Quantum Chemistry of Atoms and Molecules
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Lecture-19
Rigid Rotor: Part 2

We are studying rigid rotor and at the moment we are trying to set up Schrodinger equation for a rigid rotor. So, far we have reached a situation where we have written the Hamiltonian well we have arrived at the same Hamiltonian in two different ways right. In the last discussion we had in the previous module was that we started with the L square operator, we realize that the Hamiltonian is bound to be this L square operator divided by 2I.

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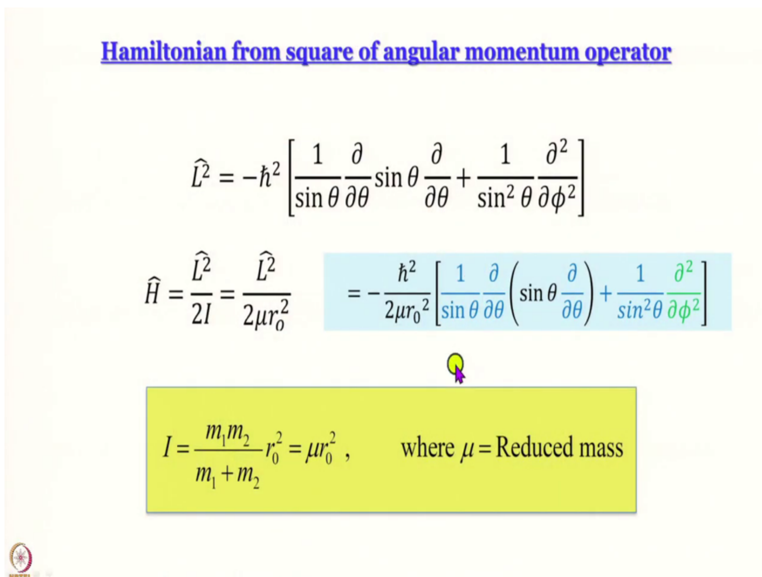

Hence we got minus h cross square by 2 mu r 0 square multiplying 1 by sine theta del del theta operating on sine theta del del theta plus 1 by sine square theta multiplying del 2 del Phi 2. And now we will define the wave function in a particular fashion and then we will try and separate the equation into individual equations in theta and Phi.

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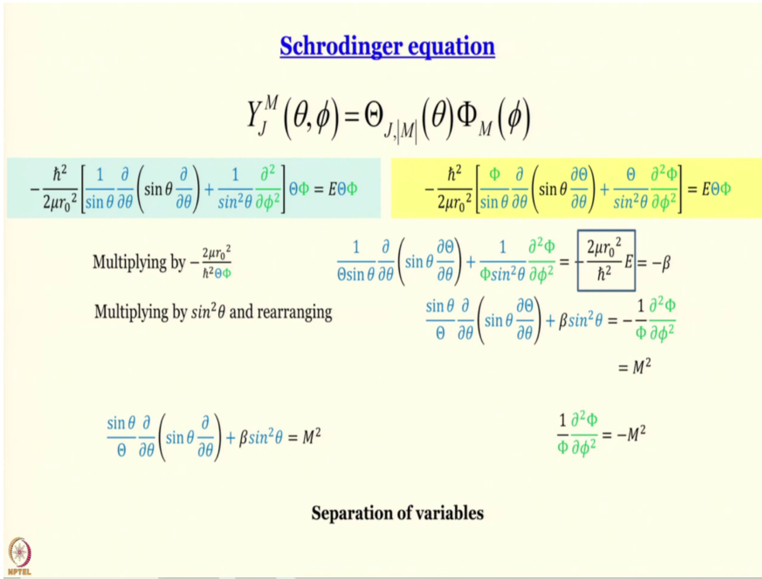

To do that first thing we do is we write the wave function as a product of a theta dependent part and a Phi dependent part. Let me just paraphrase this expression to you because generally for us Greek letters are intimidating there is nothing to be intimidated here. On the left hand Psi instead of y I have written y now y J what is J what is M this wait a little bit I will tell you what they are they are basically quantum numbers. They are functions of theta and Phi that we have written as a product of capital theta which is a function of theta.

So capital Greek letter here is a wave function small Greek letter is the variable or coordinate so capital theta is essentially the theta dependent part of the wave function and capital Phi is the small Phi coordinate dependent part. Why do we write it like this because we cannot write it as capital theta plus capital Phi can we? I mean that would be dimensionally inconsistent. We can multiply right so for separation of variables in situations like this it makes perfect sense if we take the wave function to be the product of wave functions in independent coordinates.

