INTRODUCTION TO EXACT QUANTUM MECHANICAL RESULT

In 1965 Newton proposed corpascular theory of light. According to corpuscular theory, the visible light consists of small particles which are emitted by the source. Earlier to ~~this~~ this theory Huygen suggested wave like nature for light. But corpuscular theory recieved great importance and was widely accepted by the scientists till the begining of 19th Century.

At the begining of 19th century (i.e, 1800), thomas young assumed wave theory of light and was able to explain the reflection and refraction phenomenon of light. In 1801, Thomas Young discovered the phenomenon of interference and explained the formation of Newton's rings. Earlier, Newton explained these rings in terms of corpuscular theory.

In the late 19th century and early 20th century many new discoveries were made Röntgen discovered x-rays in 1895, electron was discovered by Thomson in 1897, black body radiation was proposed by Max Planck in 1900, the phenomenon of photoelectric effect was explained by Einstien in 1905. These new discoveries were not explained by means of wave theory. These phenomenon were explain By means of new theoly known as Quantum theoly.

According to classical theoly, the absorption (or) emission of energy takes place continously but according to quantum theoly, the absorption or emission of energy takes place continously. But according to quantum theoly, the absorption or emission of energy takes place in discrete amounts. These amounts are integral multiple of a fundamental unit E_0 i.e, $0, E_0, 2E_0, \ldots$

Schrodinger Equation :

If electron has wave properties then there must be a wave equation and wave function to describe the electron if the displacement occur in y direction, mathematically these motions can be described by the functions of the form.

$$y(x,t) = f(x)\,\phi(t)$$

where $f(x)$ is independant of time (t) and $\phi(t)$ is independant of x. The general classical one dimensional wave equation has the form.

$$\frac{d^2y}{dx^2} = \frac{1}{c^2}\frac{d^2y}{dt^2} \quad \text{———} \quad ①$$

where c is called the wave velocity.

Substituting y in ①, we get

$$\frac{c^2}{f(x)}\frac{d^2f(x)}{dx^2} = \frac{1}{\phi(t)}\frac{d^2\phi(t)}{dt^2} = -\omega^2 \quad \text{———} \quad ②$$

where ω^2 is a constant.

$$\frac{1}{\phi(t)}\frac{d^2\phi(t)}{dt^2} = -\omega^2 \quad \text{———} \quad ③$$

$$\Rightarrow \frac{d^2\phi(t)}{dt^2} = -\omega^2\phi(t)$$

$$\Rightarrow \frac{d^2\phi(t)}{dt^2} + \omega^2\phi(t) = 0 \quad \text{———} \quad ④$$

$$\frac{c^2}{f(x)}\frac{d^2f(x)}{dx^2} = -\omega^2$$

$$\Rightarrow \frac{d^2f(x)}{dx^2} = \frac{-\omega^2 f(x)}{c^2}$$

$$\Rightarrow \frac{d^2f(x)}{dx^2} + \frac{\omega^2}{c^2}f(x) = 0 \quad \text{———} \quad ⑤$$

Equation ④ and ⑤ are second order differential equations

General second order differential equation can be written as

$$\frac{d^2y}{dx^2} + k^2y = 0 \quad \text{———} \quad Ⓐ$$

Solution for such equation generally can be written as

$$y = e^{mx}$$

Substituting $y = e^{mx}$ in Ⓐ, we get

$$m^2 e^{mx} + k^2 e^{mx} = 0.$$

$$\Rightarrow m^2 + k^2 = 0 \Rightarrow m^2 = -k^2 \Rightarrow m = \pm ik$$

∴ The complete solution for equation Ⓐ can be written as

$$y = A_1 e^{ikx} + A_2 e^{-ikx}$$

$$\Rightarrow y = A_1(\cos kx + i\sin kx) + A_2(\cos kx - i\sin kx)$$

$$= (A_1 + A_2)\cos kx + (A_1 - A_2)\, i\sin kx$$

$$= C\cos kx + D\sin kx$$

Similarly for equation ④ the solution can written as

$$\phi(t) = A\sin\omega t + B\cos\omega t \qquad ⑥$$

where A and B are constants which can be determined from the boundary conditions

ω is called the circular frequency and $\omega = 2\pi\nu$

∴ Equation ⑤ can be written as

$$\frac{d^2 f(x)}{dx^2} + \frac{4\pi^2\nu^2}{c^2} f(x) = 0 \qquad ⑦ \qquad \left[\nu = \frac{c}{\lambda} \Rightarrow \frac{\nu}{c} = \frac{1}{\lambda}\right.$$

$$\Rightarrow \frac{d^2 f(x)}{dx^2} + \frac{4\pi^2}{\lambda^2} f(x) = 0 \qquad ⑧$$

The general solution of equation ⑧ can be written as

$$f(x) = A_1 \exp\left[+\frac{i2\pi}{\lambda}x\right] + A_2 \exp\left[-\frac{i2\pi}{\lambda}x\right]$$

$$\text{or } f(x) = C\sin\frac{2\pi}{\lambda}x + D\cos\frac{2\pi}{\lambda}x \quad \text{——— ⑨}$$

Where A_1, A_2, C and D are constants

Imposing boundary conditions on equation ⑨ we get

i.e. (i) $f(x)=0$ at $x=0$ and

(ii) $f(x)=0$ at $x=a$

Applying first boundary condition to equation ⑨ we get

$$0 = C\sin(0) + D\cos(0)$$

$$\Rightarrow D=0$$

$$\therefore f(x) = C\sin\frac{2\pi}{\lambda}x$$

Now applying second boundary condition we get

$$0 = C\sin\frac{2\pi}{\lambda}a$$

$$\Rightarrow \sin\frac{2\pi}{\lambda}a = 0.$$

$$\Rightarrow \sin\frac{2\pi}{\lambda}a = \sin n\pi$$

$$\Rightarrow \frac{2a}{\lambda} = n \quad \text{where } n=1,2,3,\ldots\ldots$$

$$\Rightarrow a = \frac{n\lambda}{2}$$

Thus the stationary sine waves can be given by

$$f(x) = C\sin\frac{n\pi}{a}x$$

The complete solution can be written as

$$y(x,t) = C\sin\frac{n\pi}{a}x\left(A\sin 2\pi\nu t + B\cos 2\pi\nu t\right) \quad \text{——— ⑩}$$

5 T, Considering time independent part

$\psi = C \sin \frac{2\pi}{\lambda} x$.

$$\frac{\partial\psi}{\partial x} = \frac{2\pi}{\lambda} C \cos \frac{2\pi}{\lambda} x.$$

$$\frac{\partial^2\psi}{\partial x^2} = -\frac{4\pi^2}{\lambda^2} C \sin\left(\frac{2\pi}{\lambda} x\right)$$

$$\frac{\partial^2\psi}{\partial x^2} = -\frac{4\pi^2}{\lambda^2} \psi$$

$E = \frac{1}{2} mv^2 + V$ (potential energy)

$\Rightarrow (E - V) = \frac{1}{2} mv^2$ ——— ①

$E = h\nu$ and $E = mc^2$

$\Rightarrow h\nu = mc^2$

$\Rightarrow \frac{hc}{\lambda} = mc^{\cancel{2}} \Rightarrow c = \frac{h}{\lambda m}$ ⇒ Velocity $= \frac{h}{\lambda m}$

$$(E - V) = \frac{1}{2} m \frac{h^2}{\lambda^2 m^{\cancel{2}}}$$

$$= \frac{h^2}{2\lambda^2 m} \rightarrow \lambda^2 = \frac{h^2}{2m(E-V)}$$

$$\frac{\partial^2\psi}{\partial x^2} = -\frac{4\pi^2}{\frac{h^2}{2m(E-V)}} \psi$$

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

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

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$$\frac{d^2\psi}{dx^2} = -\frac{\frac{4\pi^2}{h^2}}{2m(E-V)}\psi$$

$$\Rightarrow \frac{d^2\psi}{dx^2} = \frac{-8\pi^2 m}{h^2}(E-V)\psi$$

$$\Rightarrow \frac{d^2\psi}{dx^2} + \frac{8\pi^2 m}{h^2}(E-V)\psi = 0 \quad \text{———} \quad (14)$$

Three dimensionally equation (14) can be written as

$$\frac{d^2\psi}{dx^2} + \frac{d^2\psi}{dy^2} + \frac{d^2\psi}{dz^2} + \frac{8\pi^2 m}{h^2}(E-V)\psi = 0 \quad \text{———} \quad (15)$$

Quantum - Mechanical Postulates :

Quantum mechanics was developed by analogy with the wave theory of electromagnetic radiation. A set of quantum-mechanical postulates were introduced to show the comparability of theoretical assumptions with experimental results

The Schrodinger equation is central to quantum mechanics in the same way that Newton's second law of motion is central to classical mechanics A postulate is a fundamental assumption on which theory is based and the consequences of the postulates must be compared with experiment to validate the theory.

Postulate I : The entire information about the mechanical state of a system is contained in a wave function $\psi(q,t)$. The wave function should be continuous, finite and single-valued function of time (t). The wave function ψ obeys the time-dependent Schrodinger equation.

$$\hat{H}\psi = \frac{-h}{2\pi i}\frac{\partial\psi}{\partial t}$$

Where $\hat{H}$ is Hamiltonian operator and h is planck's constant.

Postulate-II: If $d\tau$ is a differential volume element then the probability of finding the system in the volume element $d\tau$ at a specified time 't' is given by $\psi^2 d\tau$ [or $\psi\psi^* d\tau$, if ψ is a complex wave function]. ψ^2 (or $\psi\psi^*$) is thus interpreted as the probability density. This is the physical significance of the wavefunction ψ.

Postulate-III: Every dynamical variable, corresponding to a physically observable quantity, can be expressed as a linear operator.

Postulate-IV: Quantum mechanical operators corresponding to physical properties are obtained from the classical expressions for these quantities using certain well established procedures.

Eg:

observable Quantity	classical notation	Quantum mechanical notation	
		symbol	operator
position	x	$\hat{x}$	
Momentum	P_x	$\hat{P}_x$	$\frac{h}{2\pi i}\frac{d}{dx}$
kinetic energy	$E_K = \frac{P_x^2}{2m}$	$\hat{E}_K$	$\frac{-h^2}{8\pi^2 m}\frac{d^2}{dx^2}$

etc.

Postulate V: If it is supposed to measure the numerical value of physical observable property F whose operator is $\hat{F}$ then there are two possible situations.

(a) If the state of the system is given by ψ_i and ψ_i is an independent function of the operator $\hat{F}$, with eigenvalue f_i, that is

$$\hat{F}\psi_i = f_i\psi_i$$

∴ The measurement of observable F is certain to yield the numerical value f_i

(b) If ψ_i is not an eigenfunction of $\hat{F}$, then we cannot predict the result of any single measurement of the observable F. If many measurements are made on many identical systems, we may get many different results. then the quantum mechanical average of all these results ie expectation value can be given by

$$\bar{F} = \langle F \rangle = \frac{\int_{\text{all space}} \psi_i^{*} \hat{F} \psi_i \, d\tau}{\int_{\text{all space}} \psi_i^{*} \psi_i \, d\tau}$$

If the wavefunctions are normalised then $\int_{\text{all space}} \psi_i^{*} \psi_i \, d\tau = 1$

$$\therefore \langle F \rangle = \int_{\text{all space}} \psi_i^{*} \hat{F} \psi_i \, d\tau$$

The symbol $\langle \; \rangle$ is used to denote average value in Quantum mechanics and is often called the expectation value.

Operators:

It is well known that wave function describes the state of a system, so that any observable quantity can be derived from it. The mathematical process that is used for carrying out the derivation involves the concept of operators. To every physically measurable or observable quantity like position, velocity, linear momentum, angular momentum, energy etc. of a system there corresponds an operator in quantum mechanics.

