Spectroscopy Techniques for pharmaceutical & Biopharmaceutical Industries
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Lecture 13
Atomic Spectroscopy 1

Hello students! Welcome to lecture 13. Today I am going to discuss about atomic spectroscopy.

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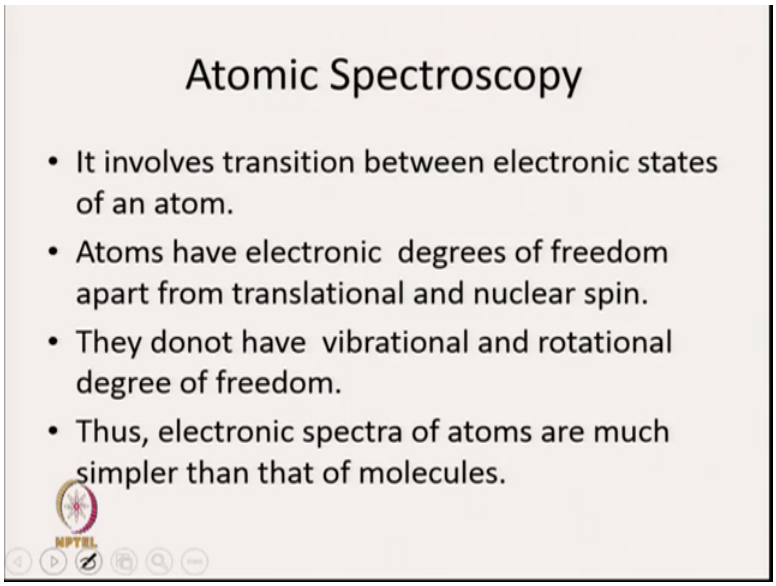

As the name suggest, atomic spectroscopy involves transition between electronic states of an atom. As you know, atoms have electronic degrees of freedom apart from transitional and nuclear spin. But they do not have vibrational and rotational degree of freedom. So electronic spectra of atoms are much simpler than that of the molecules. So today I am going to show you, how to calculate the energy associated with different electronic states of an atom.

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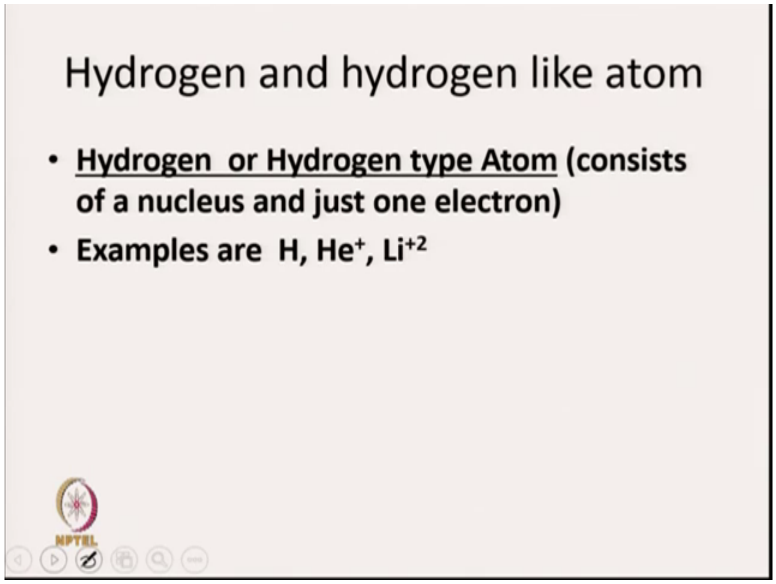

Today, I will discuss only hydrogen and hydrogen like atoms. In the next lecture, I will be discussing other atoms. So what I mean by hydrogen or hydrogen type atom is that they consist of a nucleus and just one electron. So it is a one electron system. For example, hydrogen, helium plus or lithium 2 plus.

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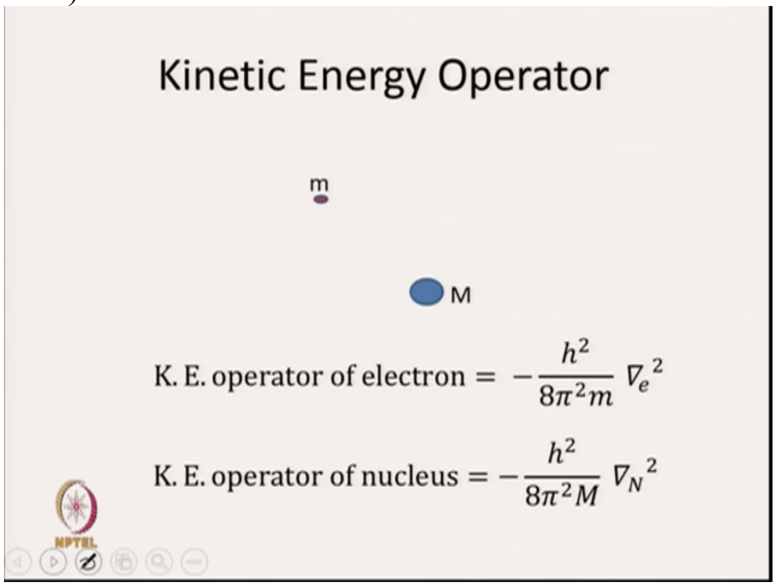

So for calculation of energy, we need to write first Schrodinger equation for an atom. So we will start with kinetic energy operator because Schrodinger equation consist of a plying Hamiltonian operator to get the energy. Hamiltonian has 2 part, kinetic energy operator and potential energy operator. So first we will look at, how to calculate in a kinetic energy operator for an atom. So atom has electrons, and electron suppose has a mass m.

And here is your nucleus with mass capital M. So these are the 2 constituents of a hydrogen like atom. There is only 1 electron and there is a nucleus. So kinetic energy operator of an electron is written by this term which we already know that minus h square by 8 pie square M delta E square, where small m is the mass of an electron. Similarly, we can write, kinetic energy operator for a nucleus. Similar way, we write the operator Minus h square by 8 pie square. Now we take, mass of, mass of the nucleus and again delta E square and delta N square is Laplacian operator with respect to electron and nucleus.

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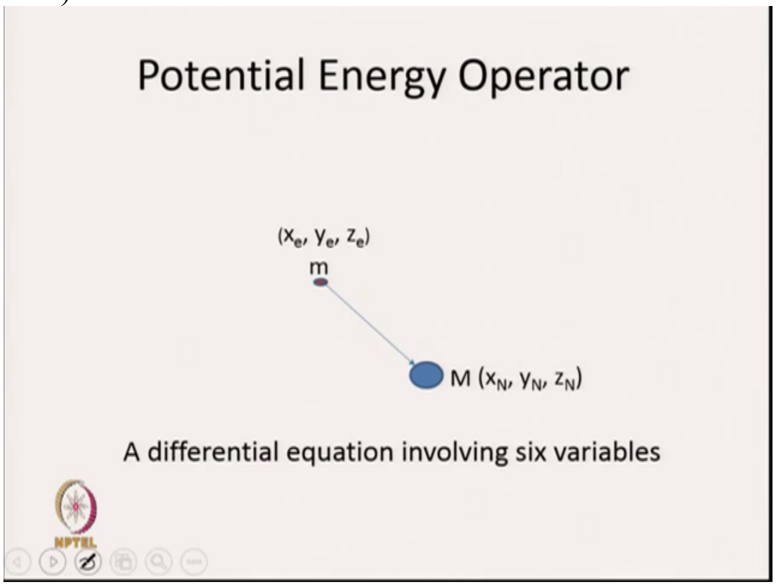

Now let us think about electron energy operator. So for calculation of potential energy, we need to know the coordinate and here, the coordinate of m is; Xe, Ye, Ze. Whereas, coordinate of nucleus is X N, Y N and Z N.

The (())(4:15) the symbol for electrons and N is the symbol for your nucleus. So as expected, this will involve 6 variables. First, what we will do is, we will try to express potential energy in terms of distance between nucleus and electron. So suppose we take a coordinate system such that the distance of nucleus from the, this is the nucleus, distance of nucleus with respect to origin is r N. And distance of electron with respect to origin is r E. Then the distance between electron and nucleus can be written with this expression; r is equal to r N minus r E.

