Concept of Chemistry for Engineering
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Lecture – 9
Hydrogen Atom: Schrodinger Equation

Having discussed free particle and particle in a box, the field is now set for us to get into Schrodinger equation of hydrogen atom.

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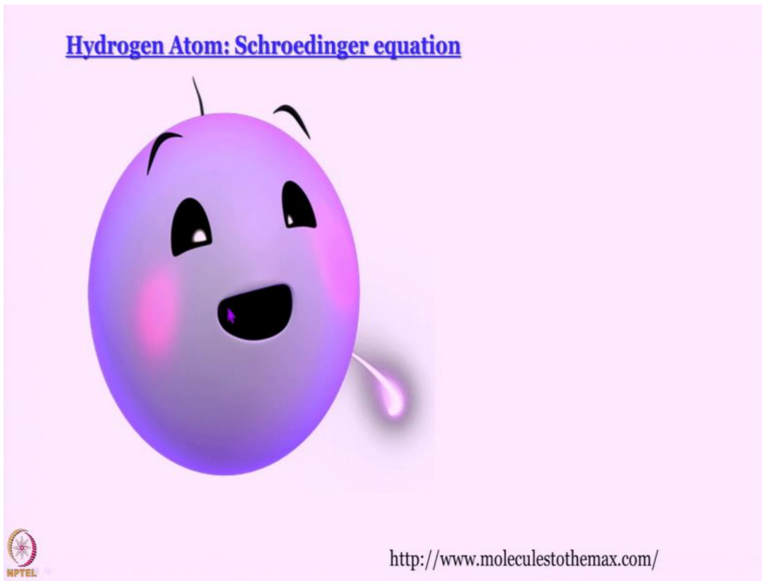

And I hope that you are as happy about it as this big fat smiling happy nucleus that we have here. And the reason why we have this cartoon here is that we should not forget that even though we said that Rutherford's model is not tenable, the basic experiment that had led to Rutherford's model, experiment performed by Marsden remember? This alpha particles shot at a gold foil, most of them go through, some of them deviate, and one in twenty thousand turn back, that experiment was not wrong.

So, the basic observation that almost the entire mass, and all the positive charge of the nucleus of the atom is centered at a point that still holds. And the fact that the negative charge, the electron in the atom is somewhere out in this vast void space in the atom, that also holds. What does not hold is that this electron goes around in circles or ellipses or whatever. But well, it does move, how does it move?

We cannot say exactly what the trajectory is, but we can write Schrodinger equation like we did for a free particle, like we did for particle in a box. And one more thing that we learned very, very important thing in the last module, was that we learnt about spherical polar coordinates. And we learned a little bit about angular momentum. So, with this, now, we are all set to talk about hydrogen atom.

As you will see, we are going to set up hydrogen, we are going to set up Schrodinger equation for hydrogen atom, then we are going to simplify it, we are going to use certain assumptions, I will show you the solution of one part of the equations. And then we are going to just share with you what the solutions of the other parts are. And what sense we can make out of them. But before we start, let us remember what we have learned so far.

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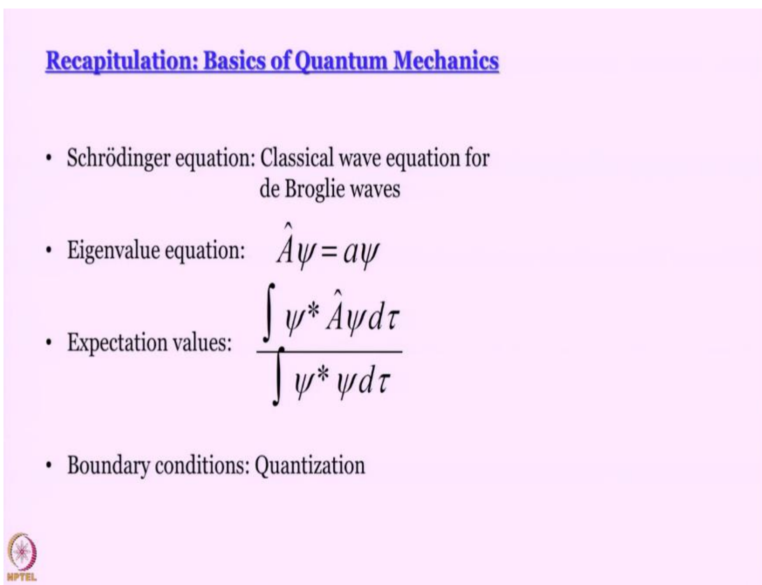

The very basic tenets of quantum mechanics are that, we are working with Schrodinger equation, we are going to write our Schrodinger equation.

$\hat{A}\psi = a\psi$

Expectation values: $\frac{\int \psi * \hat{A}\psi d\tau}{\int \psi * \psi d\tau}$

This started off as a classical wave equation for de Broglie waves. But, the realization that it is an eigenvalue equation triggered something much bigger. The postulate of quantum mechanics came about, which said that you should be able to write an eigenvalue equation for every physical observable.

So, the wave function contains all the information when the operator operates on it, it should be able to give you an eigenvalue equation, the Eigen value that you get is the value of the physical observable you are talking about. And it also sort of tells us that for every physical observable like position, momentum, energy, angular momentum, we should be able to construct an operator. And then this operator would better be Hermitian.

Because, your eigenvalues must be real, and the operators are also linear. So, these are all the postulates of quantum mechanics that we have touched upon very, very briefly. And we know already how to calculate expectation values. And one extremely important information that we have got now from our study of particularly in a box, is that quantization arises out of boundary condition. So, with this, let us now think, how we can formulate the problem of hydrogen atom in the language of quantum mechanics.

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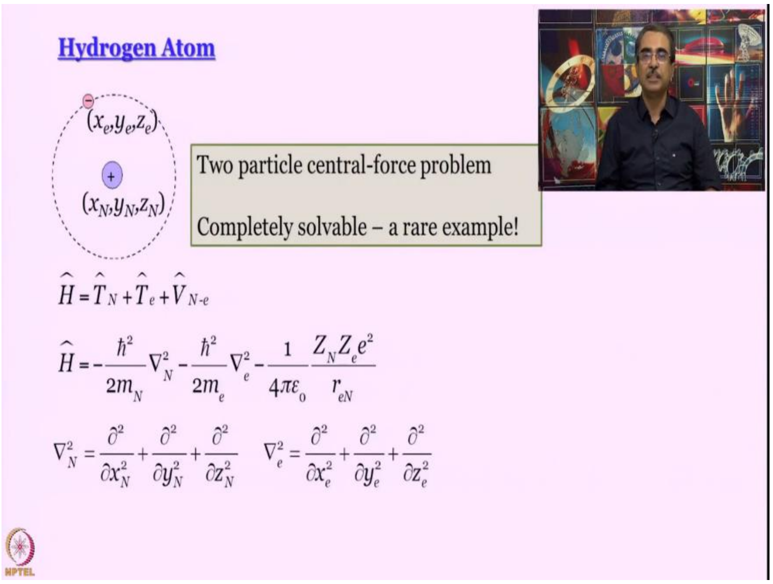

