Concepts of Chemistry for Engineering
Professor. Anindya Dutta
Department of Chemistry
Indian Institute of Technology, Bombay
Lecture No. 04
Wave functions

I hope that in the next 15 minutes or so we will sort of start to see light at the end of the tunnel. We will get to understand what this wave function is all about, what can it tell us, what kind of information it can give us, and what are the properties that it has to satisfy other than simply being a solution of wave differential equation. What else? What is the physical significance? And all that thanks to the work of this brilliant physicist, Max Born. We are going to talk about Born interpretation of this enigma of Wave function.

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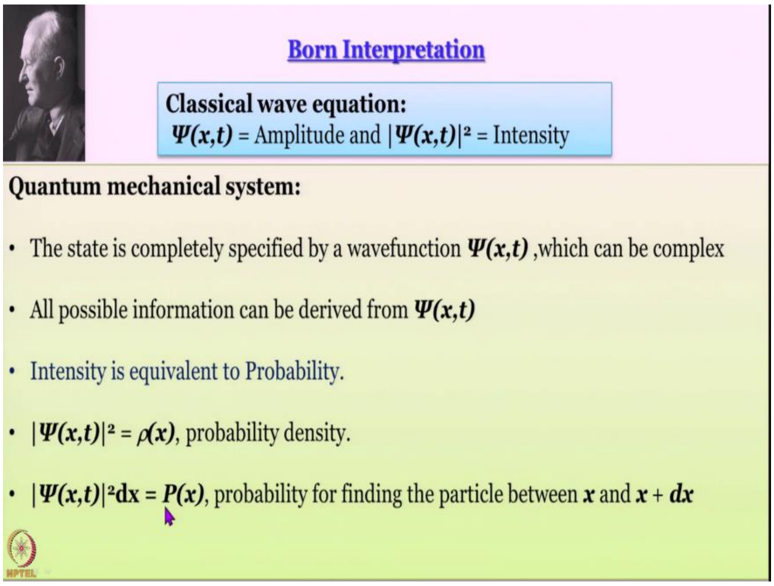

Born Interpretation

Classical wave equation:
$\Psi(x,t)$ = Amplitude and $|\Psi(x,t)|^2$ = Intensity

Quantum mechanical system:

- The state is completely specified by a wavefunction $\Psi(x,t)$,which can be complex
- All possible information can be derived from $\Psi(x,t)$
- Intensity is equivalent to Probability.
- $|\Psi(x,t)|^2 = \rho(x)$, probability density.
- $|\Psi(x,t)|^2 dx = P(x)$, probability for finding the particle between x and $x + dx$

So, Born interpretation essentially says this, in classical wave equation. remember Schrodinger equation started off as a classical wave equation of for De Broglie waves. In classical wave equation the $|\Psi(x,t)|^2$ denotes intensity of the wave. If you say, Ψ can be imaginary also. So, if you multiply the Ψ by its complex conjugate, then you get mod Ψ square which is the intensity this was known.

So, Born started thinking along this lines that we have this wave function which can be complex, can be real. It is great that all possible information can be derived from Ψ. But what is the meaning of intensity here? You are saying that this Ψ is the amplitude of matter wave. So, square of intensity of matter wave, what does it mean. Intensity of matter wave Born realized would be the something to do with probability.

What does that mean? I look at some kind of matter wave in some region I see lots of intensity, in some region I see less intensity that essentially means that in the first region it is more probable to find the particle. In the other regions probability of finding the particle is less. So, intensity is related to probability. And what he said was that this $|\Psi(x,t)|^2$is really the probability density which is written as $\rho(x)$.

What is the meaning of probability density, see it is at a point, Ψ defined at some value of x, y, z or some other coordinate? So, you cannot really talk about probability at a point you have to talk about a region. So, if it is working in one direction, we can say that, we can talk about probability of finding the particle between x and x + dx, where dx is a very small increase in length.

So, Born said that if you multiply $|\Psi(x,t)|^2$dx, then you get the probability of finding the particle between x and x + dx. So, what is dx, that is also important and you will see this is going to become most, very strongly manifested when we talk about hydrogen atom wave functions, later on. So, Born interpretation essentially says that $|\Psi(x,t)|^2$is the probability density and that is what makes life a lot simpler.

