Introductory Quantum Chemistry
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Lecture - 22
Hydrogen Atoms: Polar Co-ordinates

So, we were discussing the hydrogen atom if you remember the Hamiltonian for the hydrogen atom is this one; this is the nuclear kinetic energy, electronic kinetic energy and the interaction between the 2. And this the way this Hamiltonian is written it is not possible to apply the method of separation of variables as it is and solve the Schrodinger equation. So, therefore we changed over to the centre of mass coordinates and the relative coordinates with the transformation we discussed yesterday. And after the transformation is done what happens is that you have this kinetic energy which describes the motion of the 2 particles together as a whole; that is centre of mass motion they just execute translational motion.

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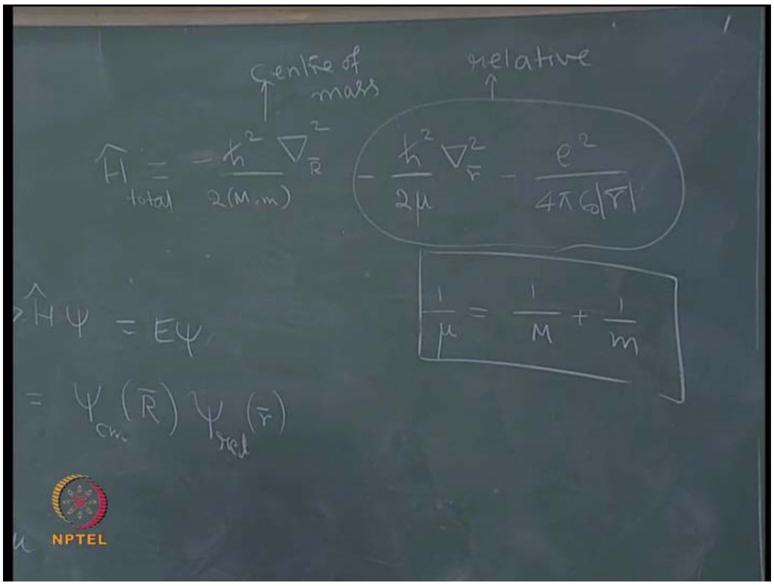

And, this part of Hamiltonian represents relative motion this represents centre of mass motion. And to the total Hamiltonian so to say right for the entire system is the sum of these 2. So, I could say that H total if you like I can add a subscript here if I want. Because now this has translational motion as well as relative motion inside it explicitly. And then what will happen this is a translational motion is simple it is just the motion of free particle. And if you wanted solve this equation I mean the Hamiltonian has to operate on psi and give you E psi.

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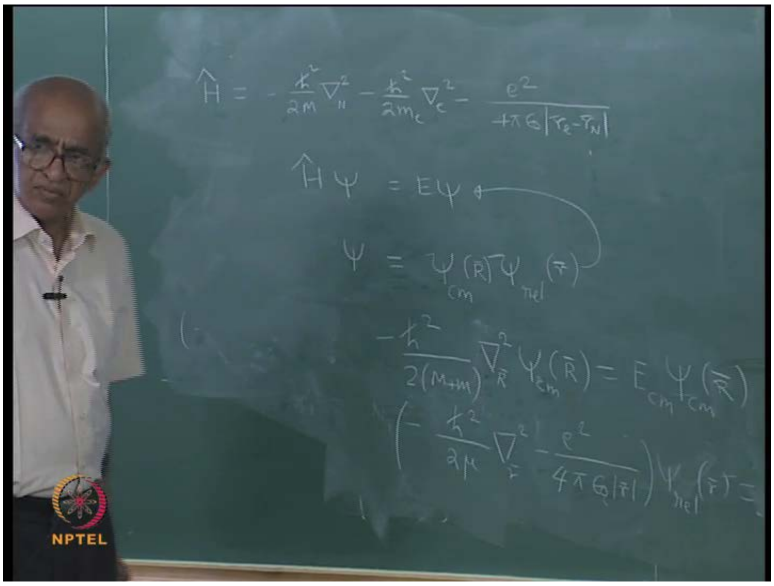

But if you want to solve the equation what you have to do is we will say that psi may be written as a product of 2 functions; I will denote both of them by psi. But one is for centre of mass motion and the other one is for relative motion. And the centre of mass motion the wave function will only depend upon centre of mass and the related motion will only depend on relative coordinates. So, this is what I expect I can take this equation over this assumption put it back into Schrodinger equation; and separate the variables very easy to separate the variables. Then, what will happen you will get an equation which will determine size centre of mass, you will also get another equation which will determine psi relative.

So, what are those equations? Well, the way they come out this is rarely easy because we have done this kind of method of separational variables once. I am not going to go through the procedure; the procedure is not difficult; what happens is you will get minus h cross square by 2 times M plus m del square operating upon psi centre of mass must be equal to a constant time psi centre of mass a constant I am not written constant. But this constant will actually represent the translational energy of the hydrogen molecule.

And, so what I will do is I will write it as E, but I will put the subscript c m; just to remind you that it is centre of mass motion. And energy this energy is the energy of the system due to its translational motion as a whole. And what will be the other equation? The other equation will be minus h cross square divided by 2 mu; well I have been sloppy here I should write an R here. Because this is differentiation with the respect to the centre of mass coordinates. Then, I will have minus h cross square by 2 mu del R square this is actually kinetic energy due to relative motion that is where this comes from. And what is that part it is actually this one right this is the one that inversely related motion; this is kinetic energy and this is potential energy.

So, therefore what will happen is that you will have minus e square divided by correct that is the potential energy; and the whole thing operated upon psi relative which will depend upon R. And that must be equal to E relative into psi relative correct and not only that see if you are looking at this psi. Here, let me be I should put a subscript this is for the total system and this psi will be total, and this E will be total and this psi will be total weight function. And what I have written here is the total weight function.