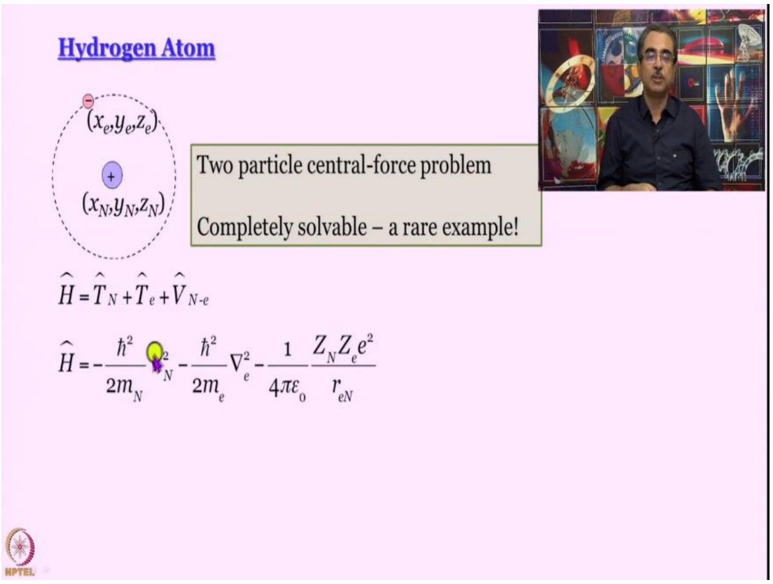

When we try to do that, the first thing that we have write down is the Hamiltonian. Now, hydrogen atom is really a two particle central force problem. What is the meaning of central force? As we said, the nucleus contains all the positive charge and the electron is a negatively charged particle. So, the electron moves in whichever way it moves under an attractive potential of the nuclear. And there are two particles, one is nucleus, one is electron and that is always a problem.

Whenever we have a two particle problem, we try and reduce it to a two one particle problems, they are much easier to handle. After we do that, this hydrogen atom Schrodinger equation is actually completely solvable. Usually, it is not. So, if you want to make fun of quantum chemist, usually tease them saying that these people have only one equation, and they do not even know how to solve it for most of the cases.

Of course, this is a not a very good thing to say and not so valid also, but well when you want to pull the leg of people this is what you do. Now, any quantum mechanical formulation of a problem starts with writing down the Hamiltonian or rather writing down the operator. If you are talking about Schrodinger equation, we have to write down Hamiltonian which is the involved operator here. So, what are the terms that the Hamiltonian will contain?

$\hat{H} = \hat{T}_{\mathrm{N}} + \hat{T}_{\mathrm{e}} + \hat{V}_{\mathrm{N\text{-}e}}$

It will contain a kinetic energy term of the nucleus, a kinetic energy term of the electron and a potential energy term for attraction between the electron and the nucleus, very simple. And we know already what the kinetic energy terms are. We know, that kinetic energy terms are like minus h cross square by $\hat{H} = -\frac{\hbar^2}{2m_N}\nabla_N^2 - \frac{\hbar^2}{2m_e}\nabla_e^2 - \frac{1}{4\pi\varepsilon_0}\frac{Z_N Z_e e^2}{r_{eN}}$. To differentiate between the two, we have written one term in capital N, one term in small e.

This means a term that is written in terms, this means a term that is expressed by the coordinates of the nucleus. And the second term is expressed in coordinates of the electron. The third term of course, it is very simple, $\frac{1}{4\pi\varepsilon_0}\frac{Z_N Z_e e^2}{r_{eN}}$. I think we are all familiar with this, very familiar. I will ask you, what is it called? Does this law have a name, I am sure you know what it is.

And we have written in SI unit for now, that is why this $\frac{1}{4\pi\varepsilon_0}$ is there. And since one of the charges is plus and one of the charges minus between proton and electron, we have a minus sign here, it is as simple as that, r_{eN} is a separation between the electron and the nucleus. So, this is the Hamiltonian.

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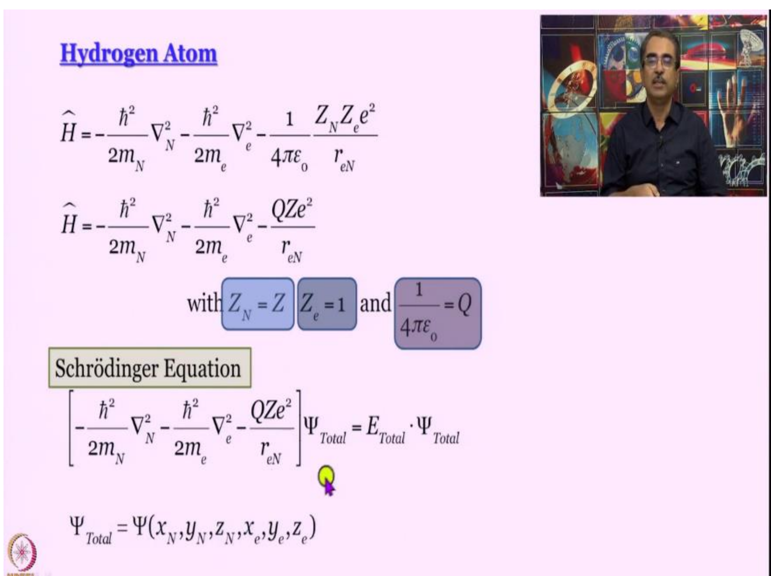

But we have to solve, we have to write it in a little simpler way before we can proceed further. Because you see, if you use that Hamiltonian and write down Schrodinger equation, this Ψ that we have here for now, we are calling this Ψ_{Total} even though Ψ_{Total} actually has a little different meaning later on, which is not really a part of this course, that we are now doing.

But generally when we talk for Ψ_{Total}, we mean a special part of Ψ multiplied by a spin part of the Ψ. We are not going to get into spin in this course. Here, when I say Ψ_{Total}, I mean the Ψ of the entire hydrogen atom, nucleus as well as electron. That Ψ is going to be a function of $x_{N,}y_N, z_N, x_e, y_e, z_{Ne}$, all the six coordinates will be there. We have to make this a little simpler.