That is a very standard technique of separation of variables right. Now what I need to do is I know the Hamiltonian already I want to take the Hamiltonian and make it operate on the wave function. And here since I am going to separate the equation into two different equations we have as discussed already written everything in theta into in blue except the sine theta and everything in Phi in green. So, our purpose will be to get all the blues on one side all the greens on one side all theta dependent terms on one side or Phi dependent terms on the other side that is what we will try to do.

So first of all look at this well look at the second term that is easier one by sine square theta del 2 del Phi 2 operating on capital theta capital Phi. Capital theta is a function of theta and not Phi so as far as Phi is concerned it is going to be constant. And capital Phi is a function of small Phi not a function of theta. So, what is forget about this one by sine square theta for the moment what is del del 2 sorry del 2 del Phi 2 of capital theta capital Phi? Capital theta is constant goes out and you are left with del 2 Phi del Phi 2.

In fact it makes perfect sense to write d Phi d 2 Phi d Phi 2 right because there is no theta anymore capital Phi is exclusively a function of small Phi. So, there is nope point of writing Delta anymore I have continued with Delta in the subsequent discussion but I hope you understand that Delta is not even required d is fine. So, the second term will be capital theta by sine square theta multiplied by d2 d Phi 2 d 2 Phi d 2 capital Phi d small Phi 2 what about this one?

Here capital Phi will be constant so we get capital Phi by sine theta multiplied by del del theta operating on sine theta del capital theta del small theta ok. So, this is what I get all right what are you trying to do we are trying to separate the equation. So, first of all let us multiply by 2 mu r 0 square divided by h cross square that is very simply to get rid of the coefficient here and we will also multiply it by 1 by capital theta capital Phi.

Why? because once we do that here we have capital Phi in the numerator if you multiply it by 1 by capital Phi capital theta then Phi and Phi cancel you are left with capital theta. So, you will get capital theta multiplied by 1 by sine theta well 1 by capital theta multiplied by sine theta then del del theta operating on sine theta d theta d theta d capital theta d small theta. So, in that first term there will be nothing in Phi anymore.

What about the second term? In the second term we are going to have well cap into this capital theta will go 1 by capital Phi sine square theta d2 capital Phi d Phi 2 so sine square theta will be there but in the next step we will get rid of it. So, this is what we get 1 by capital theta sine theta del del theta sine theta del del theta del theta del theta remember this del is not even required d is fine plus 1 by capital Phi sine square theta d2 capital Phi d Phi 2 equal to 2 mu r 0 square by h cross E.

So I have got rid of the wave function from the right hand side. But even though the first term in the on the left hand side is sorted the second is not so to get rid of that it is not very difficult to see what I have to do I have to multiply by sine square theta right but before I do that let me rewrite this minus 2 mu r0 squared multiplied by E divided by h cross square as minus beta this why minus beta because that is how it is written in solution of Schrodinger equation for hydrogen atom.

Whatever treatment we are doing now is exactly the same thing that is done for the angular part of Schrodinger equation for hydrogen atom right that is why it is so attractive other than in describing a rotating molecule in the first place. So, we will write it as minus B, so what do we do we multiply by sine square theta and then we can rearrange right. Because once you multiply by sine square theta the first term becomes sine theta by capital theta dd theta of sine theta d theta d theta second term becomes 1 by capital Phi d 2 capital Phi d Phi 2 so nothing in theta anymore.

On the right hand side you have minus B multiplied by sine square theta you are multiplying throughout by sine square theta. Remember so if I bring that minus B sine square theta to the left hand side then left hand side and if I take this 1 by capital Phi d 2 capital Phi d Phi 2 to the right hand side then the left hand side will be entirely in theta right hand side will be entirely in Phi something like this sine theta by capital theta del del theta of sine theta del theta del theta plus beta sine square theta is equal to 1 by capital Phi well minus 1 by capital Phi d 2 capital Phi d Phi 2.

Please remember the capital letters denote wave functions small letters denote coordinates and I have not written capital Phi and then small Phi in bracket because the notation is such that it is not very difficult to understand alright. So, almost done but now what we see is on the left hand side we have an expression in theta. On the right hand side we have an expression in Phi and they are equal to each other how is it possible?

