

Inadequacy of Classical Mechanics

- 1) According to the classical mechanics, as an electron is moving round the nucleus, its energy should increase. Therefore, its velocity should decrease continuously, i.e., the electron comes closer and closer to the nucleus until it collapses. This shows instability of the atom. Thus the classical mechanics fails to explain the stability of atoms.
- 2) The classical mechanics failed to explain the spectrum of hydrogen atom. According to classical theory, the excited atoms of hydrogen emit electromagnetic radiations of all wavelengths continuously. But it is observed that they emit the radiations of a certain wavelength only.
- 3) Classical mechanics explain the motion of objects, which are directly observable. When the objects are not observable even with the help of the instruments, classical concept cannot be applied i.e., the classical concepts do not hold in the region of atomic dimensions.

Quantum Theory and Atomic Spectra

Bohr Model

Bohr's theory is based on the following postulates.

- 1) The atom consists of a positively charged nucleus with electrons revolving around it.
 - 2) Electrons can move around the nucleus only in certain definite orbits.
 - 3) Electrons in each orbit have a definite energy and are at a finite distance from the nucleus. The orbits are designed as K,L,M,N etc or 1,2,3,4 etc.
 - 4) In each of these orbits, the energy of an electron remains the same. Hence an orbit is called stationary energy level.
 - 5) An electron can move from one energy level to another by quantum or photon jumps. When an electron is supplied with energy, it absorbs one quantum of energy and jumps to higher energy level. The electron is then said to be in an excited state.
 - 6) The quantum of energy absorbed or emitted is equal to the energy difference between the lower and higher energy levels of the atom: $\Delta E = E_2 - E_1 = h\nu$; where 'h' is the Plank's constant and ν is the frequency of the photon emitted or absorbed.
 - 7) The angular momentum (mvr) of an electron is an integral multiple of Plank's constant divided by 2π . $mvr = n \times \frac{h}{2\pi}$ i.e., the angular momentum is also quantised.
- n is the principal quantum number.

Bohr's Theory of Hydrogen Spectrum

1. A sample of hydrogen contains a very large number of atoms. When energy is supplied to the sample of gas, different atoms absorb different amounts of energies. So electrons in different atoms will move up to different energy levels depending upon the energy absorbed by the atoms.
2. When electrons fall back, they fall from different energy levels and reach different energy levels. We get several lines with varied wavelengths.
3. If ν is the frequency of the line emitted, then

$$\nu = \frac{2\pi^2 Me^4}{(4\pi E_0)^2 h^3} \left\{ \frac{1}{n_1^2} - \frac{1}{n_2^2} \right\}$$

where E_0 is a constant. M is the mass of the electron, e — is the charge of the electron. h —is the Planck's constant. n_1 is the principal quantum number of the lower energy level. n_2 is the principal quantum number of the higher energy level. Depending on the values of n_1 and n_2 , we get various series of spectral lines.

	Name of the series	n_1	n_2
1)	Lyman	1	2,3 etc
2)	Balmer	2	3,4 etc
3)	Paschen	3	4,5 etc
4)	Brackett	4	5,6 etc
5)	Pfund	5	6,7 etc

Thus using the above equation, the frequencies of the spectral lines are calculated.

Limitations: Each line in the original line spectrum was found to consist of a group of very fine lines. That is, every energy level consists of several sub-levels.

Failure of Bohr's model to explain atomic and molecular spectra

- 1) Bohr's model could not explain with mathematical exactness, the spectra of elements with more than one electron and molecular spectra.
- 2) de Broglie suggested that electron, like light, behaved both as a wave and as a particle. i.e. it has a dual character.
- 3) Heisenberg suggested that it is impossible to determine the exact position and the momentum of a small moving particle like electron. This principle is known as uncertainty principle.

Laws of Photoelectric Emission

Photoelectric Effect: The phenomenon of ejection of ions electrons from a metal plate, when light of a suitable wave-length falls on it is called the photoelectric effect. The electrons emitted are called photo-electrons.