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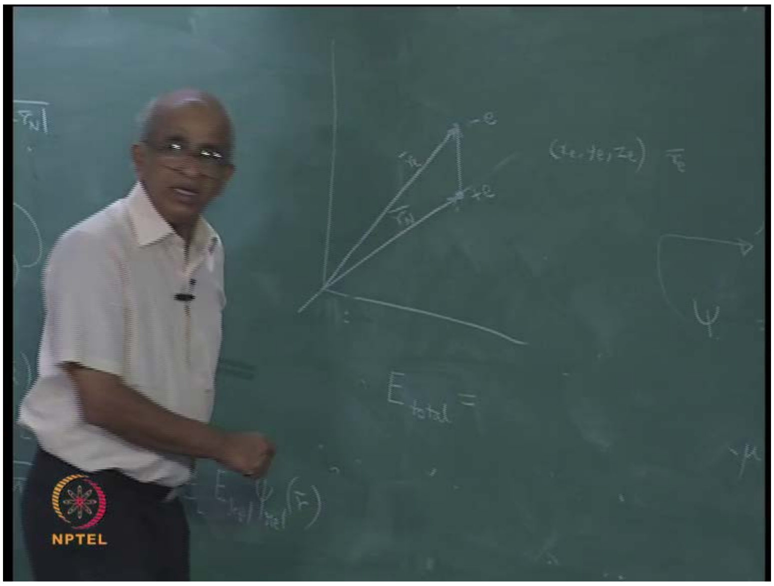

So, if you are looking at this E total what would it be? If you carried out the method of separation off variables what you will find is that E total would be found to be equal to E centre of mass plus E relative; that is what you will get you will get it from the equation which is not surprising. Because all that it says is the total at the end of the day is system is this sum of the translational energy due to the motion of the system as a whole the energy due to relative motion. Now, we are interested in the relative motion translational energy is simple I mean not difficult probably it is just a free particle moving in space; one can easily solve the equation via not terribly interested in that at the moment. So, we want to look at this equation, right. So, what we will do is we will just confine to that equation and forget about the other equations.

And, not only that I am actually going to simplify my notation; see this R I will not going to be writing anymore because it is a nuisance. But when you see the del square you have to understand this is differentiation with respect to x, y and s which are actually relative coordinates. And this relative event I am not going to write E relative also I am not going to write it fully, I am going to remove these things. But you should understand I am actually concerned with relative motion; because it is tedious to write those things again and again and again that is the only reason why we have made them. So, if you look at this what is happening is this. Let us look at it.

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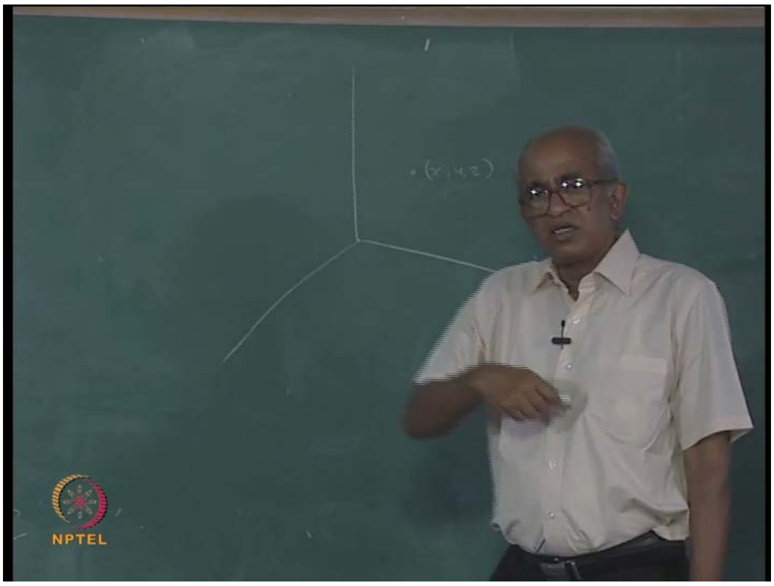

I mean the way the equation is imagine I had a particle; here is my origin. Suppose I have a coordinate system that is the origin. And I have a particle which has coordinates x, y, z correct. And imagine I want to describe the quantum mechanics of the particle single particle. What will be the kinetic energy of the particle or the operator corresponding to the kinetic energy it is going to be minus h cross square divided by 2 times the mass of the particle into del square. So, if I imagine the particle of mass mu than this will be exactly the kinetic energy of such a particle right. And further what is this term? The term actually represents the interaction with the nucleus which we can say is now here I mean it is as if it is interacting with the which is situated at the origin right. If the nucleus was at the origin then this would have been the interaction energy.

So, therefore all that you are saying is that effectively this is a equivalent to that of a single particle right moving in the presence of a nucleus; which may thought to be at the origin right. But the only thing is that we have to account for relative motion, but relative motion means both the particles are moving as it yesterday. And that is accounted for by the fact that there is this mu; it is not actually the mass of the electron, but the reduced mass, right. So, therefore this Hamiltonian is quite fine actually I mean I can imagine that the nucleus may be taken to be at the origin; which is exciting the columbic electrostatic interaction in the electron. So, with that let us try to solve this equation. How will you solve this equation? The way to solve this equation you know actually the way is use the method of separation of variables. So, what will you try? You gave me that answer because you know the answer earlier. Yeah, that is true. But suppose if I did not know that since what I would try is I would say that psi may be written; psi is a function of 3 variables x, y and z.

