Mathematics for Chemistry

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Lecture - 20

We have discussed the power series method for solving differential equations, and now we will see an application of this method. The application we will do is, what is known as spherical harmonics or these are the Eigen functions of the angular momentum operator, it which you have studied in quantum mechanics.

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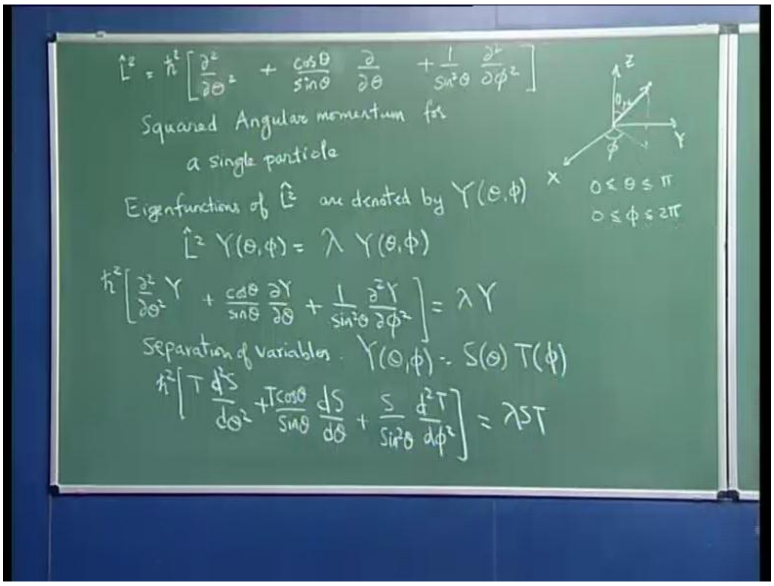

So, the angular momentum operator L square, this is the square of the angular momentum, so the L square operator, which you will learn in your quantum mechanics courses has can be written in this form, this is L square for a single particle. So, this has various terms this is an h cross square in front, then there is a derivative with respect to theta and then a second derivative with respect to theta, and you have cos theta divided by sin theta derivative with respect to theta, then you have 1 by sin square theta, second derivative with respect to phi.

And let me remind you that, r theta phi are in the spherical coordinates. So, if you have X, Y, Z then point is r theta and phi, so we are working in the spherical polar coordinates and so this theta and this phi correspond to these angles in the spherical polar coordinates.

So, and once again you should remember that 0 less than equal to theta less than equal to phi and 0 less than equal to phi 2 pi. So, we will work in these coordinates and now what we want to find out, this is the squared angular momentum for a single particle so this could be the, in the hydrogen atom it is the angular momentum associated with the electron. So, let us try now, we want to find Eigen functions of L square operator and so they are denoted by Y and Y will be function of theta and phi.

So, the Eigen functions, they will be functions of theta and phi, and they will be denoted by Y theta phi and they will satisfy L square Y theta phi is equal to some lambda Y theta phi. So, our task is to find out Y and find out lambda, so what are the Eigen values and what are the Eigen functions of this L square operator. So, let us see, how to go about this problem so first we will substitute this in this equation to get h cross square theta square Y plus dou y by dou theta plus 1 by phi square, this is equal to Y.

So, what you notice is that, this is a sum of three terms, two terms or they contain only theta and phi appears only in the third term so the natural thing to do, is a technique called separation of variable. So, use separation of variables so you say that, Y of theta phi is equal to S of theta T of phi. So, Y of theta phi is S of theta T of phi and now, if you substitute this in these equations so the second derivative with respect to S times T so second derivative with respect to theta of S times T so this will operate only on S.

So, I can take T outside in this part so I can write it in this form T now, this is d square S by d theta square and I have written this as a d square S by d theta square. Because, S is function only of theta plus cos theta by sin theta dS by d theta plus S by sin square theta d square T by d phi square is equal to lambda S T.

