Quantum Chemistry of Atoms and Molecules
Prof. Anindya Datta
Department of Chemistry
Indian Institute of Technology – Bombay

Lecture-25
Hydrogen Atom Schrodinger Equation….Continued

In this module we are going to talk about how we get magnetic and azimuthal quantum numbers in hydrogen atom. And this is by and large going to be a revision of what we had said a couple of modules ago when we talked about rigid rotor. Because this magnetic and azimuthal quantum numbers come from a an exactly similar treatment as we had done in case of rigid rotors.

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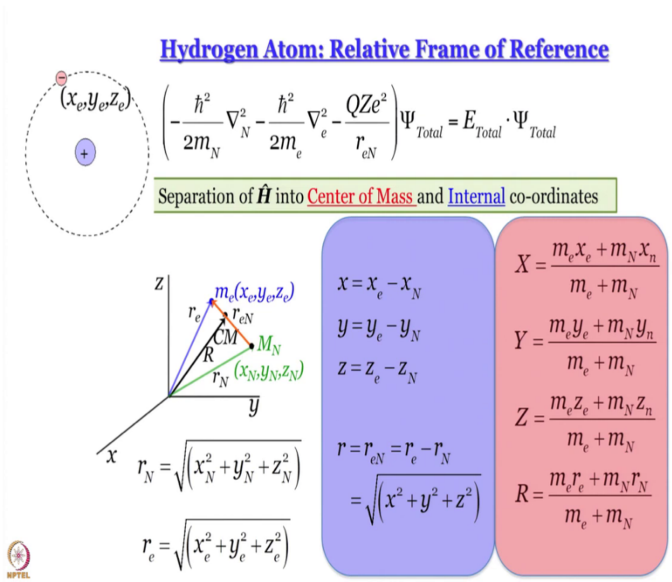

So, to recapitulate this is what we have done. So, far we have said that this hydrogen atom Schrodinger equation for hydrogen atom is written in a relative frame of reference. So, we start with this central force problem you can write the Hamiltonian in terms of nucleus and electron and then by making these substitutions x equal to x e - x N y equal to y e – x N and so on and so forth and capital X equal to mass weighted coordinates.

We can separate the equation into 2, one for the motion of the center of mass and one for the motion of electron with respect to the nucleus.

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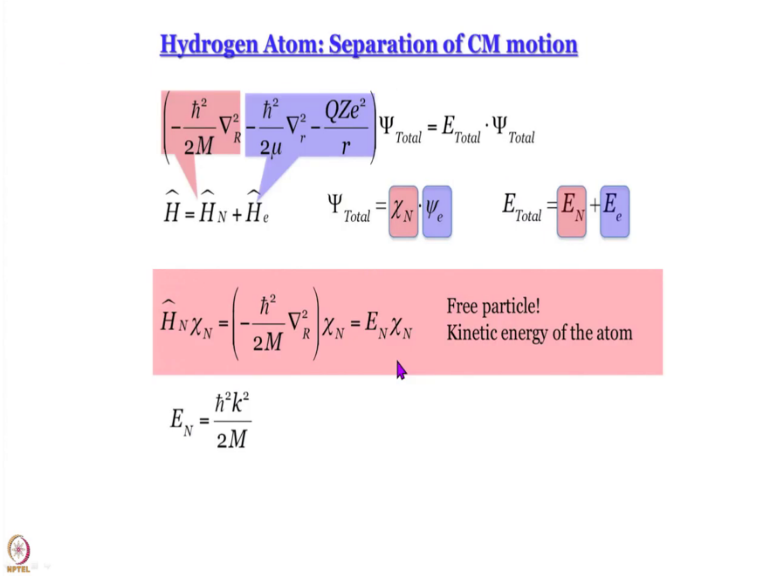

And as we have said when we do that this is what we get the first kinetic energy term minus h cross square divided by 2 Capital M to capital M means well Capital M means the mass of the atom as a whole the total mass and this is del R square this R is capital R which means this is the position vector of the center of mass. And then the second and third terms are in relative coordinates the second term is for kinetic energy due to the motion of electron with respect to the nucleus.

I am saying this again, again because it is important to understand this it is not just motion of electron in free space it is how much it moves with respect to the nucleus. How much does separation change in what kind of time right that is what we are talking about remember xe is equal to well x is equal to xe – x N, y is equal to ye minus y N z equal to z e minus z N so this is a relative frame that we are talking about.