Those variables are different they can only be positive that can only be possible if both are equal to a constant yeah then it is possible then it does not depend on theta does not depend on Phi either. So, we equate this to M square now why M square? Why not M? Why not K? Well once again the answer is you are not doing it for the first time somebody else has already done. We know very well that the subsequent treatment becomes not only easy but also meaningful if you write M square here that is why we write M square and not anything else.

What do we have we have two equations now you can write sine theta divided by capital theta dd theta of sine theta dd theta plus beta sine square theta is equal to M square that is an equation that is entirely in theta. And we can write 1 by capital Phi d to capital Phi d Phi 2 is equal to minus M square that is an equation that is entirely in Phi and not theta. So, we have achieved the separation of variable that we had set out to do.

Now we are going to solve the Phi part because very, very simple we are not going to solve the theta part because it is very non trivial but then the solution was known already when this rigid rotor business came into discussion. So, we will discuss the solutions they are very important.

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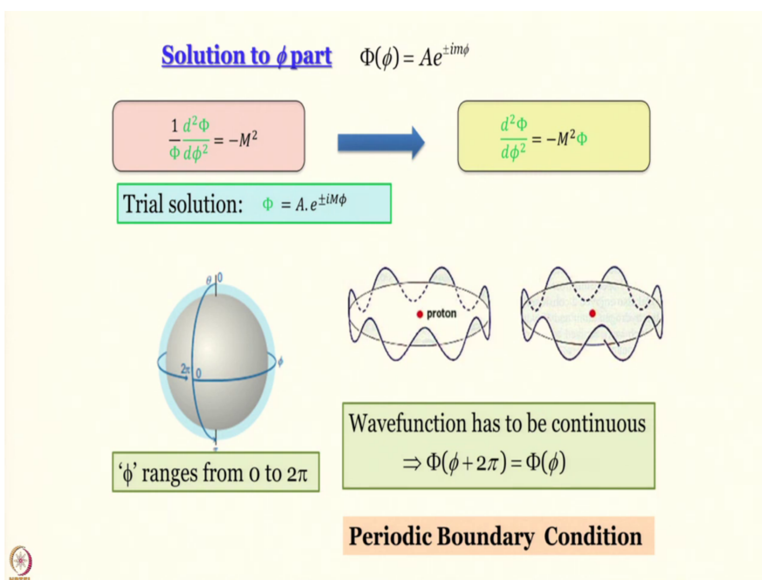

For now let us try to see whether it is possible to solve the Phi part well it is possible that it is very easy. So, 1 by capital Phi d 2 d Phi 2 is equal to minus M square this is what we have got so let us simplify a little bit. We can write d 2 Phi d Phi 2 and now I have well written d instead of del d 2 capital Phi d Phi 2 is equal to minus M square capital Phi what is the solution to this? Let us use a trial solution the trial solution will use is Phi equal to A e to the power plus minus I M Phi.

Now one might say that the most general solution is actually A 1 e to the power I M Phi - A 2 e to the power minus Phi why are we not taking that solution? Why are we taking this? We are taking this because well wave functions tell us a story, wave functions has a meaning that meaning comes out very nicely if we take a part and not the whole. And the part is as valid a solution of the differential equation then what the whole is.

So we will just work with this one at a time we will work with either plus or minus sign in the exponent. So, this is a trial solution please satisfy yourself that if you differentiate it twice you do get something like minus M square capital Phi, you get it. Differentiate once you get d Phi d Phi is equal to plus minus I M A e to the power plus minus I M Phi differentiate once again you get d to capital Phi d Phi 2 is equal to plus minus I M was there multiplied by another plus minus I M A e to the power plus minus I M Phi that is an eigen value equation.

The eigen value would be the value of whatever this d 2 capital Phi d Phi 2 might be the operator for. So, this is the equation that we are going to use I asm going to solve you know the trial solution already. Now see if you remember Phi actually ranges from 0 to 2pi that leads to a very important consequence if you remember Born interpretation. Remember one of the things that we studied from Born interpretation is that a wave function must always be continuous.

What does it mean? Ok let us say we start from some point ok, in the XY plane we go a full circle and come back to the same point. Let us say this point is associated with a coordinate Phi small Phi if we go around then the coordinate that we reach is Phi + 2 pi but it is the same point yeah so we should well single value do not continue it I made a mistake sorry. At the same point the wave function must have the same value.

