Mathematics for Chemistry
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Module – 07
Lecture - 33
Associated Legendre Polynomials, Spherical Harmonics

So in this module we have learnt about the power series method, and we saw how the power series method and we took an example of the Legendre equation, and we saw how the power series method could be used to solve the Legendre equation. And we looked at certain special cases when one of the 2 power series converges and that gave us Legendre polynomials and so these Legendre polynomials are also solutions of the Legendre differential equation, and we saw some properties of this Legendre polynomials. Now where do Legendre polynomials appear in various physical theory. So, we said that whenever we are dealing with a spherical system, and we are dealing with waves in spherical dimensions then Legendre polynomials naturally appear.

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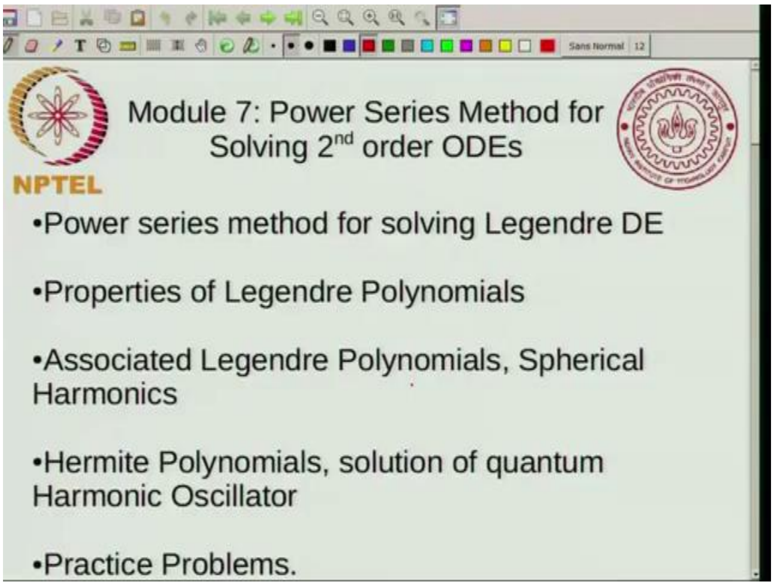

So, today I will show how where Legendre polynomials appear very naturally, when you are solving the quantum mechanical problem of a rigid rotor; and in fact the polynomial setup here are refer to as associated legendre polynomials or the spherical harmonics. So, where do they appear? So, let me describe the problem that we are that you will be solving.

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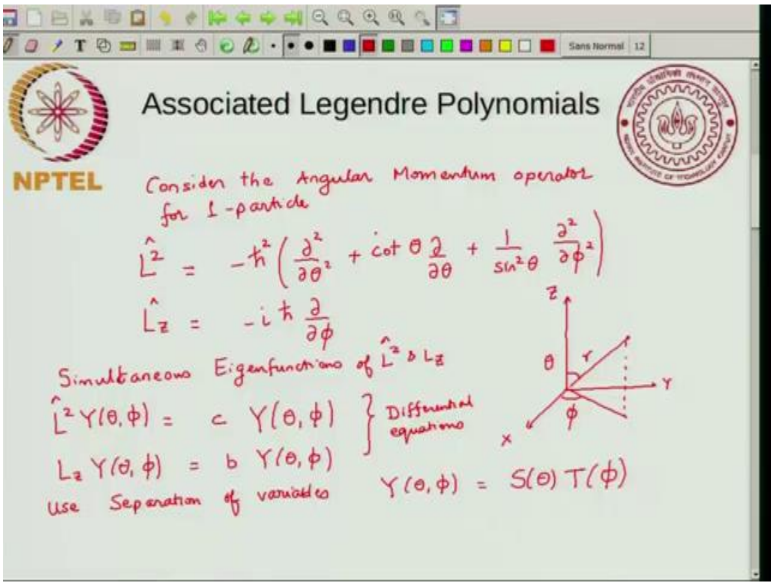