So, now we realize that we do not have to worry about matter waves, forget matter waves now. We are worried about what we can call probability waves. And at this point let me stop for a moment and pay my gratitude and respect to our respected teacher Professor Balai Chand Kundu, who we unfortunately lost last year. Professor Kundu was our teacher. He was an inorganic chemist. He taught us this portion when I was in college Presidency College Calcutta many, many years ago.

And what I say now is merely a repetition of what he had told us. I do not know whether it is written as many words in any book. So, with my deepest respects to Professor Balai Chand Kundu what we have now our probability waves. Right away the situation becomes much less disturbing. We can read these we do not have to worry about why we are not seeing matter all around why we are not saying matter wave all around, probability waves.

What about three dimensions in three dimensions, probability of finding a particle at any point defined by x, y, z will be $|\Psi(x,y,z,t)|^2 d\tau$ where $d\tau$ is the volume of the small element that we get in Cartesian coordinates we get it by increasing x to x + dx, y to y + dy and z to d + dz. When we talk about spherical polar coordinates later, we will see we get a little more interesting expression.

But the crux of the matter is Ψ tells us or rather $\Psi\Psi^*$. $\Psi^*\Psi$ is what theorists like to call it. $\Psi^*\Psi$ is your probability density. Please do not forget the density part is it going to be very important later on.

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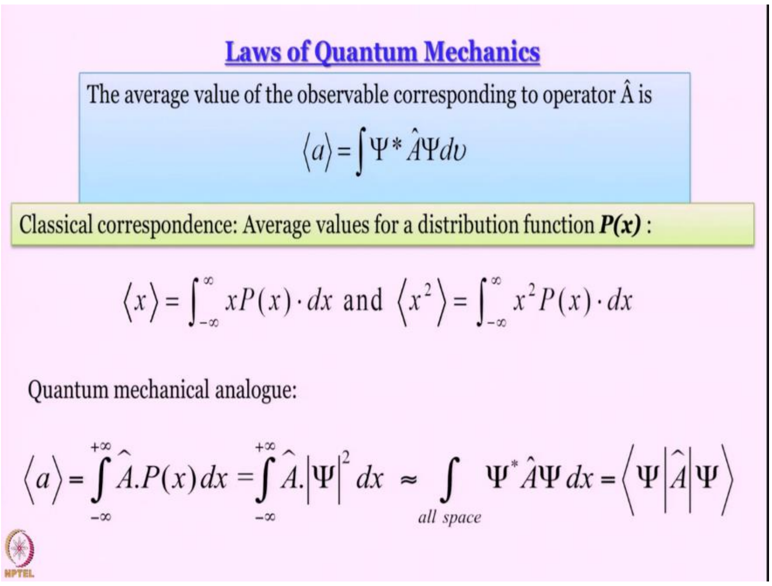

Laws of Quantum Mechanics

The average value of the observable corresponding to operator Â is

$$\langle a \rangle = \int \Psi^* \hat{A} \Psi dv$$

Classical correspondence: Average values for a distribution function ***P(x)*** :

$$\langle x \rangle = \int_{-\infty}^{\infty} xP(x) \cdot dx \text{ and } \langle x^2 \rangle = \int_{-\infty}^{\infty} x^2 P(x) \cdot dx$$

Quantum mechanical analogue:

$$\langle a \rangle = \int_{-\infty}^{+\infty} \hat{A}.P(x)dx = \int_{-\infty}^{+\infty} \hat{A}.|\Psi|^2 dx \approx \int_{all\ space} \Psi^* \hat{A} \Psi \, dx = \langle \Psi | \hat{A} | \Psi \rangle$$

Now what you can do is you can find out things like average values because some our classical treatment of mathematics the mean value is defined as integral. when I say minus infinity to plus infinity, I essentially mean the entire range of x. When you integrate over the entire range of x, then the function the average value of the function is whatever is the population distribution of a probability distribution multiplied by the function you want to work with, that gives us the average value of that function.

So, $\langle x \rangle = \int_{-\infty}^{+\infty} xP(x).dx$ and $\langle x^2 \rangle = \int_{-\infty}^{+\infty} x^2 P(x).dx$, where P(x) is the distribution function. How is the population distributed you can say or what is the probability distribution $\int_{-\infty}^{+\infty} x^2 P(x).dx$. So, that is exactly what we have written here.

