theta \cdot \frac{dY}{dz} - \sin^2 \theta \cdot \frac{d}{d\theta} \cdot \frac{dY}{dz} \right]$$

$$\text{or } -2 \cos \theta \frac{dY}{dz} - \sin \theta \cdot \frac{d}{d\theta} \cdot \frac{dY}{dz} + \left(\beta - \frac{m^2}{1-z^2} \right) Y = 0$$

$$\text{or } -2 \cos \theta \cdot \frac{dY}{dz} - \sin \theta \cdot \left(-\sin \theta \frac{d}{dz} \right) \cdot \frac{dY}{dz} + \left(\beta - \frac{m^2}{1-z^2} \right) Y = 0$$

$$\text{or } -2 \cos \theta \frac{dY}{dz} + \sin^2 \theta \cdot \frac{d}{dz} \cdot \frac{dY}{dz} + \left(\beta - \frac{m^2}{1-z^2} \right) Y = 0$$

$$\text{or } \sin^2 \theta \cdot \frac{d^2 Y}{dz^2} - 2 \cos \theta \frac{dY}{dz} + \left(\beta - \frac{m^2}{1-z^2} \right) Y = 0$$

$$(1-z^2) \cdot \frac{d^2 Y}{dz^2} - 2z \cdot \frac{dY}{dz} + \left(\beta - \frac{m^2}{(1-z^2)} \right) Y = 0 \quad (2.143)$$

$$(1-z^2) \cdot \frac{d^2 Y}{dz^2} - 2z \cdot \frac{dY}{dz} + \left(l(l+1) - \frac{m^2}{(1-z^2)} \right) Y = 0 \quad (2.144)$$

$$\therefore \beta = l(l+1)$$

Equation (2.144) is similar to *Associate Legendre Equation* and the function $P_l^m(z) = P_l^m(\cos \theta) = Y(\theta)$ is called *Associated Legendre Polynomial* of degree " l " and order " m "

$$(1-z^2) \cdot \frac{d^2 P_l^m(z)}{dz^2} - 2z \frac{d}{dz} P_l^m(z) + \left(l(l+1) - \frac{m^2}{(1-z^2)} \right) P_l^m(z) = 0$$

It is a well known equation of physics.

$$\beta = \frac{8\pi^2 I E}{h^2}$$

$$l(l+1) = \frac{8\pi^2 I E}{h^2}$$

$$E_{\text{rot}} = \frac{h^2 l(l+1)}{8\pi^2 I}$$

While considering the rotational spectra of diatomic molecules, the quantum number is usually written J rather than l

$$E_J = E_{\text{rot}} = \frac{h^2}{8\pi^2 I} \cdot J(J+1) \quad (2.145)$$

This relationship gives the eigen values of the energy of the rotator and J is known as the *rotational quantum number*.

The state of the system however, requires the specification of two quantum number J and m . It will be remembered that the relationship between two quantum numbers is

$$J \geq |m|$$

when $J = 2$, for example, then $m = +2, +1, 0, -1, -2$. There are thus five possible states of the system for $J = 2$. As the energy is determined solely by the value of J in equation (2.145) there are thus five different states of the system with the same energy. In general for any value of J , there are $(2J + 1)$ degenerate states. It may be mentioned here that this degeneracy is removed if the molecule, is placed in a magnetic field, and hence in the pressure of a magnetic field *extra liens* appear in the rotational spectrum. It should be noted that J can have the value zero, therefore, it is once again seen that a rotational motion can have zero energy. The rigid rotator serves as an approximate model for the rotational spectra of diatomic molecules. If two energy levels are defined by rotational quantum numbers J and J' , then the energy difference between the ΔE , is given by

$$\Delta E_J = \frac{h^2}{8\pi^2 I} [J'(J' + 1) - J(J + 1)] \quad \text{Joules} \quad (2.146)$$

There is a selection rule in rotational spectroscopy

$$\Delta J = \pm 1$$

We need only consider transitions in which J changes by one unit, all other transitions, being spectroscopically *forbidden*.

Equation (2.145) expresses the allowed energy in joules. In rotational region spectra are usually discussed in terms of wave number,

$$\bar{\nu} = \Delta E/hc$$

$$\text{or} \quad \epsilon_J = \frac{E_J}{hc} = \frac{h}{8\pi^2 I c} \cdot J(J + 1) \text{cm}^{-1} \quad (J = 0, 1, 2, \dots)$$

$$\text{or} \quad \bar{\nu} = BJ(J + 1) \text{cm}^{-1}$$

where B , the *rational constant*, is given by

$$B = \frac{h}{8\pi^2 I c}$$

where

h = Planck, constant

c = Velocity of light, cm s^{-1}

I = moment of Inertia

where $J = 0$, ground rotational state no rotation occurs.