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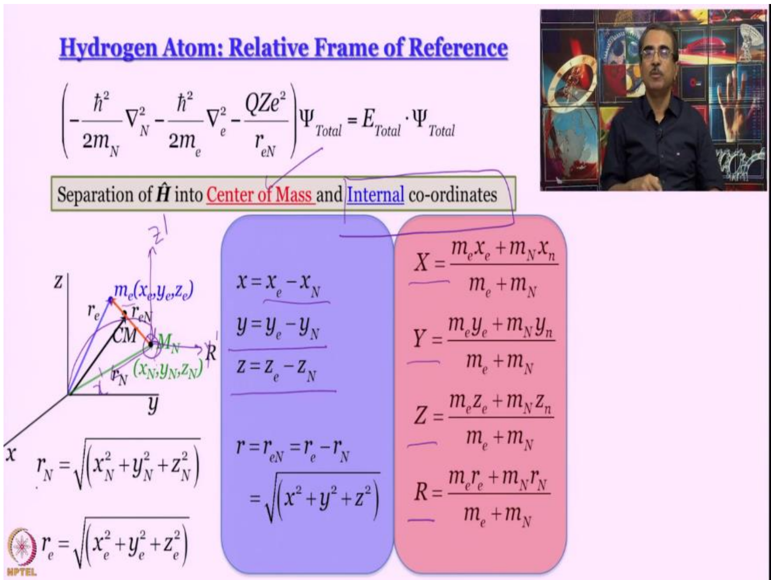

And we are not going to go through the mathematics of this, but it might help if we understand at least what the frames of references are. So, this is how we can formulate the problem. Let us say, this here is the nucleus and this is the electron. So, $x_{N,}y_N, z_N, x_e, y_e, z_{Ne}$ are the coordinates of the nucleus and the electron respectively in a space fixed coordinate system, some absolute coordinate system.

Now, the position vectors are written as r_e and r_N. Now see, if I try to write this vector, draw this vector r_{eN}, how will I get it? So, these are two vectors right, r_e and r_N. If I subtract r_N from r_e, then I get r, which is r_{eN}. And that is given by $\sqrt{(x^2 + y^2 + z^2)}$. Now, how it comes that we can show easier, but I have not even told you what x, y, z are, let me tell you that first, x is given by $x_e - x_N$, y is given by $y_e - y_N$, and z is given by $z_e - z_N$.

What am I talking about here? Where the axis are parallel. So, let us say I will draw this horizontal axis that is y, this is I call it y'. This let us say is z', and this here is x'. I hope it is not very difficult to see that x is parallel to x', y is parallel to y', z is parallel to z'. So, what is, what am I doing? I am doing a transformation of coordinates, I am moving the origin from the absolute value to where the nucleus is.

Now see, what will be the x coordinate of m_e? $x_e - x_N$ in this new frame of reference, which I have written as x y, x', y', z'. Y is going to be $y_e - y_N$, z is going to be $z_e - z_N$ as simple as that. Now, it is very simple to see what your r is. What is r? r is a position vector of the electron in this new coordinate system that I have built. Because this is a new origin, and this is the point.

So, this arrow that you see here, that is the position vector of the electron in this new transformed coordinate system. So, this coordinate system is called the internal coordinate system. What does that mean? That means, this talks about the displacement of the electron in terms of the nucleus. And the other coordinate system that we do not need to talk about in this course is this. These are mass weighted or center of mass coordinates.

When you do this, this is a very standard technique for separation of variables in problems like this. You essentially build this coordinate system, second coordinate system, which talks about the movement of the center of mass. So, the second one capital X, capital Y, capital Z that talks about movement of the center of mass. And this one, small x, small y, small z talks about movement of the smaller mass with respect to the larger mass.

And here, of course, we have to use instead of mass, we have to use reduced mass. I hope you all know what reduced mass is. The way I remember it is $\frac{1}{\mu} = \frac{1}{m_1} + \frac{1}{m_2}$. A question for you, the reduced mass suppose I have two masses, m_1 and m_2, let me give you some numbers. One mass of unit 1, another mass of unit say 1800, roughly proportional to masses of electron and nucleus.

Can you calculate the reduced mass of this system, one mass is 1 unit, the other mass is 1800 unit. So, I suggest that you stop the video right now, pause the video and work out what the reduced mass is. If you have worked it out, you will see that the reduced mass is very, very, very close to the smaller mass, 1. And that is what is important here. We will write, we will show you the equations shortly.

There you will see instead of m we have μ, but then in this system, μ is practically the mass of the electron. And capital M, the total mass is practically the mass of the proton, because their masses so very different. Now, in this system, you can do a formal separation of variables.

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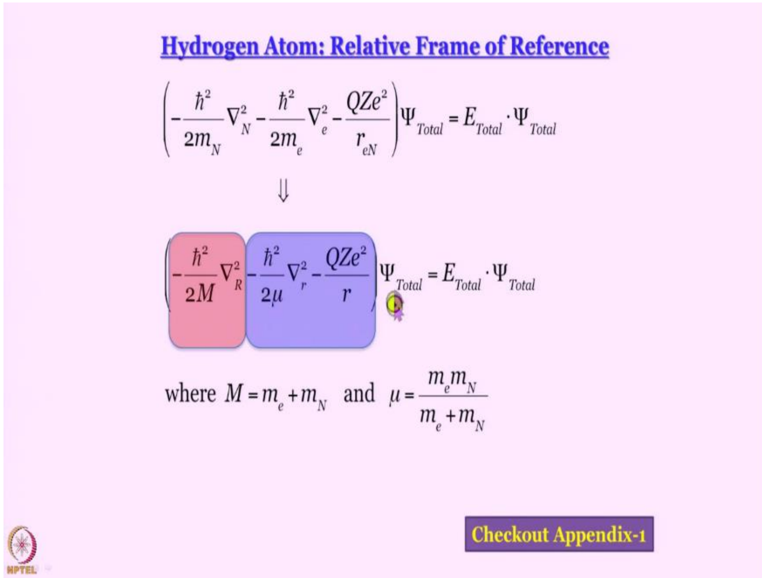

We are not going to do it here, just believe me when I say that when I write the Schrodinger equation for hydrogen atom in a relative frame of reference, then when we try to do that, first of all, I get two equations. One in terms of the center of mass coordinate, and one in terms of the relative coordinate.

$$\left[-\frac{\hbar^2}{2M}\nabla_N^2 - \frac{\hbar^2}{2\mu}\nabla_e^2 - \frac{QZe^2}{r_{eN}}\right] \Psi_{Total} = E_{Total} . \Psi_{Total}$$

So, what you see here the first term, it contains capital M, in the denominator, that is total mass, practically the mass of the proton.

$M = m_e + m_N$

And this capital R is the coordinates of the center of mass, which is essentially the proton, the nucleus, and this second one shaded in blue, that has see μ, a $-\frac{\hbar^2}{2\mu}$. What is this μ? Practically the mass of the electron.

$\mu = \frac{m_e \, m_e}{m_e + m_N}$

And here you have small r, which talks about the displacement of the electron from the nucleus. So, this is what we get. Now, how do we separate?