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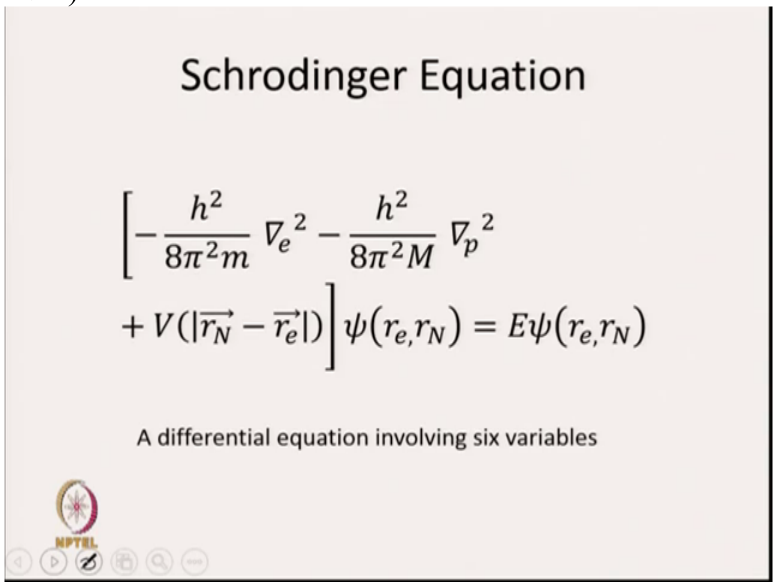

Now we know how to write kinetic energy operator and how to write potential energy operator. Let us put it in Schrodinger equation. So you have this plus this. So this is your kinetic energy operator for electron, this is kinetic energy operator for nucleus. Let us write N, since I have denoted everywhere by N.

And this is your potential energy. V as a function of r N minus r E and then wave function is a function of r E and r N. When this Hamiltonian operator is applied on this wave function, we can get your energy. You can get your energy. Here, a differential equation involves 6 variables. So we need to simplification.

So in the previous slide, I have written the Schrodinger equation which is not easy to solve. So we will do some simplification. Simplification which we do is, we divide the motion into 2 parts. One is translation motion where centre of mass is moving. So you can think of a nucleus and this is electron; and this is moving together or basically, its centre of mass is moving and then, the second motion is relative motion, which is motion of electron with respect to nucleus. So we are looking at motion, motion of electron with the nucleus.

And if we can separate it, it will be easier to solve it. Solve the Schrodinger equation. So let us look at relative motion coordinate. The way we do is; this I have already told you that R can be expressed in terms of rN and rE.

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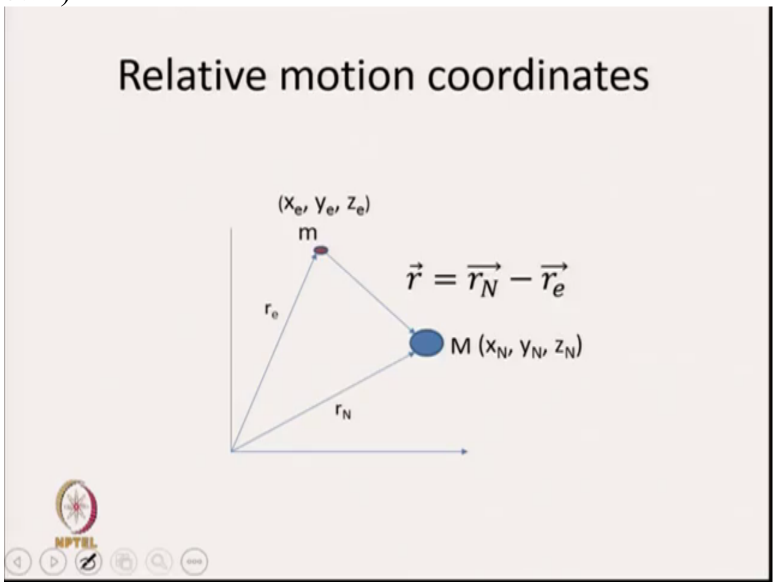

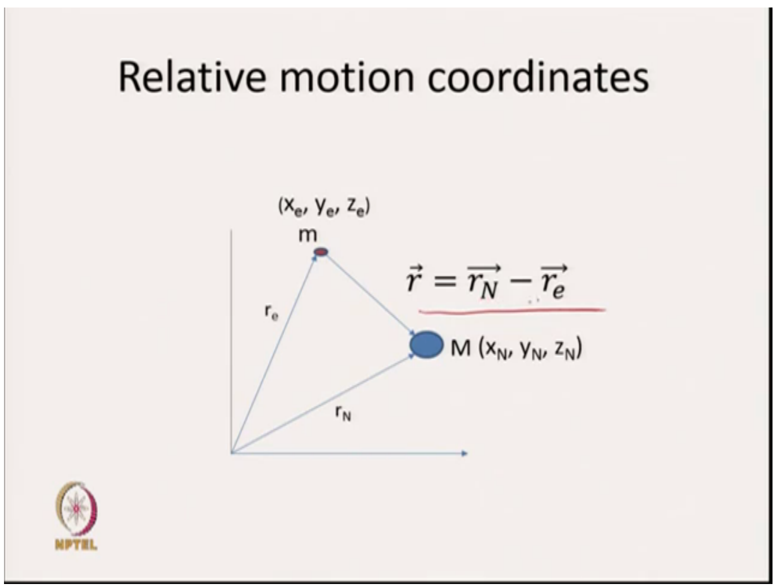

And now centre of mass coordinates. So what will happen is; let us go back one more time. This is your R; rN minus rE. And if I want to look at the coordinate of centre of mass; how we are going to write? So coordinate of centre of mass can be written as; M into rE. So this is mass into rE, plus capital M into rN, this one, divided by m plus M and now coordinate of this centre of mass is big X, big Y and big Z. Capital X and Capital Y and Capital Z, where X can be written like; MXN plus MXN divided by M plus capital M; M plus capital M. So you see, this mass of electron multiplied by X coordinate of electron plus mass of nucleus divided by mass of electron plus mass of nucleus. So this is the way, you will calculate what will be the value of X. Similarly, you can write equation for capital Y and equation for capital Z. So this is now coordinate for centre of mass.

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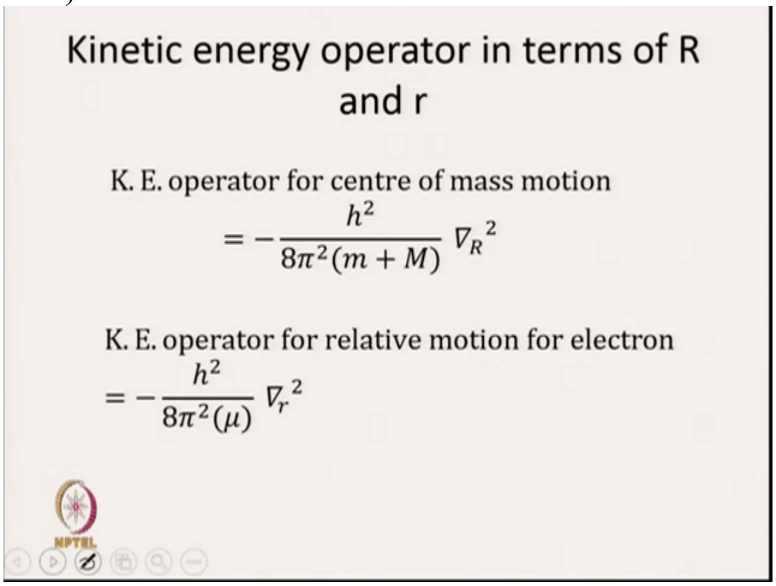

Now the next thing is to calculate kinetic energy operator in terms of capital R and small r, capital R and small r. Again, capital R denotes coordinates and centre of mass system, where R shows you coordinates for the relative motion of the electrons. So now think of; before solving, you can just think of, how to write kinetic energy for centre of mass?

