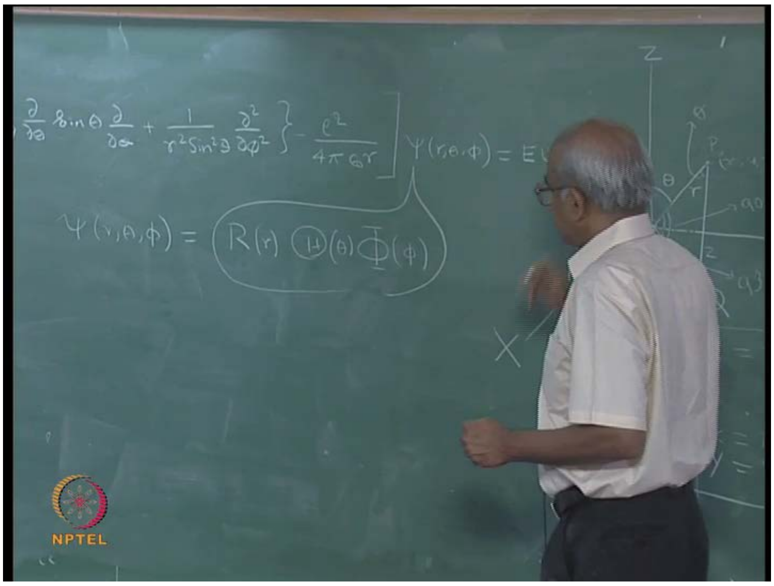
Introductory Quantum Chemistry

Prof K. L. Sebastian
Department of Inorganic and Physical Chemistry
Indian Institute of Science, Bangalore

Lecture - 23
Hydrogen Atom Continued: Separating Centre of Variables

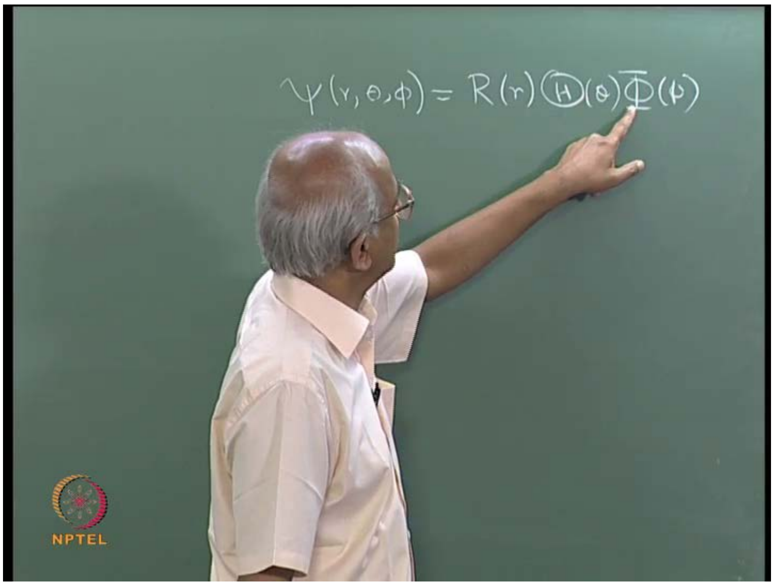
Now, what we have to do is we have to find R, capital theta and capital phi such that their product will satisfy this equation. So, to determine R, capital theta and capital phi what we have to do is we will use this product.

(Refer Slide Time: 00:32)



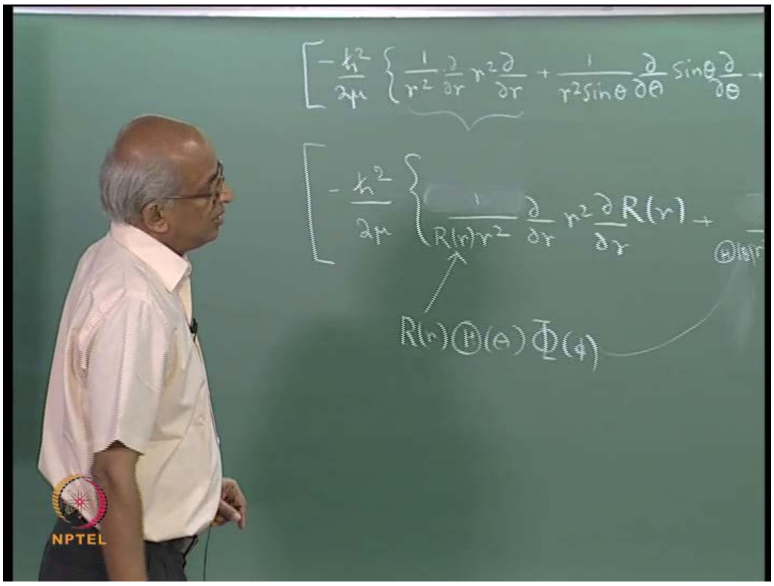
And, put it in place of psi here as well as on the right hand side; because I need space I am going to rub off this equation. But to remind you we keep it here; this is how they are Schrodinger equation. Then, we are trying to solve it using the method of separation of variables.

(Refer Slide Time: 01:11)



We assume that psi may be a product of 3 functions R, capital theta and capital psi; R is only depending on r, capital theta depending only on small theta and capital phi depending only upon small phi. So, what we do is we take this and put t into the full Schrodinger equation where ever psi occurs we are going to put that. So, let me rub of this psi and put R.

