Concepts of Chemistry for Engineering
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Lecture – 10
Hydrogen atom: Wave functions

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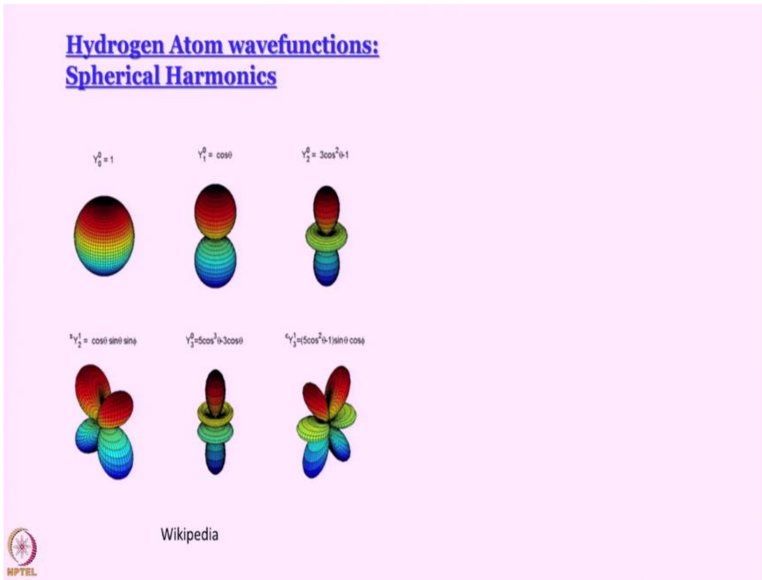

We are on our way to seeing these beautiful pictures. Well, this is slightly a little bit of a spoiler because we do not know yet of what we are talking about. But what we are showing you are depictions of hydrogen atom wave function. I think you are familiar with the shapes, you know shapes of orbitals. So, we are going to say what orbitals actually are.

What you think orbitals are may not be the correct definition. But more when we get there for now, let us just say, right now, our quest is for wave functions for hydrogen atom. And what you see here are spherical harmonics. Spherical harmonics means the solution of the angular part of Schrodinger equation. What is angular part?

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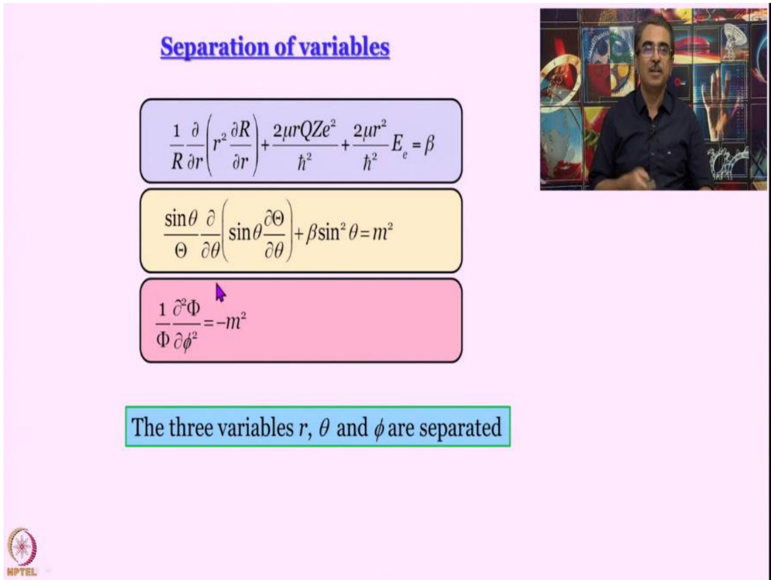

Well, this is where we were, we could separate the Schrodinger equation for hydrogen atom into three different equations, one in terms of the radial part, the second one in terms of theta, third one in terms of phi, and in case you are rusty on what r, θ and are, I recommend that you please go back to I think lecture before the last.

$$\frac{1}{R}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right)+\frac{2\mu rQZe^2}{\hbar^2}+\frac{2\mu r^2}{\hbar^2}E_e=\beta$$

$$\frac{\sin\theta}{\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta}{\partial\theta}\right)+\beta\sin^2\theta=m^2$$

$$\frac{1}{\varphi}\frac{d^2\varphi}{d\varphi^2}= -m^2$$

And that is where we had discussed spherical polar coordinates in some detail. But crux of the matter is now we are in a situation where the equations in the three variables r, θ and φ are separated, last one is simple let us, try to solve that.