And the last term is minus QZ e square by r this is a potential energy term for interaction between electron and nucleus of course this r itself is the separation between the nucleus and the electron. So, the Hamiltonian separates into H N and H e and as we see we can write the total wave function as a product of a nuclear part and the electronic part. Energy you can write as a sum of a nuclear part and the well not really nuclear part we can write energy for movement of center of mass and energy of the electron with respect to the nucleus.

So what happens is that we can collect all the terms in the center of mass coordinate and write a Schrodinger equation which is exactly the same as what we got earlier for free particle and that gives us the kinetic energy of the atom as a whole the entire hydrogen atom moving in space. Of course here the consideration is that the atom does not interact with anything else that is why there is no potential energy term.

And energy here is h cross square k square divided by 2 Capital M which is not quantized it can take up any possible value of energy. And what we are concerned about for the rest of the course is this one minus h cross square by 2 mu, mu remember is a relative is the reduced mass which is always used to reduce a two-body problem into a one body problem. So, minus h cross square by 2 mu del small r square kinetic energy of electron for movement with respect to nucleus – QZ e square by r potential energy is equal to you can see we have E e energy of the electron multiplied by Psi e.

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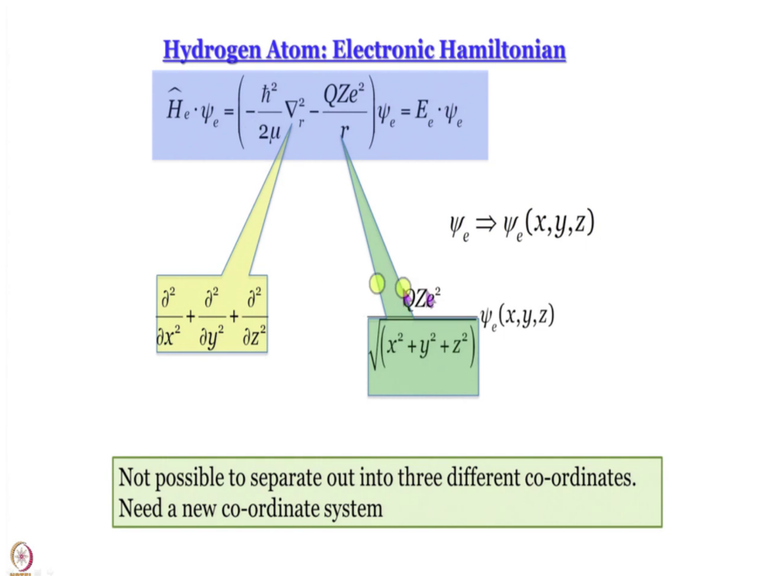

That is the electronic part of the Schrodinger equation that we deal with this is where we had a write and then we realize that there is a problem. So, this del r square is not a problem because you can write it as del 2 del x 2 + del 2 del y 2 + del 2 del z 2 the problem lies with this small r in the denominator because it is square root of x square + y square + z square how are we going to separate this. So, if we persist with the Cartesian coordinates then we really cannot proceed further.

We cannot separate this equation into smaller equations so we cannot solve it. So, we chose a different coordinate system this spherical polar coordinate.

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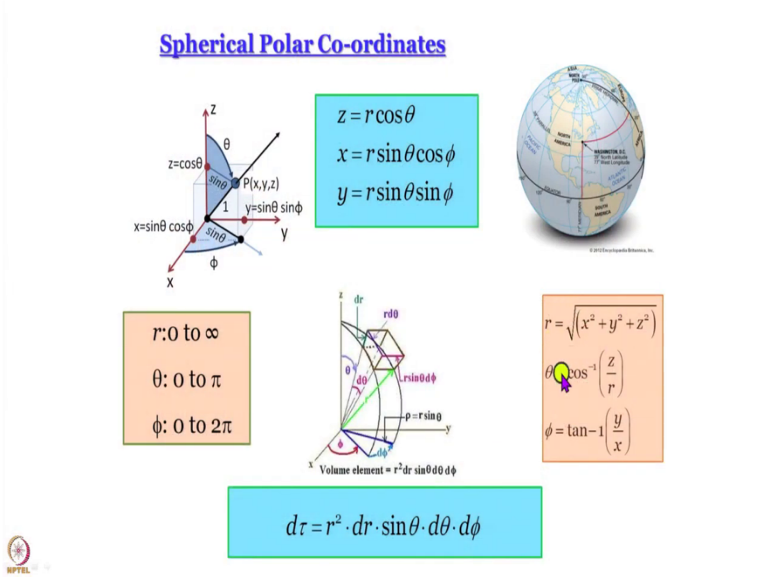

And the biggest advantage here is that this are equal to square root of x square + y square + z square which pose the problem in r trying to formulate it in terms of Cartesian coordinates that r itself is a coordinate. So, there is no issue as such and we have already gone through all these issues all these relationships earlier and this is the volume element that we are going to come back to maybe a couple of modules later .