(Refer Slide Time: 01:41)



Capital theta and capital phi and do the same thing here on this side. And now if you looked at this operator; the operator involves partial differentiation with respect to R, theta and phi. But in here this operator contains only partial differentiation with respect to R;

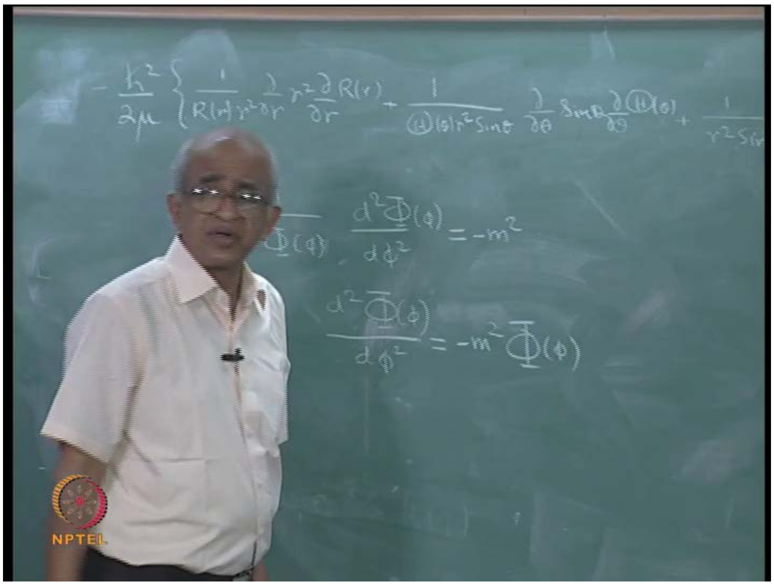
and in that partial differentiation variable theta and phi are kept constant, so there for capital theta and capital phi will be unaffected by this operator. So, therefore if I took this function inside what will happen is that; this operator will effect only R; it will not affect capital theta and capital phi. So, therefore let me write whatever the result is this. So, this operator effect capital R it does not affect the 2 things, so the 2 other things actually can taken here and written here. And similarly this operator will affect only capital theta. So, we can do a similar thing with that operator what would be the result?

The operator affects only the capital theta of theta. And similarly the last operator affects only capital phi. So, let me write that and R and capital theta are unaffected. So, I can write them here. And let me now complete this bracket; then write this term it is minus e square divided by 4 pi epsilon naught R. Yeah, well I have forgotten to put R, capital theta capital phi of phi; and that is actually equal to e into R(r), capital theta of theta capital phi of phi. And now next thing that we will do is we will divide throughout; by the wave function itself. And the reason for doing that will come clear as I proceed; we will divided throughout by the this function, I divide throughout by this function. And obviously from the left hand side this is going to go; and here from this term is also going to disappear while in this step what is going to happen?

Here, you are going to divided by R(r), capital theta of theta and capital phi of phi; obviously as far as this term is concerned there is a capita theta and a capital phi in the numerator. So, these 2 things and those 2 things will get cancelled and you will be left with R(r) in the denominator. So, without I think another the equation once more is already a long equation. So, without writing the equation once more I will just rub off this. And write 1 by R(r) and the same kind of thing is going to happen here in this we have R and capital phi in the numerator they are going to get cancelled. And you will be left with a 1 by capital theta of theta and what about this one well the R and capital theta will go you will have 1 by capital phi of phi.

Now, capital R into capital theta into phi I already told you this will disappear and this also will disappear. And because this e which is total energy which is so far away that I will do is I will bring it closer write the equation in this fashion. So, this bracket also let me just close I will put it here; this is the correct place to put it. So, this is the equation that we will use now. So, let me rewrite this equation.

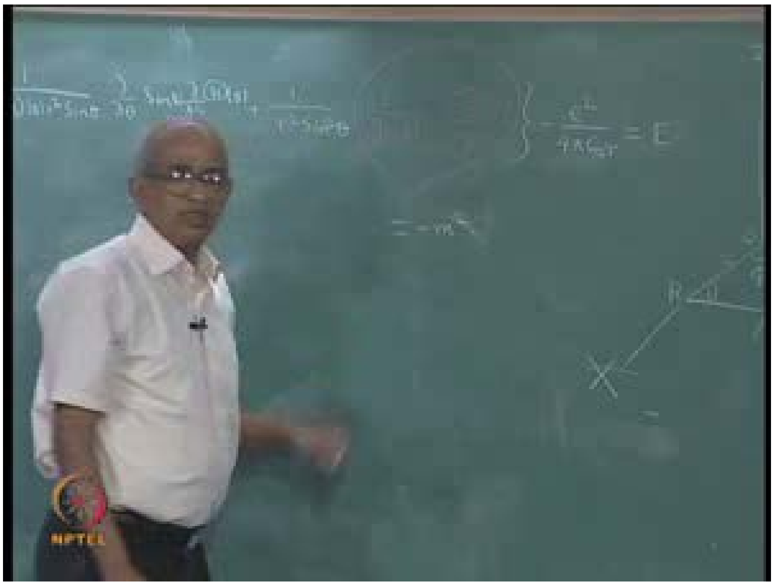
(Refer Slide Time: 07:40)



So, that is the result we can check that I have not made any mistake. But then if you will look at the expression you see I have written one part in a different color; what is the specialty of that part? If we look at it carefully you would realize that that is the only part that depends upon small phi you do not find the dependence upon small phi anywhere in the equation; that is why I used a different color. So, you have the left hand side of the equation there are R, theta and phi.

