# Quantum Chemistry of Atoms and Molecules
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## Lecture-5
## Ground Rules: Postulates of Quantum mechanics: Part II

So, far we have talked about Schrodinger equation from there we have started talking about the postulates of quantum mechanics and what has emerged is that one can use the wave function make an appropriate operator operate on it and get the value of the property of a system that we want to measure as an eigenvalue. So, we sort of have the mathematical tools shaping up slowly one question that remains to be answered is what is the wave function?

All right we do see experimentally that matter has wave nature. Why is it that we see it for; I mean what does it mean we do not really see matter flowing away or even if it is a standing wave we do not see those oscillations. So, what exactly is the meaning so when that meaning is provided by Max Born.

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But what is this wavefunction?

Google Doodle, December 11, 2017

As is given here in this cartoon that we had encountered in our previous discussion Max Born is the same person as your; as the one who had been a party to many other revelations and physics and chemistry like the Born-Haber cycle. Anybody who has studied chemistry would know about Born-Haber cycle. The other one that we know and use very frequently in spectroscopy is the Born-Oppenheimer approximation.

And of course when you take the names of Born and Oppenheimer so some other big project comes to one's mind that I leave to you to figure out, let me digress a little bit and tell you that Max Born had actually wanted to work in India after the Second World War got over he came and he stayed in Indian Institute of science for some time it is really unfortunate for reasons that I do not want to discuss you know in this course he had to go back.

Had his stay perhaps the status of science in India would have been even better than what it is already today. But anyway let us come back to the course material and see what is it that Born said? Born provided an interpretation of what the wave function is and to do that he went back once again to the point that we have referred to already three four times. And the point is that Schrodinger equation is essentially a classical equation.

It is a classical equation for de Broglie waves and if you think about a classical equation that can be written for the oscillation of a string or the oscillation is produced on the surface of a tabla diaphragm of a tabla then one thing is known for sure.

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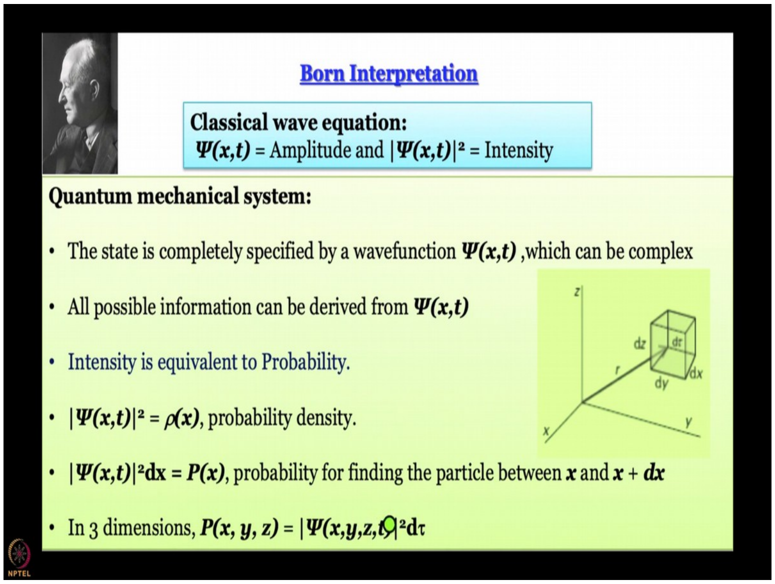

Born Interpretation

**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 $x + dx$
- In 3 dimensions, $P(x, y, z) = |\Psi(x,y,z,t)|^2 d\tau$

That this mod Psi square which means Psi star multiplied by Psi gives an idea of intensity. Think of sound waves or light for that matter electromagnetic wave of light, square of displacement has got to do with intensity. So, what one said is that that means mod Psi square of this side that we are talking about something that we got from Schrodinger equation must have to do with the intensity of de Broglie wave or matter, what is the meaning of intensity of matter?

That is what leads to a very powerful tool so as you know in quantum mechanical system we have said that the state is completely specified by wave function Psi and thus I might as well be complex you can get all possible information by using operator and now comes Born interpretation intensity is; intensity of this wave that we have Born interpreted this as something to do with probability, why so?