The way I talked about centre of mass is, this is electron and this neutron and these are moving. These are moving together and so, your mass will be replaced by M plus m, because your this whole system, mass is M plus m. So H square plus 8 phi square M plus m, delta r square.

Similarly, we can write kinetic energy for relative motion of electron and in that case, what will happen, this is nucleus and this is electron moving relative. So your centre of mass is also a bit moving. So in that case, you will use mu, which is your reduced mass for the system and here will be laplacian operator in the new coordinate and square of that. But now let us think of, how to come at this value of kinetic energy operator?

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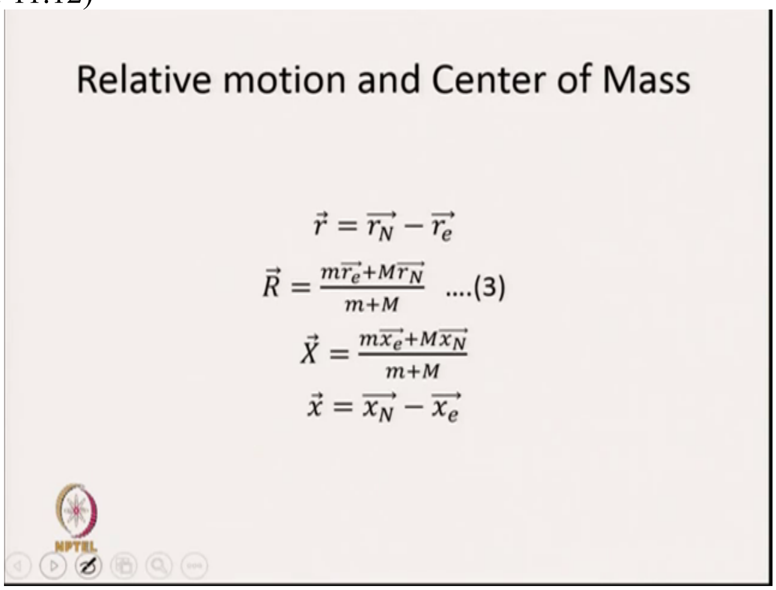

So, already I defined r is equal rN minus rE. And capital R is equal to mr plus, capital M rN divided by m plus M. So capital X can be written as mass of electron multiplied by X coordinate of electron plus, mass of nucleus multiplied by X coordinate of nucleus. And then mass of electron plus mass of nucleus. And this x, this small x tells you about coordinates in relative motion of electron system.So x is equal to Xn minus Xe. So this rN minus rE, so you can write, Xn minus Xe.

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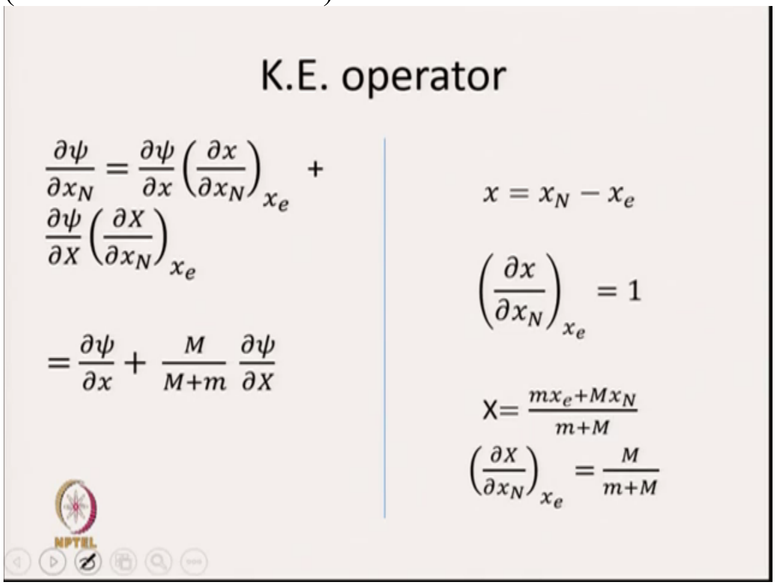

Now let us try to write kinetic energy operator in the centre of mass system. So for that, what we need to calculate is, first derivative, del psy by del X n. And the second derivative, del 2 psy by del X N S Y. So first I will explain you how to write the first derivative. So this is your differential of wave function with respect to XN, where X is, XN is coordinate of nucleus, coordinate of nucleus.

So that can be written like this - del psy by del X into del X by del x N at constant x E plus del psy by, this del capital X, multiplied by del capital X by del x N at constant x E. So why we are doing that? We need to express this term, in terms of X and capital X coordinates. So X is coordinates for relative motions and here capital X is coordinate when we are dealing with a motion of centre of mass.

Now let us calculate del X by del XN. We know that x is equal to x N minus x e. So if I differentiate this, del X by del x N at constant x e, I will get 1. And now, you calculate this, del capital X by del x n . Again capital X, we just wrote that it is equal to M into X e plus capital m in X n divided by small m plus capital M. If I differentiate this X, with respect to x n, taking x e constant, what I am going to get is divided by small m plus capital M.

So this is given here. Now I am going to plug in these two values in this equation. What I will is, del psy by del x, and this is equal to 1 and so you can multiply by 1. And this is del psy by del capital X, which is written here. And now del capital X by del x N at constant x e. And that is equal to M by small m plus capital M. So that is what is written here. So now we know first derivative, first derivative. So we have expressed first derivative in terms of capital R and small r, capital R and small r.

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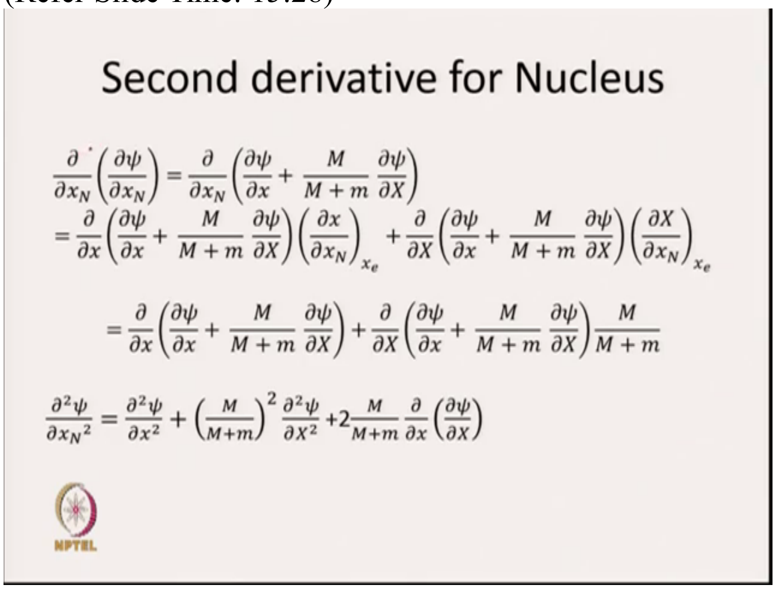

Now let us go and write the second derivative. So second derivative, again we will go in similar way. So second derivative, you can calculate by taking differential with respect to x N. For del psy by del x N, which we have just solved and what we got for del psy by del x N is this quantity. Del psy and del X plus M divided by capital M small m plus del psy by del X.

Now do similarly do this calculation. So again, del by del x I will write, then I will take this function here and then del x by del x N at constant x e. Here, you see, del by del x, now I take again this function multiplied by del X by del x n when x e is taken as constant and this we already know, del x by del x N at constant x e that is equal to 1. So I will simply write this expression and for this, I know, this is equal to m divided by capital M plus small m.

Now when you open it up, what you are going to get is del 2 psy by del x N square is del 2 psy by del x square plus, here you see, plus; this is del m divided by M plus small m square. So this comes from here. And this you see, del 2 psy by del X square. So this term; so first term came from this one, the second term came from this one. So this is for first term, this is for second term and then these two term adds up to give you twice of capital M by capital M plus small m, del by del X and del psy by del X. So this is your second derivative for centre of mass motion.