- 1) The number of Photo-electrons ejected is directly proportional to the intensity of the incident light.
- 2) The velocity of the emitted electrons increases with the increase in frequency of the incident light. i.e., there is a limiting frequency for a metal, below which no electrons are emitted. This is known as the threshold frequency (ν_0).
- 3) A part of the light energy is used up in ejecting the electrons just out of the surface. The energy depends upon the nature of the metal and is called work-function (ϕ_0).
- 4) The rest part of the energy of the striking photon is used up in imparting kinetic energy $\frac{1}{2}mv^2$ to the ejected electron.

$$h\nu = \phi_0 + \frac{1}{2}mv^2 \quad \text{and} \quad \phi_0 = h\nu_0$$

where ν_0 is the threshold frequency. Therefore,

$h\nu = h\nu_0 + \frac{1}{2}mv^2$
 This equation is called Einstein's Photoelectric equation.

Mosley's Work

- 1) When a beam of cathode rays (electrons) falls on a metal target, *x-rays* are produced. If different metals are used as anti-cathode, *x-rays* with certain wavelengths, which are more predominant than the rest are produced.
- 2) The frequency of the characteristic *x-rays* was related to the atomic number (z) of the element by the equation, $\sqrt{\nu} = a(z - b)$ where a and b are constants.

Compton Effect

A photon from *x-ray* after hitting the surface of a metal is deflected and it has less energy and comparatively larger wavelength than it had before hitting,

- 1) A photon after hitting a metal surface will have less energy and larger wavelength than it had before hitting. This is Compton effect.
- 2) If the collision is a head on, the electron would be ejected at high speed in the direction of the impact. The *x-ray* photons would lose a large fraction of energy and will be deflected through a large angle from its original path.
- 3) If the collision is a side-wise collision, the *x-ray* photon would lose less energy and it will be deflected through much smaller an angle from its original path.
- 4) If the collision is a mere touch, the *x-ray* photon would lose only a little energy and will not be deflected from its original path.

de Broglie Equation

According to de Broglie, every particle is associated with a wave. He proposed a relation between the momentum and wavelength of particles in motion.

According to Planck's quantum theory, the energy of a photon is equal to $h\nu$; i.e., $E = h\nu$

Since $\nu = \frac{C}{\lambda}$ then $E = h\frac{C}{\lambda}$

According to Einstein's mass energy relationship, $E = mc^2$.

Comparing the above two equations, $mc^2 = h\frac{C}{\lambda}$; Therefore, $mC = \frac{h}{\lambda}$

We know that, the momentum of a moving particle,

$$p = \frac{h}{\lambda} \quad (\text{or}) \quad \lambda = \frac{h}{p} \quad (\text{or}) \quad \lambda = \frac{h}{mv}$$

This equation is known as de Broglie equation.

Significance: The concept that the matter can also be considered as wave led to the concept of electrons moving around the nucleus of atom in orbitals.

Problem: Calculate de Broglie wavelength of electron moving with a velocity of 1.20×10^7 cm per second.

$$\lambda = \frac{h}{mv} = \frac{6.626 \times 10^{-27} \text{ erg s}}{(9.1 \times 10^{-28} \text{ g})(1.20 \times 10^7 \text{ cm s}^{-1})} = 6.068 \times 10^{-7} \text{ cm} = 60.68 \text{ \AA}$$

Verification of de Broglie's Equation: Davison Germer Experiment

Electrons were emitted from a hot filament. They were accelerated and were made to strike a nickel crystal. Diffraction patterns were produced which were very similar to those produced by *x-rays* and obeyed Bragg's equation, $n\lambda = 2d\sin\theta$. Davison and Germer found the value of λ to be 1.65 \AA , which is very close to that obtained from de Broglie's equation. This experiment gave direct evidence for the wave characters of electrons i.e., the concept of matter wave.