An operator is a symbol which indicates that a particular operation is to be performed on what follows the operator. In other words, an operator is a symbol for certain mathematical procedure which transforms one function into another.

For example, the symbol $\sqrt{\ }$ is the square root operator

$$\therefore \sqrt{4} = 2.$$

Another example is, if $\frac{d}{dx}$ is an operator, operating on x^n then we can obtai a new function i.e.

$$\frac{d}{dx}(x^n) = nx^{n-1}$$

$$\therefore (\text{Operator}) \cdot (\text{function}) = (\text{Another function})$$

The function on which the operation is carried out is often called an operand. An operator does not have any meaning when it stands alone. An operator is written with a symbol ^ ('hat') over head.

Addition and Subtraction of operators:

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

$$(\widehat{A+B})f = \hat{A}f + \hat{B}f$$

$$(\widehat{A-B})f = \hat{A}f - \hat{B}f$$

Where f is an operand.

The above operations can also be written as

$$\widehat{A+B} = \hat{B} + \hat{A}$$

$$\widehat{A-B} = -\hat{B} + \hat{A}$$

Multiplication of operators :

If a function is operated by two or more operators consecuti then the process is called multiplication of operators

Let $\hat{f}$ be an operand on which two operators $\hat{A}$ and $\hat{B}$ are operating consecutively

i.e. $\hat{A}\hat{B}f$ means that the function 'f' is first operated on with $\hat{B}$ to obtain a new function f', as

$$\hat{B}f = f'$$

Then f' is being operated by $\hat{A}$ to obtain the function f''

$$\hat{A}f' = f''$$

$$\therefore \hat{A}\hat{B}f = f''$$

The order of application of operators is always from right to left as they are written

If the same operator is applied several times in succession, it is written with a power

i.e. $\hat{A}\hat{A}f = \hat{A}^2 f$

For example let us suppose that operator $\hat{A}$ stands for taking the derivative w.r.to x and operator $\hat{B}$ for the multiplication by x.

$$\therefore \hat{A}\hat{B}f(x) = \hat{A}\left[\hat{B}f(x)\right] = \hat{A}\left[x\,f(x)\right] = \frac{d}{dx}\left[x\,f(x)\right] = x\frac{df(x)}{dx} + f(x)$$

$$\hat{B}\hat{A}f(x) = \hat{B}\left[\hat{A}f(x)\right] = \hat{B}\left[\frac{d}{dx}f(x)\right] = x\frac{df(x)}{dx}$$

$$\therefore \hat{A}\hat{B}f(x) \neq \hat{B}\hat{A}f(x)$$

Commuting operators:

If α and β are two operators such that $\alpha\beta f(x) = \beta\alpha f(x)$ then they are called commuting operators.

Let $\alpha = \sqrt{\ }$, $\beta = (\ )^2$ and $f(x) = x^2$. Then

$$\alpha\beta f(x) = \alpha(x^2)^2 = \alpha(x^4) = \sqrt{x^4} = x^2$$

$$\beta\alpha f(x) = \beta(\sqrt{x^2}) = \beta(x) = (x)^2 = x^2$$

In this case the operators α and β are said to commute.

If $\alpha = \beta$ then $\alpha\alpha f(x) = \alpha\alpha f(x)$.

$\therefore$ Every operator commutes with itself. It can also be concluded that any operator commutes with itself or any of its powers

i.e. $\alpha\alpha^n f(x) = \alpha^n\alpha f(x)$

Non-Commuting operators:

Let $\alpha = \frac{d}{dx}$ and $\beta = x$ and $f(x) = x^2$. Then

$$\alpha\beta f(x) = \alpha\beta(x^2) = \alpha(x \cdot x^2) = \alpha x^3 = \frac{d}{dx}(x^3) = 3x^2$$

$$\beta\alpha f(x) = \beta\frac{d}{dx}(x^2) = \beta(2x) = x(2x) = 2x^2$$

In this case, $\alpha\beta f(x) \neq \beta\alpha f(x)$. The two operators are non commuting

Commutator of a pair of operators:

If α and β are two operators, then the operator $(\alpha\beta - \beta\alpha)$ is called the commutator of the pair α and β

If α and β commute, $\alpha\beta f(x) = \beta\alpha f(x)$

$$\therefore (\alpha\beta - \beta\alpha) f(x) = 0 = 0 \cdot f(x)$$

The commutator of two commuting operators is same as multiplication by zero. The commutator of any two commuting operators is a null operator.

In the example given for non-commuting operator, $\alpha\beta f(x) = 3x^2$ and

$\beta\alpha f(x) = 2x^2$

$\therefore (\alpha\beta - \beta\alpha) f(x) = 3x^2 - 2x^2 = 1 \cdot x^2 = 1 \cdot f(x)$

In this example, the commutator of the two non-commuting operators is unit operator.

Linear operator:

If an operator when applied on the sum of two functions gives the same result as the sum of the operations on the two functions separately then the operator is said to be linear

Ex: If the value of an operator α when applied on the sum of two functions f and g and the value of the sum of the operators on f & operator on g are equal, then α is a linear operator.

$$\alpha(f+g) = \alpha f + \alpha g$$

An example of a linear operator is $\frac{d}{dx}$, because

$$\frac{d}{dx}(f+g) = \frac{df}{dx} + \frac{dg}{dx}$$

An example of a non linear operator is $\sqrt{\ }$, since

$$\sqrt{f+g} \neq \sqrt{f} + \sqrt{g}$$

Note: Operands may sometimes be functions of two or more variables, such as $f(x,y)$ and $f(x,y,z)$.

Vector operators:

Vector operators are important group of operators and can be applied on a function of several variables. A vector operator ∇ (del) is defined in cartesian co-ordinates as

$$\nabla = i\frac{\partial}{\partial x} + j\frac{\partial}{\partial y} + k\frac{\partial}{\partial z}$$

Where i, j, k are unit vectors along x, y and z axes respectively.

(a). Gradient of a scalar function ϕ:

Del operator, when applied on a scalar function, generates a vector called the gradient of ϕ

$$\nabla\phi = i\frac{\partial\phi}{\partial x} + j\frac{\partial\phi}{\partial y} + k\frac{\partial\phi}{\partial z}$$

(b). Divergence of a vector:

The scalar or dot product of ∇ operator with vector D gives a scalar function called the divergence of D or div D

$$\nabla\cdot D = \left(i\frac{\partial}{\partial x} + j\frac{\partial}{\partial y} + k\frac{\partial}{\partial z}\right)\cdot\left(iD_x + jD_y + kD_z\right)$$

$$= \frac{\partial D_x}{\partial x} + \frac{\partial D_y}{\partial y} + \frac{\partial D_z}{\partial z}$$

(c) Curl of a vector:

The cross product or vector product of the operator ∇ with a vector D gives a new vector called the curl of D.

$$\nabla \times D = \left(i\frac{\partial}{\partial x} + j\frac{\partial}{\partial y} + k\frac{\partial}{\partial z}\right)\times\left(iD_x + jD_y + kD_z\right)$$

The result is written in the determinantal form

$$\nabla \times D = \begin{vmatrix} i & j & k \\ \frac{\partial}{\partial x} & \frac{\partial}{\partial y} & \frac{\partial}{\partial z} \\ D_x & D_y & D_z \end{vmatrix}$$

(d) Laplacian operator ∇^2 (del squared)

This is the most important operator used in quantum mechanics. ~~If~~ It is formed by taking the dot product of ∇ with itself.

$$\nabla^2 = \nabla\cdot\nabla = \left(i\frac{\partial}{\partial x} + j\frac{\partial}{\partial y} + k\frac{\partial}{\partial z}\right)\cdot\left(i\frac{\partial}{\partial x} + j\frac{\partial}{\partial y} + k\frac{\partial}{\partial z}\right)$$

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

Hermitian and unitary operators:

Hermitian and unitary operators obey the eigen value in equal

$\hat{A}\psi = \lambda\psi$.

An operator $\hat{A}$ is said to be Hermitian operator if

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

Where ψ_1 and ψ_2 are two eigen functions of the operator $\hat{A}$ and ψ_1^* is complex conjugate of ψ_1. This is known as 'turn-over rule'. Hermitian operator is linear and has real eigenvalue. The existence of real eigen value can be proved as follows.

If $\hat{A}$ is a hermitian operator and ψ an eigenfunction with eigen value a then

$$\hat{A}\psi = a\psi \quad \text{———— ①}$$

Multiplying both sides of the equation with ψ^* and integrating over all space we get

$$\int \psi^* \cdot (\hat{A}\psi)\, d\tau = a\int \psi^*\psi\, d\tau \quad \text{———— ②}$$

Taking the complex conjugate of every quantity in ①

i.e. $\hat{A}^*\psi^* = a^*\psi^*$ ———— ③

Multiplying both sides with ψ and integrating

$$\int \psi \cdot (\hat{A}\psi)^*\, d\tau = a^*\int \psi\psi^*\, d\tau \quad \text{———— ④}$$

ψ^*

ψ'

The left hand side of the equations ② and ④ are equal according to the definition of hermitian operator, so that

$$a\int \psi^*\psi\, d\tau = a^*\int \psi^*\psi\, d\tau \quad \text{———— ⑤}$$

$\Rightarrow a = a^*$

This is possible only if a is real

Thus any physical quantity represented by Hermitian operator is observable and physically measureable.

Unitary operator $\hat{U}$ is also linear and is defined as

$$\int \psi_1^* \hat{U}^{-1} \psi_2 \, d\tau = \int \psi_2 \hat{U}^* \psi_1^* \, d\tau$$

Where the operator $\hat{U}^{-1}$ is the inverse of $\hat{U}$

i.e. $\hat{U}\hat{U}^{-1} = \hat{U}^{-1}\hat{U}$ and ψ_1 and ψ_2 are any two eigenfunctions of $\hat{U}$

$$\hat{U}\hat{U}^{-1} = \hat{U}^{-1}\hat{U} = 1$$

Consider the eigen value equation

$$\boxed{\hat{U}\psi = \lambda\psi} \qquad \text{———} \ ⑥$$

Where λ is eigen value

$$\therefore \hat{U}^{-1}\hat{U}\psi = \psi = \lambda.\hat{U}^{-1}\psi$$

$$\Rightarrow \hat{U}^{-1}\psi = \lambda^{-1}\psi \qquad \text{———} \ ⑦$$

∴ Inverse operator $\hat{U}^{-1}$ has the same eigenfunction as $\hat{U}$ but with reciprocal eigenvalue.

Multiply both sides of equation ⑦ with ψ^* and integrate over all the space

$$\int \psi^* \hat{U}^{-1} \psi \, d\tau = \lambda^{-1} \int \psi^* \psi \, d\tau \qquad \text{———} \ ⑧$$

Taking the complex conjugate of equation ⑥

$$\hat{U}^* \psi^* = \lambda^* . \psi^* \qquad \text{———} \ ⑨$$

Multiply both sides with ψ and integrate over all the space

$$\int \psi \hat{U}^* \psi^* \, d\tau = \lambda^* \int \psi^* \psi \, d\tau \qquad \text{———} \ ⑩$$

According to the definition of unitary operator, the left hand side of equatio ⑧ and ⑩ are equal.

$$\lambda^{-1}\int\psi^*\psi\, d\tau = \lambda^*\int\psi^*\psi\, d\tau$$

$$\Rightarrow \lambda^{-1} = \lambda^*$$

$$\Rightarrow \lambda\lambda^{-1} = \lambda\lambda^* = 1$$

Thus eigenvalues of an unitary operator have modulus one.