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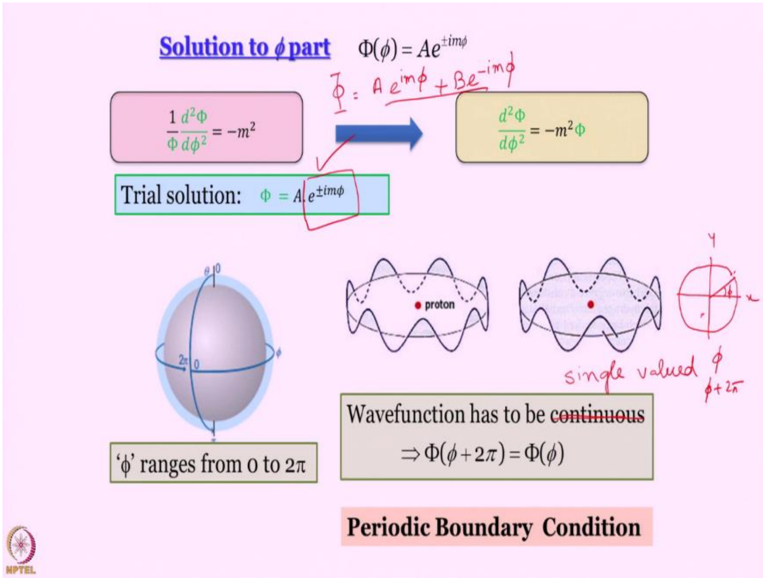

Very simple differential equation in terms in φ.

$\frac{1}{\varphi}\frac{d^2\varphi}{d\varphi^2} = -m^2$

Second order differential equation, do not you know how to solve it? I am sure you do. How do we go about solving it? Well, this is how we write it and we use a trial solution. The trial solution we are going to use is A$e^{\pm im\varphi}$. In fact, I do not even like to write $e^{\pm im\varphi}$ the $\pm$ is also not required.

You might say that, why are we using this? Mathematically it might make more sense to write something like this, that, $\Theta = \mathrm{A}e^{im\varphi} + Be^{-im\varphi}$,. Who will stop me if I write it like that? Nobody will stop me we can write it. But I write it, this solution itself is also correct. This is a complete solution.

This is a partial solution (Φ=A$e^{\pm im\varphi}$).

I prefer to work with the partial solution because that gives me access to some property of the electron in the atom. We will get there, but is this solution incorrect? No, it is correct, you can do that. And in fact, if A and B happen to equal, you know very well what the form of this thing is going to be, well not happen to be equal if A= A and B = *i*A maybe you know what it is going to boil down to?

But we are going to work with A$e^{\pm im\varphi}$. Once again, because you have the benefit of hindsight. Plug it in there as usual, I hope everybody here is sitting with a pen and paper. And I hope everybody is writing as we go along. There is the only way to understand if you just hear me speak, nothing will sink in. So, please do keep on writing, $\frac{d^2\varphi}{d\varphi^2} = -m^2\Phi$.

So, what you need to do is you need to differentiate this Φ=A$e^{\pm im\varphi}$ twice with respect to φ, do it see what you get? That is what you get just differentiate it twice, you get actually m^2. And this is why we use m^2 in the separation of variables. Because you know that then I can write this conveniently in terms of $e^{im\varphi}$. And what is m, why m and not q, we will come to that, that also will take us to actually familiar territory.

Now, one thing to remember is that φ ranges from 0 to 2π, by the way do we have quantization yet? We do not, but we are very close to it. Now, see, remember boundary condition. So, if this is our wave function of course, you can see that there is an imaginary wave function. How we are drawing it like this? Bear with me for a moment. What I am saying is, whatever is the value of the wave function, if you do not want to draw do not draw, but it has to be continuous.

And it has to be single valued. Actually, I should have written single valued here rather than continuous. This is again a persistent issue that is there with this slide I do not know why I did not change it. Wave function has to be continuous, it has to be single valued also. So, now see I start from a point and so, this is some value of φ. So, let us say this is my xy plane, this is x, this is y, this is a point I start from a point, go around in a full circle come back here. This point you can write as, this is φ, I can write it as φ, I can write it as φ + 2π also.

So, will you agree with me if I say that Φ = φ + 2π is equal to Φ = φ, why, because the wave function has to be single value, do not have to draw it like this wave function as to single valued. So, whatever is the value of Φ at φ the same value must be obtained when you go around a full circle because you have reached the same point, what is this? It is a boundary condition.