Heisenberg Uncertainty Principle

According to this principle, it is impossible to determine precisely and simultaneously both position and the momentum of a small moving particle.

If Δx is the uncertainty in position and Δp is the uncertainty in momentum, then

$$\Delta x \times \Delta p \approx \frac{h}{2\pi} \quad (\text{or}) \quad \Delta x \times m\Delta v \approx \frac{h}{2\pi}$$

Problem: An electron has a speed of 30000 cm s^{-1} accurate upto 0.001% . What is the uncertainty in locating its position? (Mass of electron = $9.1 \times 10^{-28} \text{ g}$)

$$\Delta x \times m\Delta v \approx \frac{h}{2\pi}$$

$$\Delta v \approx \frac{0.001}{100} \times 30000 = 0.3 \text{ cm s}^{-1}$$

$$\text{Therefore, } \Delta x \times 9.1 \times 10^{-28} \approx \frac{6.626 \times 10^{-27}}{2 \times 3.24} \quad \text{and} \quad \Delta x = 3.87 \text{ cm}$$

Postulates of Quantum Mechanics

(1) Any state of a system is represented by a wave function $[\psi]$ which is a function of coordinate and time i.e., $\Psi(x,t)$.

Under normalized condition, $\int \psi^* \psi d\tau = 1$. Under orthogonal condition, $\int \psi_1 \psi_2 d\tau = 0$
 ψ^* is the complex conjugate of ψ

(2) The first derivative of $\psi(x,t)$ is $\frac{\partial \psi}{\partial x}$ and its second derivative of $\Psi(x,t)$ is $\frac{\partial^2 \psi}{\partial x^2}$.

There are also continuous finite and single values for all values of x .

(3) A physically observable quantity can be represented by Hermitian operator. An operator \hat{A} is said to be Hermitian if it satisfies the following condition.

$$\int \psi_i^* \hat{A} \psi_j d\tau = \int \psi_j (\hat{A} \psi_i)^* d\tau$$

where ψ_i and ψ_j are the wave functions representing the physical states of the system.

(4) The allowed values of an observable \hat{A} are the eigen values a_i in the operator equation. $\hat{A} \psi_j = a_i \psi_j$

The above equation is known as eigen value equation. ψ_j is the eigen function. The physical properties can be measured by eigen values.

(5) The average value $\langle A \rangle$ of an observable A, corresponding to the operator \hat{A} is obtained from the relation

$$\bar{A} \equiv \langle A \rangle = \int_{-\infty}^{\infty} \psi^* \hat{A} \psi d\tau \text{ and } \psi \text{ is a normalized wave function.}$$

(6) For any state of system, solutions are obtained from Schrodinger's wave equation

$$\hat{H}\psi(x, t) = i\hbar \frac{\partial \psi(x, t)}{\partial t}$$

where \hat{H} is the Hamiltonian operator.

(7) The classical expressions are converted into quantum mechanical operator as shown below:

Classical variable	Operator
x	\hat{x}
p_x	$\hat{p}_x = -i\hbar \frac{\partial}{\partial x}$
E	$\hat{E} = i\hbar \frac{\partial}{\partial t}$

Schrodinger Wave Equation

The Schrodinger equation in one dimension is,

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{8\pi^2 M}{h^2} (E - U)\psi = 0$$

The above equation in three-dimension,

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} + \frac{8\pi^2 M}{h^2} (E - U)\psi = 0$$

Laplacian operator

$$\nabla^2 \psi = \frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} \quad \text{Therefore, } \nabla^2 \psi + \frac{8\pi^2 M}{h^2} (E - U)\psi = 0$$

Significance of ψ and ψ^2

1) The wave function ψ is a state function and it has no physical significance and it represents the amplitude of the wave.

2) ψ^2 refers to the probability of finding an electron in an extremely small volume around a point. i.e., the value of ψ^2 at any point around the nucleus gives a measure of the electronic charge density at that point (OR) the ψ^2 is the probability of finding the electron at the point at a given instant.

