CONTENTS

"DIFFERENTIATE BETWEEN ORTHOGONAL AND NORMALIZED WAVE FUNCTIONS"

Time Dependent Schrodinger Wave equation:-

This is the forth postulate of Quantum Mechanics. In 1926 Schrodinger give an wave mechanism.

Wave function is a kind of system represented by "ψ" or "Psi." This ψ describes the properties of a system. "ψ" is a complex number.

"Complex number" consist of two parts:-

Exp:- Complex No. = Real + Imaginary

$$A = x + iy$$

$$\psi = a + ib$$

The conjugate of "ψ" is "ψ^*".

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

Maximum overlap of "ψ" and "ψ^*",

$$\int_{-\infty}^{+\infty} \psi\psi^* \cdot d\psi \cdot 1$$ (Ideal conditions are three).

$$\int_{-\infty}^{+\infty} \psi^2 d\psi \cdot 1$$

Wave functions are "normalized."

⇒ Conditions for Normalization:-

When $\psi\psi^* d\psi$ becomes equal to 1, Then this is called Conditions for "<u>Normalization</u>."

Sometimes, when $\psi\psi^* d\psi$ becomes equal to "zero" than it is known as "<u>Orthogonality</u>."

$$\int_{-\infty}^{+\infty} \psi\psi^* d\psi = 0$$

$$\psi\psi^* = a^2 + b^2$$

⇒ Normalization :-

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

$$\int_{-\infty}^{+\infty} \psi_x^2 \, dx = 1$$

When the integral of wave function time its complex conjugate over the entire space available is equal to unity. Then this wave function is called "Normalized wave function". and this condition is called "Normalization".

Limits are extended from $-\infty$ to $+\infty$ and the integral must exist somewhere in that integral. If it is to exist at all. For three dimensions we can write the above equation as:-

$$\int_{-\infty}^{+\infty} \psi^2 d\tau = 1 \qquad \because d\tau = dx\,dy\,dz$$

(small volume elements).

The square of the wave function is proportional to probability of finding the particle in the given volume element. All values of wave function ψ are not acceptable. The acceptable values are:-

Those which have been normalized by multiplying the function by a proper constant. If ψ is the solution of wave equation multiplication by a constant value A then it will give "$A\psi$ (A into ψ)," which is also a solution. It means that the

"$\int_{-\infty}^{+\infty} \psi\psi^* \, dx\,dy\,dz$ is proportional to probability."

The probability of certainity is zero. Thus, the probability of electron being in the volume element is unity.

The maximum probability of existance of something in space should be unity, no matter what is the exact distribution in that region of space may be.

⇒ Use OF Normalization :-

→ Normalization is process of reducing redundancies of Data in database.

→ Essentially, normalizing the wave function means you find exact form that ensure the probability that the particle is found somewhere in space is equal to 1.

→ The process of normalization also has a constant known as:

"Constant of Normalization"

denoted by

"C."

⇒ Normalization & constant of normalization :-

Let's consider the three wave functions:

$$\psi_x = c \frac{\sin(n\pi x)}{a} \quad -(a)$$

$$\psi_y = C \frac{\sin(n\pi y)}{a} \quad -(b)$$

$$\psi_z = C \frac{\sin(n\pi z)}{z} \quad -(c)$$

In these three equations C is known as the constant of Normalization.

• Determination of value of "C" :-

. We know that for the maximum overlap, we should apply the conditions for Normalization

$$\int_b^a \psi_x \psi_x^* \, d\psi = 1 \longrightarrow (A)$$

If we put the value of ψ_x from eq(a) to equ (A) then:-

$$A \Rightarrow \int_b^a C \frac{\sin(n\pi x)}{a} \cdot C \frac{\sin(n\pi x)}{a} \, dx = 1 \longrightarrow (B)$$

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

$$c^2 \int_a^a \sin^2\left(\frac{n\pi x}{a}\right) dx = 1 \text{ --- (B)} \quad \therefore \int \sin\theta = -\cos\theta$$

We know that :-

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

$$\sin^2\theta = \frac{1-\cos 2\theta}{2}$$

So:-

$$\sin^2 \frac{(n\pi x)}{a} = \frac{1 - \cos\left(\frac{2n\pi x}{a}\right)}{2} \text{ --- (C)}$$

Put the value from (C) to equ (B).

$$B \Rightarrow c^2 \int_0^a \frac{\left(1 - \cos\left(\frac{2n\pi x}{a}\right)\right) dx}{2} = 1$$