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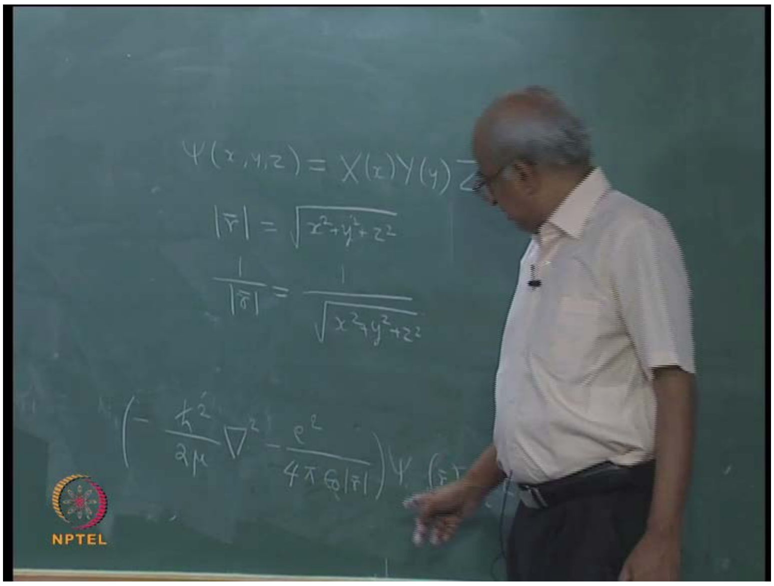

And, it may perhaps be written as X into x, Y into y, Z into z this is what you will normally try correct. But this procedure will not work; for this particular problem. Why does it not work? The answer is that if you look at this R what is the distance of the particle from the origin? R is actually the distance of the particle from the origin and it will depend on where the particle is and the relationship is actually it is equal to square root of x square plus y square plus z square.

And, the potential energy actually depends on 1 by r. So, it is actually dependent upon 1 by square root of x square plus y square plus z square; see if the method of separation of variables is to work in Cartesian coordinates. Then, he should be possible for you to write the potential energy of the system as this sum of separate terms one depending only on x, the other depending only on y; and the third only depending on z that is obviously, not possible in this potential right; that is why the method of separation of variables will not work.

But if it was possible to separate the potential into 3 separate parts; one depending on x, the other depending on y and the third depending on z. Then, it would have been possible to separate the variables in the Cartesian coordinates system, but that is not the way this potential is. But if you look at this characteristic of this potential what is the characteristic? Well, what you can say is the following say imagine I keep the distance of the particle which is of course electron from the origin fixed suppose. That means, I am thinking of all points on the surface of a sphere with surrounds the origin correct. And you can see that anywhere on surface of that sphere r will be a constant and if r is a constant the potential energy will be constant.

So, therefore this is a potential that has a spherical symmetry right that is the meaning this is a potential that has spherical symmetry. And if you have a problem with spherical symmetry; you have to make the use of a coordinate system which will explore it, that spherical symmetry of the system you should not be used Cartesian coordinates. Cartesian coordinates is appropriate if you have cubic symmetry; this is a system which has spherical symmetry. So, therefore I have to change over to a system of coordinates which would have which would use right the spherical symmetry of this system. And a system of coordinates which does that is the polar coordinates.

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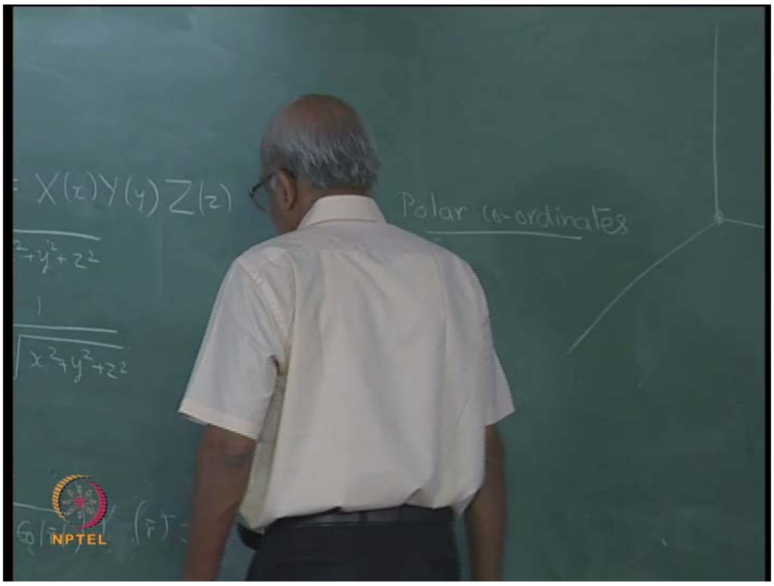

So, what are the definitions of polar coordinates but before I go into the definitions of polar coordinates let look me just look at what I have on the slides; I mean this is just the motion of the system as a whole.

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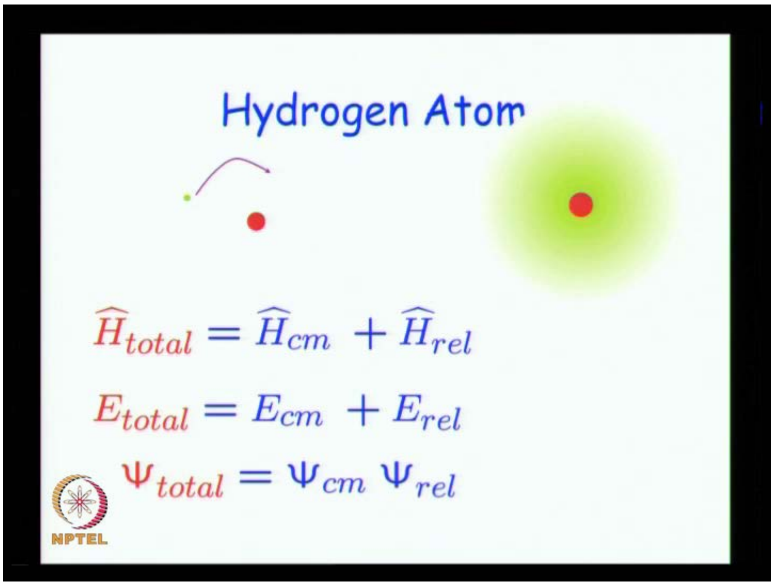

But we know that the electron is actually moving around nucleus; and the whole thing will actually move execute translational motion. And that is the reason why we said the Hamiltonian can be written like this; actually the total energy will be given by this expression the total wave function will be a product.