So from here what we can say is I do not know why we do continuous same single valued is the correct answer so capital Phi at small Phi + 2 pi essentially is equal to capital Phi at Phi ok. Since this occurs with a period of 2 pi this is called a periodic boundary condition. See what we have got here is a boundary condition remember particle in a box we are encountered boundary conditions there.

In your harmonic oscillator also we talked about boundary condition here the boundary condition arises out of not really continuity but a single valuedness and it is called periodic boundary condition. The value repeats after periods of 2 pi ok that is what is going to lead to quantization.

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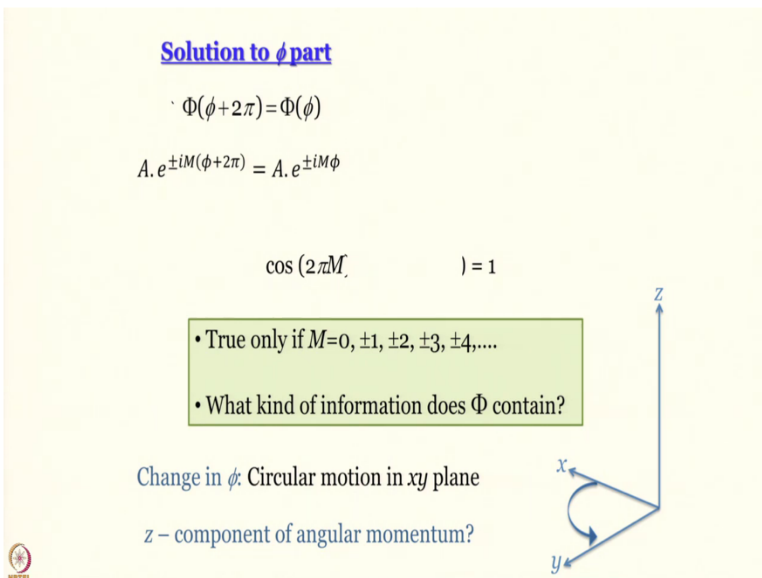

Now if capital Phi at Phi + 2 pi is equal to capital Phi at Phi then we can write a multiplied by e to the power plus minus Phi +2 pi is equal to A multiplied by e to the power plus minus I M Phi right. So, what is the solution? First solution one might think is e to the power plus minus IM phi multiplied to the power plus minus IM 2 pi is equal to e to the power plus minus IM phi e to the power I M Phi e to the power I M Phi cancel you are left with e to the power I M 2 pi is equal to 1 and it is not very difficult to figure out what will be from there.

But what we do is we use the trigonometric relationship. We know that the exponential term is really equal to cos 2 pi M plus minus I multiplied by sine 2 pi M right. So, we write this to be equal to 1. So, it turns out that cos 2 pi M is equal to 1, so this is going to be true not only for m equal to 0 but also m equal to plus minus 1 plus minus 2 plus minus 3 plus minus 4 and so on and so forth right. So, we have obtained this quantum number M which can go from 0 to infinity with increasing with integral increase integral steps of increase.

And now we have curious to know what is the story that this capital Phi tells us? What kind of information does capital Phi contain? And to say that we can use something that we know already ok. Something that is rather simple actually what is that? See what is Phi? Phi is essentially the angular displacement between the x coordinate and the projection of the position operator in the XY plane.

So suppose the projection starts from x axis and starts going round Phi increases right. So, Phi corresponds to circular motion in the XY plane from our knowledge of classical rotational dynamics we know that if you have circular motion like this then the angular momentum is like this. The angular momentum is normal to the plane of circular motion. So, here any change in Phi since it is tantamount to rotational motion in the XY plane.

We can expect that the information that will be associated with this wave function capital Phi should be the angular momentum in z direction. What is angular momentum in z direction? Nobody has said that the rigid rotor is actually rotating in XY plane it can rotate you know whichever way possible right but what we are saying is that we will talk about Phi then we only consider the motion in XY plane part.

So the angular momentum associated with that would be normal to the XY plane or other words it will be the angular momentum along z axis this is called LZ or z component of the angular momentum. So, since Phi is associated with circular motion in XY plane the information it might contain is the information about the z component of angular momentum right.