Eigenfunctions and Eigenvalues:

When a function f is operated upon by an operator α, if the function f is merely multiplied by a constant, say a, then f is called an eigenfunction or characteristic function of operator α and a is called an eigenvalue or characteristic value of the operator.

$$\alpha f = af$$

e.g. $$\frac{d}{dx}e^{kx} = k\, e^{kx}$$

Here e^{kx} is an eigenfunction of the operator $\frac{d}{dx}$ with the eigenvalue k.

Hamiltonian operator H:

The energy operator called the Hamiltonian operator can be derived as follows. The Hamiltonian function is

$$H = T + V$$

For a system of n particles

$$H = \frac{1}{2}\sum_{i=1}^{n} m_i v_i^2 + V(x_1, y_1, z_1, \ldots\ldots, x_n, y_n, z_n)$$

For a single particle

$$H = \frac{1}{2}mv^2 + V(x, y, z)$$

$$= \frac{p^2}{2m} + V(x,y,z)$$

$$= \frac{1}{2m}(P_x^2 + P_y^2 + P_z^2) + V(x,y,z)$$

The quantum mechanical Hamiltonian operator $\hat{H}$ is now given by

$$\hat{H} = \frac{1}{2m}\left[\hat{P}_x^2 + \hat{P}_y^2 + \hat{P}_z^2\right] + V(x,y,z)$$

$$= \frac{1}{2m}\left[\left(\frac{h}{2\pi i}\frac{\partial}{\partial x}\right)^2 + \left(\frac{h}{2\pi i}\frac{\partial}{\partial y}\right)^2 + \left(\frac{h}{2\pi i}\frac{\partial}{\partial z}\right)^2\right] + V(x,y,z)$$

$$= -\frac{h^2}{8\pi^2 m}\left[\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right] + V(x,y,z)$$

$$= -\frac{h^2}{8\pi^2 m}\nabla^2 + V(x,y,z)$$

If the system contains n particles, then

$$\boxed{\hat{H} = -\frac{h^2}{8\pi^2}\sum_{i=1}^{n}\frac{\nabla_i^2}{m_i} + V(x_1 y_1 z_1 \ldots\ldots x_n y_n z_n)}$$

Exercise:

Show that the operators (1) $\hat{x}$ (2) $\hat{P}_x$ and (3) $\hat{H}$ are linear and Hermitian.

1. Consider the state functions ψ and ϕ. Then

$$\hat{x}(\psi+\phi) = x(\psi+\phi) = x\psi + x\phi$$

$\therefore$ $\hat{x}$ is linear

Consider the integrals $I_1 = \int \psi^* \hat{x} \phi \, dx$ and $I_2 = \int \phi (\hat{x}\psi)^* dx$.

$\hat{x}$ is said to be Hermitian if and only if $I_1 = I_2$

$$I_1 = \int \psi^* \hat{x} \phi \, dx \Rightarrow I_1 = \int \psi^* x \phi \, dx$$

$$\Rightarrow I_1 = \int \psi^* x^* \phi \, dx \qquad [\because x^* = x, x \text{ being real}]$$

$$\Rightarrow I_1 = \int x^* \psi^* \phi \, dx$$

$$\Rightarrow I_1 = \int (\hat{x}\psi)^* \phi \, dx$$

$$\Rightarrow I_1 = I_2$$

$\therefore$ operator $\hat{x}$ is hermitian operator.

2. Let ψ and ϕ be two state functions

$$\hat{P}_x(\psi+\phi) = \frac{h}{2\pi i}\frac{\partial}{\partial x}(\psi+\phi) = \frac{h}{2\pi i}\left[\frac{\partial\psi}{\partial x} + \frac{\partial\phi}{\partial x}\right]$$

$$= \frac{h}{2\pi i}\frac{\partial\psi}{\partial x} + \frac{h}{2\pi i}\frac{\partial\phi}{\partial x} = \hat{P}_x\psi + \hat{P}_x\phi$$

$\therefore$ $\hat{P}_x$ is a linear operator.

$\hat{P}_x$ is said to be Hermitian if $\int \psi^* \hat{P}_x \phi \, dx \, [I_1] = \int (\hat{P}_x\psi)^* \phi \, dx \, [I_2]$

consider the integral $I_1 = \int \psi^* \hat{P}_x \phi \, dx$

$$\Rightarrow I_1 = \int \psi^* \frac{h}{2\pi i}\frac{\partial}{\partial x}\phi \, dx$$

In I_1 let $u = \psi^*$ and $dv = \frac{\partial\phi}{\partial x} dx$. using the formula $\int u\,dv = uv - \int v\,du$ for I_1

$$\Rightarrow I_1 = \frac{h}{2\pi i}\left[(\psi^*\phi)_{-\infty}^{+\infty} - \int \phi \frac{\partial\psi^*}{\partial x} dx\right]$$

[$\because$ where $V = \phi$ $du = \frac{\partial\psi^*}{\partial x} dx$] and $(\psi^*\phi)_{-\infty}^{+\infty} = 0$.

$$\Rightarrow I_1 = -\frac{h}{2\pi i}\int \phi \frac{\partial\psi^*}{\partial x} dx \Rightarrow I_1 = \int \phi \left(\frac{-h}{2\pi i}\frac{\partial}{\partial x}\right)\psi^* dx$$

$$\Rightarrow I_1 = \int \phi \left(\frac{h}{2\pi i}\frac{\partial}{\partial x}\psi\right)^* dx \Rightarrow I_1 = I_2$$

$\therefore$ $\hat{P}_x$ is hermitian.

3. Let ψ and ϕ be state functions

$$\hat{H}(\psi+\phi) = \left\{\left[-\frac{h^2}{8\pi^2 m}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)\right]+V(x,y,z)\right\}(\psi+\phi)$$

$$\Rightarrow \hat{H}(\psi+\phi) = -\frac{h^2}{8\pi^2 m}\nabla^2\psi + V(x,y,z)\psi - \frac{h^2}{8\pi^2 m}\nabla^2\phi + V(x,y,z)\phi$$

$$= \left[-\frac{h^2}{8\pi^2 m}\nabla^2 + V\right]\psi + \left[-\frac{h^2}{8\pi^2 m}\nabla^2 + V\right]\phi$$

$$= \hat{H}\psi + \hat{H}\phi$$

$\therefore$ $\hat{H}$ is linear

Consider the integrals $I_1 = \iiint \psi^* \hat{H}\phi \, d\tau$ and $I_2 = \iiint \phi(\hat{H}\psi)^* d\tau$

$\hat{H}$ is said to be hermitian if $I_1 = I_2$

Potential energy is the energy possessed by the system by virtue of its position.

$\therefore$ The operator part corresponding to the potential energy, namely $V(x,y,z)$ can be shown to be Hermitian.

$$\iiint \psi^* V(x,y,z)\phi \, d\tau = \iiint \phi \, [V(x,y,z)\psi]^* d\tau$$

Since $V(x,y,z)$ contains only the co-ordinates x,y,z which are real $V=V^*$

$\hat{H}$ to be hermitian, the other part of the operator should also be hermitian.

Let $I_3 = \iiint \psi^* \frac{\partial^2}{\partial x^2}\phi \, d\tau$ and $I_4 = \iiint \phi\left[\left(\frac{\partial^2}{\partial x^2}\right)\psi\right]^* d\tau$

$$I_3 = \iiint \psi^* \frac{\partial}{\partial x}\left(\frac{\partial\phi}{\partial x}\right) dx\,dy\,dz$$

Let $u = \psi^*$ and $dv = \frac{\partial}{\partial x}\left(\frac{\partial \phi}{\partial x}\right)dx$

$\therefore du = \frac{\partial \psi^*}{\partial x}dx$ and $v = \frac{\partial \phi}{\partial x}$

Applying the formula $\int u\,dv = uv - \int v\,du$

$$I_3 = \iint \left[\psi^* \frac{\partial \phi}{\partial x}\right]_{-\infty}^{+\infty} dy\,dz - \iint \frac{\partial \phi}{\partial x}\,\frac{\partial \psi^*}{\partial x}\, dx\,dy\,dz$$

As ψ and φ with their derivatives go to zero at infinity.

$$\Rightarrow I_3 = -\iiint \frac{\partial \phi}{\partial x}\,\frac{\partial \psi^*}{\partial x}\, dx\,dy\,dz$$

Now let $u = \frac{\partial \psi^*}{\partial x}$ and $dv = \frac{\partial \phi}{\partial x}\,dx$.

$$\therefore \quad du = \frac{\partial}{\partial x}\left(\frac{\partial \psi^*}{\partial x}\right)dx \qquad v = \phi$$

$$\therefore I_3 = -\left[\iint \left[\frac{\partial \psi^*}{\partial x}\,\phi\right]_{-\infty}^{+\infty} dy\,dz - \iiint \phi\,\frac{\partial}{\partial x}\left(\frac{\partial \psi^*}{\partial x}\right) dx\,dy\,dz\right]$$

$\therefore I_3 = \iiint \phi\,\frac{\partial^2 \psi^*}{\partial x^2}\, dx\,dy\,dz$ [∵ The first term in RHS is z

$$\Rightarrow I_3 = \iiint \phi \left[\left(\frac{\partial^2}{\partial x^2}\right)\psi\right]^* dx\,dy\,dz$$

$$\Rightarrow I_3 = I_4$$

∴ Hamiltonian operator $[\hat{H}]$ is Hermitian operator.

Derivation of wave equation using operator concept:

The equation for an electromagnetic radiation travelling in vacuum with velocity c is given by

$$\frac{\partial^2 y}{\partial x^2} = \frac{1}{c^2}\frac{\partial^2 y}{\partial t^2}$$

This equation is classical one dimensional wave equation. Schrodinger replaced y by ψ

$$\therefore \frac{\partial^2 \psi}{\partial x^2} = \frac{1}{c^2}\frac{\partial^2 \psi}{\partial t^2}$$

Where $\psi(x,t)$ is a function which describes the behaviour of the electron in terms of distance and time. A solution of this equation is

$$\psi(x,t) = c\,e^{i\alpha} \text{ ——— ①}$$

Where c is a constant and α is the phase

$$\alpha = 2\pi\left(\frac{x}{\lambda} - \nu t\right)$$

∴ Equation ① can be written as

$$\psi(x,t) = c\,e^{i\frac{2\pi}{\lambda}x}\,e^{-i2\pi\nu t} \text{ ——— ②}$$

$$\Rightarrow \psi(x,t) = \psi(x)\,e^{-i2\pi\nu t}$$

Where $\psi(x)$ is a function of x and independent of t and $e^{-i2\pi\nu t}$ is independent of x

Now replace ν by $\frac{E}{h}$ and λ by $\frac{h}{p}$ in equation ② $\left[\because E = mc^2 \Rightarrow mc^2 = \frac{hc}{\lambda} \Rightarrow mc = \frac{h}{\lambda} \Rightarrow p = \frac{h}{\lambda} \Rightarrow \lambda = \frac{h}{p}\right]$

$$\therefore \psi(x,t) = c\,e^{\frac{i2\pi p_x \cdot x}{h}}\,e^{-i\frac{2\pi}{h}Et} \text{ ——— ③}$$

$\boxed{\lambda = h/p}$

Differentiating ③ w.r.to t

$\boxed{\nu = E/h}$

$$\therefore \frac{\partial\psi(x,t)}{\partial t} = -c\, i\frac{2\pi E}{h}\, e^{-i\frac{2\pi E}{h}t}\, e^{i\frac{2\pi P_x}{h}x}$$

$$\Rightarrow \frac{\partial\psi(x,t)}{\partial t} = -i\frac{2\pi E}{h}\psi(x,t)$$

Rearranging the above equation we get an operator

$$-\frac{h}{2\pi i}\frac{\partial\psi}{\partial t} = E\psi \quad \text{or} \quad \hat{E}\psi = E\psi \text{ ——— ④}$$

$$\boxed{\therefore \hat{E} = -\frac{h}{2\pi i}\frac{\partial}{\partial t}}$$

The operator $\hat{E}$ when applied on ψ results in energy E multiplied by the same function.

$$\psi(x,t) = c\, e^{\frac{i2\pi P_x}{h}x}\, e^{-i\frac{2\pi E}{h}t}$$

Differentiating the above equation wrt x we get

$$\frac{\partial\psi(x,t)}{\partial x} = \frac{i2\pi P_x}{h}\, c\, e^{\frac{i2\pi P_x}{h}x}\, e^{-\frac{i2\pi E}{h}t}$$

$$\Rightarrow \frac{\partial\psi(x,t)}{\partial x} = i\frac{2\pi P_x}{h}\psi(x,t)$$

$$\Rightarrow \frac{h}{2\pi i}\frac{\partial\psi(x,t)}{\partial x} = P_x\psi(x,t)$$

$$\text{or } \hat{P}_x\psi = P_x\psi \text{ ——— ⑤}$$

Equation ⑤ is an operator equation. The operator $\boxed{\hat{P}_x = \frac{h}{2\pi i}\frac{\partial}{\partial x}}$ is called linear momentum operator.

