Advanced Mathematical Methods for Chemistry

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Module - 10
Lecture - 02
Separation of Variables

In this lecture I want to talk about one technique of solving partial differential equations. And it is a very general method that you have been using in various; I am sure you have been using in quantum mechanics. But this is a very general technique to solve partial differential equations. So, let us use this and I will take the example of the wave equation. So, let me take the wave equation.

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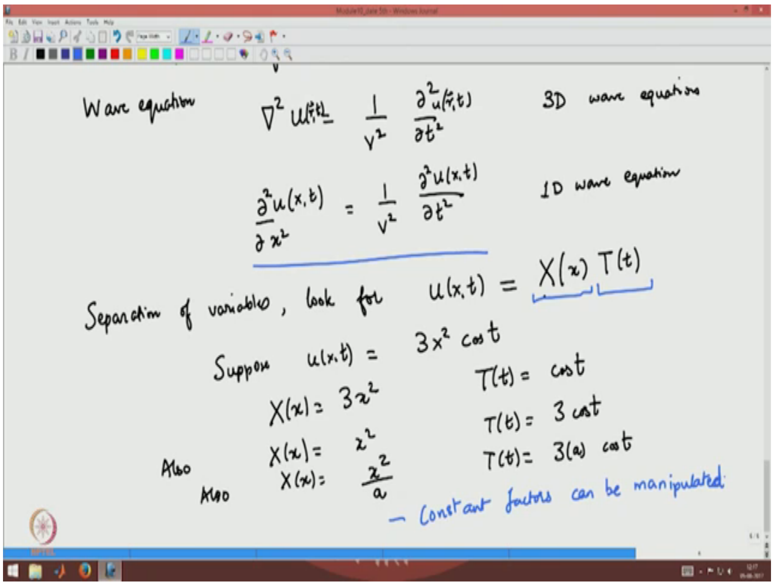

So, the wave equation we wrote as the Laplacian of u this is equal to 1 over v square dou square u by dou t square. So, this is a this is a 3 dimensional wave equation.

The 1D wave equation: so this will be this will be used suppose you have waves in a medium then this describes a propagation of waves in a medium it could be sound waves through a medium and so on. The 1D wave equation is where your spatial dimension is only one. So, what have what you have is you have dou square u by dou x square and u is only a function of x and t in this case. So, here u is a function of r and t in a 1D wave equation use only a function of x and t it is still a partial differential equation ok.

So, it is still a partial differential equation and you can write it in this form 1D wave equation. Let us consider the 1D wave equation and let us try to solve it by method of separation of variables. So, according to the method of separation of variables we look for look for a solution u of xt that is equal to some function that is only a function of x times some function that is only a function of t. So, this is a function only of x this is a function only of t. So, X of x is a is a function only of x T of t is a function only of t ok.

So, what we did is we separated it into we wrote this total function u of xt as a product of 2 functions: one which is a function only of x and the other which is a function only of t. Now the first thing you might think is that can you always do this and you know you know suppose, suppose u of xt is equal to 3 x square cos t. Then we identify we can choose then what we will say is that you will say X of x is equal to 3 x square, and T of t is equal to cos cosine of t. You can you could also say, you could also say X of x is equal to x square T of t is equal to 3 cos t.

So, I mean you can you can do various other combinations. You can you can say for example, you could also say X of x is equal to x square divided by some number a. And T of t is equal to 3 times are that number cos t. So, the message is that these constant factors are not constant factors can be you can always absorb it into one of the terms. So, the message is that constants factors can be manipulated. So, you So, you can put it wherever you want and for most part we will see that we do not really bother with the constants. But now you take another example. So, let me show that another example.