After absorption of radiation $J = 1$

The energy absorbed will be

$$\epsilon_{J=1} - \epsilon_{J=0} = 2B - 0 = 2B \text{ cm}^{-1}$$

and therefore,

$$\bar{\nu}_{J=0 \rightarrow J=1} = 2B \text{ cm}^{-1}$$

The absorption line appears at $2B \text{ cm}^{-1}$.

If now the molecule is raised $J = 1$ to $J = 2$ level of absorption of more energy, we see

$$\bar{\nu}_{J=1 \rightarrow J=2} = \epsilon_{J=2} - \epsilon_{J=1} = 6B - 2B = 4B \text{ cm}^{-1}$$

In general

$$\bar{\nu}_{J \rightarrow J+1} = 2B (J + 1) \text{ cm}^{-1}$$

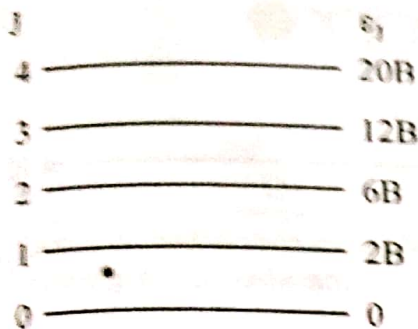


Fig. 2.25 the allowed rotational energy levels

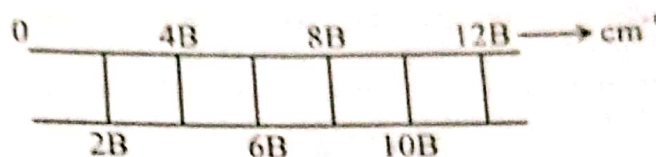


Fig. 2.26 Allowed transitions and observed rotational spectrum.

2.33 HARMONIC OSCILLATOR

A characteristic motion often observed in physical system is the simple harmonic motion (vibration or oscillation). It is a back and forth motion along the same path, in which the displacement from an equilibrium (rest) position varies periodically with time. The vibration is simple harmonic if it has a fixed time period (τ) and amplitude. A pendulum swinging through a very small angle and mass attached to a weightless spring, restricted to move along the same path, are close approximations to harmonic oscillator. Atoms in a molecule execute vibrating motion along a bond with bond length and bond angles changing periodically, these constitute tiny harmonic oscillator.

When a particle oscillates about its mean position along a straight line under the action of a force which (i) is directed towards the mean position and (ii) is proportional to the displacement at any instant from this position, the motion of the particle is said to be *simple harmonic motion* and the oscillating particle is called a *simple harmonic oscillator* or a *linear harmonic oscillator*, as the displacement is expressed in term of single coordinate.

The harmonic oscillator is an important example of periodic motion because it serves as an exact or approximate model in classical or quantum mechanics. At temperature above 0K, the atoms in a crystal are temporarily displaced from their normal positions in the structure due to absorption of thermal energy. Consequently interatomic forces obeying Hooke's law act on the displaced atoms. Under the action

of these restoring forces each atom vibrates about its normal position which is the correct position in the ideal structure. Thus, the vibrations of each atom are similar to those of a simple harmonic oscillator.

So far we have considered only the cases where the potential energy V is constant. However, in problems like those of linear harmonic oscillator, the P.E. (V) varies with displacement coordinate. The simplest examples are given by vibrations of diatomic molecules and motions of an atom in a crystal lattice. To understand the vibrations of molecules we need to understand the quantum mechanical treatment of a harmonic oscillator, and as background for that we need to review the classical treatment of a harmonic oscillator.

(i) Classical Harmonic Oscillator

The simplest example of harmonic oscillator is a mass connected to a wall by mean of an idealized spring, in the absence of gravity. As shown in the Fig. 2.27, the displacement of the mass is shown by its x -coordinate and the origin of the coordinate system is taken at the equilibrium position. The mass oscillates about its equilibrium position, and the motion is said to be harmonic if the force F due to spring is directly proportional to the displacement x from its equilibrium position x_{eq} , which we can define as the origin of x -axis.