And since this boundary condition involves a periodicity of 2π, it is called a periodic boundary condition. Even though this is a chemistry course, this is nothing to do with per-iodic something, periodic boundary condition.

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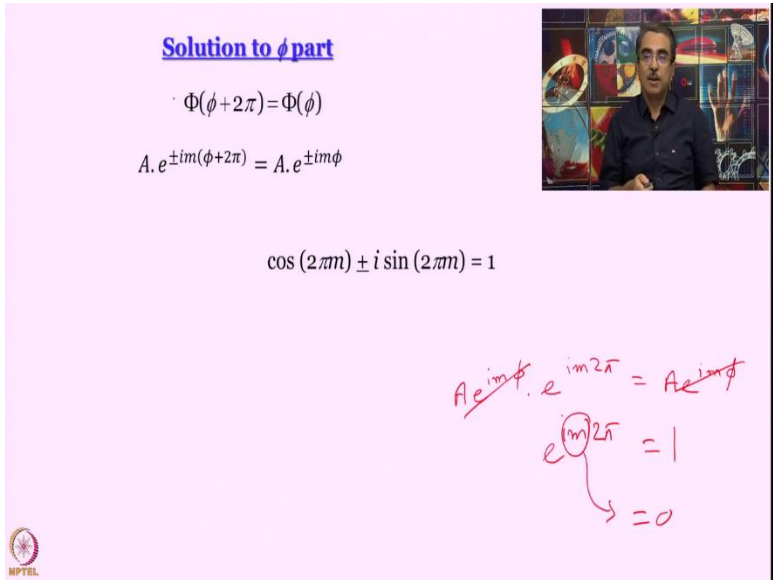

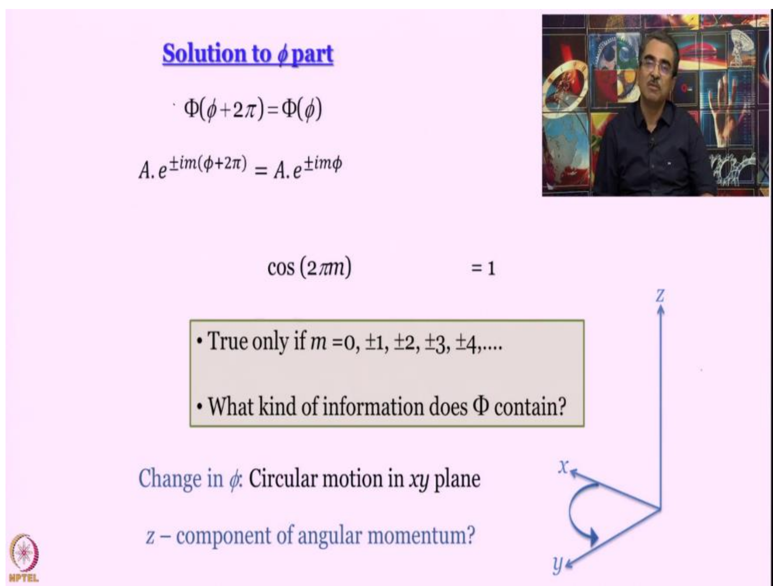

So, this is what it is, A$e^{\pm im(\varphi+2\pi)}$, I am not saying $\pm$ because I do not like it as you will see $\pm$ will come anyway later on. A$e^{\pm im(\varphi+2\pi)}$ multiplied by, A$e^{\pm im\varphi}$what is the solution? Solution is very simple I can write like this I will write and then I will erase also. I can write is equal A$e^{im\varphi}$ multiplied by $e^{im2\pi}$ to get A$e^{\pm im\varphi}$. And then these two cancel, you are left with $e^{im2\pi}$= 1.

So, easiest thing to do here is to set m = 0 then of course $e^{im2\pi}$= 1. But now, if we just write this, we actually miss out on some information. So, again there is a message for all of us how you write the wave function that is actually very important, how you write the wave function might allow you to see some things or might actually hide some things from your view. So, to get the complete picture remembering that we are dealing with a situation where there is a periodicity of 2π, periodicity of 2π means what?

What is it has periodicity of 2π? Things like angles. So, what we will do is in order to extract the complete picture, we will write this $e^{im2\pi}$ as your $\cos(2\pi m) \pm i\sin(2\pi m)$ = 1. We are going to write this in the trigonometric form. Now, what do we see? On the right hand side there is nothing in i. So, in the left hand side, this $\sin 2\pi m$ must be equal to 0 then and only then does this ($i\sin(2\pi m)$) vanish.