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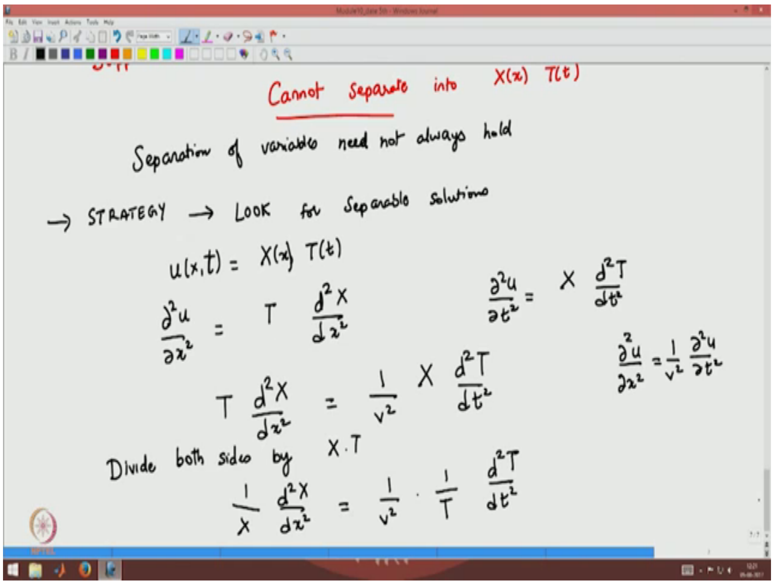

Suppose u of xt had the form let us say 3 x square cos x t ok.

So, if you had something like this, then you cannot separate into X of x times T of t. So, what I want to say is that separation of variables need not always hold. So, there might be solutions that do not have. So, the strategy is we so how do you know how do you know whether an equation you can separate the variable So, you cannot. So, what we do is our strategy is to look for separable solutions. So, there might be other solutions which are not separable, we will look only for separable solutions, ok.

So, with this strategy now let us go to the let us go to the wave equation. So, if you have u of x t xt is equal to X of x T of t then first thing you will see is that dou square u by dou x square is equal to t though, now I will have a second derivative with respect to x that is d square x by dx square x is notice that x depends only on x. So, it is a it is an ordinary derivative. And t depends only on t so; I will just take it out. And similarly dou square u by dou t square is equal to x d square t by dt square. And when you substitute these in the wave equation what you get is what you get is t times d square x by dx square is equal to 1 over v square into x d square t by dt square.

So, our wave equation once you make that substitution it has this form. So, what can you do you had a differential equation that I will just I will just write the original differential equation your original differential equation was dou square u by our dou x square is equal to dou square u by dou t square into 1 by v square. So, this was the original differential equation, and now and now we have this differential equation. So, where do we go from here, what next? Ok.

Now, what we do is after this you would divide both sides by x times t. So, when you do that then what you will get is when I divide this by tx that t will cancel. So, I will be left with 1 by x d square x by dx square is equal to 1 by v square times 1 by T d square t by dt square. V is a constant that is the speed of the wave. So now, now this is the most important part of this method of separation of variables. So, what we do is notice that the right hand side, I will just copy it again and this or we just write it here. So, the right hand side is a function only of time, ok.

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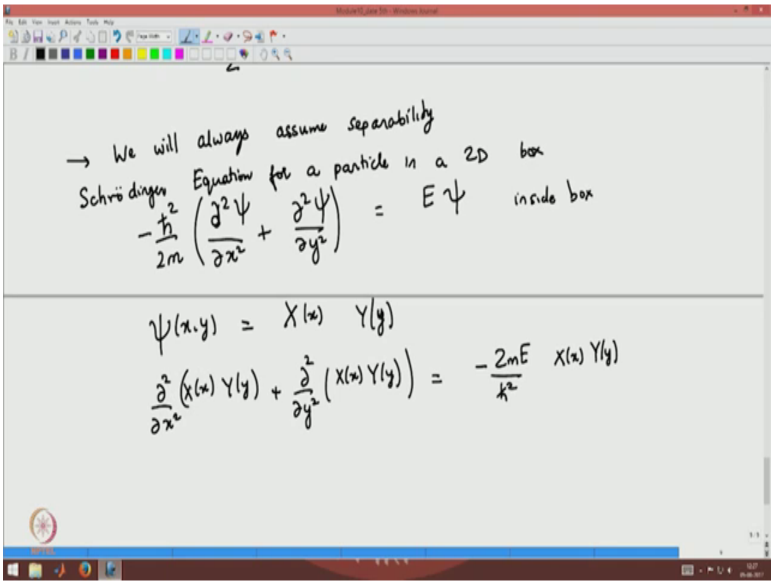

Because t is a function of time, D square by dt square of a function of time is also a function of time, and t is also a function of time v is a constant. Left hand side is a function is a function only of x. So, if you have left hand side being a function only of x and right hand side being a function only of t. And they are equal to each other. Since they are equal that necessarily this can only happen this can only be a function of x this can only be a function of time. So, the only way they can be equal leaves if both LHS and RHS are independent of x and t. Or in other words both LHS and RHS are a constant. So, what we are going to do is we are going to demand that the left hand side is a constant.