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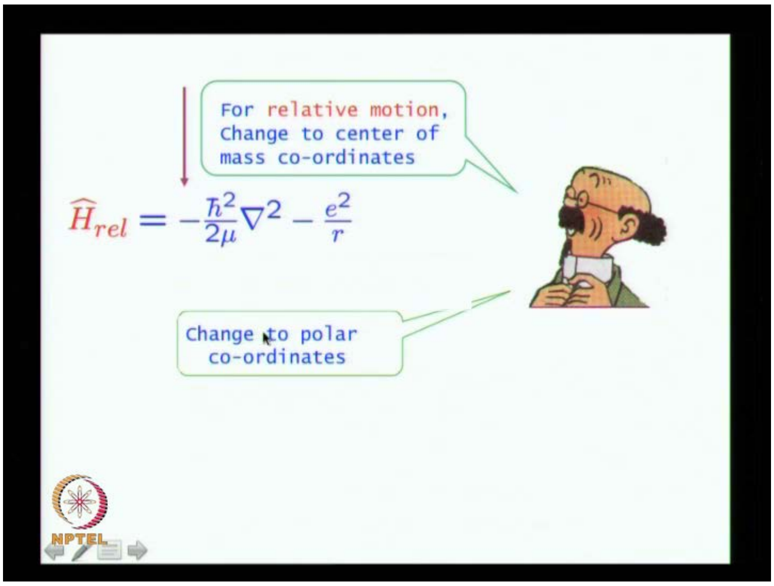

And, we are worried only about the relative motion; this is the question we are actually going to solve. And we have to change the polar coordinates.

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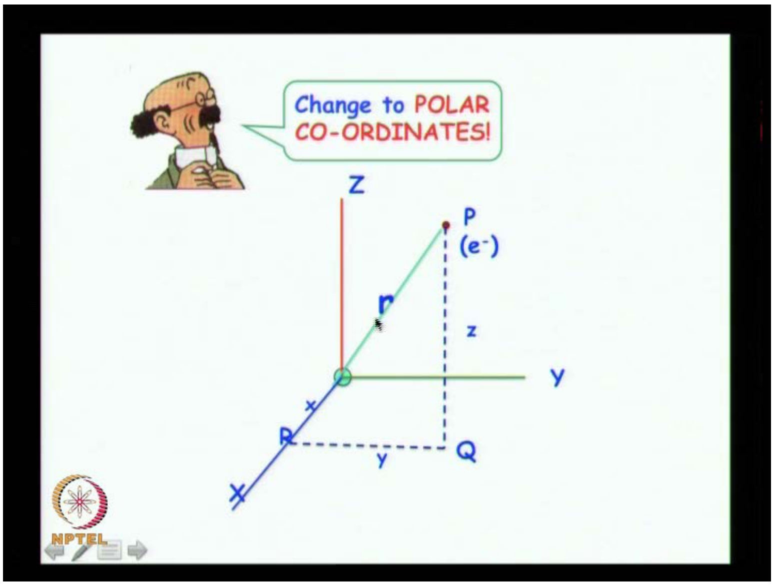

So, how do I define polar coordinates? Well, before I define polar coordinates let me just remind you what are meant by Cartesian coordinates? Imagine that we have the electron sitting there and that is the origin. And now you can imagine that the nucleus is at that origin and the electron has the coordinates x, y and z. So, it is actually quite convenient if I had a coordinate system to make use of maybe I hope you will have to imagine that there is this line joins this wall to the floor; that line I will take it to be my y axis, somewhere in the corner there is a line which is going up particularly that I will take to be my z axis. And you can imagine where there is a scale here which I mean it has to be put on the floor and that is going to be my x axis.

So, that is how things are the system of coordinates is actually shown their this is my electron. And in order to specify the position of the electron what do you do? You I mean if you like you can imagine instead of the electron you can think of the head of a person that is the point you want specify in space. How will it do that the answer is this; instead of having the picture of the person I am going to replace it with a line; there is a line. So, the height of the person I will say it as my z coordinate; actually few look at it he will see z is written there. And then from his feet you can draw up perpendicular one to the x axis; and this distance you will denote it as y coordinate and then this point R is at a distance x from the origin.

So, these are the Cartesian coordinates x, y and z; this is how the Cartesian coordinates are defined. Now, how are spherical polar coordinates are defined that you will see in a minute or in a second actually; what I do is I joined the point p to the origin right. And denote the distance of the point from the origin by the symbol R. What is R? R is nothing but the length of this vector r. So, I will denote the symbol r without the vector sign. So, what is actually our r; r is equal to square root of x square plus y square plus z square. So, in order to specify the position of the particle I can use it as one of the coordinate fine. Now, what is the minimum possible value for r? But r is the length of a vector length right. In fact, if you imagine that my head is the point just to be specified; I can imagine that my head I but of course it is difficult to manage that.