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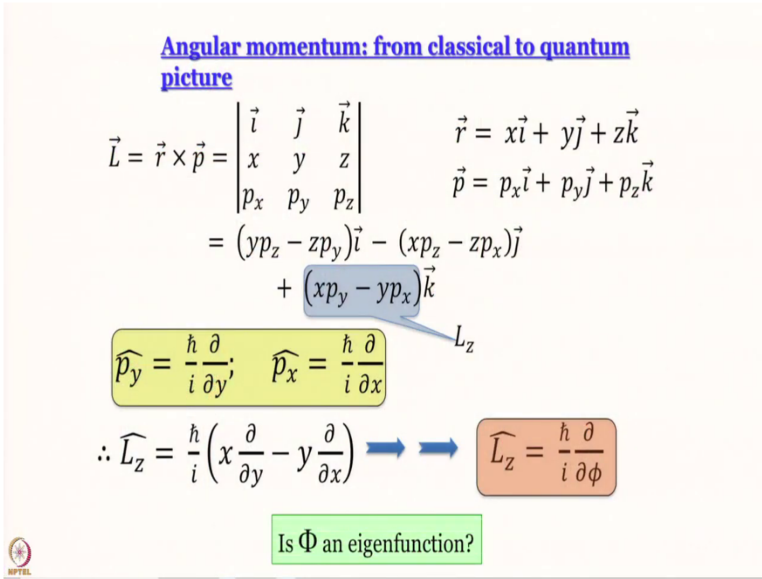

And we can convince ourselves that that is really the case by starting from the basic definition of angular momentum we will have to come back to this in the next module as well. So, L is given as r cross p so r is written as x i plus yj plus zk ijk essentially are the unit vectors along xyz axis respectively p will we have written as px i + px j + p sorry px i + py z j + pz k ok. Now when we get cross-product then what happens something like this you can write it as a determinant ijk in the first row xyz as the second row and px py pz as a third row.

What is the consequence you get something like this i multiplied by y pz - z py j multiplied by zpx p z - z px well there is a minus sign before that k multiplied by x py - ypx remember px py pz these are operators in fact xyz are also operators. So, this quantity ypz - zpy is essentially called the commutator between y pz y sorry so no mistake please delete that I got carried away there x py - y pz ok let us not the commutator it is just two operators operating simultaneously other this is what we get.

Now tell me what is the z component of angular momentum from this expression along z you have K vector so the z component of angular momentum will be x py - yp x that is your that is your Lz. So, how do i construct Lz operator it will be the same thing x operating x dot py where without forgetting that these operators minus y hat dot px hat this is Lz. Similarly one can work out that py is equal to h cross by i del del y, px is equal to h cross by del del x very simple expressions you can even remember them but not required.

But you see we never talk about px and py we hardly ever talk about it you only talk about L square the square of angular momentum and we talk about the z component of angular momentum why? Please wait until the next time we meet for the answer. So, this is Lz now knowing that the operator for py what it is? We can work out this h cross by i x del del y - y del del x this is the Lz operator.

so after little bit of hard work we get a Lz equal to h cross by i del del Phi very, very simple straightforward relationship h cross by i del del Phi that is Lz and not surprising because remember what is the operator for linear momentum it is h cross by i del del x or del del y or del del z depending on whether the motion is along x or y or z axis. Similarly now motion is along y axis you can think so Lz hat is equal to h cross by i del del Phi.

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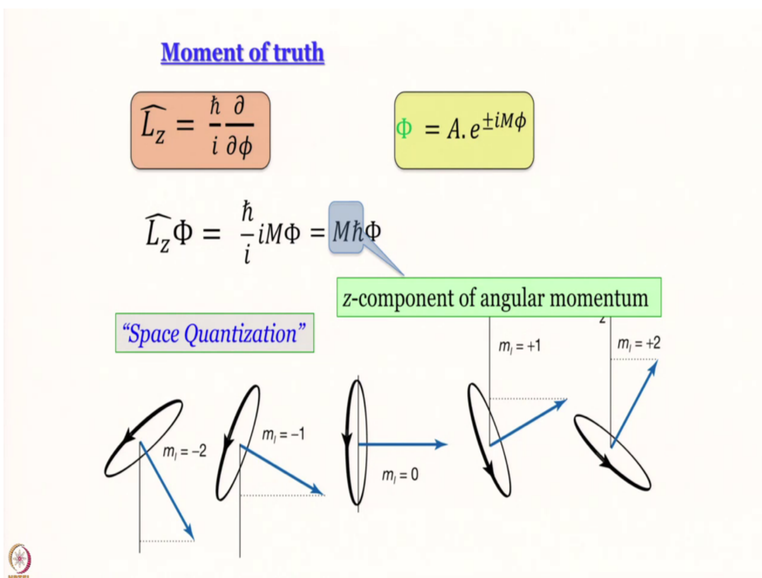

Now the question that we want to ask is we are surmised that the Phi dependent part of the wave function might contain information about Lz. So, that is a case then it should be an eigenfunction of L set and it should yield some value of Lz as its eigen value when the Lz operator operates on it, let us do that and Lz operates on capital Phi what do you get you get once again plus minus IM multiplied by A e to the power plus minus IM phi is not it. Do not forget that there is this h cross by I as well.