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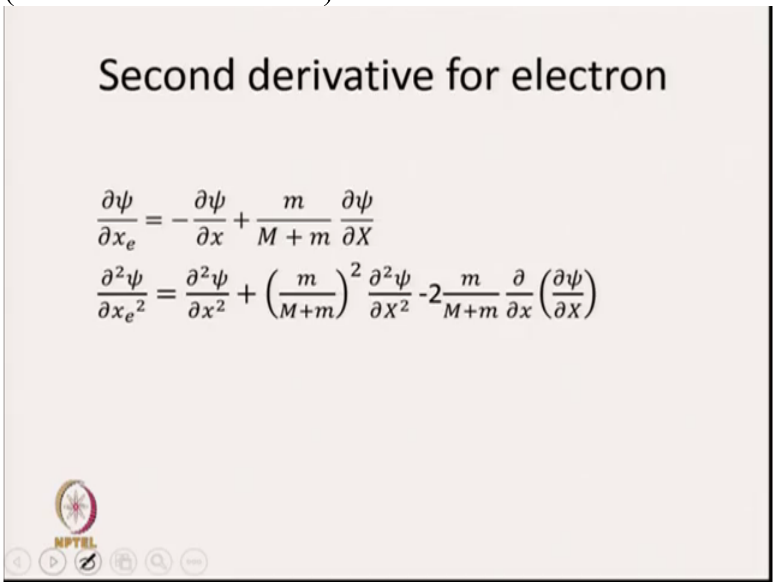

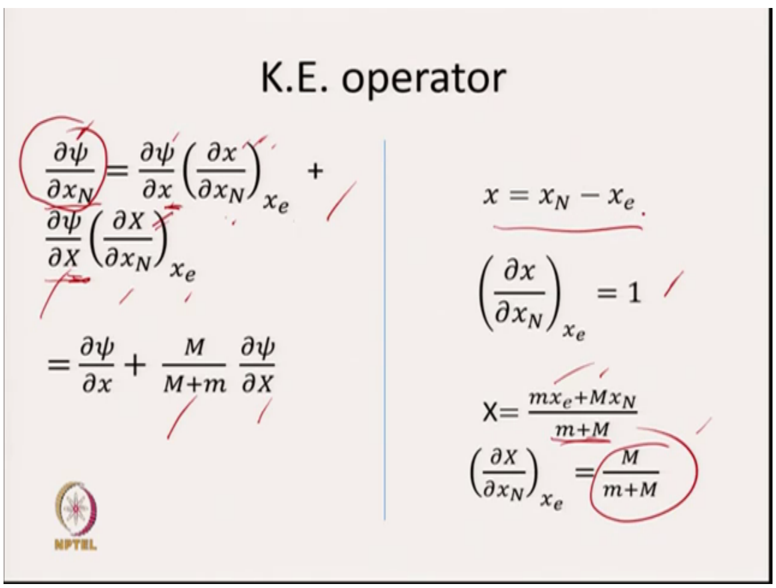

Now in the similar way, we can write the second derivative for electrons or here, I am talking about relative motion of electrons. So del psy by del x e. If you do that, what you are going to get is this. Difference only is, your this has negative sign and here, capital m is replaced by small m. That is the only difference and negative sign comes because; if you look here, this X is equal to x N minus x e.

So x N is positive and x e is minus, and so when you do del x by del x e at constant x N, you will get minus 1. And so, del psy by del x e, will be equal to del psy by del x plus small m plus capital M plus small m into del psy by del capital X. Same way we can also calculate the second derivative and what we are going to get is del square psy, del 2 psy by del x e square is equal to del 2 psy by del x square plus m divided by M plus m, capital M plus small m square, del 2 psy by del capital X square minus 2 small divided by capital M plus small m del by del x, del psy by del capital X.

If you compare with del 2 psy by del x n square, then the difference is; then you will get capital M and at this place you will get capital m. This is for centre of mass movement of centre of mass. So in that case, this will be capital M, this will be capital m and this will be positive sign . This is going to have positive sign. So once we have done this, let us go and calculate the kinetic energy operator.

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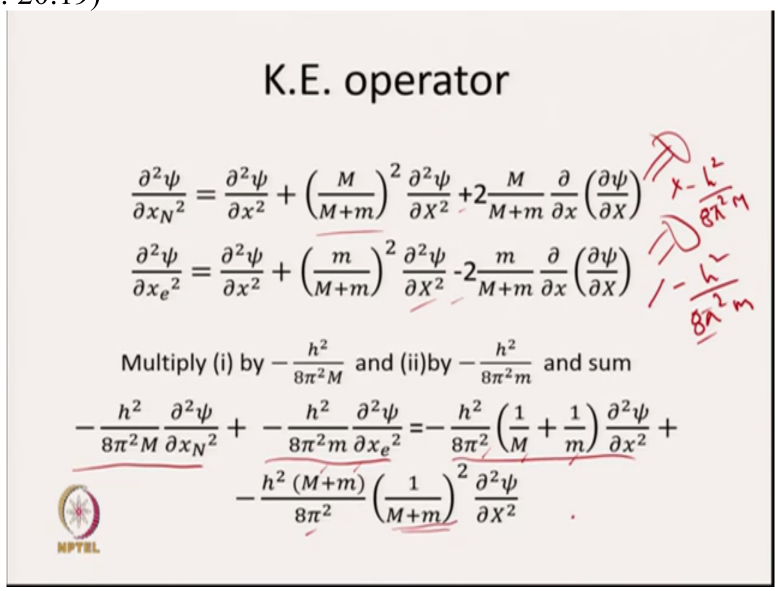

So this is the second differential of wave function with respect to x n. And this is your second differential of wave function with respect to x e. Now to calculate the sum of two kinetic energy operator, we will multiply this by minus H square by 8 pie square M and this by minus H square divided by 8 pie square small m. So the difference is, here is capital M, here is small m. When we do that, we will get this corresponding to this term corresponding to your kinetic energy operator for centre of mass motion.

And this is your kinetic energy operator for relative motion. Here, what we will get; you see del 2 psy by del x square, both have and since we have multiplied by minus h square by 8 pie square in the both terms. So minus h square by 8 phi square will be common. Here, 1 by M and this is 1 by small m. So this is for your first term. Now look at the second term, del 2 psy by del x square; what you are doing here is minus h square by 8 pie square.

Both side you are multiplying. So now the second term is 1 by M multiplied by this whole thing. So suppose I take m square out. So M square divided by m is m. And same thing if you do here, then m square divided by m is small m. So what is left? Which is common is 1 by m plus, capital M plus small m square. And this is your del 2 psy by del X 2 square. Now look at the third term, what will happen to third term? So see here, M M cancels out. Small m and small m cancels out. So plus, one has plus sign, another has minus sign.So this basically your cancels out, this cancels out. So we have this expressions for kinetic energy operator, kinetic energy operator of the whole hydrogen atom. Now we have expressed the kinetic energy operator in terms of small r and capital R.

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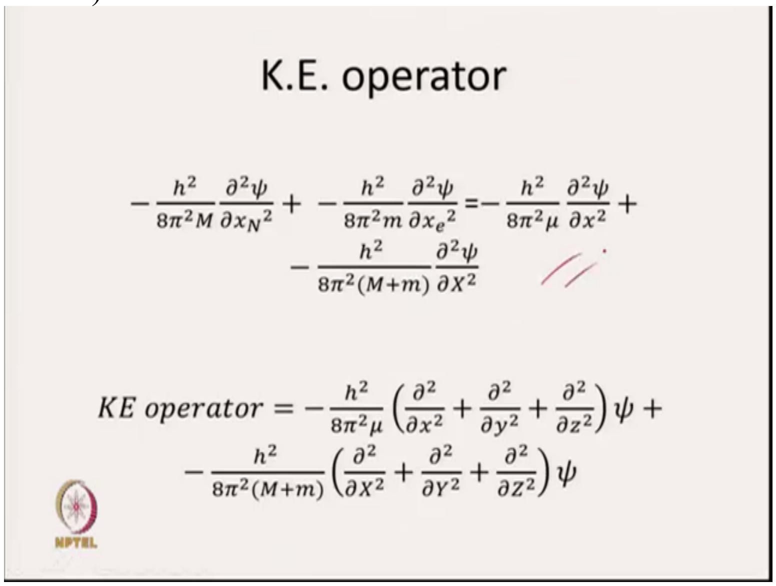