Because if you are talking about a particle and if the intensity of the particle is more at some point then at some other point what does it mean? That essentially means that the particle is it is more probable to find the particle at that point with at the first point. One can think of let us say we have a fly which has ink on its feet and let us say the fly keeps on sitting on a piece of paper. If it sits on more on a particular position more often than it does at some other position then at the first position will be more ink marks.

So the spot that is going to be darker than in the other position, so that is a very rough analog of what Born had said. What he said is that intensity of matter wave is the probability is a measure of probability of finding the particle at that particular position. So, now you do not have to talk about matter wave anymore. One can talk about probability wave which is not very difficult to handle all of a sudden things start making sense.

Because in wave mechanical treatment what we understand is we cannot have a very deterministic view but we can have a probabilistic view which can tell what is the region of space where the particle is there more probably than at some other region. And that is determined by mod Psi square. The well; the product of a wave function and its complex conjugate provided it is complex if it is not complex and it is a square.

But it is also important to remember that mod Phi square is Rho x probability density it is not the probability itself because you cannot really talk about probability at a point a point has no dimensions. When one wants to talk about probability one has to define a volume element. So, the probability in one dimension let us say is given by the mod square of Psi multiplied by dx for a particular value of x.

This is the probability of finding the particle between x and x + dx. So, it is very much x dependent because Psi itself is x dependent. In three dimensions we can write the probability is Psi xyz t mod square multiplied by d tau where d tau is the volume of a small element with size dx dy dz along x y z respectively. So, you have to define a small element how many no matter how small it may it may be and work with it in order to talk about actual probability.

In when we think in terms of Cartesian coordinates the volume of the volume element always remains same dx dy dz. So, if you think of the shape of the probability distribution it is determined by that shape of mod Psi square however and we are going to see that many times we have to deal with Cartesian polar coordinates and in this case the size of the volume element itself changes as a function of R will come to that later.

And then both become important what R is and what is mod Psi Square, we will come to it when we talk about hydrogen atom but right now it is important to understand there according to Born interpretation mod Psi square gives probability density not probability itself and when this probability density is multiplied by an appropriate volume element that is when we get the probability of finding the particle at that particular location.

And that immediately opens up other aspects of quantum mechanical treatment it leads to the next postulate.

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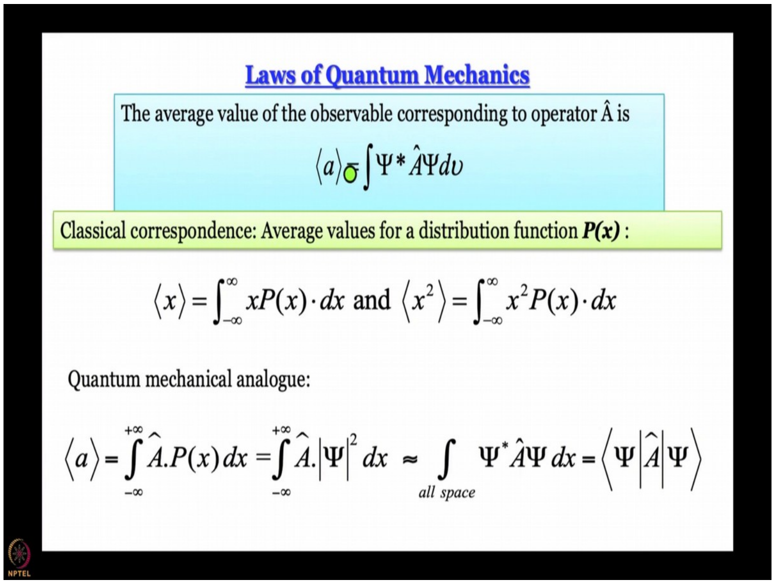

## Laws of Quantum Mechanics

The average value of the observable corresponding to operator Â is

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

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

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

Quantum mechanical analogue:

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

The next postulate of quantum mechanics is that the average value of observable corresponding to an operator is this integral Psi star A hat Psi dv I had written d tau in the previous slide did of dv and d tau mean essentially the same volume of the small volume element now where did this come from and then again let me say that this may be a little incomplete description we will see what the complete description is as we go on. Where does this come from well it comes from classical correspondence.