The total energy E of a system is the sum of potential energy and kinetic energy. For one-dimensional system the kinetic energy is $\frac{mv_x^2}{2}$, that is $\frac{P_x^2}{2m}$ and potential energy is $E_p(x,t)$

$$\therefore E = \frac{P_x^2}{2m} + E_p(x,t) \quad \text{———} ⑥ \ ★$$

If P_x in equation ⑥ is replaced by $\frac{h}{2\pi i}\frac{\partial}{\partial x}$ Then

$$\Rightarrow E = E_p(x,t) - \frac{h^2}{8\pi^2 m}\frac{\partial^2}{\partial x^2}$$

$$\Rightarrow E = -\frac{h^2}{8\pi^2 m}\frac{\partial^2}{\partial x^2} + E_p(x,t)$$

The above expression is nothing but the Hamiltonian operator

$$\Rightarrow \hat{H} = -\frac{h^2}{8\pi^2 m}\frac{\partial^2}{\partial x^2} + E_p(x,t) \quad \text{———} ⑦$$

If energy E in equation ④ is replaced by $\hat{H}$, we obtain

$$\Rightarrow -\frac{h}{2\pi i}\frac{\partial \psi}{\partial t} = \left[-\frac{h^2}{8\pi^2 m}\frac{\partial^2}{\partial x^2} + E_p(x,t)\right]\psi$$

If the above equation is extended three dimensionally. Then it can be written as

$$\Rightarrow \left[-\frac{h^2}{8\pi^2 m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right) + E_p(x,y,z,t)\right]\psi = -\frac{h}{2\pi i}\frac{\partial \psi}{\partial t} \quad \text{———} ⑧$$

The above equation is time dependent Schrodinger equation

The time-dependent wavefunction can be written as

$$\psi(x,y,z,t) = \psi(x,y,z)\boxed{e^{-i\frac{2\pi E}{h}t}} \quad \text{———} ⑨$$

Where $\psi(x,y,z)$ is the time-independent wavefunction. Differentiating ⑨ w.r.to. t we get

$$\frac{\partial \psi}{\partial t} = -i\frac{2\pi E}{h}\psi(x,y,z)e^{-i\frac{2\pi E}{h}t}$$

$$\Rightarrow \frac{\partial \psi}{\partial t} = -\frac{2\pi i}{h} E\psi$$

$$\Rightarrow -\frac{h}{2\pi i}\frac{\partial \psi}{\partial t} = E\psi$$

For stationary state potential energy E_p is independent of time.

∴ The time-dependent Schrodinger equation transforms into

$$\left[-\frac{h^2}{8\pi^2 m}\nabla^2 + E_p(x,y,z)\right]\psi(x,y,z) = E\psi(x,y,z)$$

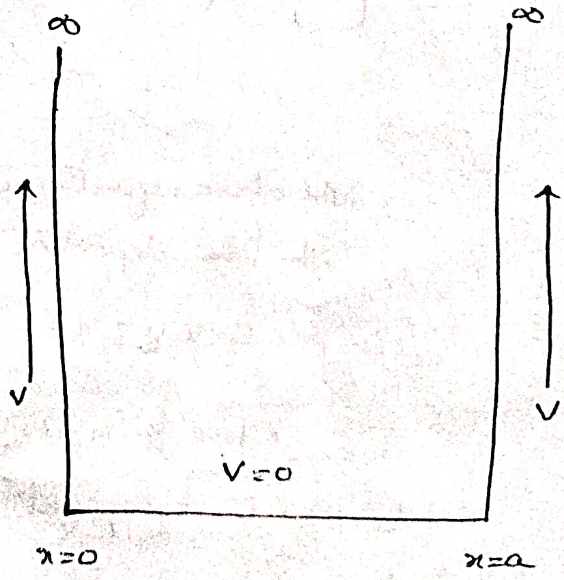
— This is time-independent Schrodinger equation and it can be compactly written as

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

Solutions of Schrodinger Equation:

(i) Particle in one dimensional box:

Consider a particle of mass 'm' moving in a box. The movement of the particle is confined between the walls of the box, which are at $x=0$ and at $x=a$. Outside the box the potential energy 'V' is taken to be infinite and with in the box the potential energy 'V' is zero. The walls of the box are infinitely height so that the particle cannot penetrate the walls. It was also supposed that the particle does not lose energy when it collides with such walls. The boundary conditions are satisfied by the particle i.e. at $x=0, \psi=0$ and at $x=a$, $\psi=0$.



One dimensional Schrodinger wave equation is

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

Inside the box the potential energy $V=0$

∴ The Schrodinger equation becomes

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

The solution for this equation can be written as

$$\psi = A \sin\left[\frac{8\pi^2 mE}{h^2}\right]^{1/2} x + B\cos\left[\frac{8\pi^2 mE}{h^2}\right]^{1/2} x$$

Applying the first boundary condition ie. at $x=0, \psi=0$.

$$\Rightarrow 0 = A \sin(0) + B \cos 0$$

$$\Rightarrow 0 = B(1) \Rightarrow B = 0.$$

∴ The wave function reduces to

$$\psi = A \sin\left[\frac{8\pi^2 m}{h^2} E\right]^{1/2} x$$

Applying the second boundary condition ie. $\psi = 0$ at $x = a$.

$$\Rightarrow 0 = A \sin\left[\frac{8\pi^2 m}{h^2} E\right]^{1/2} a$$

Since $A \neq 0$, $\sin\left[\frac{8\pi^2 m}{h^2} E\right]^{1/2} a = 0$

$$\rightarrow \left[\frac{8\pi^2 m}{h^2} E\right]^{1/2} a = n\pi$$

where $n = 1, 2, 3, \ldots$

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

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

$$\Rightarrow E = \frac{n^2 h^2}{8ma^2} \quad \text{ie. } E_n = \frac{n^2 h^2}{8ma^2} \quad \text{———} ①$$

$\psi_n = A$ … x

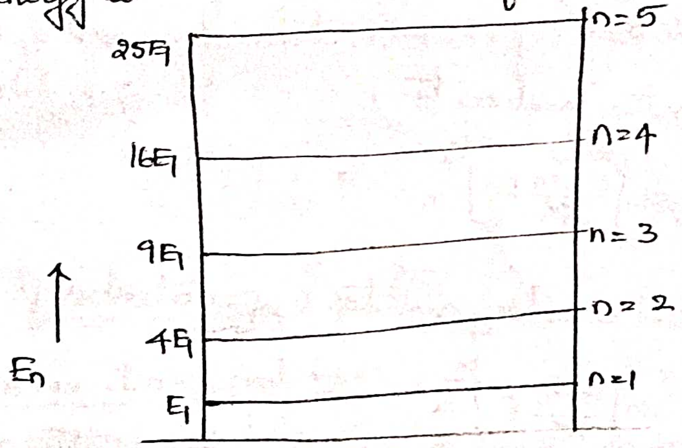
correspondingly $$\psi_n = A \sin\left(\frac{n\pi}{a}\right)x \qquad ②$$

It is clear from expression ① that inside an infinitely deep potential well, the particle can have only discrete set of values of energy i.e. the energy of the particle is quantised. The discrete energy values are given by

$$E_1 = \frac{h^2}{8ma^2} \text{ for } n=1, \quad E_2 = \frac{4h^2}{8ma^2} = 4E_1 \text{ for } n=2$$

$$E_3 = \frac{9h^2}{8ma^2} = 9E_1 \text{ for } n=3, \quad E_4 = 16\frac{h^2}{8ma^2} = 16E_1 \text{ for } n=4 \text{ and so on.}$$

The energy levels can be shown as follows.



Energy levels of a particle inside an infinite potential well.

The constant A of expression ② can be obtained by applying the normalization condition. i.e.

$$\int_0^a |\psi(x)|^2 dx = 1$$

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

$$\Rightarrow A^2 \int_0^a \frac{1}{2}\left[1 - \cos\frac{2n\pi x}{a}\right] dx = 1$$

$$\Rightarrow \frac{A^2}{2} \int_0^a \left[1 - \cos\frac{2n\pi}{a}x\right] dx = 1$$

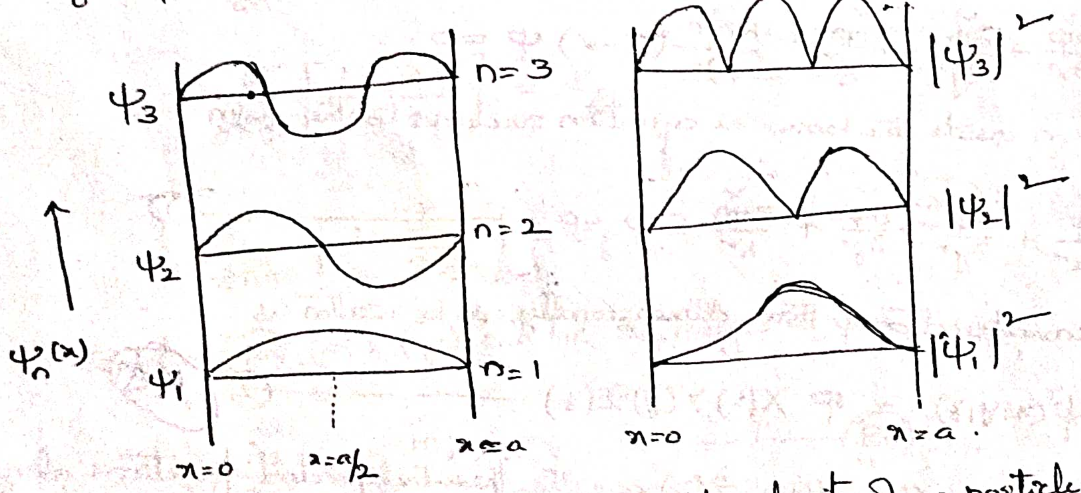
$$\rightarrow \frac{A^2}{2}\left[x - \frac{a}{2n\pi}\sin\frac{2n\pi}{a}x\right]_0^a = 1$$

$$\rightarrow \frac{A^2 a}{2} = 1 \text{ or } A^2 = \frac{2}{a} \rightarrow A = \sqrt{\frac{2}{a}}$$

$$\therefore \psi(x) = \sqrt{\frac{2}{a}} \sin\frac{n\pi}{a}x$$

This is the wavefunction for a particle enclosed in infinitely deep potential well.

The normalised wavefunctions ψ_1, ψ_2 and ψ_3 together with the probability densities $\psi_1^2, \psi_2^2, \psi_3^2$ can be plotted as follows. The probability of the particle being present is different for different quantum numbers.



Wave functions and Probability density of a particle inside an infinite potential well.