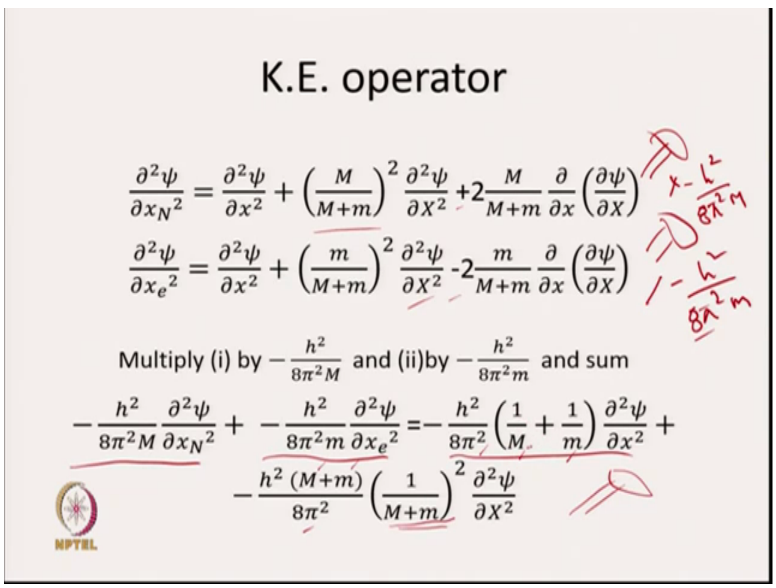

Now this is your kinetic operator; this we did with respect to a small x, which is basically x coordinate for your relative motion and this is your x coordinate for centre of mass motion. Now one thing which you will notice is that this can be written as 1 by m plus 1 by capital M plus 1 by small m can be written like 1 by mu. So you remember h square by 8 pie square into mu. So this is your inverse of reduced mass, inverse of reduced mass and that is what we are going to put it here. So here you see, this is your minus h square by 8 pie square, reduced mass into del 2 psy by del 2 square plus this.

So this is your kinetic energy operator with respect to relative motion. This is kinetic energy operator with respect to your centre of mass. This we have done with respect to X. Similarly, we can find out the second differential or kinetic energy operator with respect to Y and with respect to Z. When we do that the total kinetic energy operator will be simply here. What you will do is, in place of del square by del X square, you put del square by del X square plus del square by del Y square plus del square by del Z square.

And similarly here, you replace del square by del, capital X square by del square by del capital X square plus del square by del capital Y square plus del square by del capital Z square. So this is your kinetic energy operator.

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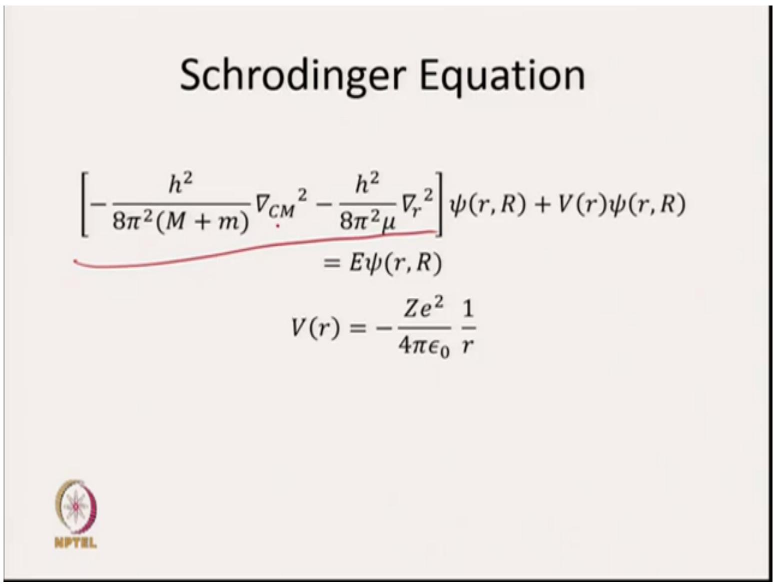

Now you can write Schrodinger equation. So this is your Schrodinger equation. And now you see this is delta cm or delta r you can write. So this is your laplacian operator and centre of mass system, laplacian operator due to relative motion of an electron and now what will be the V value. We already know that V will be Z e square by 4 pie epsilon naught, 1 by r, 4 phi epsilon naught, 1 by r. So now we know potential energy, we have expressed kinetic energy operator and centre of mass system and system where we are considering only relative motion of electron.

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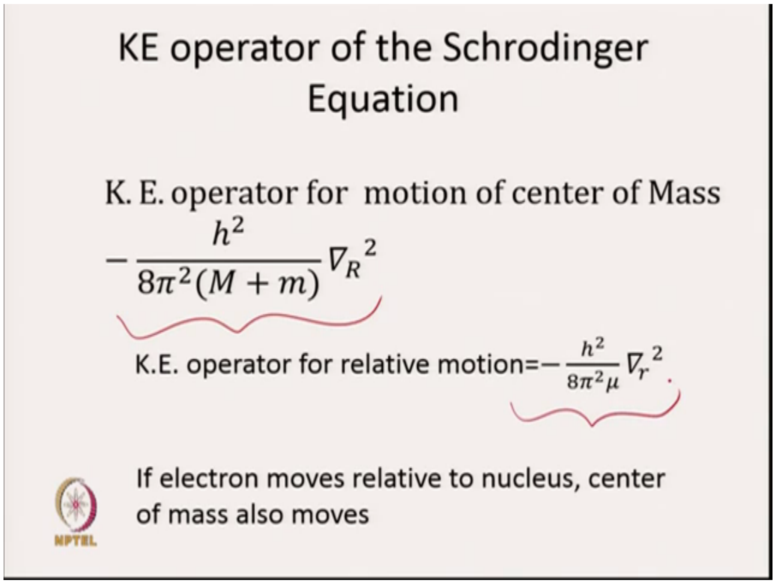

You can see that this is the kinetic operator for motion of centre for mass. This is kinetic operator for relative motion and this was the thing what I was saying was this is because of 2 system of electron and nucleus is moving together and that is why you have M plus, capital M plus small m and for relative motion, your nucleus is here and this is moving around like this. But you see, centre of mass will also be slightly changing depending on motion of electron and so you have reduced mass. So basically this is what I was saying that if electron moves relative to nucleus, centre of mass also moves and that is why there is a reduced mass.

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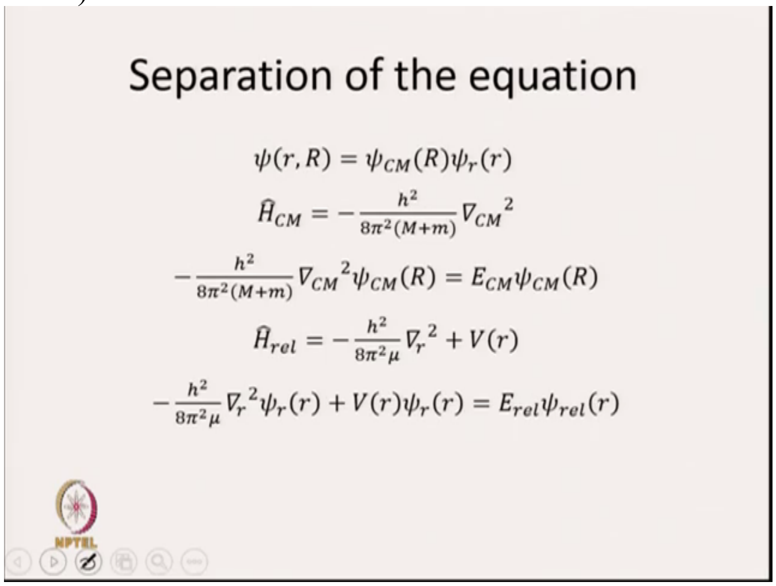

Now what I will do is, I will try to write or try to separate the equations. One equation which will deal with the motion of centre of mass and another which will deal with your motion, relative motion. Till now, we have the combined schrodinger equation. Now we have to divide into different equations if you want to solve it.

