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Quantum chemistry: Part 1

Classical mechanics best describe the behavior of macroscopic particles in terms of Newton's law of motions, but Newton's law is insufficient in itself to describe the behavior of microscopic particles. As a chemist, we are interested in chemical processes and vital information regarding the same can be extracted via studying thermodynamics which is based on classical mechanics, unfortunately we are still unaware of what taking place at the molecular/subatomic level. So there was a need for a general theory for submicroscopic systems-one comparable to Newton's equation for macroscopic bodies and this theory turns out to be the quantum theory.
Quantum mechanics can be formulated in terms of six postulates: The postulates of quantum mechanics are:

(1) The state of a system in quantum mechanics is described by a wave function Ψ (x, y, z, t) which contains all the dynamic information about the system.

(2) Every physical observable or property of a system can be represented by a corresponding linear quantum mechanical operator.

(3) The only possible values which a measurement of the property "A" can yield with arbitrary precession are the eigenvalues "a_i" of the corresponding eigen value equation $\hat{A}\Psi = a_i\Psi$.

(4) For a state described by the wave function ψ, the average, or expectation value of a property "a" for a series of measurements corresponding to the operator Â is given by:

$$\langle A\rangle = \frac{\int \Psi^* \hat{A}\, \Psi d\tau}{\int \Psi^* \Psi d\tau}$$

Where Ψ^* is the complex conjugate of Ψ.

(5) The wave function of a system varies in time according to the time-dependent Schrödinger equation or the evolution in time of a quantum mechanical system is governed by the time dependent Schrödinger equation which is expressed as:

$$\widehat{H}\Psi(x,y,z,t) = \frac{ih}{2\pi}\frac{d\Psi(x,y,z,t)}{dt} \text{ or } i\hbar\frac{d\Psi(x,y,z,t)}{dt}$$

(6) The wave function of a system of electrons must be antisymmetric with respect to the interchange of any two electrons, this postulate is the so called Pauli's exclusion principle.

Postulates 1: The state of a system is completely described by a wave function (Ψ)

Wave function:

Mathematical representation of the wave that in quantum mechanics replaces the classical concept of trajectory is called wave function, a function that contain all the dynamic information such as position, momentum etc. about a system.

Subatomic particles like electrons possess wave like properties and hence they can be described by a wave equation or more specifically by a mathematical function called the wave function. This wave function is a function of the coordinates of the parts of the system and time that completely describes the system i.e. a wave function depends both on spatial co-ordinates and as well as on time.

For a single particle residing in 3D space, we can write the wave function as:

$$\Psi = \Psi\,(x,y,z,t)$$

Similarly, for two particles system, the expression for wave function in 3D space is:

$$\Psi = \Psi\,(x_1,y_1,z_1,x_2,y_2,z_2,t)$$

For a general system, we can use generalized the expression for wave function as: $\Psi = \Psi(q_i,t)$

With certain assumptions, time can be separated from the wave function, and what remains is a time-independent state also known as the stationary state. A time-independent wave function is represented only with spatial co-ordinates as: $\Psi = \Psi(q_i)$. Until mentioned, a wave function generally represents a time independent state.

Q. Write the expression for wave function for a particle in 1 dimension. $[Ans\!: \Psi = \Psi(x)]$

Review of mathematical information:

Complex or imaginary number:

Complex number involves the imaginary unit "i", which is defined to be the square root of -1.

i.e.

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

Or

$$i^2 = -1$$

In general, a complex number is written as:

$$z = a + ib$$

Where "a" is the real part and "b" is the imaginary part of the complex number "z".

Complex conjugate:

For a complex number z, its complex conjugate (z*) is obtained simply by replacing "i" with "-i". For example, if z = a + ib, then its complex conjugate will be z* = a- ib.

Importance of complex conjugate:

Complex number multiplied by its complex conjugate will always yield a real number. For example, if z = a + ib, then z* = a - ib

Then,

$$\begin{aligned} zz^* &= (a+ib)(a-ib) \\ &= a^2 - (ib)^2 \\ &= a^2 + b^2 (real\ number) \end{aligned}$$

Q. $p_x = \frac{h}{2\pi i}\frac{d}{dx}$, then what will be the value of p_x^*

Ans: Complex conjugate is obtained by simply replacing "i" with "-i". So $p_x^* = -\frac{h}{2\pi i}\frac{d}{dx}$.

* There is no sense for taking complex conjugate of real number as it does not contain any imaginary part. If "a" is a real number than its complex conjugate a* = a.

Physical sifnificance of wave function: Born interpretation or statistical interpretation

The wave function (Ψ) itself has no physical significance, however, squared magnitude of ψ i.e. $|\psi|^2$ can be interpreted as a probability distribution or probability density for the system.

According to Heisenberg uncertainty principle, we cannot precisely measure various combinations of observables, like position and momentum. Keeping in mind the uncertainty principle, Max Born suggested that we not think of ψ as indicating a specific position of a particle, rather it indicates the probability of finding the particle over a certain region of space at any moment. Moreover, with analogy to the wave theory of radiation, in which the square of the amplitude of an electromagnetic wave in a region is interpreted as its intensity and therefore in quantum mechanics $|\psi|^2$ is interpreted as a measure of the probability of finding a particle present in a specified region.

If the wave function of a particle has the value ψ at x, then the probability of finding the particle between x and x + dx is proportional to $|\psi|^2$ dx. Since $|\psi|^2$ has to be real and positive, so it can be presented by $\Psi\Psi^*$, where $\Psi*$ is the complex conjugate of Ψ. i.e. for a particle moving in 1 D, $\Psi\Psi^*$dx or $|\psi|^2$ dx represent the probability of finding the particle and $\Psi\Psi^*$ or $|\psi|^2$ represents the corresponding probability density. Similarly, for a particle in 3D space, $|\psi|^2$ dxdydz or $|\psi|^2 d\tau$ represent the probability of finding the particle in a small volume element $d\tau = dxdydz$.

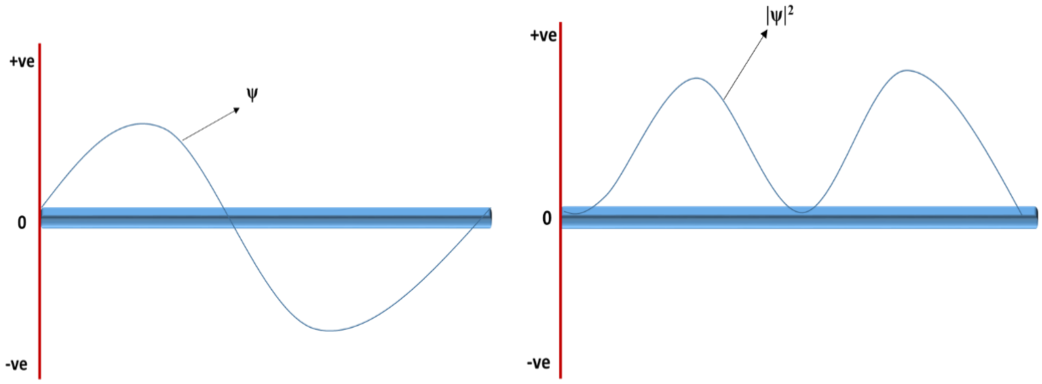


Fig: The sign of a wave function ψ has no direct physical significance, it can be positive, negative and even imaginary. But the square modulus of ψ i.e. $|\psi|^2$ or $\Psi\Psi^*$ has physical significance as it represents probability distribution which is a positive and real number.

The probability can be determined from the probability density i.e. from $|\psi|^2$. The probability P of a particle being in a certain region between points "a" and "b" in space is given by:

$$P = \int_a^b \Psi^*\Psi d\tau$$

i.e. the Born interpretation requires that a probability be evaluated over a definite region, not at a specific point in space. Thus, we should not think of ψ as giving the exact location of a particle, instead as an indicator of the probability that the particle will be in a certain region of space.

Q. What according to Born the physical significance of $|\psi|^2$.

Q. State Born's interpretation of a wave function.

Dimensions of wave function:

For 1 D:

We know for 1 D

$$P \propto \Psi^2\, dx$$

Since probability (P) is dimensionless and dx has the dimension of length (m). So to make "P" dimensionless, Ψ^2 has to be the dimension of $\frac{1}{length}$ (m^{-1}). So the dimension of wave function ψ has to be $length^{-\frac{1}{2}}\, or\, m^{-\frac{1}{2}}$ i.e. for 1 D ψ(x) has the unit of $m^{-\frac{1}{2}}$.

For 2 D:

We know for 2 D

$$P \propto \Psi^2 \, dxdy$$

Since probability (P) is dimensionless and dxdy has the dimension of length^2 (m^2). So to make “P” dimensionless, Ψ^2 has to be the dimension of $\frac{1}{length^2}$ (m^{-2}). So the dimension of wave function ψ has to be $length^{-1}$ or m^{-1} i.e. for 2 D ψ (x, y) has the unit of m^{-1}.

For 3 D:

We know for 3 D

$$P \propto \Psi^2 \, dxdydy$$

Since probability (P) is dimensionless and dxdydz has the dimension of length^3 (m^3). So to make “P” dimensionless, Ψ^2 has to be the dimension of $\frac{1}{length^3}$ (m^{-3}). So the dimension of wave function ψ has to be $length^{-\frac{3}{2}}$ or $m^{-\frac{3}{2}}$ i.e. for 3 D ψ (x, y, z) has the unit of $m^{-\frac{3}{2}}$.

Q. The one particle wave function ψ (x, y, z, t) has the dimensions of what?

Review of mathematical information:

Even function:

A function is said to be of even parity or symmetric if:

$$f(-x) = f(x)$$

For example, let a function

$$f(x) = e^{-x^2}$$

Now

$$f(-x) = e^{-(-x)^2} = e^{-x^2} = f(x)$$

i.e. e^{-x^2} is an even function

Similarly, Sin x is an even function because:

$$Sin\,(-x) = sinx$$

Odd function:

A function is said to be of odd parity or antisymmetric if:

$$f(-x) = -f(x)$$

For example, let a function

$$g(x) = x^3$$

Now

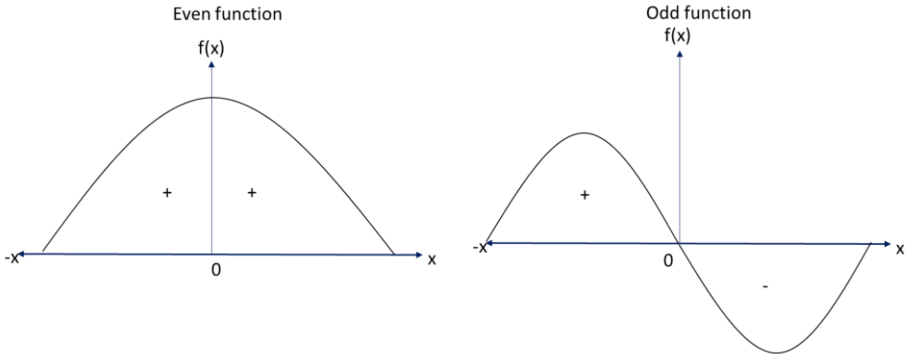
$$g(-x) = (-x)^3 = -x^3 = -g(x)$$

i.e. $x^3$is an odd function

Similarly, Cos x is an even function because:

$$Cos\,(-x) = -Cos\,x$$

Properties of even and odd functions:



(a) Integral over a symmetric interval such as $(-a, a)$ for an even function is:

$$\int_{-a}^{a} f(x)dx = \int_{-a}^{0} f(x)dx + \int_{o}^{a} f(x)dx$$

$$= \int_{o}^{a} f(-x)dx + \int_{o}^{a} f(x)dx$$

$$= \int_{o}^{a} f(x)dx + \int_{o}^{a} f(x)dx$$

$$= 2\int_{o}^{a} f(x)dx$$

i.e. for an even function integral over a symmetric interval $(-a, a)$ is twice the integral over the positive interval $(0, a)$

(b) Integral over a symmetric interval such as $(-a, a)$ for an odd function is:

$$\int_{-a}^{a} f(x)dx = \int_{-a}^{0} f(x)dx + \int_{o}^{a} f(x)dx$$

$$= \int_{o}^{a} f(-x)dx + \int_{o}^{a} f(x)dx$$

$$= -\int_{o}^{a} f(x)dx + \int_{o}^{a} f(x)dx$$

$$= 0$$

i.e. integral over a symmetric interval for an odd function just vanishes, where the positive contribution in one end is cancelled by the negative contribution over the other hand.

(c) Product of any two odd or two even function is an even function while product of any odd-even combination will yield an odd function. i.e.

$$even \times even = odd \times odd = even$$

$$odd \times even = even \times odd = odd$$

Normalization condition and normalized wave function:

Since the particle must be somewhere in space, so the total probability of finding the particle in all region of space must be 1 or 100 %. i.e.

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

Where the limits $-\infty$` and $+\infty$ are conventionally used to represent "all space".

The above equation is known as normalization equation or normalization condition and when the wave function ψ satisfies this condition then they are said to be normalized.

In general, if Ψi and Ψj are two acceptable wave functions of a system, then they are said to be normalized if:

$$\int_{-\infty}^{+\infty} \Psi_i\Psi_j\, d\tau = 1, when\ i = j$$

Orthogonal wave functions:

Two wave functions Ψi and Ψj are said to be orthogonal if:

$$\int_{-\infty}^{+\infty} \Psi_i\Psi_j\, d\tau = 0, when\ i \neq j$$

Orthonormal wave functions or orthonormal set:

When the conditions of both normality and orthogonality is satisfied by a set of wave functions then they are said to be an orthonormal set. Mathematically ortho-normality can be expressed as:

$$\int_{-\infty}^{+\infty} \Psi_i\Psi_j\, d\tau = \delta_{ij}$$

Where δ_{ij} is called Kronecker delta, which is defined as

$$\delta_{ij} = 0, if\ i \neq j$$

$$= 1, if\ i = j$$

Physical sifnificance of normalization and orthogonality condition:

Normalization condition implies that the particle is likely to be found in every region of space whatever may be the location of the region in space. Also sum of probabilities of the particle in all the regions in space must be equal to unity. i.e. the normalization condition guarantees that the probability of a particle existing in all space is 100%.

The orthogonality condition in terms of vector algebra means that the scalar product of the vectors $\Psi_i\ and\ \Psi_j$ vanishes. It is possible only when the vectors do not overlap to each other i.e. they are completely independent of one another. Likewise, in quantum mechanics, orthogonal functions are independent functions and one cannot be expressed in terms of others.

Normalization constant:

In quantum mechanics normalization condition must be fulfilled by every function. In cases where the wave function is not normalized i.e. if $\int_{-\infty}^{+\infty} \Psi^{*}\Psi d\tau \neq 1$, then the wave function must be multiplied by some constant "N" called the normalization constant such that NΨ become normalized. i.e.

$$\int_{-\infty}^{+\infty} (N\Psi)^*(N\Psi)\, d\tau = 1$$

$$=> N^2 \int_{-\infty}^{+\infty} \Psi^2\, d\tau = 1\ [\,if\ \Psi\ is\ real\ then\ \Psi = \Psi^*]$$

$$=> N = \frac{1}{\left(\int_{-\infty}^{+\infty} \Psi^2\, d\tau\right)^{\frac{1}{2}}}$$

Q. What do you mean by normalized, orthogonal and orthonormal functions? Give their physical significance. What is normalization constant?

Q. What does normalization condition means?

Q. Find the normalization constant and hence normalize the following wave functions:

(1) $\Psi = x^2, 0 \le x \le k$ (2) $\Psi = Sinx, 0 \le x \le \pi$ (3) $\Psi = a^2 - x^2, -a \le x \le a$

(4) $\Psi = Cos\left(\frac{n\pi x}{a}\right), -a \le x \le a$ (5) $\Psi = a(a - x), 0 \le x \le a$ (6) $\Psi = e^{-a|x|}, a > 0\ -\infty \le x \le \infty$

Ans:

(1) $\Psi = x^2$

Let the normalization constant = N

So the normalized wave function is $\Psi = Nx^2$

Now

$$\int_0^k (Nx^2)^2\, dx = 1$$

$$=> N^2 \int_0^k x^4\, dx = 1$$

$$=> N^2 \left[\frac{x^5}{5}\right]_0^k = 1$$

$$=> N^2 \left(\frac{k^5}{5} - 0\right) = 1$$

$$=> N = \sqrt{\frac{5}{k^5}}$$

i.e. the normalization constant is $\sqrt{\frac{5}{k^5}}$ and the normalized wave function will be $\Psi = \sqrt{\frac{5}{k^5}}\, x^2$

(2) $\Psi = Sinx, 0 \le x \le \pi$

Let the normalization constant = N

So the normalized wave function is $\Psi = N\, Sinx$

Now

$$\int_0^{\pi} (NSinx)^2\,dx = 1$$

$$=> N^2 \int_0^{\pi} Sin^2x\,dx = 1$$

$$=> \frac{N^2}{2}\int_0^{\pi} 2Sin^2x\,dx = 1$$

$$=> \frac{N^2}{2}\int_0^{\pi} (1 - Cos\ 2x)dx = 1$$

$$=> \frac{N^2}{2}\left[x - \frac{Sin\ 2x}{2}\right]_0^{\pi} = 1$$

$$=> \frac{N^2}{2}\left[\left(\pi - \frac{Sin\ 2\pi}{2}\right) - (0 - 0)\right] = 1$$

$$=> N^2 = \frac{2}{\pi}$$

$$=> N = \sqrt{\frac{2}{\pi}}$$

i.e. the normalization constant is $\sqrt{\frac{2}{\pi}}$ and the normalized wave function will be $\Psi = \sqrt{\frac{2}{\pi}}\ Sinx$

(3) $\Psi = a^2 - x^2, -a \leq x \leq a$

Let the normalization constant = N

So the normalized wave function is $\Psi = N(a^2 - x^2)$

Now

$$\int_{-a}^{a} \left(N(a^2 - x^2)\right)^2 dx = 1$$

$$=> N^2 \int_{-a}^{a} (a^2 - x^2)^2\,dx = 1$$

$$=> N^2 \int_{-a}^{a} (a^4 + x^4 - 2a^2x^2)dx = 1$$

$$=> N^2 \left[a^4x + \frac{x^5}{5} - \frac{2a^2x^3}{3}\right]_{-a}^{a} = 1$$

$$=> N^2 \left[\left(a^5 + \frac{a^5}{5} - \frac{2a^5}{3}\right) - \left(-a^5 - \frac{a^5}{5} + \frac{2a^5}{3}\right)\right] = 1$$

$$=> N^2\left[a^5+\frac{a^5}{5}-\frac{2a^5}{3}+a^5+\frac{a^5}{5}-\frac{2a^5}{3}\right]=1$$

$$=> N^2\left[2a^5+\frac{2a^5}{5}-\frac{4a^5}{3}\right]=1$$

$$=> N^2a^5\left[\frac{30+6-20}{15}\right]=1$$

$$=> N^2\frac{16a^5}{15}=1$$

$$=> N=\sqrt{\frac{15}{16a^5}}$$

i.e. the normalization constant is $\sqrt{\frac{15}{16a^5}}$ and the normalized wave function will be $\Psi=\sqrt{\frac{15}{16a^5}}(a^2-x^2)$

(4) $\Psi=Cos\left(\frac{n\pi x}{a}\right), -a\le x\le a$

Let the normalization constant = N

So the normalized wave function is $\Psi=N\ Cos\left(\frac{n\pi x}{a}\right)$

Now

$$\int_{-a}^{a}\left(N\ Cos\left(\frac{n\pi x}{a}\right)\right)^2 dx=1$$

$$=> N^2\int_{-a}^{a}Cos^2\frac{n\pi x}{a}\ dx=1$$

$$=> \frac{N^2}{2}\int_{-a}^{a}2Cos^2\frac{n\pi x}{a}\ dx=1$$

$$=> \frac{N^2}{2}\int_{-a}^{a}\left(1+Cos\frac{2n\pi x}{a}\right)dx=1$$

$$=> \frac{N^2}{2}\left[x+\frac{sin\frac{2n\pi x}{a}}{\frac{2n\pi}{a}}\right]_{-a}^{a}$$

$$=> \frac{N^2}{2}\left[x+\frac{a}{2n\pi}Sin\frac{2n\pi x}{a}\right]_{-a}^{a}$$

$$=> \frac{N^2}{2}\left[\left(a+\frac{a}{2n\pi}Sin\frac{2n\pi a}{a}\right)-\left(-a+\frac{a}{2n\pi}Sin\frac{2n\pi(-a)}{a}\right)\right]=1$$

$$=> \frac{N^2}{2}\left[\left(a+\frac{a}{2n\pi}Sin\ 2n\pi\right)-\left(-a-\frac{a}{2n\pi}Sin\ 2n\pi\right)\right]$$

$$=> \frac{N^2}{2}[(a+0)-(-a-0)]$$

$$=> \frac{N^2}{2} \times 2a = 1$$

$$=> N^2 = \frac{1}{a}$$

$$=> N = \sqrt{\frac{1}{a}}$$

i.e. the normalization constant is $\sqrt{\frac{1}{a}}$ and the normalized wave function will be $\Psi = \sqrt{\frac{1}{a}}\ Cos\left(\frac{n\pi x}{a}\right)$

(5) $\Psi = a(a-x), 0 \leq x \leq a$

Let the normalization constant = N

So the normalized wave function is $\Psi = N\ a(a-x)$

Now

$$\int_0^a [N\ a(a-x)]^2 dx = 1$$

$$=> N^2 a^2 \int_0^a (a-x)^2 dx = 1$$

$$=> N^2 a^2 \int_0^a [a^2 - 2ax + x^2] dx = 1$$

$$=> N^2 \left[a^4 x - \frac{2a^3 x^2}{2} + \frac{a^2 x^3}{3}\right]_0^a = 1$$

$$=> N^2 \left(a^5 - a^5 + \frac{a^5}{3}\right) - (0) = 1$$

$$=> N^2 \frac{a^5}{3} = 1$$

$$=> N = \sqrt{\frac{3}{a^5}}$$

i.e. the normalization constant is $\sqrt{\frac{3}{a^5}}$ and the normalized wave function will be $\Psi = \sqrt{\frac{3}{a^5}}\ a(a-x)$

(6) $\Psi = e^{-a|x|} a > 0, -\infty \leq x \leq \infty$

Ans:

Let the normalization constant = N

So the normalized wave function is $\Psi = Ne^{-a|x|}$

Now

$$\int_{-\infty}^{\infty} \left(Ne^{-a|x|}\right)^2 dx = 1$$

$$=> N^2 \int_{-\infty}^{\infty} e^{-2a|x|}\, dx = 1 - -(1)$$

Since $e^{-2a|x|}$ is an even function, so we can write

$$\int_{-\infty}^{\infty} e^{-2a|x|}\, dx = 2\int_{0}^{\infty} e^{-2a|x|}\, dx - -(1)$$

From equation (1) and (2), we have

$$2N^2 \int_{0}^{\infty} e^{-2a|x|}\, dx = 1$$

$$=> 2N^2 \left[\frac{e^{-2ax}}{-2a}\right]_0^{\infty} = 1$$

$$=> -\frac{N^2}{a}(0-1) = 1$$

$$=> N = \sqrt{a}$$

i.e. the normalization constant is $\sqrt{a}$ and the normalized wave function will be $\Psi = \sqrt{a}\, e^{-a|x|}$

[Self-test] Normalize the function over the given interval: $\Psi = sin\left(\frac{n\pi x}{a}\right), 0 \le x \le a$

Q. Show that the following sets of functions are orthogonal to each other over the given intervals:

(1) $Sin\frac{n\pi x}{a}\ and\ Cos\frac{n\pi x}{a}$, over the interval $0 \le x \le a$

(2) $\Psi_1 = x\ and\ \Psi_2 = x^2$, over the interval $-k \le x \le k$

(3) $\Psi_1 = \left(\frac{1}{2\pi}\right)^{\frac{1}{2}}, \Psi_2 = \left(\frac{1}{\pi}\right)^{\frac{1}{2}} Cos\ nx\ and\ \Psi_3 = \left(\frac{1}{\pi}\right)^{\frac{1}{2}} Sin\ nx$, over the interval o to 2π

(4) $\Psi_1 = a^2 + x^2\ and\ \Psi_2 = x(a^2 - x^2)$, over the interval $-a \le x \le a$

Ans:

(1) $Sin\frac{n\pi x}{a}\ and\ Cos\frac{n\pi x}{a}$ over the interval $0 \le x \le a$

$$\int_0^a Sin\left(\frac{n\pi x}{a}\right) Cos\left(\frac{n\pi x}{a}\right) dx$$

$$= \frac{1}{2}\int_0^a 2\, Sin\left(\frac{n\pi x}{a}\right) Cos\left(\frac{n\pi x}{a}\right) dx$$

$$= \frac{1}{2}\int_0^a Sin\frac{2n\pi x}{a} dx$$

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

$$= -\frac{1}{2} \times \frac{a}{2n\pi}\left[Cos\,\frac{2n\pi x}{a}\right]_0^a$$

$$= -\frac{1}{2} \times \frac{a}{2n\pi}\left[Cos\,\frac{2n\pi a}{a} - Cos\ 0\right]$$

$$= -\frac{1}{2} \times \frac{a}{2n\pi}[Cos 2n\pi - Cos\ 0]$$

$$= -\frac{1}{2} \times \frac{a}{2n\pi}[1 - 1]$$

$$= 0$$

So the given functions are orthogonal to each other.

(2) $\Psi_1 = x\ and\ \Psi_2 = x^2$, over the interval $-k \leq x \leq k$

$$\int_{-k}^{k} \Psi_1 \Psi_2\, dx$$

$$= \int_{-k}^{k} x x^2\, dx$$

$$= \int_{-k}^{k} x^3\, dx$$

$$= \left[\frac{x^4}{4}\right]_{-k}^{k}$$

$$= \frac{1}{4}(k^4 - (-k)^4)$$

$$= 0$$

So the given functions are orthogonal to each other.

(3) $\Psi_1 = \left(\frac{1}{2\pi}\right)^{\frac{1}{2}}, \Psi_2 = \left(\frac{1}{\pi}\right)^{\frac{1}{2}} Cos\ nx\ and\ \Psi_3 = \left(\frac{1}{\pi}\right)^{\frac{1}{2}} Sin\ nx$, over the interval 0 to 2π

$$\int_{0}^{2\pi} \Psi_1 \Psi_1 \Psi_3 dx$$

$$= \int_{0}^{2\pi} \left(\frac{1}{2\pi}\right)^{\frac{1}{2}} \left(\frac{1}{\pi}\right)^{\frac{1}{2}} Cos\ nx \left(\frac{1}{\pi}\right)^{\frac{1}{2}} Sin\ nx\ dx$$

$$= \left(\frac{1}{2\pi}\right)^{\frac{1}{2}} \left(\frac{1}{\pi}\right) \int_{0}^{2\pi} Cos\ nx\ Sin\ nx\ dx$$

$$= \left(\frac{1}{2\pi}\right)^{\frac{1}{2}} \left(\frac{1}{2\pi}\right) \int_{0}^{2\pi} 2\ Cos\ nx\ Sin\ nx\ dx$$

$$= \left(\frac{1}{2\pi}\right)^{\frac{3}{2}} \int_{0}^{2\pi} Sin\ 2nx\ dx$$

$$= \left(\frac{1}{2\pi}\right)^{\frac{3}{2}} \left[\frac{Cos\ 2nx}{2n}\right]_{0}^{2\pi}$$

$$= 2n \times \left(\frac{1}{2\pi}\right)^{\frac{3}{2}} [Cos\ 4n\pi - Cos\ 0]$$

$$= 2n \times \left(\frac{1}{2\pi}\right)^{\frac{3}{2}} [1 - 1]$$

$$= 0$$

So the given functions are orthogonal to each other.

(4) $\Psi_1 = a^2 + x^2\ and\ \Psi_2 = x(a^2 - x^2)$, over the interval $-a \leq x \leq a$

$$\int_{-a}^{a} \Psi_1 \Psi_2\ dx$$

$$= \int_{-a}^{a} \left[(a^2 + x^2)\big(x(a^2 - x^2)\big)\right] dx$$

$$= \int_{-a}^{a} [(a^2 + x^2)(xa^2 - x^3)]\ dx$$

$$= \int_{-a}^{a} (a^4x - a^2x^3 + a^2x^3 - x^5)\ dx$$

$$= \int_{-a}^{a} (a^4x - x^5)\ dx$$

$$= \left[\frac{a^4x^2}{2} - \frac{x^6}{6}\right]_{-a}^{a}$$

$$= \left[\left(\frac{a^4a^2}{2} - \frac{a^6}{6}\right) - \left(\frac{a^4(-a)^2}{2} - \frac{(-a)^6}{6}\right)\right]$$

$$= \frac{a^6}{2} - \frac{a^6}{6} - \frac{a^6}{2} + \frac{a^6}{6}$$

$$= 0$$

[Self-test]. Q. The wave functions $\psi_1 = \left(\frac{1}{\pi}\right)^{\frac{1}{2}} cosx$ and $\psi_2 = \left(\frac{1}{\pi}\right)^{\frac{1}{2}} sinx$ are defined in the interval $0 \leq x \leq 2\pi$. Examine if the functions are orthogonal to each other.

[Self-test]. Q. Show that the two wave functions $Sin\frac{\pi x}{a}\ and\ Cos\frac{\pi x}{a}$ are orthogonal over the interval $0 \leq x \leq a$

Constraints on the wave function: Concept of acceptable or well behaved wave functions

The Born interpretation puts severe restrictions on the acceptability of wave functions i.e. we can reach some general conclusions about what sort of mathematical properties ψ can or cannot have. These can be summarized as given below:

(1) Ψ must be single valued i.e. it must have only one value at each point of space.

Reasoning: In a given region of space, there is only one probability of finding a particle, it would be absurd to have two or more value of probability of finding the same particle at a specific point.

(2) The wave function must be square-integrable, in other words Ψ must be finite of the spatial coordinate

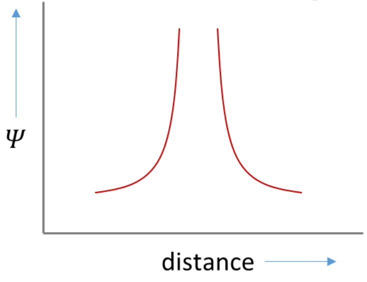
Reasoning: The wave function must be finite over any finite region, if it is infinite, then the Born integral would become equal to infinity instead of unity. i.e. if the wave function is infinite, then the Born interpretation will be useless to use as a measure of comparative probabilities, in other words the wave function could not be normalized if it is infinite.