What is the average value of 'a', to know that first of all how do you find 'a'? you have to make Â operate on Ψ. So, then in order to find the average you have to multiply by Ψ^* integrate over all space, $\langle a \rangle = \int \Psi^* \hat{A}\Psi dv$. So, that is how we get the average value of any quantity that we get. We are going to work out at least one problem maybe in the next module while revising, that is where this meaning of this average value and later on most probable value these will become much clearer I hope.

So, this is how remember we calculate average value. Now what we have written here is the expression for let us take a check on that we will come back and say it later.

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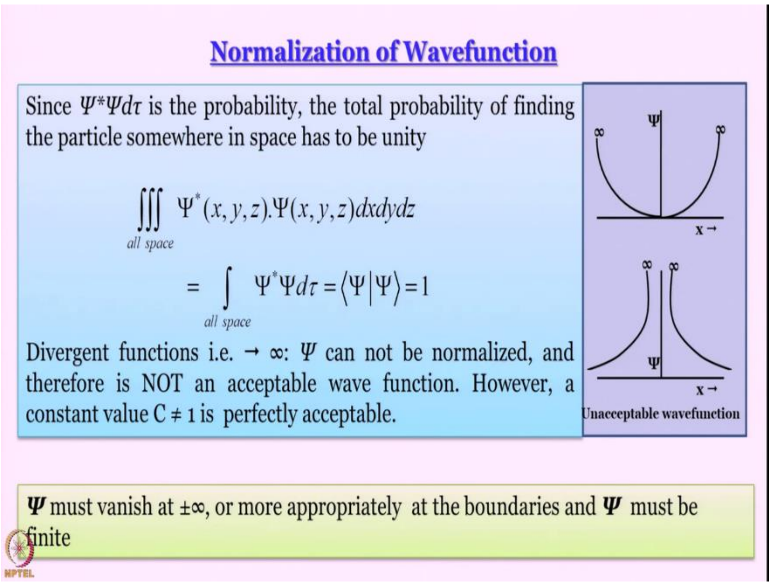

Normalization of Wavefunction

Since $\Psi^*\Psi d\tau$ is the probability, the total probability of finding the particle somewhere in space has to be unity

$$\iiint_{all\ space} \Psi^*(x,y,z).\Psi(x,y,z)dxdydz$$

$$= \int_{all\ space} \Psi^*\Psi d\tau = \langle\Psi|\Psi\rangle = 1$$

Divergent functions i.e. → ∞: Ψ can not be normalized, and therefore is NOT an acceptable wave function. However, a constant value $C \neq 1$ is perfectly acceptable.

Unacceptable wavefunction

Ψ must vanish at ±∞, or more appropriately at the boundaries and **Ψ** must be finite

Next thing that we want to discuss is normalization of a function. So, if $\Psi^*\Psi$ is probability density and you integrate over all the entire range of your coordinates what should you get, the particle has to be somewhere or the other. So, $\int \Psi^*(x,y,z)\,\Psi(x.y,z)dxdydz$ if you are working in Cartesian space is equal to 1. This condition is called the normalization condition.

So, obviously divergent functions they cannot be normalized look at the function here cannot be normalized naturally look at the function here cannot be normalized is becoming infinity at least at one point. So, what you see is that some of the values of Ψ which may be absolutely valid solutions of the wave equation. They are not going to satisfy Born condition and if they do not satisfy Born condition, then they are what we call unacceptable.

Acceptable values are acceptable wave functions are those that satisfy Born condition. We will come to the remaining Born conditions also. First condition we have said is normalization. You should be able to normalize it to 1.