So, $\cos(2\pi m)$ = 1 holds when m = 0, $\pm 1, \pm 2, \pm 3,$ so, on and so forth. We have got the possible values of m from here. Now, we have got quantization. Not n quantization of energy something else to know what the something else is, we have to think what kind of information does Φ contain? So, what we can think is this. This is what φ is. It is an angle, angular displacement from x axis in x y plane.

So, a circular motion in x y plane would that not involve an angular momentum along z axis? Yeah, if you have circular motion and x y plane, you are going to have an angular momentum along Z axis depending on the direction of rotation, it can point up can, it can point down but it will be along Z axis anyway. So, now we asked is it possible that the information contained φ is that of Z component of angular momentum, makes sense, but we have to verify it.

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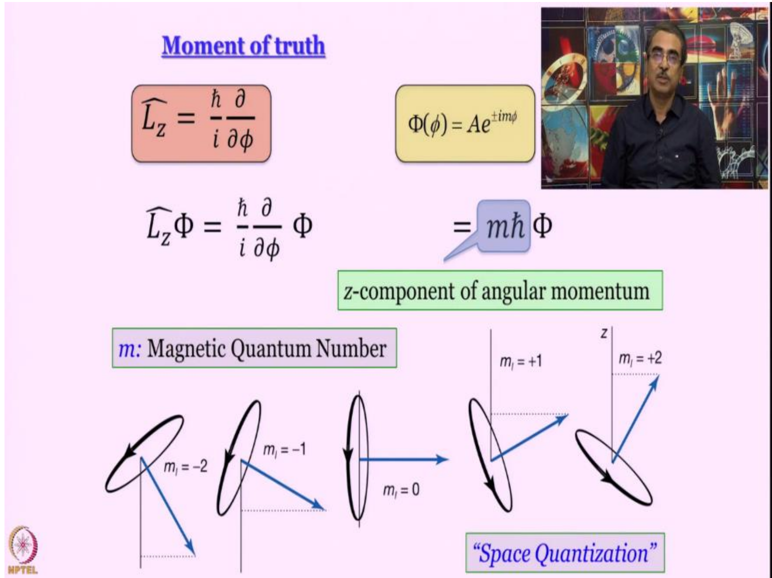

So, this here is $\hat{L}_z$ hat operator that we talked about earlier, $\hat{L}_z = \frac{\hbar}{i}\frac{\partial}{\partial\varphi}\Phi$. This is a wave function make $\hat{L}_z$ operate on Φ, what you get? Is what you get, m$\hbar\Phi$ don't' you, an eigenvalue equation with a real Eigenvalue, m$\hbar$ and remembering that m = 0, 1, 2, 3, rather 0, $\pm1, \pm2, \pm3,$. Now, you see why I do not like to write $\pm$ here, because in any case, naturally, the solution contains $\pm$.

So, this is your Z component of angular momentum. m is our familiar magnetic quantum number. That is why we wrote m^2 and nothing else. So, what does it tell us, it tells us that since m = 0, $\pm1, \pm2,$ so on and so forth, we get back to the same kind of inference that we had from both theory. Angular momentum can point in different directions. The only thing is, since we cannot really talk about the trajectory of an electron in a quantum mechanical system anymore, we might as well shade these orbits.

But we should not shade the arrows. So, these arrows denote the direction of angular momentum, what we learn is that the angular momentum vector can take up only specific orientations in space. With respect to z, what is z? Well, to know what orientation it is, you have to apply a magnetic field that is what defines the direction of z.

Remember, before making the measurement, the system exists in an entangled state, only upon making the measurement, the wave function collapses into an Eigen function, which you see. So, we arrive at space quantization, space quantization was a term that was actually from old Quantum theory, we arrive at space quantization, using quantum mechanics.

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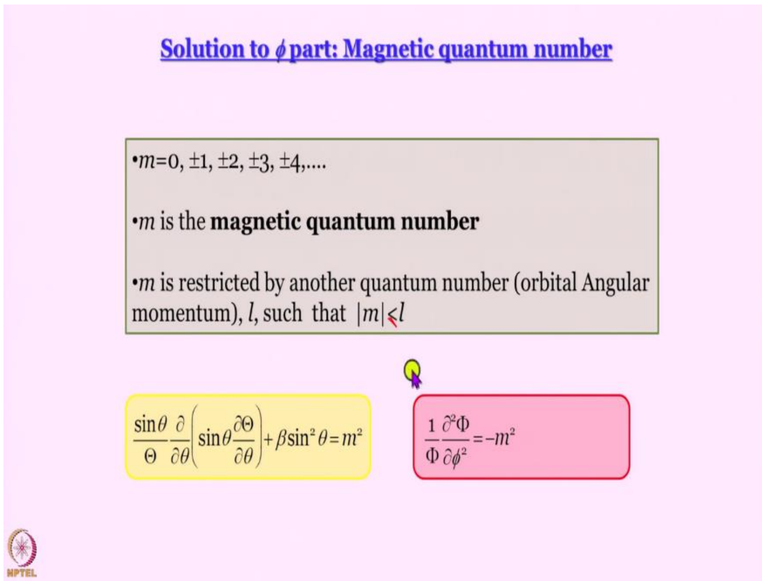