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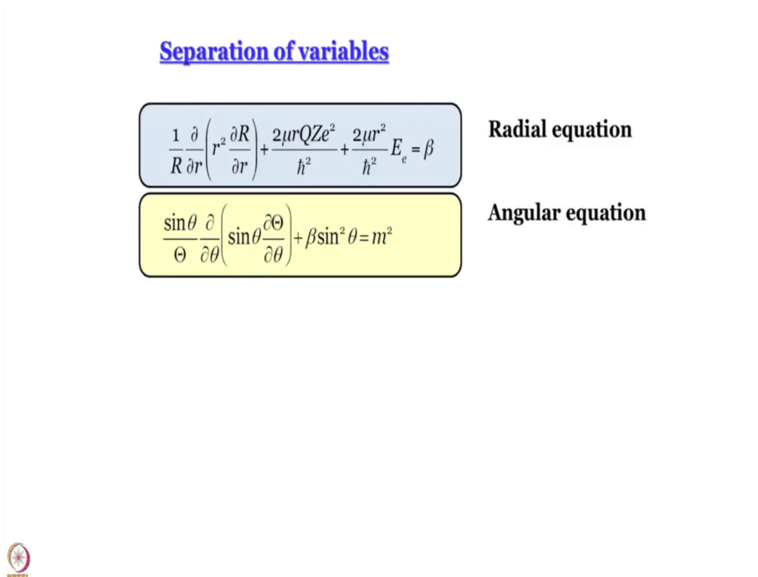

So with that this is where we had stopped, we had been able to separate the variables we are able to separate the equations into 2, one in terms of the radius R only we call that the radial equation and the other one is in terms of theta and Phi we call it the angular equation. Please remember that for spherical polar coordinates there are two classes of coordinates one is R which is a length and theta and Phi together are angular coordinates their angles.

Now I am not going through the detail of separation of this angular equation into the Phi part and theta part once again because we have done it while discussing rigid rotor already.

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Separation of variables

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

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

$$\frac{1}{\Phi}\frac{\partial^2\Phi}{\partial\phi^2}=-m^2$$

The three variables r, θ and ϕ are separated

So I just request you to recall what we had talked about there the theta part is sine theta by capital theta. The capital theta is the theta dependent part of the wave function del del theta of sine theta del capital theta del theta and again let me say that this del is not really required anymore might as well write d because there is nothing other than theta in this entire equation. So, d d theta of sine theta d capital theta d theta plus beta sine square theta is equal to M square.

So this is the theta dependent part only theta terms are there nothing else and the Phi dependent part is very, very simple 1 by capital Phi d 2 capital Phi d Phi 2 is equal to minus M square thus the three variables R theta and Phi are separated from each other. Now you might notice that we have written instead of capital M we have written a small m here there is a convention because when we talk about rigid rotor and when we talk about hydrogen atom we want to use a little bit of different convention for the two so that right from what we write it is quite clear what we are talking about.

So it is just a matter of convention that we are going to write small m instead of capital M when we talk about hydrogen atom. Now small m in terms of hydrogen atom should ring a bell. We all know what small m is in terms of hydrogen atom and I am not talking about mass here remember the quantum numbers N L M S, M is that M it is really the magnetic quantum number but we will arrive at it shortly.

What I just told you was really a spoiler I told you what is going to come and the way we will proceed is that will once again go through the solution of the Phi part only we are not going to explicitly solve the theta dependent part and the r dependent part because that is too much of mathematics and we do not want to; this is really a chemistry course we do not want this to become a maths course. We will tell you the solutions you do not have to remember the solutions except for the general form. And then we try and plot them later on and see what they look like right.