In classical mechanics it is known that if you have a population distribution function P of x it can be anything Gaussian, Lorentzian something two-sided exponential then the average value is given average value of some property x, x here and need not be real x, some variable the average value is given by x multiplied by the population distribution integrated over all space. Essentially what that means is that you take the population distribution and this multiply and plot all over space.

The area is what will give you the average value, for x square is given by the same thing as I said expand in a function we replace x or x square by some arbitration f this is what the equation will be. So, this was again known from classical mechanics. And according to Born interpretation what is P of x? P of x is essentially the probability distribution right so that is mod Psi square. So, according to Born interpretation the quantum mechanical analog would be something like this.

How do I know what the value of x is I have to make the operator a operate on the population distribution itself so and then integrate over all space so a operates on mod Psi square dx mod Psi square means Psi star Psi, so I can take psi star out and I am left with integral over all space Psi star A hat the operator Psi dx and as said earlier we often write it in the convenient bracket notation where the bra vector contains the complex conjugate or Psi, Psi in bra vector means it is complex conjugate.

The ket vector contains a hat psi the second line is actually not required but it is there just so that it looks symmetric it is alright if I don't even write this second line. But this is how in bracket notation we represent this integral and the take-home message from this slide is how to find an average value this average value is also called the expectation value. And what it means is that you perform a large number of measurements remember from the last module what happens when you perform measurements successively we are not talking about that.

They are saying we have the system in an entangled State then we make a measurement we get some value because of wave function collapse. Then we let the system be and when we let the system be once again the states get entangled we wait for a sufficient time make one more measurement now I get some value of the variable once again maybe the same as what we got earlier maybe not the same as what we got earlier.

So we keep on making a large number of measurements one lakh measurements one crore measurements whatever we can and then when we do that we get a large number of values different eigen values what is the average value average value an expectation value is given conveniently by this. So, one way is to keep on doing it at different times otherwise theoretically what you can do is you can just work out this integral and you will get the expectation value.

Once again this description is not complete we will come back to what the complete description is this is really the numerator of it there can be something in the denominator provided wave function does not satisfy a particular condition.

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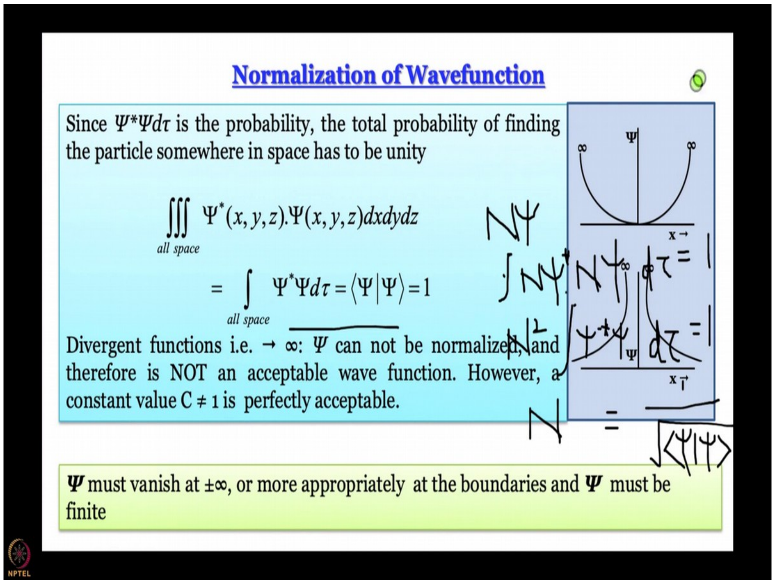

## Normalization of Wavefunction

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

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

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

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

$\Psi$ must vanish at ±∞, or more appropriately at the boundaries and $\Psi$ must be finite

$$N\Psi$$

$$\int N\Psi^* N\Psi \, d\tau = 1$$

$$N^2 \int \Psi^*\Psi \, d\tau = 1$$

$$N = \frac{1}{\sqrt{\langle\Psi|\Psi\rangle}}$$

And that particular condition is that of normalization. So, once we accept Born wave function Born interpretation of wave function we also have to accept that these wave functions have to be normalized. What is the meaning of normalization? Well, see Psi star Psi d tau is the probability of finding the particle at some particular point within a volume element at some particular point. Now if I just integrate this over all space integral of Psi star Psi d tau over all space what does it give me probability of some of finding the particle somewhere in the universe.