This is the solution to the magnetic quantum number then, this is what we have learned so far, m = 0, $\pm1, \pm2, \pm3, \pm4, ...$ magnetic quantum number. Now, it is restricted by another quantum number (l).

$$|m| \leq l$$

Where does that come from? That comes from solution of the θ dependent part of the equation. And we will show you why magnitude of m has to be, now here I better correct this mistake. Because in my regular class, at least one student has been very worked up about this.

So, let me correct it here. Less than equal to l. So, what do we do here? Now, with the knowledge of m, we go back, and we have to work out this θ dependent part of the wave equation, which is formidable, we will not do it.

$$\frac{\sin\theta}{\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta}{\partial\theta}\right) + \beta sin^2\theta = m^2$$

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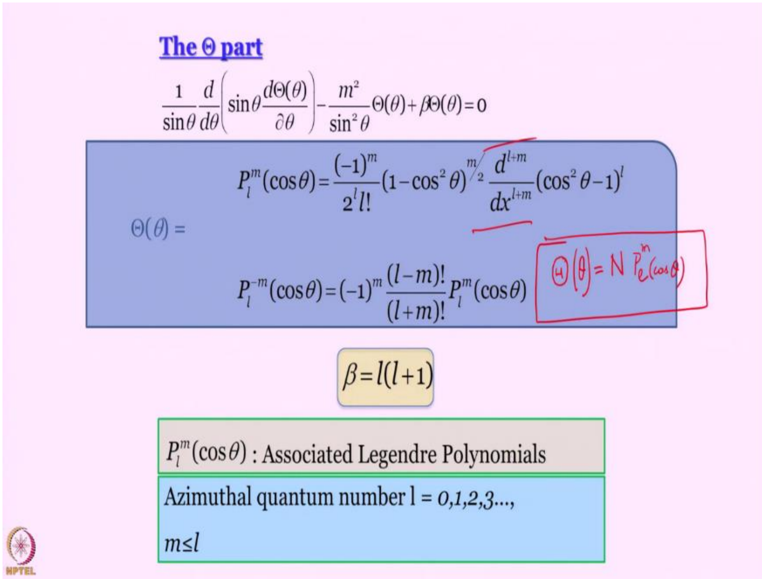

And fortunately, the solution of this θ dependent part was already known by the time this Schrodinger equation was being done.

$$\frac{1}{\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta(\theta)}{d\theta}\right) - \frac{m^2}{sin^2\theta}\Theta(\theta)+\ \beta\Theta(\theta)=0$$

That is how science progresses. To start with, you are driven by curiosity, you just work out, as somebody had said, why do you want to climb the mountain? Because it is there.

So, you want to work out some mathematics, because it is a challenging problem not because by doing that you will be able to develop a product, or you will be able to sell it, or you will be able to make money or you will be able to solve the energy crisis of the planet earth, not necessarily, those are all big problems, you should do it. What I am saying is that curiosity driven research, so called curiosity driven research is also a very, very important thing to do, for the progress of knowledge of mankind.

So, when this kind of equation was solved, there was no idea that this is going to be used in Schrodinger equation for hydrogen atom, people just did it for the fun of it.

$$P_l^m(\cos\theta) = \frac{(-1)^m}{2^l l!}(1-cos^2\theta)^{m/2}\frac{d^{l+m}}{dx^{l+m}}(cos^2\theta-1)^l$$

$$P_l^{-m}(\cos\theta) = (-1)^m\frac{(l-m)!}{(l+m)!}P_l^m(cos\theta)$$

And it became useful because it was known that the solution is in terms of some polynomials in $\sin\theta$, do not worry about these terms. All I want to say is that Θ, I will write it, because I am afraid that some of us might get scared when looking at all this and some of us might stop thinking, please do not.