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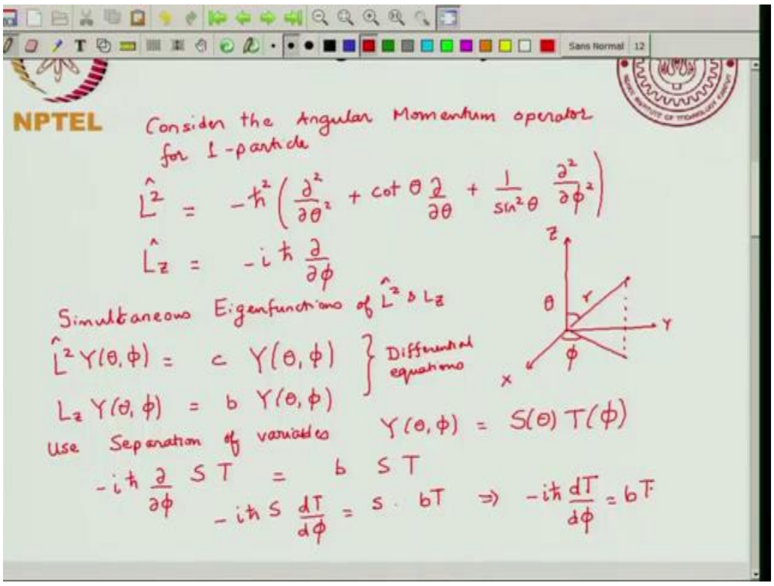

So, you consider the angular momentum operator, so the angular momentum operator for a single particular, for one particle. Now this operator in quantum mechanics, so I will write the operator for L square, the square angular momentum; so this is given by minus h bar square, dou square by dou theta square, plus cotangent of theta, dou by dou theta plus 1 by sine square theta, dou square by dou phi square. So, this is the operator for the squared angular momentum, and the operator for the z component of the angular momentum is given by minus i h bar, dou by dou phi.

So, this is the operator and remember we are using spherical polar coordinates. So, in spherical polar coordinates you can imagine that if these are your axis x y z, then if you have a point r which has coordinates x y z, then we express the coordinates in terms of r theta phi where r is this distance, theta is the angle with the z axis, and phi is this angle that the projection of this vector on to the x y plane makes with the x axis. So, we are using spherical polar coordinates, and in spherical polar coordinates these are the operators for L square and L z.

Now, the problem that we are interested in is, we are we are interested in finding is a simultaneous what are known in quantum mechanics has Eigen functions of L square and L z. We denote these functions as y of theta phi, so this is the simultaneous Eigen function of L square and L z and what are the properties of Y? So, it should satisfy that if you take L square operated on Y, you should get some constant I will call that constant as c times. So, c is independent of theta and phi, and then if you take the L z operator on Y theta phi you should get some other constant b times Y of theta and phi. So, this is what we are looking, we are trying to find the y that satisfies these 2 conditions.

So, you want to find a Y that satisfies these 2 conditions, and these 2 conditions will give you some differential equations. So, before we do that, we need now this is a function of 2 variables, so will use separation of variables. So, you say Y of theta phi is written as a function S which is only a function of theta times T which is only a function of phi. So, we start with this and if you take this Y of theta phi equal to S of theta into T f phi and you substitute in this equation. So, let me emphasize that these 2 are differential equations.

Because L square has is a L square has a representation that involves derivatives, similarly L z also has a derivative. So, the second case is this is a first order differential equation and for L square you have a second order partial differential equation that includes both theta and phi. Now if you use separation of variables then let us say you substitute in the second equation. So, substitute in the second equation, what we will get is minus i h bar, dou by dou phi of S times T is equal to b times S times T. I am not showing the theta and phi dependence of S and T, now what you can do is you can take since this derivative operation only of the phi part.

So, I can write this as minus i h bar S d T by d phi, equal to S times b T. I am deliberately writing the S in front and what you can do is you can cancel the S, you can just cancel the S on both sides and this gives you the relation minus i h bar d T by d phi equal to b T. So, this is the differential equation for T, and it is a really simple differential equation. So, notice that by separation of variables, you went from a partial differential equation. So, this was because L z and L square involved partial derivatives. So, L z it is a partial differential equation for Y and from that you went to an ordinary differentially equation for T.