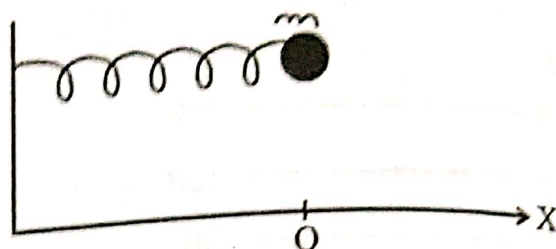


Fig. 2.27 Mass m connected to a wall by a spring in the absence of gravity

The work done in stretching spring to a distance dx is equal to the product of force times distance. This work is stored in the form of P.E. (V). To get the overall charge, one has to integrate the equation (2.148).

$$F = -kx \quad (2.147)$$

The negative sign comes from the fact that the force F is opposite to the displacement x . The probability constant k , referred to a force constant, is small for a weak spring and large for a stiff spring. Recall from physics that a force can be expressed as the negative derivative of the potential energy.

$$-\frac{dV}{dx} = F$$

$$\text{or } dV = -F \cdot dx \quad (2.148)$$

The work done in stretching spring to a distance dx is equal to the product of force times distance. This work is stored in the form of P.E. (V). To get the overall charge, one has to integrate the equation (2.148).

$$dV = - \int_0^x F \cdot dx$$

$$V = - \int_0^x F \cdot dx$$

$$V = \int_0^x kx \cdot dx$$

$$V = \frac{1}{2} kx^2 \quad (2.149)$$

Now according to the second law of motion

$$F = ma \quad (2.150)$$

where a is the acceleration of mass m subjected to a force F . Comparing Eqs. (2.147) and (2.150), we get

$$ma = -kx \quad \left(\because a = \frac{d^2x}{dt^2} \right)$$

$$\frac{d^2x}{dt^2} = -\left(\frac{k}{m}\right)x$$

$$\text{or} \quad \frac{d^2x}{dt^2} + \left(\frac{k}{m}\right)x = 0 \quad (2.151)$$

It is a second order differential equation. The general solution of this equation is

$$x = A \sin \left(\frac{k}{m}\right)^{1/2} t \quad (2.152)$$

Also from simple harmonic motion, we know that

$$x = A \sin 2\pi\nu t \quad (2.153)$$

Comparing the above two equations, we get

$$A \sin 2\pi\nu t = A \sin \left(\frac{k}{m}\right)^{1/2} t$$

$$\nu = \frac{1}{2\pi} \sqrt{\frac{k}{m}}$$

$$\bar{\nu}c = \frac{1}{2\pi} \sqrt{\frac{k}{m}} \quad \left(\because \nu = \frac{c}{\lambda} = \bar{\nu}c \right)$$

$$\text{or} \quad \bar{\nu} (\text{cm}^{-1}) = \frac{1}{2\pi c} \sqrt{\frac{k}{m}} \quad (2.154)$$

For two particles connected to each other through a weightless spring (as in diatomic molecular), we use the term reduced mass, μ

$$\bar{\nu} (\text{cm}^{-1}) = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}} \quad (2.155)$$

Eqs (2.154) and (2.155) gives the vibrational frequencies of a linear harmonic oscillators. If we take the potential energy to be zero where $x = 0$, then the path of the

motion will be parabola (Fig. 2.28). At the extreme points of oscillation, all the energy is potential ($E = V = \frac{1}{2} kx^2$) while at the equilibrium ($x = 0$), all the energy is kinetic.

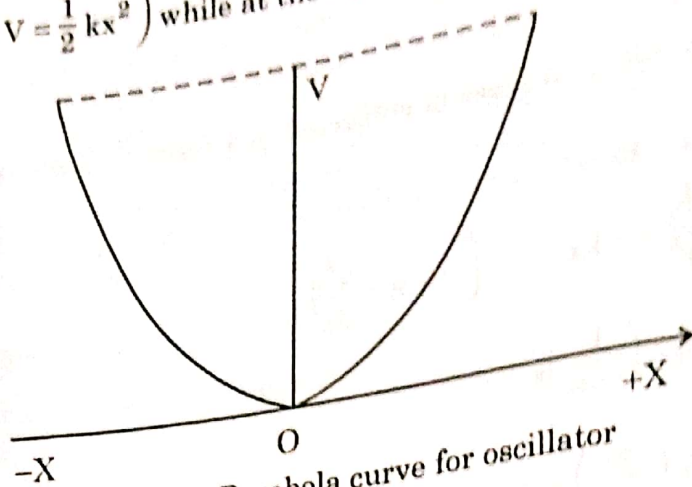


Fig. 2.28 Parabola curve for oscillator

(ii) Quantum Mechanical Harmonic Oscillator

The time-independent Schrodinger wave equation for linear motion of a particle along the x -axis is given as follows:

$$\frac{d^2\Psi}{dx^2} + \frac{8\pi^2m}{h^2} (E - V)\Psi = 0 \quad (2.156)$$

where E is the total energy of the particle, V is the potential energy and Ψ is the wave function of the particle, which is a function of x -alone.