But I can imagine that it has been put there then the value of r would be 0 or I might be standing far away from the origin in which case the value of r would be extremely large. So, therefore r can actually vary from the minimum value of 0 right to a maximum value of infinity. So, if you say that r is equal to 10 feet; that means, I am standing somewhere here so that my head is a distance of 10 feet from the origin. But even if I moved a little bit actually I can move in such a fashion that the distance does not change r is still 10. So, if I tell you that the point is at a distance of 10 feet what it means is that; the point is anywhere on the surface of a sphere of radius 10 feet correct. You did not know where exactly the point is all that we can say is. If you specify the value for r all that you can now is it is on somewhere on the surface having that radius, but where exactly would it be on that sphere for that you need additional coordinates right.

So, what are the additional coordinates you will use? Well, you can imagine that the point p is joined to the origin; that is the line which has the length r. And if you want to specify orientation of this line in space; how will you specify the orientation? One coordinate you can use to specify the orientation of this line in space is this angle; the angle between the red line and the line that joins the origin to the point P. Well, if this is your point; imagine that this point origin is joined to that point.

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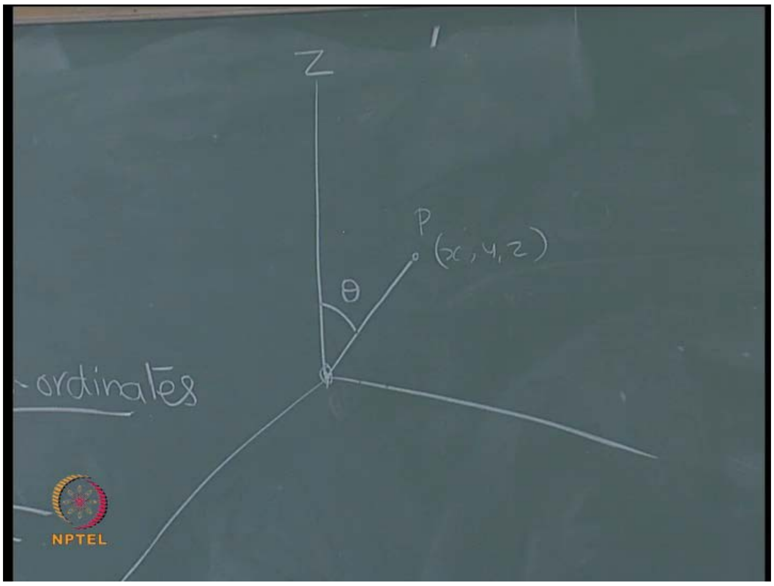

And, you can specify this angle theta which is the angle between the positive direction of the z axis. And the line that joins origin to that point p. Now, suppose theta is 0.

Suppose then you can immediately say that the point is somewhere along the z axis right. Suppose then I say theta is equal to 30 degrees I do not give you any more information. Then, where is the point what would be your answer? Well, the answer would be the following imagine that this is your z axis; and you think of cone like this one such that it is a round z axis difficult to do this right this is the z axis. And you think of cone having such a shape such that the internal angle, this internal angle is how much 30 degrees. And if you think about it for any point on the surface of this cone, you can think of a line joining that point to the origin; and you will find that the angle is actually 30 degrees. So, therefore if I say that theta has a value 30 degrees all that you can say that is that the point has to be somewhere around the surface of this cone. Now, suppose if I increase the value of theta to 45 degrees what would happen the cone would expand a little bit; you can go on to make it 60 cone would have expanded more.

And, suppose if I would go on to increase the angle to 90 degrees then what would happen? The cone would have opened up. And what would be that plane it would actually be the x y plane right. So, any point on the x y plane value of theta equal to 90 degrees. And suppose if I went on increasing theta further more let us say to 120 degrees then what would happen is that the cone points in the opposite direction; earlier the tip of the cone was pointing down. But now the tip of the cone is pointing up correct and the point could be anywhere on the surface of this cone. But when you go on increasing the value of theta eventually when the value of theta rate is 1280 degrees; what would happen the cone would degenerate into the negative z axis, correct. So, it should be obvious to you that any point in this space has a value of theta which lies between 0 and 180; that is enough I do not need anything more; any point in space would have a value of theta which lies between 0 and 180 degrees.

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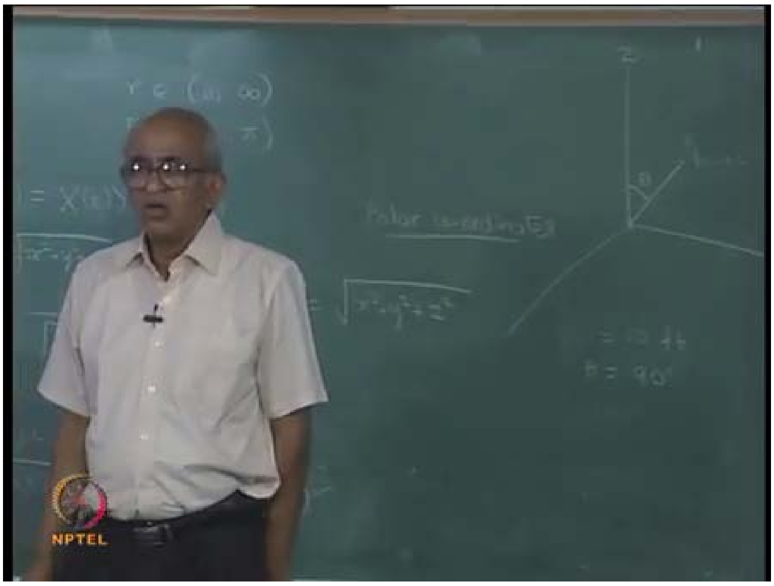

So, theta actually we can say it has to be between 0 and phi in radiance I was speaking in terms of degrees, but in radiance should be 0 and phi. So, now if I told you that that r is equal to 10 feet and theta is equal to 90 degrees suppose; what will you say? Well, the first statement implies that it is on the surface of a sphere having radius 10 feet, the second statement implies says that it is in x y plane. So, therefore these 2 combined together tell me that the point is somewhere along a circle of radius 10 feet lying in the x y plane; that still does not enable me to specify the point exactly; which means that I need one more additional coordination right.