So the way we do it is let us take wave function which is a function of r and capital R as a multiple for wave function of centre of mass, which is a function of capital R multiplied by wave function associated with relative motion and it is a function of small r. So if you do that, the H we are going to write as Hamiltonian for the centre of mass is minus H square by 8 pie square capital M plus small m, laplacian operator for centre of mass square.

And then we can write this equation; so if I apply Hamiltonian operator on the wave function, we are going to get the energy due to the motion of centre of mass. Hamiltonian for relative motion can be written in this term. So minus H square by 8 pie square reduced mass into laplacian operator square plus laplacian operator; this is whole laplacian operator. So laplacian operator plus potential energy which is a function of R, potential energy which is a function of R.

So now you see, in centre of mass there is no potential energy. In the relative motion, you have a potential energy term. We are looking at the energy levels of an electron so we are more interested in the energy associated with electronic levels. Schrodinger equation for relative motion will be written like this. Schrodinger equation for relative motion will be given by this this is your Hamiltonian, when applied on function, it will give you the energy of electronic levels, energy of electronic levels.

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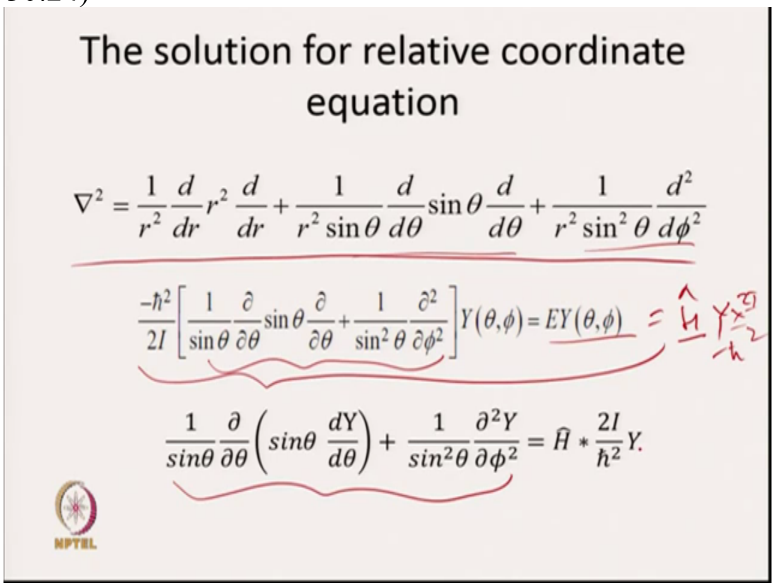

So we are going to see the solution for relative coordinate equation. We are going to see the solution for Schrodinger equation for relative coordinate equation. So this I have already discussed in the rotation chapter when I was discussing about rotational motion. That for 3 dimensional motion, what we need to do is express Laplacian in terms of polar coordinates. Now what I will do is, first I will write the Laplacian operator in polar coordinates and then we will see how to apply in hydrogen atom.

So we know that in the rotational motion chapter we have seen that minus h square by 2I, this term multiplied by r square plus this term multiplied by r square and applied to spherical harmonics, it will give you energy multiplied by spherical harmonics. So if you see this, this should be equal to your e multiplied by 2 i. This is basically h Hamiltonian y. So if we write this operator, 1 by sine theta, del by del theta, sine theta del y by del theta plus 1 by sine square theta del square y by del psy square. That should be equal to h multiplied by, here 2i is there, so 2i minus h cross square, minus h cross square. So this is h into 2i by h cross square into I.

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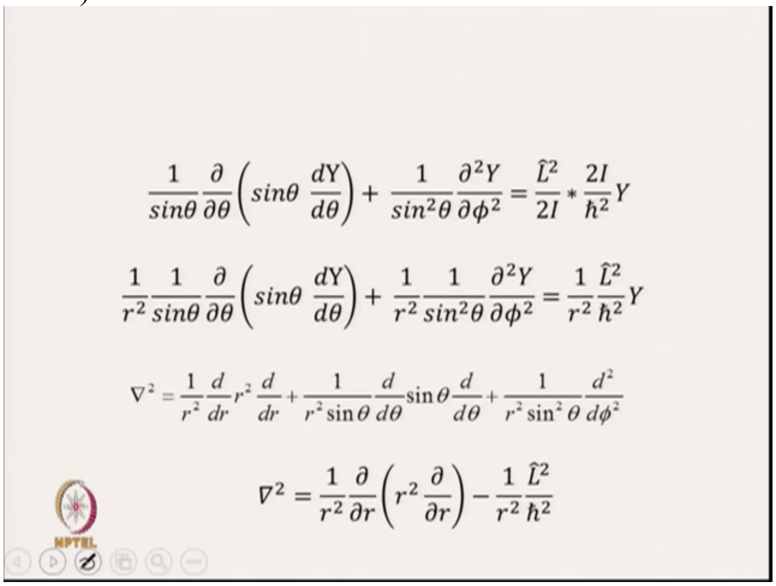

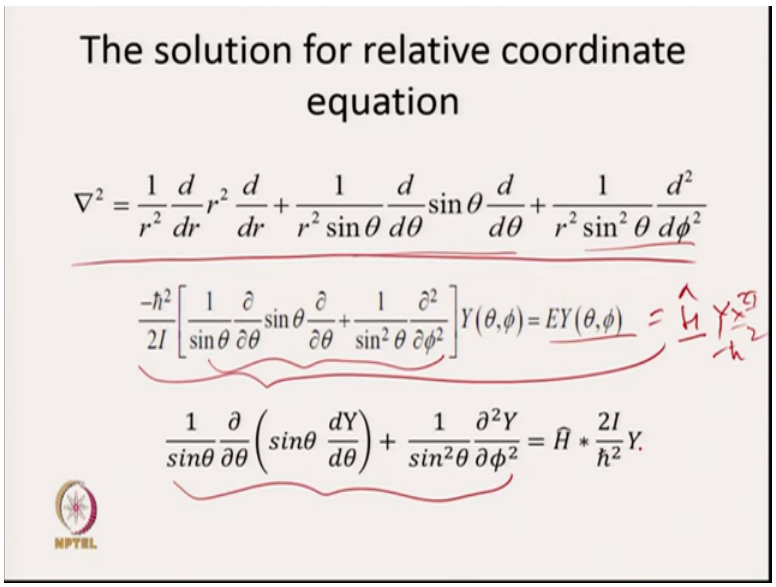

And then this is the same thing, which I have taken from the last slide. So this is your h multiplied by 2i by h cross square into y and Hamiltonian operator is equal to l square by 2i operator. So this whole thing will be equal to l square by 2i, multiplied by 2i divided by h cross square, cross square. And so you see, 2i 2i cancels out and so what we have is this whole term is equal to l square divided by h cross square into y. Now you divide that by r square.

What I will get is 1 by r square l square operator divided by h cross square into y. And your Laplacian operator is equal to this what we discussed earlier. So this del square will be equal to this term, that is what I have written here. minus, so here was the minus term, so I missed this, So please correct it. So minus and sum of this is equal to 1 by r square l square operator divided by h cross square. So now this is your whole, this is your expression for Laplacian operator, expression for Laplacian operator.