Mathematical Formulation of Quantum Mechanics Operator, Functions etc.

The mathematical operation such as differentiation, integration, multiplication, addition, subtraction etc., can be represented by a symbol known as operator.

An operator \hat{Q} is a mathematical operation which may be applied to a function $f(x)$ which changes the function into another function; i.e., $\hat{Q} f(x) = g(x)$

Ex: $f(x) = x^2$; $\frac{d}{dx}(x^2) = 2x$; $\int x^2 = \frac{x^3}{3}$; $x \times x^2 = x^3$; $\sqrt{x^2} = x$; $(x^2)^2 = x^4$

The function on which the operation is carried out is called operand.

Addition and Subtraction operator

New operators can be constructed by adding and subtracting operators. If \hat{A} and \hat{B} are two different operators, then the new operators $\widehat{A+B}$ and $\widehat{A-B}$ can be defined as

$$\widehat{A+B}f = \hat{A}f + \hat{B}f \quad \text{and} \quad \widehat{A-B}f = \hat{A}f - \hat{B}f \quad \text{where } f \text{ is an operand.}$$

Multiplication Operator

The constructive operation with 2 or more operators on a function may be called the multiplication of operators. Let, \hat{A} and \hat{B} represent two different operators and f is an operand then, the expression $\hat{A}\hat{B}f$ means that the function " f " is first operated on with \hat{B} to obtain a new function f' , which is then operated on with \hat{A} to obtain the final function f'' .

$$\hat{B}f = f' \quad \text{and} \quad \hat{A}f' = f''$$

If the same operators are applied several times in succession then it can be written as $\hat{A}\hat{A}f = \hat{A}^2f$

Linear Operator

If an operator operating on sum of the two functions gives the same result as the sum of the operators on two functions separately, then the operator is said to be linear. If \hat{A} is a linear operator and f and g are two functions then

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

Multiplication is a linear operator; but, square and square root are not linear operators.

Example: $a(b+c) = ab + ac$; $(a+b)^2 \neq a^2 + b^2$; $\sqrt{f+g} \neq \sqrt{f} + \sqrt{g}$

Commutators

Using any two operators A and B it is possible to construct a new operator.

If $\widehat{AB-BA}$ is a commutator, then it can be written as $[A,B]$. If these two operators commute then,

$$[A,B] = \hat{A}\hat{B} - \hat{B}\hat{A} = 0 \quad ; \quad \text{Ex.:} \quad \left[\frac{d}{dx}, x \right] = \frac{d}{dx}x - x\frac{d}{dx} = 1$$

Vector Operator

A vector operator ∇ is defined as $\nabla = i\frac{\partial}{\partial x} + j\frac{\partial}{\partial y} + k\frac{\partial}{\partial z}$

$$\nabla\psi = i\frac{\partial\psi}{\partial x} + j\frac{\partial\psi}{\partial y} + k\frac{\partial\psi}{\partial z} \quad \text{where } i, j, k \text{ are unit vectors along } x, y, z \text{ axis.}$$

Laplacian operator

It is defined as $\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$

Eigen values and Eigen functions

Let Ψ be the well behaved function of the state of the system. When \hat{A} operates on the function such that it satisfies the condition $\hat{A}\Psi = \lambda\Psi$, where Ψ is the eigen function; λ is eigen value.

Example: i) $\frac{d}{dx} e^{kx} = k \times e^{kx}$ $k =$ eigen value $e^{kx} =$ eigen function

ii) $\frac{d^2}{dx^2} \sin 4x = -16 \sin 4x$; $\sin 4x =$ eigen function $-16 =$ eigen value

Problem: Find out whether the following functions are eigen functions or not. If it is the eigen function, find out the eigen value:

	Operator	Function
i)	$\frac{d}{dx}$	K
ii)	$\frac{d}{dx}$	$\cos kx$
iii)	$\frac{d^2}{dx^2}$	e^{-x^2}
iv)	$-\frac{d^2}{dx^2}$	$\cos 4x$

Answer

K is not an eigen function.