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

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

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

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

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$$\frac{c^2}{2}\left[(a-0)-\Big|_0^a \frac{a}{2n\pi}\sin\frac{2n\pi x}{a}\Big|\right]=1$$

$$\frac{c^2}{2}\left[a-\frac{a}{2n\pi}\left(\sin\frac{2\pi n \cancel{a}}{\cancel{a}}-\sin\frac{2\pi n}{a}(0)\right)\right]=1$$

As we know:-

$\sin 0, \sin 2\pi, \sin 3\pi, \sin n\pi = 0$

So we get:-

$$\frac{c^2}{2}a-0=1$$

$$\frac{c^2}{2}a=1$$

$$c^2a=2$$

$$c^2=\frac{2}{a}$$

$$c=\sqrt{\frac{2}{a}}$$

This c is known as "constant of Normalization"

So, by putting the value of c in eq (a), (b), (c),

We get:-

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

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

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

By putting values of
ψ_x, ψ_y, ψ_z in equation

$$\psi_{xyz} = \psi_x \cdot \psi_y \cdot \psi_z$$

$$\psi_{xyz} = \sqrt{\frac{2}{a}} \cdot \sqrt{\frac{2}{a}} \cdot \sqrt{\frac{2}{a}} \cdot$$

$$\sin\left(\frac{n\pi x}{a}\right) \cdot \sin\left(\frac{n\pi y}{a}\right) \cdot \sin\left(\frac{n\pi z}{a}\right)$$

This equation gives total wave function of particle moving ino 3·D box.

⇒ How to normalize a wave function:-

Normalizing a wave function means multiplying it by a constant to ensure that the sum of the probabilities for finding the particle equals to 1.

Mathematically:- This means integrating $\psi^*(x)\psi(x)\,dx$ over all space should equal to 1.

$$\int_{-\infty}^{+\infty} \psi^*_{(x)} \psi_{(x)}\, dx = 1$$

Example #01:-

The $n=2$ state for a particle in a box of length $L=1$

Unnormalized = $\psi_x = \sin(2\pi x)$

Normalized = $\psi_x = \sqrt{2}\sin(2\pi x)$

Unnormalized = Probability sum to 0.5

Normalized = Probability sum to 1.0

As we Know:-

$$\psi_x = \sin(2\pi x)$$

Let's check is it normalized?

$$\int_{-\infty}^{+\infty} \psi^*_{(x)} \psi_{(x)}\, dx = \int_0^1 [\sin(2\pi x)][\sin(2\pi x)]\,dx$$

$$= \int_0^1 \sin^2(2\pi x)\,dx$$

$$= \frac{1}{2\pi} \int_0^{2\pi} \sin^2 u \, du$$

$$= \frac{1}{2\pi} \int_0^{2\pi} \sin^2 u \, du$$

$$= \frac{1}{2\pi} \pi$$

$$= \frac{1}{2} \Rightarrow \underline{\text{Not normalized}}$$

To convert it into a normalized wave function we multiply it by a constant "A".

$$\psi(x) = A \sin(2\pi x)$$

What value of A will make it Normalized.

$$\int \psi^*(x)\psi(x)\,dx = \int_0^1 [A\sin(2\pi x)]\,[A\sin(2\pi x)]\,dx$$

$$= A^2 \int_0^1 \sin^2(2\pi x)\,dx$$

$$\frac{A^2}{2} = 1 \Rightarrow \text{If Normalized}$$

$$\frac{A^2}{2} = 1 \Rightarrow A^2 = 2$$

$$A = \sqrt{2}$$

And our normalized wave function is:-

$$\psi_{(x)} = \sqrt{2} \sin(2\pi x)$$

Example #02

Normalize a wavefunction for a particle in a box of length L give by:

$$\psi_{(x)} = x(L-x)$$

$$\int \psi^*_{(x)} \psi_{(x)} dx = \int_0^L [Ax(L-x)] [Ax(L-x)] dx$$

$$= A^2 \int_0^L x^2 (L-x)^2 dx$$

$$= A^2 \int_0^L x^4 . 2Lx^3 + L^2 x^2 dx$$

$$A^2\left[\frac{x^5}{5}-\frac{2Lx^4}{4}+\frac{L^2x^3}{3}\right]_{x-0}^{x-L}$$

$$= \frac{A^2L^5}{30} = 1 \quad \text{If Normalized}$$

$$= A^2 = \frac{30}{L^5}$$

$$= A = \sqrt{\frac{30}{L^5}}$$

So, our final Normalized wave function is :-

$$\psi_x = \sqrt{\frac{30}{L^5}}\, x\,(L-x)$$

ORTHOGONALITY

Definition:-

There are many acceptable solutions to Schrodinger Wave Equation for a particular system.