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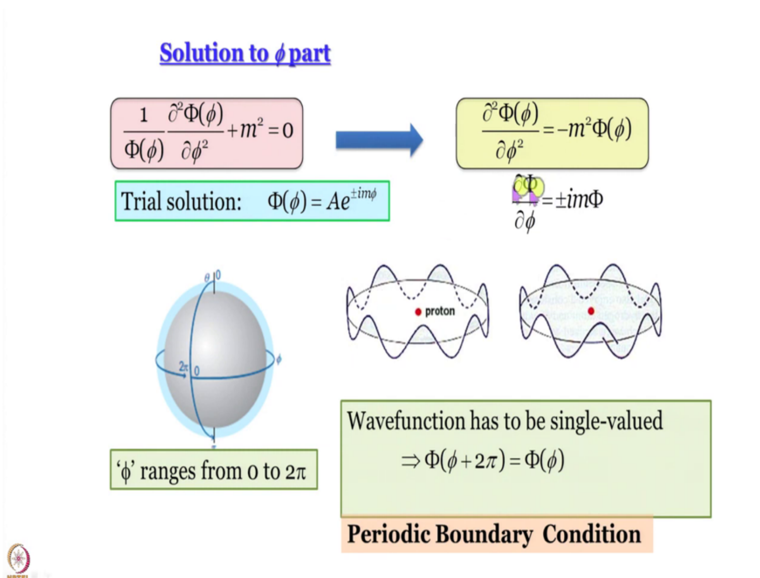

So, let us proceed so solution to the Phi part is known to us we know that the solution is A multiplied by e to the power plus minus im Phi once again here we use small m and A is worked out in one of the tutorial problems assignment problems that turns out to be 1 by root over 2 pi.

So, and then once again we use a periodic boundary condition the wave function has to be single valued. So, you start from a particular value of Phi go around a full circle come back to the same point the wave function must have the same value once again.

Which means capital Phi for Phi is equal to capital Phi for Phi + 2 pi ok. We will start from Phi go around a full circle come back to the same point. As we have discussed while talking about Born interpretation this wave functions have to be single valued in order to satisfy or in order to conform with the Born interpretation. So, that is why that is what gives rise to this periodic boundary condition.

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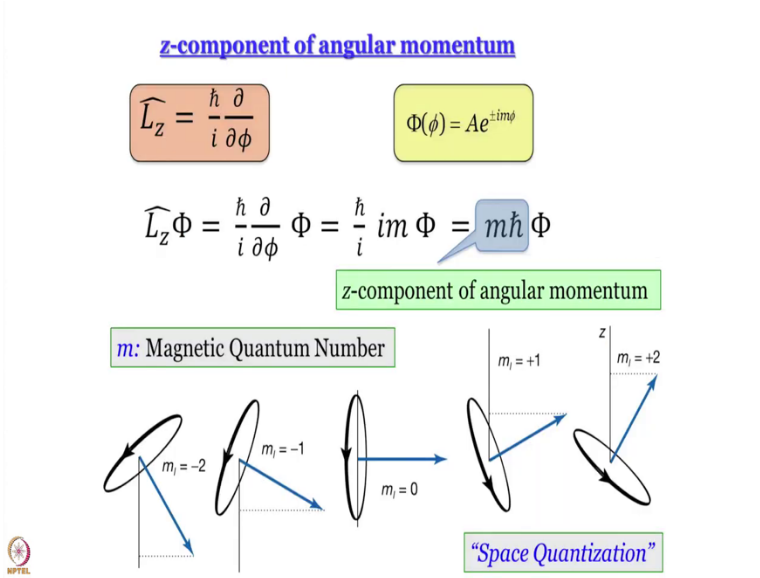

And then what we discussed earlier is that that is what leads to quantization of M. M can only take up values of 0 plus minus 1 plus minus 2 and so on and so forth. Please go back and recall our discussion of rigid rotor that is where we have worked it out. The only thing is I noticed that whenever I talked about that at that time I kept on saying M goes from 0 1 2 3 4 up to infinity let us not forget minus 1 minus 2 up to minus infinity also.

So in principle it can go up to plus minus infinity shortly we will see that there is actually a limit as far as the small m in hydrogen atom is concerned. And also similar to or exactly like Capital M for rigid rotor small m here denotes the Z component of angular momentum if you make the angular momentum operator operate on capital Phi then you get mh cross multiplied by capital

Phi and eigenvalue equation. The eigenvalue is mh cross so that is the Z component of angular momentum and M is called magnetic quantum number.

Why, because if you apply a magnetic field or even an electric field across along the z axis then all that matters all the quantity that determines the kind of interaction with this magnetic field along the z Direction is the z component of the field right. You have some magnetic moment of the electron it can point this way or this way or whatever right. So, if it is like this then the z component is more if it is like this then said component is 0.