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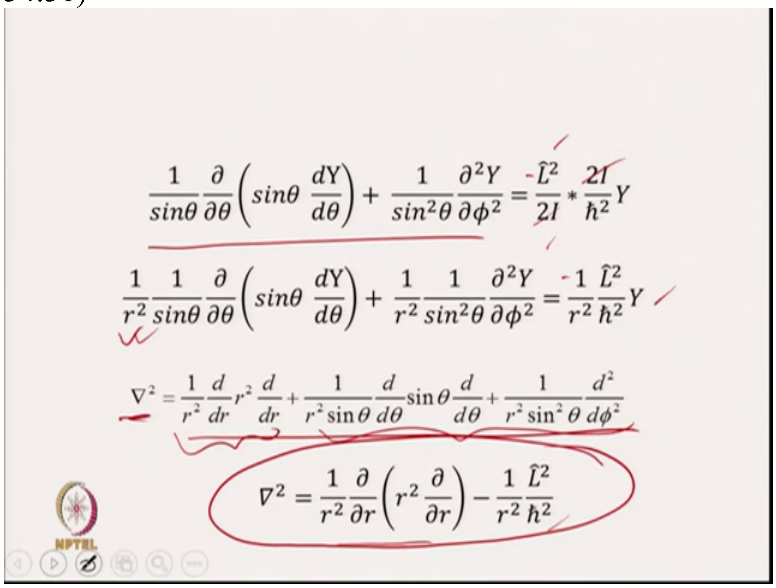

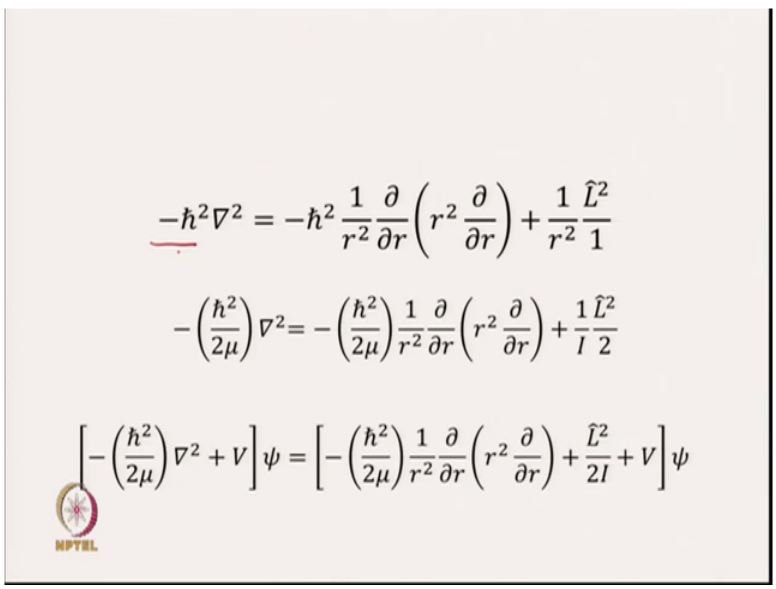

Now, if you look back, this is your Laplacian operator. Now what I am doing is, I am now multiplying by minus h cross square. So simply, I multiplied here and if you go back, there was h cross square, so this h cross square and this h cross square will cancel out. So I am writing one one. So l square operator by r square. And then, if you divide by 2, divide by 2 mu, which is reduced mass, then you will write minus h cross square by 2 mu. And here 1 by 2 mu r square, which is equal to 2 y and now I can write, whole Hamiltonian for the electron in a relative coordinate system. And this will be equal to your this expression. So why we are doing that, because what we are trying to do is, the terms which is function of theta and psy, we try to express in terms of angular momentum operator because we already know the solution of that, already know the solution of that and so if you put the values, which we obtained in the rotational spectroscopy, we need not have to separate, r theta and phy, r theta and phi and I will show you this.

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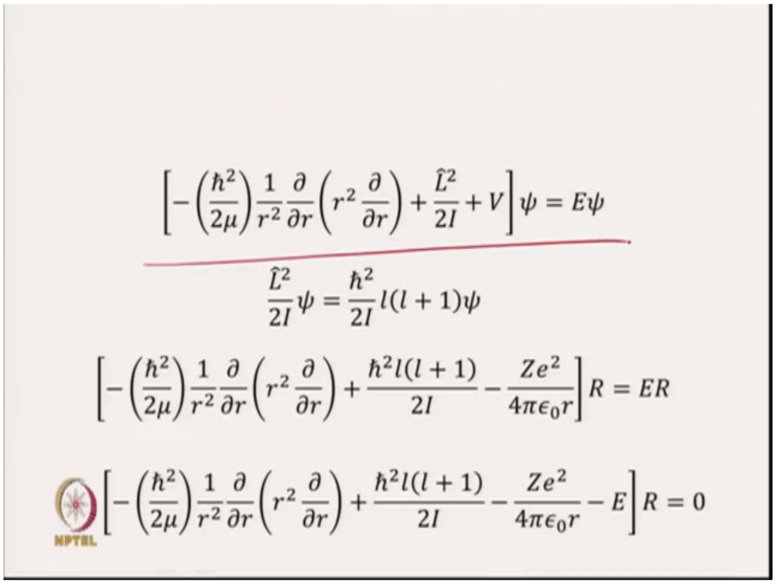

So this was the equation which I got in the last slide. And this was the expression which we derived when we were discussing rotational motion. So I am going to put it here. When I plug in here, I get this value. We get this value. Minus h cross square L, l plus 1 minus 1 by 2i. And now I put also the value of V. And this is your Schrodinger equation and if you take ER this side, your this differential equation and now it is easy to solve, it is easy to solve.

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$$\psi(\vec{r}) = \psi(r,\theta,\phi) = R(r)Y(\theta,\phi) = \frac{u(r)}{r}Y(\theta,\phi)$$

$$-\left(\frac{\hbar^2}{2\mu}\right)\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\frac{u(r)}{r}\right) + \left[\frac{\hbar^2 l(l+1)}{2I} - \frac{Ze^2}{4\pi\epsilon_0 r} - E\right]\frac{u(r)}{r} = 0$$

$$\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\frac{u(r)}{r}\right) = \frac{\partial}{\partial r}\left(r^2\left(\frac{1}{r}\frac{\partial u(r)}{\partial r} - \frac{u(r)}{r^2}\right)\right)$$

$$\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\frac{u(r)}{r}\right) = \frac{\partial}{\partial r}\left(r^2\left(\frac{1}{r}\frac{\partial u(r)}{\partial r} - \frac{u(r)}{r^2}\right)\right)$$

Now let us see, how we will solve it. Again I will make another simplification. What we will do is, already we express the psy which is basically as a function of r and this relative motion coordinate system. This psy is a function of r theta phi. And we are separating this in terms of r r into spherical harmonics. And now what we are going to do is just put this r, this radial wave function in terms of u r by r. u is another function of r divided by r.

Again we are going to simplify it, nothing else. So when you do that, what you are going to get is; you see here, I have got here is your psy r, u r by r and here again psy r by u r. That is what I have done. Now good thing is, if you do that, this will be further simplified. And that is why we did it. So how does it look like when I put psy r as u r by r. So see here, del by del r, r square, del by del r , u r by r is equal to del by del r, r square, and now differentiate this. First differential we are doing so 1 bye r of u r by r minus, this will be plus, but since so u r will take as a constant.

And differential of 1 by r with respect to r will be minus 1 by r square. So minus term comes here. So u r by r square. So this is for this differential. You will get this term. If I do this differential, I will get this term. Now what I will do, I will multiply by r square. So that is what we are doing, multiplying by R square.

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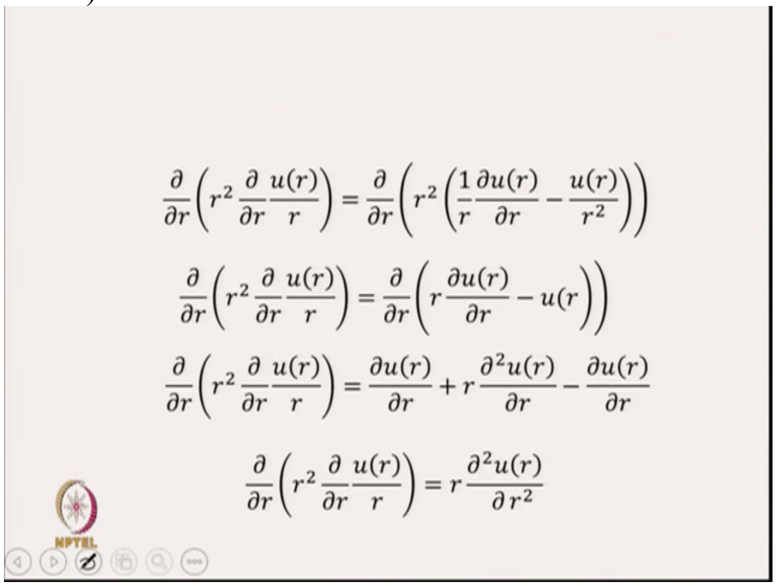

And as we multiply by r square, what we are going to see? So this is the same thing what I have got in the previous slide. We have to multiply by r square. When we do that, what we will get is r square by r is r and u r by r square is u r. Now if I do this differential, what I am going to get is del r by del r cancels out. So del ur by del r. Now what I will do is, I take R constant, and take differential for this. So plus r del 2 u by del r and minus, now for this second term differential; del u r by del r. Now you see, this terms cancels out. So this whole term becomes r into del square ur by d r. So now you will understand why we replaced the R with ur divided by small r.