And, that coordinate I am going to introduce now. So, what I do is I think of this line p q right p q was actually that person; p q was that person. So, I take that person I mean imagine that I myself is that person. So, I take p q and you can see that I myself am parallel to the z axis. And therefore I can think of a plane which contains myself and the z axis right. And if I can specify the orientation of this plane that is fine; then you would know where the point is; that will be my final coordinate. In order to specify the final coordinate of the point it is enough if I specify the orientation of this plane. And how do I specify the orientation of this plane I make use of a coordinate which I refer to as phi.

Pi is the angle look at this angle; it is the angle between the positive direction of the x axis correct. And this plane consisting of the line p q and o z; o is the origin and the positive direction of the z axis. So, there is a plane found by p q o and z and to specify the orientation of that plane you make use of that angle y correct. And now suppose you see I am standing somewhere here so that my head is in the, which plane would you like let me say in the x z plane. Suppose, I am standing somewhere there unfortunately in this room I cannot do that. But anyway suppose I am standing there such that my head is in the x z plane what would be the value of y? It will be 0, but suppose than if I am able to standing there and then I start moving like this. And if I moved like this obviously increasing the value of y. And now if I am in this plane of the board remember on the y axis is down there and z axis is there.

So, if I put my head in the plane of the board; obviously the value of y would be 90 degrees. Then, imagine I go around right; if I go around what will happen the value of y would go on increasing eventually when I am back where I started the value of y would have increased to 360 or 2 phi radius correct.

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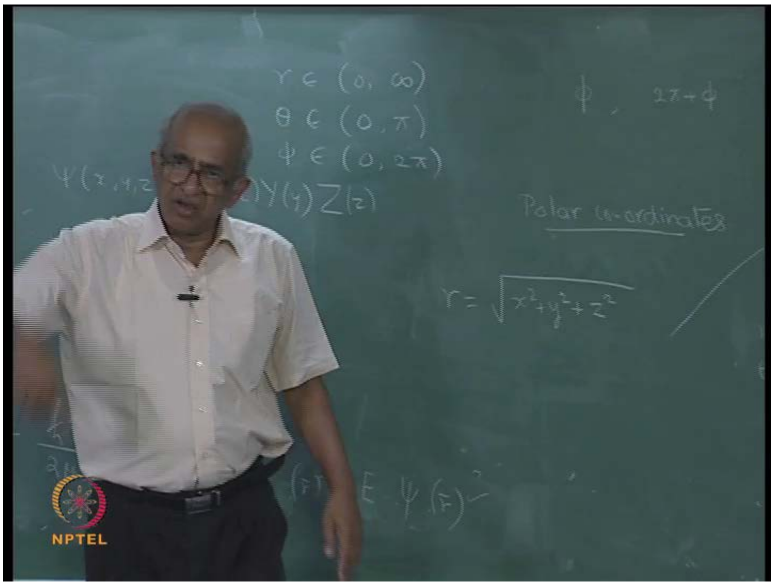

So, therefore to specify any arbitrary point space I need to allow phi to radiance between 0 and 2 phi radiance correct; we can also think about it in this fashion. Suppose am standing here so that the value of y is 45 when I am standing here. And then I go around and come back here; I go around the origin and come back here what will happen 5 would have been increased; it would have reached the value 360 and if I then would have continued I can say 361, 362 etc. And I would have reached here 405 degrees correct. So, I could have said that while y for me here is 45 degrees or equally well I could have said 405.

So, the point I am trying to convey is that a particular point coordinate which has a phi coordinate equal to something which we denote as phi; it is equally well to say that it is coordinate is 2 phi plus phi or in other words phi and 2 phi plus phi r equivalent correct they refer to the same point. Any point it is coordinate this particular coordinate is phi or you can also say that it is coordinate is 2 phi plus phi it is equally fine both refer to the same point right this is something which we will be using later. But as far as any point in space is concerned it is enough if I allowed phi to vary from 0 to 2 phi.

But if I want I can allow I can think of phi as continuously changing variable running from 0 to any number; the only condition is that any value you are phi if you add 2 phi nothing happens the point remains unchanged. So, whatever I have told you is given in this slide r belongs to 0 to infinity, theta belongs to 0 to phi; phi belongs to 0 to 2 phi.

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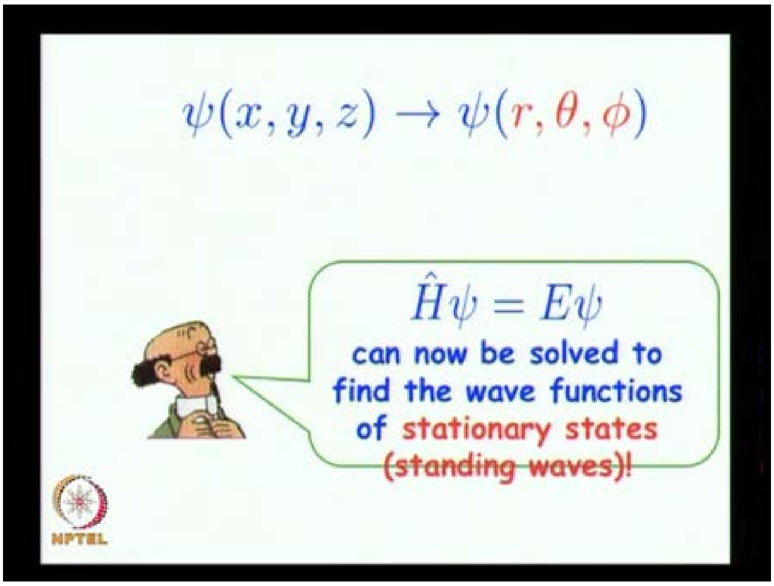

Now, what is going to happen is that my wave function which is x, y and z.