If it is like this then that component is negative right. So, it is the magnetic quantum number M that determines the interaction with magnetic field and that is why this was discovered in the experimental study of Zeeman effect. Remember in Zeeman effect it was observed that the number of lines in hydrogen atom spectrum splits increases upon applying a magnetic field and it was explained by this kind of space quantization.

In the within the ambit of Bohr Sommerfeld model the electron is expected to go around in a circular or elliptic circle and so a circular or elliptic orbit and correspondingly there has to be an angular momentum which is normal to the plane of rotation. Now here in quantum mechanics we should eliminate this circular path because as we have said many times we cannot talk about the trajectory that is not allowed because that would violate uncertainty principle.

Interestingly we can still talk about this blue arrow the angular momentum vector and we can talk about this allowed orientations of the angular momentum vector. So, we come back to the same point where the allowed orientations are plus m to minus m through 0 that is there are 2m plus so sorry +L to –L will come to that later on. So, that is what gives us the allowed orientations or now we can say allowed values of theta. So, that is called space quantization.

Only specific values of small theta can be taken up by this angular momentum vector right. So, that is space quantization in terms of quantum mechanics. How many values of m? We will come to that shortly. So, please remember that now we should not draw these circular or elliptic orbits anymore but we still have to retain the angular momentum vectors and they are allowed discrete orientations. So, crux of the matter is that this m is a quantum number that determines the z component of angular momentum.

And therefore or in other words it determines the angle at which the angular momentum vector is oriented. See the angular moment length of the arrow is same for all right what determines the length of the arrow or other in other words the magnitude of the angular momentum we will come to that shortly. What we are saying is that given a particular total angular momentum orientations it can take up in space are determined by the values of m.

This mh cross will give us the preferred not preferred allowed values of theta or allowed orientations of the angular momentum vector.

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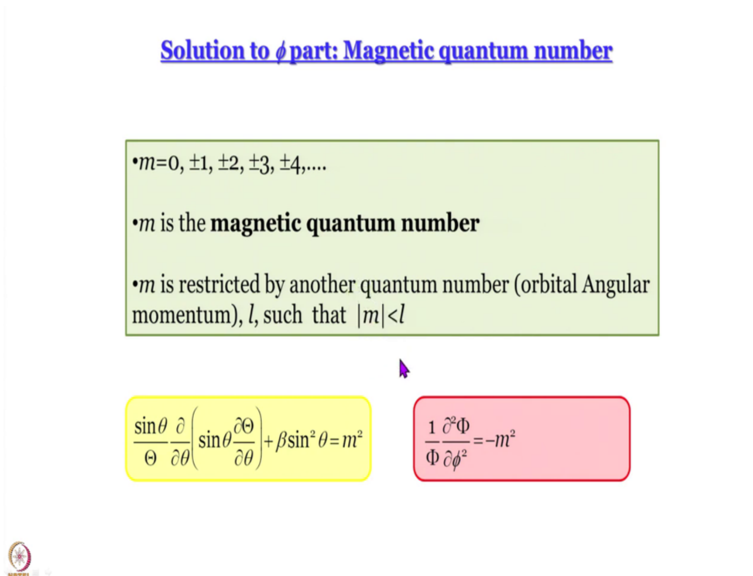

So solution of Phi part gives magnetic quantum number as we said as we learn from rigid rotor m can take up values of 0 plus minus 1 plus minus 2 plus minus 3 plus minus 4 and so on and so forth we call it the magnetic quantum number. And now we talk about the restriction it does not really go up to plus minus infinity, M is restricted by another quantum number which is called the orbital or azimuthal quantum number small l.

Remember small l it came in Bohr treatment as well subsidiary quantum number azimuthal quantum number so m is restricted by another quantum numbers such that magnitude of m is less than l. Why is that so? Because if you recall the two equations that arose from the angular part one is 1 by capital Phi d 2 capital Phi d Phi 2 is equal to - m square the other one was something in theta equal to m square. So, m square actually is the bridge between the equation in Phi and equation in theta.

When you solve the equation in Phi you get the allowed values of m when you solve the equation in theta then you get the limit to the allowed values of m and that turns out to be mod m less than l. Unfortunately solving it is beyond the scope of what we want this course to be so we are not going to do it in this course. We will take it axiomatically for now. And similarly the same thing is going to happen for l and principal quantum number n ok.

