B.Sc. SEMESTER-I

MJC(T)/MIC(T)

Inorganic Chemistry

Atomic Structure and Chemical Bonding

Atomic Structure- Normalized and Orthogonal Wave Function

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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

$$\int_{0}^{\pi} (NSinx)^2\, dx = 1$$

$$=> N^2 \int_{0}^{\pi} Sin^2 x\, dx = 1$$

$$=> \frac{N^2}{2} \int_{0}^{\pi} 2Sin^2 x\, dx = 1$$

$$=> \frac{N^2}{2} \int_{0}^{\pi} (1 - Cos\ 2x)dx = 1$$

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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) $\Psi = a(a-x), 0 \le x \le a$

Let the normalization constant = N

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

Now

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

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

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

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

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

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

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

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

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: $\Psi = sin\left(\frac{n\pi x}{a}\right), 0 \leq x \leq a$

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 $0 \leq x \leq a$

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

(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 $-a \leq x \leq a$

Ans:

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

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

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

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

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

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

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

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

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

$$= 0$$

So the given functions are orthogonal to each other.

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

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

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

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

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

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

$$= 0$$

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 $0 \leq x \leq a$