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

Each wave function has a corresponding energy value E. for only two wave function ψ_n and ψ_m coresponding to the energy values En & Em. The following condition must be fulfilled.

$$\int_{-\infty}^{+\infty} \psi_n \psi_m \, dx = 0$$

Such a condition is called condition of orthogonality of wave function. The two functions ψ_n & ψ_m are send to be orthogonal to each other.

From this it multiplied that the orthogonality is a relationship b/w two wavefunctions and a single wave function itself cannot be labbled as orthogonal. They must be orthogonal with respect to some other wave function.

There is an exception in Orthogonality. When 2 or more wave functions corresponds to same energy level. Then these are called degenarate levels. Wave function for dengenarate level are not always Orthogonal to one another but they are orthogonal to all other wave functions that are solutions of some wave function.

"In vector form the term Orthogonal" means "Perpendicular". For Perpendicular vectors, their dot product is zero. Orthogonal means scaler Product = 0. For functions, scaler product is the integral of the product of functions values. For instance, "sin & cos" are two orthogonal functions. Often used to describe waves.

Derivation for orthogonal wave function:-

If an electron exists in the two Quantum states corresponding to two wave functions (ψ_l, ψ_m) and fulfill the condition.

$$\int_{-\infty}^{+\infty} \psi_l \cdot \psi_m d\tau = 0 \quad \text{—— (i)}$$

Let consider that

$$\psi_x = \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi x}{a}\right) \quad \text{—— (2a)}$$

Let $n = l$ in eq (2a)

$$\psi_l = \sqrt{\frac{2}{a}} \sin\left(\frac{l\pi x}{a}\right) \quad \text{—— (2b)}$$

$$\psi_m = \sqrt{\frac{2}{a}} \sin\left(\frac{m\pi x}{a}\right) \quad \text{—— (2c)}$$

In the case of 3-D box

but (2b) and (2c) in (1).

$$\int_0^a \left[\sqrt{\frac{2}{a}} \sin\left(\frac{l n \pi x}{a}\right) \cdot \sqrt{\frac{2}{a}} \sin\left(\frac{m\pi x}{a}\right)\right] dx = 0$$

$$\frac{2}{a} \int_0^a \left[\sin\left(\frac{l\pi x}{a}\right) \cdot \sin\left(\frac{m\pi x}{a}\right)\right] dx = 0$$

As we know :-

$$2\sin A \cdot \sin B = \cos(A-B) - \cos(A+B)$$

$$\frac{1}{a} \int_0^a \left[2\sin\left(\frac{l\pi x}{a}\right) \cdot \sin\left(\frac{m\bar{\pi} x}{a}\right)\right] dx = 0$$

$$\frac{1}{a} \int_0^a \left[\cos\left(\left(\frac{l\pi x}{a}\right) - \left(\frac{m\pi x}{a}\right)\right) - \cos\left(\frac{l\pi x}{a} + \frac{m\pi x}{a}\right)\right] dx = 0$$

$$\frac{1}{a} \int_0^a \cos \frac{\pi x}{a} (l-m)\, dx - \frac{1}{a} \int_0^a \cos \frac{\pi x}{a} (l+m)\, dx = 0$$

$$\frac{1}{a} \left. \frac{\sin \bar{\pi} x (l-m)}{\frac{\pi}{a}(l-m)} \right]_0^a - \frac{1}{a} \left. \frac{\sin \left(\frac{\pi x}{a}\right)(l+m)}{\frac{\pi}{a}(l+m)} \right]_0^a = 0$$

$$\frac{1}{a} \cdot \frac{a}{\pi (l-m} \left[\frac{\sin(a)(l-m)}{a} - \frac{\sin(0)(l-m)}{a} \right] - \frac{1}{a} \frac{a}{\pi(l+m)} \left[\frac{\sin \bar{\pi}(a)(l+m)}{a} - 0 \right] = 0$$

$$\frac{1}{\pi(l-m)} \left[\sin \pi (l-m) - 0\right] - \frac{1}{\pi(l+m)} \left[\sin \pi (l+m) - 0\right] = 0$$

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If $l = 1$ them $m = 0, 1, 1$

for $(l-m)$

$l - m = 1 = 0 = 1$

$l - m = 1 - (-1) = 2$

$l - m = 1 - (+1) = 0$

for $(l+m)$

$l + m = 1 + 0 = 1$

$l + m = 1 + (-1) = 0$

$l + m = 1 + (+1) = 2$

This equation can be satisfied only, If 0, $\sin 1\pi$, $\sin 2\pi$ is equal to zero.