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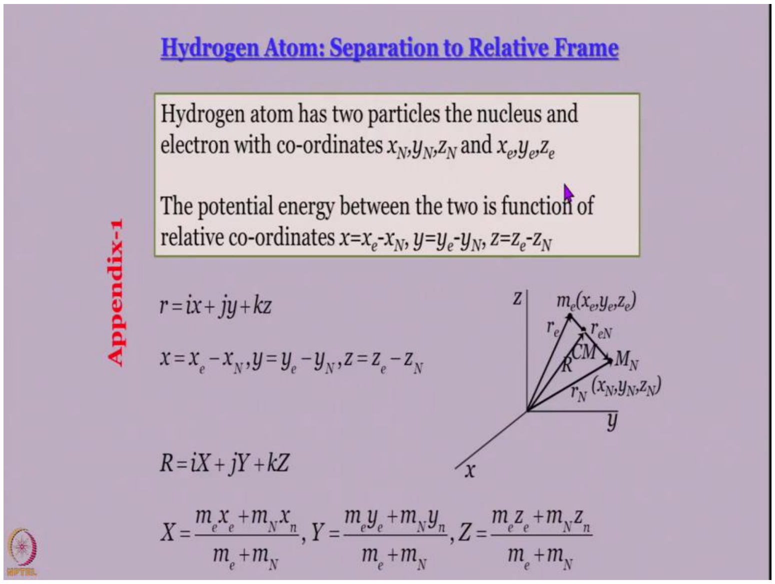

We separate in this manner.

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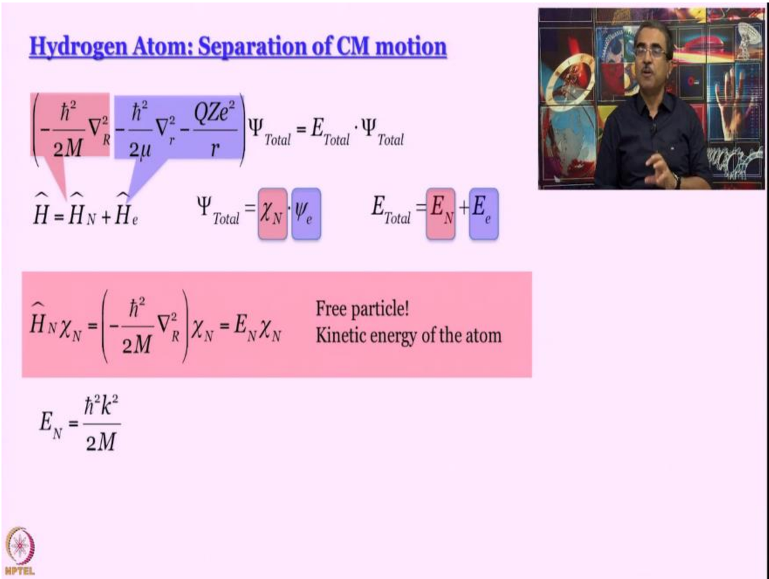

Well, first of all, this separation is done in this way I am not going to talk about it. Whoever is mathematically inclined is welcome to go through all those. We are, we do not really need to do this, let us take it axiomatically. So, we have got two equations, one like this.

$$\left[-\frac{\hbar^2}{2m_N}\nabla_N^2 - \frac{\hbar^2}{2m_e}\nabla_e^2 - \frac{QZe^2}{r_{eN}}\right]\Psi_{Total} = E_{Total}.\Psi_{Total}$$

The first term, I will call it $\widehat{H_N}$, because that is the only term on the left hand side, which is in terms of the capital mass, a capital M mass, which is sort of the mass of the nucleus, as I have said several times.

$$\widehat{H} = \widehat{H_N} + \widehat{H_e}$$

Second, and third terms together make up the Hamiltonian for the electron. Again, why electron? Because μ is practically the mass of the electron. Did I say it too many times? But I have said it, but that is all right. Now, how do I write wave function? To write wave, to separate this equation, what we do is we write the wave function as a product of two wave functions. One in terms of the center of mass.

$$\Psi_{Total} = \chi_N . \psi_e$$

Well, since it is practically the nucleus, I call it χ_N and one in terms of the electron ψ_e. So, why are we doing this? Remember particle into the 2D box, there also since x and y directions were independent, we took the wave function to be a product of a wave function in x and a wave functions in y. Here also the nuclear and the electronic coordinates are independent after separation of variables. That is why we can write the wave function as a product of a nuclear factor and an electronic factor.

So, when we put that in, what will the energy be? Naturally energy will be a sum of the center of mass, that is the nucleus and the reduced mass that is the electron, $E_N + E_e$. And what you see is, this color coding is used to highlight, which part is associated with nucleus, which part is associated with electron. So, now essentially we collect all the terms in the nucleus coordinates. So, from the left hand side what will I get? $-\frac{\hbar^2}{2M}\nabla_R^2$.

That operates on, see when it operates some χ and ψ, what will happen? ψ_e is a constant it will come out. So, we are doing separation of variables, I will not do it in very much of detail here, because we are going to do it in little more detail slightly later, for another equation. So, if you do not understand what we are doing here, please wait up a little bit. Let us do that, and you can come back and do it yourself.

$$\widehat{H_N} . \chi_N = \left[-\frac{\hbar^2}{2m_N}\nabla_N^2\right] \chi_N = E_N . \chi_N$$

Crux of the matter is, we get one equation as $\widehat{H_N}.\chi_N = \left[-\frac{\hbar^2}{2m_N}\nabla_N^2\right]\ \chi_N = E_N.\chi_N$. And $\widehat{H_N}$ here is only the kinetic energy operator. Does that ring a bell? Have you encountered Schrodinger equation like this? Actually we have, we have encountered it when we talked about free particle. So, this is what gives us the kinetic energy of the atom as a whole. And remember, this is not quantized.

$E_N = \frac{\hbar^2 k^2}{2M}$, k can take up any values. So, essentially the atom as a whole if you look at the atom as a whole, you will see it undergoing translational motion and this translational motion energy, translational energy is not going to be quantized. This is very important to understand. That being said, we do not worry about it anymore, because we are not interested in the movement or atom as a whole. We are interested in movement of the electron with respect to the nucleus.