So, if the left hand side is a constant you get 1 over x d square x by dx square equal to I will just call it c. And the right hand side you will get 1 over v square t d square t by dt square is equal to c. So, thus both the left hand side and right hand side are constant. And now what happened is you get 2 ordinary differential equations after separating variables. This is an ordinary differential equation that only involves x, this is an ordinary differential equation that only involves t. So, you have these 2 ordinary differential equations and basically you have converted your problem of solving the PDE to us all to a problem of solving 2 odes ok.

Now this is a general strategy this strategy of separation of variables is something that you use for various differential equations. And in fact, in fact this is the in all the problems we will always assume. So, at least in this course we will always assume separability. For example: if you take if you take the Schrödinger equation for a particle in 2 d box. So, this is given by minus 2 d box between then I will I will just write the equation then I will then we will discuss it ok.

So, you have d dou square psi by dou x square plus dou square psi by dou y square equal to e psi inside box. So, when you have this then what is done is you write you take this and you write you write psi of xy psi a function of xy in that, I write it as X of x times Y of y when you do this then what we will get is this equation will nicely factor out. So, if you go if you what will give when I take the second derivative then I just have d square by d x square. So, let me let me write this in a slightly different way.

So, I will write d square by dx square of X of x Y of y plus dou square by dou y square of X of x Y of y is equal to minus 2 m e by h cross square, and what I will get a psi is X of x Y of y. And what you notice is that since this is separable I can write this as I can write this as y times d square psi by d square x by dx square.

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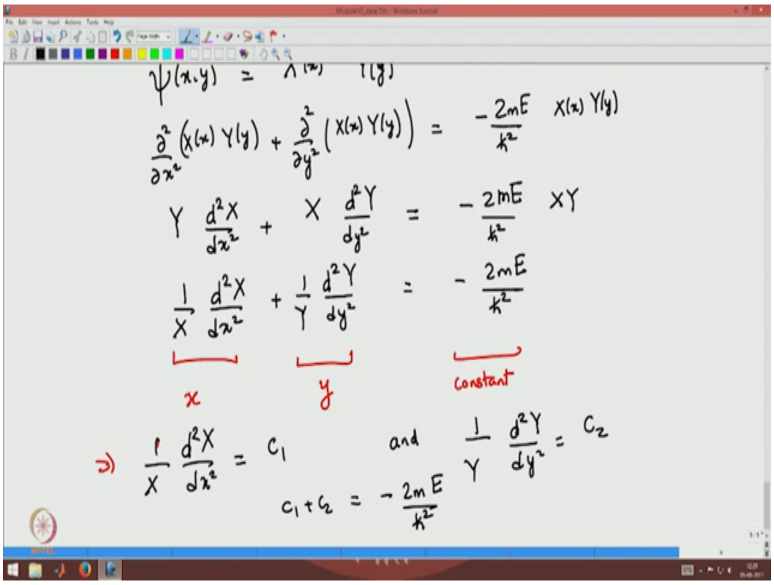

So, y times d square x by dx square, plus x times d square y by dy square is equal to minus 2 m e by h cross square x times y. And now and now if you divide by x y if you divide by x y then what you will get is that d square x by dx square into 1 by x plus d square y by dy square into 1 by y is equal to minus 2 m e by h cross square.

Now what you notice is that in this case this is a function only of x, this is a function only of y and this is a constant. So, that implies that implies that that 1 over x d square x by dx square is equal to c 1 and 1 over y d square y by dy square is equal to c 2, and c 1 plus c 2 is equal to minus 2 m e by h, h cross square. And what is done typically at this point is that is that you use a notation choose c 1 is equal to 2 m E x divided by h cross square.