(3) Ψ and its 1st derivatives (slope) i.e. $\frac{\partial\Psi}{\partial x},\frac{\partial\Psi}{\partial y},\frac{\partial\Psi}{\partial z}$ must be continuous. It means that there can be no kinks in the function and no sharp steps are permitted.

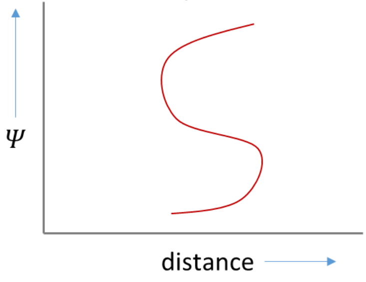
Reasoning: The wave function must be continuous everywhere. That is, there are no sudden jumps in the probability density when moving through space. For example, there is a certain probability of finding an electron at a given distance from the nucleus, there will be a slightly different probability if the distance is changed slightly. The probability does not change drastically if the distance is changed slightly. i.e. the probability function does not have discontinuities and hence the wave function must be continuous. If the wave function has a discontinuity such as a sharp step upwards or downwards, this can be seen as a limiting case of a very rapid change in the function. Such a rapid change would mean that the derivative of the function was very large (either a very large positive or negative number). In the limit of a step function, this would imply an infinite derivative.

Graphical representation of some of the unacceptable wave function:

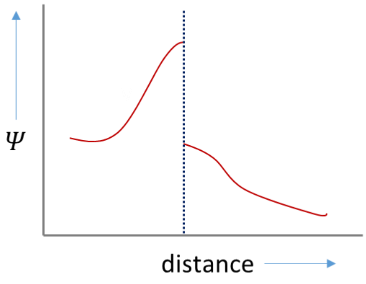
Unacceptable as it is
infinite over a finite region



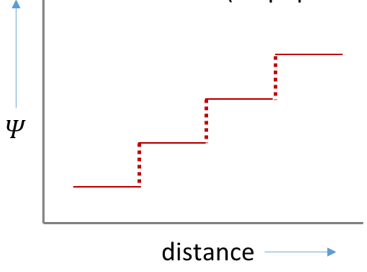
Unacceptable as it is
multiple valued



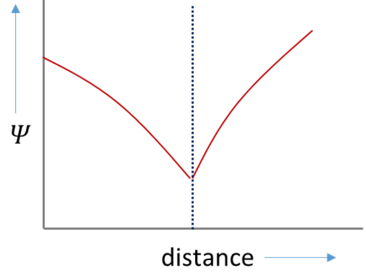
Unacceptable as it is
discontinuous



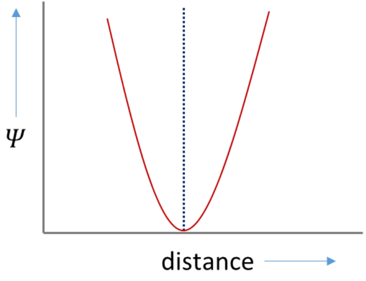
Unacceptable as it is
discontinuous (steps present)



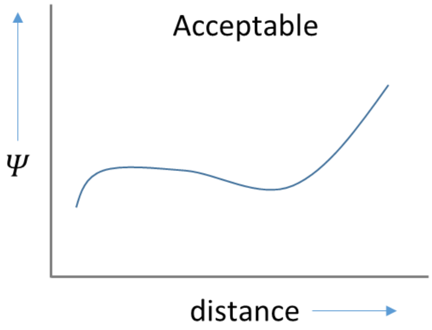
Unacceptable as its
1st derivative (slope) is
discontinuous

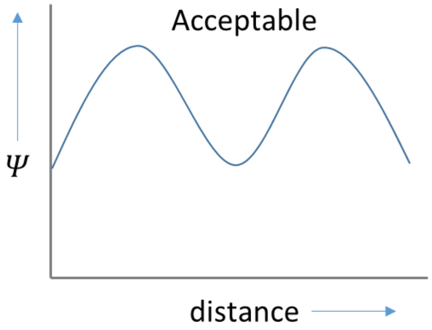


Unacceptable as it is
not quadratically integrable



Graphical representation of some acceptable wave functions:





Q. Discuss the characteristics of acceptable wave function clearly explaining the conditions of acceptance.

Q. One of the condition for a well behaved function is that the function must be single valued. State why it is so.

Q. Indicate which of the following wave functions are acceptable and which are not within the interval $[-\infty, \infty]$. State why they are accepted and why they are not.

(1) $\Psi = x$ (2) $\Psi = x^2$ (3) $\Psi = Sin\, x$ (4) $\Psi = e^x$ (5) $\Psi = e^{-x}$ (6) $\Psi = e^{-x^2}$ (7) $\Psi = \tan x$

(8) $\Psi = Cosec\, x$ (9) $\Psi = Sinx + Cos\, x$

Ans:

(1) $\Psi = x$ is not acceptable because as $x \to \infty, \Psi \to \infty$ i.e. it is not bounded (diverged).

(2) $\Psi = x^2$ is not acceptable because as $x \to \infty, \Psi \to \infty$ i.e. it is not bounded

(3) $\Psi = Sin\, x$ is acceptable as values of Sin x line between -1 to +1. i.e. it is bounded.

(4) $\Psi = e^x$ is not acceptable because as $x \to \infty, \Psi \to \infty$ i.e. it is not bounded.

(5) $\Psi = e^{-x}$ is not acceptable because as $x \to -\infty, \Psi \to \infty$ i.e. it is not bounded.

(6) $\Psi = e^{-x^2}$ is acceptable because as $x \to \pm\infty, \Psi \to 0$ i.e. it is bounded

(7) $\Psi = \tan x$ is not acceptable because as $x \to \frac{\pi}{2}, \Psi \to \infty$ i.e. it is not bounded.

(8) $\Psi = Cosec\, x$ is not acceptable because as $x \to 0, \Psi \to \infty$ i.e. it is not bounded

(9) $\Psi = Sinx + Cos\, x$ is acceptable as values of Sin x and Cos x always lies between -1 to +1. i.e. it is bounded.

Q. Indicate which of the following wave functions are acceptable and which are not. For those that are not, state why.

(a) $f(x) = \pm\sqrt{x}, x \geq 0$ (b) $\Psi = \frac{1}{\sqrt{2}} Sin\frac{x}{2}, -\frac{\pi}{2} \leq x \leq \frac{\pi}{2}$ (c) $\Psi = \frac{1}{4-x}, 0 \leq x \leq 10$

(d) $\Psi = \frac{1}{4-x}, 0 \leq x \leq 3$ (e) $\Psi = e^{-x}, 0 \leq x \leq \infty$ (f) $\psi = \frac{Sin\, x}{x}\ (0 \leq x \leq \infty)$

(g) $\psi = Sin^{-1}x, -1 \leq x \leq 1$ (h) $\Psi = e^{-|x|}, -\infty \leq x \leq \infty$

Ans:

(a) Not acceptable, because the function is multi valued.

(b) Acceptable, because it meets all criteria for acceptable wave functions

(c) Not acceptable, because the function approaches infinity for x = 4, which is a part of the given interval range.

(d) Acceptable, because the function meets all criteria for acceptable wave functions within the stated range of the variable x.

(e) Acceptable, as it is single valued, finite continuous and quadratically integrable over the interval $0 \leq x \leq \infty$.

(f) Acceptable because as $x \rightarrow 0, \frac{Sin\, x}{x} \rightarrow 1$

(g) Not acceptable as Sin^{-1} x is a multi-valued function (for example Sin^{-1} 1 $= \frac{\pi}{2}, \frac{\pi}{2} + 2\pi, \frac{\pi}{2} + 4\pi$ ....)

(h) At $x = -\infty, \Psi = e^{-|x|} = e^{-\infty} = 0$ and at $x = \infty, \Psi = e^{-|x|} = e^{-\infty} = 0$

So the function is bound and it seems like acceptable, but 1st derivative of $e^{-|x|}$ is not continuous at x = 0, so it is an unacceptable wave function.

Postulates 2: For every dynamical variable (classical observable) there is a corresponding linear quantum mechanical operator

Dynamic variable or observable: A measurable property of a system such as position, momentum, energy etc. are called dynamic variable or observable.

Operator: An operator is a rule for transforming a given function into another function. A caret over the mathematical symbol is used to designate an operator. For example if an operator $\hat{A}$ operate on a function say $f(x)$, then it will convert it into a new function $g(x)$. Mathematically, we can say that:

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

Algebra of Operators:

Addition:

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

Subtraction:

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

Product:

The product of two operators is defined as:

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

Operator $\hat{B}$ first act on the function $f(x)$ and in next the operator $\hat{A}$ act on resulting function. In general, the order of application of operators is always from right to left. For example if two operator say $\frac{d}{dx}\ and\ x$ operate on a function $f(x)$, then we have

$$\frac{d}{dx}x[f(x)] = \frac{d}{dx}[xf(x)]$$

$$= x\frac{d}{dx}f(x) + f(x)$$

* If the same operator is applied in succession then it is written as power, for example $\hat{A}\hat{A}\hat{A}f(x) = \hat{A}^3 f(x)$

Associative law: Associative law holds good for operators, i.e.

$$\hat{A}\left(\hat{B}\hat{C}\right) = \left(\hat{A}\hat{B}\right)\hat{C}$$

Commutative law: The commutative law does not generally hold for operators. i.e.

$$\hat{A}\hat{B} \neq \hat{B}\hat{A}$$

Commutator: Using any two operator say $\hat{A}\ and\ \hat{B}$, it is possible to construct a new operator $(\hat{A}\hat{B} - \hat{B}\hat{A})$, called the commutator of the two operator $\hat{A}\ and\ \hat{B}$ which is usually written as $\left[\hat{A}, \hat{B}\right]$, i.e.

$$Commutator\ \left[\hat{A}, \hat{B}\right] = (\hat{A}\hat{B} - \hat{B}\hat{A})$$

If the result of two operations is the same irrespective of the sequence in which the operations are performed, then the two operators are said to be commute with each other i.e. if two operates commute then $\hat{A}\hat{B} = \hat{B}\hat{A}$ and hence we can write:

$$\left[\hat{A}, \hat{B}\right] = \hat{A}\hat{B} - \hat{B}\hat{A} = 0$$

If two operators do not commute then $\hat{A}\hat{B} \neq \hat{B}\hat{A}$, and hence $\left[\hat{A}, \hat{B}\right] \neq 0$

* Any operator commute with itself or any power of it i.e. $\left[\hat{A}, \hat{A}\right] = 0$ and $\left[\hat{A}, \hat{A}^n\right] = 0, n = 1,2,3$ ...

Q. Prove that: $\left[\hat{A}, \hat{B}\right] = -\left[\hat{B}, \hat{A}\right]$

Ans:

$$\begin{aligned}\left[\hat{A}, \hat{B}\right] &= \hat{A}\hat{B} - \hat{B}\hat{A} \\ &= -\hat{B}\hat{A} + \hat{A}\hat{B} \\ &= -\left[\hat{B}\hat{A} - \hat{A}\hat{B}\right] \\ &= -\left[\hat{B}, \hat{A}\right]\end{aligned}$$

Q. Find whether the following operators commute with each other or not? In cases where they do not commute evaluate the commutator.

(a) $\left[x, \frac{d}{dx}\right]$ (b) $\left[y, \frac{d}{dx}\right]$ (c) $\left[\frac{d}{dx}, \frac{d^2}{dx^2}\right]$ (d)$\left[\frac{d^2}{dx^2}, x\frac{d}{dx}\right]$ (e) $\left[z^3, \frac{d}{dz}\right]$ (f) $\left[3y^2, \frac{d}{dy}\right]$ (g) $\left[\frac{d}{dx}, x^n\right]$

Ans:

(a) $\left[x, \frac{d}{dx}\right]$

Let Ψ be the operand function ;

Now

$$\begin{aligned}\left[x, \frac{d}{dx}\right]\Psi &= \left(x\frac{d}{dx} - \frac{d}{dx}x\right)\Psi \\ &= x\frac{d\Psi}{dx} - \frac{d}{dx}(x\Psi) \\ &= x\frac{d\Psi}{dx} - x\frac{d\Psi}{dx} - \Psi \\ &= \left(x\frac{d}{dx} - x\frac{d}{dx} - 1\right)\Psi \\ &= -\Psi\end{aligned}$$

Now removing the operand function Ψ from both sides we have

$$\left[x, \frac{d}{dx}\right] = -1\ (not\ zero)$$

So the two operator $x\ and\ \frac{d}{dx}$ do not commute with each other and their commutator is -1.

(b) $\left[y, \frac{d}{dx}\right]$

Let Ψ be the operand function

Now

$$\begin{aligned}\left[y, \frac{d}{dx}\right]\Psi &= \left(y\frac{d}{dx} - \frac{d}{dx}y\right)\Psi \\ &= y\frac{d\Psi}{dx} - \frac{d}{dx}(y\Psi) \\ &= y\frac{d\Psi}{dx} - y\frac{d\Psi}{dx} - \Psi\frac{dy}{dx} \\ &= y\frac{d\Psi}{dx} - y\frac{d\Psi}{dx} - 0 \\ &= \left(y\frac{d}{dx} - y\frac{d}{dx}\right)\Psi \\ &= 0\end{aligned}$$

$$i.e. \left[y, \frac{d}{dx}\right] = 0$$

So the two operators $y\ and\ \frac{d}{dx}$ commute with each other's

(c) $\left[\frac{d}{dx}, \frac{d^2}{dx^2}\right]$

Let Ψ be the operand function

$$\begin{aligned}\left[\frac{d}{dx}, \frac{d^2}{dx^2}\right]\Psi &= \left(\frac{d}{dx}\frac{d^2}{dx^2} - \frac{d^2}{dx^2}\frac{d}{dx}\right)\Psi \\ &= \frac{d}{dx}\frac{d^2\Psi}{dx^2} - \frac{d^2}{dx^2}\frac{d\Psi}{dx} \\ &= \frac{d^3\Psi}{dx^3} - \frac{d^3\Psi}{dx^3} \\ &= 0\end{aligned}$$

$$i.e. \left[\frac{d}{dx}, \frac{d^2}{dx^2}\right] = 0$$

So the operators $\frac{d}{dx}\ and\ \frac{d^2}{dx^2}$ with each other, in other words we can say that the 1st and 2nd derivative commute with each other.

(d) $\left[\frac{d^2}{dx^2}, x\frac{d}{dx}\right]$

Let Ψ be the operand function

$$\left[\frac{d^2}{dx^2}, x\frac{d}{dx}\right]\Psi = \left(\frac{d^2}{dx^2}x\frac{d}{dx} - x\frac{d}{dx}\frac{d^2}{dx^2}\right)\Psi$$

$$= \frac{d^2}{dx^2}x\frac{d\Psi}{dx} - x\frac{d}{dx}\frac{d^2\Psi}{dx^2}$$

$$= \frac{d}{dx}\frac{d}{dx}\left(x\frac{d\Psi}{dx}\right) - x\frac{d^3\Psi}{dx^3}$$

$$= \frac{d}{dx}\left[x\frac{d^2\Psi}{dx^2} + \frac{d\Psi}{dx}\right] - x\frac{d^3\Psi}{dx^3}$$

$$= \frac{d}{dx}\left(x\frac{d^2\Psi}{dx^2}\right) + \frac{d}{dx}\frac{d\Psi}{dx} - x\frac{d^3\Psi}{dx^3}$$

$$= x\frac{d^3\Psi}{dx^3} + \frac{d^2\Psi}{dx^2} + \frac{d^2\Psi}{dx^2} - x\frac{d^3\Psi}{dx^3}$$

$$= \left(x\frac{d^3}{dx^3} + 2\frac{d^2}{dx^2} - x\frac{d^3}{dx^3}\right)\Psi$$

$$= \left(2\frac{d^2}{dx^2}\right)\Psi$$

Now removing the operand function Ψ from both sides we have

$$\left[\frac{d^2}{dx^2}, x\frac{d}{dx}\right] = 2\frac{d^2}{dx^2}$$

So the two operator $\frac{d^2}{dx^2}$ $and\ x\frac{d}{dx}$ do not commute with each other and their commutator is $2\frac{d^2}{dx^2}$.

(e) $\left[x^3, \frac{d}{dx}\right]$

Let Ψ be the operand function

Now

$$\left[x^3, \frac{d}{dx}\right]\Psi = \left(x^3\frac{d}{dx} - \frac{d}{dx}x^3\right)\Psi$$

$$= x^3\frac{d\Psi}{dx} - \frac{d}{dx}(x^3\Psi)$$

$$= x^3\frac{d\Psi}{dx} - \left[x^3\frac{d\Psi}{dx} + \Psi\frac{d}{dx}(x^3)\right]$$

$$= x^3\frac{d\Psi}{dx} - \left[x^3\frac{d\Psi}{dx} + 3x^2\Psi\right]$$

$$= \left(x^3\frac{d}{dx} - x^3\frac{d}{dx} - 3x^2\right)\Psi$$

$$= -3x^2\Psi$$

$$i.e.\left[x^3, \frac{d}{dx}\right] = -3x^2$$

So the two operators $x^3 \ and \ \frac{d}{dx}$ do not commute with each other and their commutator is $-3x^2$.

(g) $\left[\frac{d}{dx}, x^n\right]$

Ans:

Let Ψ be the operand function

Now

$$\left[\frac{d}{dx}, x^n\right]\Psi = \left(\frac{d}{dx}x^n - x^n\frac{d}{dx}\right)\Psi$$

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

$$= x^n\frac{d\Psi}{dx} + \Psi n x^{n-1} - x^n\frac{d\Psi}{dx}$$

$$= nx^{n-1}\Psi$$

$$i.e.\left[\frac{d}{dx}, x^n\right] = nx^{n-1} \neq 0$$

So the two operators $\frac{d}{dx}$ $and x^n$ do not commute with each other and their commutator is nx^{n-1}.

Q. Find the expressions for the following operators

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

(b) $\left(x\frac{d}{dx}\right)^2$

(c) $\left(\frac{d}{dx}x\right)^2$

Ans:

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

Let the operand function is Ψ

Now

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

$$= \left(\frac{d}{dx} + x\right)\left[\left(\frac{d}{dx} + x\right)\Psi\right]$$

$$= \left(\frac{d}{dx} + x\right)\left(\frac{d\Psi}{dx} + x\Psi\right)$$

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

$$= \frac{d^2\Psi}{dx^2} + x\frac{d\Psi}{dx} + \Psi + x\frac{d\Psi}{dx} + x^2\Psi$$

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

Removing the operand function from both sides we have:

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

(b) $\left(x\frac{d}{dx}\right)^2$

Let the operand function is Ψ

Now

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

$$= \left(x\frac{d}{dx}\right)\left(x\frac{d\Psi}{dx}\right)$$

$$= x\left[\frac{d}{dx}\left(x\frac{d\Psi}{dx}\right)\right]$$

$$= x\left[x\frac{d^2\Psi}{dx^2} + \frac{d\Psi}{dx}\frac{dx}{dx}\right]$$

$$= x^2\frac{d^2\Psi}{dx^2} + x\frac{d\Psi}{dx}$$

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

Removing the operand function from both sides we have:

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

(c) $\left(\frac{d}{dx}x\right)^2$

Let the operand function is Ψ

Now

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

$$= \left(\frac{d}{dx}x\right)\left[\frac{d}{dx}(x\Psi)\right]$$

$$= \frac{d}{dx}x\left[x\frac{d\Psi}{dx} + \Psi\right]$$

$$= \frac{d}{dx}\left[x^2\frac{d\Psi}{dx} + x\Psi\right]$$

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

$$= x^2\frac{d^2\Psi}{dx^2} + \frac{d\Psi}{dx}2x + x\frac{d\Psi}{dx} + \Psi$$

$$= x^2\frac{d^2\Psi}{dx^2} + 3x\frac{d\Psi}{dx} + \Psi$$

$$= \left(x^2\frac{d^2}{dx^2} + 3x\frac{d}{dx} + 1\right)\Psi$$

Removing the operand function from both sides we have:

$$\left(\frac{d}{dx}x\right)^2 = x^2\frac{d^2}{dx^2} + 3x\frac{d}{dx} + 1$$

Del or vector operator $(\hat{\nabla})$:

It is a vector operator whose Cartesian co-ordinate representation is:

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

Where i, j, k are unit vectors.

Laplacian operator $(\hat{\nabla}^2)$:

The scalar product of del operator $(\hat{\nabla})$ is called the Laplacian operator

i.e.

$$\hat{\nabla}^2 = \hat{\nabla}.\hat{\nabla}$$

$$= \left(i\frac{\partial}{\partial x} + j\frac{\partial}{\partial y} + k\frac{\delta}{\delta z}\right).\left(i\frac{\partial}{\partial x} + j\frac{\partial}{\partial y} + k\frac{\delta}{\delta z}\right)$$

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

Linear operator:

Rule of thumb: Operators encountered in quantum mechanics are all linear.

If in operating on the sum of two functions, an operator gives the same result as the sum of the operations on the two functions separately, then the operator is said to be linear.

Thus an operator say $\hat{A}$ is said to be linear if it satisfies the following two properties:

$$(1)\ \hat{A}[f(x) + g(x)] = \hat{A}f(x) + \hat{A}g(x)$$

$$(2)\hat{A}[f_1(x)] = c\,\hat{A}f_1(x)$$

Where $f(x), g(x)\ and\ f_1(x)$ are functions and "c" is a constant.

For example, $\frac{d}{dx}\ (differentation), \int dx\ (intregation), multiplication$ etc. are linear operators because:

$$Differentation: \frac{d}{dx}[f(x) + g(x)] = \frac{d}{dx}f(x) + \frac{d}{dx}g(x)\ and\ \frac{d}{dx}[cf(x)] = c\frac{d}{dx}[f(x)]$$

$$Integration: \int [f(x) + g(x)]dx = \int f(x)dx + \int g(x)dx\ and \int cf(x)dx = c\int f(x)dx$$

But square root , $taking\ square, exponential, logarithim$ etc. are non-linear operator because:

$$Square\ root{:}\sqrt{f(x)+g(x)} \neq \sqrt{f(x)}+\sqrt{g(x)}\ and\ \sqrt{cf(x)} \neq c\sqrt{f(x)}$$

$$Exponential{:}\ e^{f(x)+g(x)} \neq e^{f(x)}+e^{g(x)} and\ e^{cf(x)} \neq ce^{f(x)}$$

Note: The linear character of the operator is related to the superposition of states and waves reinforcing each other in the process.

Q. State true of false with reason: $\hat{O}[f(x)+g(x)]$ is always equal to $\hat{O}f(x)+\ \hat{O}g(x)$.

Ans: False, it is true only when the given operator $\hat{O}$ is linear in nature.

Q. Determine whether the following operators are linear and which are nonlinear:

(a) $\hat{A}\Psi=\lambda\Psi, where\ \lambda\ is\ a\ constat$ (b) $\hat{B}\Psi=\Psi^*$ (c) $\hat{O}\Psi=\Psi^2$ (d) $\hat{D}\Psi=\frac{d\Psi}{dx}$ (e) $\hat{O}\Psi=\frac{1}{\Psi}$

(f) $\hat{O}\Psi=x^2\,\Psi$ (g) $\hat{O}=-i\hbar\frac{d}{dx}$

Ans:

(a) $\hat{A}\Psi=\lambda\Psi, where\ \lambda\ is\ a\ constat$

In this case the operator $\hat{A}=\lambda$

Now $\hat{A}=\lambda$ will be linear if

$$\hat{A}[f(x)+g(x)]=\hat{A}f(x)+\hat{A}g(x)\ and\ \hat{A}[cf_1(x)]=c\,\hat{A}f_1(x)$$

Now

$$L.H.S=\hat{A}[f(x)+g(x)]$$
$$=\lambda[f(x)+g(x)]$$
$$=\lambda f(x)+\lambda g(x)$$
$$R.H.S.=\hat{A}f(x)+\hat{A}g(x)$$
$$=\lambda f(x)+\lambda g(x)$$
$$i.e. L.H.S=R.H.S.$$

Again

$$\lambda[cf_1(x)]=\boldsymbol{c}\lambda[f_1(x)]$$

i.e. $\hat{A}=\lambda$ is a linear operator

(b) $\hat{B}\Psi=\Psi^*$

In this case the operator $\hat{B}$ is simply taking the complex conjugate

Now $\hat{B}$ will be linear if

$$\hat{B}[f(x)+g(x)]=\hat{B}f(x)+\hat{B}g(x)\ and\ \ \hat{B}[\boldsymbol{c}f_1(x)]=c\,\hat{B}f_1(x)$$

Now

$$L.H.S=\hat{B}[f(x)+g(x)]$$
$$=[f(x)+g(x)]^*$$

$$R.H.S. = \hat{B}f(x) + \hat{B}g(x)$$

$$= [f(x)]^* + [g(x)]^*$$

Since

$$[f(x) + g(x)]^* \neq [f(x)]^* + [g(x)]^*$$

$$i.e.\ L.H.S. \neq R.H.S.$$

So the operator $\hat{B}$ which stands for taking complex conjugate of the function is a non-linear operator.

(c) $\hat{O}\Psi = \Psi^2$

In this case the operator $\hat{O}$ is simply taking square

Now $\hat{O}$ will be linear if

$$\hat{O}[f(x) + g(x)] = \hat{O}f(x) + \hat{O}g(x)\ and\ \hat{O}[cf_1(x)] = c\,\hat{O}f_1(x)$$

Now

$$L.H.S = \hat{O}[f(x) + g(x)]$$

$$= [f(x) + g(x)]^2$$

$$= f^2(x) + g^2(x) + 2f(x)g(x)$$

$$R.H.S = \hat{O}f(x) + \hat{O}g(x)$$

$$= f^2(x) + g^2(x)$$

$$i.e.\ L.H.S \neq R.H.S.$$

So the operator $\hat{O}$ which stands for taking square of the function is a non-linear operator.

(d) $\widehat{D}\Psi = \frac{d\Psi}{dx}$

In this case the operator $\widehat{D} = \frac{d}{dx}$

Now $\widehat{D} = \frac{d}{dx}$ will be linear if

$$\widehat{D}[f(x) + g(x)] = \widehat{D}f(x) + \widehat{D}g(x)\ and\ \widehat{D}[\boldsymbol{c}f_1(x)] = c\,\widehat{D}f_1(x)$$

Now

$$L.H.S = \widehat{D}[f(x) + g(x)]$$

$$= \frac{d}{dx}[f(x) + g(x)]$$

$$= \frac{d}{dx}\,f(x) + \frac{d}{dx}g(x)$$

$$R.H.S. = \widehat{D}f(x) + \widehat{D}g(x)$$

$$= \frac{d}{dx}\,f(x) + \frac{d}{dx}g(x)$$

$$i.e.\ L.H.S \neq R.H.S$$

And

$$\frac{d}{dx}[cf_1(x)] = \boldsymbol{c}\frac{d}{dx}f_1(x)$$

So $\hat{D} = \frac{d}{dx}$ is a linear operator.

$(e)\ \hat{O}\Psi = \frac{1}{\Psi}$

In this case the operator $\hat{O}$ is stand for taking reciprocal of the function

Now $\hat{O}$ will be linear if

$$\hat{O}[f(x) + g(x)] = \hat{O}f(x) + \hat{O}g(x)\ and\ \ \hat{O}[cf_1(x)] = c\ \hat{O}f_1(x)$$

Now

$$L.H.S = \hat{O}[f(x) + g(x)]$$

$$= \frac{1}{f(x) + g(x)}$$

$$R.H.S = \hat{O}f(x) + \hat{O}g(x)$$

$$= \frac{1}{f(x)} + \frac{1}{g(x)}$$

Since

$$\frac{1}{f(x) + g(x)} \neq \frac{1}{f(x)} + \frac{1}{g(x)}$$

$$i.e. L.H.S \neq R.H.S.$$

So the operator $\hat{O}$ which stands for taking reciprocal of the function is non-linear operator.

$(f)\ \hat{O}\Psi = x^2\ \Psi$

In this case the operator $\hat{O}$ stand for simply multiplying by x^2 (mind that it is not for taking square of the function)

Now $\hat{O}$ will be linear if

$$\hat{O}[f(x) + g(x)] = \hat{O}f(x) + \hat{O}g(x)\ \ and\ \ \hat{O}[cf_1(x)] = c\ \hat{O}f_1(x)$$

Now

$$L.H.S = \hat{O}[f(x) + g(x)]$$

$$= x^2[f(x) + g(x)]$$

$$= x^2f(x) +\ x^2g(x)$$

$$R.H.S = \hat{O}f(x) + \hat{O}g(x)$$

$$= x^2f(x) +\ x^2g(x)$$

$$L.H.S = R.H.S.$$

Again

$$x^2[cf_1(x)] = \boldsymbol{c}x^2f_1(x)$$

i.e. the operator $\hat{O}$ which stand for simply multiplying the function by x^2 is linear.

(g) $\hat{O}\Psi = -i\hbar\frac{d\Psi}{dx}$

In this case the operator $\hat{O} = -i\hbar\frac{d}{dx}$

Now $\hat{O} = -i\hbar\frac{d}{dx}$ will be linear if

$$\hat{O}[f(x) + g(x)] = \hat{O}f(x) + \hat{O}g(x)\ and\ \ \hat{O}[\boldsymbol{c}f_1(x)] = c\ \hat{O}f_1(x)$$

Now

$$\begin{aligned} L.H.S &= \hat{O}[f(x) + g(x)] \\ &= -i\hbar\frac{d}{dx}[f(x) + g(x)] \\ &= -i\hbar\frac{d}{dx}f(x) - i\hbar\frac{d}{dx}g(x) \\ R.H.S &= \hat{O}f(x) + \hat{O}g(x) \\ &= -i\hbar\frac{d}{dx}f(x) - i\hbar\frac{d}{dx}g(x) \\ i.e. L.H.S &= R.H.S. \end{aligned}$$

Again

$$-i\hbar\frac{d}{dx}[cf_1(x)] = -\boldsymbol{c}i\hbar\frac{d}{dx}f_1(x)$$

So $\hat{O} = -i\hbar\frac{d}{dx}$ is a linear operator.