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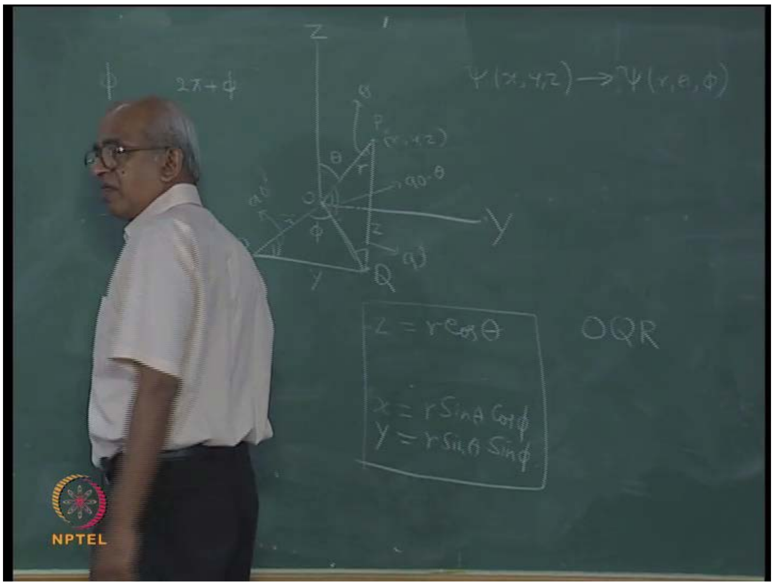

We decided that we do not want x, y and z, but instead we want to change over to r, theta, phi. So, therefore we will get rid of x y and z and express everything in terms of r, theta, phi. So, naturally I have to express x y and z in terms of r, theta, phi. So, how will I do that? Well, this is my point p and if you remember I will just mark coordinates here this is p q. And that point is R, this distance is x this distance is y and that is z; X, Y and Z. And this angle is phi right this is how the point is and we have also shown all the coordinates this is r; and the origin is as I have been telling you denoted by the symbol O. So, it is actually a matter of simple trigonometry to find a relation between x, y and z and r theta phi. So, just to illustrate this is the coordinate z and what is this angle or maybe what is this angle? Well, you have to remember that p q is myself.

So, if I am standing here imagine my feet is joined to the origin and this angle is nothing but the angle between myself and the line joined the feet to the origin. And therefore this angle will be 90degrees even though it does not appear to be 90 in the picture. Because you see three-dimensional things trying to represent on a blackboard which is two-dimensional. So, therefore what I am saying is that this is actually is a right angle triangle in 3 dimensions right; r the hypotenuse triangle and z this height is one of the sides. And how much would this angle be when we entered this total angle obviously will be 90 degrees and this much is only theta. Therefore, the angle that is remaining is 90 minus theta right and if this angle is 90 minus theta this is 90 degrees. And then naturally this angle has to be equal to theta correct. And therefore it can immediately say that z equal to r cos theta correct; we are just making use of simple trigonometry.

And, how much should be this length o q should be how much? That is the other side of the right angle triangle it must be equal to r sine theta fine. And then we see you can say well if you think of this angle; how much is that angle? Well, you have to think of that model you this is myself and here is the perpendicular from the point where I am standing to the x axis this line is actually perpendicular to the x axis. And therefore this angle has to be 90 degrees even though it does not appear to be. So, this is another right angle triangle and using trigonometry you can show that x must be equal to r sine theta cos phi and y must be equal to r sine theta sine phi. And therefore if you wanted in this essentially very simple trigonometry all that you have to do is you have to worry about this triangle what is the triangle actually OQR. If you worry about that right angle triangle realize that OQ is its Hypotenuse right x and y are its sides.

And, this angle is equal to phi; OQ we had already found out OQ was found to be r sine theta. So, therefore what happens x and y should be r sine theta cos phi and y should be equal to r sine theta sine phi. So, this is fairly simple the derivation. And what we have to do is see you have to make use of these relationships correct. What is it that I want to do? I want to change from Cartesian coordinates to polar coordinates. Now, when you look at the equation I want to solve what is the equation? The equation is written here psi is equal to E psi, but when you look at this equation you will realize that there is del square there. What is del square? Del square in words partial differentiation with respect to x, y and z right. In fact, there this kinetic energy due to motion in the escalation, kinetic energy due to the motion in the y direction and as well as in the z direction contained in there and in the Cartesian coordinates.

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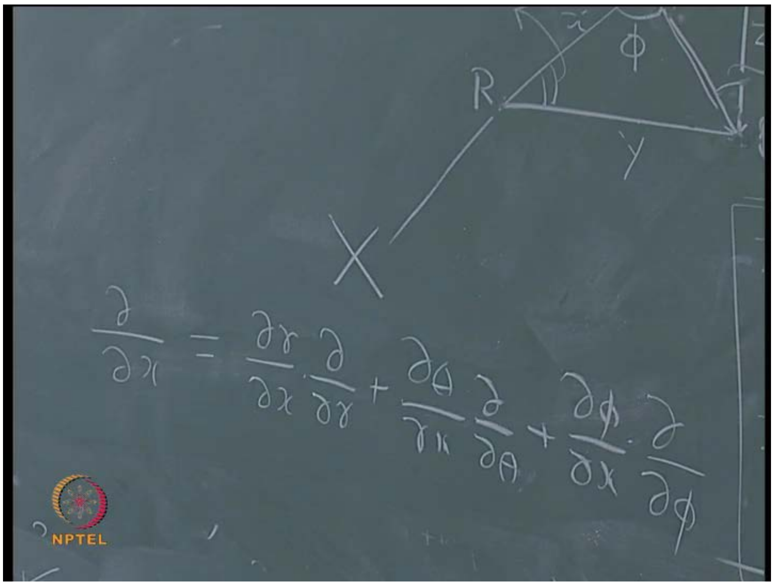