From the above plotting of wave functions & Probability functions it is clear that wave functions becomes $(n-1)$ times zero in this region in addition to becoming zero at the walls of the box i.e. there are $(n-1)$ internal nodes.

If the potential energy inside the box is not zero, then the energy can be given by

$$E_n = \frac{n^2h^2}{8ma^2} + V$$

$E_1 = \frac{h^2}{8ma^2}$ for n=1 is the lowest energy possessed by the particle in the box [Because n cannot be zero, $E_1 \neq 0$]. This lowest irremovable energy, E_1 is known as the zero point energy.

(ii) Particle in three dimensional box:

Consider a particle placed in three dimensional rectangular box having sides a_x, a_y and a_z. The potential energy of the particle is zero inside the box and infinite outside the box.

The three dimensional Schrodinger equation can be written as

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

As V=0 inside the box the equation reduces to the form

$$\frac{\partial^2\psi}{\partial x^2}+\frac{\partial^2\psi}{\partial y^2}+\frac{\partial^2\psi}{\partial z^2}+\frac{8\pi^2 m}{h^2}E\psi = 0. \quad \text{———} ①$$

The wave function ψ three dimensionally can be written as

$$\psi(x,y,z) = \cancel{\psi}\, X(x)\,Y(y)\,Z(z) \quad \text{———} ②$$

Where X(x), Y(y), Z(z) are the three independent functions along the three co-ordinates x, y, and z respectively.

Simply ② can be written as

$$\psi = XYZ \quad \text{———} ③$$

$$\therefore \frac{\partial\psi}{\partial x} = YZ\frac{\partial X}{\partial x} \Rightarrow \frac{\partial^2\psi}{\partial x^2} = YZ\frac{\partial^2 X}{\partial x^2} \quad \text{———} \text{(4a)}$$

Similarly $\frac{\partial\psi}{\partial y} = XZ\frac{\partial Y}{\partial y} \rightarrow \frac{\partial^2\psi}{\partial y^2} = XZ\frac{\partial^2 Y}{\partial y^2}$ ——— (4b)

& $\frac{\partial\psi}{\partial z} = XY\frac{\partial Z}{\partial z} \Rightarrow \frac{\partial^2\psi}{\partial z^2} = XY\frac{\partial^2 Z}{\partial z^2}$ ——— (4c)

Substituting 4a, 4b, 4c in ① and divide the equation with XYZ

$$-\frac{h^2}{8\pi^2 m}\left[\frac{1}{X}\frac{\partial^2 X}{\partial x^2}+\frac{1}{Y}\frac{\partial^2 Y}{\partial y^2}+\frac{1}{Z}\frac{\partial^2 Z}{\partial z^2}\right] = E \quad \text{———} \quad ⑤$$

If the total energy E is written as the sum of three energy components along the three Co-ordinates ie. $E = E_x + E_y + E_z$ Then equation ⑤ can be written as three different equations.

$$-\frac{h^2}{8\pi^2 m}\left[\frac{1}{X}\frac{\partial^2 X}{\partial x^2}\right] = E_x \quad \text{———} \quad (7a)$$

$$-\frac{h^2}{8\pi^2 m}\left[\frac{1}{Y}\frac{\partial^2 Y}{\partial y^2}\right] = E_y \quad \text{———} \quad (7b)$$

$$-\frac{h^2}{8\pi^2 m}\left[\frac{1}{Z}\frac{\partial^2 Z}{\partial z^2}\right] = E_z \quad \text{———} \quad (7c)$$

Equation (7a), (7b), (7c) can be rearranged as

$$\frac{\partial^2 X}{\partial x^2} + \frac{8\pi^2 m}{h^2}E_x X = 0 \quad \text{———} \quad (8a)$$

$$\frac{\partial^2 Y}{\partial y^2} + \frac{8\pi^2 m}{h^2}E_y Y = 0 \quad \text{———} \quad (8b)$$

$$\frac{\partial^2 Z}{\partial z^2} + \frac{8\pi^2 m}{h^2}E_z Z = 0 \quad \text{———} \quad (8c)$$

The solutions for the equations (8a), (8b), (8c) can be written as

$$X = \sqrt{\frac{2}{a_x}} \sin\left[\frac{n_x \pi}{a_x} x\right], \quad Y = \sqrt{\frac{2}{a_y}} \sin\left(\frac{n_y \pi y}{a_y}\right) \quad Z = \sqrt{\frac{2}{a_z}} \sin\left[\frac{n_z \pi}{a_z} z\right]$$

$$\therefore \quad \psi = XYZ$$

$$\Rightarrow \psi = \sqrt{\frac{8}{V}} \sin\left(\frac{n_x \pi x}{a_x}\right) \sin\left(\frac{n_y \pi y}{a_y}\right) \sin\left(\frac{n_z \pi z}{a_z}\right) \quad \text{———} ⑧$$

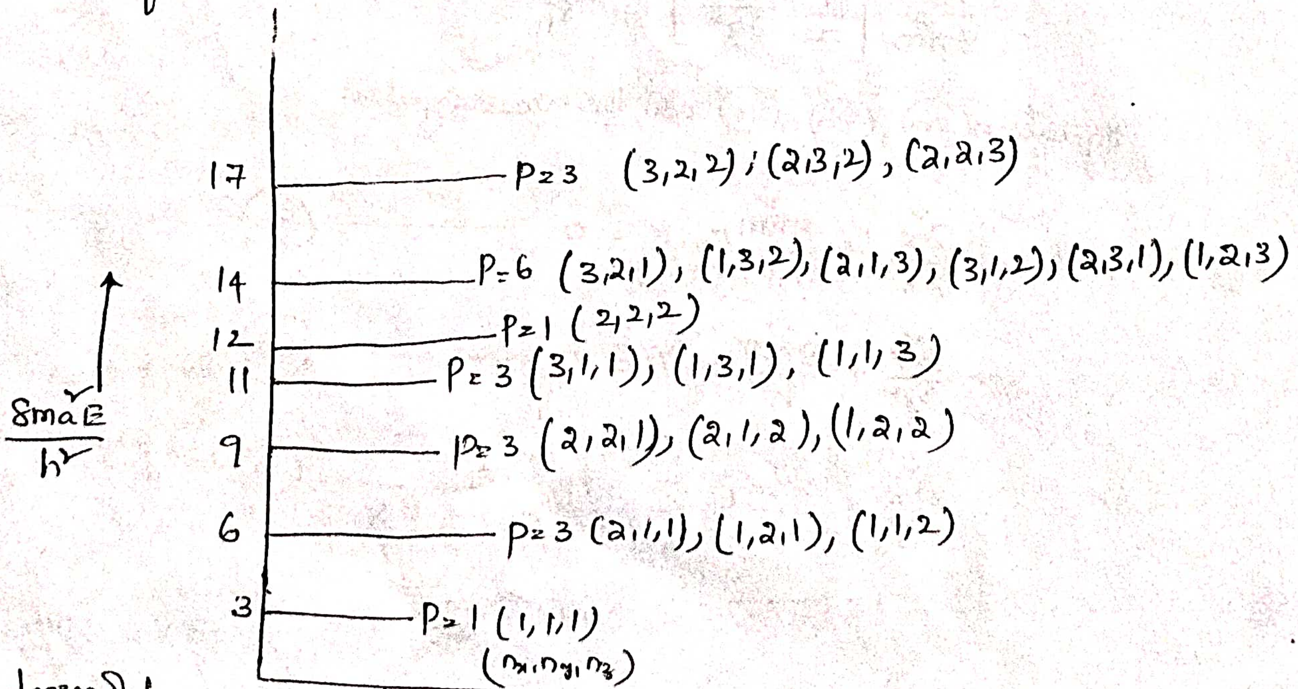
From the concept of particle in one dimensional box, energy for the particle in three dimensional box can be written as

$$E = \frac{h^2}{8m}\left[\frac{n_x^2}{a_x^2} + \frac{n_y^2}{a_y^2} + \frac{n_z^2}{a_z^2}\right] \quad \text{———} ⑨$$

If the box is a cubical box i.e. $a_x = a_y = a_z$ then

$$E = \frac{h^2}{8ma^2}\left[n_x^2 + n_y^2 + n_z^2\right] \quad \text{———} ⑩$$

For a particle enclosed in a cubical box the energy levels for few states can be shown as follows.



Energy levels, degree of degeneracy P and quantum number for a particle in a Cubical box

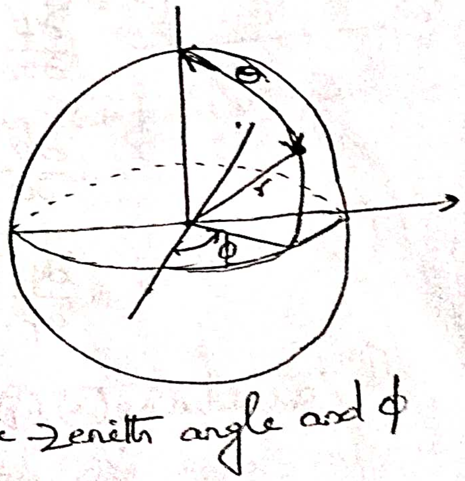
When there is only one wavefunction corresponding to a particular eigen value, the level is ~~so~~ known as nondegenerate but when there are a number of wave functions corresponding to a single eigen value, the level is known as degenerate. From the figure it is obvious that the energy level corresponding to the energy $h^2/8ma^2$ when $n_x=n_y=n_z=1$ is non degenerate. Similarly with $n_x=n_y=n_z=2$, $n_x=n_y=n_z=3$ and so on will be non-degenerate. In case of the energy $[h^2/8ma^2 \times 6]$ n_x, n_y & n_z may have values $(2,1,1)$; $(1,2,1)$; $(1,1,2)$ ie energy is the same but there will be 3 wavefunctions hence this is a degenerate level with g-degeneracy: Similarly we can consider the degeneracy of other levels.

Transformation of Co-ordinates:

The Schrodinger equation more generally ~~be~~ can be given by

$$\frac{\partial^2\psi}{\partial x^2}+\frac{\partial^2\psi}{\partial y^2}+\frac{\partial^2\psi}{\partial z^2}+\frac{8\pi^2\mu}{h^2}\left[E+\frac{ze^2}{4\pi\epsilon_0 r}\right]\psi=0.$$

Where $-\frac{ze^2}{4\pi\epsilon_0 r}$ is potential energy for hydrogen $[z=1]$ ~~atom~~ and hydrogen like atoms.



It will be more convenient to express the above equation in spherical polar co-ordinates r, θ, ϕ, where r is length of the radius vector θ the angle between the axis of the sphere and the length of the radius vector and ϕ the angle between a fixed meridian plane and the meridian plane in which r is measured. θ is called the zenith angle and ϕ the azimuthal angle.

The relation between polar co-ordinates and cartesian co-ordinates is

$r^2=x^2+y^2+z^2$, $z=r\cos\theta$, $y=r\sin\theta\sin\phi$, $x=r\sin\theta\cos\phi$

The Schrodinger equation in polar co-ordinates can be obtained by transforming the equation from cartesian co-ordinates.

The Schrodinger equation in Spherical polar Co-ordinates is

$$\frac{1}{r^2}\left[\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right)+\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2\psi}{\partial\phi^2}\right]+\frac{8\pi^2\mu}{h^2}\left[E+\frac{Ze^2}{4\pi\epsilon_0 r}\right]\psi=0$$

Separation of Variables:

The Schrodinger equation in spherical polar co-ordinates can be readily separated into three independent equations each involving only one co-ordinate.