Importance of operator in quantum mechanics: The principal mathematical deference between classical mechanics and quantum mechanics is that whereas in the former physical observables are represented by functions (such as position as a function of time), in quantum mechanics they are represented by mathematical operators. Since quantum mechanics postulates that the state of a system is given by a wave function that contain all the dynamic information, so how does one determine the value of various observables (say, position or momentum or energy) from a wave function. The answer lies in the 2nd postulates of quantum mechanics which states that in order to determine the value of an observable, we have to perform some mathematical operation on a wave function and this operation is represented by an operator.

Construction of quantum mechanical operators from the corresponding classical observable:

Two basic classical observables are position and the corresponding linear momentum. In classical mechanics, they are designated as q and p_q. Other observables are basically various combinations of these two basic observables. So all quantum mechanical operators can be constructed from these two classical observable. The process of converting an observable form a classical system to the corresponding operator for the quantum mechanical system is formalized by the following rules:

(1) Each Cartesian co-ordinates "q" is replaced by the operator $\hat{q}$,which is nothing but multiplying the concerned wave function by that coordinate i.e.

$$\hat{q} = q \times (concerned\ wave\ function)$$

For example, the position operator for the x- coordinate is $\hat{x} = x \times$,for y-coordinate is $\hat{y} = y \times$ and for z-coordinate is $\hat{z} = z \times$

(2) Each Cartesian component of linear momentum p_q is represented in differential form as:

$$\hat{p}_q = \frac{h}{2\pi i}\frac{\partial}{\partial q} or \frac{ħ}{i}\frac{\partial}{\partial q}\ or - iħ\frac{\partial}{\partial q}$$

Where $ħ = \frac{h}{2\pi}$. The quantity $\frac{1}{i} = -i$, because $i(-i) = 1$.

i.e. the x, y, z component of linear momentum can be represented with the corresponding quantum mechanical operators as:

$$\hat{p}_x = \frac{h}{2\pi i}\ \frac{\partial}{\partial x} or \frac{ħ}{i}\frac{\partial}{\partial x}\ or - iħ\frac{\partial}{\partial x}$$

$$\hat{p}_y = \frac{h}{2\pi i}\ \frac{\partial}{\partial y} or \frac{ħ}{i}\frac{\partial}{\partial y}\ or - iħ\frac{\partial}{\partial y}$$

$$\hat{p}_z = \frac{h}{2\pi i}\ \frac{\partial}{\partial z} or \frac{ħ}{i}\frac{\partial}{\partial z}\ or - iħ\frac{\partial}{\partial z}$$

The other operators corresponding to various observable can be constructed by combining the position and linear momentum operators as shown in the below example:

Operator for potential energy $(\hat{V})$:

$$\hat{V}(q) = V(q) \times$$

So for:

$$1D: \hat{V}(x) = V(x) \times$$

$$2D: \hat{V}(x, y) = V(x, y) \times$$

$$3D: \hat{V}(x, y, x) = V(x, y, z) \times$$

Operator for $\hat{p}_q{}^2$:

$$\hat{p}_q{}^2 = \left(\frac{h}{2\pi i}\ \frac{\partial}{\partial q}\right)^2$$

$$= -\frac{h^2}{4\pi^2}\frac{\partial^2}{\partial q^2}\ or - ħ^2\ \frac{\partial^2}{\partial q^2}$$

Operator for kinetic energy $(\hat{T})$:

We know

$$Kinetic\ energy\ (T) = \frac{1}{2}mv^2$$

$$= \frac{1}{2m}m^2v^2$$

$$= \frac{p^2}{2m} - -(1)$$

For 3D space, we can write

$$p^2 = p_x^2 + p_y^2 + p_z^2 - -(2)$$

From equation (1) and (2), we have

$$T = \frac{1}{2m}\left(p_x^2 + p_y^2 + p_z^2\right)$$

So

$$\widehat{T} = \frac{1}{2m}\left(\hat{p}_x{}^2 + \hat{p}_y{}^2 + \hat{p}_z{}^2\right)$$

$$= \frac{1}{2m}\left(-\frac{h^2}{4\pi^2}\frac{\partial^2}{\partial x^2}\right) + \left(-\frac{h^2}{4\pi^2}\frac{\partial^2}{\partial y^2}\right) + \left(\frac{h^2}{4\pi^2}\frac{\partial^2}{\partial z^2}\right)$$

$$= -\frac{h^2}{2m4\pi^2}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right)$$

$$= -\frac{h^2}{8\pi^2 m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right) \; or - \frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right)$$

$$= -\frac{h^2}{8\pi^2 m}\widehat{\nabla}^2 or \; -\frac{\hbar^2}{2m}\widehat{\nabla}^2$$

i.e. for 3D in can write

$$\widehat{T} = -\frac{h^2}{8\pi^2 m}\widehat{\nabla}^2 \; or - \frac{\hbar^2}{2m}\widehat{\nabla}^2$$

Similarly, it can be shown that:

For 2D:

$$\widehat{T} = -\frac{h^2}{8\pi^2 m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2}\right) \; or - \frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2}\right)$$

For 1 D:

$$\widehat{T} = -\frac{h^2}{8\pi^2 m}\frac{\partial^2}{\partial x^2} \; or - \frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}$$

Operator for total energy $(\widehat{\boldsymbol{H}})$:

We know

$$Total\ energy\ (E) = kinetic\ enrgy\ (T) + Potential\ energy\ (V)$$

In quantum mechanics the total energy of a system is expressed by the operator $(\widehat{H})$, which is called the "Hamiltonian" operator.

i.e.

$$\widehat{H} = \widehat{T} + \widehat{V}$$

For 3D:

$$\widehat{H} = \widehat{T} + \widehat{V}$$

$$= -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right) + \widehat{V}(x, y, z)$$

For 2D:

$$\widehat{H} = \widehat{T} + \widehat{V}$$

$$= -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2}\right) + \widehat{V}(x, y)$$

For 1D:

$$\hat{H} = \hat{T} + \hat{V}$$

$$= -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2}\right) + \hat{V}(x)$$

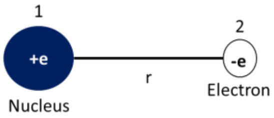
Q. What do you mean by Hamiltonian operator? Write down the expressions for Hamiltonian operators for a particle of mass "m" in one, two and three dimensions respectively.

Q. Write the Hamiltonian operators for the following systems:

(a) H-atom (b) H_2-molecule (c) He atom

Ans:

(a) H-atom is a two particle system, it has a nucleus and an electron which can be represented as:



Here

$$\hat{V} = -\frac{e^2}{r}$$

And

$$\hat{T} = -\frac{\hbar^2}{2m}\hat{\nabla}_2^{\ 2}$$

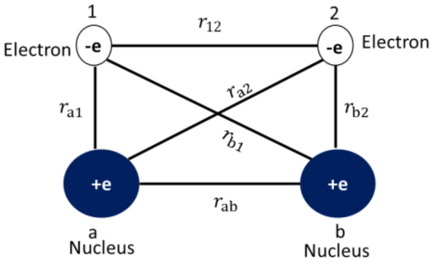
Since nucleus (particle 1) is stationary, so its kinetic energy is zero and hence we will consider only the kinetic energy operator for the electron (particle 2) only.

Now

$$\hat{H} = \hat{T} + \hat{V}$$

$$= -\frac{\hbar^2}{2m}\hat{\nabla}_2^{\ 2} - \frac{e^2}{r}$$

(b) H_2-molecule is a four particle system, it has two nuclei and two electrons which can be shown as:



Here

$$\hat{V} = \frac{e^2}{r_{ab}} + \frac{e^2}{r_{12}} - \frac{e^2}{r_{a1}} - \frac{e^2}{r_{a2}} - \frac{e^2}{r_{b1}} - \frac{e^2}{r_{b2}}$$

And

$$\hat{T} = -\frac{\hbar^2}{2m}\left(\hat{\nabla}_1^{\ 2} + \hat{\nabla}_2^{\ 2}\right)$$

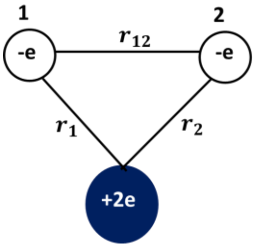
Since nucleus (particle a and b) is stationary, so their kinetic energies are zero and hence we will consider only the kinetic energy operator for the two electron (particle 1 and particle 2) only.

Now

$$\hat{H} = \hat{T} + \hat{V}$$

$$= -\frac{\hbar^2}{2m}\left(\hat{\nabla}_1{}^2 + \hat{\nabla}_2{}^2\right) + \left(\frac{e^2}{r_{ab}} + \frac{e^2}{r_{12}} - \frac{e^2}{r_{a1}} - \frac{e^2}{r_{a2}} - \frac{e^2}{r_{b1}} - \frac{e^2}{r_{b2}}\right)$$

(3) He atom is a three particle system it has one nucleus (+2 charge) and two electrons which can be shown ass below:



Here

$$\hat{V} = \frac{e^2}{r_{12}} - \frac{2e^2}{r_1} - \frac{2e^2}{r_2}$$

And

$$\hat{T} = -\frac{\hbar^2}{2m}\left(\hat{\nabla}_1{}^2 + \hat{\nabla}_2{}^2\right)$$

Since nucleus is stationary, so its kinetic energy is zero and hence we will consider only the kinetic energy operator for the two electron (particle 1 and particle 2) only.

Now

$$\hat{H} = \hat{T} + \hat{V}$$

$$= -\frac{\hbar^2}{2m}\left(\hat{\nabla}_1{}^2 + \hat{\nabla}_2{}^2\right) + \left(\frac{e^2}{r_{12}} - \frac{2e^2}{r_1} - \frac{2e^2}{r_2}\right)$$

Q. Verify that $\hat{\nabla}^2 + \hat{V}$ i.e. $\hat{H}$ is a linear operator.

Ans:

$$\hat{\nabla}^2(f+g) = \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right)(f+g)$$

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

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

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

$$= \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right)(f) + \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right)(g)$$

$$= \hat{\nabla}^2(f) + \hat{\nabla}^2(g)$$

Again

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

Since both $\hat{\nabla}^2$ and $\hat{V}$ are linear, so $\hat{\nabla}^2 + \hat{V}$ $i.e. \hat{H}$ is also linear.

Postulates 3: It give us idea about eigen functions and eigen values.

Eigen value equation:

In general, when an operator operates on a function, the outcome is an another function. i.e.

$$\hat{O}\Psi(x) = \phi(x)$$

However, in certain cases, when an operator say $\hat{A}$ operates on a function say $\Psi(x)$, the outcome of the operation is the same function multiplied by a constant. i.e.

$$\hat{A}\Psi(x) = \lambda \times \Psi(x)$$

In such cases the function Ψ(x) is said to be an eigen function of the operator $\hat{A}$ and the corresponding constant "λ" is called the eigen value. Such an equation which satisfy eigen function-eigen value relationship is called an eigenvalue equation.

Physical significance of eigen value equation:

The combination of operator and function yield an expression that could be mathematically evaluated. However, not all operator/function combinations are mathematically possible, or yield meaningful results (For example if $\hat{A} = \ln$ and $\Psi = -10$, then $\hat{A}\Psi$ cannot be evaluated as logarithm of negative number does not exist). So to yield meaningful result from operator/function combinations in quantum mechanics, they should follow an eigen function-eigen value relation. The speciality of eigen value equation is that the eigen values that result from eigen-function/operator combination is the only possible values of the observables that are obtainable with arbitrary precession in a single measurement.

Let's elaborate this concept by taking an eigen value equation:

$$\hat{M}\Psi_M = c\Psi_M$$

Suppose we want to determine a property M (which may be energy, momentum etc.) of a system. Now if we know both the wave function Ψ_M and operator $\hat{M}$ corresponding to the observable M and if the wave function Ψ_M is an eigen function of the operator $\hat{M}$, then the measurement of the property M is certain to give the value "c" as a result. If the wave function Ψ_M is not an eigen function of the operator $\hat{M}$ then the result of measuring the property M cannot be predicted precisely.

Q. What do you mean by eigenvalue equation? Write with example what the constant in eigen value equation indicates.

Q. State whether the following functions are eigen functions or not of the given operators. If so, evaluate the corresponding eigen values:

(a) $\Psi = 8e^{4x}, \hat{A} = \frac{d}{dx}$ (b) $\Psi = Sin\ nx,\ \hat{A} = \frac{d}{dx}$ (c) $\Psi = Sin\ nx, \hat{A} = \frac{d^2}{dx^2}$ (d) $\Psi = e^{-ax}, \hat{A} = \frac{d}{dx}$

(e) $\Psi = e^{-ax^2}, \hat{A} = \frac{d}{dx}$ (f) $\Psi = e^{-ax^2}, \hat{A} = \frac{d^2}{dx^2}$ (g) $\Psi = e^{-ax^2}, \hat{A} = \frac{1}{x}\frac{d}{dx}$ (h) $\Psi = f(x), \hat{A} = c\ \times$, where "c" is a constant (i) $\Psi = e^{-ikx}, \hat{A} = \frac{d^2}{dx^2}$ (j) $\Psi = Sin\ nx + Cos\ nx,\ \hat{A} = \frac{d^2}{dx^2}$ (k) $\Psi = 37, \hat{A} = \frac{d}{dx}$

(l) $\Psi = Cos\ x + i \sin x\ , \hat{A} = \frac{d}{dx}$

Ans:

(a) $\Psi = 8e^{4x}, \hat{A} = \frac{d}{dx}$

Now

$$\hat{A}\Psi = \frac{d}{dx}(8e^{4x})$$
$$= 8 \times 4e^{4x}$$
$$= 4(8e^{4x})$$
$$= 4\Psi$$

i.e. $8e^{4x}$ is an eigen function of the operator $\frac{d}{dx}$ with eigen value of 4.

(b) $\Psi = Sin\, nx, \hat{A} = \frac{d}{dx}$

Now

$$\hat{A}\Psi = \frac{d}{dx}(Sin\, nx)$$
$$= (n)\, Cos\, nx$$

Since after operation the original function is not regenerated so $Sin\, nx$ is not a eigen function of the operator $\frac{d}{dx}$

(c) $\Psi = Sin\, nx, \hat{A} = \frac{d^2}{dx^2}$

Now

$$\hat{A}\Psi = \frac{d^2}{dx^2}(Sin\, nx)$$
$$= \frac{d}{dx}\frac{d}{dx}(Sin\, nx)$$
$$= \frac{d}{dx}(n\, Cos\, nx)$$
$$= (-n^2)\, Sin\, nx$$
$$= (-n^2)\Psi$$

i.e. $Sin\, nx$ is an eigen function of the operator $\frac{d^2}{dx^2}$ with eigen value of $-n^2$.

(d) $\Psi = e^{-ax}, \hat{A} = \frac{d}{dx}$

Now

$$\hat{A}\Psi = \frac{d}{dx}(e^{-ax})$$
$$= (-a)e^{-ax}$$
$$= (-a)\Psi$$

i.e. e^{-ax} is an eigen function of the operator $\frac{d}{dx}$ with eigen value of $-a$.

(e) $\Psi = e^{-ax^2}, \hat{A} = \frac{d}{dx}$

Now

$$\hat{A}\Psi = \frac{d}{dx}\left(e^{-ax^2}\right)$$

$$= (-a)e^{-ax^2}\frac{d}{dx}(x^2)$$

$$= -2axe^{-ax^2}$$

This is not an eigenvalue equation because although the original function is reproduced, it is not multiplied by a constant. Instead, it is multiplied by another function $-2ax$. So $e^{-ax^2}$is not an eigen function of the operator $\frac{d}{dx}$.

(f) $\Psi = e^{-ax^2}, \hat{A} = \frac{d^2}{dx^2}$

Now

$$\hat{A}\Psi = \frac{d^2}{dx^2}\left(e^{-ax^2}\right)$$

$$= \frac{d}{dx}\frac{d}{dx}\left(e^{-ax^2}\right)$$

$$= \frac{d}{dx}\left(-2ax\, e^{-ax^2}\right)$$

$$= (-2a)\frac{d}{dx}\left(x\, e^{-ax^2}\right)$$

$$= (-2a)\left[x\frac{dy}{dx}\left(e^{-ax^2}\right) + \ e^{-ax^2}\frac{dx}{dx}\right]$$

$$= (-2a)\left[\left(-2ax^2e^{-ax^2}\right) + \ e^{-ax^2}\right]$$

$$= 4a^2x^2\, e^{-ax^2} - 2a\, e^{-ax^2}$$

$$= (4a^2x^2 - 2a)\, e^{-ax^2}$$

This is not an eigenvalue equation because although the original function is reproduced, it is not multiplied by a constant. Instead, it is multiplied by another function$(4a^2x^2 - 2a)$. So $e^{-ax^2}$is not an eigen function of the operator $\frac{d^2}{dx^2}$.

(g) $\Psi = e^{-ax^2}, \hat{A} = \frac{1}{x}\frac{d}{dx}$

Now

$$\hat{A}\Psi = \frac{1}{x}\frac{d}{dx}\left(e^{-ax^2}\right)$$

$$= \frac{1}{x} \times (-a)e^{-ax^2}\frac{d}{dx}(x^2)$$

$$= \frac{1}{x} \times (-a)e^{-ax^2} \times 2x$$

$$= (-2a)e^{-ax^2}$$

$$= (-2a)\Psi$$

i.e. e^{-ax^2} is a n eigen function of the operator $\frac{1}{x}\frac{d}{dx}$ with eigen value of $-2a$.

(h) $\Psi = f(x), \hat{A} = c\times$, where "c" is a constant.

Now

$$\hat{A}\Psi = c \times f(x)$$

$$= c\Psi$$

i.e. $f(x)$ is an eigen function of the operator $c\times$.

(i) $\Psi = e^{-ikx}, \hat{A} = \frac{d^2}{dx^2}$

Now

$$\hat{A}\Psi = \frac{d^2}{dx^2}\left(e^{-ikx}\right)$$

$$= \frac{d}{dx}\frac{d}{dx}\left(e^{-ikx}\right)$$

$$= \frac{d}{dx}\left(-ike^{-ikx}\right)$$

$$= (-ik)\frac{d}{dx}\left(e^{-ikx}\right)$$

$$= (-ik)(-ik)e^{-ikx}$$

$$= i^2k^2e^{-ikx}$$

$$= -k^2e^{-ikx}$$

$$= -k^2\Psi$$

i.e. e^{-ikx} is an eigen function of the operator $\frac{d^2}{dx^2}$ with eigen value of $-k^2$.

(j) $\Psi = Sin\,nx + Cos\,nx, \hat{A} = \frac{d^2}{dx^2}$

Now

$$\hat{A}\Psi = \frac{d^2}{dx^2}(Sin\,nx + Cos\,nx)$$

$$= \frac{d}{dx}\frac{d}{dx}(Sin\,nx + Cos\,nx)$$

$$= \frac{d}{dx}[n\,Cos\,nx - n\,Sin\,nx]$$

$$= n\frac{d}{dx}(Cos\,nx - Sin\,nx)$$

$$= n[-n\,Sin\,nx - n\,Cos\,nx]$$

$$= n \times (-n)[Sin\,nx + Cos\,nx]$$

$$= -n^2\Psi$$

i.e. $Sin\ nx + Cos\ nx$ is an eigen function of the operator $\frac{d^2}{dx^2}$ with eigen value of $-n^2$.

(k) $\Psi = 37, \hat{A} = \frac{d}{dx}$

$$\hat{A}\Psi = \frac{d}{dx}(37)$$
$$= 0 \times \Psi$$

i.e. 37 is an eigen function of the operator $\frac{d}{dx}$ which eigen value is zero.

(l) $\Psi = Cos\ x + i\ \mathrm{Sin}\ x, \hat{A} = \frac{d}{dx}$

Now

$$\hat{A}\Psi = \frac{d}{dx}(Cos\ x + i\ \mathrm{Sin}\ x)$$
$$= -Sin\ x + i\ Cos\ x$$
$$= i^2\ Sin\ x + i\ Cos\ x$$
$$= i\ (Cos\ x\ + i\ Sin\ x)$$
$$= i\Psi$$

i.e. $Cos\ x + i\ \mathrm{Sin}\ x$ is an eigen function of the operator with eigen value of “i".

Q. Which of the following functions are eigen functions of the operator $\frac{d^2}{dx^2}$

(i) 4 Cos 3x (ii) Cos $\frac{x}{4}$ (iii) 5x^2 (iv) $\frac{1}{x}$ (v) tan x (vi) ln 2x

Ans:

(i) 4 Cos 3x

$$\hat{A}\Psi = \frac{d^2}{dx^2}(4\ Cos\ 3x)$$
$$= \frac{d}{dx}\frac{d}{dx}(4\ Cos\ 3x)$$
$$= \frac{d}{dx}(-3 \times 4\ Sin\ 3x)$$
$$= -3 \times 3 \times 4\ Cos\ 3x$$
$$= -9\Psi$$

i.e. 4 Cos 3x is an eigen function of the operator $\frac{d^2}{dx^2}$ with eigen value of -9.

(ii) Cos $\frac{x}{4}$

$$\hat{A}\Psi = \frac{d^2}{dx^2}\left(Cos\ \frac{x}{4}\right)$$
$$= \frac{d}{dx}\frac{d}{dx}\left(Cos\ \frac{x}{4}\right)$$

$$= \frac{d}{dx}\left(-\frac{1}{4} Sin\ \frac{x}{4}\right)$$

$$= -\frac{1}{4} \times \frac{1}{4}\ Cos \frac{x}{4}$$

$$= -\frac{1}{16}\Psi$$

i.e. $Cos\ \frac{x}{4}$ is an eigen function of the operator $\frac{d^2}{dx^2}$ with eigen value of $-\frac{1}{16}$.

(iii) $5x^2$

$$\hat{A}\Psi = \frac{d^2}{dx^2}(5x^2)$$

$$= \frac{d}{dx}\frac{d}{dx}(5x^2)$$

$$= \frac{d}{dx}(2 \times 5x)$$

$$= 10$$

i.e. $5x^2$ is not an eigen function of the operator $\frac{d^2}{dx^2}$.

(iv) $\frac{1}{x}$

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

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

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

$$= \frac{2}{x^3}$$

i.e. $\frac{1}{x}$ is not an eigen function of the operator $\frac{d^2}{dx^2}$.

(v) tan x

$$\hat{A}\Psi = \frac{d^2}{dx^2}(\tan x)$$

$$= \frac{d}{dx}\frac{d}{dx}(\tan x)$$

$$= \frac{d}{dx}(Sec^2\ x)$$

$$= 2Sec\ x \frac{d}{dx}(Sec\ x)$$

$$= 2\ Sec\ x\ (Sec\ x \tan x)$$

$$= 2\ Sec^2 x \tan x$$

$$= 2\ Sec^2 x\ \Psi$$

i.e. tan x is an eigen function of the operator $\frac{d^2}{dx^2}$ with eigen value of 2 Sec^2x.

(vi) ln 2x

$$\begin{aligned}\hat{A}\Psi &= \frac{d^2}{dx^2}(\ln 2x)\\ &= \frac{d}{dx}\frac{d}{dx}(\ln 2x)\\ &= \frac{d}{dx}\left(\frac{1}{2x}\times 2\right)\\ &= \frac{d}{dx}\left(\frac{1}{x}\right)\\ &= -\frac{1}{x^2}\end{aligned}$$

i.e. ln 2x is not an eigen function of the operator $\frac{d^2}{dx^2}$.

Q. Show that e^{ax} is an eigen function of the operator $\frac{d^n}{dx^n}$. What is the eigen value?

Ans:

Here, $\Psi = e^{ax}\ and\ \hat{A} = \frac{d^n}{dx^n}$

So

$$\begin{aligned}\hat{A}\,\Psi &= \frac{d^n}{dx^n}(e^{ax}\ )\\ &= a^n e^{ax}\end{aligned}$$

i.e. e^{ax} is an eigen function of the operator $\frac{d^n}{dx^n}$ and the eigen value is a^n

Q. Show that e^{ikx} is an eigen function of the operator $\hat{p}_x$

Ans:

Here, $\Psi = e^{ikx}\ and\ \hat{A} = \hat{p}_x = -i\hbar\frac{d}{dx}$

So

$$\begin{aligned}\hat{p}_x\Psi &= -i\hbar\frac{d}{dx}\left(e^{ikx}\right)\\ &= (-i\hbar)(ik)e^{ikx}\\ &= \hbar k e^{ikx}\end{aligned}$$

e^{ikx} is an eigen function of the operator $\hat{p}_x$ and the eigen value is $\hbar k$.

Q. Show that $\frac{1}{\pi}\sin(nx)$ is an eigen function of the operator $-\frac{h^2}{8\pi^2 m}\frac{d^2}{dx^2}$. What is the eigen value.

Ans:

Here $\Psi = \frac{1}{\pi}\sin(nx)\ \ and\ \hat{A} = -\frac{h^2}{8\pi^2 m}\frac{d^2}{dx^2}$

Now

$$\hat{A}\Psi = -\frac{h^2}{8\pi^2 m}\frac{d^2}{dx^2}\left(\frac{1}{\pi}\sin(nx)\right)$$

$$= -\frac{h^2}{8\pi^2 m}\frac{d}{dx}\frac{d}{dx}\left(\frac{1}{\pi}\sin(nx)\right)$$

$$= -\frac{h^2}{8\pi^2 m}\frac{d}{dx}\left(\frac{n}{\pi}\ Cos\ nx\right)$$

$$= \left(-\frac{h^2}{8\pi^2 m}\right)\left(-\frac{n^2}{\pi}\ Sin\ nx\right)$$

$$= \frac{n^2h^2}{8\pi^2 m}\left(\frac{1}{\pi}\ Sin\ nx\right)$$

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

i.e. $\frac{1}{\pi}\sin(nx)$ is an eigen function of the operator $-\frac{h^2}{8\pi^2 m}\frac{d^2}{dx^2}$ with eigen value of $\frac{n^2h^2}{8\pi^2 m}$.

Q. Is the wave function $\Psi = \left(\frac{2}{L}\right)^{\frac{1}{2}} sin\left(\frac{\pi x}{L}\right)$ for particle in a box is an eigen function of the operator $\frac{d^2}{dx^2}$. If so what are the eigen value.

Ans:

Here $\Psi = \left(\frac{2}{L}\right)^{\frac{1}{2}} sin\left(\frac{\pi x}{L}\right)\ and\ \hat{A} = \frac{d^2}{dx^2}$

$$\hat{A}\Psi = \frac{d^2}{dx^2}\left(\left(\frac{2}{L}\right)^{\frac{1}{2}} \mathrm{Sin}\frac{\pi x}{L}\right)$$

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

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

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

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

$$= -\left(\frac{\pi}{L}\right)^2\left(\frac{2}{L}\right)^{\frac{1}{2}} Sin\ \frac{\pi x}{L}$$

$$= -\left(\frac{\pi}{L}\right)^2\Psi$$

i.e. $\Psi = \left(\frac{2}{L}\right)^{\frac{1}{2}} sin\left(\frac{\pi x}{L}\right)$ is an eigen function of the operator $\frac{d^2}{dx^2}$ with eigen value of $-\left(\frac{\pi}{L}\right)^2$.

Q. Show that the function $\psi = Cos\ ax\ Cos\ by\ Cos\ cz$ is a an eigen function of the Laplacian operator $\hat{\nabla}^2$. What is the eigen value.

Ans:

We know

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

So

$$\hat{\nabla}^2 \Psi = \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right)(Cos\ ax\ Cos\ by\ Cos\ cz)$$

$$= (Cos\ by\ Cos\ cz)\frac{\partial^2}{\partial x^2}(Cos\ ax) + Cos\ ax\ Cos\ cz\frac{\partial^2}{\partial y^2}(Cos\ by) + Cos\ ax\ Cos\ by\frac{\partial^2}{\partial z^2}(Cos\ cz)$$

$$= (Cos\ by\ Cos\ cz)\frac{d}{dx}\frac{d}{dx}(Cos\ ax) + (Cos\ ax\ Cos\ cz)\frac{d}{dy}\frac{d}{dy}(Cos\ by) + Cos\ ax\ Cos\ by\frac{d}{dz}\frac{d}{dz}(Cos\ cz)$$

$$= (Cos\ by\ Cos\ cz)\frac{d}{dx}(-a\ Sin\ ax) + (Cos\ ax\ Cos\ cz)\frac{d}{dy}(-b\ Sin\ by) + (Cos\ ax\ Cos\ by)\frac{d}{dz}(-c\ Sin\ cz)$$

$$= (Cos\ by\ Cos\ cz)(-a^2 Cos\ ax) + (Cos\ ay\ Cos\ cz)(-b^2 Cos\ by) + (Cos\ ax\ Cos\ by)(-c^2 Cos\ cz)$$

$$= -(a^2 + b^2 + c^2)(Cos\ ax\ Cos\ by\ Cos\ cz)$$

$$= -(a^2 + b^2 + c^2)\Psi$$

i.e. the function $\psi = Cosax\ Cosby\ Coscz$ is a an eigen function of the Laplacian operator $\hat{\nabla}^2$ with eigen value $-(a^2 + b^2 + c^2)$

[Self-test]. Show that the function $\psi = Sin\ k_1 x\ Sin\ k_2 y\ Sin\ k_3 z$ is a an eigen function of the Laplacian operator $\hat{\nabla}^2$. What is the eigen value. [Ans: Eigen value is $-\left({k_1}^2 + {k_2}^2 + {k_3}^2\right)$].

Q. What are the eigen function and eigen value of the operator $\frac{d}{dx}$.

Ans:

Let the eigen function is $f(x)$

Now According to eigen value equation, we have

$$\frac{d}{dx}f(x) = kf(x)$$

$$=> \frac{df(x)}{f(x)} = kdx$$

Integrating both sides we have,

$$lnf(x) = kx + c$$

$$=> f(x) = e^{kx+c}$$

$$=> f(x) = e^c e^{kx}$$

$$=> f(x) = c' e^{kx}$$

i.e. the eigen function of $\frac{d}{dx}$ is $c' e^{kx}$

Now

$$\frac{d}{dx}\left(c/e^{kx}\right) = kc/e^{kx}$$

i.e. the eigen value is “k”.

Determining the value of an observable from operator/function combination:

If we know the wave function and the operator corresponding to the concerned observable and if the wave function is an eigen function of the operator of interest, then the corresponding eigen value obtained from operator/wave function commination will give us the value of that observable**.**

Q. What is the linear momentum of a free particle described by the wave functions (a) $\psi\ (x) = e^{ikx}$ (b) $\psi\ (x) = e^{-ikx}$. What conclusions can be drawn from the results.