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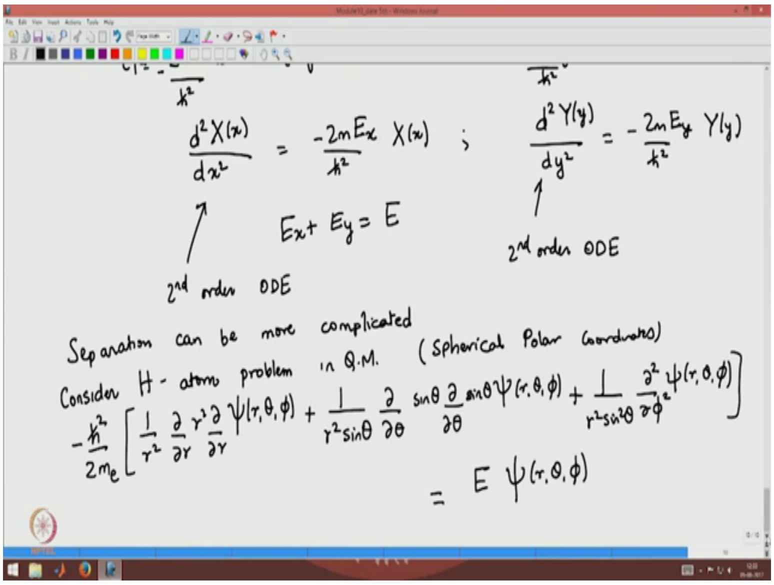

So, this is defined define E x le c 2 is equal to 2 m E y by h cross square. So, you write it you write it with a minus sign.

So, you write it in this form. And the reason for doing this is that what you will get is you will get you will get 2 equations you will get 2 equations. So, the first equation will be d square X of x divided by dx square now let me d square is equal to minus 2 m E x by h cross square psi or not psi X of x. And you have a very similar equation d square psi Y of y divided by dy square is equal to minus 2 m E y by h cross square Y of y, and you have E x plus E y equal to E.

So, E x and E y have a physical interpretation as the energy in the x direction and the energy in the y direction, or the energy in the in the x part of the motion and energy due to the y part of the motion. So, what we did was we converted our the PDE into 2 odes in each of these can be solved individually, this is a second order ODE. Similarly this is also a second order ODE. So, this is the general strategy that that we are going to use now in these cases the separation was very easy, because your Laplacian just had a second derivative with respect to S and x and second derivative with respect to y ok.

Now you can imagine that separation can be more complicated. So, for example, let us consider the hydrogen atom problem in Q.M. So, here we use spherical polar coordinates. So now, now the Schrödinger equation looks like minus h cross square by 2 m e, e is a mass of the, m e is a mass of the electron. And now what you have is

Laplacian and the Laplacian in spherical polar coordinates has this form 1 over r square dou by dou r of R r square dou by dou r of now psi is a function of r theta phi plus 1 by r square sin theta dou by dou theta of sin theta dou by dou theta of sin theta psi of r theta phi plus 1 over r square sin square theta. And what you have is dou square by dou phi square of psi of r theta phi; this is equal to e times psi of r theta phi.

Now in this case when you separate variables you write psi of r theta phi is equal to a part that depends only on r.

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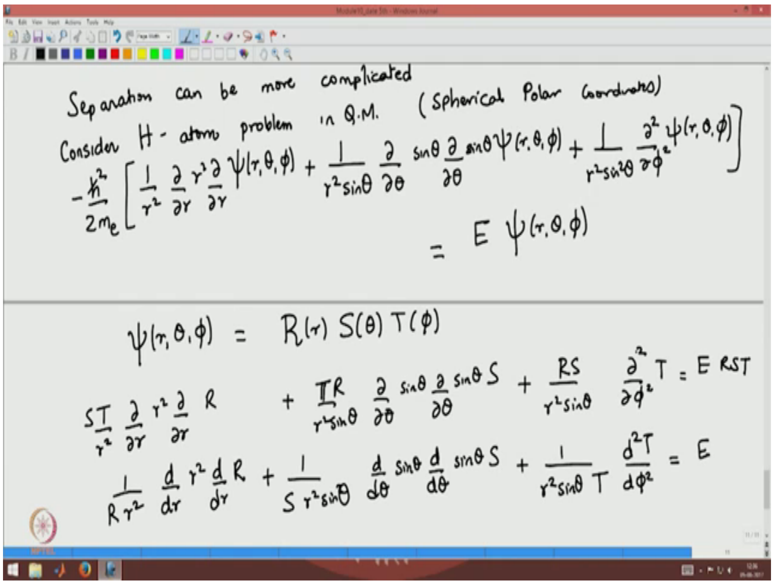

And a part that depends on theta and phi the part that depends on theta and phi, I will write as S of theta T of phi. And I will actually separation of variables in this case is slightly more tricky. So, when you go ahead and you and you substitute. So, what you will get is I will tell you again I will take the h cross square into a m e on the right hand side. So, what I will write is 1 over r square dou by dou r of r square dou by dou r of RST plus 1 by r square sin theta dou by dou theta sin theta dou by dou theta of RST. Now let me let me simplify this. So, the S and t part in this case, I can take it here outside ST. Now this depends this derivative depends only on theta. So, I can write this as sin theta s, and I can take t and r here plus.