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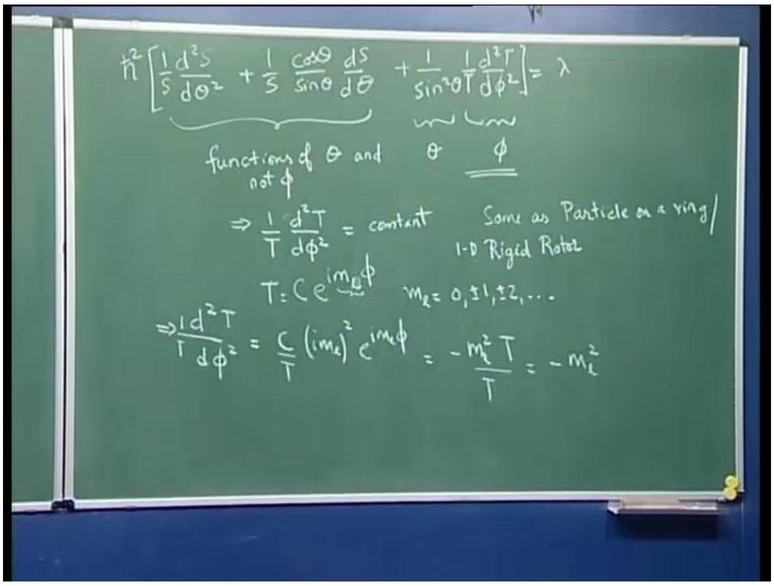

Now, if I divide by S T, I will get h cross square plus d theta plus what I will get is, theta phi square, this is equal to lambda. So, now, notice that, the right hand side is a constant, left hand side is a function of theta and phi, so this is a function only of theta, this is also a function only of theta. So, these two are functions of theta and not phi, so these two are independent to phi now, this is a function of theta, this is a function of phi.

So, if all this has to add to a constant then this whole thing has to be independent of phi and that means, there should be 1 by t here sorry so that means, this term has to be independent of phi. So, since the right hand side is independent of phi, the left hand side should also be independent of phi and this so if this is dependent on phi then nothing in here can cancel that dependence.

So, the only way, in which this can be true is, if this is independent of phi so that implies d square T by d phi square 1 by T. Now, this has to be independent of phi and since T is only of function of phi, this has to be a constant and d square T by d phi square is constant times T, this is same as the particle on a ring or a rigid rotor, 1-D rigid rotor. So, in other words, this has a solution, the solution is T is equal to some constant e to the i m L phi where, m L is equal to 0 plus minus 1 plus minus 2 and so on.

So, this part I am assuming that, you know how to work this out, what we get is that then d square T by d phi square will just give m L square. It will just give m L square times t or minus m L square times t so you can write this so you can replace this whole quantity by just minus m L square. So, then the equation for so this implies d square T by d phi square is equal to some constant i m L square e to the i m L phi, this is equal to minus m L square T.

So, that is d square T by d phi square and so if I divide this by T so I take 1 over T here, T here, 1 over T here and this gives you minus m L square. So, then you can replace this whole thing by minus m L square and if you do that then you will get an equation that involves only S and theta.

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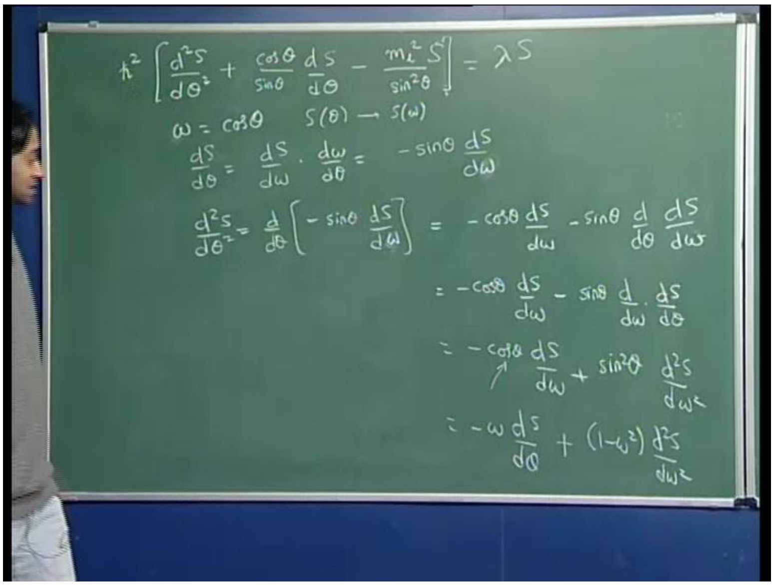

So, let us substitute this in this expression to get h cross square, I will take the S to the right hand side so I will get d square S by d theta square plus cos theta by sin theta d S by d theta minus m L square by sin square theta, m L square S by theta is equal to lambda S. So, this is our ordinary second order differential equation where, S is a function of theta, so S is a function of theta and this is just an ordinary second order differential equation.