Ans: To determine to value of momentum in the x-coordinate, we have to operate on the given wave functions by the corresponding linear momentum operator namely $\hat{p}_x = -i\hbar\frac{d}{dx}$.

(a) For $\psi\ (x) = e^{ikx}$

$$\hat{p}_x\psi\ (x) = -i\hbar\frac{d}{dx}\left(e^{ikx}\right)$$
$$= -i\hbar(ik)e^{ikx}$$
$$= +k\hbar\ \psi\ (x)$$

This is an eigenvalue equation, with eigenvalue +kħ. It follows that a measurement of the momentum will give the value $p_x = +\ k\hbar$.

(b) For $\psi\ (x) = e^{-ikx}$

$$\hat{p}_x\psi\ (x) = -i\hbar\frac{d}{dx}\left(e^{-ikx}\right)$$
$$= -i\hbar(-ik)e^{ikx}$$
$$= -k\hbar\ \psi\ (x)$$

Now the eigenvalue is – $k\hbar$, so momentum $p_x = -\ k\hbar$.

i.e. in case (a) the momentum is positive, meaning that the particle is travelling in the positive x-direction, whereas in case (b) the particle is moving in the opposite direction i.e. in negative x-direction.

Q. Show that the average value of momentum of a particle described by the wave function e^{ikx} is ħk, where k is a constant

Q. What is the kinetic energy of a particle described by the wave function Cos kx.

Ans: To determine to value of kinetic energy in the x-coordinate, we have to operate on the given wave functions by the corresponding kinetic energy operator namely $\hat{T} = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}$

Now

$$\hat{T}\psi\ (x) = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}(Cos\ kx)$$
$$= -\frac{\hbar^2}{2m}\frac{\partial}{\partial x}\frac{\partial}{\partial x}\ (Cos\ kx)$$
$$= -\frac{\hbar^2}{2m}\frac{\partial}{\partial x}(-\ k\ Sin\ Kx)$$

$$= \frac{k\hbar^2}{2m}\frac{\partial}{\partial x}(\,Sin\,Kx)$$

$$= \frac{k^2\hbar^2}{2m}\ Cos\,kx$$

$$= \frac{k^2\hbar^2}{2m}\Psi$$

i.e. Kinetic energy of the particle is $\frac{k^2\hbar^2}{2m}$

Linear combination, linearly independent functions and principle of superposition:

Linear combination: In mathematics, a linear combination is an expression constructed from a set of terms by multiplying each term by a constant and adding the results. For example, a linear combination of x and y would be any expression of the form ax + by, where “a” and “b” are constants.

Linearly independent functions: A set of functions $f_1, f_2, \dots f_n$ are said to be linearly independent if there exist no relation as such:

$$c_1f_1 + c_2f_2 + \cdots c_nf_n = 0$$

$$or \sum_n c_nf_n = 0$$

Except under the conditions where all the co-efficient are zero i.e. when $c_1 = c_2 = \cdots c_n = 0$. In other words, it means that no member of such set can be expressed as a linear combination of the remaining members. For example Sin x and Cos x constitute a set of linearly independent function as in $Sinx = (1 - Cos^2x)^{\frac{1}{2}}$, they are not linearly related. On the other hand $Sin^2x\ and\ Cos^2x$ are not linearly independent (or simply linearly dependent) as in $Sin^2x = 1 - Cos^2x$ they are related linearly, where one is expressed in terms of other.

Principle of superposition: If $\Psi_1, \Psi_2, \dots \Psi_n$ be a set of linearly independent wave functions, then their linear combination must result in a state function of the system.

i.e.

$$\phi = c_1\Psi_1 + c_2\Psi_2 + \cdots c_n\Psi_n = \sum_n c_n\Psi_n$$

Where $c_1, c_2 \dots c_n$ are constants called the expansion coefficients or Fourier coefficients .

Degenerate eigen functions: If two functions when operated by the same operator produces the same eigen value, then they are said to be degenerate.

Theorm: Linear combination of a set of degenerate eigen function of a linear operator is also an eigen function of the same operator with same eigen value.

Proof:

Let Ψ_1 and Ψ_2 be the two degenerate eigen functions of the linear operator $\hat{O}$ having the same eigen value λ, then we have:

$$\hat{O}\Psi_1 = \lambda\Psi_1$$

And

$$\hat{O}\Psi_2 = \lambda\Psi_2$$

Now linear combination of Ψ_1 and Ψ_2 can be shown as:

$$\phi = c_1\Psi_1 + c_2\Psi_2$$

Now

$$\begin{aligned}\hat{O}\phi &= \hat{O}(c_1\Psi_1 + c_2\Psi_2)\\ &= \hat{O}(c_1\Psi_1) + \hat{O}(c_2\Psi_2)\\ &= c_1\hat{O}\Psi_1 + c_2\hat{O}\Psi_2\\ &= c_1\lambda\Psi_1 + c_2\lambda\Psi_2\\ &= \lambda(c_1\Psi_1 + c_2\Psi_2)\\ &= \lambda\phi\end{aligned}$$

i.e. linear combination of Ψ_1 and Ψ_2 is also an eigen function of the operator $\hat{O}$ having the same eigen value

Q. If Ψ_1 and Ψ_2 be the two degenerate eigen functions of the linear operator $\hat{O}$ having the same eigen value λ, then show that the linear combination of Ψ_1 and Ψ_2 is also an eigen function of the operator $\hat{O}$ having the same eigen value.

Hermitian operator:

Rule of thumb: Operators encountered in quantum mechanics are all linear and as well as Hermitian.

Operators and wave functions may be complex or imaginary, but eigen value of quantum mechanical operators must be real because they are the only possible measured value and measured values of observable are always real. This places a restriction on possible quantum mechanical operators. Operators that have the property to yield real eigen value are called Hermitian operators. A Hermitian operator say $\hat{A}$ always obey the below given relation:

$$\begin{aligned}\int \Psi^*\hat{A}\phi\, d\tau &= \int \phi\left(\hat{A}\Psi\right)^*\, d\tau\\ &= \int \phi\hat{A}^*\Psi^* d\tau\\ &= \left(\int \phi^*\, \hat{A}\Psi\, d\tau\right)^*\end{aligned}$$

The above expression is known as the definition of Hermiticity.

Q. What is Hermitian operator.

Confirming the hermiticity of operators:

Hermiticity of position operator ($\hat{x}$):

We know

$$\hat{x} = x$$

Now

$$\begin{aligned}\int \Psi^* x\phi\, dx &= \int \phi x\Psi^*\, dx\\ &= \left(\int \phi^* x\Psi\, dx\right)^*\end{aligned}$$

Here we use the fact that $(\phi^*)^* = \phi \ and \ x^* = x \ as \ x \ is \ real$

Hermiticity of momentum operator ($\hat{p}_x$):

$$\mathit{Required\ intergral}: \int u dv = uv - \int v du$$

We know

$$\hat{p}_x = -i\hbar \frac{d}{dx}$$

Now

$$\int_{-\infty}^{\infty} \Psi^* \hat{p}_x \phi \, dx = \int_{-\infty}^{\infty} \Psi^* \left(-i\hbar \frac{d}{dx}\right) \phi \, dx$$

$$= -i\hbar \int_{-\infty}^{\infty} \Psi^* \frac{d\phi}{dx} \, dx$$

$$= -i\hbar \int_{-\infty}^{\infty} \Psi^* d\phi$$

$$= -i\hbar \left\{ [\Psi^* \phi]_{-\infty}^{\infty} - \int_{-\infty}^{\infty} \phi d\Psi^* \right\}$$

Now $[\Psi^* \phi]_{-\infty}^{\infty} = 0$, as both the functions are well behaved and hence they must vanished at infinity, so the above expression reduces to

$$\int_{-\infty}^{\infty} \Psi^* \hat{p}_x \phi \, dx = (-i\hbar) \left\{ - \int_{-\infty}^{\infty} \phi d\Psi^* \right\}$$

$$= i\hbar \int_{-\infty}^{\infty} \phi d\Psi^*$$

$$= i\hbar \int_{-\infty}^{\infty} \phi \frac{d\Psi^*}{dx} dx$$

$$= i\hbar \int_{-\infty}^{\infty} \phi \frac{d}{dx} \Psi^* dx$$

$$= \int_{-\infty}^{\infty} \phi \, (i\hbar) \frac{d}{dx} \Psi^* dx$$

$$= \left(\int_{-\infty}^{\infty} \phi^* \, (-i\hbar) \frac{d}{dx} \Psi \, dx \right)^*$$

$$= \left(\int_{-\infty}^{\infty} \phi^* \, \hat{p}_x \Psi \, dx \right)^*$$

Properties of Hermitian operators:

(1) Eigen values of Hermitian operators are real

Proof:

Let Ψ and ϕ are two equal eigen function (i.e. $\Psi = \phi$) of the Hermitian operator $\hat{A}$ with eigen value λ

Now

$$\hat{A}\Psi = \lambda\Psi$$

Since $\hat{A}$ is Hermitian, so from definition of hermiticity we have:

$$\int \Psi^{*}\hat{A}\,\Psi d\tau = \int \Psi\left(\hat{A}\Psi\right)^{*} d\tau$$

$$=> \int \Psi^{*}\lambda\Psi d\tau = \int \Psi(\lambda\Psi)^{*}\, d\tau$$

$$=> \lambda\int \Psi^{*}\Psi d\tau = \lambda^{*}\int \Psi\Psi^{*}\, d\tau$$

$$=> \lambda\int |\Psi|^{2} d\tau = \lambda^{*}\int |\Psi|^{2}\, d\tau$$

$$=> (\lambda - \lambda^{*})\int |\Psi|^{2}\, d\tau = 0$$

Since

$$\int |\Psi|^{2}\, d\tau \neq 0$$

So

$$(\lambda - \lambda^{*}) = 0$$

$$=> \ \lambda = \lambda^{*}$$

Now only a real number is equal to its complex conjugate, so the eigenvalue “λ" must be real.

Q. Show that the eigen value of a Hermitian operator is real.

(2) If the eigen functions of a Hermitian operator have different eigen values, then they are orthogonal to each other.

Proof:

Let Ψ *and* ϕ be the two eigen functions of the Hermitian operator $\hat{A}$ with eigen values λ_1 *and* λ_2 respectively, then we have from eigen value equation:

$$\hat{A}\Psi = \lambda_1\Psi$$

And

$$\hat{A}\phi = \lambda_2\phi$$

From definition of hermiticity we have:

$$\int \Psi^{*}\hat{A}\phi\, d\tau = \int \phi\left(\hat{A}\Psi\right)^{*} d\tau$$

$$=> \int \Psi^* \lambda_2 \phi \, d\tau = \int \phi (\lambda_1 \Psi)^* \, d\tau$$

$$=> \lambda_2 \int \Psi^* \phi \, d\tau = \int \phi \lambda_1^* \Psi^* \, d\tau$$

$$=> \lambda_2 \int \Psi^* \phi \, d\tau = \lambda_1^* \int \Psi^* \phi \, d\tau$$

$$=> \lambda_2 \int \Psi^* \phi \, d\tau = \lambda_1^* \int \Psi^* \phi \, d\tau$$

$$=> (\lambda_2 - \lambda_1^*) \int \Psi^* \phi \, d\tau = 0$$

Since Hermitian operators have real eigen values, so we can write $\lambda_1^* = \lambda_1$, So the above equation can be written as:

$$=> (\lambda_2 - \lambda_1) \int \Psi^* \phi \, d\tau = 0$$

Since the two eigen values are different i.e. $(\lambda_2 - \lambda_1) \neq 0$, therefore it must be the case that $\int \Psi^* \phi \, d\tau = 0$. That is, the two eigen functions are orthogonal, as was to be proved.

Q. Prove that if the Eigen functions of a Hermitian operator have different eigenvalues then they are orthogonal to each other.

Gram-Schmidt orthogonalization technique:

We have Seen that two eigen functions of a Hermitian operator that corresponds to different eigenvalues are orthogonal, but if the eigen functions are degenerate (same eigen value) then they need not be orthogonal. Nevertheless, in the case of degeneracy, we can construct eigen functions that will be orthogonal to one another via applying Gram-Schmidt orthogonalization technique.

Let us consider tow degenerate eigen functions $\phi_1 \; and \; \phi_2$ of an operator $\hat{B}$ with the same eigen value of "a"

Now

$$\hat{B}\phi_1 = a\phi_1 \; and \; \hat{B}\phi_2 = a\phi_2$$

Since $\phi_1 \; and \; \phi_2$ are degenerate and hence they need not to be orthogonal, but we can take linear combination of $\phi_1 \; and \; \phi_2$ to construct two eigen functions $\Psi_1 \; and \; \Psi_2$ such that they become orthogonal to each other. We chose

$$\Psi_1 = \phi_1 \; and \; \Psi_2 = \phi_2 + c\phi_1$$

Where the constant "c" is chosen to ensure orthogonality

Since $\Psi_1 \; and \; \Psi_2$ are orthogonal, so

$$\int \Psi_1 \Psi_2 d\tau = 0$$

$$=> \int \phi_1 (\phi_2 + c\phi_1) = 0$$

$$=> \int \phi_1 \, \phi_2 d\tau + c \int {\phi_1}^2 d\tau = 0$$

$$=> c = -\frac{\int \phi_1 \, \phi_2 d\tau}{\int {\phi_1}^2 d\tau}$$

$$=> c = -\int \phi_1\, \phi_2 d\tau$$

So the two orthogonal functions are $\Psi_1 = \phi_1\ and\ \Psi_2 = \phi_2 - \phi_1 \int \phi_1\, \phi_2 d\tau$

Q. Using Schmidt orthogonalization technique, orthogonalized the following non-orthogonal functions over the interval $0 \leq x \leq a$.The functions are: $\phi_1 = 1, \phi_2 = x\ and\ \phi_3 = x^2$

Ans:

Let

$$\Psi_1 = \phi_1 = 1$$

$$\Psi_2 = \phi_2 + c\phi_1 = x + c$$

$$\Psi_3 = \phi_3 + c_1\phi_1 + c_2\phi_2 = x^2 + c_1 + c_2 x$$

Now using orthogonalization condition we have:

$$\int_0^1 \Psi_1 \Psi_2 dx = 0$$

$$=> \int_0^1 1(x + c)dx = 0$$

$$=> \left[\frac{x^2}{2}\right]_0^1 + c[x]_0^1 = 0$$

$$=> \frac{1}{2} + c = 0$$

$$=> c = -\frac{1}{2}$$

i.e.

$$\Psi_2 = x - \frac{1}{2}$$

Similarly,

$$\int_0^1 \Psi_1 \Psi_2 dx = 0$$

$$=> \int_0^1 1(x^2 + c_1 + c_2 x)dx = 0$$

$$=> \left[\frac{x^3}{3}\right]_0^1 + c_1[x]_0^1 + c_2\left[\frac{x^2}{2}\right]_0^1 = 0$$

$$=> \frac{1}{3} + c_1 + \frac{c_2}{2} = 0$$

$$=> \frac{2}{3} + 2c_1 + c_2 = 0$$

$$=> 2c_1 + c_2 = -\frac{2}{3}$$

Again

$$\int_0^1 \Psi_2 \Psi_3 dx = 0$$

$$=> \int_0^1 \left(x - \frac{1}{2}\right)(x^2 + c_1 + c_2 x)dx = 0$$

$$=> \int_0^1 \left[x^3 + c_1 x + c_2 x^2 - \frac{1}{2}(x^2 + c_1 + c_2 x)\right] dx = 0$$

$$=> \left[\frac{x^4}{4}\right]_0^1 + c_1 \left[\frac{x^2}{2}\right]_0^1 + c_2 \left[\frac{x^3}{3}\right]_0^1 - \frac{1}{2}\left\{\left[\frac{x^3}{3}\right]_0^1 + c_1 [x]_0^1 + c_2 \left[\frac{x^2}{2}\right]_0^1\right\} = 0$$

$$=> \frac{1}{4} + \frac{c_1}{2} + \frac{c_2}{3} - \frac{1}{2}\left(\frac{1}{3} + c_1 + \frac{c_2}{2}\right) = 0$$

$$=> c_2 = -1$$

Since we have

$$2c_1 + c_2 = -\frac{2}{3}$$

$$=> 2c_1 - 1 = -\frac{2}{3}$$

$$=> c_1 = \frac{1}{6}$$

So

$$\Psi_3 = x^2 + \frac{1}{6} - x$$

i.e. the orthogonal functions are: $\Psi_1 = 1, \Psi_2 = x - \frac{1}{2}$ $and\ \Psi_3 = x^2 + \frac{1}{6} - x$

Basis function, complete set and expanding a wave function on orthonormal basis:

A general function can be expanded in terms of all the eigen functions of an operator. If ϕ is a general function and $\Psi_1, \Psi_2 \dots \Psi_n$ are the different eigen functions (orthonormal set) of the operator corresponding to the observable of interest, then the general function ϕ can be expressed as a linear combination in the form of:

$$\phi = c_1 \Psi_1 + c_2 \Psi_2 + \cdots c_n \Psi_n$$

$$= \sum_n c_n \Psi_n$$

Where the orthonormal set of eigen functions $\{\Psi_n\}$ i.e. $(\Psi_1, \Psi_2, \dots \Psi_n)$ as a whole are called complete set in the sense that any arbitrary function can be expressed as a linear combination of them and each individual functions that are used to construct the complete set is called the basis functions. The above expression that expanded a wave function in terms of orthonormal set is known as Fourier expansion.

Theorm: If two linear operators $\hat{A}\ and\ \hat{B}$ have the same complete set of eigen functions then they commute i.e. $[\hat{A}, \hat{B}] = 0$.

Proof:

Let $\phi_n(x)$ be the common complete set of eigen functions of the operators $\hat{A}\ and\ \hat{B}$. Now according to eigen value equation we have:

$$\hat{A}\phi_n(x) = a_n\phi_n(x) - -(a)$$

And

$$\hat{B}\phi_n(x) = B_n\phi_n(x) - -(b)$$

Now let's assume an arbitrary function $f(x)$ which can be expanded in terms of complete set of eigen function of the operator $\hat{A}\ and\ \hat{B}$ i.e. in terms of ϕ_n as:

$$f(x) = \sum_n c_n\phi_n(x) - -(1)$$

Now we must show that

$$[\hat{A},\hat{B}]\, f(x) = (\hat{A}\hat{B} - \hat{B}\hat{A})f(x) = 0$$

Now

$$\begin{aligned}
[\hat{A},\hat{B}]\, f(x) &= [\hat{A},\hat{B}]\sum_n c_n\phi_n(x) \\
&= \sum_n c_n[\hat{A},\hat{B}]\ \phi_n(x) \\
&= \sum_n c_n(\hat{A}\hat{B} - \hat{B}\hat{A})\ \phi_n(x) \\
&= \sum_n c_n[\hat{A}\hat{B}\phi_n(x) - \hat{B}\hat{A}\phi_n(x)] \\
&= \sum_n c_n[\hat{A}b_n\phi_n(x) - \hat{B}a_n\phi_n(x)] \\
&= \sum_n c_n[b_n\hat{A}\phi_n(x) - a_n\hat{B}\phi_n(x)] \\
&= \sum_n c_n[b_na_n\phi_n(x) - a_nb_n\phi_n(x)] \\
&= \sum_n b_na_nc_n[\phi_n(x) - \phi_n(x)] \\
&= 0
\end{aligned}$$

i.e. $[\hat{A},\hat{B}] = 0$, hence proved.

Theorm: If two operator $\hat{A}\ and\ \hat{B}$ commute i.e. if $[\hat{A},\hat{B}] = 0$, then they have the same set of eigen functions.

Proof:

If Ψ_i is an eigen function of the operator $\hat{A}$, then we can write

$$\hat{A}\Psi_i = a_i\Psi_i - -(1)$$

Now let's suppose that the eigen values are non-degenerate $(a_1, a_2, a_3 \ldots etc. are\ not\ equal)$ i.e. there is only one eigen value with respect to a single function, for example, eigen value a_1 for the function Ψ_1, eigen value a_2 for the function Ψ_2 and so on.

Since $\hat{A}\ and\ \hat{B}$ commute, so we can write

$$[\hat{A}, \hat{B}] = 0$$

$$=> [\hat{A}, \hat{B}]\Psi_i = 0$$

$$=> (\hat{A}\hat{B} - \hat{B}\hat{A})\Psi_i = 0$$

$$=> \hat{A}\hat{B}\Psi_i - \hat{B}\hat{A}\Psi_i = 0$$

$$=> \hat{A}\hat{B}\Psi_i = \hat{B}\hat{A}\Psi_i$$

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

$$=> \hat{A}(\hat{B}\Psi_i) = a_i\hat{B}\Psi_i - -(2)$$

Equation (2) implies that $\hat{B}\Psi_i$ is also an eigen function of the operator $\hat{A}$ with same eigen value "a_i" as predicted by equation (1). Since we assume that the eigen values are non-degenerate, but we found that both the function $\Psi_i\ and\ \hat{B}\Psi_i$ has the same eigen value (degenerate eigen value). This is possible only when $\hat{B}\Psi_i$ and differ from Ψ_i only by a constant factor, i.e.

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

This means that Ψ_i is also an eigen function of the operator $\hat{B}$. So in conclusion we can say that the operator $\hat{A}\ and\ \hat{B}$ has the same set of eigen function namely Ψ_i.

Average value or arithmetic mean:

The average value of a measurement of a property say "A" is simply the arithmetic mean which is denoted by the symbol < A >, i.e.

$$\langle A \rangle = \frac{1}{N}\sum_{i=1}^{N} a_i$$

Alternatively, we can also write:

$$\langle A \rangle = \frac{1}{N}\sum_{i=1}^{N} n_a\, a$$

Where $\langle A \rangle$ is the average value of the property A, "N" is the total number of measurements, "a_i" is the observed value of A, "n_a" is the number of times "a" is observed and "a" is a possible value of A.

Let's a class of 9 students take a quiz and receive grades as: 0, 20, 20, 60, 60, 80, 80, 80, 100.

Now the average grade will be:

$$\langle Grade \rangle = \frac{1}{N}\sum_{i=1}^{N} f_i = \frac{0 + 30 + 30 + 50 + 50 + 70 + 70 + 70 + 100}{9} = 52.22$$

Or

$$\langle Grade \rangle = \frac{1}{N}\sum_{i=1}^{N} n_f\, f = \frac{1(0) + 2(30) + 2(50) + 3(70) + 1(100)}{9} = 52.22$$

Postulate 4: It gives us idea about average or expectation value.

The eigen value equation says that when the wave function is an eigen function of an operator, the corresponding observable have a definite or precise value. However, when the wave function is not an eigen function of an operator this does not imply that we cannot extract any information from the wave function. In such cases, instead of a definite or precise single value of the observable, a number of possible values of the observable will be forthcoming from the concerned wave function and from this large collection we can simply calculate the average or expectation value.

Expression of average or expectation value in quantum mechanics:

We know

$$\langle A \rangle = \frac{1}{N}\sum_{i=1}^{N} n_a\, a$$

$$= \sum_{i=1}^{N}\left(\frac{n_a}{N}\right) a$$

$$= \sum_{i=1}^{N} p_a a - -(1)$$

Where $p_a = \frac{n_a}{N}$ is the probability of observing the value of "a".

Now we can make three changes in equation (1):

(a) The summation over the infinitesimal probabilities in equation (1) can be replaces by an integration over all region of space.

(b) Probability p_a can be replaces by $|\Psi|^2 d\tau \; or \; \Psi\Psi^* d\tau$ (From Born interpretation).

(c) The value of the observable i.e. "a" can be replaces by the corresponding quantum mechanical operator $\hat{A}$.

With these changes we can re-write equation (1) as:

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

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

This is the required expression for average or expectation value of a property "A" when the wave function is normalized i.e. when $\int_{-\infty}^{\infty} \Psi^*\Psi d\tau = 1$.

When the wave function is not normalized then we have the expression for average value of a property "A" as:

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

Q. A function is defined as $\Psi = x$, find the average value of position in the range $0 \le x \le 1$.

Ans:

Here, $\Psi = x \; and \; \hat{A} = x$

So

$$\langle x \rangle = \frac{\int_0^1 x^* x x dx}{\int_0^1 x^* x d\tau}$$

$$= \frac{\int_0^1 x^3 dx}{\int_0^1 x^2 dx}$$

$$= \frac{\left[\frac{x^4}{4}\right]_0^a}{\left[\frac{x^3}{3}\right]_0^a}$$

$$= \frac{\frac{1}{4} - 0}{\frac{1}{3} - 0}$$

$$= \frac{3}{4}$$

Q. Describe the term expectation value of observable in quantum mechanics. Give the relation of it with the wave function.

Q. If the state function of a system is Ψ, then write the expression for expectation value of a physical quantity denoted by “M”.

Physical significance of average or expectation value:

Case a: When the wave function is an eigen function of the corresponding operator

Let Ψ is a normalized eigen function of the operator $\hat{A}$ with eigen value of “a”, i.e. $\hat{A}\Psi = \mathrm{a}\Psi$, then we have:

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

$$= \int_{-\infty}^{\infty} \Psi^* a \Psi d\tau$$

$$= a \int_{-\infty}^{\infty} \Psi^* \Psi d\tau$$

$$= a$$

i.e. in such case the average or expectation value is equal to the eigen value of the observable. In other words, we can say that when the wave function is an eigen function of the corresponding operator, then the determination of the property will always yield one result, namely the corresponding eigenvalue.

Case b: When the wave function is not an eigen function of the corresponding operator

Let Ψ is a normalized wave function which is not an eigen function of the operator of interest say $\hat{A}$. Although Ψ is not an eigen function of the operator $\hat{A}$, but we can expressed Ψ as a linear combination of eigen functions of $\hat{A}$ as:

$$\Psi = \sum_n c_n \Psi_n \,, where\ \hat{A}\Psi_n = a_n \Psi_n$$

Now

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

$$= \int_{-\infty}^{\infty} \left(\sum_n c_n \Psi_n \right)^* \hat{A} \left(\sum_n c_n \Psi_n \right) d\tau$$

$$= \sum_n c_n c_n^* \int_{-\infty}^{\infty} \Psi_n^* \hat{A}\, \Psi_n d\tau$$

$$= \sum_n |c_n|^2 \int_{-\infty}^{\infty} \Psi_n^* a_n \Psi_n d\tau$$

$$= \sum_n |c_n|^2 \, a_n \int_{-\infty}^{\infty} \Psi_n^* \Psi_n d\tau$$

$$= \sum_n |c_n|^2 \, a_n - - - (a)$$

i.e. the expectation value is a weighted sum of the eigenvalues of A, the contribution of a particular eigenvalue to the sum being determined by the square modulus of the corresponding coefficient ($|c_n|^2$) in the expansion of the wave function.

We know that

$$\langle A \rangle = \sum_{n=1}^{N} p_n a_n - -(b)$$

Comparing equation (a) and (b) we have

$$p_n = |c_n|^2$$

i.e. probability of observing the value of a particular eigen value a_n is equal to the square modulus of the corresponding coefficient ($|c_n|^2$).

Again total probability must be always equal to 1, so we can write

$$\sum_{n=1}^{N} |c_n|^2 = 1$$

Let's make it clarify with an example: Suppose $\Psi_1\ and\ \Psi_2$ are two normalized eigen function of the operator $\hat{A}$ with eigen values $a_1\ and\ a_2$. i.e.

$$\hat{A}\Psi_1 = a_1 \Psi_1\ and\ \hat{A}\Psi_2 = a_2 \Psi_2$$

Now consider the linear combination of the two wave function i.e.

$$\Psi = c_1 \Psi_1 + c_2 \Psi_2$$

Now Ψ is not necessarily an eigen function of the operator $\hat{A}$. Now the average value $\langle A \rangle$ of the associated wave function Ψ is:

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

$$= \int_{-\infty}^{\infty} (c_1\Psi_1 + c_2\Psi_2)^* \hat{A} (c_1\Psi_1 + c_2\Psi_2) d\tau$$

$$= \int_{-\infty}^{\infty} (c_1\Psi_1 + c_2\Psi_2)^* \left(c_1\hat{A}\Psi_1 + c_2\hat{A}\,\Psi_2\right) d\tau$$

$$= \int_{-\infty}^{\infty} (c_1^*\Psi_1^* + c_2^*\Psi_2^*) \left(c_1 a_1 \Psi_1 + c_2 a_2 \hat{A}\,\Psi_2\right) d\tau$$

$$= c_1^* c_1 a_1 \int_{-\infty}^{\infty} \Psi_1^* \Psi_1 d\tau + c_2^* c_1 a_1 \int_{-\infty}^{\infty} \Psi_2^* \Psi_1 d\tau + c_1^* c_2 a_a \int_{-\infty}^{\infty} \Psi_1^* \Psi_2 d\tau + c_2^* c_2 a_2 \int_{-\infty}^{\infty} \Psi_2^* \Psi_2 d\tau$$

$$= |c_1|^2 a_1 + |c_2|^2 a_2$$

The interpretation of this expression is that in a series of measurements each individual measurement yields either a_1 or a_2, but that the probability of a_1 occurring is $|c_1|^2$, and likewise the probability of a_2 occurring is $|c_2|^2$. The average is the sum of the two eigenvalues, but with each weighted according to the probability that it will occur in a measurement.

Q. The wave function Ψ for a certain system is given as a linear combination of two linearly independent wave functions Ψ_1 *and* Ψ_2 with energy eigen values E_1 and E_2 respectively as:

$$\Psi = \sqrt{\frac{1}{3}}\Psi_1 + \sqrt{\frac{2}{3}}\Psi_2$$

What is the probability that the systems energy will be observed to be E_1?

Ans: The measurement of an eigen value is proportional to the square modulus of the co-efficient,

So probability of measurement of $E_1 = \left(\sqrt{\frac{1}{3}}\right)^2 = \frac{1}{3} = 33.33\ \%$

Q. The wave function Ψ for a certain system is given as a linear combination of three linearly independent wave functions Ψ_1 ,Ψ_2 *and* Ψ_3 as:

$$\Psi = \frac{1}{2}\Psi_1 + \frac{1}{4}\Psi_2 + c_3\Psi_2$$

Evaluate the value of c_3.