This is all you need to remember, $\Theta(\theta) = NP_l^m(cos\theta)$ (N=normalization constant).

I will just write N for now, multiplied by a polynomial, so I will write it like this and is characterized by l as well as m, two quantum numbers and this polynomial is in $cos\theta$. Polynomial is in $cos\theta$, forget about this d/dx, it is very scary we will not go there. Please remember this Θ is equal to a constant, a normalization constant multiplied by a polynomial in $\cos\theta$.

What are polynomials in $\cos\theta$? It can be 1, it can be something in $\cos\theta$, something in $cos^2\theta + \cos\theta$ whatever. But these are special kinds of polynomials, they belong to a family of polynomials is called associated Legendre polynomials. So, in this series of polynomials, each polynomial can be related to the previous one and the later one, if you multiply it by $\cos\theta$

We do not need to go into that they are called recursion relations, but that is what gives the name associated Legendre polynomials. Well, what is the meaning of Legendre? Legendre was the name of a famous scientist or mathematician. So, capital theta is equal to $\Theta(\theta) = NP_l^m(\cos\theta)$. And for the umpteenth time, the polynomial is not in θ, not in x y z, this Legendre polynomial is in $\cos\theta$, please remember.

So, that gives rise to this azimuthal quantum number l= 0, 1, 2, 3, see from solution of θ dependent part, you do not get that limit of l, you know very well that l ≤n-1, you do not get that you only get the information that they can be 0 and positive integers. The other thing that comes out from here is $|m| \leq$l, how we will see. One more thing that is very important remember β, $\beta$is here in this equation also.

Beta turns out to be $\beta = l(l+1)$, where l is your secondary quantum number l =0, 1, 2. In fact, my animation is a little problematic here, this beta expression should have come first, l expression should have come later sorry about that, but at least now, everything is there in front of you.

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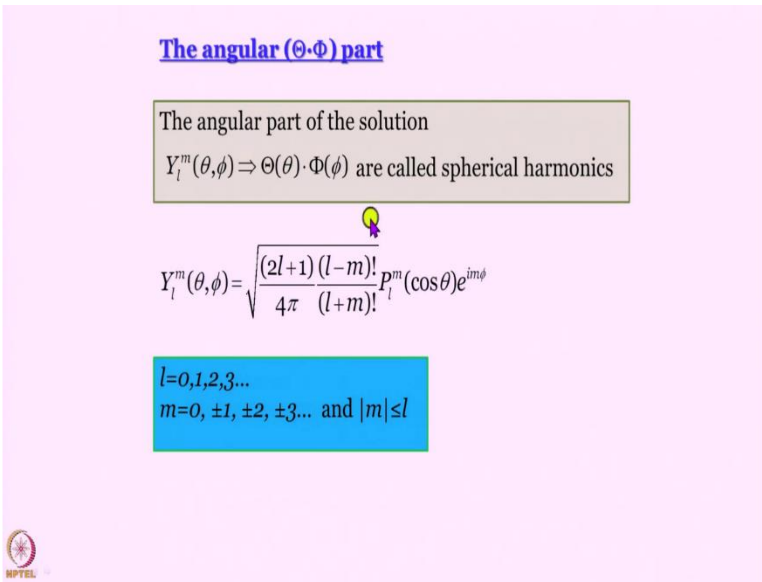

So, this is what it is, we have got spherical harmonics, spherical harmonics are the angular part of the solution of Schrodinger equation for hydrogen atom.

$$Y_l^m(\theta,\varphi) = \Theta(\theta).\Phi(\varphi)$$

$$Y_l^m(\theta,\varphi) = \sqrt{\frac{(2l+1)}{4\pi}\frac{(l-m)!}{(l+m)!}}\,P_l^m(\cos\theta)\,e^{im\varphi}$$

Once again kindly forget this, just think this is N$P_l^m(\cos\theta)$ and this polynomial depends on what l is, what m is multiplied by $e^{im\varphi}$. One more thing.