It is homogeneous, each term has just one power of S now, but you notice that, there is cos theta and sin theta appearing here similarly, there is a sin square theta. So, what we will do is, we will do a small transformation so put w equal to cos theta, so then S of theta goes to S of w and dS by d theta equal to d S by dw into dw by d theta is equal to, dw by d theta is minus sin theta d theta.

And then if you take d square S by d theta square is equal to d by d theta of minus sin theta dS by d theta sorry dS by dw. And now, you can use the pair rule so you will get minus cos theta dS by dw and you will get a second term that is, minus sin theta into d square S by dw square into minus sin theta square so that is, plus sin square theta. So, you just differentiate the first term and then if you differentiate the second term, you get d by d theta d by dw of dS by d theta, for dS by d theta you substitute this term.

And so what we will do is, we have to do this a little more carefully let us look at the second term little more carefully. So, first term you take the derivative of this with respect to theta, for the second term what you will get is, minus sin theta, you will get d by d theta of dS by dw and you can write this as, cos theta dS by dw minus sin theta d by dw of dS by d theta.

And so S here is expressed as a function of theta and if you write dS by d theta, you substitute this term minus sin theta dS by dw. So, then you will get plus sin square theta and it becomes d by dw of dS by dw that is, d square S by d w square. And now, what you will say is that, cos theta is w and sin square theta is 1 minus cos square theta that is, 1 minus w square so that is the second derivative with respect to theta.

And what we will do is, we will take the h cross square to the right and now, we can rewrite this equation so what we will do is, we will substitute for dS by d theta and d square S by d theta square. So, when we do that, and for convenience, I will take the h cross square to the right hand side.

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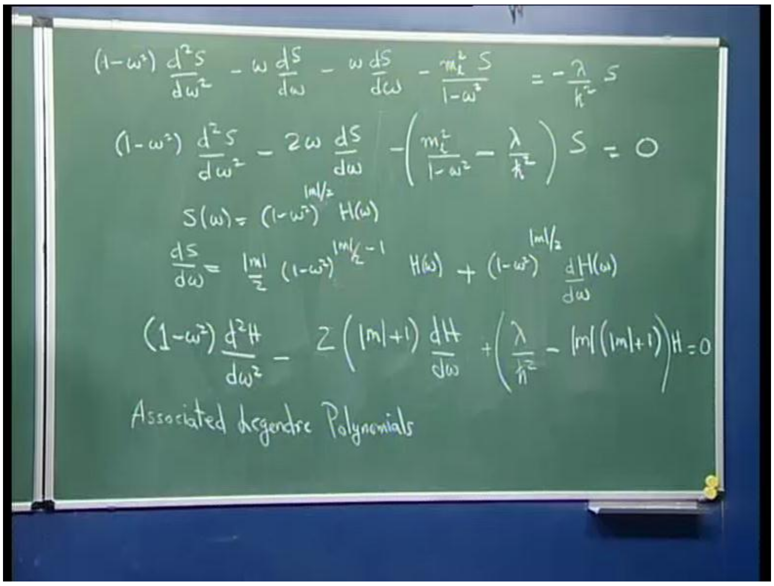

So, I will get 1 minus w square d square S by dw square minus w dS by dw so that is this term then I get plus cos theta by sin theta dS by d theta. Remember, dS by d theta was minus cos theta dS by dw so even though sorry minus sin theta dS by dw so the sin thetas will cancel. So, you will just get minus cos theta, cos theta is w, minus w dS by d w, this is from this term so from this term, you substitute this expression for dS by d theta and the sin thetas will cancel.

So, you have minus cos theta dS by dw and minus cos theta is same as minus w, minus m L square, what you have is, you just have S divided by sin square theta is 1 minus cos square theta so 1 minus w square. So, this is equal to lambda by h cross square S, this is and if you want, I can combine these two terms to write this in this form, 1 minus omega square d square S by d omega square minus 2 omega dS by d omega minus m L square S by 1 minus omega square and plus lambda by h cross square sorry there should be a, I had missed out a minus sign here.

So, write in the angular momentum operator, there should be a minus sign and so there should have been a minus sign all along so I can put this minus sign here and this will be plus, equal to 0 minus this. So, I can write this in this form so this is like S double prime, S prime and S, so it is written exactly like a homogeneous equation. Now, so one of the things to notice is that, this has a 1 minus w square and you would prefer not to have this 1 minus w square.