Ans:

We know

$$\sum_{n=1}^{N} |c_n|^2 = 1$$

$$=> \left(\frac{1}{2}\right)^2 + \left(\frac{1}{4}\right)^2 + (c_3)^2 = 1$$

$$=> (c_3)^2 = 1 - \frac{1}{4} - \frac{1}{16}$$

$$=> (c_3)^2 = \frac{11}{16}$$

$$=> c_3 = \frac{\sqrt{11}}{4}$$

i.e. the value of the missing coefficient c_3 is $\frac{\sqrt{11}}{4}$

Bracket notation and matrix notation in quantum mechanics:

In quantum mechanics, the definite integral over all space of an operator sandwiched between two functions occurs often, and various abbreviations are used to represent this calculus (integral) formalisms in simplified notation:

Dirac bracket notation: In this notation, the wave function of a system say Ψ is given by a quantity called "ket" and is represented as "$| >$" and the complex conjugate of the wave function i.e. Ψ^* is given by a quantity called bra and is represented as "$< |$".

So the eigen value equation: $\hat{A}\Psi = a\Psi$ can be expressed in terms of bracket notation as:

$$\hat{A}\,|\Psi> = a\,|\Psi>$$

Again a general integral formalism can be written in bracket notation as:

$$\int \Psi_m^* \hat{A} \Psi_n = \langle \Psi_m | \hat{A} | \Psi_n \rangle \; or \; \langle m | \hat{A} | n \rangle$$

Note: (a) If the operator $\hat{A} = 1$, then it is not shown in bracket notation i.e. instead of writing $\langle \Psi_m | 1 | \Psi_n \rangle$ we can simply write it as $\langle \Psi_m | \Psi_n \rangle$. (b) $\int \Psi_m^* \Psi_n = \langle m | n \rangle = \langle n | m \rangle^*$

Similarly, the expression for expectation value can be written in bracket notation as:

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

$$= \frac{\langle \Psi | \hat{A} | \Psi \rangle}{\langle \Psi | \Psi \rangle}$$

Matrix notation: It is an abbreviated form of Dirac bracket notation where the integral is written as a matrix element of the corresponding operator

i.e.

$$\langle m | \hat{A} | n \rangle = A_{mn}$$

Simultaneous observable, complementary observable and uncertainty principle:

Simultaneous observable: If two operators commute with each other, then simultaneous measurements of the physical properties (observable) represented by the two operators can be precisely evaluated**.** Such pairs of observables for which $[A, B] = AB - BA = 0$ and hence can be be specified simultaneously is called simultaneous observable. For example: all three position operators $\hat{x}, \hat{y}$ and $\hat{z}$ commute with one another i.e.$[\hat{x}, \hat{y}] = [\hat{x}, \hat{z}] = [\hat{y}, \hat{z}] = 0$, so there is no constraint on the complete specification of position. The same is true of the three operators for the components of linear momentum i.e.$[\hat{p}_x, \hat{p}_y] = [\hat{p}_x, \hat{p}_z] = [\hat{p}_y, \hat{p}_z] = 0$, so all three components can be determined simultaneously.

* Since position operator and potential energy operator simply represents multiplicative operation, so order of operation involving them will be irrelevant. Hence $\hat{x}\hat{V}(x) = \hat{V}(x)\hat{x}$ $i.e.$ $[\hat{x}, \hat{V}(x)] = 0$.

Complementary observable and uncertainty principle: If two operators do not commute with each other, then simultaneous measurements of the physical properties (observable) represented by the two operators cannot be precisely evaluated**.** Such pairs of observables for which $[A, B] = AB - BA \neq 0$

and hence cannot be specified simultaneously is called complementary observable. For example: the position operator corresponding to “x” coordinate ($\hat{x}$) and the momentum operator in the same co-ordinate i.e. $\hat{p}_x$ do not commute with each other i.e. $[\hat{x}\ ,\hat{p}_x] \neq 0$. So precise simultaneous determination of the position on the x-axis and the momentum parallel to x-axis is not possible which is the statement of Heisenberg uncertainty principle.

Q. Define complementary observable with one example.

Q. Show that `$[\hat{x},\hat{p}_x] \neq 0, but \left[\hat{x},\hat{p}_y\right] = [\hat{x},\hat{p}_z] = 0$. What conclusion can be drawn from the result.

Ans:

Let the operand function is Ψ

Now

$$[\hat{x},\hat{p}_x]\Psi = \hat{x}\hat{p}_x\Psi - \hat{p}_x\hat{x}\Psi$$

$$= x\frac{h}{2\pi i}\frac{d}{dx}(\Psi) - \frac{h}{2\pi i}\frac{d}{dx}x(\Psi)$$

$$= x\frac{h}{2\pi i}\frac{d\Psi}{dx} - \frac{h}{2\pi i}\frac{d}{dx}(x\Psi)$$

$$= x\frac{h}{2\pi i}\frac{d\Psi}{dx} - x\frac{h}{2\pi i}\frac{d\Psi}{dx} - \frac{h}{2\pi i}\Psi$$

$$= -\frac{h}{2\pi i}\Psi \ or \ i\hbar \ \Psi$$

Removing the arbitrary function from both sides, we have

$$[\hat{x},\hat{p}_x] = -\frac{h}{2\pi i} or \ i\hbar \ \neq 0$$

Again

$$\left[\hat{x},\hat{p}_y\right]\Psi = \hat{x}\hat{p}_y\Psi - \hat{p}_y\hat{x}\Psi$$

$$= x\frac{h}{2\pi i}\frac{d}{dy}(\Psi) - \frac{h}{2\pi i}\frac{d}{dy}x(\Psi)$$

$$= x\frac{h}{2\pi i}\frac{d\Psi}{dy} - \frac{h}{2\pi i}\frac{d}{dy}(x\Psi)$$

$$= x\frac{h}{2\pi i}\frac{d\Psi}{dx} - x\frac{h}{2\pi i}\frac{d\Psi}{dy} - \Psi\frac{h}{2\pi i}\frac{dx}{dy}$$

$$= 0$$

i.e.

$$\left[\hat{x},\hat{p}_y\right] = 0$$

Similarly, we can show that:

$$[\hat{x},\hat{p}_z] = 0$$

So the conclusion is that simultaneous specification of the position in x-axis and momentum parallel to x-axis cannot be determined precisely, but the simultaneous specification of the position on x-axis and the momentum parallel to y or z axis can be determined simultaneous with arbitrary precession.

Q. Show that: $[\hat{x}, \hat{p}_x\ ] = \frac{ih}{2\pi}$

Q. Show that momentum operator $\hat{p}_x$ in x-direction commute with the kinetic energy operator $\hat{T}_x$in the same direction.

Ans:

We know

$$\hat{p}_x = \frac{\hbar}{i}\frac{d}{dx}\ and\ \hat{T}_x = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2}$$

Now

$$\hat{p}_x\hat{T}_x\Psi = \left(\frac{\hbar}{i}\frac{d}{dx}\right)\left(-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\right)\Psi$$

$$= -\frac{\hbar^3}{2im}\frac{d}{dx}\frac{d^2\Psi}{dx^2}$$

$$= -\frac{\hbar^3}{2im}\frac{d^3\Psi}{dx^3}$$

Again

$$\hat{T}_x\hat{p}_x\Psi = \left(-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\right)\left(\frac{\hbar}{i}\frac{d}{dx}\right)\Psi$$

$$= -\frac{\hbar^3}{2im}\frac{d^2}{dx^2}\frac{d\Psi}{dx}$$

$$= -\frac{\hbar^3}{2im}\frac{d^3\Psi}{dx^3}$$

Now

$$\hat{p}_x\hat{T}_x\Psi - \hat{T}_x\hat{p}_x\Psi = -\frac{\hbar^3}{2im}\frac{d^3\Psi}{dx^3} - \left(-\frac{\hbar^3}{2im}\frac{d^3\Psi}{dx^3}\right)$$

$$=> \left(\hat{p}_x\hat{T}_x - \hat{T}_x\hat{p}_x\right)\Psi = 0\Psi$$

$$=> \left(\hat{p}_x\hat{T}_x - \hat{T}_x\hat{p}_x\right) = 0$$

$$=> \left[\hat{p}_x, \hat{T}_x\right] = 0$$

i.e. $\hat{p}_x\ and\ \hat{T}_x$ commute with each other and hence simultaneous determination of linear momentum and kinetic energy in the same direction is possible with arbitrary precession.

Properties of commutator:

(a) $\left[\hat{A}, \hat{B}\right] = -\left[\hat{B}, \hat{A}\right]$

(b) $\left[\hat{A}, \hat{A}\right] = \left[\hat{A}, \hat{A}^n\right] = 0$

(c) $\left[\hat{A}, \hat{B} + \hat{C}\right] = \left[\hat{A}, \hat{B}\right] + \left[\hat{A}, \hat{C}\right]\ or\ \left[\hat{A} + \hat{B}, \hat{C}\right] = \left[\hat{A}, \hat{C}\right] + \left[\hat{B}, \hat{C}\right]$

(d) $\left[\hat{A}, \hat{B}\hat{C}\right] = \left[\hat{A}, \hat{B}\right]\hat{C} + \hat{B}\left[\hat{A}, \hat{C}\right]\ or\ \left[\hat{A}\hat{B}, \hat{C}\right] = \left[\hat{A}, \hat{C}\right]\hat{B} + \hat{A}\left[\hat{B}, \hat{C}\right]$

(e) $\left[k\hat{A}, \hat{B}\right] = \left[\hat{A}, k\hat{B}\right] = k\left[\hat{A}, \hat{B}\right]$ and $\left[m\hat{A}, n\hat{B}\right] = mn\left[\hat{A}, \hat{B}\right]$

(f) If $\left[\hat{A},\hat{B}\right]=0\ and\ \left[\hat{A},\hat{C}\right]=0, then\ \left[\hat{B},\hat{C}\right]=0$

Q. Find (a) $\left[x^n,\frac{d}{dx}\right]$(b) $\left[\frac{d}{dx},\frac{d^4}{dx^4}\right]$ (c) $\left[\hat{T}_x,\hat{p}_x\right]$ (d)$[\hat{x},\hat{p}_x^2]$

Ans:

(a) $\left[x^n,\frac{d}{dx}\right]$

We know

$$\left[\frac{d}{dx},x^n\right]=nx^{n-1}$$

Using the property of commutator: $\left[\hat{A},\hat{B}\right]=-\left[\hat{B},\hat{A}\right]$

We have

$$\left[x^n,\frac{d}{dx}\right]=-nx^{n-1}$$

(b) $\left[\frac{d}{dx},\frac{d^4}{dx^4}\right]$

Ans:

Here

$$\hat{A}=\frac{d}{dx}\ and\ \hat{A}^4=\ \frac{d^4}{dx^4}$$

Using the property of commutator: $\left[\hat{A},\hat{A}^n\right]=0$

We have

$$\left[\frac{d}{dx},\frac{d^4}{dx^4}\right]=0$$

(c) $\left[\hat{T}_x,\hat{p}_x\right]$

Ans:

We know

$$\hat{T}_x=-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\ and\ \hat{p}_x=-i\hbar\frac{d}{dx}$$

Now

$$\left[\hat{T}_x,\hat{p}_x\right]=\left[-\frac{\hbar^2}{2m}\frac{d^2}{dx^2},-i\hbar\frac{d}{dx}\right]--(1)$$

Using the property of commutator: $\left[m\hat{A},n\hat{B}\right]=mn\left[\hat{A},\hat{B}\right]$ in equation (1), we have

$$\left[\hat{T}_x,\hat{p}_x\right]=\frac{i\hbar^3}{2m}\left[\frac{d^2}{dx^2},\frac{d}{dx}\right]--(2)$$

Using the property of commutator: $\left[\hat{A},\hat{A}^n\right]=0$ in equation (2), we have

$$\left[\hat{T}_x,\hat{p}_x\right]=0$$

(d) $[\hat{x},\hat{p}_x^2]$

Ans:

Using the property of commutator: $\left[\hat{A},\hat{B}\hat{C}\right]=\left[\hat{A},\hat{B}\right]\hat{C}+\hat{B}\left[\hat{A},\hat{C}\right]$, we have

$$[\hat{x},\hat{p}_x^2]=[\hat{x},\hat{p}_x\hat{p}_x]$$

$$=[\hat{x},\hat{p}_x]\hat{p}_x+\hat{p}_x[\hat{x},\hat{p}_x]--(1)$$

We know

$$[\hat{x},\hat{p}_x]=i\hbar\ and\ \hat{p}_x=\frac{\hbar}{i}\frac{d}{dx}$$

Putting these values in equation (1), we have

$$[\hat{x},\hat{p}_x]\hat{p}_x=i\hbar\frac{\hbar}{i}\frac{d}{dx}+\frac{\hbar}{i}\frac{d}{dx}i\hbar$$

$$=\hbar^2\frac{d}{dx}+\hbar^2\frac{d}{dx}$$

$$=2\hbar^2\frac{d}{dx}$$

Quantum mechanical waves and Schrodinger equation:

The classical one dimensional wave equation is:

$$\frac{\partial^2u}{\partial x^2}=\frac{1}{c^2}\frac{\partial^2u}{\partial t^2}--(1)$$

Where u is the amplitude of vibration and c is the velocity at which the wave propagates. This differential equation possesses two variables viz. spatial coordinates (x) and time (t) and hence the amplitude is a function of these two variables i.e. $u(x,t)$. Now the spatial part can be written as Ψ(x) and the temporal part as Cos ωt.

Now applying the principle of separation of variables we can write:

$$u(x,t)=\Psi(x)\times Cos\ \omega t--(2)$$

Now

$$\frac{\partial^2u(x,t)}{\partial t^2}=\frac{\partial^2}{\partial t^2}[\Psi(x)Cos\ \omega t]$$

$$=-\omega^2\Psi(x)Cos\ \omega t--(3)$$

And

$$\frac{\partial^2u(x,t)}{\partial x^2}=\frac{\partial^2}{\partial x^2}[\Psi(x)Cos\ \omega t]$$

$$=Cos\ \omega t\frac{\partial^2\Psi(x)}{\partial x^2}--(4)$$

From equation (1), (3) and (4), we can write

$$Cos\ \omega t\frac{\partial^2\Psi(x)}{\partial x^2}=-\frac{\omega^2}{c^2}\Psi(x)Cos\ \omega t$$

$$=>\frac{\partial^2\Psi(x)}{\partial x^2}=-\frac{\omega^2}{c^2}\Psi(x)$$

$$=> \frac{\partial^2 \Psi(x)}{\partial x^2} + \frac{\omega^2}{c^2}\Psi(x) = 0 - - - (4)$$

We know

$$\omega = 2\pi v \; and \; c = v\lambda$$

Putting these values in equation (5), we have

$$\frac{\partial^2 \Psi(x)}{\partial x^2} + \frac{4\pi^2 v^2}{v^2 \lambda^2}\Psi(x) = 0$$

$$=> \frac{\partial^2 \Psi(x)}{\partial x^2} + \frac{4\pi^2}{\lambda^2}\Psi(x) = 0 - -(5)$$

We know

$$E = T + V$$

$$=> E = \frac{P^2}{2m} + V(x)$$

$$=> \frac{P^2}{2m} = E - V(x)$$

$$=> P = [2m(E - V(x))]^{\frac{1}{2}}$$

From De-Broglie hypothesis of wave-particle dual nature, we have

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

$$= \frac{h}{[2m(E - V(x))]^{\frac{1}{2}}}$$

So

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

Putting the value of λ^2 in equation (5), we have

$$\frac{\partial^2 \Psi(x)}{\partial x^2} + \frac{4\pi^2}{\frac{h^2}{[2m(E - V(x)]}}\Psi(x) = 0$$

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

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

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

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

$$=> \left[-\frac{h^2}{8\pi^2 m}\frac{\partial^2}{\partial x^2} + V(x)\right]\Psi(x) = E\Psi(x)$$

The above expression is the time-independent Schrödinger equation in one dimension.

If we consider that the wave propagates in 3 D space, then we can write

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

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

$$=>\hat{H}\Psi(x,y,z)=E\Psi(x,y,z)$$

The above expression is the time-independent Schrödinger equation in three dimension which is derived from classical wave equation via incorporating De-Broglie equation.

Q. Deduce Schrodinger equation on the basis of classical concept

Q. Show that the classical wave equation of stationary wave is consistent with Schrodinger equation if de Broglie relation is used.

Using quantum mechanics on some simple systems:

(1) Free particle in motion in one dimension:

By free particle, we mean that the particle is not under the action of any force. The dissociation of an electron from an atom, radioactive decay of alpha or beta particle are some examples of free particles. The potential energy of such a particle is constant and can be taken as zero for convenience. So the total energy is solely due to the kinetic motion of the particle.

The Schrodinger equation for 1 D is:

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

$$or\ \left[-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}+V(x)\right]\Psi(x)=E\Psi(x)$$

Since the potential energy for a free particle is assumed to be zero, so we can write

$$-\frac{\hbar^2}{2m}\frac{\partial^2\Psi(x)}{\partial x^2}=E\Psi(x)--(1)$$

This is a 2nd order differential equation, whose general solution will be:

$$\Psi=Ae^{ikx}+Be^{-ikx} or\ A\cos kx+B\sin kx$$

[Euler's theorem, $e^{ikx}=\cos kx+i\sin kx$]

Now

$$-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\left(Ae^{ikx}+Be^{-ikx}\right)=-\frac{\hbar^2}{2m}\left[A(ik)^2e^{ikx}+B(-ik)^2e^{-ikx}\right]$$

$$=-\frac{\hbar^2(ik)^2}{2m}\left(Ae^{ikx}+Be^{-ikx}\right)$$

$$=\frac{k^2\hbar^2}{2m}\left(Ae^{ikx}+Be^{-ikx}\right)--(2)$$

Comparing equation (1) and (2), we have

$$E = \frac{k^2\hbar^2}{2m}$$

i.e. the wave function and energy expressions for a free particle in one dimension are:

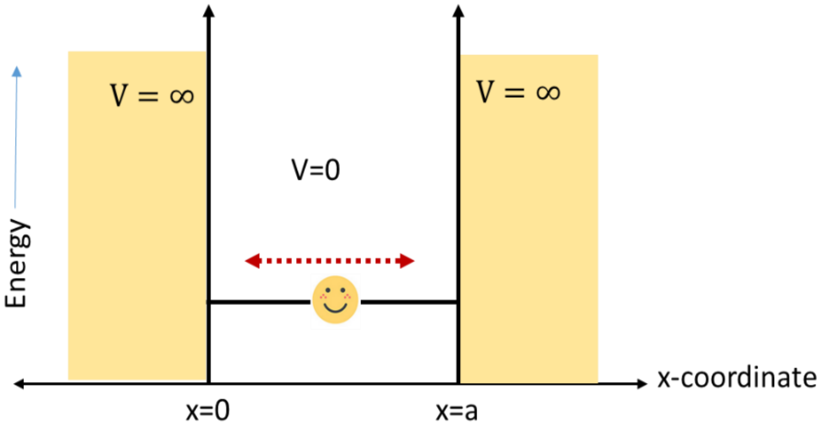
$$\Psi = Ae^{ikx} + Be^{-ikx} \; and \; E = \frac{k^2\hbar^2}{2m}$$

The wave function is acceptable for any value of k, so the energy term that involve k^2 *can* take any non-negative value, including zero. i.e. we can say that for a free particle $E \geq 0$. As a result, the translational energy of a free particle is not quantized.

Q. For free particle how can you show that its energy is not quantized. What is the restriction imposed on its energy? Give one example of free particle.

(2) Confined motion:

(a) Particle in a one dimensional box:



Consider a box in which a particle of mass “m” is confined to move in a one-dimensional space of length “a” between two impenetrable walls. The potential energy is zero inside the box but rises abruptly to infinity at the walls located at x = 0 and x = a to ensure that the particle cannot escape from the box. Therefor potential energy is infinite outside the box indicating no probability of finding the particle outside.
i.e.

$$\begin{aligned} V(x) &= 0\,, 0 \leq x \leq a \\ &= \infty, x > 0, x < 0 \end{aligned}$$

Schrodinger equation for outside of the box:

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

$$=> -\frac{\hbar^2}{2m}\frac{\partial^2\Psi}{\partial x^2} + \infty\Psi = \infty\Psi$$

$$=> \frac{\hbar^2}{2m}\frac{\partial^2\Psi}{\partial x^2} = \infty\Psi$$

$$=> \frac{\partial^2\Psi}{\partial x^2} = \infty\Psi$$

Now $\frac{\partial^2\Psi}{\partial x^2}$ is finite only when $\Psi = 0$ or $\Psi^2 = 0$, i.e. there is no probability of finding the particle outside the box.

Schrodinger equation for inside of the box:

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

$$=> -\frac{ħ^2}{2m}\frac{\partial^2\Psi}{\partial x^2} + 0\Psi = E\Psi$$

$$=> -\frac{ħ^2}{2m}\frac{\partial^2\Psi}{\partial x^2} = E\Psi$$

$$=> -\frac{ħ^2}{2m}\frac{\partial^2\Psi}{\partial x^2} - E\Psi = 0$$

$$=> \frac{ħ^2}{2m}\frac{\partial^2\Psi}{\partial x^2} + E\Psi = 0$$

$$=> \frac{\partial^2\Psi}{\partial x^2} + \frac{2mE}{ħ^2}\Psi = 0 - -(1)$$

Let

$$k^2 = \frac{2mE}{ħ^2} - -(2)$$

From equation (1) and (2), we have

$$\frac{\partial^2\Psi}{\partial x^2} + k^2\Psi = 0$$

This is a 2nd order differential solution whose general solution is:

$$\Psi = A\ Sin\ kx + B\ Cos\ kx - -(1)$$

An acceptable wave function must be finite, so the wave function must be vanished (become zero) at the two boundary of the box.

i.e.

$$\Psi = 0\ \ at\ x = 0\ and\ at\ x = a$$

Now applying the boundary condition of $\Psi = 0\ at\ x = 0$ in equation (1), we have

$$0 = A\ Sin\ k0 + B\ Cos\ k0$$

$$=> B = 0$$

Putting the value of B in equation (1), we have

$$\Psi = A\ Sin\ kx - -(2)$$

Again, applying the boundary condition of $\Psi = 0\ at\ x = a$ in equation (2), we have

$$0 = A\ Sin\ ka$$

$$=> Sin\ ka = 0$$

$$=> ka = n\pi$$

$$=> k = \frac{n\pi}{a} - -(3)$$

Where n =1,2,3…

Putting the value of "k" in equation (2), we have

$$\Psi = A\,Sin\,\frac{n\pi x}{a}$$

Comparing equation (2) and (3), we have

$$\frac{2mE}{\hbar^2} = \left(\frac{n\pi}{a}\right)^2$$

$$=> E = \frac{n^2\pi^2\hbar^2}{2ma^2}\ or\ \frac{n^2h^2}{8ma^2}$$

Where n =1,2, 3…. called the quantum numbers.

i.e. for a particle in 1 D box the expression for wave function and energy are:

$$\Psi_n = A\,Sin\,\frac{n\pi x}{a}\ and\ E_n = \frac{n^2\pi^2\hbar^2}{2ma^2}\ or\ \frac{n^2h^2}{8ma^2}$$

Since n =1,2,3… i.e. "n" can have only discrete value and hence the energy value is restricted to having only certain values. So the energy of the particle in the box is quantized. This quantization arises from the boundary conditions that ψ must satisfy. The need to satisfy boundary conditions implies that only certain wave functions are acceptable, and hence restricts the eigenvalues of energy to discrete values.

The values of "n" cannot be zero i.e. $n \neq 0$, if n = 0, then

$$k = \frac{n\pi}{a} = 0$$

So the wave function becomes as:

$$\Psi = A\,Sin\,\frac{n\pi x}{a} = 0$$

i.e. n = 0, lead to the conclusion that $\Psi = 0\ or\ \Psi^2 = 0$, i.e. the particle is not inside the box, which is absurd, as it goes against our initial assumption that the particle lies inside the box. So value of "n" cannot be zero.

Q. Set up and solve the Schrodinger equation for a particle in 1 D box for wavelength and energy.

Q. The wave function for a particle in 1 D box is: $\Psi = A\,Sin\,k\frac{n\pi x}{a}$. State why the value of quantum number "n" cannot be zero.

Q. Justify the quantization of energy for a particle in 1 D box.

Q. What will happen if the walls of a particle in 1D box are suddenly removed.

Ans: The quantization of energy in particle in 1 D box arise due to boundary conditions that restrict the particle motion within the box. If the walls box of the is removed, then the particle will become a free particle. So for this unbound particle, restriction in its energy as imposed by boundary condition will no longer valid and hence its energy quantization will disappear.

Zero-point energy (ZPE) and uncertainty principle:

Zero-point energy is the lowest possible nonzero value of energy possess by a system. Since for a particle in 1 D box $n \neq 0$, so the lowest possible energy state (ZPE) corresponds to n =1 quantum state.

i.e.

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

i.e. for a particle in 1 D box, the particle is not at rest even at absolute zero (0 K) as they possess some kinetic energy and hence some finite momentum. This existence of zero-point energy can be accounted for by the Heisenberg uncertainty principle. If the particle could possess zero kinetic energy, then its speed would also be zero, consequently there would be no uncertainty in determining its momentum (ΔP) and as a result its uncertainty in position (Δx) would then be infinite. But the particle lies within the box of length "a" and hence the uncertainty in determining the particle's position cannot exceed the box length "a", therefore, zero kinetic energy would violate the Heisenberg uncertainty principle and hence it is not possible.

Q. What do you mean by zero-point energy? Find the find expression for zero-point energy for a particle in 1 D box.

Q. Why a particle in a box cannot have zero energy quantum mechanically or justify the existence of ZPE for a particle confined in 1 D box.

Q. An electron is confined to a molecule of length 1 nm. Considering the electron to be a particle in 1D box, where potential energy is zero, (a) calculate its minimum energy (b) What electronic speed this minimum energy will corresponds to.

Ans:

(a) The minimum energy possess by a particle in 1 D box is the zero-point energy which is:

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

Now

m = 9.1 × 10^{-31} kg, $a = 10^{-9} m, h = 6.63 \times 10^{-34} Js$

So

$$E_{ZPE} = \frac{(6.63 \times 10^{-34}\, Js)^2}{8 \times 9.1 \times 10^{-31} kg \times (10^{-9}\, m)^2}$$

$$= 6.04\ \times 10^{-20} J$$

(b) Since potential energy is zero i.e. V = 0, so total energy is solely due to kinetic energy i.e.

$$E = T = \frac{1}{2} m v^2$$

$$=> v = \sqrt{\frac{2E}{m}}$$

$$= \sqrt{\frac{2\ \times 6.04 \times 10^{-20} J}{9.1 \times 10^{-31}\, kg}}$$

$$= 3.65 \times 10^5 ms^{-1}$$

Normalization of the wave function for a particle in a 1D box:

We have the wave function for a particle in 1 D box as:

$$\Psi_n = A\, Sin\, \frac{n\pi x}{a}$$

Here "A" is an arbitrary constant i.e. the wave function is not normalized yet. In order to ensure that the particle lies within the box with probability of finding it to be unity between x= 0 to x = a, it must be normalized. i.e.

$$\int_0^a \Psi_n{}^*\Psi_n dx = 1$$

$$=> \int_0^a \left(A\, Sin\, \frac{n\pi x}{a}\right)^2 dx = 1$$

$$=> \int_0^a A^2 Sin^2 \frac{n\pi x}{a} = 1$$

$$=> \frac{A^2}{2}\int_0^a 2\, Sin^2 \frac{n\pi x}{a} = 1$$

$$=> \frac{A^2}{2}\int_0^a \left(1 - Cos\, \frac{2n\pi x}{a}\right) dx = 1$$

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

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

$$=> \frac{A^2}{2}\left[\left(a - \frac{a}{2n\pi} Sin\, \frac{2n\pi a}{a}\right) - \left(0 - \frac{a}{2n\pi} Sin\, \frac{2n\pi 0}{a}\right)\right] = 1$$

$$=> \frac{A^2}{2}[(a-0)-(0-0)] = 1$$

$$=> \frac{A^2 a}{2} = 1$$

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

So the normalized wave function is: $\Psi_n = \sqrt{\frac{2}{a}}\, Sin\, \frac{n\pi x}{a}$

Q. Deduce the expression for normalized wave function for a particle in 1 D box.

Q. Show that the wave function for a particle in 1 D box is not an eigen function of the linear momentum operator $\hat{p}_x$but of $\hat{P}_x^2$.

Ans:

The normalized wave function for a particle in 1 D box is:

$$\Psi_n = \sqrt{\frac{2}{a}}\, Sin\, \frac{n\pi x}{a}$$

We know

$$\hat{p}_x = -i\hbar \frac{d}{dx} and\ \hat{P}_x^2 = -\hbar^2 \frac{d^2}{dx^2}$$

Now

$$\hat{p}_x \Psi_n = -i\hbar \frac{d}{dx}\left(\sqrt{\frac{2}{a}}\, Sin\, \frac{n\pi x}{a}\right)$$

$$= -i\hbar \left(\frac{2}{a}\right)^{\frac{1}{2}} \frac{d}{dx}\left(Sin\, \frac{n\pi x}{a}\right)$$

$$= -i\hbar \left(\frac{2}{a}\right)^{\frac{1}{2}} \left(\frac{n\pi}{a}\right) Cos\, \frac{n\pi x}{a}$$

$$\neq Constnat \times \Psi_n$$

i.e. $\Psi_n = \sqrt{\frac{2}{a}}\, Sin\, \frac{n\pi x}{a}$ is not an eigen function of the linear momentum operator $\hat{p}_x$.