$\cos kx$ is not an eigen function

e^{-x^2} is an eigen function with an eigen value of 4

$\cos 4x$ is an eigen function with an eigen value of 16.

Hermitian Operator

An \hat{A} is said to be hermitian if it is equal to its adjoint under the condition,

$$\int \psi_1^* \hat{A} \psi_2 d\tau = \int \psi_1^* \hat{A}^* \psi_2 d\tau = \int (\psi_1 \hat{A})^* \psi_2 d\tau$$

Where Ψ_1 and Ψ_2 are the eigen values functions of the operator \hat{A} . This is known as Turn-over rule.

Unitary operator

If the inverse and the adjoint of the operator are equal then the operator is known as the unitary operator.

If \hat{U} is an unitary operator, then $U^* = U^{-1}$; $\hat{U} \times U^{-1} = 1$ then $\hat{U} \times \hat{U}^* = 1$

Particle in One Dimensional Box

Suppose an electron of mass ' m_e ' moves in x direction $x = 0$ to $x = a$. Outside this box the potential energy $v = \alpha$ and within this region $v = 0$. The schrodinger equation is

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

(1)

Inside the box the schrodinger wave equation is

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{8\pi^2 m_e}{h^2} E \psi = 0 \quad (2)$$

Outside the box the schrodinger equation is

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{8\pi^2 m_e}{h^2} (E - \infty) \psi = 0 \quad (3)$$

We know that $H \Psi = E \Psi$ (4)

From equation (2)

$$\frac{\partial^2 \psi}{\partial x^2} = -\frac{8\pi^2 m_e}{h^2} E \psi \quad \text{and} \quad E \psi = -\frac{h^2}{8\pi^2 m_e} \frac{\partial^2 \psi}{\partial x^2}$$

Therefore, $H = -\frac{h^2}{8\pi^2 m_e} \frac{\partial}{\partial x^2}$

In the equation (2) put $\frac{8\pi^2 m_e}{h^2} = k^2$ (5)

\therefore We get $\frac{\partial^2 \psi}{\partial x^2} + k^2 \psi = 0$

For the above equation the solution is $\psi = C \cos kx + D \sin ka$

Applying the boundary conditions if $x = 0$, then $\psi = 0$

$\therefore 0 = C \cos 0 + D \sin 0$ and therefore $C = 0$

If $x = a$ $\psi = 0$ then, $0 = D \sin ka$

$\therefore ka = n\pi$ $\therefore k = \frac{n\pi}{a}$

$\therefore \psi = D \sin \frac{n\pi}{a} x$

From the equation (5) $E = \frac{k^2 h^2}{8\pi^2 m_e}$

Substituting the value of k $E = \frac{n^2 \pi^2 h^2}{8\pi^2 m_e a^2}$

Therefore, $E = \frac{n^2 h^2}{8m_e a^2}$

The lowest kinetic energy is called zero point energy if $n = 1$; $E_0 = \frac{h^2}{8m_e a^2}$