But this part alone depends only upon phi while everything else depends upon R and theta; see if we have this kind of equation what we can you do? You can rearrange this first you see you will take this term to other side. Then, you will multiply by the inverse of this after which you will take these terms also to the other side; eventually you can rearrange in such a fashion that only this term is left on the left hand side. And what about the right hand side? Right hand side will be some function of R and theta and whenever you have such an equation we know that. So, you want the left hand side you have a function of phi and on the right hand side you have some function of R and theta; if such an such a thing has to be satisfied both of them must be equal to a constants. So, therefore this function of phi definitely must be equal to a constant and I am going to call that constant right.

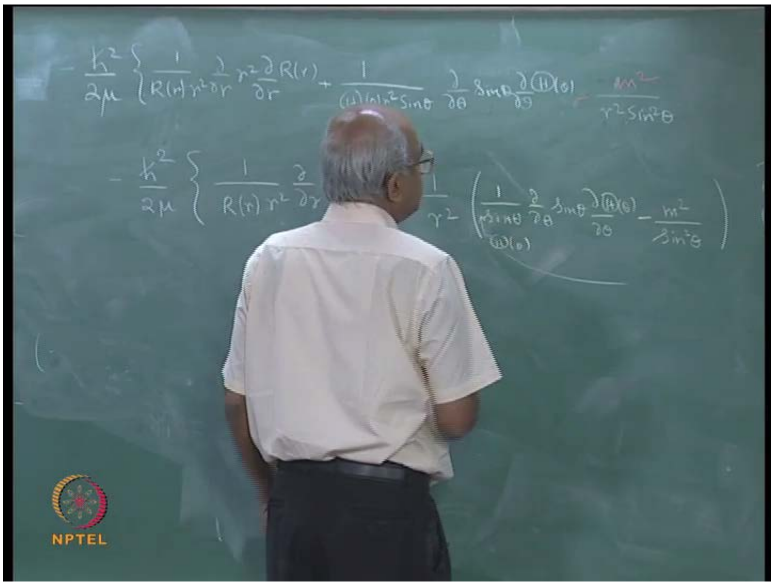
(Refer Slide Time: 11:16)



So, I am let to the conclusion that this must be equal to a constant which I will denote as minus m square you can have any notation for it. But standard notation is used to use minus m square you should not confused with the electron; this is not the mass of the electron eventually it will train out to be the magnetic quantum number. And there magnetic quantum number is usually denoted by in simple m. So, I am not going to be change the notation. So, what is the conclusion? The conclusion is this object has to be equal to minus m square which actually tells me that 1 by capital phi of phi. Well, it is not really necessary to use partial derivative notation here because phi capital phi depends only upon small phi. So, I could have written this as d square capital phi by d phi square is equal to minus m square; as the equation that I give. So, if you multiply by capital phi what happens you will get d square capital phi by d phi square is equal to minus m square capital phi of phi this is a fairly simple differential equation; that you can solve right not difficult to solve at all.

So, there for we have successfully found what phi should be we will solve it later, but we have found an equation in that capital phi satisfies right. And so then what will I do next? Well, this is equal to minus m square. So, instead of this part I can actually say I will put minus m square because it has to be equal to a constant. So, let us put minus m square minus m square that term instead of that term we just write minus m square. And what happens you have this equation correct. And I am going to write this equation once more, but because I will need this equation later may be I will write I will move it to this side.

(Refer Slide Time: 14:13)



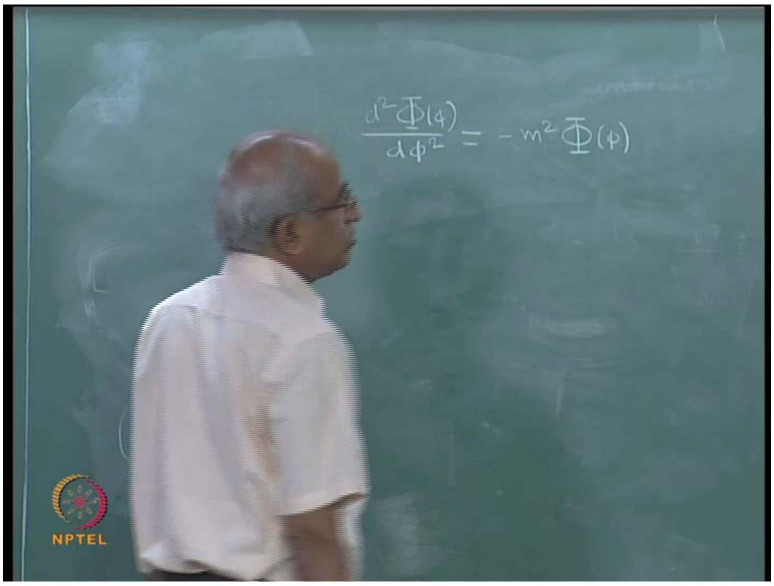
So, I will write this equation once more minus h cross square by 2 mu 1 by capital R(r); r square dou by dou R, r square dou R by dou R plus 1 by R square you can see there is a 1 by R square here and another 1 by R square there. So, let me write it as a common factor, but this inside this bracket it is actually 1 by sine theta dou by dou theta sine theta dou capital theta by dou theta minus m square divided by sine square theta right. And of course we have 1 by R square I have taken that out. And then plus well actually not plus, but minus e square divided by 4 pi epsilon 0 R is equal to e right. Now, if we look at this equation what do you find the portion that they have written with the yellow color depends only upon theta while everything else is either constant or dependent on r. So, what can you do? You can rearrange this you can rearrange it in such a fashion that only this term is left on the left hand side only this term remains on the left hand side.