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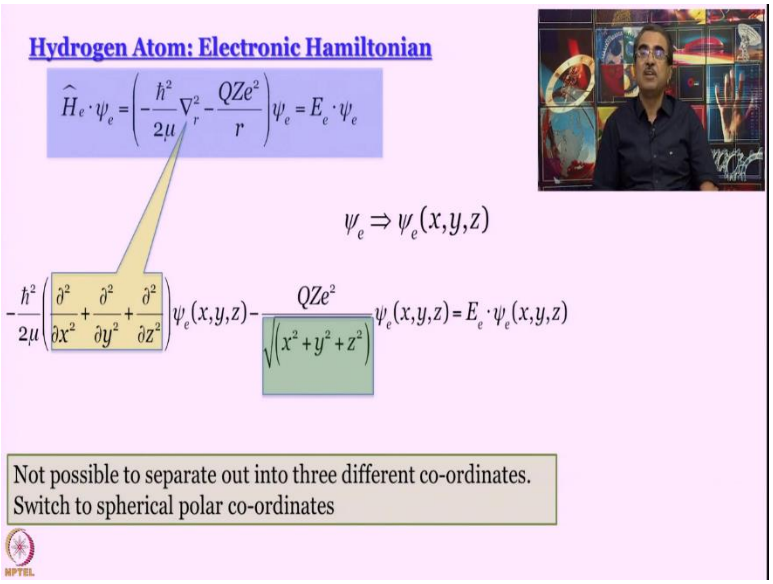

For that for the rest of this discussion, we are going to focus on the electronic part of Schrodinger equation. Now, if you have not understood anything we have said so far, it does not matter. If you can believe that, we have to formulate this Schrodinger equation for the electronic part, and ∇_r^2 is the kinetic energy, well $-\frac{\hbar^2}{2\mu}\nabla_r^2$ is the kinetic energy operator for the electron.

$$\widehat{H_N}.\psi_e = -\frac{\hbar^2}{2\mu}\nabla_r^2 - \frac{QZe^2}{r}\psi_e = E_N\,.\,\psi_e$$

This one is the potential, then I think you can understand the rest of the discussion, no problem. Now, this is our Hamiltonian. And in fact this is our Schrodinger equation, ∇_r^2 as you know is $\frac{\partial^2}{\partial x^2}$ + $\frac{\partial^2}{\partial y^2}$ + $\frac{\partial^2}{\partial z^2}$. And r as we have said already is, $\sqrt{(x^2 + y^2 + z^2)}$. So, if you want you can write it like this, you can write it out and this is going to be your Schrodinger equation in terms of x, y and z. Is it okay?

Can we work like this, can we just write is equal to $E_e \cdot \psi_e$? And try to solve it? Actually, we cannot. Because see, earlier when we talk about, talked about 2d, 3d box, we could separate it very nicely. Here the problem is, here we have a term in $\sqrt{(x^2 + y^2 + z^2)}$, you cannot separate it. So, your Cartesian coordinates will not work. What should work?

Well, if you go back to the original form of the equation, here we have written r, and the problem is that we cannot separate r into x, y and z. So, if you cannot separate it, can you work with it? Is there a coordinate system in which r itself is a coordinate? Actually there is, and we know what it is, that is spherical polar coordinate.

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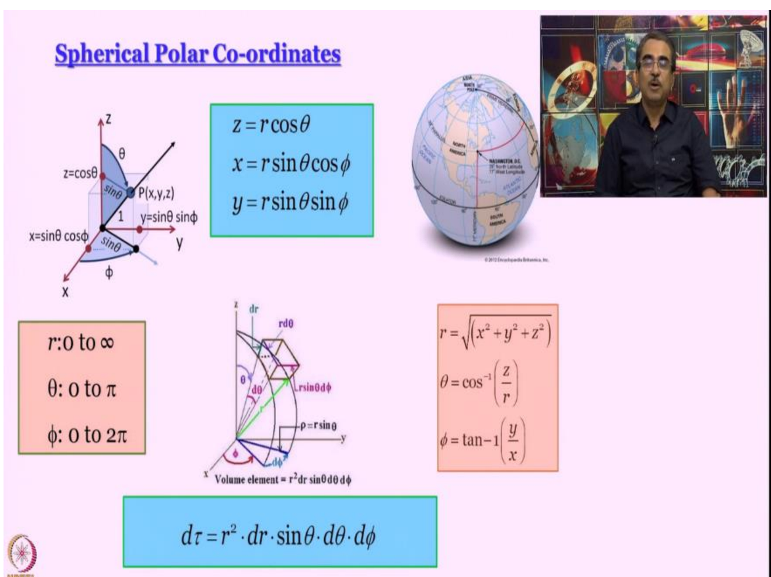

So, we need to formulate Schrodinger equation in terms of spherical polar coordinates. I will not repeat all these relations, and expression for your volume element and all, because we have discussed already. Suffice to say, that we need to now reformulate the problem in terms of spherical polar coordinates, easier said than done.

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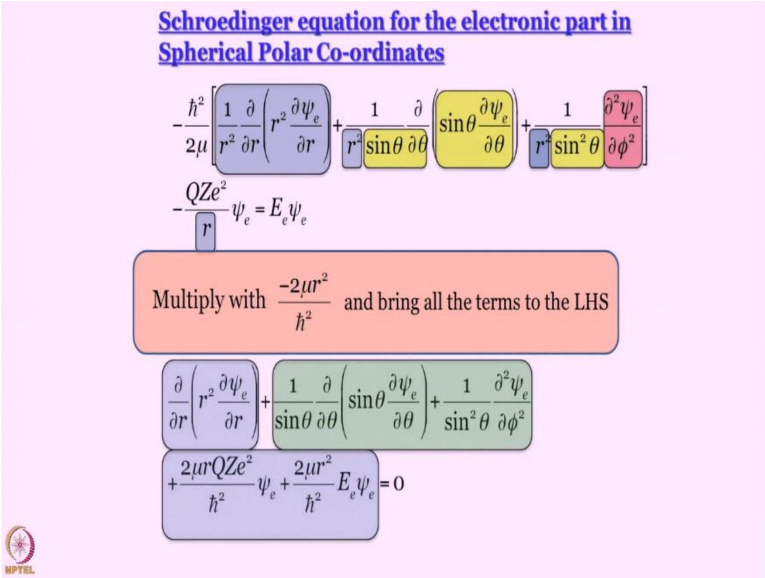

Because when we try to do that, I have removed all the slides, usually in my regular classes, we have a lot of fun showing thirteen slides that we are not going to discuss. That, those thirteen slides tell us, how to go over from $\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}$- this big scary expression that we have. What we have written here is kinetic energy operated in spherical coordinates.

$$\frac{-\hbar^2}{2\mu}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)+\frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{r^2\sin^2\theta}\right]$$

You have to believe me on this, or you have to actually do the transformation yourself. If you want to do it, suit yourself. I am not about to do it. I am not about to do it here. That being said, do you have to remember this? No. Please do not. Nobody needs to remember anything in a course like this. And in case, this is used by some colleges by teachers, my request to teachers is that we should never ask questions like, write down the kinetic energy operator in spherical polar coordinates.

We need to use our brain, not just as a storage device rather we have to use it as a processor. So, let us do that, let us focus on understanding rather than memorizing things. This is something that is available in many resources, we will just use it. How do I write the Hamiltonian operator? This is the kinetic energy operator. So, to get to the Hamiltonian operator, I just have to add the kinetic, potential energy term.

$$\frac{-\hbar^2}{2\mu}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi_e}{\partial r}\right)+\frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi_e}{\partial\theta}\right)+\frac{1}{r^2\sin^2\theta}\frac{\partial^2\psi_e}{\partial\varphi^2}\right]-\frac{QZe^2}{r}\psi_e=E_e.\psi_e$$

Here it is, how do I write Schrodinger equation. Now, this Hamiltonian in spherical polar coordinates has to operate on the wave function. Let us do that, this is your Schrodinger equation now. So, this here is Schrodinger equation for the electronic part in spherical polar coordinates. And see, what we have. These are the terms in r. These are the terms in θ. And these are in φ. The first term is only in r.