Characteristic of Wave Function

We know that the energy of the particle in one dimensional box is

$$E = \frac{n^2 h^2}{8m_e a^2}$$

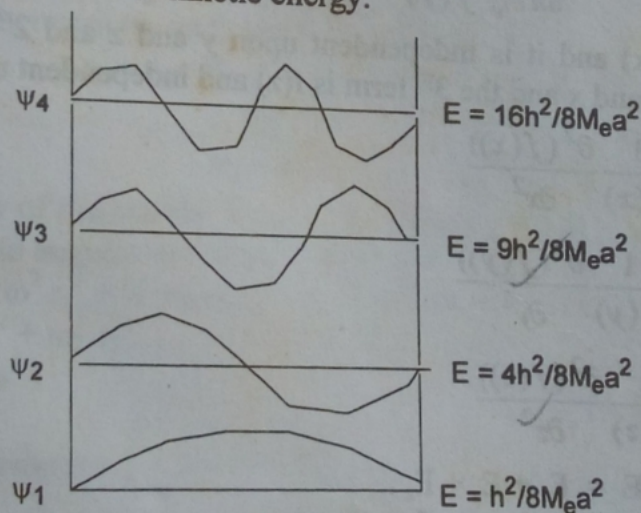
When $n = 1$ $E = \frac{h^2}{8m_e a^2}$

When $n = 2$ $E = \frac{4h^2}{8m_e a^2}$

When $n = 3$ $E = \frac{9h^2}{8m_e a^2}$

The normalised wave function is $\psi = \sqrt{\frac{2}{a}} \sin \frac{n\pi}{a} x$

A few wave functions and the corresponding energy levels are shown graphically in the following figure. It should be noted that the wave functions are alternatively symmetrical and antisymmetrical with respect to reflection. There are points inside the box, where the wave function $\psi = 0$. These points are called nodes. As the value of n increases, the number of nodes on the wave also increases. For the state, whose wave function is ψ_{n_2} , has $(n-1)$ nodes inside the box. Increasing the number of nodes decreases the wavelength, which corresponds to increase in kinetic energy.



Particle in a 3 Dimensional Box

Consider an electron in a 3 dimensional box. Let the length of the box be 'a' and the volume of the box be a^3 . Let the potential energy $v = 0$ (outside) and inside the box

$$v = \alpha.$$

$$v_x = 0 \quad 0 < x < a \quad v_x = \alpha$$

$$v_y = 0 \quad 0 < y < a \quad v_y = \alpha$$

$$v_z = 0 \quad 0 < z < a \quad v_z = \alpha$$

Inside the box Schrodinger wave equation is:

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} + \frac{8\pi^2 m_e}{h^2} E \psi = 0 \quad (1)$$

The wave function $\psi(x, y, z) = f(x) f(y) f(z)$. Differentiating the above equation we get

$$\frac{\partial^2 \psi}{\partial x^2} = f(y) f(z) \frac{\partial^2 f(x)}{\partial x^2}$$

$$\frac{\partial^2 \psi}{\partial y^2} = f(x) f(z) \frac{\partial^2 f(y)}{\partial y^2}$$

$$\frac{\partial^2 \psi}{\partial z^2} = f(x) f(y) \frac{\partial^2 f(z)}{\partial z^2}$$

Substituting these values in equation (1), we get

$$f(y) f(z) \frac{\partial^2 f(x)}{\partial x^2} + f(x) f(z) \frac{\partial^2 f(y)}{\partial y^2} + f(x) f(y) \frac{\partial^2 f(z)}{\partial z^2} + \frac{8\pi^2 m_e}{h^2} E f(x) f(y) f(z) = 0$$

Multiplying the above equation by $\frac{h^2}{8\pi^2 m_e} \times \frac{1}{f(x) f(y) f(z)}$

$$\frac{h^2}{8\pi^2 m_e} \frac{1}{f(x)} \frac{\partial^2 (f(x))}{\partial x^2} + \frac{h^2}{8\pi^2 m_e} \frac{1}{f(y)} \frac{\partial^2 (f(y))}{\partial y^2} + \frac{h^2}{8\pi^2 m_e} \frac{1}{f(z)} \frac{\partial^2 (f(z))}{\partial z^2} + E = 0$$

The first term is $f(x)$ and it is independent upon y and z and 2nd term is $f(y)$ and it is independent upon z and x and the 3rd term is $f(z)$ and independent upon x and y .

$$\therefore E_x = -\frac{h^2}{8\pi^2 m_e} \frac{1}{f(x)} \frac{\partial^2 (f(x))}{\partial x^2}$$

$$E_y = -\frac{h^2}{8\pi^2 m_e} \frac{1}{f(y)} \frac{\partial^2 (f(y))}{\partial y^2}$$

$$E_z = -\frac{h^2}{8\pi^2 m_e} \frac{1}{f(z)} \frac{\partial^2 (f(z))}{\partial z^2}$$

\therefore The total energy $E = E_x + E_y + E_z$.