Because, when w equal to plus or minus 1, this solution will have some divergences and also you have a 1 minus w square in the denominator here. So, w equal to 1 will not be a regular singular point, if you have this 1 minus w square in the denominator. So then you make the substitution and the substitution will make is the following will say, S of w H of w, I think that is, 1 raise to m by 2 H of w.

So, you make this substitution and then you calculate the value of d square S by dw square and you calculate the value of dS by dw and d square S by d w square. So, if I do dS by dw is equal to, so we will get m by 2 raise to absolute value of m plus by 2 dH by dw, dH of w. And similarly you do the same for d square S by dw square, you take the second derivative and you plug it into this, I would not go into the details of that but what you will end up with then you can cancel essentially, this factor you will be able to cancel.

So, ultimately, if you do all the rearrangements, you will get an equation of the following form w square d square minus 2 absolute value of m plus 1 dw plus lambda S, lambda by h cross square minus absolute value of m plus 1, H equal to zero. So, this is what, you will end up with now, if m is an integer, this is and the solutions of this looks very much like the Legendre differential equation.

It looks very similar to the Legendre differential equation and only thing is, if m is an integer, there is this additional factor, m by definition has to be an integer. So, if this is an integer, this is also a kind of Legendre differential equation and the polynomials you get are called the associated Legendre polynomials. The polynomials that you will get, when you solve these equations are called the associated Legendre polynomials, they are very similar to the Legendre polynomials.

But, let us go and work out, how you get these so here, we have a differential equation and we are going to use the power series method to solve this differential equation. So, now, in this case, 1 minus w square or w equal to plus minus 1 becomes a regular singular point.

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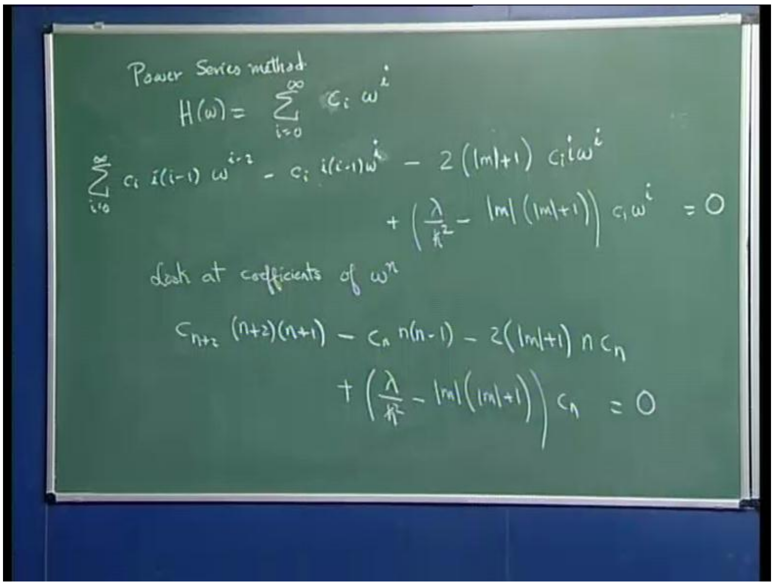

And you can use the power series method so the power series method now, we will say, H of w is equal to infinity C i w raise to i. So, if you do this then you substitute in this equation, what you will get is infinity, first term will be second derivative so C i into i i minus 1 w raise to i minus 2 minus, the second term will be C i i, i minus 1 w square. The third term I have twice derivative, 2 m plus 1 there should be a w, so that was missing, there should have been a w here.

So, minus 2 plus 1, now w d by dH so if I do this, I will get C i w raise to i into i, that is due to this term and then you have this constant plus lambda by h cross square, this one is equal to 0. So, here, I substituted in this. And now, you can immediately see the recursion relation so look at coefficients of w raise to n now, you will have a coefficient of w raise to n, when i equal to n plus 2 in this.

So, you will have C n plus 2 n plus 2 n plus 1 minus in this case, you will have c n n, n minus 1 so w raise to i and then you have minus 2 plus 1. Now, in this case, you will have n C n w raise to n so n C n is the coefficient of w raise to n followed by this whole constant multiplied by C n. So, followed by equal to 0 now, you notice that, all these terms are proportional to C n so we can take all those terms to the right hand side and you can write C n plus 2 in terms of C n and that is the recursion relation, you will get.