And, then you will say that a function of theta is equal to a some function of R; theta and R are both independent variables. So, in the spirit of method of separation of variables you will have to say that both of them are equal to a constant. So, that specifically implies that that this must be equal to a constant let me write that equation; there is a minor mistake in what I have written I have forgotten to write this capital theta that should have come here. So, let me write that also capital theta of theta will be occurring here. So, 1 by capital theta of theta sine theta dou by dou theta sin theta dou by dou theta operating upon capital theta of theta minus m square by sine square theta must be equal to a constant; that is what I am saying. And what I will do is I will use the symbol minus beta for this constant. So, therefore if I like I can rearrange this I can rearrange this and get an equation for differential equation for capital theta. So, how will I rearrange it? I will first take beta to this side and then multiply throughout by capital theta. So, let me write that result 1 by sine theta dou by dou theta sine theta dou capital theta by dou theta plus beta minus m square by sine square theta into capital theta is equal to 0; that is the equation for capital theta.

And, it is an ordinary differential equation in fact it is not really necessary to put partial derivative notation. Because the function on which these things operate are just functions of the variables theta alone. So, you could have just put d and not only that this whole thing is equal to a constant. So, therefore I can put instead of that whole thing I can put minus beta; and if we put minus beta what happens you get an equation for look at what has had happened this is just an equation for R. So, what is that equation? I will have to write it somewhere that equation I will write in the middle. Well, I will I will multiply throughout by R. So, that it appears as a nice differential equation.

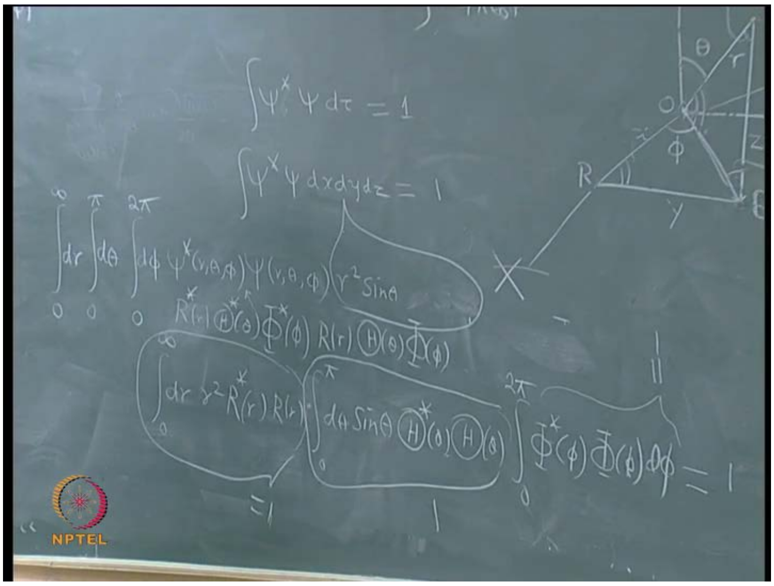
So, that is how it is fine. So, we have at arrived at 3 separate ordinary differential equations and I would like to solve these 3 equations. And of course I have any solutions that I find I will have to be acceptable; I mean that is the condition that we have to impose. So, we start with the first equation because it is the simplest.

(Refer Slide Time: 21:38)



So, the first equations says that d square capital phi by d phi square is equal to minus m square capital phi of phi. Now, I shall I would also like to remind you that any function that you get has to be normalized.

(Refer Slide Time: 22:17)



So, what does that means that actually means if you took psi star psi. And integrated over the full volume element sorry integrated over the over the full space you multiplied by the volume element d toe and integrate over the entire space; the answer must be equal to 1. And in Cartesian coordinates actually this is a reasonably simple expression you will have to take d x into d y into d z and the answer has to be 1. But we have decided to through away Cartesian coordinates and express everything in terms of R, theta, phi. So, what does that mean? It means that this psi that I find which will be a function of R, theta, phi; I will have to multiply it by its own complex conjugate R, theta, phi. Then, I will have to multiply it by the volume element d toe.

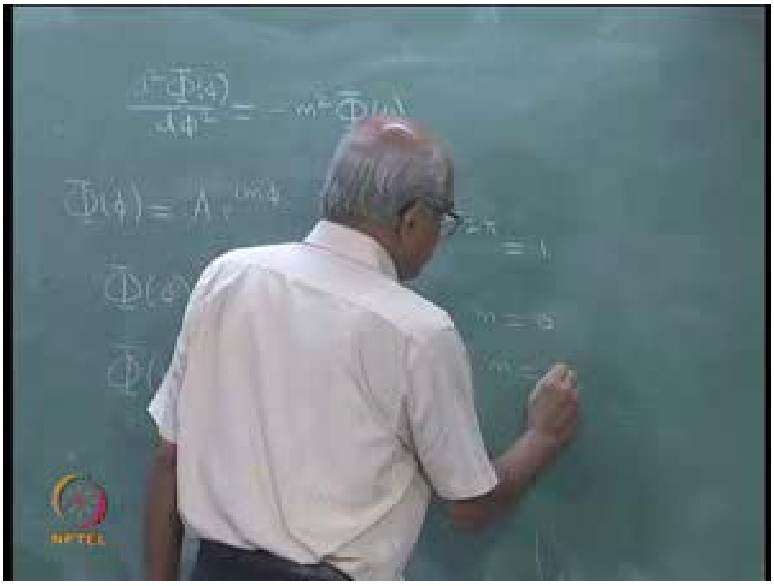
So, that means this volume element d toe has to be expressed in terms of R, theta, phi right. Here, the expression for volume element in terms of Cartesian coordinates is simple it is just d x into d y into d z. But the expression for the volume element in terms of spherical polar coordinates is slightly more complex. We I will not describe discuss this but I will just say that in polar coordinates what happens is that the volume element actually becomes R square sine theta d r into d theta into d phi; that is what happens this is just your d toe. And you have to integrate over the entire space how will you do the integrations over the entire space? It will be a triple integral because you have 3 variables. Now, the variable R will vary minimum possible value if you remember is 0 it will go to infinity right just remind you that this integration over R what I will do is I will remove this d r from there and put it here.