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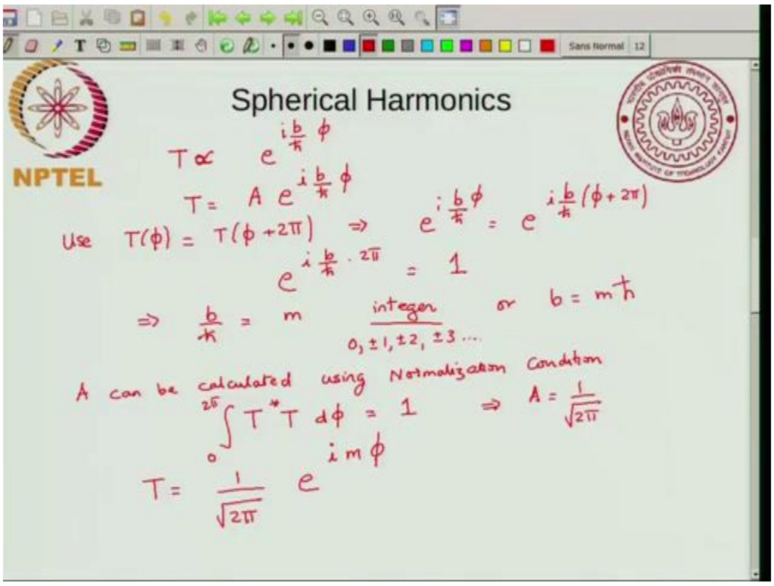

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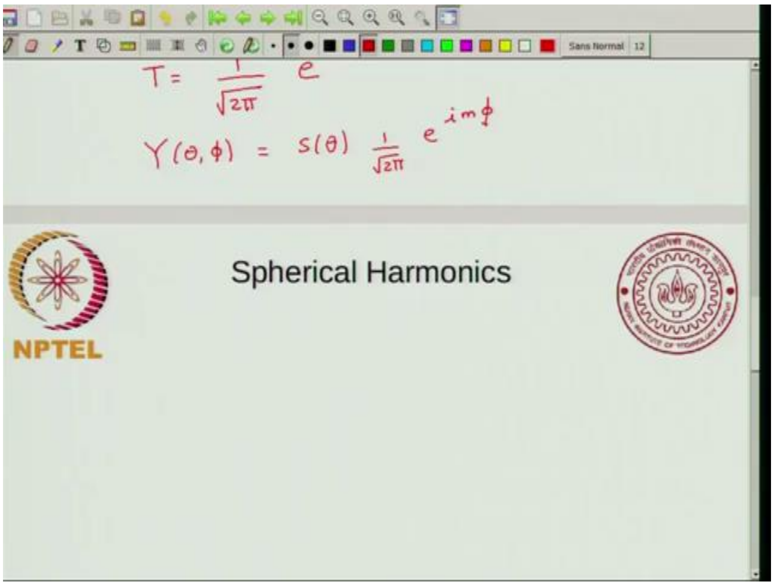

Now, when you do this, so you can solve this you can show that T is equal to or T S proportional to I will say it is proportional to, e to the i h bar phi, T is actually proportional to i h bar or sorry i b phi. So, just write it correctly. So, it is equal to. So, what we will have is if you take the exponential. So, you have b divided by i h cross. So, that is i b divided by h bar. So, T is proportional to this. So, I can write T as a constant a times e to the i b h by h cross phi. So, let me call that constant A e to the i, b by h bar phi. So, this is the solution of the phi part and just for you know you can use a T of phi equal to T of phi plus 2 phi, this is because your angle phi varies from 0 to 2 pi, and if you rotate by a if you increase your angle by 2 pi then you get back to the original angle. So, this implies A is equal to 1 by root 2 pi and this you can show using normalization.

. So, sorry before I do that; so we will come back to a just a minute. So, if you use this then what you will get is that e to the i b pi by h bar is equal to e to the i, b by h bar phi plus 2 pi and if you cancel the e to the i b phi by h bar, you get e to the i b by h bar into 2 pi is equal to 1 and. So, you know that. So, if b by h bar was an integer then e to the 2 pi I into any integer is 1. So, this implies that b by h bar equal to m integer m has to be an integer. So, this say set of or b equal to m h bar, this is commonly referred to as a quantization of the z component of angular momentum.