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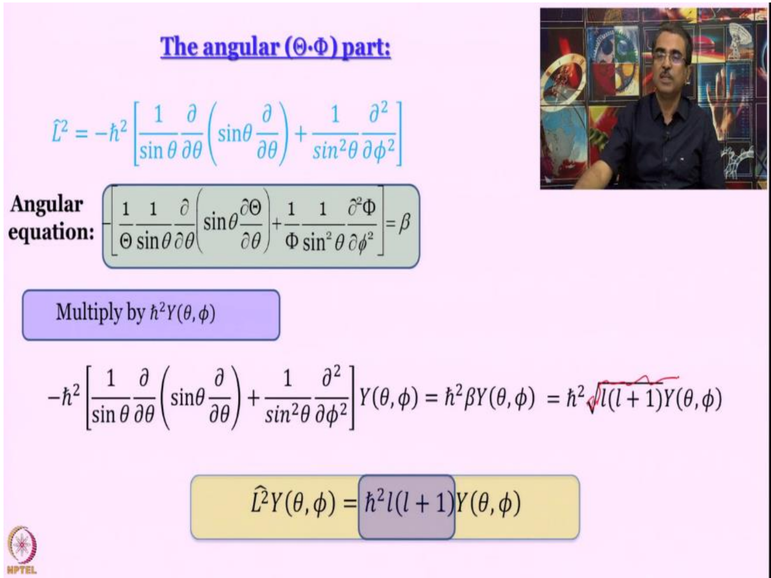

I should have animated this sorry about that. But, now, I take you back to this $\hat{L}^2$operator. See $\hat{L}^2$ operator as we had shown a couple of lectures ago is $-\hbar^2\left[\frac{1}{\sin\theta}\left(\frac{\partial}{\partial\theta}\sin\theta\right)\frac{\partial}{\partial\theta}+\frac{1}{sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right]$. If you remember, this is the angular equation, how do I go from angular equation to just $\hat{L}^2$ multiplied by $-\hbar^2$.

Y(Θ,Φ) that is how you get it. So, you do that this is what turns out.

$\hat{L}^2 Y(\Theta,\Phi) = \hbar^2 l(l+1)Y(\theta,\varphi)$

So, on the left hand side, now, you have the $\hat{L}^2$ operator, $\hat{L}^2 = -\hbar^2\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right]$.

that operates on spherical harmonics to give you what β remember what β is? $\beta = \sqrt{l(l+1)}$. So, $\hbar^2$multiplied by, I have made a little bit of mistake here the square root sign should not be there, there is no square root sign.

So, this I should remove is

$-\hbar^2\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right]Y(\theta,\varphi) = \hbar^2\beta Y(\theta,\varphi) = \hbar^2 l(l+1)Y(\theta,\varphi)$. That is what β is remember, remember beta is $\beta = \sqrt{l(l+1)}$. So, finally, you get an eigenvalue equation for $\hat{L}^2$. $\hat{L}^2$, what is $\hat{L}^2$? This square of total angular momentum operator that operates on the angular part to give you $\hbar^2 l(l+1)Y(\theta,\varphi)$. What is the value of the total angular momentum then?

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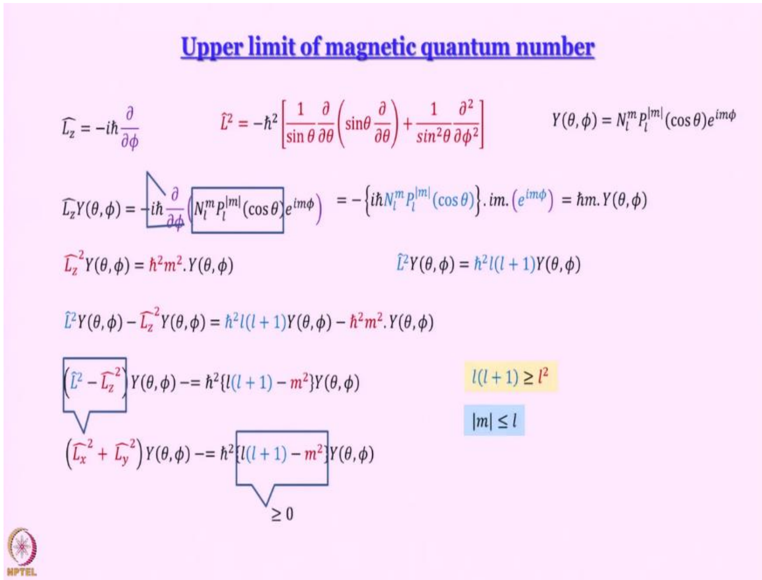