Now, I have 1 over r square sin theta, and what I have is RS dou square by dou phi square of T, and all these all these partial derivatives will become ordinary derivatives. This is equal to E times RST. Now if I divide by RST, if I if I divide by R times S times

T, then in the first term the S t will cancel. So, what I will have is 1 over R r square dou by dou. now let me write it explicitly as d by dr of r square d by dr of R plus 1 over S r square sin square sin theta and if we write d by d theta of sin theta d by d theta of sin theta times S plus 1 over r square sin theta times a t d square T by d phi square is equal to E ok.

Now what you notice is that I will just do one part of this separation, is that here this is only term which has phi dependence.

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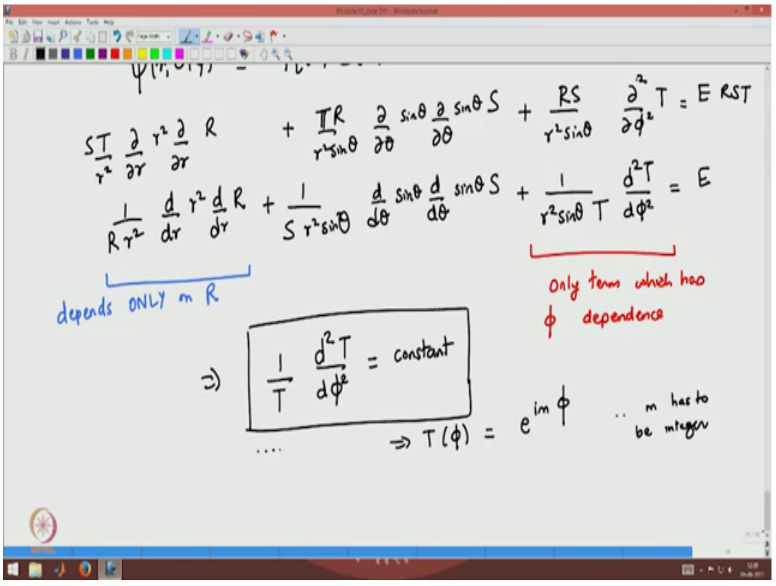

So, this is the only term that has phi dependence. And so, immediately you can say that this phi dependence has to be a constant. So, you have some of 3 terms and you have on the right hand side you have something that is independent of phi. So obviously, this phi dependent term has to be a constant. So, this implies that 1 over t d square t by d phi square equal to constant. So, this is this is one of the things that will do and so and so this implies that T of phi is equal to we will just write it as e to the I m phi ok

So, this constant you can show that it should be equal to minus m square and eventually after some work. So, after some work you will get T of phi should be e to the I m phi and with some, I won t write the as I said as I said earlier that you can always put a constant factor in front of this, but we would not bother with that. And for various other reasons for various other reasons m has to be integer.

So, in this way you can separate and you can solve for t and then once you solve for t then you eliminate t from this equation you still have r and s, but you notice that this term depends only on r on r. And so, and so, the theta dependent terms are only there in the second and third. So, what you can do is you can set this part the theta part to a constant, and then and then you can you can go ahead and solve that equation ok.

So, the So, what is done is that So, the second and third terms have the theta dependent terms, now what you will get is what is done after this is that is that you write 1 over t d square t by d phi square is equal to minus m square.