So, m is an integer; m is an integer means it can be 0, plus minus 1, plus minus 2, plus minus 3 and so on. So, this is the part of the T now if you take this T and you will substitute in the L square expression. So, you take the form of T and you substitute in the expression for L square operator, then what you will get is. So, that is what we are going to do before I do that I will just say that that A can be calculated using normalization condition. So, the normalization condition is integral 0 to 2 pi psi star psi or rather T star T. T star T d phi equal to 1, this implies you can easily show that a is equal to 1 by square root of 2 pi, because the complex conjugate of T is just this multiplied by the minus sign. So, it is just e to the minus i b by h cross phi and so I can write with this I can write T is equal to 1 by root 2 pi, e to the i m h phi e to the i m phi.

So this is my expression for T and now I can take this expression for T and substitute in the expression in the equation for L square. So, the equation for L square is this. So, L square has this has this long expression and L square psi L square y is equal to c y. So, we are going to use that x we are going to substitute y equal to. So, I can write y of theta phi is equal to S of theta times 1 by root 2 pi, e to the i m phi when I substitute this form of y into the expression into the into the Eigen value equation for L square what I will get is the following.

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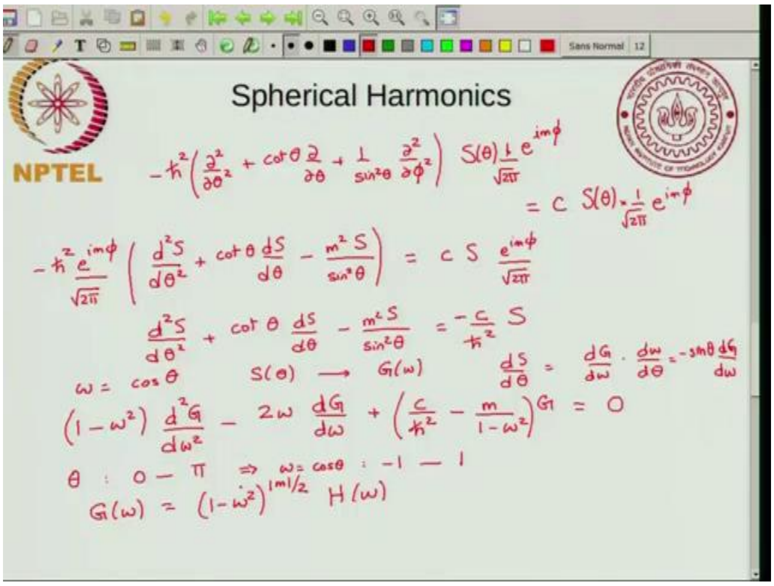

So, what I will get I will just write it explicitly, minus h bar square and you have dou square by dou theta square, plus cotangent of theta, dou by dou theta plus 1 by sine square theta, dou square by dou phi square and what you have y instead of y, I will write S of theta which is only a function of theta, and then you have 1 by root 2 pi, e to the I m phi and this is equal to a constant c times y itself and y is S of theta times one by root 2 pi e to the i m phi.

So this is our equation this is a differential equation and now will take this inside, when you take this inside this is the first the third term is the only one that has derivative with respect to phi. So, the first 2 terms do not have derivatives with respect to phi, and when you take the second derivative with respect to phi you will just get minus m square; minus m square I have times the same function. So, what I get is I can write this as minus h bar square and I will have e to the i m phi, and divided by root 2 pi and then what I will have is I will have d square S by d theta square, plus cotangent of theta d S by d theta plus rather will become minus m square S by sine square theta.

So, I have m squared minus m square times e to the i m phi, e to the i m phi took outside so this is what I am left with, and this is equal to c S e to the i m phi by root 2 pi. So, I can just cancel the e to the i m phi on both sides, and what I am left with is a differential equation that involves only S, and let me write down the differential equation I will take the h square to that side. So, what I will have is d square S by d theta square, plus cotangent of theta d S by d theta, minus m square S divided by sine square theta is equal to c by h bar square into S, a with a minus I minus c by h bar square.