And, then I have to integrate over theta; theta I told you to cover the entire space you need to allow it to range from 0 to phi. So, therefore you will have 0 to phi d theta. So, I can remove d theta from there and then finally you have d phi let me put d phi here that is a third integration. And that will have to range from 0 to 2 pi; that is why we will have to do the integral right. And now if I looked at my wave function what is happened the wave function has been assumed to be a product correct. So, what is the nature of the product it is going to be R, capital theta, capital phi everything star multiplied by R(r), capital theta of small theta and capital phi of small phi correct.

So, if you substitute this product here you would realize that the integrals that you can you have to perform; they become 3 separate integrals that it should be clear to you. And what are those integrals? Let me just write those integrals one of them will be integral 0 to infinity d r; I will just collect to the terms that depend upon R, dr r square R star R. And the next integral will be integral 0 to phi d theta sine theta capital theta of theta star capital theta; and integral 0 to 2 phi capital phi star phi capital phi of phi d phi. And this must be equal to unity correct this is the normalization condition. And so what we will do is you see and I am going to solve this equation. Similarly, there are equations for R and capital theta which also have to be solved, but after having found those solutions. What I will do is I will impose conditions on them which will say that this must be this integral must be equal 1. And I shall impose condition on theta saying that this must be equal to 1 and this other integral that also must be equal to 1.

So, that once I have found functions in this fashion I am I showed that the wave function the total wave function is normalized; you see each one of them is equal to 1 then the product has to be equal to 1. So, that is what I will be imposing. So, therefore what happens is that this differential equation I am going to solve and adjust in it in such a fashion that this condition which is a normalization condition is satisfied as per as that part is concerned. Similarly, when I have capital theta I will have to normalize it normalize that; and similarly R also has to be normalized. So, what is the solution of this equation is the next question? Answer I very simple any constant a into e to the power of I m phi satisfies that differential equation.

(Refer Slide Time: 28:47)

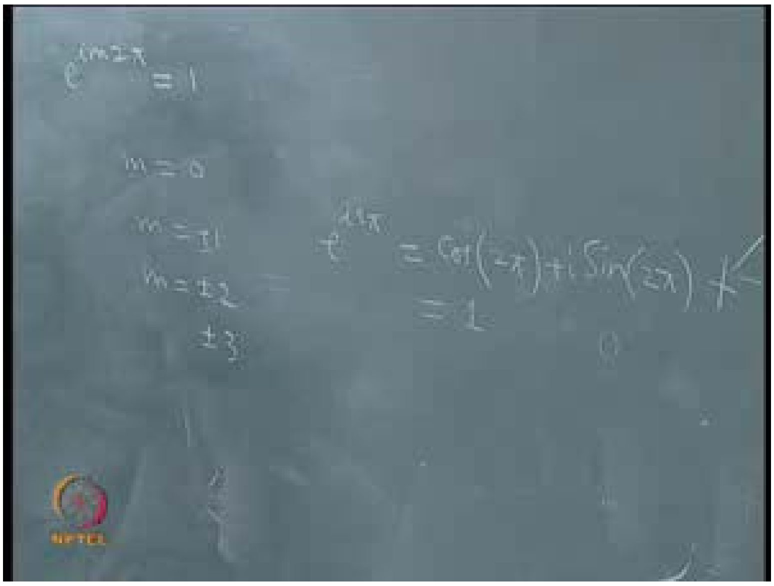


Answer I very simple any constant a into e to the power of i m phi satisfies that differential equation. But then the question arises whether this is an acceptable solution; see suppose I am thinking of having my head as I said in the x is that plane; but that is not very precise actually. Suppose, I am standing somewhere here this is me and here is my head this is the positive x direction and that is the z axis. So, my head is in the plane formed by the positive x axis and the z axis. So, if that is the where I was standing then you know that the value phi is equal to 0. But you can also say that the same in the plane the value of phi can be thought of as three sixty which is 2 phi radians. So, phi equal to 0 and phi equal to 2 pi are completely equivalent right any for any point you can say that phi equal to 0 or equivalently phi is equal to 2 pi. So, therefore let me say I am going to evaluate the value of this function in that plane anywhere in that plane what will I do?

So, while I may say the value of small phi is 0. So, what will happen I will get the answer to be A e to the power of 0 which is obviously is 1. But one of you may say no no I do not want that value of the angle phi. But what I will do is I will put 2 phi right; see if you put 2 phi what will happen? The answer that you will get will be A e to the power of i m 2 pi. And if the function is to be single valued these 2 answers have to be the same you cannot have a different answer. And then what is the condition? The condition would be that e to the power of i m 2 pi must be equal to 1.