Now

$$\hat{P}_x^2 \Psi_n = -\hbar^2 \frac{d^2}{dx^2}\left(\sqrt{\frac{2}{a}}\, Sin\, \frac{n\pi x}{a}\right)$$

$$= -\hbar^2 \frac{d}{dx}\frac{d}{dx}\left(\sqrt{\frac{2}{a}}\, Sin\, \frac{n\pi x}{a}\right)$$

$$= -\hbar^2 \frac{d}{dx}\left[\left(\frac{2}{a}\right)^{\frac{1}{2}} \left(\frac{n\pi}{a}\right) Cos\, \frac{n\pi x}{a}\right]$$

$$= -\hbar^2 \left(\frac{n\pi}{a}\right)\left(\frac{2}{a}\right)^{\frac{1}{2}} \frac{d}{dx}\left(Cos\, \frac{n\pi x}{a}\right)$$

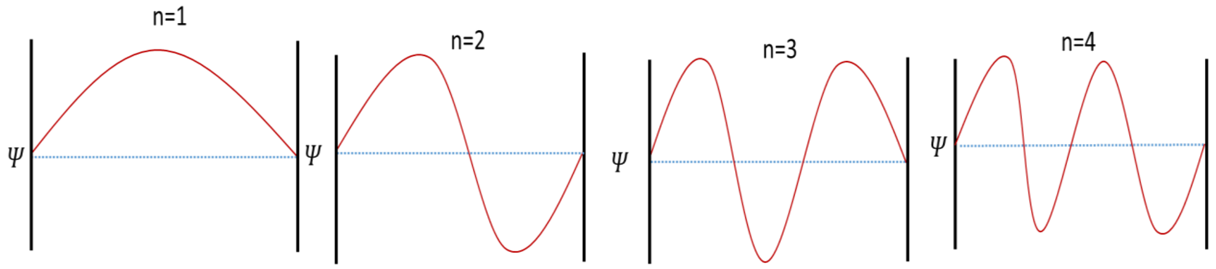
$$= -\hbar^2 \left(\frac{n\pi}{a}\right)\left(\frac{2}{a}\right)^{\frac{1}{2}} \left(-\frac{n\pi}{a}\right) Sin\, \frac{n\pi x}{a}$$

$$= \frac{\hbar^2 n^2 \pi^2}{a^2}\left(\frac{2}{a}\right)^{\frac{1}{2}} Sin\, \frac{n\pi x}{a}$$

$$= \frac{n^2 h^2}{4a^2}\Psi_n$$

i.e. $\Psi_n = \sqrt{\frac{2}{a}}\, Sin\, \frac{n\pi x}{a}$ is an eigen function of the operator $\hat{P}_x^2$ with eigen value of $\frac{n^2h^2}{4a^2}$.

Properties of wave function (Ψ_n) for a particle in 1 D box:



(1) The wave functions are all sine functions with the same maximum amplitude but different wavelengths. The wave length (λ_n) varies as $\frac{2a}{n}$ i.e. the wavelength gets shorter as "n" increases.
(2) Wave functions are alternatively symmetric and antisymmetric with respect to a mirror plane placed at the center of the box. Wave functions associated with all odd number of "n" is symmetric and that of all even number of "n" is antisymmetric.

(3) The boundary condition implies that the wave functions must vanished at the two ends of the box i.e. $\Psi = 0 \; at \; x = 0 \; and \; x = a$. But besides the boundaries, there are points inside the box where the wave function is zero. These points are called nodes. There are zero probability of finding the particles at the nodes. With increase in the value of quantum number "n", number of nodes increases. Basically in a specified quantum state "n", there is n-1 number of nodes present.

Nodal theorm: This theorm states that the ground state for a system is node-less, and that the energy of a quantum state increases with an increasing number of nodes.

Expression for wave length associated with particle wave in 1 D box:

We know

$$E_n = \frac{n^2h^2}{8ma^2} - -(1)$$

Again

$$E_n = T + V$$

But for a particle in 1 D box, V = 0

So

$$\begin{aligned} E_n &= T \\ &= \frac{1}{2}mv^2 \\ &= \frac{P^2}{2m} - -(2) \end{aligned}$$

From equation (1) and (2), we have

$$\frac{n^2h^2}{8ma^2} = \frac{P^2}{2m}$$

$$=> a^2 = \frac{n^2h^2}{4P^2} - -(3)$$

From De Broglie hypothesis we have

$$P = \frac{h}{\lambda_n}$$

Putting the value of "P" in equation (3), we have

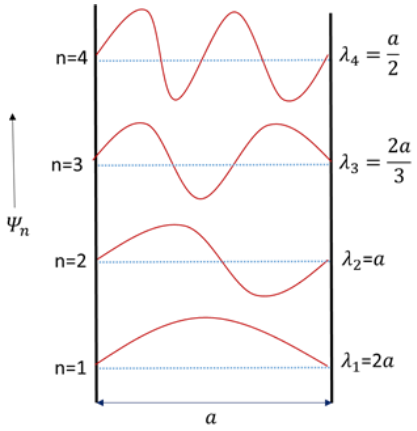
$$a^2 = \frac{n^2h^2}{4\left(\frac{h}{\lambda_n}\right)^2}$$

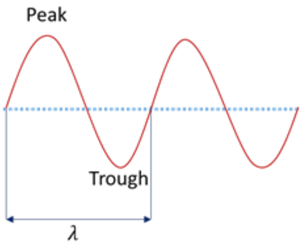
$$=> a^2 = \frac{n^2\lambda_n^2}{4}$$

$$=> a = n\left(\frac{\lambda_n}{2}\right)$$

$$=> \lambda_n = \frac{2a}{n}$$

i.e. for $n = 1\ state\ \ \lambda_1 = 2a, n = 2\ state\ \lambda_2 = a, n = 3\ state\ \lambda_3 = \frac{2a}{3}$ and so on

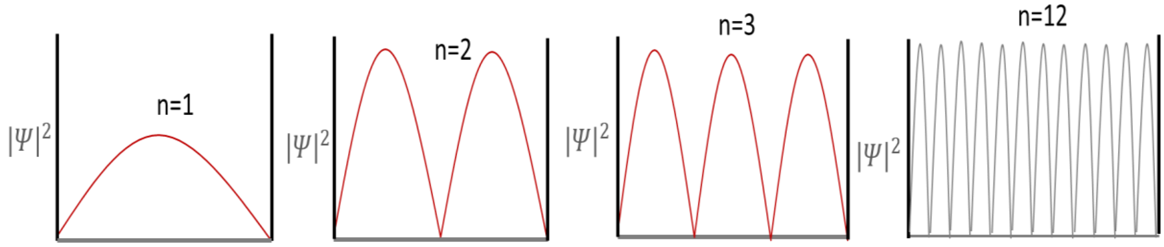




Q. A particle with mass “m” is moving in a 1D box of length “a” where the potential is zero. Show that the wavelength associated with the particle is $\frac{2a}{n}$

Q. Show that length of a particle in 1 D box is an integral multiple of $\frac{\lambda_n}{2}$, where λ_n is the wave length associated the particle wave. [Hint: We have to prove that $a = n\left(\frac{\lambda_n}{2}\right)$]

Properties of probability density $\left(\Psi_n^2\right)$ for a particle in 1 D box:



(1) The probability density for a particle in 1 D box is $\Psi_n^2 = \left(\sqrt{\frac{2}{a}}\ Sin\ \frac{n\pi x}{a}\right)^2 = \frac{2}{a}Sin^2\left(\frac{n\pi x}{a}\right)$

(2) Ψ_n^2 i.e. probability density has the same number of maxima as the quantum number “n”. The most probable location of the particle corresponds to the maxima in the probability density plot. At high quantum number $(n \geq 2)$ there are point within the box called nodes where $\Psi_n^2 = 0$. i.e. in these points the probability of finding the particle is zero.

(3) In classical mechanics, the probability of finding the particle is the same at all points along the box. This is because the particle has constant energy, hence constant speed, we would expect the particle to spend equal time in each line segment between 0 to a. However, quantum mechanical solution shows that the probability density is not uniform as the particle spent more time in some segment represented by the maxima’s and spent no time at some segments represented by the minima’s. But as we go to higher energy states, the maxima and minima come closer together and hence probability density (Ψ_n^2) become more and more uniform as the quantum number “n” increases. i.e. as the value of the quantum number increases, the probability density oscillates more and more. For very high values of “n” there are so many oscillations that we would not expect to observe anything other than a constant or uniform value for the probability density. Classically this is just what we would expect for a particle in a box.

This is the so called Bohr's correspondence principle which states that classical mechanics resembles with quantum mechanics in the limit of very high quantum number. The large quantum-number limit is known as the classical limit.

Q. Give the plots of Ψ and Ψ^2 against co-ordinate for n = 2 state of a particle in 1 D box of length "a" where potential energy is zero.

Q. Explain Bohr's Correspondence principle.

Q. For a particle in a 1 D box of length "a" find the probability of finding the particle in the region $0 \leq x \leq \frac{a}{4}$ in ground state (n =1) and in 1st excited state (n = 2).

Ans:

We know

$$\Psi_n = \sqrt{\frac{2}{a}}\, Sin\, \frac{n\pi x}{a}$$

Now

$$P = \int_0^{\frac{a}{4}} \Psi_n^2 dx$$

$$= \int_0^{\frac{a}{4}} \left(\sqrt{\frac{2}{a}}\, Sin\, \frac{n\pi x}{a}\right)^2 dx$$

$$= \frac{2}{a}\int_0^{\frac{a}{4}} Sin^2\left(\frac{n\pi x}{a}\right) dx$$

$$= \frac{2}{2a}\int_0^{\frac{a}{4}} 2Sin^2\left(\frac{n\pi x}{a}\right) dx$$

$$= \frac{1}{a}\int_0^{\frac{a}{4}} \left[1 - Cos\, \frac{2n\pi x}{a}\right] dx$$

$$= \frac{1}{a}\left[[x]_0^{\frac{a}{4}} - \frac{a}{2n\pi}\left[Sin\, \frac{2n\pi x}{a}\right]_0^{\frac{a}{4}}\right]$$

$$= \frac{1}{a}\left[\left(\frac{a}{4} - 0\right) - \frac{a}{2n\pi}\left(Sin\, \frac{2n\pi\frac{a}{4}}{a} - Sin\, \frac{n\pi 0}{a}\right)\right]$$

$$= \frac{1}{a}\left[\frac{a}{4} - \frac{a}{2n\pi}\, Sin\, \frac{n\pi}{2}\right]$$

$$= \frac{1}{4} - \frac{1}{2n\pi}\, Sin\, \frac{n\pi}{2}$$

For ground state i.e. for n =1

$$P = \frac{1}{4} - \frac{1}{2\pi}\, Sin\, \frac{\pi}{2}$$

$$= \frac{1}{4} - \frac{1}{2 \times 3.14} \times 1$$

$$= 0.0908$$

For 1st excited state i.e. for n = 2

$$P = \frac{1}{4} - \frac{1}{2 \times 2 \times \pi}\, Sin\, \frac{2\pi}{2}$$

$$= \frac{1}{4} - \frac{1}{4\pi}\, Sin\, \pi$$

$$= \frac{1}{4}\ or\ 0.25$$

Q. For a particle in 1 D box of length “a” find the probability of finding the particle in between 0 to $\frac{a}{2}$ in the ground state (n =1).

Ans:

We know

$$\Psi_n = \sqrt{\frac{2}{a}}\, Sin\, \frac{n\pi x}{a}$$

So

$$\Psi_1 = \sqrt{\frac{2}{a}}\, Sin\, \frac{\pi x}{a}$$

Now

$$P = \int_0^{\frac{a}{2}} \Psi_1^2 dx$$

$$= \int_0^{\frac{a}{2}} \left(\sqrt{\frac{2}{a}}\, Sin\, \frac{\pi x}{a} \right)^2 dx$$

$$= \frac{2}{a} \int_0^{\frac{a}{2}} Sin^2 \left(\frac{\pi x}{a} \right) dx$$

$$= \frac{2}{2a} \int_0^{\frac{a}{2}} 2Sin^2 \left(\frac{\pi x}{a} \right) dx$$

$$= \frac{1}{a} \int_0^{\frac{a}{4}} \left[1 - Cos\, \frac{2\pi x}{a} \right] dx$$

$$= \frac{1}{a} \left[[x]_0^{\frac{a}{2}} - \frac{a}{2\pi} \left[Sin\, \frac{2\pi x}{a} \right]_0^{\frac{a}{2}} \right]$$

$$= \frac{1}{a}\left[\left(\frac{a}{2} - 0\right) - \frac{a}{2\pi}\left(Sin\ \frac{2\pi\frac{a}{2}}{a} - Sin\ \frac{\pi 0}{a}\right)\right]$$

$$= \frac{1}{a}\left[\frac{a}{2} - \frac{a}{2\pi}\ Sin\ \pi\ \right]$$

$$= \frac{1}{2}$$

Q. Evaluate the probability of finding a particle in the vicinity of center of a 1 D box of length 1 nm for n =1 state.

Ans:

In the vicinity of center, the position is not precisely measured. so we can say the particle lies in between x_1= 0.49 nm and x_2 = 0.51 nm

Now

$$dx = x_2 - x_1$$

$$= (0.51 - 0.49)\ nm$$

$$= 0.02\ nm$$

We are given that:

Length of the box $(a) = 1\ nm$

Quantum state (n) =1

Position of the particle (x) = center of the box $= \frac{a}{2} = \frac{1}{2}\ nm = 0.50\ nm$

We know

$$\Psi_n = \sqrt{\frac{2}{a}}\ Sin\ \frac{n\pi x}{a}$$

So

$$\Psi_1 = \sqrt{\frac{2}{a}}\ Sin\ \frac{\pi x}{a}$$

Now

$$P = \Psi_1^2 dx$$

$$= \left(\sqrt{\frac{2}{a}}\ Sin\ \frac{\pi x}{a}\right)^2\ dx$$

$$= \frac{2}{a} Sin^2\left(\frac{\pi x}{a}\right) dx$$

$$= \frac{2}{1\ nm} \times Sin^2\left(\frac{\pi \times 0.50\ nm}{1\ nm}\right) \times 0.02\ nm$$

$$= 0.04$$

Q. The size of a nucleus is 10^{-12} cm. Treating it as a 1 D box show why the electron does not exist in the box i.e. in the nucleus. Given mass of electron (m_e) = 9.1×10^{-31} kg

Ans:

An electron will be there in the nucleus if its columbic potential energy is greater that the zero-point energy, otherwise it will escape from the nucleus.

Now

$$E_{ZPE} = \frac{h^2}{8m_e a^2}$$

$$= \frac{(6.63 \times 10^{-34}\, Js)^2}{8 \times 9.1 \times 10^{-31} kg \times (10^{-14}\, m)^2}$$

$$= 6.04\ \times 10^{-10}\, J$$

Now

$$E_{Coulombic} = -\frac{e^2}{r}$$

$$= -\frac{(1.6\ \times 10^{-19}\, C)^2}{10^{-14}\, m}$$

$$= -2.6 \times 10^{-24} J$$

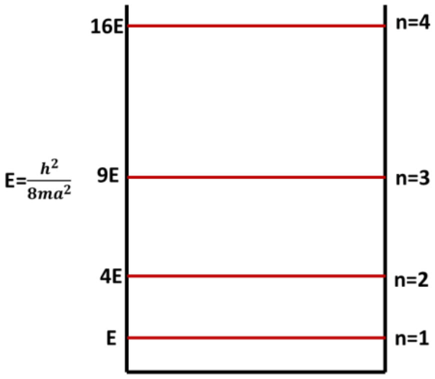
i.e. zero-point energy is greater than the Coulombic attraction energy, so the nucleus does not have enough energy to hold the electron by electrostatic forces of attraction.

Properties of energy for a particle in 1 D box:

We know

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

i.e. the energy levels increase as n^2, and hence their separation increases as the quantum number increases.



Q. Calculate and draw energy levels from E_1 to E_6 in eV for an electron in 1 D box of length 12Å.

Ans:

We know

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

Given, $a = 12\ \text{Å}\ or\ 12\ \times 10^{-10} m, m = 9.1 \times 10^{-31}\ kg$

Now

$$E_n = \frac{n^2 \times (6.63 \times 10^{-34}\ Js)^2}{8 \times 9.1 \times 10^{-31} kg \times (12 \times 10^{-10}\ m)^2}$$

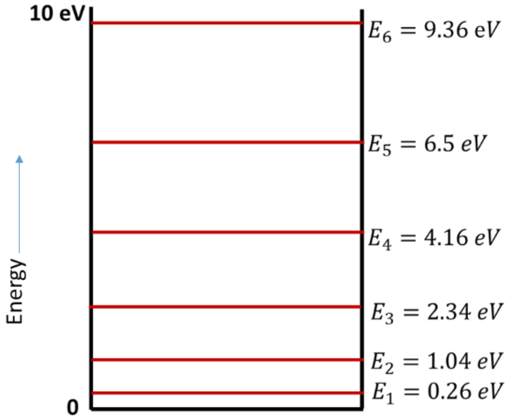
$$= 4.16 \times 10^{-20} n^2 J$$

$$= \frac{4.16 \times 10^{-20} n^2}{1.6 \times 10^{-19}}\ eV$$

$$= 0.26\, n^2\ eV$$

So

$$E_1 = 0.26\ eV, E_2 = 1.04\ eV, E_3 = 2.34\ eV, E_4 = 4.16\ eV, E_5 = 6.5\ eV, E_6 = 9.36\ eV$$



Separation between adjacent energy levels (ΔE):

We know

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

So, the separation between adjacent energy levels with quantum numbers n and n + 1 is

$$\Delta E = E_{n+1} - E_n$$

$$= \frac{(n+1)^2h^2}{8ma^2} - \frac{n^2h^2}{8ma^2}$$

$$= \frac{h^2}{8ma^2}[(n+1)^2 - n^2]$$

$$= \frac{h^2}{8ma^2}(n^2 + 2n + 1 - n^2)$$

$$= (2n+1)\frac{h^2}{8ma^2}$$

$$i.e. \Delta E \propto \frac{1}{a^2}\ and\ \frac{1}{m}$$

$\Delta E \propto \frac{1}{a^2}$ means that smaller the box length or the more tightly a particle is confined, the greater is the spacing between the allowed energy levels and hence more is the extent of quantization of energy. Alternatively, as the box is made wider, the separation between energies decreases and the energy levels get closer together. In the limit of a very large box (macroscopic dimensions), the energy levels are so close together that the quantization disappears entirely and an energy continuum will be observed. Atoms and molecules free to move in normal laboratory-sized vessels therefore have non -quantized translational energy. $\Delta E \propto \frac{1}{m}$ means that the separation between allowed energy levels decreases as mass of the particle increases. Ultimately, for a macroscopic object, "m" is so large that the energy levels are too closely spaced to be distinguished from the continuum of levels expected in classical mechanics. In other words, for heavier particle quantization of energy almost vanishes.

Thus we can say that quantization of energies persists only with spatial confinement involving microscopic particles.

Q. Calculate the spacing between energy levels for (a) an electron of mass 10^{-30} kg in a 1D box of length 1 Å (b) A ball bearing mass of 1 g in a box of length 10 cm (c) comment on energy spacing in the two cases.

Ans:

(a)

$$\Delta E = (2n+1)\frac{h^2}{8ma^2}$$

$$= (2n+1)\frac{(6.63 \times 10^{-34}\, Js)^2}{8 \times 10^{-30} kg \times (10^{-10}\, m)^2}$$

$$= (2n+1) \times 5.445 \times 10^{-18}\, J$$

(b)

$$\Delta E = (2n+1)\frac{h^2}{8ma^2}$$

$$= (2n+1)\frac{(6.63 \times 10^{-34}\, Js)^2}{8 \times 10^{-3} kg \times (10^{-1}\, m)^2}$$

$$= (2n+1) \times 5.445 \times 10^{-63}\, J$$

(c) In the 2nd case energy spacing is negligible which implies that with increasing particle size and box length energy spacing decreases i.e. energy quantization almost vanishes.

Q. What is the wavelength of light absorbed when an electron in a linear molecule of 10 Å makes a transition from the energy level n =1 to n = 2?

Ans:

We know

$$\Delta E = (2n+1)\frac{h^2}{8ma^2}$$

$$= (2 \times 1 + 1)\frac{h^2}{8ma^2}$$

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

$$= \frac{3 \times (6.63 \times 10^{-34}\, Js)^2}{8 \times 9.1 \times 10^{-31} kg \times (10 \times 10^{-10}\, m)^2}$$

$$= 1.81\ \times 10^{-19}\, J$$

Now

$$\Delta E = \frac{hc}{\lambda}$$

$$=> \lambda = \frac{hc}{\Delta E}$$

$$= \frac{6.63\ \times 10^{-34}\, Js \times 3 \times 10^{8}\, ms^{-1}}{1.81\ \times 10^{-19}\, J}$$

$$= 1.09 \times 10^{-6}\, m$$

[Self -test]: Find the wave length of radiation emitted when a particle of mass 9.0 × 10^{-31} kg in a 1 D box of length 3 Å undergoes a transition from n=3 level to ground level.

[Self-test]: (a) For a particle of mass 9.1 ×10^{-31} kg in a certain one-dimensional box, the n = 3 to n = 2 transition occurs at a frequency 4 × 10^{14} s^{-1}. Find the length of the box. [Ans: 1.07 nm]

Average or expectation value of observables for a particle in 1 d box:

For a particle in a 1 D box, the expression for normalized wave function is:

$$\Psi_n = \sqrt{\frac{2}{a}}\, Sin\, \frac{n\pi x}{a}$$

So the expression for expectation value of a property A will be:

$$\langle A \rangle = \int_0^a \Psi^* \hat{A} \Psi dx$$

$$= \int_0^a \left(\sqrt{\frac{2}{a}}\, Sin\, \frac{n\pi x}{a} \right)^* \hat{A} \sqrt{\frac{2}{a}}\, Sin\, \frac{n\pi x}{a} dx$$

(a) Expectation value for position $\langle x \rangle$:

$$Required\ intergal: \int uvdx = u \int vdx - \int \frac{du}{dx}\left(\int vdx\right) dx$$

$$\langle x \rangle = \int_0^a \left(\sqrt{\frac{2}{a}}\, Sin\, \frac{n\pi x}{a} \right)^* x \sqrt{\frac{2}{a}}\, Sin\, \frac{n\pi x}{a} dx$$

$$= \frac{2}{a} \int_0^a Sin\, \frac{n\pi x}{a} x\ \ Sin\, \frac{n\pi x}{a} dx$$

$$= \frac{2}{a} \int_0^a x\, Sin^2\, \frac{n\pi x}{a} dx$$

Let

$$b = \frac{n\pi}{a}$$

So

$$\langle x \rangle = \frac{2}{a}\int_0^a x\, Sin^2\, bx\, dx$$

$$= \frac{2}{a}\int_0^a x\, \left[\frac{1 - Cos\ 2bx}{2}\right] dx$$

$$= \frac{2}{2a}\int_0^a x\,(1 - Cos\ 2bx)\, dx$$

$$= \frac{1}{a}\int_0^a x\, dx - \frac{1}{a}\int_0^a x\, Cos\ 2bx\, dx$$

$$= \frac{1}{a}\left[\frac{x^2}{2}\right]_0^a - \frac{1}{a}\left\{\left[\frac{x\, Sin\ 2bx}{2b}\right]_0^a - \int_0^a \frac{Sin\ 2bx}{2b}\, dx\right\}$$

$$= \frac{1}{a}\left[\frac{x^2}{2}\right]_0^a - \frac{1}{a}\left\{\frac{1}{2b}[x\, Sin\ 2bx]_0^a - \frac{1}{2b}\left[\left(-\frac{Cos\ 2bx}{2b}\right)\right]_0^a\right\}$$

$$= \frac{1}{a}\left[\frac{x^2}{2}\right]_0^a - \frac{1}{a}\frac{1}{2b}[x\, Sin\ 2bx]_0^a - \frac{1}{a}\frac{1}{2b^2}[\, Cos\ 2bx]_0^a$$

$$= \frac{1}{a}\left[\frac{x^2}{2}\right]_0^a - \frac{1}{2n\pi}\left[x\, Sin\ \frac{2n\pi x}{a}\right]_0^a - \frac{a}{2n^2\pi^2}\left[\, Cos\ \frac{2n\pi x}{a}\right]_0^a$$

$$= \frac{1}{a}\left[\left(\frac{a^2}{2} - 0\right) - (0 - 0) - \frac{a}{2n^2\pi^2}(1 - 1)\right]$$

$$= \frac{a}{2}$$

i.e. $\langle x \rangle = \frac{a}{2}$ implies that the average location of the particle is at the center of the box. Thee particle should spend as much time on one side as on the other, so its average position would be in the middle of the box.

(b) Expectation value for momentum $\langle p_x \rangle$:

$$\langle p_x \rangle = \int_0^a \left(\sqrt{\frac{2}{a}}\, Sin\ \frac{n\pi x}{a}\right)^* \hat{p}_x \sqrt{\frac{2}{a}}\, Sin\ \frac{n\pi x}{a} dx$$

$$= \int_0^a \left(\sqrt{\frac{2}{a}}\, Sin\ \frac{n\pi x}{a}\right)^* - i\hbar\frac{d}{dx}\sqrt{\frac{2}{a}}\, Sin\ \frac{n\pi x}{a} dx$$

$$= -i\hbar\frac{2}{a}\int_0^a Sin\ \frac{n\pi x}{a}\frac{d}{dx}\left(Sin\ \frac{n\pi x}{a}\right) dx$$

$$= -i\hbar\frac{2}{a}\int_0^a Sin\ \frac{n\pi x}{a}\left(\frac{n\pi}{a}\right)Cos\ \frac{n\pi x}{a}\ dx$$

$$= -\frac{i\hbar 2n\pi}{a^2}\int_0^a Sin\ \frac{n\pi x}{a}Cos\ \frac{n\pi x}{a}\ dx$$

$$= -\frac{i\hbar 2n\pi}{2a^2}\int_0^a 2\ Sin\ \frac{n\pi x}{a}Cos\ \frac{n\pi x}{a}\ dx$$

$$= -\frac{i\hbar n\pi}{a^2}\int_0^a Sin\ \frac{2n\pi x}{a}\ dx$$

$$= -\frac{i\hbar n\pi}{a^2}\times\left(-\frac{a}{2n\pi}\right)\left[Cos\ \frac{2n\pi x}{a}\right]_0^a$$

$$= -\frac{i\hbar n\pi}{a^2}\times\left(-\frac{a}{2n\pi}\right)[Cos\ 2n\pi - Cos\ 0]$$

$$= -\frac{i\hbar n\pi}{a^2}\times\left(-\frac{a}{2n\pi}\right)[1-1]$$

$$= 0$$

$\langle p_x\rangle = 0$ implies that the particle is likely to be moving equally in both + x and –x direction.

Q. Show that for a particle in 1 D box show that the average value of momentum along x - axis is zero.

(c) Expectation value for $\langle p_x^2\rangle$:

$$\langle p_x^2\rangle = \int_0^a \left(\sqrt{\frac{2}{a}}\ Sin\ \frac{n\pi x}{a}\right)^* \hat{p}_x^2 \sqrt{\frac{2}{a}}\ Sin\ \frac{n\pi x}{a}dx$$

$$= \int_0^a \left(\sqrt{\frac{2}{a}}\ Sin\ \frac{n\pi x}{a}\right)^* - \hbar^2\frac{d^2}{dx^2}\sqrt{\frac{2}{a}}\ Sin\ \frac{n\pi x}{a}dx$$

$$= -\frac{2\hbar^2}{a}\int_0^a Sin\ \frac{n\pi x}{a}\ \frac{d^2}{dx^2}\left(Sin\ \frac{n\pi x}{a}\right)dx$$

$$= -\frac{2\hbar^2}{a}\int_0^a Sin\frac{n\pi x}{a}\left(-\frac{n^2\pi^2}{a^2}\right)Sin\ \frac{n\pi x}{a}\ dx$$

$$= -\frac{2\hbar^2}{a}\left(-\frac{n^2\pi^2}{a^2}\right)\int_0^a Sin\frac{n\pi x}{a}\ Sin\ \frac{n\pi x}{a}\ dx$$

$$= \frac{2n^2\hbar^2\pi^2}{a^3}\int_0^a Sin^2\frac{n\pi x}{a}\ dx$$

$$= \frac{2n^2\hbar^2\pi^2}{2a^3}\int_0^a 2\,Sin^2\frac{n\pi x}{a}\;\;dx$$

$$= \frac{n^2\hbar^2\pi^2}{a^3}\int_0^a \left(1 - Cos\;\frac{2n\pi x}{a}\right)\;dx$$

$$= \frac{n^2\hbar^2\pi^2}{a^3}\left[[x]_0^a - \frac{a}{2n\pi}\left[Sin\;\frac{2n\pi x}{a}\right]_0^a\right]$$

$$= \frac{n^2\hbar^2\pi^2}{a^3}\times a$$

$$= \frac{n^2\hbar^2\pi^2}{a^2}$$

$$= \frac{n^2h^2}{4a^2}$$

$$= \frac{n^2h^2 \times 2m}{4a^2 \times 2m}$$

$$= 2m \times \frac{n^2h^2}{48a^2}$$

$$= 2mE$$

(d) Expectation value for total energy $\langle E\rangle$:

We know for a particle in 1 D box: V = 0, So E = T i.e. $\widehat{H} = \widehat{T}$

Now

$$\langle E\rangle = \int_0^a \left(\sqrt{\frac{2}{a}}\;Sin\;\frac{n\pi x}{a}\right)^* \widehat{H}\sqrt{\frac{2}{a}}\;Sin\;\frac{n\pi x}{a}dx$$

$$= \int_0^a \left(\sqrt{\frac{2}{a}}\;Sin\;\frac{n\pi x}{a}\right)^* - \frac{\hbar^2}{2m}\frac{d^2}{dx^2}\sqrt{\frac{2}{a}}\;Sin\;\frac{n\pi x}{a}dx$$

$$= -\frac{\hbar^2}{2m}\times\frac{2}{a}\int_0^a Sin\;\frac{n\pi x}{a}\;\frac{d^2}{dx^2}\left(Sin\;\frac{n\pi x}{a}\right)dx$$

$$= -\frac{\hbar^2}{ma}\times\left(-\frac{n^2\pi^2}{a^2}\right)\int_0^a Sin^2\;\frac{n\pi x}{a}\;dx$$

$$= \frac{n^2h^2}{4ma^3}\int_0^a Sin^2\;\frac{n\pi x}{a}\;dx$$

$$= \frac{n^2h^2}{8ma^3}\int_0^a 2\,Sin^2\;\frac{n\pi x}{a}\;dx$$

$$= \frac{n^2h^2}{8ma^3}\int_0^a \left(1 - Cos\ \frac{2n\pi x}{a}\right)\ dx$$

$$= \frac{n^2h^2}{8ma^3}\left[[x]_0^a - \frac{a}{2n\pi}\left[Sin\ \frac{2n\pi x}{a}\right]_0^a\right]$$

$$= \frac{n^2h^2}{8ma^3} \times a$$

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

i.e. $\langle E\rangle = \langle T\rangle = \frac{n^2h^2}{8ma^2}$

Q. A particle of mass m is moving in a box of length “a”, where potential energy is zero. Calculate the average kinetic energy of the particle.