Second term is a mixture of r and θtheta, the third term contains r and θ and φ. So, we will have to find a way of separating these equations. And this is what we are saying that we are going to do it at least for this part of the discussion. How do you do it? Well, first of all, let us see how we can simplify further. If I multiply by $\frac{-2\mu r^2}{\hbar^2}$, what happens? This r^2 gets eliminated.

So, at least the second term becomes only in terms of θ, except for the wave function of course. The third term, the operator part is only in terms of θ and φ. So, r is eliminated from second and third terms. And then we bring this $E_e.\psi_e$ to the left hand side. Again, I recommend that you keep on pausing the video, writing down what we should get in the next step. And you come back and see the video after that.

That way, you will understand better. I hope you are doing that. Now, I will show you what the answer is if you do this, this is what we get.

$$\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi_e}{\partial r}\right)+\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi_e}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2\psi_e}{\partial\varphi^2}+\frac{2\mu r^2 QZe^2}{\hbar^2}\psi_e+\frac{2\mu r^2}{\hbar^2}E_e.\psi_e=0$$

First term becomes $\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi_e}{\partial r}\right)$, yeah? You have multiplied by $\frac{-2\mu r^2}{\hbar^2}$. What does the second term become? r^2 would go, 2μ would go, $\hbar^2$ would go, you are left with $\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi_e}{\partial\theta}\right)$.

What about the last term? It becomes $\frac{1}{\sin^2\theta}\frac{\partial^2\psi_e}{\partial\varphi^2}$. And since you have brought whatever was on the right hand side to left hand side, the last term that you get is $\frac{-2\mu r^2 QZe^2}{\hbar^2}$. What is Q? We have defined Q to take care of all these constants $\frac{1}{4\pi\varepsilon_0}$ and all that. So, that will be $\frac{2\mu r^2}{\hbar^2}E_e.\psi_e = 0$

So, this second last term is the potential energy term, the last term is what was there on the right hand side. Now, these are in terms of r, only r except for the wave function. These are in terms of θ and φ, there are two kinds of coordinates, r is the line and θ and φ are angles. So, first, as a first step if you can separate r from θ, φ, that is good enough.

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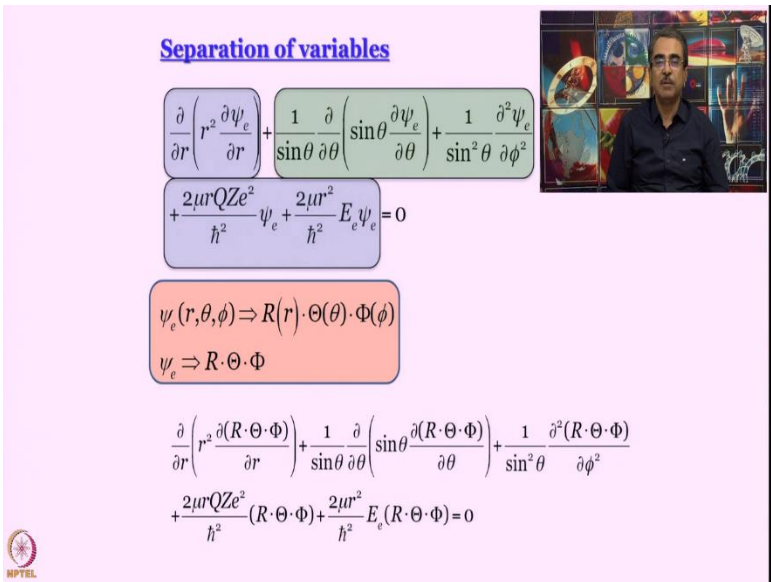

How do I do it? Again I have to define my wave function in a particular manner. So, let us define the wave function as a product of an r dependent part, a θ dependent part and a φ dependent part.

$$\psi_e(R, \theta, \varphi) = R(r).\Theta(\theta).\Phi(\varphi)$$

We often, do not even write this small r, small θ, small φ in brackets. We just write capital R, capital Θ, capital Φ.

$$\psi_e = R.\Theta.\Phi$$

What is capital R? Wave function, what is capital Θ? Wave function, what is Φ capital? Wave function, capital R is a wave function that is written only in terms of small r, capital Θ is a function of θ only not r, not φ. Capital Φ is a function of φ only not r, not θ.

So, small letters are coordinates, capital letters are wave functions. How are we okay? How is it that we can write it? Well, we are doing separation of variables and these are all independent coordinates. So, let us write that, this is what your equation becomes.

$$\frac{\partial}{\partial r}\left(r^2\frac{\partial(R.\Theta.\Phi)}{\partial r}\right)+\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial(R.\Theta.\Phi)}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2(R.\Theta.\Phi)}{\partial\varphi^2}+\frac{2\mu r^2QZe^2}{\hbar^2}(R.\Theta.\Phi)+\frac{2\mu r^2}{\hbar^2}E_e.(R.\Theta.\Phi)=0$$

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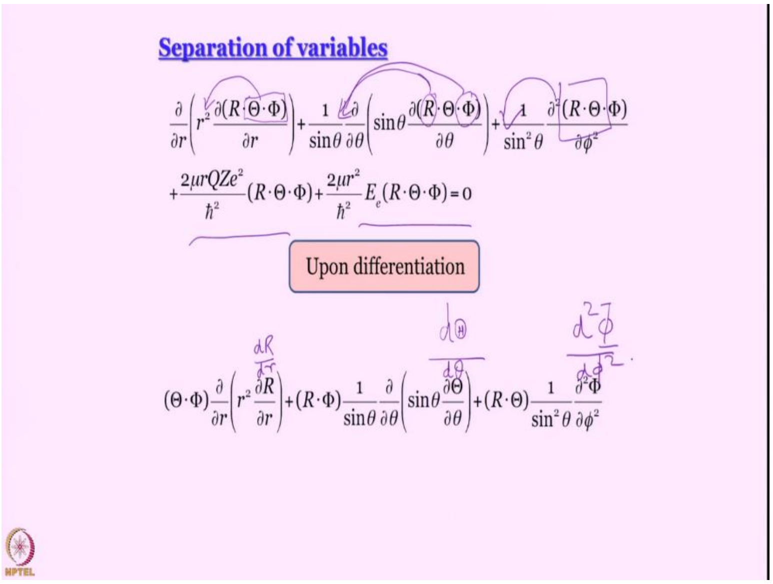

Now, what? What happens when you try to differentiate? Well, this is the step that we had skipped earlier. So, let me at least draw some arrows here. And let me show you, let us take the first term. When I differentiate see this Θ, Θ and Φ, they are not functions of R. So, as far as R is concerned, they are constants, so they are going to come out. Similarly, in the second one, capital R, and Φ, these are not functions of small r.