Let $\psi(r,\theta,\phi)$ be written as the product of the three functions: $R(r)$, which depends upon r alone; $\Theta(\theta)$, which depends upon θ alone and $\Phi(\phi)$, which depends upon ϕ alone. Thus,

$$\psi(r,\theta,\phi) = R(r)\Theta(\theta)\Phi(\phi) \qquad ①$$

Equation ① in a simpler form can be written as

$$\psi = R\Theta\Phi \qquad ②$$

$$\therefore \frac{\partial\psi}{\partial r} = \Theta\Phi\frac{\partial R}{\partial r} \qquad ③$$

$$\frac{\partial\psi}{\partial\theta} = R\Phi\frac{\partial\Theta}{\partial\theta} \qquad ④$$

$$\frac{\partial\psi}{\partial\phi} = R\Theta\frac{\partial\Phi}{\partial\phi} \Rightarrow \frac{\partial^2\psi}{\partial\phi^2} = R\Theta\frac{\partial^2\Phi}{\partial\phi^2} \qquad ⑤$$

Substituting ③, ④ and ⑤ in Schrodinge equation

$$\frac{1}{r^2}\left[\Theta\Phi\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right)+\frac{R\Phi}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta}{\partial\theta}\right)+\frac{R\Theta}{\sin^2\theta}\frac{\partial^2\Phi}{\partial\phi^2}\right]+\frac{8\pi^2\mu}{h^2}\left[E+\frac{Ze^2}{4\pi\epsilon_0 r}\right]R\Theta\Phi=0 \qquad ⑥$$

Multiplying each team in equation ⑥ by the factor $r^2\sin^2\theta/R\Theta\Phi$, we get

$$\frac{\sin^2\theta}{R}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right)+\frac{\sin\theta}{\Theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta}{\partial\theta}\right)+\frac{1}{\Phi}\frac{\partial^2\Phi}{\partial\phi^2}+\frac{8\pi^2\mu}{h^2}\left[E+\frac{Ze^2}{4\pi\epsilon_0 r}\right]r^2\sin^2\theta=0 \quad ⑦$$

In equation ⑦ the third term is a function of ϕ only, while the other terms are independent of ϕ

$$\therefore -\frac{1}{\phi}\frac{\partial^2\Phi}{\partial\phi^2}=\frac{\sin^2\theta}{R}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right)+\frac{\sin\theta}{\Theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta}{\partial\theta}\right)+\frac{8\pi^2\mu}{h^2}\left[E+\frac{Ze^2}{4\pi\epsilon_0 r}\right]r^2\sin^2\theta \quad ⑧$$

Since the two sides of equation ⑧ are functions of different variables, they will be equal only if each side is equal to the same constant.

$$-\frac{1}{\Phi}\frac{\partial^2\Phi}{\partial\phi^2}=m^2 \quad ⑨$$

$$\frac{\sin^2\theta}{R}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right)+\frac{\sin\theta}{\Theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta}{\partial\theta}\right)+\frac{8\pi^2\mu}{h^2}\left[E+\frac{Ze^2}{4\pi\epsilon_0 r}\right]r^2\sin^2\theta=m^2 \quad ⑩$$

Where m^2 is a constant.

Dividing eq each term in ⑩ by $\sin^2\theta$ and rearranging changes to the form

$$\frac{1}{R}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right)+\frac{8\pi^2\mu}{h^2}\left[E+\frac{Ze^2}{4\pi\epsilon_0 r}\right]r^2=\frac{m^2}{\sin^2\theta}-\frac{1}{\Theta\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta}{\partial\theta}\right) \quad ⑪$$

In equation ⑪ the two sides having different variables are equal only if they are equal to a constant L. Now equation ⑪ can be written as two different equations.

$$\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta}{\partial\theta}\right)+\left(L-\frac{m^2}{\sin^2\theta}\right)\Theta=0 \quad ⑫$$

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right)+\frac{8\pi^2\mu}{h^2}\left[E+\frac{Ze^2}{4\pi\epsilon_0 r}\right]R-\left(\frac{L}{r^2}\right)R=0 \quad ⑬$$

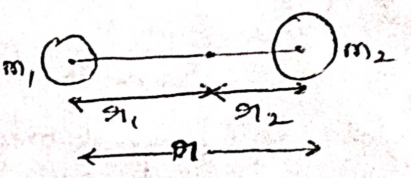
Equations ⑨, ⑫ & ⑬ are three different equations in terms of three different variables

(iii) Rigid Rotor & Rigid Rotator :

Consider a diatomic molecule which consists of two atoms of masses m_1 and m_2 rigidly joined by a weightless link of length 'r'. The centre of gravity of the system is assumed to be fixed at the origin of the co-ordinate system. Let the distance of m_1 from the centre of gravity be r_1 and the distance of m_2 be r_2.

$\therefore m_1 r_1 = m_2 r_2$, $r_1 + r_2 = r$ and $I = m_1 r_1^2 + m_2 r_2^2$

$\Rightarrow r_1 = \frac{m_2 r}{m_1+m_2}$, $r_2 = \frac{m_1 r}{m_1+m_2}$ and $I = \mu r^2$



The kinetic energy of rotation of the atoms joined together by a bond can be given by

$$K.E = \frac{1}{2} m_1 v_1^2 + \frac{1}{2} m_2 v_2^2$$

Where v_1 and v_2 are the velocities of masses m_1 and m_2 respectively

$$K.E = \frac{1}{2} m_1 r_1^2 \omega^2 + \frac{1}{2} m_2 r_2^2 \omega^2$$

$$= \frac{1}{2} \omega^2 (m_1 r_1^2 + m_2 r_2^2)$$

$$= \frac{1}{2} I \omega^2$$

$$\Rightarrow K.E. = \frac{L^2}{2I}$$

where ω is angular velocity and I is moment of inertia.

As no forces acts on the rotator, the potential energy $(V) = 0$.

$\therefore$ The Hamiltonian operator may be written as

$$\hat{H} = \frac{\hat{L}^2}{2I}$$

The Schrodinger equation in polar co-ordinates can be given by.

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

Since r is a constant the above equation can be written as

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

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

The above equation consists of two angular variables θ and φ and hence the wave function ψ can be written as

$$\psi=\Theta(\theta)\,\Phi(\phi) \quad \text{———} ②$$

$$\frac{\partial\psi}{\partial\theta}=\Phi(\phi)\frac{\partial\Theta}{\partial\theta} \quad \text{———} ③$$

$$\text{and } \frac{\partial\psi}{\partial\phi}=\Theta(\theta)\frac{\partial\Phi}{\partial\phi} \Rightarrow \frac{\partial^2\psi}{\partial\phi^2}=\Theta(\theta)\frac{\partial^2\Phi}{\partial\phi^2} \quad \text{———} ④$$

Substituting equations ③ and ④ in ① we get

$$\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\,\Phi(\phi)\frac{\partial\Theta}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\Theta(\theta)\frac{\partial^2\Phi}{\partial\phi^2}+\frac{8\pi^2 I}{h^2}E\,\Theta(\theta)\Phi(\phi)=0 \quad \text{———} ⑤$$

Dividing equation ⑤ with Θ(θ)Φ(φ)

$$\frac{1}{\Theta(\theta)\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta}{\partial\theta}\right)+\frac{1}{\Phi(\phi)\sin^2\theta}\frac{\partial^2\Phi}{\partial\phi^2}+\frac{8\pi^2 I}{h^2}E=0 \quad \text{———} ⑥$$

Multiplying equation ⑥ with $\sin^2\theta$

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

$$\Rightarrow \frac{\sin\theta}{\Theta(\theta)}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta}{\partial\theta}\right)+\frac{8\pi^2 I}{h^2}E\sin^2\theta=-\frac{1}{\Phi(\phi)}\frac{\partial^2\Phi}{\partial\phi^2} \quad \text{———} ⑦$$

The left hand expression and right hand expression in equation ⑦ are expressed in terms of two different variables. These two expressions will be equal to a constant i.e. $-\frac{1}{\Phi(\phi)}\frac{\partial^2\Phi}{\partial\phi^2} = m^2$ ——— ⑧

$$\frac{\sin\theta}{\Theta(\theta)}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta}{\partial\theta}\right)+\frac{8\pi^2 I}{h^2}E\sin^2\theta = m^2 \text{ ——— } ⑨$$

The solution for equation ⑧ can be written as

$$\Phi(\phi) = Ce^{\pm im\phi} \text{ ——— (9a)}$$

The normalised solution of ⑨ can be written as $\Phi_{\pm m}(\phi) = \frac{1}{\sqrt{2\pi}}e^{(\pm im\phi)}$ $(m = 0, 1, 2, 3, \cdots)$

Equation ⑨ can be written as

$$\frac{\sin\theta}{\Theta(\theta)}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta}{\partial\theta}\right)+\frac{8\pi^2 I}{h^2}E\sin^2\theta = m^2$$

Dividing the above equation with $\sin^2\theta$

$$\Rightarrow \frac{1}{\sin\theta\,\Theta(\theta)}\frac{\partial}{\partial\theta}\left[(\sin\theta)\frac{\partial\Theta}{\partial\theta}\right]+\frac{8\pi^2 I}{h^2}E = \frac{m^2}{\sin^2\theta}$$

$$\Rightarrow \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta}{\partial\theta}\right)+\left(\frac{8\pi^2 I}{h^2}E-\frac{m^2}{\sin^2\theta}\right)\Theta(\theta) = 0$$

$$\Rightarrow \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta}{\partial\theta}\right)+\left(\beta-\frac{m^2}{\sin^2\theta}\right)\Theta(\theta) = 0 \text{ ——— } ⑩$$

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

$\Rightarrow E = \frac{h^2\beta}{8\pi^2 I}$ $\Rightarrow E = \frac{h^2 l(l+1)}{8\pi^2 I}$ ⑪ where $\beta = l(l+1)$ and l is either zero or positive number.

The solution of equation ⑩ is associated with Legendre polynomials $P_l^{|m|}(\cos\theta)$ where l is either zero or a positive integer and further $l \geq |m|$. The normalised solution of equation ⑩ is

$$\Theta(\theta) = \Theta_{l,\pm m}(\theta) = \sqrt{\frac{(2l+1)}{2}\cdot\frac{(l-|m|)!}{(l+|m|)!}}\,P_l^{|m|}(\cos\theta)$$

☆ Where $P_l^{|m|}(\cos\theta) = \sin^{|m|}\theta\,\frac{d^{|m|}}{d(\cos\theta)^{|m|}}P_l\cos\theta$

The restriction on 'l' leads to quantisation of the kinetic energy of rotation given by equation ⑪.

(iv) Hydrogen atom & Hydrogen like atoms :

The nucleus of hydrogen atom consists of a proton of charge 'e'. This proton exerts coulombic force of attraction on the electron of charge '-e' at a distance r. The coulombic force can be given by

$$F = \frac{-e^2}{4\pi\epsilon_0 r^2}$$

The potential energy of the electron is zero at infinite distance. The potential energy of the electron at a distance 'r' is given by

$$E_p = \int_r^\infty F \cdot dr \Rightarrow E_p = -\frac{e^2}{4\pi\epsilon_0 r} \quad \text{———} ①$$

Hence the Hamiltonian operator takes the form

$$\hat{H} = -\frac{h^2}{8\pi^2 m}\nabla^2 - \frac{e^2}{4\pi\epsilon_0 r} \quad \text{———} ②$$

The Schrodinger equation for the hydrogen atom can be given by

$$\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2} + \frac{8\pi^2 m_e}{h^2}\left[E + \frac{e^2}{4\pi\epsilon_0 r}\right]\psi = 0$$

In general the above equation can be written as

$$\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2} + \frac{8\pi^2 \mu}{h^2}\left[E + \frac{Ze^2}{4\pi\epsilon_0 r}\right]\psi = 0$$

Where μ is reduced mass and Z is atomic number.