Variance (σ^2) and standard deviation(σ):

Variance of a measurement of property say “y” is defined as:

$$\sigma_y^2 = \langle y^2\rangle - \langle y\rangle^2$$

The square root of variance is known as standard deviation:

i.e.

$$\sigma_y = \left(\sigma_y^2\right)^{\frac{1}{2}} = \left(\langle y^2\rangle - \langle y\rangle^2\right)^{\frac{1}{2}}$$

Uncertainty Principle from expectation values of 1 D box:

For a particle in 1 D box:

$$(i)\ \langle x\rangle = \frac{a}{2}, so\ \langle x\rangle^2 = \frac{a^2}{4}$$

$$(ii)\ \langle x^2\rangle = \frac{2}{a}\int_0^a x^2 sin^2\frac{n\pi x}{a}dx$$

$$= \left(\frac{a}{2\pi n}\right)^2\left(4\frac{\pi^2n^2}{3} - 2\right)$$

$$= \frac{a^2}{3} - \frac{a^2}{2\pi^2n^2}$$

$$(iii)\ \langle p_x\rangle = 0$$

And

$$(iv)\ \langle p_x^2\rangle = \frac{n^2h^2}{4a^2}$$

Now, uncertainty in position is simply the standard deviation in position. i.e.

$$\Delta x = \sigma_x = \left(\langle x^2\rangle - \langle x\rangle^2\right)^{\frac{1}{2}}$$

$$= \left[\left(\frac{a^2}{3} - \frac{a^2}{2\pi^2n^2}\right) - \frac{a^2}{4}\right]^{\frac{1}{2}}$$

$$= \left[\left(\frac{a^2}{12} - \frac{a^2}{2\pi^2 n^2}\right)\right]^{\frac{1}{2}}$$

$$= \left[\left(\frac{a}{2\pi n}\right)^2 \left(\frac{\pi^2 n^2}{3} - 2\right)\right]^{\frac{1}{2}}$$

$$= \left(\frac{a}{2\pi n}\right)\left[\left(\frac{\pi^2 n^2}{3} - 2\right)\right]^{\frac{1}{2}}$$

Similarly, uncertainty in momentum is simply the standard deviation in momentum i.e.

$$\Delta p_x = \sigma_{p_x} = \left(\langle p_x^2\rangle - \langle p_x\rangle^2\right)^{\frac{1}{2}}$$

$$= \left[\left(\frac{n^2 h^2}{4a^2}\right) - 0\right]^{\frac{1}{2}}$$

$$= \frac{nh}{2a}$$

Now

$$\Delta x \Delta p_x = \sigma_x \sigma_x$$

$$= \left(\frac{a}{2\pi n}\right)\left[\left(\frac{\pi^2 n^2}{3} - 2\right)\right]^{\frac{1}{2}}\left(\frac{nh}{2a}\right)$$

$$= \frac{h}{4\pi}\left[\left(\frac{\pi^2 n^2}{3} - 2\right)\right]^{\frac{1}{2}}$$

$$= \frac{\hbar}{2}\left[\left(\frac{\pi^2 n^2}{3} - 2\right)\right]^{\frac{1}{2}}$$

Since the term within square root is greater than 1, so we can write

$$\Delta x \Delta p_x > \frac{\hbar}{2}$$

i.e. the product of $\Delta x \Delta p_x$ for a particle in a box is in agreement with Heisenberg uncertainty principle as it is always greater than $\frac{\hbar}{2}$.

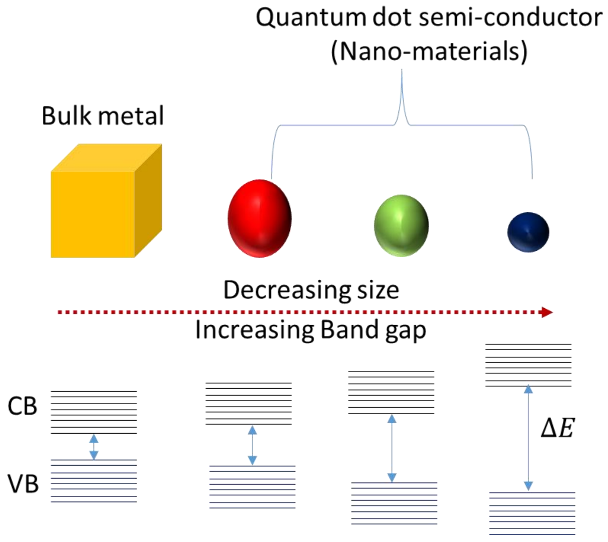
Application of particle in 1 D box model:

(1) Quantum confinement: If the diameter of a molecule is reduced to nano-meter size regime, it experiences electronic as well as optical properties which considerably differ from the properties of bulk materials. This effect is known as quantum confinement effects.

We know

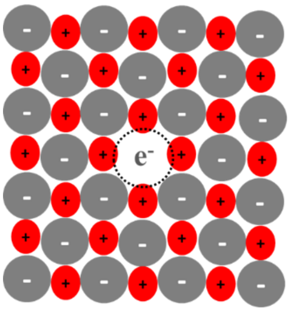
$$\Delta E = (2n+1)\frac{h^2}{8ma^2}$$

If the size of the material is reduced to nano scale regime, then the energy separation (ΔE) between adjacent energy levels get increases and hence a material which act as a metallic conductor in its bulk state now behave like a semi-conductor in its nano scale state.



Moreover, due to the increase in energy spacing as a result of size downscaling, the associated wavelength of absorption by the material of interest also changes and hence material in its nano scale regime shows different colour as compared to its bulk counterpart. For e.g. the colour of gold nano particle is purple instead of golden.

(2) Origin of F-center or colour center:



F-center is an anion vacancy containing a free electron surrounded by several cationic species. The electron is free to move within the hole but it cannot escae beyond the hole as it has to cross the infinite potential energy barrier of surrounding cationic Species. So it a classic example of particle in 1 D box and hence energy of the trapped electron is quantised. Therefore, a series of energy levels are available for the electron within this box and the energy required to transfer from one level to another falls in the visible part of the electromagnetic spectrum leading to its colouration.

(3) Free electron model of conjugated polyenes:

In conjugated polyenes, the mobile π electrons are free to move through the entire length of the molecule via conjugation, but the electrons cannot escape beyond its molecular length. So the π electrons is said to have a finite potential energy when it is "on" the molecule and an infinite potential energy when it is "off" the molecule. This model is very much analogous to the particle in a box model and is known as free electron model.

In molecules, the electronic transition takes place from highest occupied molecular orbital (HOMO) to lowest unoccupied molecular orbital (LUMO). Now aufbau principle says that the π electrons must be filled in the π molecular orbitals starting from the lowest energy level and Pauli's principle says that each π molecular orbital accommodate at max two electrons. Now if "N" is the number of atoms in conjugation or number of total π electrons, then the quantum number corresponding to HOMO will be $\frac{N}{2}$. So the quantum for the LUMO which lies in the next higher energy level will be $\frac{N}{2}+1$.

Now

$$\Delta E = \frac{h^2}{8ma^2}\left[\left(\frac{N}{2}+1\right)^2 - \left(\frac{N}{2}\right)^2\right]$$

$$= \frac{h^2}{8ma^2}(N+1)$$

And the expression for the corresponding wave length is:

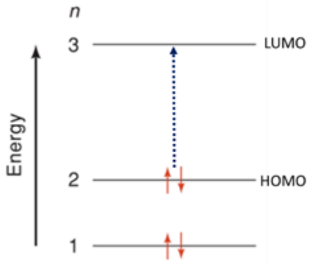
$$\lambda = \frac{hc}{\Delta E} = \frac{8ma^2c}{h(N+1)}$$

Q. Treating π electrons in butadiene as a particle in 1 D box, calculate the lowest absorption frequency of the absorbed radiation, given that the length of the butadiene molecule to be 0.56 nm.

Ans:

Butadiene has 4 carbon atoms or 4 π electrons,

So in the ground state, the quantum number for HOMO $= \frac{4}{2} = 2$ and the quantum number for LUMO $= \frac{4}{2} + 1 =$



Now

$$\Delta E = \frac{h^2}{8ma^2}(N+1)$$

$$= \frac{(6.63 \times 10^{-34}\, Js)^2}{8 \times 9.1 \times 10^{-31} kg \times (0.56 \times 10^{-9}\, m)^2}(4+1)$$

$$= 9.63 \times 10^{-19} J$$

Now

$$\vartheta = \frac{\Delta E}{h}$$

$$= \frac{9.63 \times 10^{-19} J}{6.63 \times 10^{-34} Js}$$

$$= 1.45 \times 10^{15}\, Hz$$

Q. β-Carotene is a linear polyene in which 10 single and 11 double bonds alternate along a chain of 22 carbon atoms. If each carbon-carbon bond length is taken to be 140 pm, the length of the molecular box in β-carotene is 2.94 nm. Estimate the wavelength of the light absorbed by this molecule when it undergoes a transition from its ground state to the next higher excited state

Ans:

Given

N = 22, $a = 2.94\ nm\ or\ 2.94\ \times 10^{-9}\ m$

Now

$$\Delta E = \frac{h^2}{8ma^2}(N+1)$$

$$= \frac{(6.63 \times 10^{-34}\ Js)^2}{8 \times 9.1 \times 10^{-31} kg \times (2.94\ \times 10^{-9}\ m)^2}(22+1)$$

$$= 1.60\ \times 10^{-19} J$$

Now

$$\lambda = \frac{hc}{\Delta E}$$

$$= \frac{6.63 \times 10^{-34}\ Js \times 3 \times 10^{8}\ ms^{-1}}{1.60\ \times 10^{-19} J}$$

$$= 12.40 \times 10^{-7} m$$

$$= 1240\ nm$$

Separation of variables:

If a function is a product of "n" numbers of functions each depending on just one variable, then we can write:

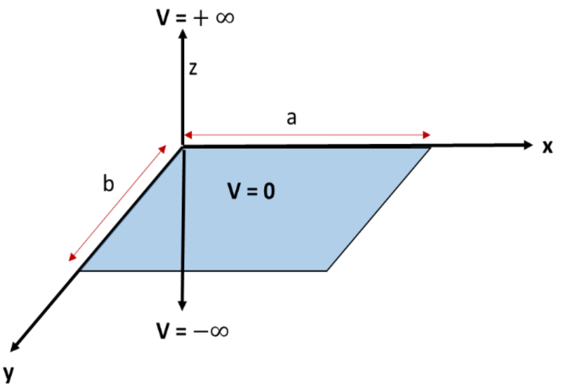
$$\Psi(x_1, x_{2,} x_3 \ldots x_n) = f(x_1) \times g(x_2) \times h(x_3) \ldots . \times z(x_n)$$

For example, the 2 D wave function $\Psi(x, y)$ can be written as product of two functions each depending one just one co-ordinate as:

$$\Psi(x, y) = X(x)Y(y)$$

where X(x) is a function only of x (that is, independent of y), Y(y) is a function solely of y (that is, independent of x).

Particle in a two dimensional box:



In the model for a particle in a two-dimensional box, the particle is free to move about in two independent Cartesian coordinates, x and y having dimensions "a" and "b" respectively. The potential energy is zero when the particle is in the planar box and infinite elsewhere.

i.e.

$$V(x,y) = 0\ for\ 0 \le x \le a;\ 0 \le y \le b$$

$$= 0, otherwise$$

Now the corresponding Schrodinger equation for 2D space is:

$$\hat{H}\Psi(x,y) = E\Psi(x,y)$$

$$=> -\frac{ħ^2}{2m}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}\right)\Psi(x,y) = E\Psi(x,y) --(1)$$

From separation of variables we have

$$\Psi(x,y) = X(x)Y(y)$$

Dropping the parenthetical variables on the functions we can write

$$\Psi(x,y) = XY --(2)$$

From equation (1) and (2), we have

$$-\frac{ħ^2}{2m}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}\right)XY = EXY$$

$$=> \left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}\right)XY = -\frac{2mE}{ħ^2}XY$$

$$=> \frac{\partial^2}{\partial x^2}(XY)+\frac{\partial^2}{\partial y^2}(XY) = -\frac{2mE}{ħ^2}XY$$

$$=> Y\frac{\partial^2 X}{\partial x^2}+X\frac{\partial^2 Y}{\partial y^2} = -\frac{2mE}{ħ^2}XY$$

Dividing both sided by XY, we have

$$\frac{1}{X}\frac{\partial^2 X}{\partial x^2}+\frac{1}{Y}\frac{\partial^2 Y}{\partial y^2} = -\frac{2mE}{ħ^2}$$

The L.H.S. of the above equation is the summation of two terms and each term is a function of only one variable. Since, the summation is a constant, so it is possible only if each contributing term in L.H.S. is also a constant quantity. Now let

$$\frac{1}{X}\frac{\partial^2 X}{\partial x^2} = -\frac{2mE_x}{ħ^2}$$

$$=> \frac{1}{X}\frac{\partial^2 X}{\partial x^2}+\frac{2mE_x}{ħ^2} = 0 --(3)$$

Similarly,

$$\frac{1}{Y}\frac{\partial^2 Y}{\partial Y^2} = -\frac{2mE_y}{ħ^2}$$

$$=> \frac{1}{Y}\frac{\partial^2 Y}{\partial y^2}+\frac{2mE_y}{ħ^2} = 0 --(4)$$

Clearly,

$$E = E_x + E_y$$

Equation (3) and (4) has the same form as the Schrödinger equation for the one-dimensional particle-in-a box. Therefor solutions for these equations can be written as:

$$X(x) = \sqrt{\frac{2}{a}}\, Sin\, \frac{n_x \pi x}{a}$$

The corresponding energy expressions is:

$$E_x = \frac{n_x^2 h^2}{8ma^2}$$

And

$$Y(y) = \sqrt{\frac{2}{b}}\, Sin\, \frac{n_y \pi y}{b}$$

The corresponding energy expressions is:

$$E_y = \frac{n_y^2 h^2}{8mb^2}$$

Since

$$\Psi(x, y) = X(x)Y(y)$$

So the expression for complete wave function is:

$$\Psi(x, y) = \sqrt{\frac{2}{a}}\, Sin\, \frac{n_x \pi x}{a} \sqrt{\frac{2}{b}}\, Sin\, \frac{n_y \pi y}{b}$$

$$= \sqrt{\frac{4}{ab}}\; Sin\, \frac{n_x \pi x}{a} Sin\, \frac{n_y \pi y}{b}$$

If the 2 D box is a square, then $a = b$, in such cases we can write:

$$\Psi(x, y) = \frac{2}{a}\; Sin\, \frac{n_x \pi x}{a} Sin\, \frac{n_y \pi y}{a}$$

Again

$$E = E_x + E_y$$

So the expression for total energy is:

$$E_{n_x, n_y} = \frac{n_x^2 h^2}{8ma^2} + \frac{n_y^2 h^2}{8mb^2}$$

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

If the 2 D box is a square, then $a = b$, in such cases we can write:

$$E_{n_x, n_y} = \frac{h^2}{8ma^2}\left(n_x^2 + n_y^2\right)$$

Q. Derive the expression for the energy and wave function of a particle in a two dimensional box.

Ground state wave function and ZPE for a particle in 2 D box:

For a particle in 2 D box, the ground state is specified at $n_x = 1$, $n_y = 1$

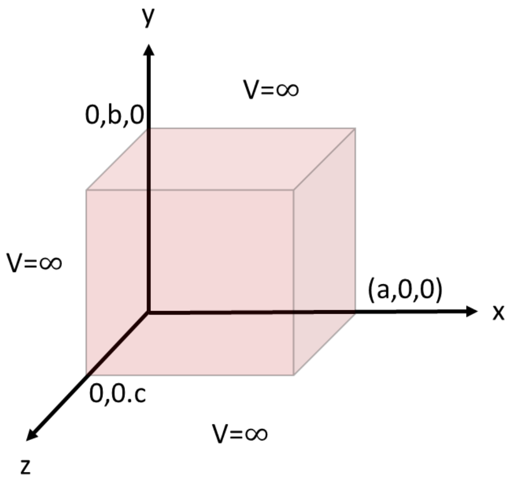
So the expression for ground state wave function is

$$\Psi(1,1) = \sqrt{\frac{4}{ab}}\, Sin\, \frac{\pi x}{a}\, Sin\, \frac{\pi y}{b}$$

And expression for ZPE:

$$E_{11} = \frac{h^2}{8m}\left(\frac{1}{a^2} + \frac{1}{b^2}\right)$$

Particle in a three dimensional box:



Consider a particle of mass "m" confined in a box of dimensions a, b, and c in the x, y, and z directions, respectively. The potential energy inside the box is assumed to be zero and it is infinite outside of the box.

i.e.

$$V(x,y,z) = 0\ for\ 0 \le x \le a;\ 0 \le y \le b;\ 0 \le z \le c$$

$$= \infty, otherwise$$

Now the corresponding Schrodinger equation for 3D space is:

$$\hat{H}\Psi(x,y,z) = E\Psi(x,y,z)$$

$$=> -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right)\Psi(x,y,z) = E\Psi(x,y,z) --(1)$$

From separation of variables we have

$$\Psi(x,y,z) = X(x)Y(y)Z(z)$$

Dropping the parenthetical variables on the functions we can write

$$\Psi(x,y,z) = XYZ --(2)$$

From equation (1) and (2), we have

$$-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)XYZ = EXYZ$$

$$=> \left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)XYZ = -\frac{2mE}{\hbar^2}XYZ$$

$$=> \frac{\partial^2}{\partial x^2}(XYZ)+\frac{\partial^2}{\partial y^2}(XYZ)+\frac{\partial^2}{\partial z^2}(XYZ) = -\frac{2mE}{\hbar^2}XYZ$$

$$=> YZ\frac{\partial^2 X}{\partial x^2}+XZ\frac{\partial^2 Y}{\partial y^2}+XY\frac{\partial^2 Z}{\partial z^2} = -\frac{2mE}{\hbar^2}XYZ$$

Dividing both sided by XYZ, we have

$$\frac{1}{X}\frac{\partial^2 X}{\partial x^2}+\frac{1}{Y}\frac{\partial^2 Y}{\partial y^2}+\frac{1}{Z}\frac{\partial^2 Z}{\partial z^2} = -\frac{2mE}{\hbar^2}$$

The L.H.S. of the above equation is the summation of three terms and each term is a function of only one variable. Since, the summation (in R.H.S.) is a constant, so it is possible only if each contributing term in L.H.S. is also a constant quantity. Now let

$$\frac{1}{X}\frac{\partial^2 X}{\partial x^2} = -\frac{2mE_x}{\hbar^2}$$

$$=> \frac{1}{X}\frac{\partial^2 X}{\partial x^2}+\frac{2mE_x}{\hbar^2} = 0 --(3)$$

Similarly,

$$\frac{1}{Y}\frac{\partial^2 Y}{\partial Y^2} = -\frac{2mE_y}{\hbar^2}$$

$$=> \frac{1}{Y}\frac{\partial^2 Y}{\partial y^2}+\frac{2mE_y}{\hbar^2} = 0 --(4)$$

And

$$\frac{1}{Z}\frac{\partial^2 Z}{\partial z^2} = -\frac{2mE_Z}{\hbar^2}$$

$$=> \frac{1}{Z}\frac{\partial^2 Z}{\partial z^2}+\frac{2mE_Z}{\hbar^2} = 0 --(5)$$

Clearly,

$$E = E_x + E_y + E_z$$

Equation (3), (4) and (5) has the same form as the Schrödinger equation for the one-dimensional particle-in-a box. Therefor solutions for these equations can be written as:

$$X(x) = \sqrt{\frac{2}{a}}\,Sin\,\frac{n_x\pi x}{a}$$

The corresponding energy expressions is:

$$E_x = \frac{n_x^2 h^2}{8ma^2}$$

Similarly

$$Y(y) = \sqrt{\frac{2}{b}}\, Sin\, \frac{n_y \pi y}{b}$$

The corresponding energy expressions is:

$$E_y = \frac{n_y^2 h^2}{8mb^2}$$

And

$$Z(z) = \sqrt{\frac{2}{c}}\, Sin\, \frac{n_z \pi y}{b}$$

The corresponding energy expressions is:

$$E_z = \frac{n_z^2 h^2}{8mc^2}$$

Since

$$\Psi(x, y, z) = X(x)Y(y)Z(z)$$

So the expression for complete wave function is:

$$\Psi(x, y, z) = \sqrt{\frac{2}{a}}\, Sin\, \frac{n_x \pi x}{a} \sqrt{\frac{2}{b}}\, Sin\, \frac{n_y \pi y}{b} \sqrt{\frac{2}{c}}\, Sin\, \frac{n_z \pi y}{c}$$

$$= \sqrt{\frac{8}{abc}}\, Sin\, \frac{n_x \pi x}{a} Sin\, \frac{n_y \pi y}{b} Sin\, \frac{n_z \pi y}{c}$$

Again

$$E = E_x + E_y + E_z$$

So the expression for total energy is:

$$E_{n_{x,}n_{y,}n_z} = \frac{n_x^2 h^2}{8ma^2} + \frac{n_y^2 h^2}{8mb^2} + \frac{n_z^2 h^2}{8mc^2}$$

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

ZPE for a particle in 3D box:

The ground state with lowest possible energy (ZPE) corresponds to the state with n_x=1, n_y=1 and n_z=1 i.e.

$$E_{111} or\ E_{ZPE} = \frac{h^2}{8m}\left(\frac{1}{a^2} + \frac{1}{b^2} + \frac{1}{c^2}\right)$$

Q. Find the expression for total energy of a particle with mass “m” having co-ordinate (x, y, z) Or A particle of mass “m” is moving within a box of lengths a, b and c along x, y and z axis respectively. The potential energy within the box is zero and outside the box it is infinity. Solve the time independent Schrodinger equation for the particle to get the values of the wave function and the energy.

Q. Find the lowest kinetic energy of an electron in a 3D box of lengths 0.1×10^{-13} cm, 1.5×10^{-13} cm and 2×10^{-13} cm assuming potential energy to be zero.

Ans:

Since the potential energy is zero, so the total energy will be equal to the kinetic energy.

Now for the lowest energy state $n_x=1$, $n_y=1$ and $n_z=1$

So

$$E_{111} = \frac{h^2}{8m}\left(\frac{1}{a^2}+\frac{1}{b^2}+\frac{1}{c^2}\right)$$

$$= \frac{(6.63\times10^{-34}Js)^2}{8\times9.1\times10^{-31}kg}\left(\frac{1}{(0.1\times10^{-15}m)^2}+\frac{1}{(1.5\times10^{-15}m)^2}+\frac{1}{(2\times10^{-15}\,m)^2}\right)$$

$$= 6.067\times10^{-8}J$$

[Self-test]. Find the lowest energy of a particle of mass 9.0 X 10^{-31} kg enclosed in a 3 D box of lengths 1.0×10^{-15} m, 2.0×10^{-15} m and 3.0×10^{-15} m assuming its potential energy to be zero.

State: In quantum mechanics a state is defined by a set of quantum numbers namely n_x, n_y and n_z which specify an independent wave function. For example, for $n_x=1$, $n_y=1$ and $n_z=1$, the state is defined as "111" which corresponds to the wave function $\Psi_{111} = \sqrt{\frac{2}{a}}\,Sin\,\frac{\pi x}{a}\sqrt{\frac{2}{b}}\,Sin\,\frac{\pi y}{b}\sqrt{\frac{2}{c}}\,Sin\,\frac{\pi y}{c}$.

Symmetry, degenerate state and degree of degeneracy of energy level:

If different states of a system as defined by different wave functions corresponds to same energy level, then they are said to be degenerate state. The number of states which occupy the same energy level is called the degree of degeneracy (g) of that energy level. If there is only one state in an energy level then it is called non-degenerate i.e. g =1, if there are two states corresponding to same energy level, then the energy level is called twofold (or doubly) degenerate i.e. g=2, if there are three states, it is threefold (or triply) degenerate i.e. g =3 and so on.

Elaboration with reference to particle in a 3D box:

For a particle in 3-D box, the total energy depends on not only the quantum numbers n_x, n_y, and n_z but also on the individual dimensions of the box a, b, and c. Now a special case occur for a cubic box where the sides of the box are equal i.e. $a = b = c$. In such cases we have

$$E_{n_x,n_y,n_z} = \frac{h^2}{8ma^2}\left(n_x^2+n_y^2+n_z^2\right)$$

Now for the lowest energy level, only one state is possible as defined by $n_x=1$, $n_y=1$ and $n_z=1$.

$$\Psi_{111} = \sqrt{\frac{8}{a^3}}\;Sin\,\frac{\pi x}{a}Sin\,\frac{\pi y}{a}Sin\,\frac{\pi y}{a}\;and\;E_{111} = \frac{3h^2}{8ma^2}$$

For the next higher energy level, we have three possible state viz. $n_x=2$, $n_y=1$, $n_z=1$ or $n_x=1$, $n_y=2$, $n_z=1$ or $n_x=1$, $n_y=1$, $n_z=2$. The corresponding wavelength and energy expressions are:

$$\Psi_{211} = \sqrt{\frac{8}{a^3}}\;Sin\,\frac{2\pi x}{a}Sin\,\frac{\pi y}{a}Sin\,\frac{\pi y}{a}\;and\;E_{211} = \frac{6h^2}{8ma^2}$$

$$\Psi_{121} = \sqrt{\frac{8}{a^3}}\;Sin\,\frac{\pi x}{a}Sin\,\frac{2\pi y}{a}Sin\,\frac{\pi y}{a}\;and\;E_{211} = \frac{6h^2}{8ma^2}$$

$$\Psi_{112} = \sqrt{\frac{8}{a^3}}\ Sin\ \frac{\pi x}{a} Sin\ \frac{\pi y}{a} Sin\ \frac{2\pi y}{a}\ and\ E_{112} = \frac{6h^2}{8ma^2}$$

Although the states 211, 121 and 112 represents different wave functions they correspond to the same energy level namely $\frac{6h^2}{8ma^2}$. So the states 211, 121 and 112 are said to be degenerate and degree of degeneracy is three (g = 3).

This types of detergency occur only when the general rectangular box $(a \neq b \neq c)$ becomes a cube $(a = b = c)$ and degeneracy is lifted when symmetry is destroyed by making sides of the box different. So this might be considered degeneracy by symmetry. So in general we expect degeneracies to be present in systems that have some element of symmetry and hence have high degree of symmetry. So for a particle in a 3 D box the degeneracy can be lowered or lifted by simply lowering the symmetry i.e. by making distortion to the system via chanting the edges of the box.

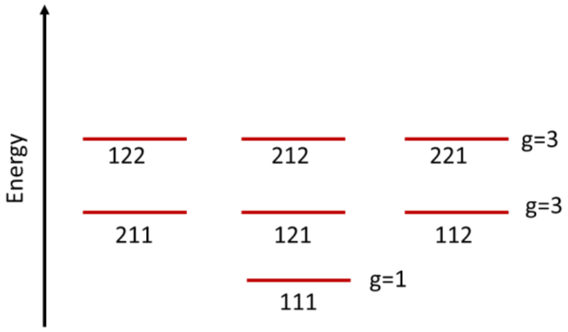


Fig: Energies of the lowest few states of a particle in a cubic box along with the corresponding degree of degeneracies.

Q. Use the results of particle in a 3 D box to explain degeneracy.

Q. What do you mean degree of degeneracy? How degeneracy of a system can be lowered?

Accidental degeneracy:

Sometimes degeneracy is encountered where energy levels are not apparently related by symmetry. This is the case when all the dimensions are not equivalent but one of the dimensions is an integral multiple of other (such as a =2b). Degeneracy of this kind is known as accidental degeneracy. For example, 22 and 41 states of a particle in 2 D box where a=2b are accidently degenerate:

$$\Psi(2,2) = \sqrt{\frac{4}{2b^2}}\ Sin\ \frac{2\pi x}{2b}\ Sin\ \frac{2\pi y}{b}\ and\ E_{22} = \frac{h^2}{8m}\left(\frac{2^2}{(2b)^2} + \frac{2^2}{b^2}\right) = \frac{5h^2}{8mb^2}$$

$$\Psi(4,1) = \sqrt{\frac{4}{2b^2}}\ Sin\ \frac{4\pi x}{2b}\ Sin\ \frac{\pi y}{b}\ and\ E_{41} = \frac{h^2}{8m}\left(\frac{4^2}{(2b)^2} + \frac{1^2}{b^2}\right) = \frac{5h^2}{8mb^2}$$

i.e. although the state 22 and 41 are symmetrically not equivalent, they possess the same energy of $\frac{5h^2}{8mb^2}$. So the state 22 and 44 are accidently degenerate.

Similarly, for a cubical box, although the states 333 and 511 have no common quantum numbers in their corresponding wave functions, but their energy values are exactly the same.

$$E_{333} = \frac{h^2}{8ma^2}(3^2 + 3^2 + 3^2) = \frac{27h^2}{8ma^2}$$

$$E_{333} = \frac{h^2}{8ma^2}(5^2 + 1^2 + 1^2) = \frac{27h^2}{8ma^2}$$

So the states 333 and 511 are said to be accidentally degenerate.

Q. For a particle in a 3D box with $L_x = L_y = L_{\frac{z}{2}}$, what would be the energy when n_x=1, n_y=2 and n_z=2 and when n_x=1, n_y=1 and n_z= 4.

Ans:

We know

$$E_{n_{x,}n_{y,}n_z} = \frac{h^2}{8m}\left(\frac{n_x^2}{a^2} + \frac{n_y^2}{b^2} + \frac{n_z^2}{c^2}\right)$$

So

$$E_{122} = \frac{h^2}{8m}\left(\frac{1}{\left(\frac{L_z}{2}\right)^2} + \frac{2^2}{\left(\frac{L_z}{2}\right)^2} + \frac{2^2}{(L_z)^2}\right)$$

$$= \frac{h^2}{8m}\left(\frac{4}{{L_z}^2} + \frac{16}{{L_z}^2} + \frac{4}{(L_z)^2}\right)$$

$$= \frac{3h^2}{mL_z}$$

And

$$E_{114} = \frac{h^2}{8m}\left(\frac{1}{\left(\frac{L_z}{2}\right)^2} + \frac{1}{\left(\frac{L_z}{2}\right)^2} + \frac{4^2}{(L_z)^2}\right)$$

$$= \frac{h^2}{8m}\left(\frac{4}{{L_z}^2} + \frac{4}{{L_z}^2} + \frac{16}{(L_z)^2}\right)$$

$$= \frac{3h^2}{mL_z}$$

i.e. $E_{122} = E_{114}$, so the given states are accidently degenerate.