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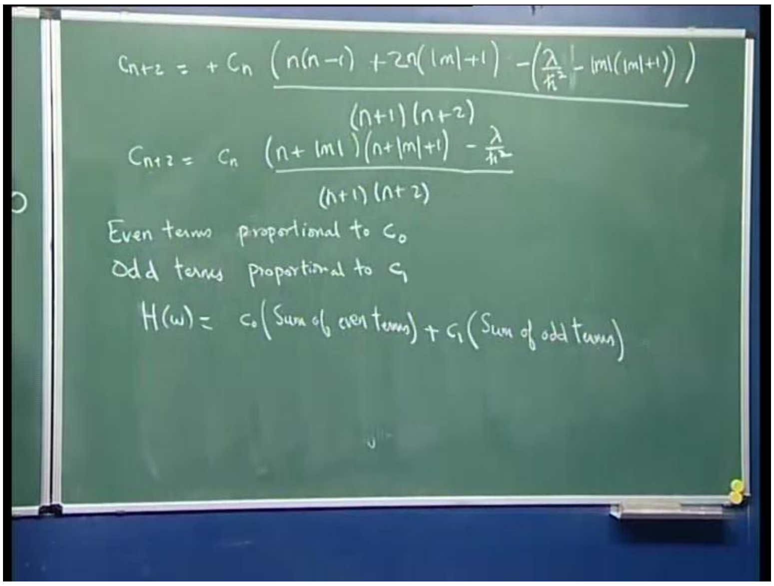

So, then I can write C n plus 2 is equal to minus C n or you can write it as plus C n times whatever, is remaining on the right. So, what is remaining on the right was, n n minus one minus 2 plus 1 times n, 2 n so put plus and that, should be of minus this whole thing. So, then I can write it as minus lambda by h cross square minus m plus 1 so this whole thing divided by n plus 1 n plus 2.

So, that is the recursion relation and what you can do is, you can simplify this, you can take this m m plus 1 over here and you can rewrite the whole thing in a slightly simpler looking form, in the following form. So, you can write C n, n plus m plus 1 minus lambda by h cross square divided by n plus 1, n plus 2. So, I can just take this inside here and I can write it in this form so this the recursion relation and if you work out the various terms in this, you will get two types of terms.

So, you will get even and odd terms, even terms will be proportional to C 0, odd terms proportional to C 1. So, then you have general H of w, it can be written as a linear combination of C 0 times sum of even terms plus C 1 times sum of odd terms. So, and we can do this because the recursion relation relates C n plus 2 to C n so it will relate C 2 to C 0. And then similarly, C 4 will be related to C 2 but C 2 is already related to c 0 so C 4 will be related to C 0 and so on so we can write this in this form and you can solve.

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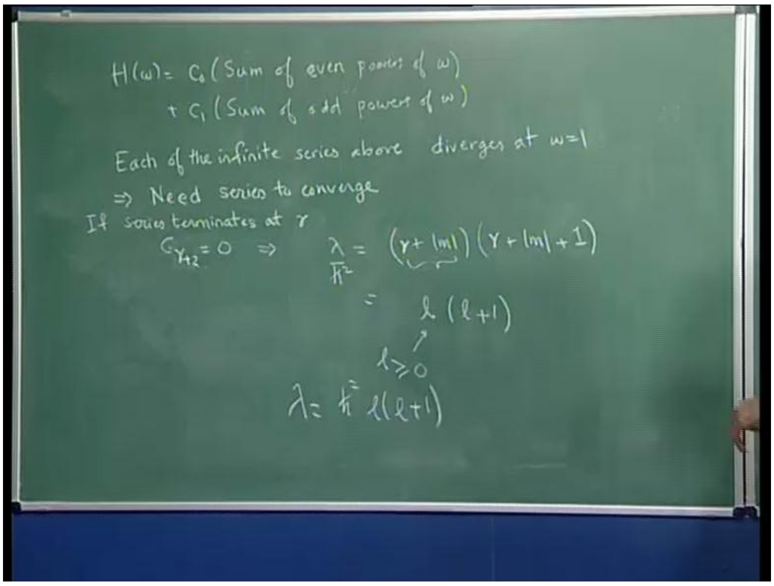

So, eventually, what you can do is, you can write H of w is equal to C 0 sum of even powers of w plus C 1 times sum of odd powers of w and typically, each of these will be an infinite series. So, this will be an infinite series, this will be an infinite series now, once again we need, if this series so each of the infinite series above diverges at w is equal to 1. So, when w becomes 1 then both these series will go to infinity so then that implies, but it is not good, if it diverges at w equal to 1.