So, this is the differential equation that we have to solve for a S, and what we will do is we will make a few changes we will make a change of variables, will change the variable because we see the sine squared theta appearing here, and you see a cotangent theta appearing here. Now we want to write it we want to get an algebraic we want an equation without all these sine and cosines. So, we change the variable you put w equal to cosine theta.

So, when you put w is equal to cosine theta then you then instead of your function S of theta, you have a function g of w. I am just using a different symbol g you can write you can you can also write it as S of w, but I will use a different symbol g of w, because S of theta becomes is basically equal to g of w. So, then what you can dou then if you if you take any derivative d S by d theta is d S by d or. So, I can write d S by d theta is equal to d G by d w into d w by d theta, and you know I can d d w by d theta is just minus sine theta. So, I can use this iteratively I can. So, this is just minus sine theta d G by d w, and I just go ahead and I you know make all these substitutions and put in this equation. So, the minus sine square theta will find that it eventually cancels this factor. So, what you will get is a differential equation that looks in the following form.

So, I will just write the final equation you can easily work it out. So, you'll get 1 minus w square. So, the sine square theta is gives you a 1 minus cos square theta. So, and that is 1 minus w square, and what we will get is d square g by d w square minus 2 w d G by d w plus c by h bar square times minus m divided by 1 minus w square, G equal to 0 and you can see what has happened this almost looks like a Legendre differential equation yeah not exactly like one, but it almost looks like one also notice that the range of allowed values of w, this w is cos theta and theta varies from theta goes from 0 to pi. So, this implies w equal to cos theta that varies from minus 1 to 1. So, the range of w is minus 1 to 1.

Now, what we will do is we do not want this additional m term there. So, what we will do is we will do a small change in this because we have a 1 over 1 minus w square is the denominator, which we would not like to have. So, it looks a lot like the Legendre differential equation if you look at this, but there is a 1 minus w square here. So, to get rid of that we will make a substitution; so you use G of w is equal to 1 minus w square raise to m by 2 H w.

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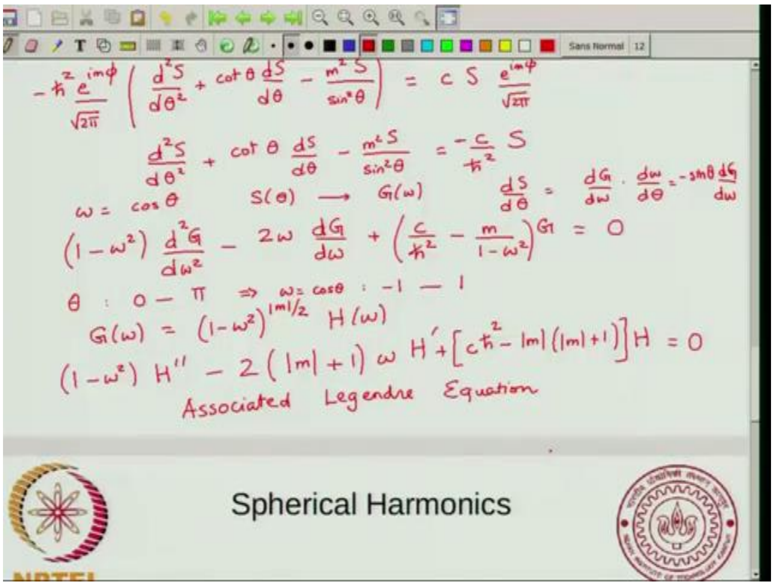

So, I am again defining this new function H in this form. So, I am writing g as this and it will become obvious y we are doing this. So, when you do this then the differential equation you do this and you substitute everywhere you substitute in each of these terms, then you can write the differential equation in the following form 1 minus w square, now I will just call it I would not write a second derivative I will just write it as H double prime which is second derivative with respect to w, minus 2 and what I have is absolute value of m plus 1 w h prime plus what I will have c h bar square minus absolute value of m, absolute value of m plus one H equal to 0.

Now this equation is I mean with whatever constant you have in this last term, this is of the form of what is called an associated Legendre equation, and this is what is used to I mean I mean we use the properties of this of this equation. Now I am you can work out the solution of this using the power series method, and that is what we are going to do, but I will just do a few steps and then and then we look at the implications of the results. So, what we are going to do is we are going to write this in the form of a power series. So, the power series or what we are going to say is that H of w, you are going to write it as sum over j equal to 0 to infinity and what we will write is a j w of j.