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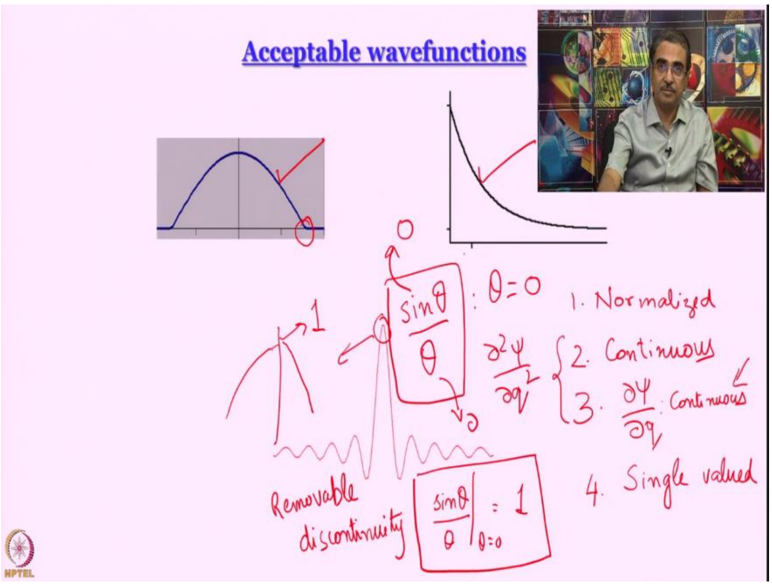

Acceptable wavefunctions

$\frac{\sin\theta}{\theta}$: $\theta = 0$

1. Normalized
2. Continuous
3. $\frac{\partial\Psi}{\partial q}$: Continuous
4. Single valued

These are some examples of acceptable wave functions. Let us see what it should be, what are the conditions of acceptability? First is it should be normalized. What if I give you a wave function that is not normalized? If I give you an un-normalized wave function something like Ψ, this is a not normalized, we can always say that I will normalize it by multiplying it with N.

What do I mean? I mean that N has to be chosen in such a way that N can be actually complex quantity also. So, $N^*N \int \Psi^* \Psi d\tau$ that has to be equal to 1. This is really the normalization condition. So, if I give you a un-normalized wave function no big deal you can multiply it by some constant and you can normalize it.

It is something as doable. We are going to encounter several examples of normalization in subsequent classes. Second condition that is very very important is that it has to be continuous. Third condition is this $\frac{\partial\Psi}{\partial q}$, I will write the first derivative that also should be continuous. Now these come from the requirement not so much from Born interpretation but these come from the requirement of the differential equation per se.

So, there is a little bit of difference between these two and the first one. See we are working with something like $\frac{\partial^2\Psi}{\partial q^2}$, second derivative. So, these are the conditions for the second derivative to exist. As you will see that this condition number three especially is often violated. We are going to see some examples. And the last condition I want to talk about is that it must be single valued.

What is the meaning of single valued? If you have a function which has more than one value at any given x, then what is the probability density at that point? You cannot have more than one values of probability density at a point, that is a problematic situation. So, it must be single valued in order to satisfy Born condition. So, this is a perfectly acceptable condition you can think, is it actually not perfect? Let us look, what about this?

It is continuous single value, everything is fine. Look at this point, at this point there is a discontinuity of $\frac{\partial \Psi}{\partial q}$ but as you will see this is taken as an acceptable function in some cases that we are going to discuss soon. So, this $\frac{\partial \Psi}{\partial q}$ is a condition that is not so stringent. What about this let me write the functional form of this one, I think this is $\frac{\sin\theta}{\theta}$.

At first look you might think that it is not acceptable. Why? Because what is the value of $\frac{\sin\theta}{\theta}$, for θ = 0. Denominator is 0. Numerator is also 0. So, 0 by 0, undefined. However, if you look at the function if you zoom in. zoom in as much as you want, what do you see? At values very, very small values of θ. If you approach from the right the value is going to be nearly 1.

If you approach from the left, then also the value will be nearly 1 and the limit exists because from both sides you approach the value of 1. So, what we do is. we set this value $\frac{\sin\theta}{\theta}$ and write like this at $\frac{\sin\theta}{\theta}|_{\theta=0} = 1$. What is 1? 1 is essentially the limiting value of $\frac{\sin\theta}{\theta}$ for theta tending to 0. So, the value of $\frac{\sin\theta}{\theta}$ is defined to be 1 and this is called a removable discontinuity. So, this is acceptable.