So, they are, sorry they are not functions of θ. So, they are also going to come out. And in the third term, we are differentiating with respect to φ. So, capital R and Θ which are not functions of Φ, they are constants as far as this differentiation is concerned. And last two terms you do not even have to worry about, because they are just products. So, that is what we get. And again please pause, work it out yourself and then only see the next step. When you do that, this is what you get.

$$(\Theta.\Phi)\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right)+(R.\Phi)\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta}{\partial\theta}\right)+(R.\Theta)\frac{1}{\sin^2\theta}\frac{\partial^2\Phi}{\partial\varphi^2}+\frac{2\mu r^2QZe^2}{\hbar^2}(R.\Theta.\Phi)+\frac{2\mu r^2}{\hbar^2}E_e.(R.\Theta.\Phi)=0$$

$(\Theta.\Phi)\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right)$. In fact, there is no need to write del here anymore, because I do not have a partial derivative any longer, is not it? So, it is absolutely okay and it is desirable that I write $\frac{dR}{dr}$, that is actually better. Similarly, the second term we have, (R.Φ) outside $\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta}{\partial\theta}\right)$.

So, again I can write actually $\frac{d\Theta}{d\theta}$. There is no need of writing that $\partial\Theta$ any longer. And finally, in the third term, (R.Φ) come out and you are left with $\frac{1}{\sin^2\theta}\frac{\partial^2\Phi}{\partial\varphi^2}$, again it is better to write $\frac{d^2\varphi}{d\varphi^2}$. Remember $\frac{d^2\varphi}{d\varphi^2}$ wave function, φ dependent wave function as small φ is the coordinate. So, and these are the other terms.

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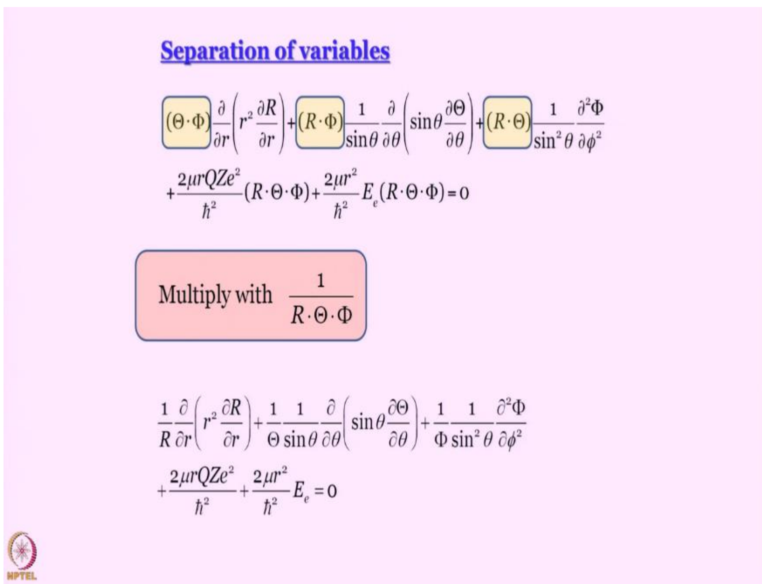

What is the next step? Obviously, you do not want this (Θ.Φ) in the first term, you want to get rid of it. The easiest way of doing it is to divide by (R. Θ.Φ), do it and see what you get. Yeah? Multiply by $\frac{1}{(R.\Theta.\Phi)}$, please do it yourself. This is what you get, $\frac{1}{R}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right)$. This, and this, I am not going to read out everything here. This is what you get. And now have a look.

$$\frac{1}{R}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right)+\frac{1}{\Theta}\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta}{\partial\theta}\right)+\frac{1}{\Phi}\frac{1}{\sin^2\theta}\frac{\partial^2\Phi}{\partial\varphi^2}+\frac{2\mu r^2QZe^2}{\hbar^2}+\frac{2\mu r^2}{\hbar^2}E_e=0$$

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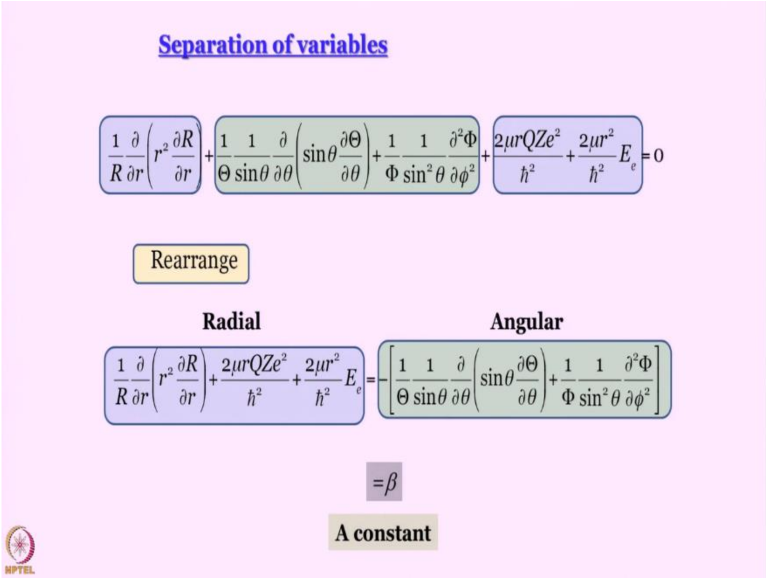

Well, I have written a little more neatly here. Now, see, these are the terms in r, no θ, no φ. These two terms are in terms of θ, φ only, no r. These are equal to 0, rearrange a little bit.

$\frac{1}{R}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right) + \frac{2\mu r^2 QZe^2}{\hbar^2} + \frac{2\mu r^2}{\hbar^2}E_e = -\left[\frac{1}{\Theta}\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta}{\partial\theta}\right) + \frac{1}{\Phi}\frac{1}{\sin^2\theta}\frac{\partial^2\Phi}{\partial\varphi^2}\right]$ These are equal to each other, but left hand side is in terms of r, right hand side is in terms of θ, φ, they are independent coordinates. So, this radial and angular parts, the part in radial and part in angular coordinates, the part in r and part in θ, φ, they must be equal to some constant, we write it β.

Why? Because left hand side is in terms of r, small r. Right hand side is in terms of θ φ, how can they not be constant? They have to be a constant, a very simple mathematical tool that is used universally.