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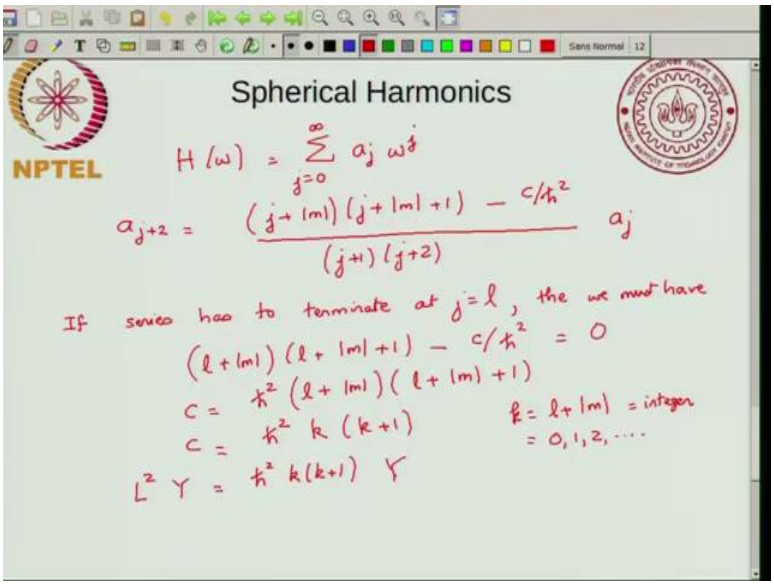

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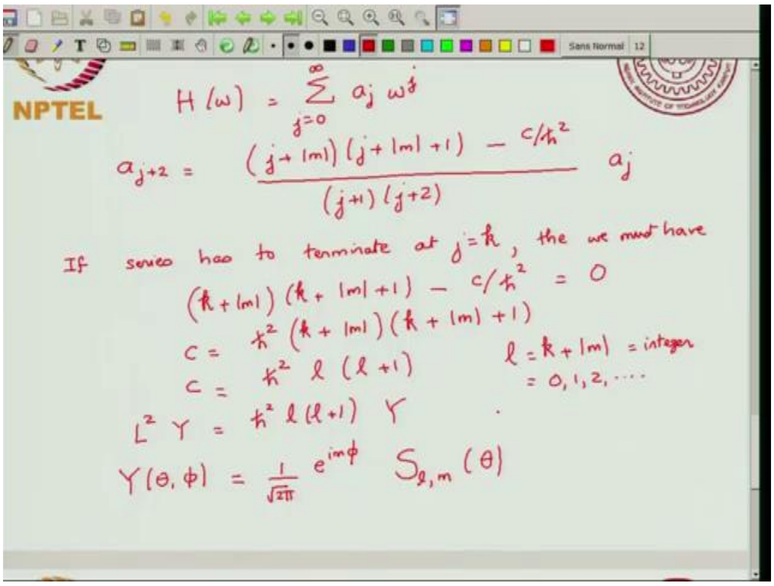

I will just write it as a j, w of j and I have used the letter j and this is what you do in the power series method. Now if you substitute in this you will get the recursion relation that looks like a j plus 2 is equal to j plus absolute value of m, j plus absolute value of m plus 1 minus c divided by h bar square. So, this should be c divided by h bar square. So, divided by h bar square I am this should have been c divided by h bar square in the differential equation. So, this the whole thing divided by j plus 1, j plus 2 times a j. And you can see from here that it looks a lot like recursion relation for the Legendre polynomials. In fact, these polynomials are called associated Legendre polynomials which are closely related to the Legendre polynomials.

Now what we said is that if this series has to terminate. So, if series has to terminate has to terminate at j equal to l, then we must have this numerator when j equal to l should go to 0. So, you should have l plus m, l plus mod m plus 1 minus c by h bar square equal to 0 or you will get the relation which is you will get c is equal to h bar square l plus m, l plus mode m plus 1.