Now the particle would better be somewhere in the universe right otherwise and what are you talking about. So, probability of finding the particle somewhere in the universe is equal to one will definitely find it. So, integral of Psi Psi star d tau which can also be written as sign bra vector sign ket vector bracket Psi Psi is it has to be equal to one. This is the normalization condition. So, for born of one condition for born approximation interpretation to hold one interpreted;

For born interpretation to hold the wave functions have to be normalized this is what was not accounted for in our earlier discussion of your expectation value. The earlier expression holds only if one can; one works with normalized wave function otherwise it does not. It is not difficult to normalize away function that is unnormalized by itself one just has 2 multiply by n multiplication by n and integration over all space should give it give us one.

So we can do it here please forgive my poor handwriting especially using a mouse what we are saying is that suppose Psi is not normalized and let us say upon multiplying it by n it becomes normalized then this integral here has to be rewritten, how do we rewrite we can rewrite as integral N Psi multiplied by N Psi d tau that is a d is equal to 1. Now N is constant well I should write star here. I can take N outside the integral so I can write n square integral Psi star Psi d tau equal to 1.

What is N then? N can simply be written as 1 divided by square root of since I am tired of writing that integral I write in the bracket notation integral Psi star Psi d tau so this is how one finds out the normalization constant and in the tutorial we are going to have problems not only now but also later on how one can work it out once you do it, it will be very easy. But now one thing is normalization, second thing is that we understand that you cannot normalize a function that is divergent.

So also Psi has to vanish when the x-variable or whatever is the coordinate becomes plus infinity or minus infinity so let us move bounded right and that the boundaries Psi must be finite. So, functions like these two are not allowed. The first function is not allowed because at x equal to infinity the function becomes infinity so you can never integrate this function and get one. Second function is also not allowed because it becomes infinity in the middle.

So we see that as a result of Born interpretation some conditions some restrictions start coming on the wave function these are unacceptable wave functions as we have said already. These are some examples of acceptable wave function.

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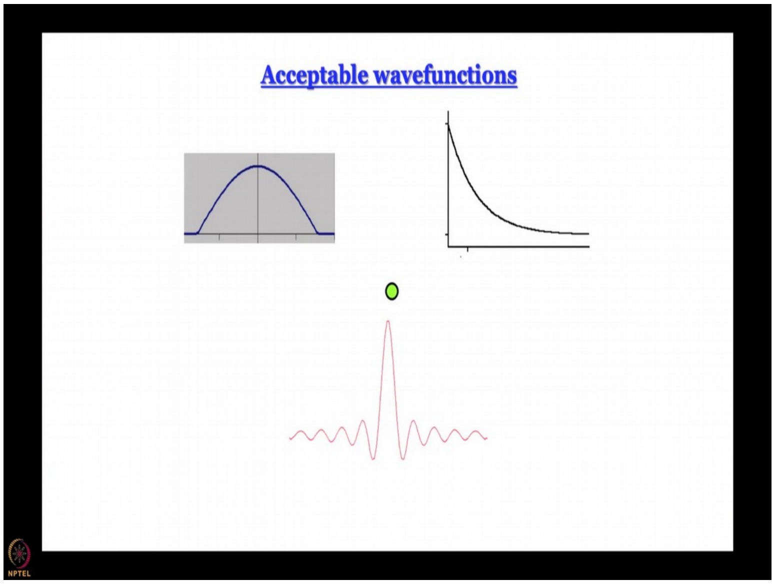

Acceptable wavefunctions

Let us look at the first one, it becomes zero at long distances on both sides. So, here you have something you can always integrate it and get one by multiplying it by the appropriate constant you can ensure that the area under this curve is 1. What about the second one? Here the function becomes 0 asymptotically so it is still integral and you can still get a normalization constant for which the area under the curve is going to be 1.

This is a plot of sine x by x and this is something that actually appears in many different problems and is a favorite question with many examiner's because sine x by x at x equal to 0 is if you want to be orthodox not defined because x equal to 0 and at x equal to 0 sine x is also equal to 0 so you have a 0 by 0 situation you do not know what it is? Is it too small it is it too large fortunately we know what it is?