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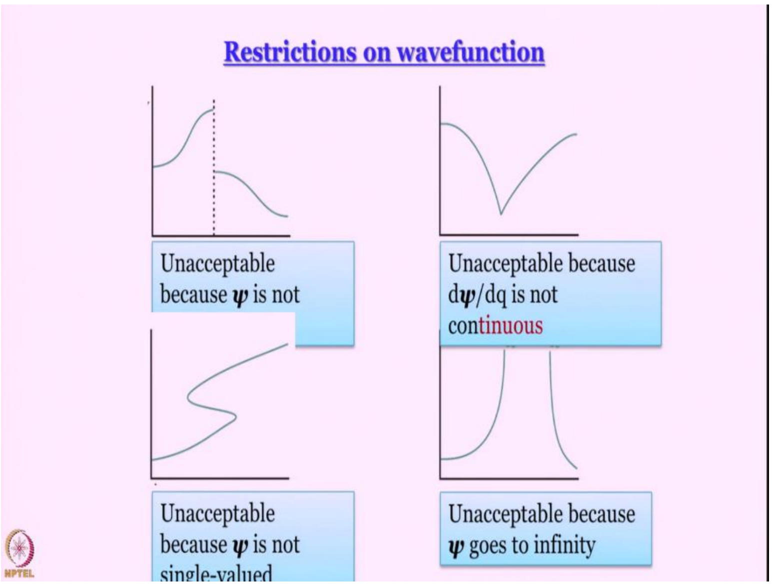

Restrictions on wavefunction

Unacceptable because ψ is not

Unacceptable because $d\psi/dq$ is not continuous

Unacceptable because ψ is not single-valued

Unacceptable because ψ goes to infinity

Let us show you some examples of unacceptable wave functions. This one is unacceptable. Why? Because it is not continuous. It is like $\frac{\sin\theta}{\theta}$ but the same value is not obtained if you approach from left hand. from right. So, it is unacceptable. What about this? This is also unacceptable because $\frac{\partial\Psi}{\partial q}$ is not continuous. But given the system something like this might become acceptable as you will see.

This is definitely not acceptable because it is multivalued. It is not single valued this is what we are saying. And this is not acceptable we have discussed this already because Ψ equals to infinity. So, what you see is that there are several restrictions on the wave function that arise out of Born interpretation. And these restrictions give us what are called boundary conditions.

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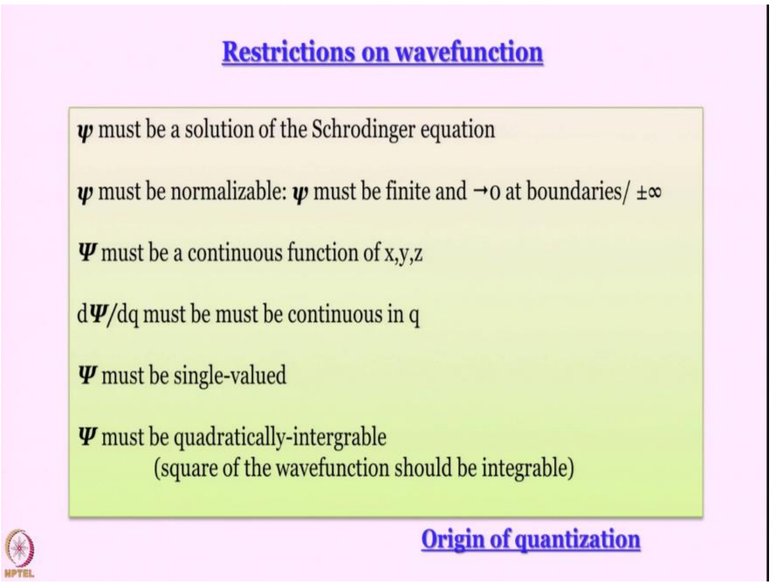

Restrictions on wavefunction

ψ must be a solution of the Schrodinger equation

ψ must be normalizable: ψ must be finite and $\rightarrow 0$ at boundaries/ $\pm\infty$

Ψ must be a continuous function of x,y,z

dΨ/dq must be must be continuous in q

Ψ must be single-valued

Ψ must be quadratically-intergrable
(square of the wavefunction should be integrable)

Origin of quantization

And these boundary conditions bring in quantization as we are going to see. So, all these conditions that are there, they bring in restrictions and these restrictions eventually bring about quantization. So, the origin of quantization lies in Born interpretation. So, even though in Schrodinger equation we do not see any quantum number. Quantum numbers are going to arise the moment we try to apply these boundary conditions. And this is something that comes out beautifully when we discuss free particle and particle in a box. That is what we are going to take up next.