It is actually quite straightforward you will have dou x square upon dou x square plus dou x square upon dou y square plus dou square upon dou z square correct; this is how they have got the del square operatories correct. But now I am saying that I do not use x, y or z I want to use the coordinates r theta phi right. That means, this partial differentiation with respect to x has to be expressed in terms of partial differentiation with respect to the new variables r theta and phi. And similarly with reference to partial differentiation to y as well as z has to be expressed; this is a very very lengthy algebra is involved here. So, I will not be doing algebra but let me just remind you how it may be done. So, you can say that dou by dou x partial differentiation with respect to x may be written as dou r by dou x into dou by dou r plus dou theta by dou x into dou by dou theta plus dou phi by dou x into dou by dou phi; this is only dou x.

Now, you have to evaluate dou r by dou x dou theta by dou x dou phi by dou x. And then you will have another similar expression dou by dou y yet another one for dou by dou z right. So, you have to do all these things after which you have to calculate dou square upon dou x square dou square upon dou y square dou square upon dou z square you can see that it is quite messy; and then you have to add up all these things right. So, this is a fair a lengthy in algebra this is one way to do it; it may take a one hour to do it, but we will not do that. And therefore we will have to believe me when I say that del square has an expression that I am going to write. So, if you did all these things what happens to the Hamiltonian?

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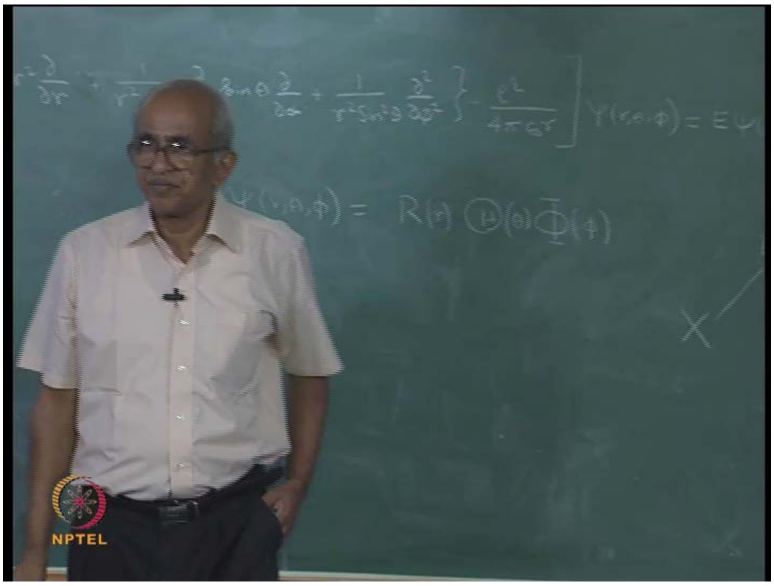

Well, the answer this minus h cross square by 2 mu. So, this is the first term that you will find; second term involves differentiation with respect to theta. Third term involving differentiation with respect to phi; what am I writing now the potential energy. And the potential energy only contains only magnitude of r the number r that we have been talking about. So, 4 phi epsilon 0 r. So, this is your Hamiltonian operator and the whole thing operating upon psi. Now, you have to imagine that psi is a function r theta and phi. And the answer must be equal to the energy psi E multiplied by psi r theta phi. So, this is the full form of Schrodinger equation written in polar coordinates; and if you look at this expression you really wonder if any progress has been made. Because this actually looks more complex than the previous equation, but interestingly you can manipulate this equation and find the solution.

But even though we have not derived this equation actually you can have physical interpretations for the different terms in the equation. So, you can look at this term the first term; the first term onwards differentiation with respect to what may be referred to as the radial coordinate r. See if you have the electron the electron can be moving in the radial direction which is moving in all directions. But there is a component which is moving in the radial direction right; there is a component in the radial direction. So, therefore what will happen is that there will be a kinetic energy due to the change in the value of r right. And that is this term we have 2 differentiations with respect to r actually; a little bit more complex than what we have in the Cartesian coordinates the meaning is the same.

This term represents the kinetic energy operator associated with radial motion. Then, of course you can see that the electron is not moving radially alone it is moving in other directions also. So, if it is moving in other directions what is going to happen? You will have kinetic energy associated with theta motion as well as with phi motions. So, these are those kinetic energies you can see that there is differentiation with respect to theta here. And that is simply happening because this represents the kinetic energy associated with theta motion and this represents the kinetic energy associated with phi motion. So, these are the physical meanings of the different terms. And this term of course simply represents in the potential energy due to the fact that there is a electrostatic reaction between the electron and the nucleus.

Now, what we will do is we will say that psi R theta Phi is a function of three variables we want to solve this we only know one method actually. We have discussed only one method for solving this kind of differential equations; what is that one method? We will say that it may be written as a product of 3 functions which I am going to write as R this symbol is capital theta and this symbol this PHI. And what I will assume is that capital R only depends on r capital theta only depends on small theta and PHI only depends on phi. So, we divide the wave function into 3 separate parts. So, the wave function is a product of 3 separate parts each part only depending on one coordinate. And then he will have to R, capital theta and PHI in such a fashion that the product obeys the original Schrodinger equation; that is the way we proceed. I shall continue in my next lecture.

So, thank you for listening.