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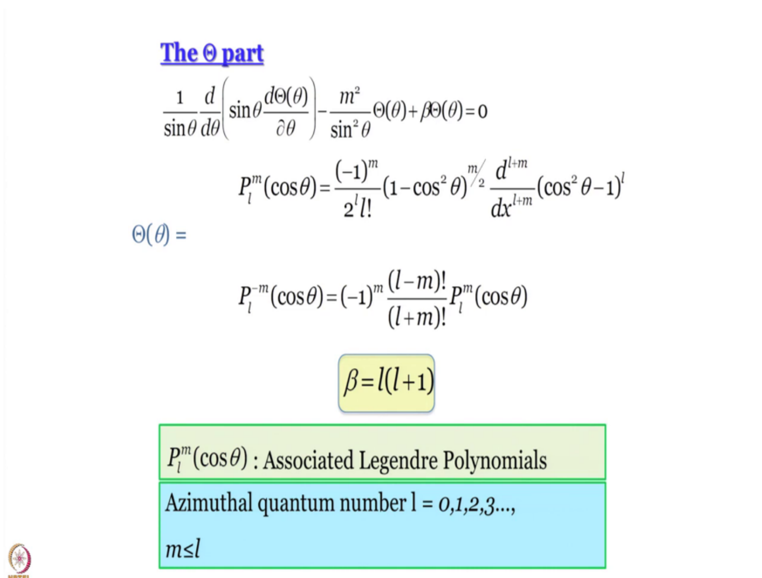

Now let us move on to the theta part. In the theta part this here is the equation and you know the solution already. The solution is what is called Associated Legendre polynomial in cos theta and this as you can see is associated with another quantum number l. You see this just now I have a look at this expressions for the Associated Legendre polynomials here you have l - m factorial in the denominator you have l + m factorial minus 1 is raised to the power m.

And the polynomial itself is a function of l as well as m so these conditions when you work this out when we get when we apply boundary conditions to these wave functions we get the allowed values of l to be 0 1 2 3 and so on and so forth. We also get that yet the condition that they should have been a mod sign here mod m, modulus of m absolute value of m has to be less than or equal to l that is things that we know already 2l + 1 values of m are there.

So going back to the picture we showed earlier for l equal to 2m can take up values of 2 1 0 -1 -2 5 values 5 is 2l + 1 where l equal to 2 ok right that also this part also leads us to a very important phenomenon that beta is equal to l into l + 1 what is beta? You remember this is beta and as will show later on this beta is there in the theta part as well as the r dependent part of the equation. So, beta is the bridge between the theta part and our part of the Schrodinger equation.

So here we get B is equal to l into l + 1 and that has some profound application as we will see shortly.

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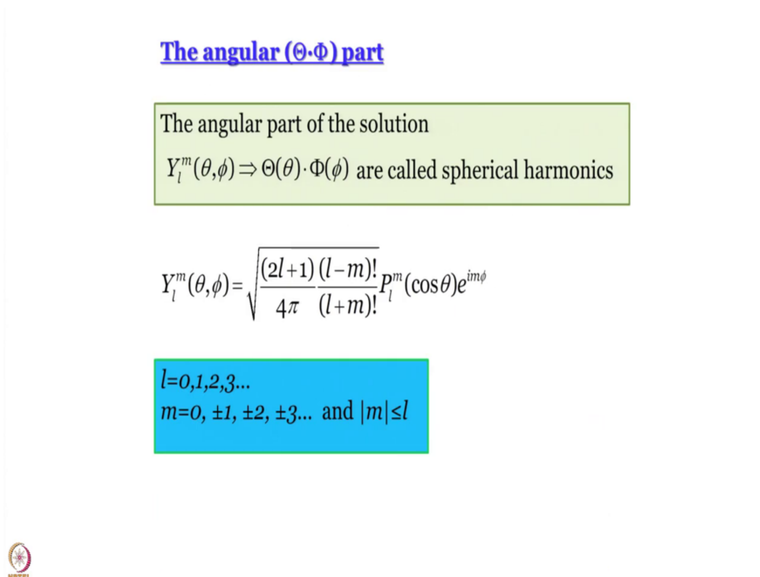

But before we go there let us just summarize this part. The angular part is the same as what we got for a rigid rotor we have a constant which is a function of l and m multiplied by a Legendre polynomial in cos theta this form of Legendre polynomial depends on l as well as m that is multiplied by e to the power im Phi and l ranges from 0 1 2 3 is in principle up to infinity. But again when we discuss the ‘r’ dependent part in the next module we will put a limit to the values allowed values of l there as well.

And m is 0 plus minus 1 plus minus 2 plus minus 3 mod M less than equal to l we have said this several times sorry for the repetition but I wanted to say this before going to the next step all right.