So you multiply by that then you get h cross remains h cross and this i in the denominator cancels the i that was coming here from the differentiation M is left. So, you are left with Lz operating on Phi is analogous to well it gives you Mh cross multiplied by Phi. So, M h cross is the eigen value for your z component of angular momentum M is a quantum number what is the range of m, m right now we have said from 0 to infinity.

Later on we will see that some limit actually does come in. so, Mh cross is indeed the z component of angular momentum what does it mean? What does it mean that z component of angular momentum is quantized what does it mean by that? What it means is that if you think of this rotation of the rigid rotor let us say it rotates in this plane then the plane can have only certain given orientations why? Because the arrow can only point in certain directions.

Let us take an example let us say M is equal to well let us say half, M equal to half so what is the orientation that it will take, half h cross into well half h cross well half h cross is going to be the eigen value that will be the z component from there you can work out what the angle will be. So, only certain angles are allowed and it takes us back to the familiar concept of space quantization that had arisen during Bohr Sommerfeld theory of hydrogen atom.

So what we see here is that by using quantum mechanics we see that for a rigid rotor, the angular momentum can only point in certain specific directions and that means that the plane of rotation can only take up certain specific directions, space quantization. So, this is what we have.

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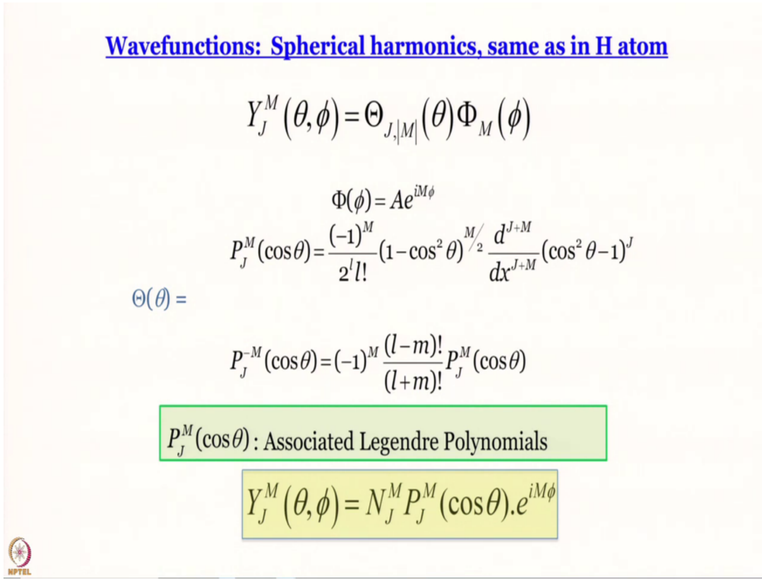

Well next part of the story I just tell you that we said that the total wave function is theta dependent part minus x Phi dependent part. We have worked out the Phi dependent part one thing that we are not worked out is a normalization constant that will do during the assignments. And the solution of the theta dependent part we are not going to do it. Believe me when I say that the solution is again some kind of a polynomial but a polynomial in cos theta it is not x square or y square is z square or even theta it is something in cos square theta.

And we show you specific values when we talk about hydrogen atom. And again these polymers these polynomials are actually very special polynomials they are associated legendre polynomials which means that one can write a similar recursion relations among these polynomials as one could for the harmonic oscillator wave functions right. So, the crux of the matter is that the wave function that is called spherical harmonics is given by a product of a Phi dependent part and a theta dependent part there should be a normalization constant here.

The Phi dependent part is A to the power plus minus IM Phi and the theta dependent part it is enough if you remember that it is a polynomial in cos theta. So, finally well here we have put in the constant and this is what the wave function is. We have the Hamiltonian we have the wave function the next step is to apply the Hamiltonian on the wave function and extract energy.