Because if we go a little bit away from 0 they on this side or this side what is the value? It is close to 1. So, what I am saying is limit for x tending to 0 sine x by x is actually 1 so we can use that limit and with the understanding that this function is discontinuous at only one particular point well the discontinuity is a problem right. If it is discontinuous then we do not know what the probability is at that point, so we cannot integrate and get 1.

But here this is a special case of what is called removable discontinuity. Since the discontinuity is only at that point and the limits from the two sides converge being might as well substitute the value at that point by the limit and say that this is as good as a continuous function and therefore it is acceptable. Now let us see some examples of unacceptable wave functions here we have one.

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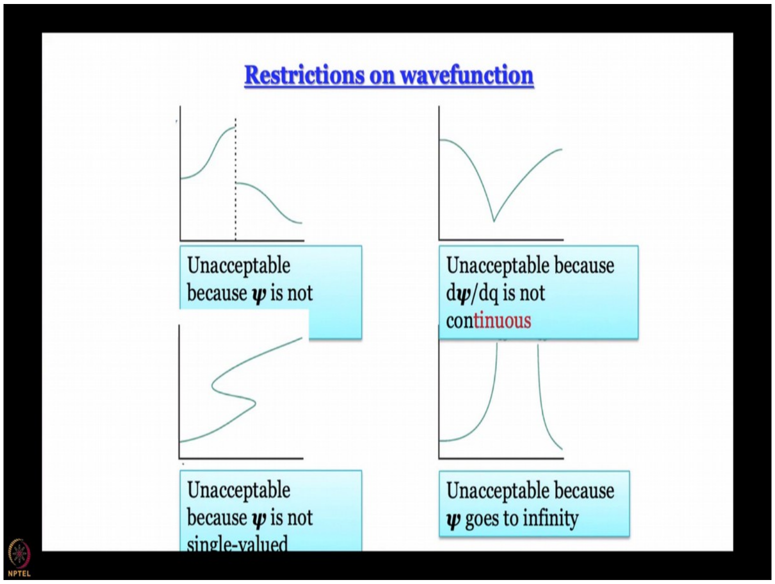

Restrictions on wavefunction

Unacceptable because $\psi$ is not

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

Unacceptable because $\psi$ is not single-valued

Unacceptable because $\psi$ goes to infinity

So, here what we have is that once again we have a discontinuity at a single point but then if you approach from the right you have some value if you approach from the left you have some other value. So, you cannot really like write a limit this is not a converging situation. So, you do have discontinuity at this particular point and therefore it is unacceptable. What about this function it is continuous but here we are sharp break.

From most of the applications it is unacceptable because dpsi dq is not continuous but this is really not one of the most stringent conditions there is a condition and we are going to point it out when we drive it where we are fine with the wave function even though this is really not met. Third, this one is also not acceptable why because look at this point we have 1, 2, 3 values of Psi which means there are three different probabilities of finding the particle in that particular point makes no sense.

And it is okay that quantum mechanics is not determinist that is why we were working with probability. But if there is an uncertainty in probability that is not an acceptable situation so multiple multivalued wave functions are not acceptable Psi has to be single value. And finally this is not acceptable for the reason that we have said already it is good that we are showing it once again because since I decided to scribble on that slide you could not really see that diagram there.

So here it becomes infinity at some point right if it becomes infinity then you cannot integrate and get 1. So, what we see is that many of the wave functions that may arise as a result of solution of Schrodinger equation or any eigenvalue equation are not allowed because they do not satisfy this requirement imposed; they do not satisfy some requirement or the other that get imposed because of Born interpretation that mod Psi square is probability density.

Remember we do not have quantization so far, does this mean quantization we will see but let us summarize first. What we see about the wave function this enigmatic wave function that we are talking about in this module is that first of all of course it is a solution of Schrodinger equation