The above equation in cartesian co-ordinates can be transformed into equation in Spherical polar co-ordinates.

$$\frac{1}{r^2}\left[\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right)+\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2\psi}{\partial\phi^2}\right]$$

$$+\frac{8\pi^2 m_e}{h^2}\left[E+\frac{Ze^2}{r}\right]\psi=0. \qquad ①$$

The equation ① on separation yields the following three equations each containing one variable

$$\frac{1}{\Phi}\frac{\partial^2\Phi}{\partial\phi^2}=-m^2 \qquad ②$$

$$\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left[\sin\theta\frac{\partial\Theta}{\partial\theta}\right]+\left(\beta-\frac{m^2}{\sin^2\theta}\right)\Theta=0 \qquad ③$$

$$\frac{1}{R}\frac{\partial}{\partial r}\left[r^2\frac{\partial R}{\partial r}\right]+\frac{8\pi^2 m_e}{h^2}\left[E+\frac{Ze^2}{r}\right]r^2=\beta \qquad ④$$

In these equations, m^2 and β are constants that arise from the separation of variables and β is replaced by $l(l+1)$. The solutions for equations ② + ③ are ~~similar~~ same as those found for the rigid rotor.

Equation ④ can be written as

$$\frac{1}{R}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right)+\frac{8\pi^2 m_e}{h^2}\left[E+\frac{Ze^2}{r}\right]r^2=l(l+1)$$

This ~~can~~ may be written as

$$\frac{\partial}{\partial r}\left[r^2\frac{\partial R}{\partial r}\right]-\frac{\rho^2 R}{4}+\delta\rho R-l(l+1)R=0 \qquad ⑤$$

Where $\alpha^2=-\frac{8\pi^2 m_e E}{h^2}$ $\qquad \delta=\frac{4\pi^2 m_e Z e^2}{h^2\alpha}$

$\rho=2\alpha r$ $\qquad \frac{\partial}{\partial r}=2\alpha\frac{\partial}{\partial\rho}$

The solutions for equations ② and ③ are same as those discussed in case of rigid rotor.

Equation ⑤ may be rewritten as

$$\frac{\partial^2 R}{\partial \rho^2} + \frac{2}{\rho}\frac{\partial R}{\partial \rho} - \frac{R}{4} + \frac{\delta R}{\rho} - l(l+1)\frac{R}{\rho^2} = 0 \quad \text{———} \quad \textcircled{6}$$

For large values of ρ, this reduces to

$$\frac{\partial^2 R}{\partial \rho^2} - \frac{R}{4} = 0 \quad \text{———} \quad \textcircled{7}$$

The solution for ⑦ can be written as

$$R = e^{-1/2\,\rho} \quad \text{———} \quad \textcircled{8}$$

The complete solution for equation ⑥ includes Laguerre polynomials of degree $(n-l-1)$ and the solution for ⑥ is

$$R_{n,l}(r) = -\sqrt{\frac{4(n-l-1)!}{2n\,[(n+l)!]^3}\left(\frac{2Z}{na_0}\right)^3}\left[\frac{2Zr}{na_0}\right]^l e^{\left(-\frac{Zr}{na_0}\right)} L_{n+1}^{2l+1}\left[\frac{2Zr}{na_0}\right] \quad \text{———} \quad \textcircled{9}.$$

Where $a_0 = \dfrac{h^2}{4\pi^2 Z e^2 \mu}$ when m_e is replaced by μ.

Approximation Methods:

For certain systems it is possible to solve the Schrodinger's equation exactly and therefore their true wave functions, energies and other properties can be obtained. But for most of the systems of chemical interest the Schrodinger equation cannot be solved exactly. Because in such systems, the presence of more than one electron introduces the electron repulsion terms. (e^2/r_{ij} where r_{ij} is the distance between electron i and electron j) in the hamiltonian.

The separation of variables for the systems having more than one electron is not possible owing to the dependence of r_{ij} on θ and ϕ coordinates. Hence, for such systems having more than one electron it is not possible to obtain an exact solution of the wave equation and can be solved approximately. Even for ~~[illegible]~~ the systems having one electron, sometimes it is not possible to solve the wave equation if the system is not in a spherically symmetrical potential field.

The approximate solution of the wave equation can be obtained by two methods. They are

(1) the perturbation method
& (2) the variation method.

The perturbation method is suitable for a system which deviates from the exact solution to lesser extent The variation method is applicable for the system whose wave function can be guessed This trial wave function might suitable to be close to the true wave function of the system concerned and the mean energy is then calculated. This mean energy is taken to be the energy of the system. But in many cases, it is difficult to guess how the true wave function will be.

For convenience, in the above methods the integral forms can be denoted in brackets as shown

$$\int f \cdot \hat{A} \cdot g \, d\tau = \langle f|A|g\rangle$$

The variation theorem:

If the approximate wave function of a system is guessed basing on physical and chemical considerations generally, then the energy of the system is approximately given by

$$E = \frac{\langle\psi|H|\psi\rangle}{\langle\psi|\psi\rangle} \quad \text{------} ①$$

If the guessed wave function ψ is normalised then E can be written as

$$E = \langle\psi|H|\psi\rangle \quad ②$$

Where $\hat{H}$ is the Hamiltonian operator of the system.

The energy 'E' calculated using the above equation will be always greater than the true energy E_0 (which is the lowest eigenvalue of $\hat{H}$) of the system in its ground state.

If several guesses of wave function, say ψ_1 and ψ_2 etc are made which lead to the eigen values E_1 and E_2 respectively according to equations ① & ② then there are two possibilities i.e. either $E_1 < E_2$ or $E_2 < E_1$

If $E_1 < E_2$ and E_1 is the better approximation to the true energy E_0 ~~and~~ than E_2 then ψ_1 is a better wavefunction of the system than ψ_2

Thus the variation theorem is stated as, "If ψ be the trial wave function of a system whose Hamiltonian $\hat{H}$ has a discrete eigenvalue, then $\langle\psi|H|\psi\rangle \geq E_0$ where E_0 is the lowest exact eigenvalue of $\hat{H}$ assuming that the trial wave function ψ is normalised."

Proof: We have to prove that the eigenvalue of approximate wave function ψ is greater than the exact eigenvalue E_0.

Let $\phi_1, \phi_2, \phi_3, \ldots$ be the set of normalised and mutually orthogonal eigenfunctions of $\hat{H}$ with discrete eigen values such as E_1, E_2, E_3 etc respective

$$\therefore \hat{H}\phi_i = E_i\phi_i \qquad i = 1, 2, 3, \ldots \quad ③$$

Let $\psi = \sum_i c_i\phi_i$

Since ψ is normalised wave function $\langle\psi|\psi\rangle = 1$

i.e. $\int \psi^2 d\tau = 1 \Rightarrow \int \left(\sum_i c_i\phi_i\right)^2 d\tau = 1$

$\Rightarrow \int [c_1\phi_1 + c_2\phi_2 + c_3\phi_3 + \ldots]^2 d\tau = 1 \Rightarrow \sum c_i^2 = 1$ [$\because \phi_i$ is normalised wave function]

It is well known that $\langle\phi_i|H|\phi_i\rangle = E_i$ ④

and $\langle\phi_i|H|\phi_j\rangle = E_j\langle\phi_i|\phi_j\rangle = 0$ [$\because \phi_i$ and ϕ_j are orthogonal] ⑤

Consider the integral

$$E = \langle \psi | H | \psi \rangle$$

$$\Rightarrow E = \langle \sum_i c_i \phi_i | H | \sum_j c_j \phi_j \rangle$$

$$\Rightarrow E = \sum_{i=j} c_i^2 \langle \phi_i | H | \phi_i \rangle + \sum_{i \neq j} c_i c_j \langle \phi_i | H | \phi_j \rangle$$ ⑥

$$\Rightarrow E = \sum_i c_i^2 E_i + \sum_{i \neq j} c_i c_j (0)$$ [∵ from equations ④ and ⑤]

$$\Rightarrow E = \sum_i c_i^2 E_i$$

$$\Rightarrow E - E_0 = \sum_i c_i^2 E_i - E_0$$

Where E_0 is the lowest exact eigen value of $\hat{H}$

$$\therefore E - E_0 = \sum_i c_i^2 E_i - \sum_i c_i^2 E_0$$ $[\because \sum_i c_i^2 = 1]$

$$= \sum_i c_i^2 [E_i - E_0]$$

The quantity $E_i - E_0$ must be positive or zero for all values of i and since c_i^2 is always positive.

$$\Rightarrow E_i - E_0 \geq 0$$

$$\Rightarrow E_i \geq E_0$$

Hence we can write that $E - E_0 \geq 0 \Rightarrow E \geq E_0$

$$\Rightarrow \langle \psi | H | \psi \rangle \geq E_0$$

Application of variation method to Hydrogen atom:

The application of variation method involves the following steps:

1. A trial wave function ψ with some variable parameter should be chosen.
2. The integral $\langle\psi|H|\psi\rangle$ should be calculated.
3. The integral always gives an upper bound to the true energy value unless the choosen wave function ψ ~~happens~~ happens to be the exact one, minimise the integral with respect to the variable parameter.
4. The ψ with optimum value of the parameter is the best approximation to the true wave function and the lowest value of $\langle\psi|H|\psi\rangle$ is the nearest approximation to the true energy.

Apply the variation method to the simple case ie. hydrogen atom for which schrodinger equation is exactly solvable. This is to show how powerful is the variation method and the extent to which the results of variation method differ from the exact values.

The Hamiltonian operator in atomic units is

$$\hat{H} = -\frac{1}{2}\nabla^2 - \frac{1}{r}$$

Where ∇^2 is Laplacian operator in terms of polar co-ordinates.

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

The system like hydrogen atom is spherically symmetrical.

If ψ is the wave function then $\hat{H}\psi = E\psi$ where E is the energy of the system. The wave function of the form $\psi = e^{-\gamma r}$ can be choosen

$$\therefore \hat{H}\psi = -\frac{1}{2}\frac{1}{r^2}\frac{\partial}{\partial r}\left[r^2\frac{\partial(e^{-\gamma r})}{\partial r}\right] - \frac{1}{r}e^{-\gamma r}$$

$$= -\frac{1}{2}\frac{1}{r^2}\left\{\frac{\partial}{\partial r}\left[r^2(-\gamma)e^{-\gamma r}\right]\right\} - \frac{1}{r}e^{-\gamma r}$$

$$= \frac{1}{2}\frac{\gamma}{r^2}\left\{\frac{\partial}{\partial r}\left(r^2 e^{-\gamma r}\right)\right\} - \frac{1}{r}e^{-\gamma r}$$

$$= \frac{1}{2}\frac{\gamma}{r^2}\left\{2r e^{-\gamma r} + r^2(-\gamma)e^{-\gamma r}\right\} - \frac{1}{r}e^{-\gamma r}$$

$$= \frac{1}{2}\left\{\frac{2\gamma}{r}e^{-\gamma r} - \gamma^2 e^{-\gamma r}\right\} - \frac{1}{r}e^{-\gamma r}$$

$$= -\frac{1}{2}\left[\gamma^2 - \frac{2\gamma}{r}\right]e^{-\gamma r} - \frac{1}{r}e^{-\gamma r}$$

$$\Rightarrow \hat{H}\psi = \left\{-\frac{1}{2}\left(\gamma^2 - \frac{2\gamma}{r}\right) - \frac{1}{r}\right\}e^{-\gamma r}$$

The energy of the system can be given by

$$E = \frac{\langle\psi|H|\psi\rangle}{\langle\psi|\psi\rangle} \text{ ——— } ①$$

By making use of standard integrals to evaluate the integrals in equation ① the value of energy can be given by

$$E = \left[\frac{\gamma^2}{2} - \gamma\right]$$

The energy E of the system will be minimum if $\frac{\partial E}{\partial \gamma} = 0$

$$\therefore \frac{\partial E}{\partial \gamma} = \left[\frac{2\gamma}{2} - 1\right] = 0 \Rightarrow (\gamma - 1) = 0 \Rightarrow \gamma = 1$$

Hence the lowest eigenvalue is

$$E = \left[\frac{\gamma^2}{2} - \gamma\right] = \frac{1}{2} - 1 = -\tfrac{1}{2} \quad \text{[in atomic units]}$$

The corresponding eigen function is

$$\psi = e^{-r}$$

The above eigen value and eigen function represents the exact eigen value and eigen function of the hydrogen atom in its ground state.