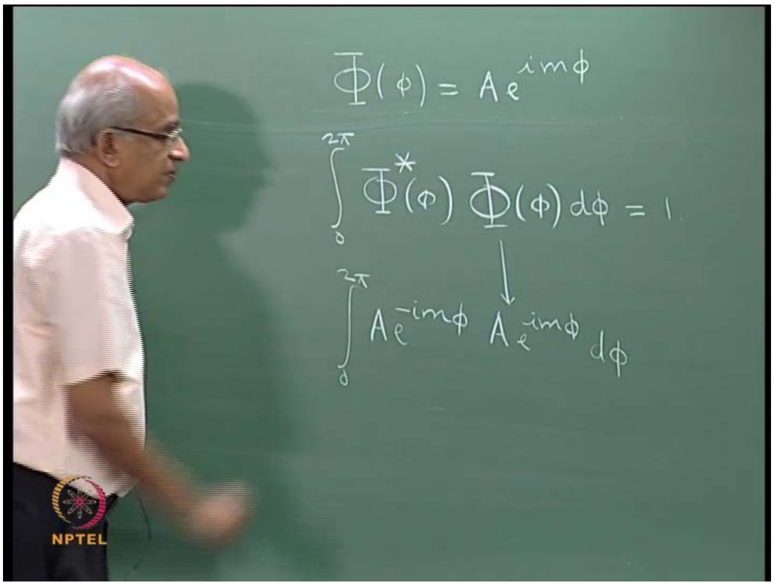
So, therefore you realize that this m is not arbitrary; m cannot have any value I mean we introduced it as a constant we did not know what its value was; but now we realized that this m has to be such that e to the power of i m 2 pi must be 1. So, what are the different possible values of m which will satisfy this condition? The first possibility is to have m is equal to 0.

(Refer Slide Time: 32:22)



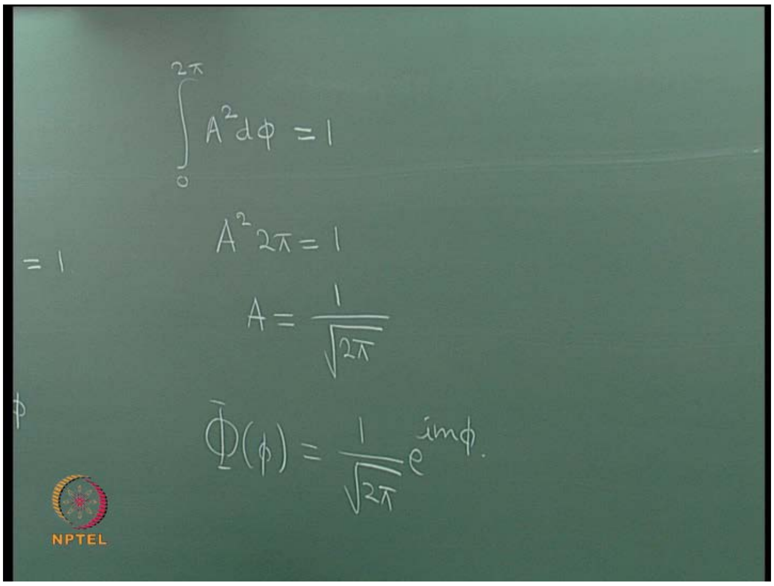
The next possibility is m is equal to plus 1 because if you put m equal to plus 1 you will have e to the power of i 2 pi. But there is a theorem of de moiver which tells me that e to the power of i theta is equal to cos theta plus i sine theta; there is a theorem due to de moiver where he says that. So, therefore if you had e to the power of i 2 pi then it will be cos 2 pi plus i sine 2 pi and sine 2 pi is 0, cos 2 pi is 1. So, even when m is equal to plus 1 you find that the condition is satisfied, but we can easily verify that m may be minus 1 not only plus or minus 1. But m can also have the values plus or minus 2 plus or minus 3 extra. So, therefore in order to satisfy this condition the value of m should be 0; I mean could be 0 plus or minus 1 plus or minus 2 extra; any positive or negative integer are 0.

(Refer Slide Time: 34:19)



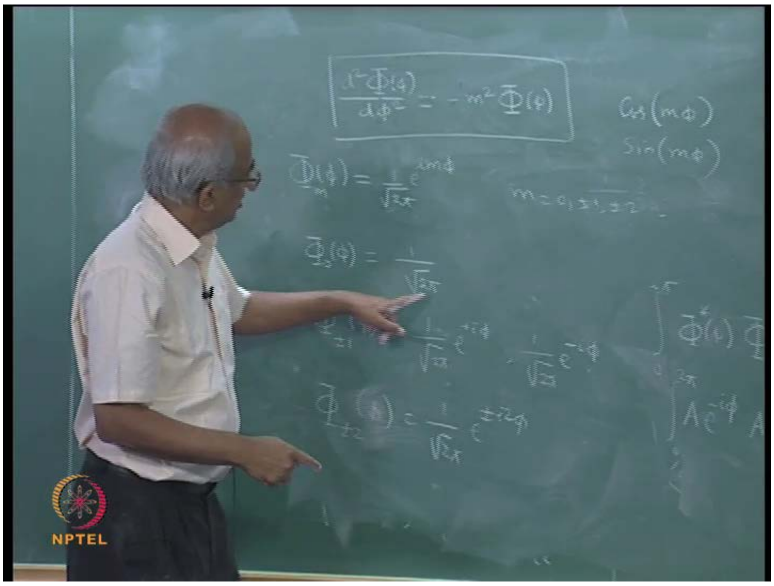
And, then the next question will be what should be the value of A? Well, this is your wave function you know that I have to use A in such a fashion that the wave function multiplied by its own complex conjugate integral from 0 to 2 pi must be equal to 1; this is what I have to do. So, if you use this condition for this particular function what is going to happen is this will be A e to the power of i m phi complex conjugate of phi will be A e to the power of minus i m phi. And you have to multiply by d phi and integrate from 0 to 2 pi. And it is obvious that in this expression this e to the power of plus i m phi will be exactly cancelled by e to the power of minus i m phi. So, these two will cancel each other.