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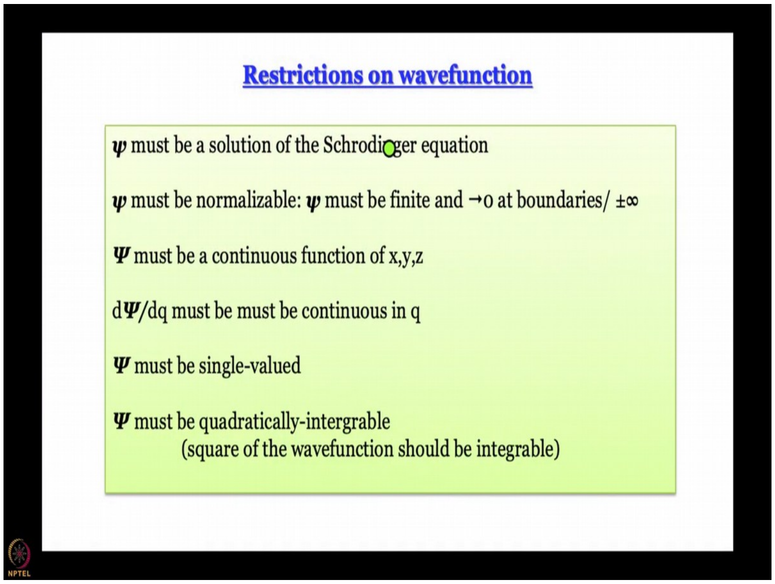

**Restrictions on wavefunction**

$\psi$ must be a solution of the Schrodinger equation

$\psi$ must be normalizable: $\psi$ must be finite and →0 at boundaries/ ±∞

$\Psi$ must be a continuous function of x,y,z

$d\Psi/dq$ must be must be continuous in q

$\Psi$ must be single-valued

$\Psi$ must be quadratically-intergrable
(square of the wavefunction should be integrable)

Now we bring this condition that it has to be normalizable Psi must be finite and it must tend to 0 at boundaries, boundaries means boundaries can be at plus minus infinity must be continuous well these two basically mean the same here we have written xyz here we have written in terms of q must be single valued and should we quadratically integral I had rather not write the mass here. So, when you impose so many restrictions many of the wave functions become disallowed only some wave functions are left.

And remember each wave function corresponds to a particular energy. So, what you are saying is that many of the energies are not allowed only some are, this is a different way of saying that energies are quantized. So, what we are proposing is that we get quantization as a result of what are called boundary conditions which in turn arise out of Born interpretation. So, born interpretation not only gives us sort of a sense of what the wave function really means it also leads to quantization which had remained elusive so far.

So what we will do is that we are going to demonstrate this point by working with some exactly solvable systems.

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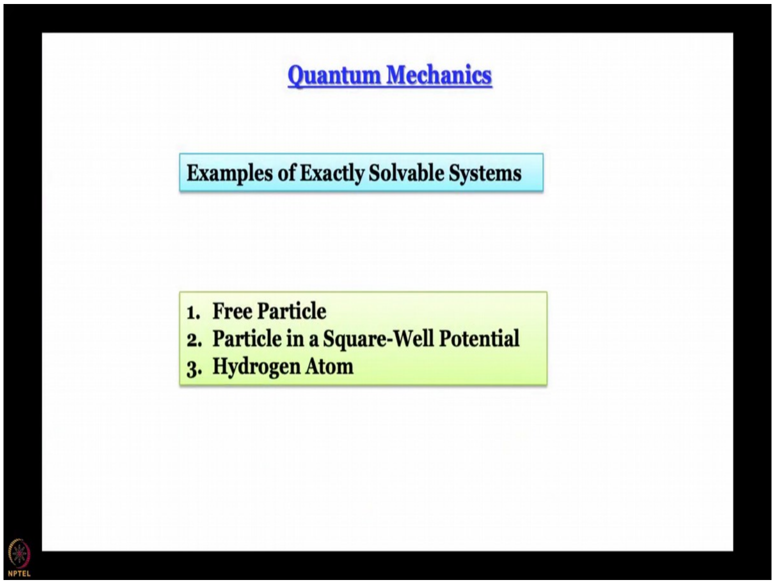

Quantum Mechanics

Examples of Exactly Solvable Systems

1. Free Particle
2. Particle in a Square-Well Potential
3. Hydrogen Atom

In the next few minutes that we have today we are going to introduce the quantum mechanics of a free particle. A free particle means something that moves without interacting with anything else so it thinks that there is nothing else in the universe. So, if it thinks there is nothing else in the universe what it means is that it does not experience any potential energy because potential energy arises as a virtual position.