Because, then the series will go to infinity and if H of w goes to infinity then the wave function will go to infinity. So, then we need series to converge so you need at least one of these two series to be to converge and to be finite. So, at least one of these series should be truncated and this condition is that, C n plus 2 equal to 0 or C m plus 2 converge. So, if series terminates at C m, so if one of these series terminates at C m then C m plus 2 has to be 0.

So, this implies lambda by h cross square is equal to n plus m, n plus m plus 1 it sorry terminates not at C m I should, let me call it C r so just to differentiate from this m, I will call it C r at r then C r plus 2 equal to 0 implies, this times r plus 1, r plus m plus 1. So, now, m absolute value of m is a positive integer, r is also a positive integer so then r plus m will be some other integer, we call this l, l is greater than or equal to 0 so l then this becomes l plus 1.

Therefore, we conclude that, the Eigen value of angular momentum has to be h cross square l l plus 1. So, if the Eigen value of angular momentum is h cross square l l plus 1 then the series will converge at, it will get truncate at this value of r. So, we went through this argument, and now what we have identified that, your angular momentum, Eigen functions have to be of this form, h cross square into some integer greater than or equal to 0 times that integer plus 1.

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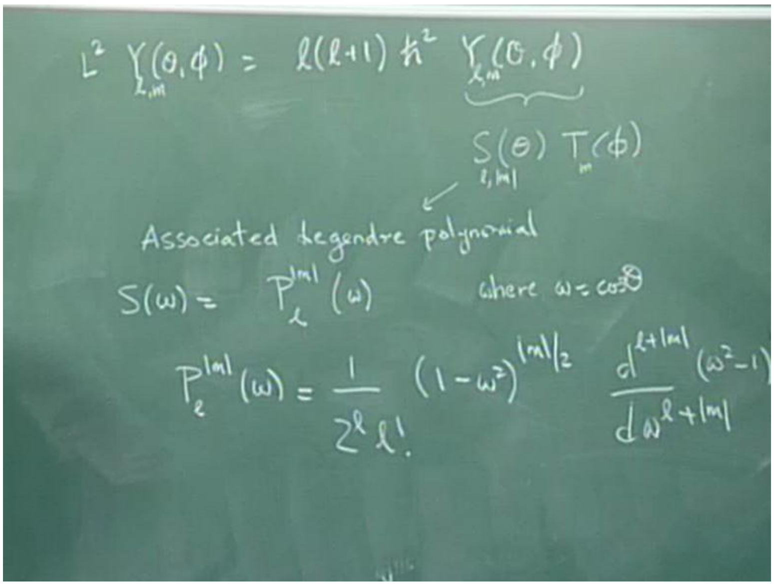

So, in other words, L square times Y of theta phi is equal to l l plus 1 h cross square Y of theta phi and notice that, Y is quantized by l so we can write this as l. Also this m value, so m value decides the wave function, the phi part of the wave function so it is actually quantized by both l and m so you can write it in this form. And this function Y l m, we wrote as S of theta T of phi now, T of phi depends on m, S of theta depends on l and absolute value of m.

Now, this S of theta, this is called the associated Legendre polynomial so we write this as S of w is equal to P l absolute value of m of w where, w equal to cos theta. Now, what is this P l absolute value of m w, this is closely related to the Legendre polynomials that we saw earlier. So, I will mention the Rodrigues formula for P l absolute value of m w, is equal to 2 l plus omega 2 l.

So, this is the Rodrigues formula, by which you can generate all these I mean, this is not, you can actually derive the exact forms of P l m of w by starting from the recursion relations, just as we did in the case of Legendre polynomials.

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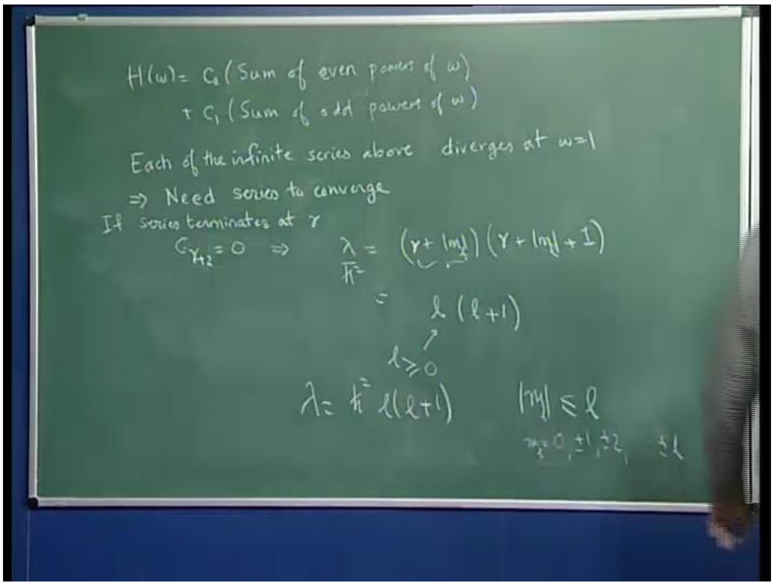