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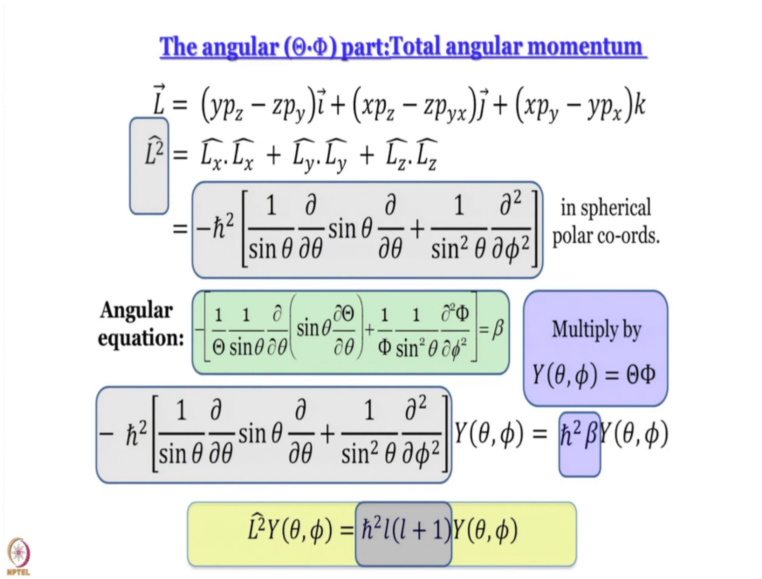

Now here we have discussed angular momentum in detail earlier. So, this we know very well is the l square operator and now look at the angular equation. As we have said in our discussion of rigid rotor as well you can go very easily from the Hamiltonian of angular equation to the l square operator simply by multiplying is h cross square. So, once we do that we can try and manipulate and get an eigenvalue equation in l squared, so this is what we will do.

First of all we will just multiply by capital theta capital Phi so what will happen this capital theta will cancel and you get capital Phi in the numerator here this capital Phi will get cancelled and you get capital theta in the numerator. Now let us multiply by h cross square so on the left hand side what we have is minus h cross square capital Phi by sine theta d well del capital theta del theta B is fine here until now sine theta del capital theta del theta plus capital theta by sine square theta multiplied by del 2 capital Phi del Phi 2 that is equal to h square beta capital Phi capital theta.

Now see I might as well write it like this if you go back to the earlier one I can there is no harm if I take this capital Phi inside this operator in theta because capital Phi is constant with respect to theta anyway. Similarly I can take this capital theta inside this capital Phi so this is what we will write. And hence of course we have to multiply by sine square theta so that this goes there is no need actually.

So we get this there is no need to do that actually. So, here let us see what we have on the left hand side minus h cross square 1 by sine theta del del theta operating on sine theta del del theta same thing as here plus 1 by sine square theta del 2 del Phi 2 same thing as we have here. So, on the left hand side we have the l square operator operating on the spherical harmonics the theta phi dependent wave function of hydrogen atom that gives us back the same wave function multiplied by h cross square multiplied by beta.

What does that mean that means that square of total angular momentum is h cross square beta and if you remember that beta is l into l +1 you might as well substitute that so we get that we get the result that the square of total angular momentum is h cross square multiplied by l into l + 1. So, from there what we might as well write is you can write something like this angular momentum and just write it so that we are not confused between the quantity and the operator.

Angular momentum well it is better to write total angular momentum here that turns out to be root over l into l + 1 multiplied by h cross right a universal result that keeps back to will haunt us time and again. So, what we have understood then is that we can figure out the total angular momentum from the theta dependent part. So, remember we talked about the length of the arrow this here is the length of the arrow root over l into l+1 multiplied by h cross.

And what is the z component z component is mh cross. So, if I draw this let me just draw this picture once, let us say this here is as z axis this dotted arrow this is your angular momentum vector maybe I just make it a solid arrow it looks horrible well, it is not supposed to be so wavy it is just that my hand is not very stable on this surface. So, what we get is first of all this is theta this length turns out to be root over l into l + 1 and I will write h cross in the beginning.

And if I drop a perpendicular here on z axis what is this length this is mh cross, so what do we get from there? What is the relationship between m and l and theta?Very simple trigonometry so one can actually work out the orientation of the angular momentum vector if we know m and if you know l right that is what once again takes back that takes us back to space quantization. Since only discrete values of m are allowed discrete values of l are allowed discrete values of theta are allowed and that in other words is space quantization right.