So you it takes two to tango you need to have two different things to have a potential energy between them. So, if you have a free electron which feels that there's nothing else there's no potential energy vx equal to 0. Then we are going to put this in a same free particle in a square well potential and finally we are going to go on to our first atom that is the hydrogen atom. So, let us quickly talk about the quantum mechanics of free particle we are going to perhaps come back and revise it in the next module.

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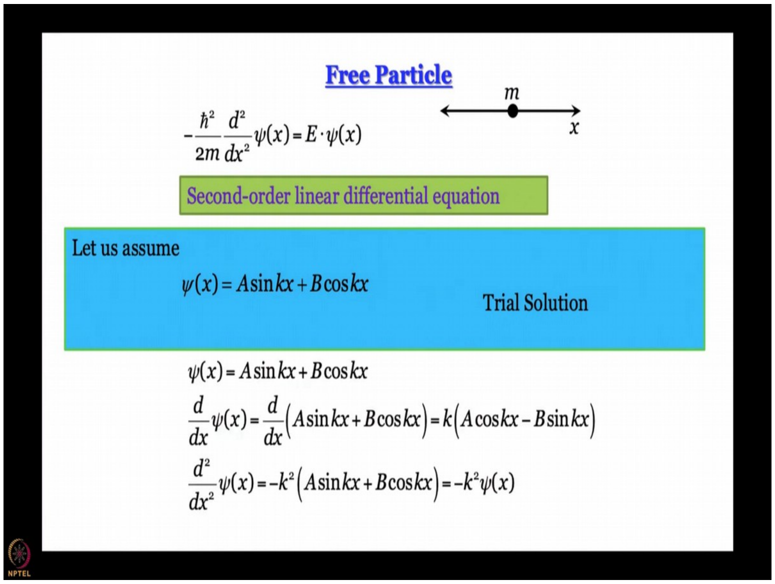

## Free Particle

$$-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\psi(x)=E\cdot\psi(x)$$

Second-order linear differential equation

Let us assume

$$\psi(x)=A\sin kx+B\cos kx$$

Trial Solution

$$\psi(x)=A\sin kx+B\cos kx$$

$$\frac{d}{dx}\psi(x)=\frac{d}{dx}\left(A\sin kx+B\cos kx\right)=k\left(A\cos kx-B\sin kx\right)$$

$$\frac{d^2}{dx^2}\psi(x)=-k^2\left(A\sin kx+B\cos kx\right)=-k^2\psi(x)$$

So this here is our time dependent Schrodinger equation as we know as we said in a free particle there is no potential energy. So, we should set vx to be equal to 0 no external forces that is it realistic? It can be, approximately we are going to discuss some actual chemical systems where the electron behaves more or less like a free particle. So, put vx equal to 0 the equation boils down to this -h cross square by 2 m no sense writing del anymore d 2 dx 2 Psi of x equal to e multiplied by Psi of x.

This is the equation for a free particle which moves along one dimension. So, free particle in one dimensional space if we want a free particle in 3d space all we have to do is write three times del del x 2 del 2 del y 2 then 2 del z 2 it is not difficult alright. So, this is a differential equation as long as we restrict to a single dimension is quite simple I think all of us will be able to solve it, so I leave it to you to solve this equation by yourself all of us have done it in class 11, 12 if you have studied maths.

So what we do is we take a trial solution and the most general trial solution would be A sine kx + B cos kx and when all we have to do is take this function A sine kx + B cos kx differentiate twice then multiplied by -h cross square by 2 m. When we do that what do we get we get d2 dx 2 Psi of x is equal to -k square multiplied by Psi of x ok take it and plug it in the Schrodinger equation.