And l is an integer; m already we showed to be an integer. So, l plus mod m is an another integer we will call it k, we call it k. So, this is h bar square k, k plus 1. So, k is equal to l plus mod m this is an integer this is a positive integer equal to integer, and you know when you wrote the series l can be anything from 0, 1, 2, 3 etcetera. So, this is equal to 0, 1, 2 etcetera. So, absolute value of m has to be 0, 1, 2 etcetera. So, l plus m will go from

0, 1, 2 etcetera. So, we got that. So, this is the Eigen value of l square. So, what you can say that l square y is equal to h cross square k, k plus 1 where k is some integers y.

This is a very well known results that we use we use this to characterize the states of a rigid rotor in quantum mechanics. So, we saw how we can get this by using the power series method. A few more points I want to make just to complete. So, when the sum will when the series terminates then the solution. So, this Y of theta phi takes the form take the following form. So, I can write it as 1 by root 2 pi, e to the i m phi times what I have is something that is S, now S is a function of theta and phi, but it depends on these 2 quantum numbers what I would like to use the notation. So, change notations. So, I just like to make a small change of notation, let me call this place where the series terminates as k. So, I will just make this change of notation. So, where the series terminates I will call it k, and I will use the l to denote the value of k plus. So, I will call this k and I will use the notation l; just to be consistent with what you are used to seeing in various books. So, use a notation l, l plus 1 where you have l equal to k plus m.

Just to be consistent with the notations that you are used to seeing. So, I said this series has to terminate at j equal to k, then you must have this relation. Now this l, this now your Y has this form, so you have e to the i m phi, now this S depends not only on it depends on l and it depends on m; S l m of theta. So, this is the function of theta, now what is this function of theta; this will be related to the solution this will be related to the polynomial that you get from the power series solution, so that polynomial.

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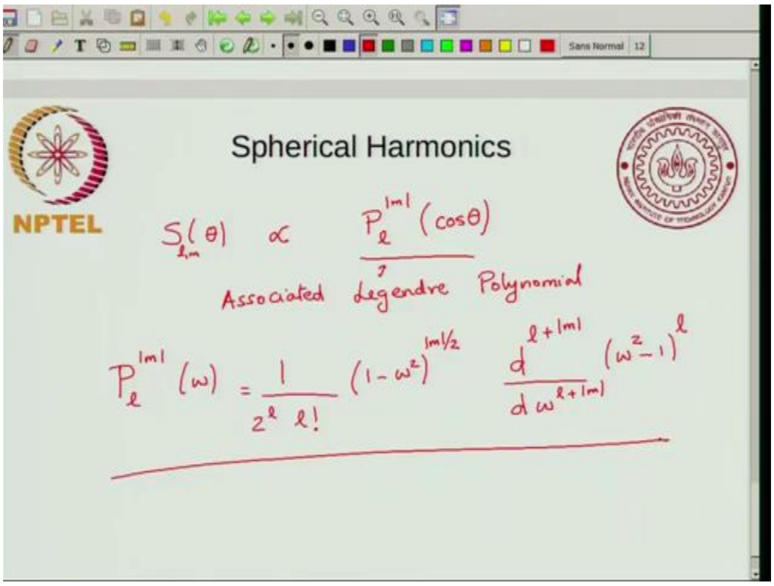

So, you can show that S of S l m of theta. So, this is proportional to we would not bother about the concept of proportionality. So, P l the notation is P l m off now the variable. So, we remember what we had was a w, w was cos theta.

So the variable in which we wrote the associated Legendre equation was w which is cos theta. So, this polynomial is called the associated Legendre polynomial, it is closely related to the Legendre polynomial. So, Legendre polynomial you just had P l m; now you have P l m and m. So, what is the expression I will just write the expression? So, if I write P l m of w. So, I can write this as. So, there are some constants at the beginning just like in the Legendre polynomial, then you have 1 minus w square raised to absolute value of m by 2, and then you have exactly like the legendre polynomial, but instead of just l you have l plus m or w square minus 1. So, instead of 1 minus w square you have w square minus 1 raised to it. So, this is the associated Legendre polynomial which appears naturally in solution of the rigid rotor problem in quantum mechanics and with this I will stop today's lecture.

So, in the next class we will look at another differential equation called the Hermite equation and we look at Hermite polynomials which appear in that solution.

Thank you.