(Refer Slide Time: 35:20)



And, you will be left with integral 0 to 2 pi A square d phi is equal to 1P; remembering that A square is just a constant I feel I never referred to as normalization constant. This integral can be easily done you will find that A square into 2 pi is equal to 1 which implies that a suitable value for the normalization constant is A equal to 1 by square root of 2 pi. As a result of which the normalized wave function this capital phi will become capital phi of phi is equal to 1 by square root of 2 pi E to the power of i m phi . So, therefore we have found the complete I mean the all the possible solutions of this equation. The solutions are of the form phi is equal to equal to 1 by square root of 2 pi correct because I find that A square into 2 pi is equal to 1.

(Refer Slide Time: 36:30)



That means, A is equal to 1 by square root of 2 pi. So, 1 by square root of 2 pi into e to the power of phi m phi is the solution. Now, this m can have the value as 0 plus or minus 1 plus or minus 2 extra. Specifically, if you put m equal to 0 what is the answer that you get? You get just a constant. Well, you see that this solution this function actually depends upon a number m right which we will refer to as a quantum number; specifically it is referred to as a magnetic quantum number. And to in to denote its dependence we will put a subscript pi m.

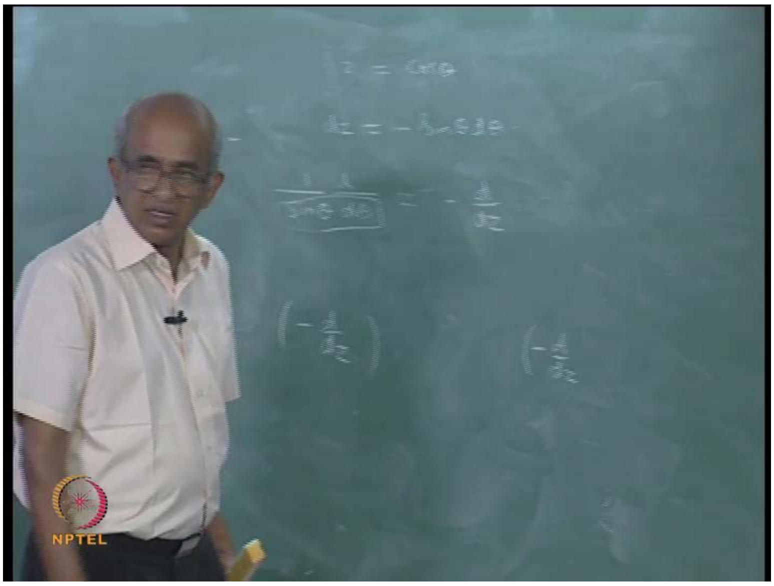
So, if I am looking at phi 0 of small phi it is going to be 1 by square root of 2 pi. What will happen to this part? If m is 0 it is just a constant. And then you can think of phi either plus 1 or minus 1; what will you find? You will find that the answer is 1 by square root of 2 pi e to the power of either plus i phi or 1 by square root of 2 pi e to the power of minus i phi. And similarly you can go ahead you can say that phi is equal to plus or minus 2of phi 1 by square root 2 pi e to the power of may be plus or minus; I will write both together i 2 phi and so on right. Now, you will realize that m is equal to plus or minus 1 or m is equal to plus or minus 2; the solutions that we have written actually are complex right. But if one is choosy one wants a real solution not a complex solution; that is that can be done that can be arrived. Because after all the original differential equation is says this d square phi by d phi square is minus m square capital phi is what the equation tells you.

And, we have written as complex solution by saying e to the power of i m phi. But instead I could have said that the solution may be of the form cos m phi right; you can see that that this actually satisfies that equation right; you just carry out 2 differentiations you will find that this actually satisfies that equations. So, it is possible to say instead of saying e to the power of i m phi; you could have said that a possible solution is cos m phi. And another possible solution is sine m phi correct; this is another possibility the nice thing about this possibility is that there is no square root of minus 1 occurring in this solution. So, if you want you can adapt such a solution and then of course it will have its own normalization factor.

The normalization factor is not found to be the same as this one; you can actually carry out that process of normalization. And you will find that the normalization factor is square root of 1 by square root of pi in both the cases not 1 by square root of 2 pi. So, therefore if you want I mean as far as this function is concerned it does not really matter right; I mean I do not have to worry. But as far as these this is these are concerned you see I can actually see you I will have a solution; which I will write as phi is equal to let me just write to the left 1 by square root of pi cos simplify is the solution right here value of m is 1. So, I will have one as a subscript but specifically the value of m is 1 and I have chosen a cosine function.

So, I will put a subscript c and say that this is one possible solution; while what is the other possible solution I will have phi 1 s. Why do I put s there? Because I am choosing the sine. So, phi 1 s phi and that will be equal to 1 by square root of pi into sine phi. So, instead of choosing this 2 solutions equally well I can chose these 2 also as my solutions; the thing is you see many a times we want to be working with real functions; particularly these are going to lead to you to atomic orbitals. And atomic orbitals normally chemists are happier if the functions are real usually or instead of this what will you do? Instead of these 2 functions you can do exactly the same thing what is going to happen is that you will have a function which will be a cosine of 2 pi. And another function which will contain sine of 2 pi; you can do it for all the other solutions also. And in fact we will be using these solutions when we discuss the atomic orbitals; that is the reason why I am telling you this. But there is of course nothing wrong if you want to say if you want to use this functions; they are also completely fine. So, now we have to look at the next equation which is actually more complex; this is the equation that we have to worry about. So, we will look at that equation and remember that theta is the variable that will range from 0 to pi; I have already told you that. And there is actually sine theta occurring here in this expression. So, what we what we will find convenient is to introduce a new variable.