We know that the normalized wave function

$$f(x) = \sqrt{\frac{2}{a}} \sin \frac{n\pi}{a} x; \quad f(y) = \sqrt{\frac{2}{a}} \sin \frac{n\pi}{a} y; \quad \text{and} \quad f(z) = \sqrt{\frac{2}{a}} \sin \frac{n\pi}{a} z$$

The total wave function $\psi = f(x) f(y) f(z)$

$$\psi = \sqrt{\frac{8}{a^3}} \sin \frac{n\pi}{a} x \cdot \sin \frac{n\pi}{a} y \cdot \sin \frac{n\pi}{a} z$$

$$E_x = \frac{n_x^2 h^2}{8m_e a^2} ; E_y = \frac{n_y^2 h^2}{8m_e a^2} ; E_z = \frac{n_z^2 h^2}{8m_e a^2}$$

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

When the value for $n_x = n_y = n_z = 1$

$$\therefore \text{Zero point energy} = E_0 = \frac{3h^2}{8m_e a^2}$$

Problem: Find out the kinetic energy of the electron in a rectangular box of dimensions 1×10^{-13} cm, 1.5×10^{-13} cm and 2×10^{-13} cm.

$$E = \frac{h^2}{8m_e a^2} (n_x^2 + n_y^2 + n_z^2) = \frac{h^2 (n_x^2 + n_y^2 + n_z^2)}{8m_e (a_x^2 + a_y^2 + a_z^2)}$$

$$= \frac{(6.626 \times 10^{-28})^2}{8 \times 9.018 \times 10^{-28} [(1 \times 10^{-13})^2 + (1.5 \times 10^{-13})^2 + (2 \times 10^{-13})^2]} = 1.014 \text{ erg}$$

Rigid Rotator

Let us consider a diatomic molecule, which consists of two atoms of masses m_1 and m_2 . Distance between the nuclei is 'r'. Let the distance between the centre of gravity and m_1 is ' r_1 ' and the distance between m_2 and centre of gravity is ' r_2 '.

$$m_1 r_1 = m_2 r_2 ; r_1 + r_2 = R$$

$$r_1 = \frac{m_2 r}{m_1 + m_2} ; r_2 = \frac{m_1 r}{m_1 + m_2}$$

The total kinetic energy of the system = $\frac{1}{2} m_1 v_1^2 + \frac{1}{2} m_2 v_2^2$

The velocity is related to angular velocity; $v = \omega r$
 K.E. = $\frac{1}{2} m_1 \omega^2 r_1^2 + \frac{1}{2} m_2 \omega^2 r_2^2 = \frac{1}{2} \omega^2 [m_1 r_1^2 + m_2 r_2^2]$

We know that $I = m_1 r_1^2 + m_2 r_2^2$

Therefore, K.E. = $\frac{1}{2} \omega^2 I$

$$L = I\omega$$

The total angular momentum = L

$$\text{K.E.} = \frac{1}{2} \omega^2 I \times \frac{I}{I} = \frac{1}{2} \omega^2 \times \frac{I^2}{I} = \frac{L^2}{2I}$$

The Hamiltonian operator $H = \text{K.E.} + \text{P.E.};$ But $\text{P.E} = 0$

$$\hat{H} = \frac{L^2}{2I} \text{ (or) } \hat{H} = \frac{-h^2}{8\pi^2 I} \frac{\partial^2}{\partial \phi^2}$$

To solve this problem, it is more convenient to use this expression for L^2 in spherical co-ordinates.

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

The equation contains two angular variables θ and ϕ .