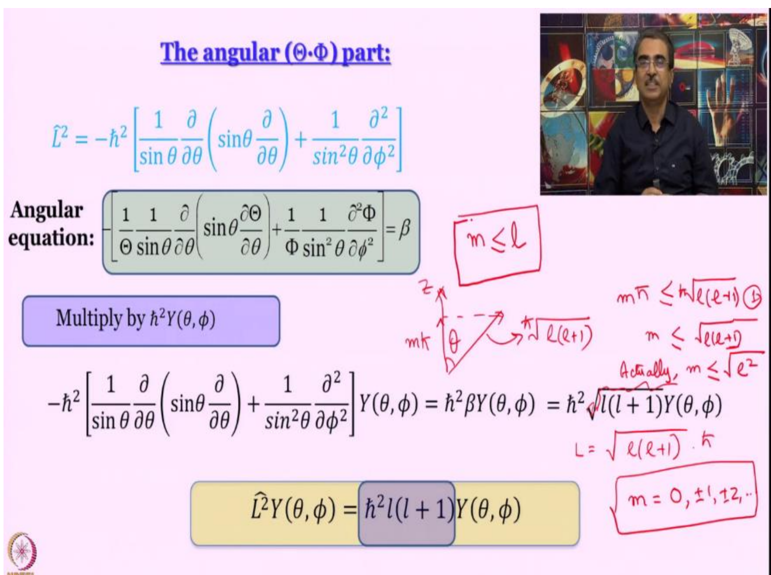

Total angular momentum then is equal to now I will write, I can write like this L=$\sqrt{l(l+1)}$ ħ . Now, if I try to draw something, let us see what I get, this is my z axis and this is the angular momentum vector what is the length here, $\sqrt{l(l+1)}$ ħ remember what the z component is, z component of angular momentum was we found out mħ.

So, can I say that mħ ≤ $\sqrt{l(l+1)}$, make sense. Z component of the angular momentum in the best case scenario would be equal to $\sqrt{l(l+1)}$ is not it? Because this z component here can never be more than the length of the arrow whose component it is, this is θ. So, mħ $\leq \sqrt{l(l+1)}$ that is my first equation.

So, m, well I forgot the ħ here, mħ $\leq \sqrt{l(l+1)}$. Can I make it a little better? Remember what are the values of m, m = 0, $\pm 1, \pm 2,$ so on and so forth. So, it has to be 0 or some positive or negative integers. So, $\sqrt{l(l+1)}$ will it ever be like that, can it be, it can be 0. But suppose $l = 1$, what is $\sqrt{l(l+1)}$,$\sqrt{2}$, that is not an integer.

So, the best case scenario actually turns out to be m $\leq \sqrt{l^2}$ to get rid of that 1. Because, m = 0, $\pm 1, \pm 2,$ and so on and so forth. So, what does that mean? It means, m$\leq$ l is, we have all learned this expression.

Now, we know how it comes, it comes because mħ is the z component of angular momentum root over $\sqrt{l(l+1)}$ is the total angular momentum, z component can never be more than the total angular momentum that is why m$\leq$ l. So, we have arrived at an expression that we have all learned while studying in eleven and twelve.

These are more formal ways of doing it using operators, I think it should be elementary for you now. It is just that it looks a little scary. So, I will not do it, I encourage you to try and work this out yourself. It says the same thing you, it turns out that $\widehat{L_z^2},$

$\left(\hat{L}^2 - \widehat{L_z^2},\right) Y(\theta,\varphi) = -\hbar^2\{l(l+1) - m^2\} Y(\theta,\varphi)$, that operator is written as

$\left(\widehat{L_x^2}, + \widehat{L_y^2},\right) Y(\theta,\varphi) = -\hbar^2\{l(l+1) - m^2\} Y(\theta,\varphi)$, it turns out that eigenvalue of that operator is $-\hbar^2\{l(l+1) - m^2\}$.

Now, $\left(\widehat{L_x^2}, + \widehat{L_y^2},\right)$ that has to be a positive quantity. So, it turns out that this$\{l(l+1) - m^2\} \geq 0$. And then the rest of it is very simple. That is what we have learned today, we have talked about the angular part and we have talked about the angular equation, we have learned how to solve the φ dependent part, we have shown you the solutions of θ dependent part.

And we learned that from the angular part, we can get two very important quantities of hydrogen atom, well of electron and hydrogen atom, total angular momentum, which is determined by the secondary quantum number L and Z component of angular momentum determined by the magnetic quantum number m. Where are those beautiful pictures that I drew at the beginning? We have not got there yet, we will.

Let us wait a little bit before getting there. Let us think of the coordinate that we have neglected so far poor good old small r the radius. Let us see what the r dependent part of the wave function is. Then we will bring together the r dependent, θdependent, φ dependent part and we will talk about the shapes of the wave functions. And that time, we will also formally say, what an orbital is. So, homework for you now, before you see the next videos, is find out from whatever resources you have what is an orbital.