Now, the other thing is that, from this expression, we can say that, m has to be less than equal to l. So, m has to be less than or equal to l and we already said that, therefore m is equal to 0 plus minus 1 plus minus 2 up to plus minus l. So, that is the other thing we can conclude from this argument, we called it m l, so m l.

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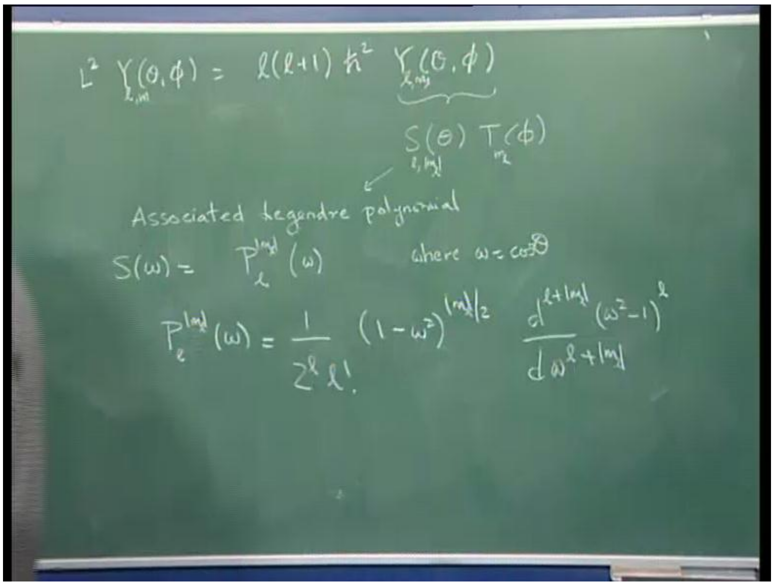

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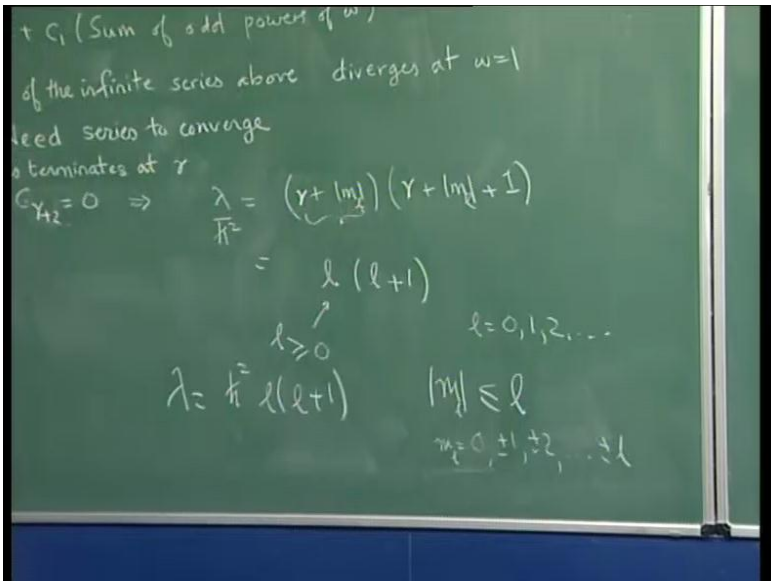

So, the point is that, this is what, we found from this whole discussion is that, l is equal to 0, 1, 2 dot dot dot, it can be anything but m l has to be 0 plus minus 1 plus minus 2 up to plus minus l. And this will be familiar for those, who have seen the, this is the orbital quantum number, this is the angular momentum quantum number. So, this is the orbital quantum number in the case of hydrogen atom, this is the angular momentum quantum number and you can actually show, you can actually put these wave functions and you can calculate this.