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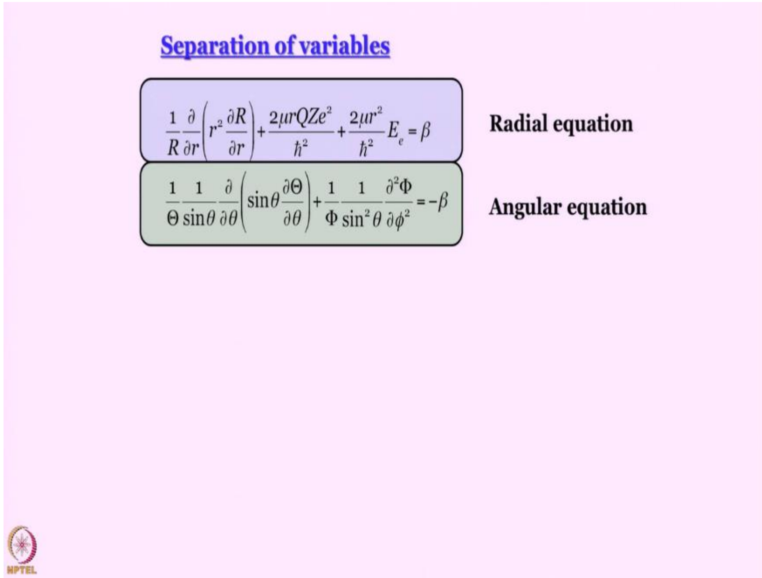

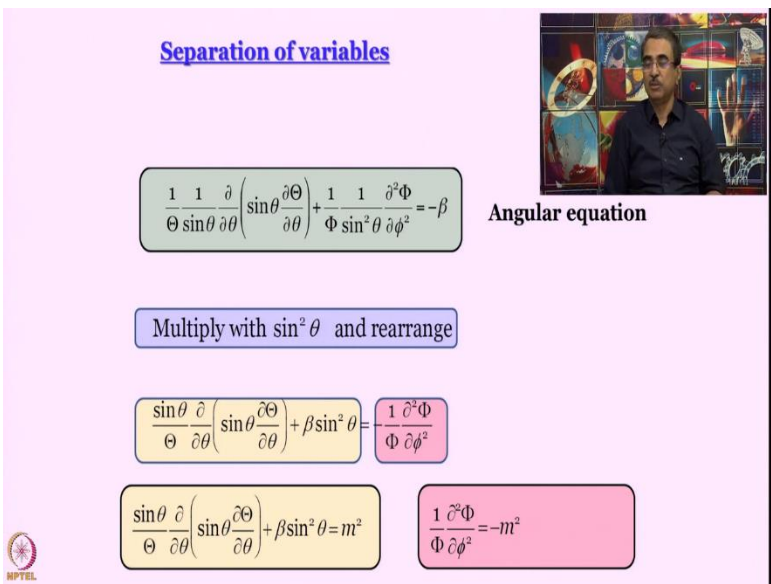

So, when you do that, you get two equations. The first one is called the radial equation. Second one is called angular equation.

$$\frac{1}{R}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right) + \frac{2\mu r^2 QZe^2}{\hbar^2} + \frac{2\mu r^2}{\hbar^2}E_e = \beta$$

$$\left[\frac{1}{\Theta}\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta}{\partial\theta}\right) + \frac{1}{\Phi}\frac{1}{\sin^2\theta}\frac{\partial^2\Phi}{\partial\varphi^2}\right] = -\beta$$

And please note that they are connected by β. They are not independent of each other. For example, in the Schrodinger equation for 2D, particle in a 2D box, the two, the equations were independent.

Here, they are not independent, they are actually correlated by β. And I do not have to do anything more for the radial part. It is sorted. But Angular equation, I have to still work a little more, because we have θ and φ, mixture of those. How do I do it? Same thing, first of all multiplied by $\sin^2\theta$, this is what you get.

$$\frac{\sin\theta}{\Theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta}{\partial\theta}\right)+\ \beta\sin^2\theta\ =\ \frac{-1}{\Phi}\frac{\partial^2\Phi}{\partial\varphi^2}$$

First term is only in θ, second term is only in theta. Well, then I take this just, I sort of inter change sides. So, now left side is in θ, right side is in φ. Again, these are going to be equal to some constant, this constant I call m^2.

$$\frac{\sin\theta}{\Theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta}{\partial\theta}\right)+\ \beta\sin^2\theta\ =m^2$$

$$\frac{-1}{\Phi}\frac{\partial^2\Phi}{\partial\varphi^2}=\ -m^2$$

Now, why m^2? Why not k? Because I know what we are going to do later. We are not the first people doing it here. It is absolutely okay if you write k or whatever you want to write, but I know that life becomes simpler and meaningful, if I write m^2 here, that is the only reason why it has been written this way.

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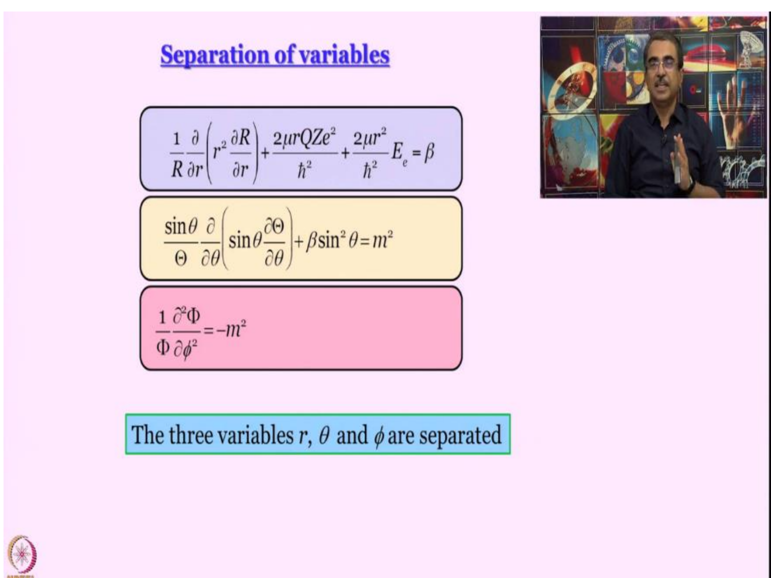

So, we have three equations. One, a function of r, one, one in terms of r, one in terms of θ, one in terms of φ. They are separated. What we are going to do next is that we are going to try to solve this simple one. And while I am speaking, many of you would have solved it also.

$$\frac{1}{R}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right) + \frac{2\mu r^2 QZe^2}{\hbar^2} + \frac{2\mu r^2}{\hbar^2}E_e = \beta$$

$$\frac{\sin\theta}{\Theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta}{\partial\theta}\right) + \beta\sin^2\theta = m^2$$

$$\frac{-1}{\Phi}\frac{\partial^2\Phi}{\partial\varphi^2} = -m^2$$

But let us take a break now. We will come back and we will solve this. And we will tell you what the solutions are of the r dependent part and the θ dependent part.