$0, \sin 1\pi, \sin 2\pi = 0$

Therefore, it has been proved that both of the wave functions are orthogonal to each other.

So, the wave function that are the solution of Schrodinger Wave Equation. are the orthogonal to each other. Thee product should be equal to zero.

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Examples for Orthogonality:-

Show that

$$[1, \cos x, \sin x, \cos 2x, \cdots]$$

for an orthogonal set on $[-\pi, \pi]$.

Example #01

Show: $(1, \cos(nx)) = 0$

$$= \int_{-\pi}^{+\pi} \cos(nx)\, dx$$

$$= \frac{1}{n} \Big| \sin(nx) \Big|_{-\pi}^{+\pi}$$

$$= \frac{1}{n} [\sin(n\pi) - \sin(-n\pi)]$$

Bothare multiple of π

So:- $\frac{1}{n} [0 - 0] = 0$

So function $(1, \cos(nx))$ is orthogonal.

Example #02:-

Show: $(1, \sin(nx)) = 0$

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If $l = 1$ them $m = 0{\cdot}11$

for $(l-m)$

$l - m = 1 = 0 = 1$

$l - m = 1 - (-1) = 2$

$l - m = 1 - (+1) = 0$

for $(l+m)$

$l + m = 1 + 0 = 1$

$l + m = 1 + (-1) = 0$

$l + m = 1 + (+1) = 2$

This equation can be satisfied only, If 0, $\sin 1\pi$, $\sin 2\pi$ is equal to zero.

$0, \sin 1\pi, \sin 2\pi = 0$

Therefore, it has been proved that both of the wave functions are orthogonal to each other.

So, the wave function that are the solution of Schrodinger Wave Equation are the orthogonal to each other. Their product should be equal to zero.

$$\int_{-\pi}^{\pi} \sin(nx)\,dx$$

$$= -\frac{1}{n}\Big|\cos(nx)\Big|_{-\pi}^{\pi}$$

$$= -\frac{1}{n}\left[\cos(nx) - \cos(-nx)\right] \quad \therefore \cos(-\theta) = \cos\theta$$

$$= -\frac{1}{n}\left\{\cos(n\pi) - \cos(\pi n)\right\}$$

$$= 0$$

Example #03:-

Show:- $\left[\sin(nx), \sin(mx)\right] = 0 \quad n \neq m$

$$\int_{-\pi}^{\pi} \sin(nx)\cdot\sin(mx)\,dx$$

$\therefore \quad \sin A\cdot\sin B = \frac{1}{2}\left[\cos(A-B) - \cos(A+B)\right]$

So:-

$$= \int_{-\pi}^{\pi} \frac{1}{2}\left[\cos(nx-mx) - \cos(nx+mx)\right]dx$$

$$= \frac{1}{2}\int_{-\pi}^{\pi}\left[\cos(n-m)x - \cos(n+m)x\right]dx$$

$$= \frac{1}{2}\left|\frac{1}{n-m}\sin(n-m)x - \frac{1}{n+m}\sin(n+m)x\right|_{-\pi}^{\pi}$$

$$= \frac{1}{2}\left[\frac{1}{n-m}\underbrace{\sin(n-m)\pi}_{0} - \frac{1}{n+m}\underbrace{\sin(n+m)\pi}_{0}\right] -$$

$$\left[\frac{1}{n-m}\sin\underbrace{(n-m)(-\pi)}_{0} - \frac{1}{n+m}\sin\underbrace{(n+m)(-\pi)}_{0}\right]$$

$$=0$$

Because we know that:-

sin (multiply of π) = 0

So the above equation becomes equal to "zero".

→ Orthonormal Wave Function:-

If $\psi_1 \psi_2 = 1$ the wave function is normalized. If $\psi_1 \psi_2 = 0$, then the wave function is the orthogonal. If the wave function is both Orthogonal and Normalized then it is called "Orthonormal wavefunction."

⇒ Conditions for Orthonormality:-

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

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

The above relations can be combined as:

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

"δ_{mn} called Kromecker detta"

It can be defined as:

$$\delta_{nm} \begin{Bmatrix} 0 & \text{for } n \neq m \\ 1 & \text{for } n \neq m \end{Bmatrix} \quad -(A)$$

The wave function that satisfied the condition (A). is called "Orthonormal wave function"