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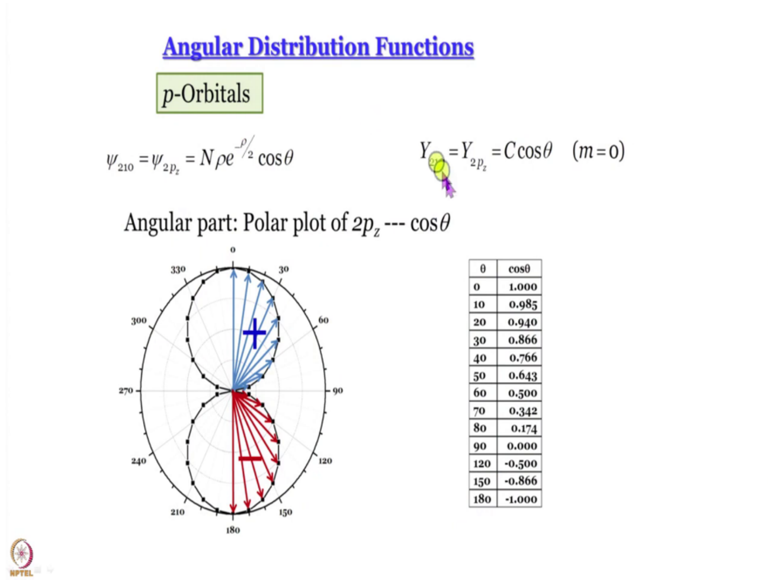

And then just to remind you we can a very convenient way of drawing this angular distribution functions and we will a parts of Schrodinger equation is by using polar plots ok. What I have written here is the total wave function of Psi 2 P Z or Psi where N equal to 2 l equal to 1 and m equal to 0 ok. So, again it is a spoiler but you get something like this if you forget the radial part you are left with the angular part cos theta.

The what about Phi but where is the Phi part e to the power im Phi m is equal to 0 remember 2 1 0 means m equal to 0. So, that Phi part is essentially becomes 1. We will discuss later what happens when the Phi part is nonzero well when Phi well m is nonzero, so the Phi part is what am I saying so we will see later on what happens when this Phi part does not conveniently become 1 or a constant we will see how to deal with that.

But for now the only angular part that we need to concern ourselves with is cos theta how do you plot cos theta? I will just do a quick recap of what we had discussed 2 or 3 modules earlier. This is a polar graph paper remember the independent axis is the angle dependent axis is a length.

Here is a table with in increments of 10 degrees of theta and cos theta there is a function we are interested in. For theta equal to 0 cos theta is 1 so this length is 1.

For theta equal to 90 degrees cos theta is obviously 0 so this is 0 and from theta equal to 0 to 90 degrees cos theta keeps increasing then it goes from maximum and then it decreases to 0. So, it keeps decreasing from 1 to 0 so this is how the lengths of the arrows is going to decrease remember the length is what determines the value of cos theta. So, you get this kind of a curve what happens when you go beyond 90 degrees you start getting negative values there is no way in which we can show negative here.

So, what we do is we use a different color and we write the sign of the function cos theta explicitly in the relevant parts of the curves. And also please remember that theta ranges from 0 to 180 degrees so you should not draw anything beyond 180 degrees. So, this is a way of designating your angular part of the wave function. Now I would like you to think something look at this curve and think a little bit.

See this curve is valid for any value of Phi is not it. So, let us say I have a; so this plane that we are shown here is the plane where you have theta as one axis and function of theta cos theta in this case as the other. Let us now consider a perpendicular plane and let us say this angle is Phi does it matter what Phi is, for all values of Phi right from 0 to 2pi whatever is the value of cos theta for a particular value of theta will remain the same right.

So we can think that if we just rotate it around by 360 degrees what are we going to get? You are going to get something that looks like a dumbbell is not it right. For all values of Phi since its Phi independent will get same values. If there is a Phi dependence then there will be modulation then it becomes a little more complicated. But since there is no Phi dependence here we will get two loaves one with positive sine of cos theta, one with negative sine of cos theta does it remind you of something does not it look exactly like the pure orbital that we are used to seeing in textbook.

Two lobes plus on one and minus on the other well the pictures that you saw there we are sort of constructed like this. But we will have more to talk about how to designate? how to show orbitals? Well how to show the wave functions in the subsequent modules. So, now we are done with our discussion of the angular part next we are going to discuss the radial part of the wave function.