Q. Find the degree of degeneracy of the following energy levels: $(a)\,\frac{9\,h^2}{8ma^2}$ $(b)\,\frac{12h^2}{8ma^2}$ $(c)\,\frac{14\,h^2}{8ma^2}$ $(d)\,\frac{17h^2}{8ma^2}$

Ans:

(a)

$$E_{n_{x,}n_{y,}n_z} = \frac{9\,h^2}{8ma^2}$$

$$=> \frac{h^2}{8ma^2}\left(n_x^2 + n_y^2 + n_z^2\right) = \frac{9\,h^2}{8ma^2}$$

$$=> n_x^2 + n_y^2 + n_z^2 = 9$$

Now

$$2^2 + 2^2 + 1^2 = 9$$

So the possible degenerate states are 221, 212, 122. i.e. g =3 for the energy level $\frac{9\,h^2}{8ma^2}$.

(b)

$$E_{n_{x,}n_{y,}n_z} = \frac{12\,h^2}{8ma^2}$$

$$=> \frac{h^2}{8ma^2}\left(n_x^2 + n_y^2 + n_z^2\right) = \frac{12\,h^2}{8ma^2}$$

$$=> n_x^2 + n_y^2 + n_z^2 = 12$$

Now

$$2^2 + 2^2 + 2^2 = 12$$

So the only possible state is 222. i.e. g =1 for the energy level $\frac{12\,h^2}{8ma^2}$.

(c)

$$E_{n_{x,}n_{y,}n_z} = \frac{14\,h^2}{8ma^2}$$

$$=> \frac{h^2}{8ma^2}\left(n_x^2 + n_y^2 + n_z^2\right) = \frac{14\,h^2}{8ma^2}$$

$$=> n_x^2 + n_y^2 + n_z^2 = 14$$

Now

$$3^2 + 2^2 + 1^2 = 14$$

So the possible degenerate states are 321, 231, 213,123, 132 and 312 i.e. g =6 for the energy level $\frac{14\,h^2}{8ma^2}$

(d)

$$E_{n_{x,}n_{y,}n_z} = \frac{17\,h^2}{8ma^2}$$

$$=> \frac{h^2}{8ma^2}\left(n_x^2 + n_y^2 + n_z^2\right) = \frac{17\,h^2}{8ma^2}$$

$$=> n_x^2 + n_y^2 + n_z^2 = 17$$

Now

$$3^2 + 2^2 + 2^2 = 17$$

So the possible degenerate states are 322, 232 and 223. i.e. g =3 for the energy level $\frac{17\,h^2}{8ma^2}$.

Q. Far a particle in a cubic box of edge length “a”

(a) How many states have energies in the range 0 to $\frac{16h^2}{8ma^2}$

(b) How many energy level lies in this range?

(c) Draw the energy level diagram indicating the degenerate states and the corresponding degree of degeneracy.

Ans:

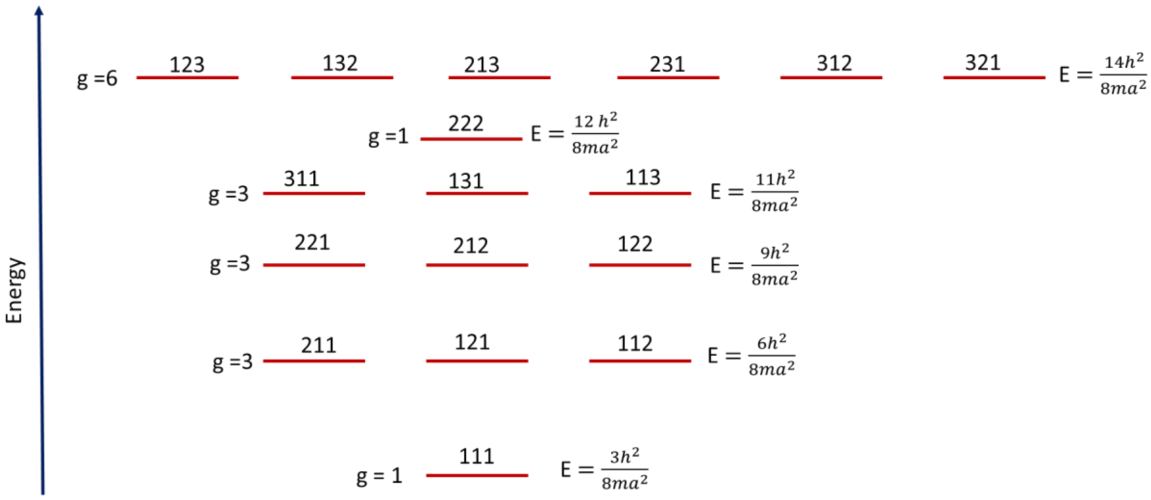
(a)

Quantum number	Possible states	Degeneracy (g)	Energy level
1, 1, 1 (G.S.)	111	1	$\frac{3\,h^2}{8ma^2}$
2, 1, 1 (1st E.S.)	211, 121, 112	3	$\frac{6\,h^2}{8ma^2}$
2,2, 1 (2nd E.S.)	221, 212, 122	3	$\frac{9\,h^2}{8ma^2}$
2, 2, 2	222	1	$\frac{12\,h^2}{8ma^2}$
3, 1, 1	311, 113, 131	3	$\frac{11\,h^2}{8ma^2}$
3,2,1	123, 132, 213, 231, 321, 312	6	$\frac{14\,h^2}{8ma^2}$

i.e. the total number of states in the energy range 0 to $\frac{16\,h^2}{8ma^2}$ is 17

(b) Number of energy levels that lies within the given energy range is 6

(c)



Q. Let a cube of edge length 1.2 nm within which potential energy is zero contain 10 electrons. Considering ground state, explain with diagram how these electrons occupy different states. Calculate the ΔE for the 1st excited state of this system

Ans:

The energy expression for cubical box is:

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

$$= \frac{(6.63 \times 10^{-34} Js)^2}{8 \times 9.1 \times 10^{-31} kg \times (1.2 \times 10^{-9} m)^2}\left(n_x^2 + n_y^2 + n_z^2\right)$$

$$= \left(n_x^2 + n_y^2 + n_z^2\right) \times 4.1834 \times 10^{-20} J$$

The energy levels and distribution of electrons are as shown below:

Quantum numbers n_x	 n_y	 n_z	Energy (J)	Electron distribution
3	1	1	$(11) \times 4.1834 \times 10^{-20} J$	☐ ↑ ΔE
1	2	2	$(9) \times 4.1834 \times 10^{-20} J$	[↑] [↑] ☐
2	1	2		
2	2	1		
1	1	2	$(6) \times 4.1834 \times 10^{-20} J$	[↑↓] [↑↓] [↑↓]
1	2	1		
2	1	1		
1	1	1	$(3) \times 4.1834 \times 10^{-20} J$	[↑↓]

The electrons are distributed following:

(a) aufbau principle according to which the lowest energy levels are filled first.

(b) Pauli's exclusion principle which states that each energy level can accommodate maximum of 2 electrons

(c) Hund's rule which states that energy levels are singly filled before pairing

Now the 1st excited state is obtained when the electron in the triply degenerate level of energy $(9) \times 4.1834 \times 10^{-20} J$ is promoted to the non-degenerate level of energy $(11) \times 4.1834 \times 10^{-20} J$.

So

$$\Delta E = (11) \times 4.1834 \times 10^{-20} J - (9) \times 4.1834 \times 10^{-20} J$$

$$= 2 \times 4.1834 \times 10^{-20} J \text{ or } 8.366 \times 10^{-20} J$$

Q. Calculate the ground state energy of electron in (i) 1D box length 3 × 10^{-10} m and (ii) a cubical box of edge length 10^{-10} m in eV. Comment on feasibility of using this cubical box model for an electron in a H-atom.

Ans:

(a) For a particle in 1 D box, in ground state

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

$$= \frac{(6.63 \times 10^{-34} Js)^2}{8 \times 9.1 \times 10^{-31} kg \times (3 \times 10^{-10} m)^2}$$

$$= 0.0671 \times 10^{-17} J$$

$$= 4.19\ eV$$

(b) For a particle in 3 D box, in ground state

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

$$= \frac{(6.63 \times 10^{-34} Js)^2}{8 \times 9.1 \times 10^{-31} kg \times (1 \times 10^{-10} m)^2}(1+1+1)$$

$$= 1.81 \times 10^{-17}\, J$$

$$= 112\, eV$$

But the experimental ground state energy for H-atom is 13.6 eV. So this cubical model cannot be used for an electron in a H-atom

Q. For a particle in a 3 D box of dimensions $a = b \neq c$, find the energies of the particle with quantum numbers 1and 2 and hence indicate the degeneracies of the levels.

Ans:

With quantum number 1and 2, the possible states are 112,121,211,221 212 and 122

Now

$$E_{112} = \frac{h^2}{8m}\left(\frac{1}{a^2} + \frac{1}{a^2} + \frac{2^2}{c^2}\right) = \frac{h^2}{4m}\left(\frac{1}{a^2} + \frac{2}{c^2}\right)$$

$$E_{121} = \frac{h^2}{8m}\left(\frac{1}{a^2} + \frac{2^2}{a^2} + \frac{1}{c^2}\right) = \frac{h^2}{8m}\left(\frac{5}{a^2} + \frac{1}{c^2}\right)$$

$$E_{211} = \frac{h^2}{8m}\left(\frac{2^2}{a^2} + \frac{1}{a^2} + \frac{1}{c^2}\right) = \frac{h^2}{8m}\left(\frac{5}{a^2} + \frac{1}{c^2}\right)$$

$$E_{221} = \frac{h^2}{8m}\left(\frac{2^2}{a^2} + \frac{2^2}{a^2} + \frac{1}{c^2}\right) = \frac{h^2}{8m}\left(\frac{8}{a^2} + \frac{1}{c^2}\right)$$

$$E_{212} = \frac{h^2}{8m}\left(\frac{2^2}{a^2} + \frac{1}{a^2} + \frac{2^2}{c^2}\right) = \frac{h^2}{8m}\left(\frac{5}{a^2} + \frac{4}{c^2}\right)$$

$$E_{122} = \frac{h^2}{8m}\left(\frac{1}{a^2} + \frac{2^2}{a^2} + \frac{2^2}{c^2}\right) = \frac{h^2}{8m}\left(\frac{5}{a^2} + \frac{4}{c^2}\right)$$

Clearly, 112 and 221 states are non-degenerate, 121 and 211 states are doubly degenerate and 212 and 122 states are doubly degenerate.

Quantum mechanical tunnelling:

Tunnelling is a quantum mechanical phenomenon which denotes the penetration of a particle into a classically forbidden region or the passage of a particle through a potential energy barrier that is higher in energy than the particle's kinetic energy**.**

In particle in a 1 D box model, the particle is trapped within infinite potential energy barrier on both sides of the box to ensure that it cannot penetrate through the box. However, a new quantum-mechanical feature appears when the potential walls surrounding the particle were not infinitely high rather slightly higher than the kinetic energy possess by the particle. Let's consider a particle with kinetic energy "E" is approaching a potential barrier of "V" such that E < V. Classical physics predicts that such a particle with not have enough energy (E < V) cannot surmount the barrier and will not be able to reach to the other side, instead it will be reflected back by the barrier. However, quantum mechanics predicts wave character of particle which have probabilistic interpretation with the consequence that there is a finite probability that the particle will penetrate through the potential energy barrier and appear to the other side even though E < V. This is the so called tunnelling phenomena.

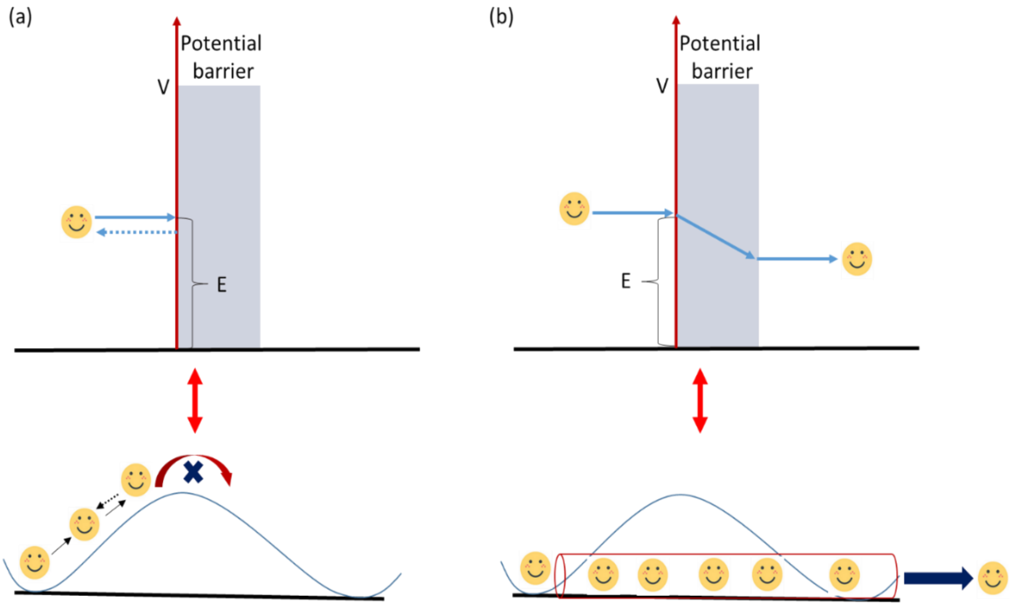


Fig: (a) Classically the particle with E < V will be reflected by the barrier and hence cannot make its journey to the other side (b) Quantum mechanically such a particle is tunnelled through the barrier and make it journey to the other side of the barrier.

A particle arriving from the left of the barrier (region I) has an oscillating wave function but inside the barrier (region II) the wave function decays exponentially rather than oscillates. Provided the barrier is not too wide the wave function emerges to the right, but with reduced amplitude; it then continues to oscillate once it is back in a region (region III) where it has zero potential energy. The probability of finding the particle is proportional to the square of the amplitude function. Since after tunnelling, the amplitude of the transmitted wave decreases, so transmission probability is very low. However, quantum tunnelling does not violate the law of energy conservation. The particle does not gain or lose energy while tunnelling. Instead, it appears on the other side of the barrier with the same energy it had before and hence it persist the same de Broglie wave length to that of incident wave.

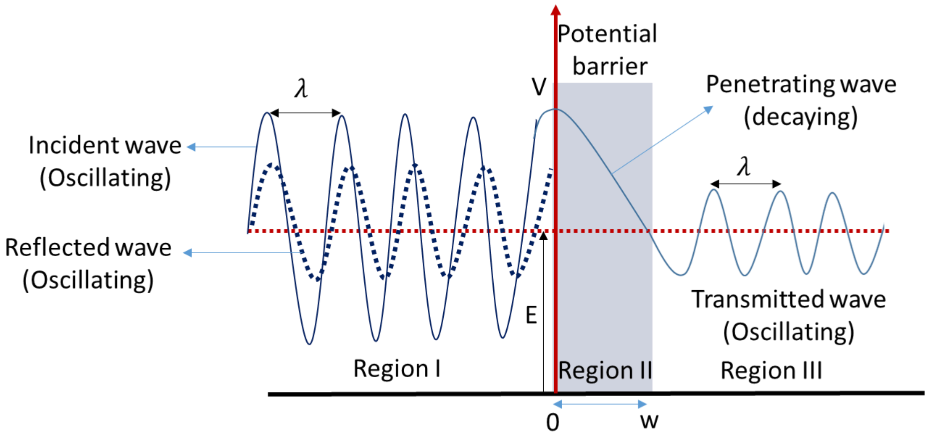


Fig: Schematic diagram showing tunnelling through a finite potential barrier. The particle is moving from left to right. Most of the incident wave of the particle is reflected back. A small part of the wave penetrates the barrier, emerging on the other side with diminished amplitude but with the same de Broglie wavelength and hence with the same energy to that of incident wave.

Solving Schrodinger equation for evaluating transmission probability:

In treating the barrier penetration problem, we encountered three regions in which the particle may exist. Our task is to determine the wave function for the particle in each region:

(1) On the left of the barrier (region I), i.e. for the particle moving toward the barrier, it can be described by a wave equation similar to that presented for the particle in a box with V = 0, So

$$\Psi_I = Ae^{ikx} + Be^{-ikx}, where\ k = \frac{\sqrt{2mE}}{\hbar}$$

Ψ_I consist of two terms, the 1st term $\left(Ae^{ikx}\right)$ is for the incident wave moving towards right and the 2nd term $\left(Be^{-ikx}\right)$ is for the reflected wave travelling to the left. A and B are the amplitudes of the incident and reflected waves, respectively.

Now reflection co-efficient/probability (R) which is the fraction of total wave reflected by the barrier is defined as the ratio of reflection probability to that of incident probability.

$$R = \frac{\left|\Psi_{ref}\right|^2}{|\Psi_{inc}|^2} = \frac{|B|^2}{|A|^2}$$

(2) For the region (region II) representing the potential barrier (0 ≤ x ≤ W), where the potential energy is constant "V" the expression for Schrodinger is:

$$-\frac{\hbar^2}{2m}\frac{d^2\Psi}{dx^2} + V\Psi = E\Psi$$

Provided E < V, the above expression can be algebraically rearranged as:

$$\frac{2m(V-E)}{\hbar^2}\Psi = \frac{d^2\Psi}{dx^2}$$

The general solution for the above 2nd order differential equation is:

$$\Psi_{II} = Ce^{jx} + De^{-jx}, where\ j = \frac{\sqrt{2m(V-E)}}{\hbar}$$

There are two terms in Ψ_{II}, the 1st term for the wave that penetrates through the barrier from the left to right and the 2nd term for the wave that partially reflected by the right end of the barrier. Moreover, the exponentials term in Ψ_{II} have real exponents, instead of imaginary component. So unlike the oscillating nature of the function in region I, the wave function in region II is decaying in nature.

(3) To the right of the barrier (x > w) i.e. in region III, where V = 0 again, the wave function has the expression:

$$\Psi_{III} = Fe^{ikx}$$

Since in region III there is no reflection, so Ψ_{III} the transmitted wave consist of just one term only. Here F is the amplitude of the transmitted wave

Now the transmission co-efficient or transmission probability or tunnelling probability is defined as ratio between transition probability to incident probability, i.e.

$$T = \frac{|\Psi_{trans}|^2}{|\Psi_{inc}|^2} = \frac{|F|^2}{|A|^2}$$

An acceptable wave function must be continuous at the edges of the barrier, so at the boundaries i.e. at x = 0 and x = w, both ψ and $\frac{d\psi}{dx}$ must be continuous i.e. the wave functions in adjacent regions must join smoothly.

So at x = 0

$$\Psi_I = \Psi_{II}$$

$$=> Ae^{ikx} + Be^{-ikx} = Ce^{kx} + De^{-kx}$$

$$=> Ae^{0} + Be^{0} = Ce^{0} + De^{0} \; [\,putting\ x = 0]$$

$$=> A + B = C + D - -(1)$$

Again

$$\frac{d\Psi_I}{dx} = \frac{d\Psi_{II}}{dx}$$

$$=> \frac{d}{dx}\left(Ae^{ikx} + Be^{-ikx}\right) = \frac{d}{dx}\left(Ce^{jx} + De^{-jx}\right)$$

$$=> ikAe^{ikx} - ikBe^{-ikx} = jCe^{jx} - jDe^{-jx}$$

$$=> ikAe^{0} - ikBe^{-0} = jCe^{0} - jDe^{0}[\,putting\ x = 0]$$

$$=> ikA - ikB = jC - jD - -(2)$$

At x = w

$$\Psi_{II} = \Psi_{III}$$

$$=> Ce^{kx} + De^{-kx} = Fe^{ikx}$$

$$=> Ce^{kw} + De^{-kw} = Fe^{ikw}[\,putting\ x = w] - -(3)$$

And

$$\frac{d\Psi_{II}}{dx} = \frac{d\Psi_{III}}{dx}$$

$$=> \frac{d}{dx}\left(Ce^{jx} + De^{-jx}\right) = \frac{d}{dx}\left(Fe^{ikx}\right)$$

$$=> jCe^{jx} - jDe^{-jx} = ikFe^{ikx}$$

$$=> jCe^{jw} - jDe^{-jw} = ikFe^{ikw}[\,putting\ x = 0] - -(4)$$

Solving the equation (1), (2), (3) and (4) with tedious algebraic manipulation and further simplification we have

$$T = \frac{|F|^2}{|A|^2}$$

$$= \left\{1 + \frac{\left(e^{jw} - e^{-jw}\right)^2}{16\varepsilon(1-\varepsilon)}\right\}^{-1}$$

Where $\varepsilon = \frac{E}{V}$

Properties of transmission probability (T):

(1) Summation of transmission and reflection probability is equal to unity i.e. T + R =1

(2) T = 0 when $E \ll V$ i.e. there is negligible tunnelling when the energy of the particle is much lower than the height of the barrier.

(3) T increases when energy of the particle (E) approaches to the potential energy barrier (V). i.e. the probability of tunnelling increases as the energy of the particle rises to match the height of the barrier.

(4) T approaches, but still less than 1 for E > V. ie. there is still a probability of the particle being reflected by the barrier even when it should classically pass over the barrier.

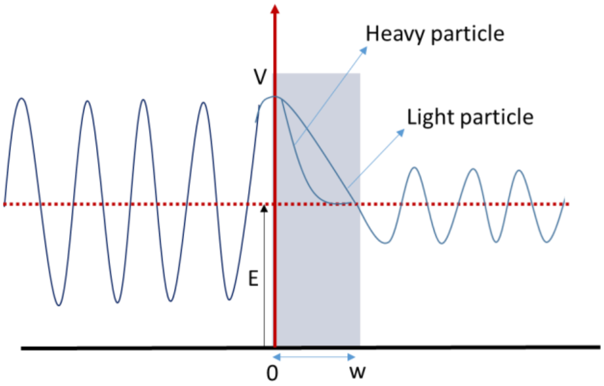
(5) $T \approx 1$ for some energies, so the wave function in this case if fully transmitted. This is the so called resonance transmission and occur due to wave functions interference where the reflected waves are fully suppressed. In terms of classical concept this happen when E >> V.

(6) If the width of the potential energy barrier is very high such that jw >>1, then the expression for tunnelling probability become:

$$T = 16\varepsilon(1-\varepsilon)e^{-2jw}$$

$$= \frac{16E(V-E)}{V^2}e^{-2jw}, where\ j = \frac{\sqrt{2m(V-E)}}{\hbar}$$

i.e. tunnelling probability decreases with increase in barrier width (w), barrier height (V) and mass of the particle $\left(j \propto m^{\frac{1}{2}}\right)$. So tunnelling is very important for subatomic particles only.



(7) If the potential energy barrier is low such that E is slightly smaller than V and if the width of the (w) is wide, then the expression for tunnelling probability become:

$$T \approx e^{-2jw}$$

Q. What is the energy of a particle that sufficiently tunnelled through a potential energy barrier:

(a) Less than the initial energy (b) Greater than the initial energy (c) Equal to the initial energy

Q. An electron with a total energy of 6 eV approaches a potential energy barrier of height 12 eV, if the width of the barrier is 0.18 nm, find the tunnelling probability? What is the probability of reflection for the same electron?

Ans:

Given

E = 6 eV, V = 12 eV and w = 0.18 nm

We know

$$T = 16\varepsilon(1-\varepsilon)e^{-2jw}$$

$$= \frac{16E(V-E)}{V^2}e^{-2jw}$$

And

$$j = \frac{\sqrt{2m(V-E)}}{\hbar}$$

$$= 2\pi\frac{\sqrt{2m(V-E)}}{h}$$

$$= 2\times 3.14\frac{\sqrt{2\times 9.1\times 10^{-34}kg\ (12-6)\times 1.6\times 10^{-19}J}}{6.63\times 10^{-34}Js}$$

$$= 12.6\ nm^{-1}$$

* Value of exponential terms is dimensionless, since “w” has the dimension of nm, so to make e^{-2jw} dimensionless “j” has to be dimension of nm^{-1}.

Now

$$T = \frac{16E(V-E)}{V^2}e^{-2jw}$$

$$= \frac{16\times 6\ eV\ \times (12-6)eV}{(12\ eV)^2}\times e^{-2\times 12.6nm^{-1}\times 0.18\ nm}$$

$$= 0.44\ or\ 44\ \%$$

Now

$$R = 1 - T$$

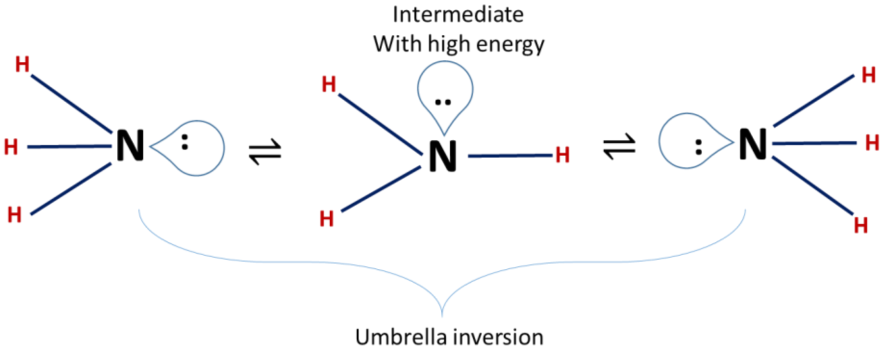
$$= 1 - 0.44$$

$$= 0.56\ or\ 56\%$$

Applications of the concept quantum tunneling:

(1) Nuclear fusion: One of the most vital applications of quantum tunnelling is in nuclear fusion, the process that powers the sun. For fusion to occur, atomic nuclei must come very close together to produce effective combination, however the columbic repulsion barrier induced by the positive nuclei of the combining atoms makes this approach impossible. Nevertheless, quantum mechanics put no restriction on this approach as the wave function of the corresponding nuclei can penetrate through this potential energy barrier via tunnelling. Though this probability is still low, the extremely large number of nuclei in the core of a star is sufficient to sustain a steady fusion reaction.

(2) Ammonia inversion or umbrella inversion: A molecule of ammonia NH_3 typically exists in triangular pyramidal shape where the three H atoms formed the base, and the N atom the apex of the pyramid and hence it looks like an umbrella. There is also an equivalent mirror image configuration possible for NH_3 which is obtained via inverting the molecule. When we compare both the conformation it seems like a strong wind blows an umbrella inside out and hence the process in known as umbrella inversion.



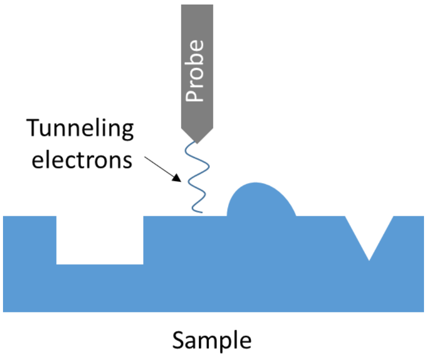
Although the left-hand and right hand molecules are obviously equivalent and so have equal energy, the intermediate structure has higher energy. In fact, this intermediate stands for 25 kJmol^{-1} columbic barrier which is 10 times greater than thermal energy at room temperature and therefore the inversion of NH_3 is hindered from classical view point. However, the occurrence of quantum tunnelling make it possible for the molecule to adopt the inverted configuration even at room temperature although its thermal motion is less energetic than the potential energy barrier.

(3) α particle decay: α decay is a process wherein a nucleus spontaneously decays by emitting an α (He^{2+}) particle.

The α particle being at the center of the nucleus is surrounded by other positively charged protons and therefore behaves like a particle trapped in a box where the potential barriers are the result of electrostatic repulsion due to other positively charged protons present. This potential barrier has a height in the order of 250 MeV, whereas the α possess kinetic energy in the order of 2-9 MeV. Since the kinetic energy of the α particle is smaller than the columbic potential energy and hence classically there is no chance for the particle to decay from the nucleus. Gamow suggested that the α particle, being a quantum mechanical object, has wavelike properties that enable it to penetrate the high potential barrier through quantum tunnelling.

(4) Scanning tunnelling microscope (STM): Principle of operation of STM is based on the quantum mechanical tunnelling, in which the wavelike properties of electrons permit them to "tunnel" beyond the surface of a solid into regions of space that are forbidden to them under the rules of classical physics.

A probe with a sharp tip which provides tunnelling electrons is allowed to move across the surface of a solid under examination. A small voltage is applied between the probe tip and the surface, causing electrons to tunnel across the gap. Now probability of finding such tunnelling electrons decreases exponentially as the distance of the tip from the surface increases. The STM makes use of this extreme sensitivity to distance. As the probe is scanned over the surface, it registers variations in the amount of tunnelling electron which is measured as a current (since current is the flow of electrons. This information can be processed to provide a topographical image of the surface



Postulate 5: It describe how the wave function of a system varies with time

Time dependent Schrodinger equation hold good only for stationary states whose probability distributions don't vary over time. So to describe the evolution of a quantum mechanical system with time, it is necessary to use the time-dependent Schrodinger equation which can be expressed as:

$$\hat{H}\Psi(x,t) = i\hbar\frac{d\Psi(x,t)}{dt}$$

Assuming the separability of time and position, the time dependent wave function can be written as:

$$\Psi(x,t) = \Psi(x)e^{-\frac{iEt}{\hbar}}$$

Where E is the total energy of the system

Now

$$Probability\ density = \Psi(x,t)\Psi^*(x,t)$$

$$= \left[\Psi(x)\ e^{-\frac{iEt}{\hbar}}\right]\left[\Psi(x)\ e^{-\frac{iEt}{\hbar}}\right]^*$$

$$= \left[\Psi(x)e^{-\frac{iEt}{\hbar}}\right]\left[\left[\Psi^*(x)\ e^{\frac{iEt}{\hbar}}\right]\right]$$

$$= \Psi(x)\Psi^*(x)$$

Thus for a conservative system where time can be separated from position probability density is independent of time and hence $\Psi(x)$ alone are called stationary state.