Perturbation Theory:

Perturbation method is applied when the system deviates from the exact solution to a lesser extent. The application of this method to the system is based on the following conditions.

(1) The Hamiltonian can be decomposed into two parts.

$$\hat{H} = \hat{H}^{(0)} + \lambda\hat{v}$$

Where $\lambda\hat{v}$ is the perturbation and λ is expansion parameter.

(2) The eigen values and eigenfunctions of the unperturbed Hamiltonian $\hat{H}^{(0)}$ are known.

(3) $\hat{H}^{(0)} \geq \lambda\hat{v}$

Let $\psi^{(0)}$ be the wavefunction of $\hat{H}^{(0)}$ with eigen value $E^{(0)}$. Then the unperturbed equation can be written as

$$\hat{H}^{(0)}\psi^{(0)} = E^{(0)}\psi^{(0)} \quad \text{———} ①$$

The perturbed equation can be written as

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

$$\rightarrow [\hat{H}^{(0)} + \lambda\hat{v}]\psi = E\psi \quad \text{———} ②$$

Where ψ is the wavefunction of the Hamiltonian $\hat{H}$ with eigen value E.

In equation ②, if $\lambda = 0$ then the equation ② reduces to equation ① and then E becomes $E^{(0)}$ and ψ becomes $\psi^{(0)}$. From this we can say that the effect of perturbation $\lambda\hat{v}$ changes slightly the unperturbed eigen value $E^{(0)}$ to E and the eigen function $\psi^{(0)}$ to ψ.

Hence we can say that ψ and E are functions of λ and they can be written as

$$\psi = \psi^{(0)} + \lambda\psi^{(1)} + \lambda^2\psi^{(2)} + \lambda^3\psi^{(3)} + \cdots\cdots \quad \text{———} ③$$

$$E = E^{(0)} + \lambda E^{(1)} + \lambda^2 E^{(2)} + \lambda^3 E^{(3)} + \cdots\cdots \quad \text{———} ④$$

Where $\psi^{(1)}, \psi^{(2)}, \ldots\ldots$ and $E^{(1)}, E^{(2)} \ldots$ are independant of λ

, $\psi^{(1)}, \psi^{(2)}$ .... are chosen such that they are orthogonal to $\psi^{(0)}$ which is assumed to be normalised. Substituting equations ③ and ④ in ②

$$\hat{H}^{(0)}[\psi^{(0)}+\lambda\psi^{(1)}+\lambda^2\psi^{(2)}+\dots]+\lambda\hat{V}[\psi^{(0)}+\lambda\psi^{(1)}+\lambda^2\psi^{(2)}+\dots]$$

$$=[E^{0}+\lambda E^{(1)}+\lambda^2 E^{(2)}+\dots][\psi^{(0)}+\lambda\psi^{(1)}+\lambda^2\psi^{(2)}+\lambda^3\psi^{(3)}+\dots] \qquad \textcircled{5}$$

The eigenfunction and eigenvalue of the above equation can be determined to certain order of accuracy. If $\psi^{(0)}$ and $E^{(0)}$ are the approximate solutions to the perturbed system then it is called as the zeroth order of approximation to the true solution of the perturbed system. To obtain more accurate eigen function one has to retain more number of terms in the series.

$$\hat{H}^{(0)}\psi^{(0)} = E^{(0)}\psi^{(0)} \qquad \textcircled{6}$$

In first order perturbation theory, the approximation of the true solution is obtained by retaining the second terms in the series ③ and ④

i.e. $\hat{H}^{(0)}\psi^{(1)}+\hat{V}\psi^{(0)} = E^{(1)}\psi^{(0)}+E^{(0)}\psi^{(1)}$ [compare coefficients of λ]

$$\rightarrow [\hat{H}^{(0)}-E^{(0)}]\psi^{(1)} = -\hat{V}\psi^{(0)}+E^{(1)}\psi^{(0)} \qquad \textcircled{7}$$

Similarly the equation for second order perturbation theory can be written as

$$\hat{H}^{(0)}\psi^{(2)}+\hat{V}\psi^{(1)} = E^{(2)}\psi^{(0)}+E^{(1)}\psi^{(1)}+E^{(0)}\psi^{(2)}$$

$$\Rightarrow [\hat{H}^{(0)}-E^{(0)}]\psi^{(2)} = -\hat{V}\psi^{(1)}+E^{(1)}\psi^{(1)}+E^{(2)}\psi^{(0)} \qquad \textcircled{8}$$

The solution of equation ⑦ gives $\psi^{(1)}$ and $E^{(1)}$ and the solution of equation ⑧ gives $\psi^{(2)}$ and $E^{(2)}$

The energy of first order perturbation can be obtained by multiplying equation ⑦ with $\psi^{(0)}$ and integrating over the entire space.

$$\langle\psi^{(0)}|H^{(0)}-E^{(0)}|\psi^{(1)}\rangle = -\langle\psi^{(0)}|V|\psi^{(0)}\rangle+E^{(1)}\langle\psi^{(0)}|\psi^{(0)}\rangle \qquad \textcircled{9}$$

Since $\hat{H}^{(0)}$ is a hermitian operator we can write

$$\langle \psi^{(0)} | H^{(0)} - E^{(0)} | \psi^{(1)} \rangle = \langle \psi^{(1)} | \hat{H}^{(0)} - E^{(0)} | \psi^{(0)} \rangle$$

We know that $\langle \psi^{(1)} | \hat{H}^{(0)} - E^{(0)} | \psi^{(0)} \rangle = 0$

$\therefore E^{(1)} = \langle \psi^{(0)} | V | \psi^{(0)} \rangle$ ———— ⑩

To solve equation ⑦ it is necessary to expand $\psi^{(1)}$ in terms of the complete set of eigenfunctions of the unperturbed Hamiltonian $H^{(0)}$

The unperturbed equation can be written as

$\hat{H}^{(0)} \psi_i^{(0)} = E_i^{(0)} \psi_i^{(0)}$ ———— ⑪

with $i = 1, 2, 3, 4 \ldots\ldots$

Where $E_i^{(0)}$ is non-degenerate i.e. there is only one normalised eigenfunction belonging to each $E_i^{(0)}$

Let $\psi_i^{(1)} = \sum_{i \neq j} c_{ij} \psi_j^{(0)}$ ———— ⑫

Multiply equation ⑫ with $\psi_i^{(0)}$ and integrate over the whole space

$$\Rightarrow \langle \psi_i^{(0)} | \psi_i^{(1)} \rangle = \sum_{i \neq j} c_{ij} \langle \psi_i^{(0)} | \psi_j^{(0)} \rangle$$

$$= 0.$$

Since $\psi_i^{(0)}, \psi_j^{(0)}$ are orthonormal

This ensures that $\psi_i^{(1)}$ is orthogonal to $\psi_i^{(0)}$

Substitute equation ⑫ in ⑦

i.e. $\left[\hat{H}^{(0)} - E_i^{(0)} \right] \sum_{i \neq j} c_{ij} \psi_j^{(0)} = - \hat{V} \psi_i^{(0)} + E_i^{(1)} \psi_i^{(0)}$

$\Rightarrow \sum_{i \neq j} c_{ij} \left[E_j^{(0)} - E_i^{(0)} \right] \psi_j^{(0)} = - \hat{V} \psi_i^{(0)} + E_i^{(1)} \psi_i^{(0)}$ ———— ⑬

Multiply equation ⑬ with $\psi_i^{(0)}$ and integrate over entire space.

$$\Rightarrow \sum_{i\neq j} c_{ij}\left[E_j^{(0)} - E_i^{(0)}\right] \langle \psi_i^{(0)} | \psi_j^{(0)} \rangle = -\langle \psi_i^{(0)} | V | \psi_i^{(0)} \rangle + E_i^{(1)} \langle \psi_i^{(0)} | \psi_i^{(0)} \rangle$$

$$\Rightarrow \sum_{i\neq j} c_{ij}\left[E_j^{(0)} - E_i^{(0)}\right] (0) = -\langle \psi_i^{(0)} | V | \psi_i^{(0)} \rangle + E_i^{(1)} \langle \psi_i^{(0)} | \psi_i^{(0)} \rangle$$

$$\Rightarrow E_i^{(1)} = \langle \psi_i^{(0)} | V | \psi_i^{(0)} \rangle$$
———— ⑭

Equation ⑬ can be expanded as

$$c_{i1}\left[E_1^{(0)} - E_i^{(0)}\right]\psi_1^{(0)} + c_{i2}\left[E_2^{(0)} - E_i^{(0)}\right]\psi_2^{(0)} + c_{i3}\left[E_3^{(0)} - E_i^{(0)}\right]\psi_3^{(0)} + \dots$$

$$= -V\psi_i^{(0)} + E_i^{(1)}\psi_i^{(0)}$$
———— ⑮

The value c_{i1} can be obtained by multiplying ⑮ with $\psi_1^{(0)}$ and integrating

$$c_{i1}\left[E_1^{(0)} - E_i^{(0)}\right]\langle \psi_1^{(0)} | \psi_1^{(0)} \rangle + c_{i2}\left[E_2^{(0)} - E_i^{(0)}\right]\langle \psi_1^{(0)} | \psi_2^{(0)} \rangle + \dots$$

$$= -\langle \psi_1^{(0)} | V | \psi_i^{(0)} \rangle + E_i^{(1)} \langle \psi_1^{(0)} | \psi_i^{(0)} \rangle$$

$$\Rightarrow c_{i1} = -\frac{\langle \psi_1^{(0)} | V | \psi_i^{(0)} \rangle}{E_1^{(0)} - E_i^{(0)}}$$
———— ⑯

Similarly $$c_{i2} = -\frac{\langle \psi_2^{(0)} | V | \psi_i^{(0)} \rangle}{E_2^{(0)} - E_i^{(0)}}$$
———— ⑰

In general

$$c_{ij} = -\frac{\langle \psi_j^{(0)} | V | \psi_i^{(0)} \rangle}{E_j^{(0)} - E_i^{(0)}}$$
———— ⑱

Substituting ⑱ in ⑫ we get

$$\psi_i^{(1)} = -\sum_{i\neq j} \frac{\langle \psi_j^{(0)}|V|\psi_i^{(0)}\rangle}{E_j^{(0)}-E_i^{(0)}}\,\psi_j^{(0)}$$

$$= \sum_{i\neq j} \frac{\langle \psi_j^{(0)}|V|\psi_i^{(0)}\rangle}{E_i^{(0)}-E_j^{(0)}}\,\psi_j^{(0)} \tag{19}$$

The results of the non-degenerate first order perturbation theory are

$$E_i = E_i^{(0)} + \lambda E_i^{(1)}$$

$$\Rightarrow E_i = E_i^{(0)} + \lambda \langle \psi_i^{(0)}|V|\psi_i^{(0)}\rangle \tag{20}$$

$$\psi_i = \psi_i^{(0)} + \lambda \psi_i^{(1)}$$

$$\Rightarrow \psi_i = \psi_i^{(0)} + \lambda \left[\sum_{i\neq j} \frac{\langle \psi_j^{(0)}|V|\psi_i^{(0)}\rangle}{E_i^{(0)}-E_j^{(0)}}\,\psi_j^{(0)}\right] \tag{21}$$

If there is degeneracy in $E^{(0)}$ values equation ㉑ is not valid.