(Refer Slide Time: 43:23)



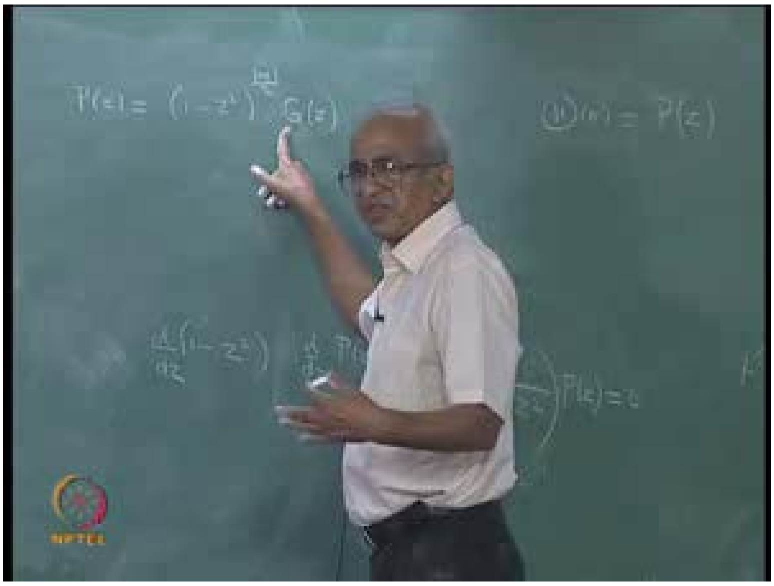
So, we are going to rewrite this equation in terms of a new variable; which I will denote as z. Now, this can be confusing because this is not your z coordinate. In fact, it would have been better for me to denote this by some other symbol I mean I can do that. But the reason why I thought I will use this z is you see most of the notations that I am using are from book, the famous classic book buy Pauling and Wilson introduction to quantum mechanics with the application in chemistry. So, that I mean for using notations from that book is that if you if anybody if anyone of you wants to look at the derivation; you should be able to use that book. And so it is better that I use the same notations as the book, but there is a minor difference that I have done the minor difference is that you see that book is the old book. And therefore everything is in CGS units while here because we have decided to through away that system of units and use psi. So, I have modified things. So, that it is everything is in SI.

So, we I mean I actually I prefer to use instead of z; I would have been happier to use mu. But I hope there is no confusion and I can use z but if you wish I can of course use mu. And close it I have no difficulties, but it is better that I use z. So, let us let us just say z, but remember this is not the z coordinate. So, if you have the z coordinator sorry z equal to cos theta then naturally you will say how much what is d z? See, I am this equation I am going to express in terms of the new variable z; that is the aim. So, if z I define to be cos theta then d z will be minus sine theta d theta. And therefore if you had something like d by d theta sine theta; suppose we have something like d by sorry 1 by sine theta d by d theta what is it actually; that is nothing, but minus of d by d z correct, see d z is minus sine theta d theta.

So, therefore 1 by sine theta d by d theta this whole thing is minus d z correct. So, that is why it is minus d by d z. And now you will see the reason why this is convenient because you have 1 by sine theta d theta here right. And then you may say well there is a sine square sine theta here what I am going to do is I will put sine square here and introduce another sine theta here. So, that there also I have sine theta d theta right. So, let us see what happens to this equation this equation? This equation the way it is written it is going to be become minus d by d z right I am just writing this operator; then there is another sine theta d theta. So, therefore so I will have another minus d by d z right and that is going to operate upon theta. But theta I am going to change the variable now I have a new variable. And therefore I will say this function capital theta of theta is actually equal to some new function P of z .right.

Because I mean the function will change when you change the variable. So, therefore I will say P is going to be here, P is actually defined to be d capital theta of theta. So, I have written this part, I have written sine theta d theta; I should take care of sin square theta. But I know that sine square theta is 1 minus 1 minus cos square theta. So, therefore I can account for the by putting 1 minus z square here, right. So, therefore I have taken complete care of this part of the equation; then what about the other part? The other part is going to be plus beta minus m square divided by sine square theta that is very easy that is nothing but 1 minus cos square theta. So, this is actually equal to 1 minus z square; and then I have capital theta here capital theta is my P, so there for this is what happens to that equation right. So, you can see that it is little bit simpler not too much difficult, but of course this negative sign and that negative sign are going to cancel. So, you can say this is what has happened to that equation. Now, you see this it can be rewritten in a slightly similar form by making a substitution this is going to take little bit of time.

(Refer Slide Time: 49:49)



So, I will do it in a next lecture. But now I want to do is I want to say that this P z I am going to write it as 1 minus the magnitude of m by 2 sorry 1 minus z square to the power of m by 2 integer function of G; z it is a unknown function actually. And then I will ask what is the differential equation that G (z); the reason is not actually very obvious. But what happens is that if you made this substitution; then the equation that you get for G can be solved by the method; that we discussed yesterday by the series expansion procedure where you will say that g may be written as power series in z remember.

Yesterday we discussed the harmonic oscillator where we had a function H and this H was written as a power series in the variable x; in exactly the same fashion you make this substitution you will get an equation for G. And that equation can be solved by assuming a power series expansion. And once you have a power series expansion what is the result that you would have expect? You could get a recursion relation and you will want to terminate the finite power of z; and you will have to impose a condition which i. So, we will see that in a afternoon. Thank you for listening.