The total wave function $\psi = \Theta(\theta)\Phi(\phi) = \Theta\Phi$

The equation is multiplied by $\sin^2\theta/\Theta\Phi$ and separating the variables θ and ϕ ,

$$\frac{\sin\theta}{\Theta} \frac{\partial}{\partial\theta} \left(\sin\theta \frac{d\Theta}{d\theta} \right) + \frac{8\pi^2 IE}{h^2} \sin^2\theta = -\frac{1}{\Phi} \frac{\partial^2\Phi}{\partial\phi^2}$$

Putting LHS as M_2 , we get
$$\frac{\partial^2\Phi}{\partial\phi^2} + \Phi M^2 = 0$$

The solutions are

$$\Phi(\phi) = \frac{1}{\sqrt{2\pi}} \exp(\pm im\phi)$$

$$\Theta(\theta) = \sqrt{\frac{(2l+1)(l-|M|)!}{2(l+|M|)!}} P_l^{|M|} \cos\theta \quad \text{where } M = 0, 1, 2, 3, \dots$$

$$\text{Total wave function } \psi = \sqrt{\frac{(2l+1)(l-|M|)!}{2(l+|M|)!}} P_l^{|M|} \cos\theta \times \frac{1}{\sqrt{2\pi}} \exp(\pm im\phi)$$

The corresponding eigen value of ψ_{em} is $\frac{8\pi^2 IE}{h^2} = l(l+1)$ and $E_l = \frac{h^2}{8\pi^2 I} l(l+1)$

l is the rotational quantum numbers = 0, 1, 2,etc.

The energy of the system E is given by
$$E = \frac{l(l+1)h^2}{8\pi^2 I}$$

Harmonic Oscillator

The total energy of the single particle of mass 'm', $\hat{H} = \text{K.E.} + \text{P.E.} = \frac{1}{2}mv^2 + V$

$$= \frac{m^2 v^2}{2m} + V = \frac{p^2}{2m} + V$$

We know that $p_x = \frac{h}{2\pi i} \frac{\partial}{\partial x}$; $\hat{H} = -\frac{h^2}{8\pi^2 m} \frac{\partial^2}{\partial x^2} + V$

Consider a system of particle of mass 'm' attracted by a force proportional to the displacement of the particle is given by the expression, $f = -kx$
The potential energy of such particle is equal to its integral of the force over the distance its axis

$$V = -\int_0^x f dx ; V = \int_0^x kx dx = \frac{1}{2} kx^2$$

$$\therefore \hat{H} = -\frac{h^2}{8\pi^2 m_e} \frac{d^2}{dx^2} + \frac{1}{2} k x^2$$

The wave equation for the system is

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{8\pi^2 m_e}{h^2} (E - \frac{1}{2} k x^2) \psi = 0$$

Put $\alpha = \frac{8\pi^2 m_e E}{h^2}$ and $\beta = \frac{2\pi}{h} \sqrt{m_e k}$ and $\beta^2 = \frac{4\pi^2 m_e k}{h^2}$

Therefore, $\frac{\partial^2 \psi}{\partial x^2} + (\alpha - \beta^2 x^2) \psi = 0$

$$\frac{\partial^2 \psi}{\partial x^2} + (\alpha - \beta^2 x^2) \psi = 0 \text{ where } \xi = \text{the change of variable} = x\sqrt{\beta}$$

Dividing by β gives $\frac{\partial^2 \psi}{\partial \phi^2} + \left(\frac{\alpha}{\beta} - \xi^2\right) \psi = 0$

For the above equation the solution is,

$$\psi_n = \left(\frac{1}{2^n n! \sqrt{\pi}}\right)^{1/2} \exp\left(-\frac{\xi^2}{2}\right) H_n(\xi)$$

The energy of the system is given by

$$E = (n + \frac{1}{2}) h\nu_0$$

where n = vibration quantum number values of $n = 0, 1, 2, 3, \dots$

The state with $n = 0$ is the vibration ground state which possess energy $\frac{1}{2} h\nu_0$ called zero point energy.