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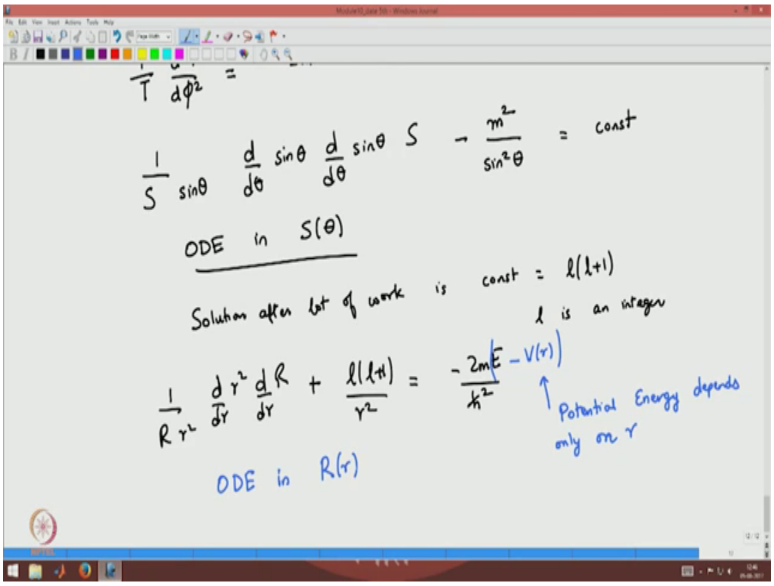

You can work this out. So, if you take T of phi equal to e to the I m phi then d square t by d phi square is just minus m square t and then if you divide by T you will just get minus m square. So, then what you are what your equation becomes, is that you can replace this whole thing by just minus m square. And since this term depends only on r then the remaining term has to be the theta dependent term here has to be a constant.

So, then what I can write is that 1 over S sin theta now square sin square theta should be a square there should be a square in front of the in front of the t term. So, the there should be a sin square theta there. So, what happens here is that you have 1 over S sin theta, I am not I am not I am not bothering with the r part, times d by d theta of sin theta d by d theta of sin theta S plus or no now it will become minus m square divided by sin square theta equal to constant ok.

And now this is an ODE in S of theta. So, this is a ode S of S of theta and you can solve this. So, you can solve this and this gives you in terms of associated legendre polynomials. And then and then once you have once you have the ode in S then you use that solution and then and then you are left with, after you put the ode for S. What you will get is; you will get a differential equation in r. Now incidentally I can just I can just tell what the solution looks like. So, this solution after lot of work is that is constant equal to l, l plus 1 h cross square. So, l, l is just l, l plus 1 sorry it is just l, l plus 1, where l is an integer.

So, finally the So, this is something that that you will see in your quantum mechanics course, but what will what you will eventually find after all this is that l has to be an integer and this should be a constant. And so, and so now, the final differential equation in r has a form 1 over R r square d by dr of r square d by dr of R plus l, l plus 1 is equal to minus 2 m e by h cross square. So, let us just go back see where we started. So, we had this equation we took the minus 2 m. So, we are left with this part and then oh they should be in r square l, l plus 1 divided by r square I should I should mention one other term there is one other term that I had I had missed out in the Schrödinger equation ok.

So, there is the potential energy term. So, the potential energy term is a function only of r. So, it is 1 over 4 pi epsilon e square by r this is a function only of r. So, this is this would not contribute to the remaining terms. So, let me just call this v of r and So, I just have to carry that v of r here v of r here it would not affect this equation it would not affect this equation, but you should have another term; so e minus v of r. So, that is that is what the equation will look like. So, the potential energy term only on r only on only on the radial coordinate should be your minus sign. So, this is a attraction between the electron and the nucleus alright.

Finally, what happens is that this is a radial part of the Schrödinger equation. This is this is a ODE in R of r. So, this is how the separation of variables takes place and you can see that when you are dealing with Cartesian coordinates usually things look simple. But there are certain problems that are not that where Cartesian coordinates are just not convenient and this hydrogen atom was one problem. Because you had a center the nucleus was at the center, and your electron was radially located outward from the nucleus it was it was radially. So, it made sense to use spherical polar coordinates, which were centered at the nucleus.

So, you could have other problems the most common example is like you could have something like a circular drum. So, if you are looking at the wave equation of a drum, in that case we will be using you will be using cylindrical color you will be using cylindrical coordinates or you will be using plain polar coordinates.

And in that case to the separation of variables will become a little more involved. But what I want to emphasize is that once you have done the separation of variables then you get back ordinary differential equations and these ordinary differential equations can be solved using the methods that we have already seen. But it is not it is not always straightforward to get this separation of variables.

So, in the next class we look at we look at the nature of solutions. I will take the particular example of a circular drum, because this is very it illustrates; I mean we will see the whole machinery of not only of separation of variables, but you would also see of actually solving the PDE.

Thank you.