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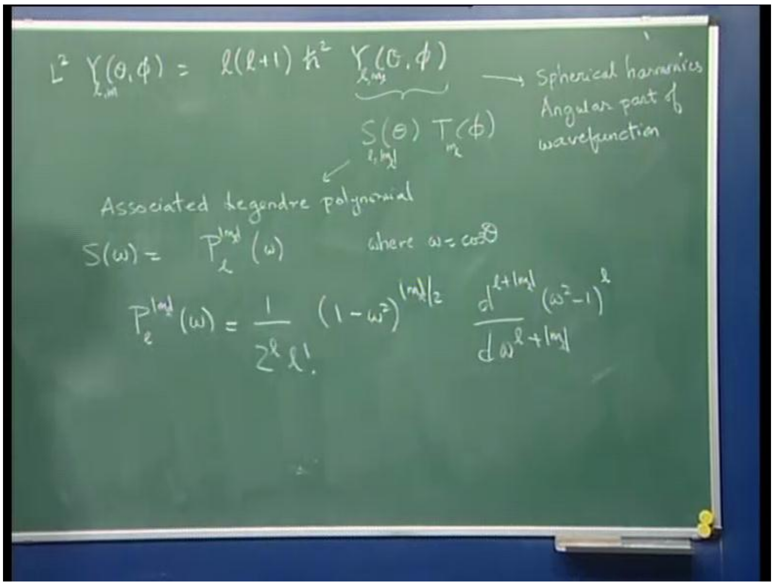

Now, this part is the so S times T gives you Y l m m l of theta phi, this is also called as spherical harmonics or it also called the angular part of wave function. So, what we have done is, to solve the angular part of the wave function for the Eigen functions of the Hamiltonian operator. We found that, the angular part of the wave function for Eigen functions of the Hamiltonian are also Eigen function of angular momentum square operator and so Y l m is that Eigen functions of the angular momentum square operator.

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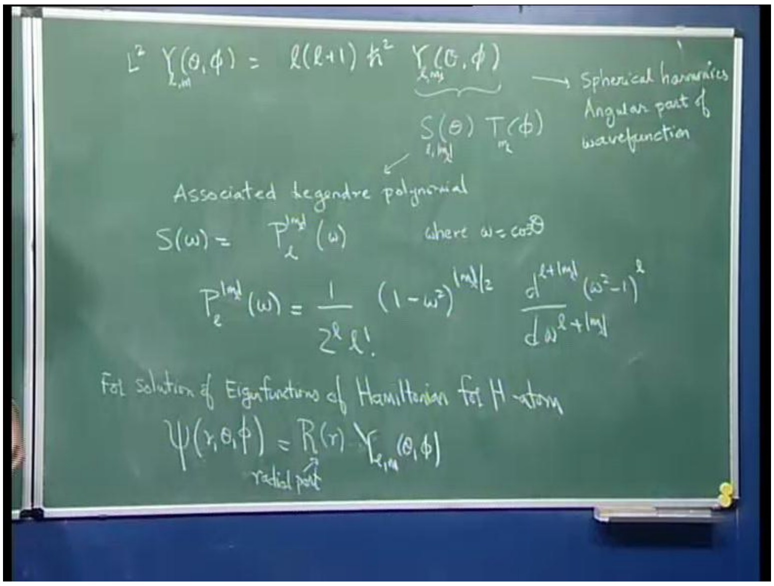

So, when you write the, so for solution of Eigen functions of Hamiltonian, for hydrogen atom so the psi will be a function of r theta phi so we will write this as a radial part, this is a radial part times Y l m of theta phi. So, Y l m theta phi is a angular part and the angular part of the wave function is the same as the Eigen functions of L square operator. So, this is we have seen in this exercise, we have seen how to solve for the angular part of this wave function.

Now, I would not be talking about the radial part of the wave function of the hydrogen atom but you might have seen it in your quantum chemistry courses. The radial part of the solution of the hydrogen atom can also be solved using the power series method but you have to use the modified power series method or the Frobenius method. So, when you write the differential equation for the radial part of the wave function, the most elegant and simple way to do it, is the Frobenius method or the modified power series method.

So, what you have seen by this is that, when you need to solve differential equations, the power series method is a very useful method, when the direct power series method does not work, you can use the modified power series method or the Frobenius method. Now, at this point, this will be all that, I will talk about the power series method, in the next class what I will do is, to look at in a one property of the power series method, that has to do with orthogonal Eigen functions.

So, we will look at conditions, when the solutions of differential equation gives you or orthogonal to each other, and this will be the last part of this discussion on differential equations.