For a linear oscillator along the x -axis with angular frequency ω under a restoring force proportional to the displacement x , the potential energy is given by

$$V = \frac{1}{2} kx^2$$

From classical treatment of harmonic oscillator, we know that

$$v = \frac{\omega}{2\pi} = \frac{1}{2\pi} \sqrt{\frac{k}{m}}$$

$$k = 4\pi^2 v^2 m$$

$$\text{hence } V = 2\pi^2 v^2 m x^2 \quad (2.157)$$

Therefore, the Schrodinger wave equation for this system is

$$\frac{d^2\Psi}{dx^2} + \frac{8\pi^2m}{h^2} (E - 2\pi^2 v^2 m x^2) \Psi = 0 \quad (2.158)$$

and the problem is to find the well-behaved functions which satisfy equation (2.158) and the allowed energy levels. Equation (2.158) may be written in the form

$$\frac{d^2\Psi}{dx^2} + \frac{8\pi^2mE}{h^2} - \frac{16\pi^4 v^2 m^2 X^2}{h^2} \Psi = 0$$

$$\text{or } \frac{d^2\Psi}{dx^2} + \left(\frac{8\pi^2 mE}{h^2} - \alpha^2 x^2 \right) \Psi = 0$$

$$\therefore \alpha^2 = \frac{16\pi^4 v^2 m^2}{h^2} \quad \text{and} \quad \alpha = \frac{4\pi^2 vm}{h}$$

Here

$$\frac{d^2\Psi}{dx^2} + \left(\frac{8\pi^2 mE}{h^2} - \alpha^2 x^2 \right) \Psi = 0 \quad (2.159)$$

In order to simplify Eq.(2.159), let us introduce a dimensionless variable q , which is related to x by the equation

$$q = \sqrt{\alpha} X \quad (2.160)$$

If the variable is to be changed in this way, then in the first term of Eq. (2.159) Ψ must be differentiated with respect to q rather than with respect to x and relationship between d^2/dq^2 and $\frac{d^2}{dx^2}$ must be established

$$\text{Let } \frac{d}{dx} = \frac{d}{dq} \cdot \frac{dq}{dx}$$

and from Eq.(2.160)

$$\frac{dq}{dx} = \sqrt{\alpha}$$

hence

$$\frac{d}{dx} = \frac{d}{dq} \sqrt{\alpha} \quad (2.161)$$

In order to arrive at an expression for d^2/dx^2 , Eq. (2.161) must be differentiated again with respect to x .

$$\frac{d^2}{dx^2} = \frac{d}{dx} \left(\frac{d}{dq} \sqrt{\alpha} \right)$$

Substituting the value of d/dx from Eq.(2.161), we get

$$\frac{d^2}{dx^2} = \frac{d}{dq} \sqrt{\alpha} \left(\frac{d}{dq} \sqrt{\alpha} \right)$$

$$\frac{d^2}{dx^2} = \alpha \cdot \frac{d^2}{dq^2} \quad (2.162)$$

Using the relationship and that given by Eq.(2.160), we may write Eq. (2.159) as

$$\alpha \cdot \frac{d^2\Psi}{dq^2} + \left(\frac{8\pi^2 mE}{h^2} - \frac{\alpha^2 q^2}{\alpha} \right) \Psi = 0 \quad \therefore q = \sqrt{\alpha} x, \quad x^2 = q^2/\alpha$$

$$\text{or } \alpha \cdot \frac{d^2\Psi}{dq^2} + \left(\frac{8\pi^2 m E}{h^2} - \alpha q^2 \right) \Psi = 0$$

Divide this equation by α

(2.163)

$$\frac{d^2\Psi}{dq^2} + \left(\frac{8\pi^2 m E}{\alpha h^2} - q^2 \right) \Psi = 0$$

Substituting the value of $\alpha = 4\pi^2 v m / h$, we get

$$\frac{d^2\Psi}{dq^2} + \left(\frac{8\pi^2 m E h}{h^2 4\pi v^2 m} - q^2 \right) \Psi = 0$$

$$\text{or } \frac{d^2\Psi}{dq^2} + \left(\frac{2E}{vh} - q^2 \right) \Psi = 0$$

$$\text{Let } \beta = \frac{2E}{vh}$$

(2.164)

$$\frac{d^2\Psi}{dq^2} + (\beta - q^2)\Psi = 0$$

Eq. (2.164) is a second order differential equation. It is a simple equation in the sense that it is free of the quantities like π , m , h etc. and since the variable q is dimensionless, the equation is purely algebraic. The approach is to find an approximate solution of this equation, which thus may be modified to give an exact solutions.

It is not easy to solve equation (2.164), however an asymptotic solutions can be obtained for very large value of q .