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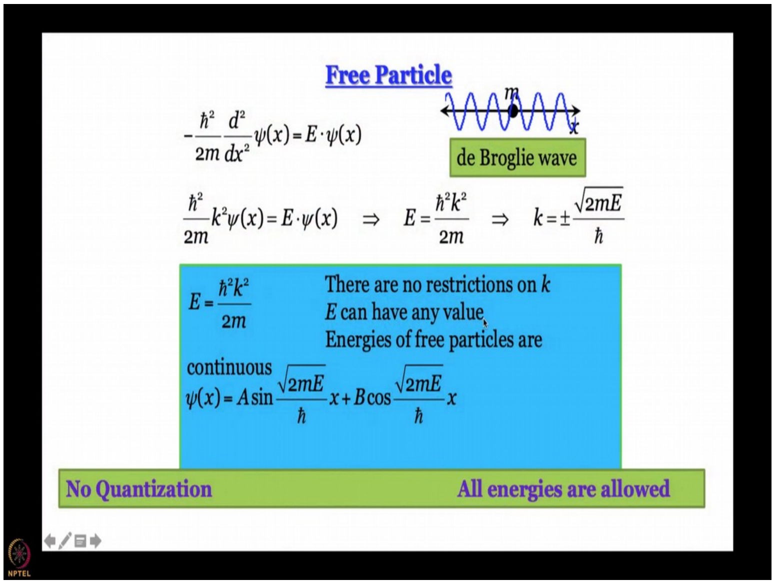

**Free Particle**

$$-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\psi(x)=E\cdot\psi(x)$$

$$\frac{\hbar^2}{2m}k^2\psi(x)=E\cdot\psi(x)\quad\Rightarrow\quad E=\frac{\hbar^2k^2}{2m}\quad\Rightarrow\quad k=\pm\frac{\sqrt{2mE}}{\hbar}$$

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

There are no restrictions on $k$

$E$ can have any value

Energies of free particles are continuous

$$\psi(x)=A\sin\frac{\sqrt{2mE}}{\hbar}x+B\cos\frac{\sqrt{2mE}}{\hbar}x$$

No Quantization All energies are allowed

We get remember right hand side eiganvalue is E, so when we take this k square Psi of x multiplied by h cross square by 2m we get E Psi x, so E turns out to be there is a -k remember E turns out to be h cross square k square divided by 2 m which means k is equal to root over 2 mE by h cross. So, you have got an expression for energy of the free particle by using Schrodinger equation and these calls for celebration because for the first time in this course we have actually solved a Schrodinger equation and got the value of an energy.

Do we have quantization? Actually we do not, we do not have quantization here because there is no restriction on the value of k, k can be anything therefore E can be anything, no quantization.

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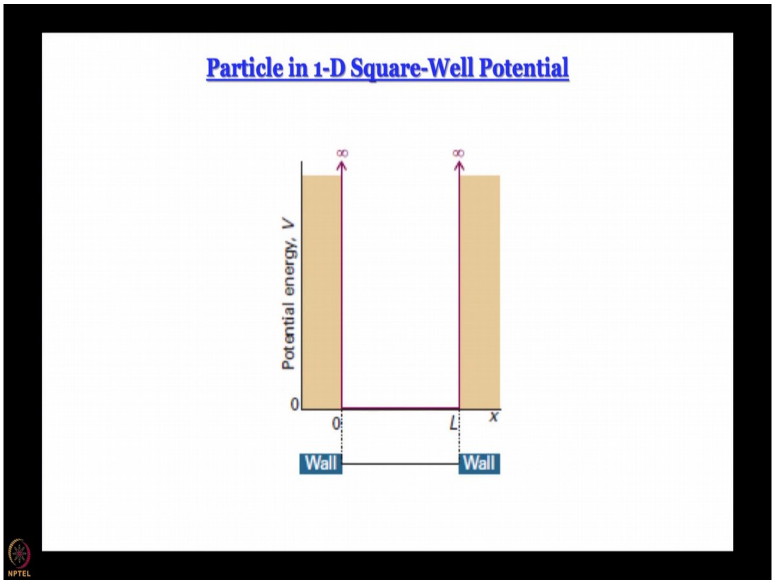

Particle in 1-D Square-Well Potential

So, we will see that quantization will arise when we restrict this same free particle within some boundary when we put it in what is called particle in a 1 V Square L potential. And before we do that we will also have something more to say about whether this wave function that we got for a free particle is really all that great or not that is what we are going to take up in the next module. So, with this we have completed the first week of this course.

We have introduced ourselves we have learned why classical mechanics fails, why Bohr model does not work beyond a certain extent even though it gives all the right values. We have learned how wave mechanics begins and we have learned what the probabilistic interpretation of born is for the wave function. What we have not got is how does quantization come that is what we will obtain when we start discussing this one-dimensional square well potential next week.