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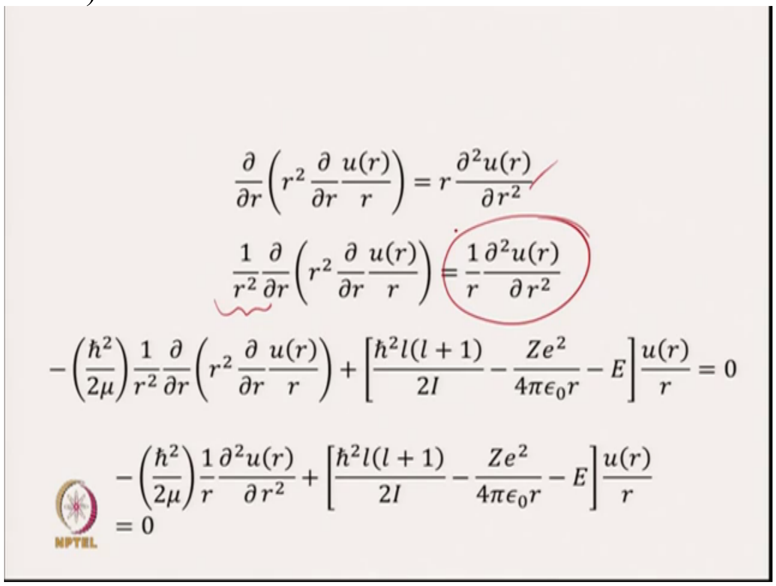

So wave function, radial wave function, R by your u which is a function of R divided by small r. Now we have got this. Let us multiply by 1 by r square. When we do that, we will get this equation, 1 by r del square ur by del r. Now this was the equation, which we got earlier. And this we have already solved. This whole thing, and so I am going to put this in place of this. And when I do that this is our new Schrodinger equation. This is our new Schrodinger equation. I have done nothing, I have simply plugged in the value obtained here in this equation. So this is the thing which we get.

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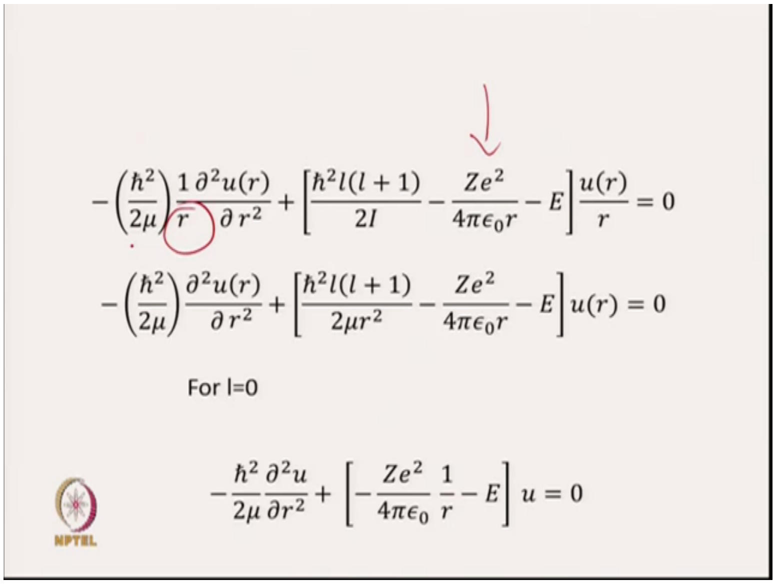

Now again this is from the previous slide. This equation I have got from a previous slide. Now let us look at this. This has, this two r terms. So there are 2 terms in this equation. Both have small r in the denominator but since small r is not going to be infinity and so the other part must be equal to 0. And that is what we are going to write. So we just remove the small r from the denominator. Now, we are going to see the solution.

So what we will do is, we will, you see again this is a complicated equation. So the way I simplify it is; let us go and see, what will be its differential equation for different value of l. You see there are different values of l. This expression has l Quantum number. So what I am going to do is - write the differential equation for different value of l and then start with a equation which is a guess equation and then you try to find out the second differential and see what value of E and wave function you get. So if I take l is equal to 0, this whole things goes away. And then we have this differential equation, for which I am going to see the solution.

So let us look for solution of differential equation for l is equal to 0. If you go back again, this differential equation if you see, this is your second order differential with respect to r. The second term has 1 by R and third term is your constant. In fact, we know the solution of this kind of differential equation and that is why I first put l is equal to 0 and I am trying to look at the solution. And these are the very well known differential equation, so solution is already known.

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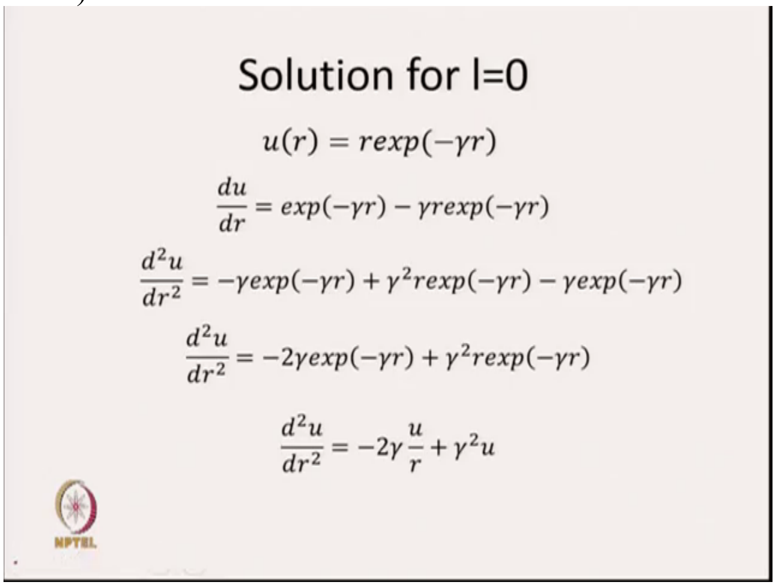

What is the solution? Solution is your ur is equal to r exponential minus some constant multiplied by r. This is your constant. Now let us see what we get, when we differentiate this. So let us do first differential. What you will get is, e del dr by, dr is 1. So this is constant, and you are differentiating first R.

So this will give you this quantity. Now what I am going to do? I am going to take R as constant. I am going to differentiate this and what we will get is minus gamma into exponential minus Gamma. So R multiplied by minus gamma exponential minus Gamma R. So this is your first differential. Now let us go and do, second differential. Differential for second expression is only 1 term. So this is exponential multiplied by differential of minus gamma R with respect to r and that will give you gamma minus.

Now differentiate for this one. Again I am going to take r as constant. If I take r as constant, what I am going to get is exponential minus gamma r and if I multiplied by the differential of minus gamma R, which is minus gamma. And you have minus gamma already here. So minus gamma into minus gamma is plus gamma square. So this when we have taken r as a constant. Now we will take this exponential term as a constant and we will differentiate r. So d r by dr is 1 and so you are going to get minus exponential minus gamma R.

And if you look at here, what we will get is gamma exponential minus gamma r, and minus exponential minus gamma r. So these 2 terms combine to give a minus 2 gamma exponential minus gamma r plus gamma square r exponential minus gamma r and that means that d 2 u by dr square is minus 2 gamma u by r plus gamma square into u and this is the kind of differential equation you have. So here you see, this is the second differential of u and this is your, with respect to r, and this is simply a constant multiplied by a function.

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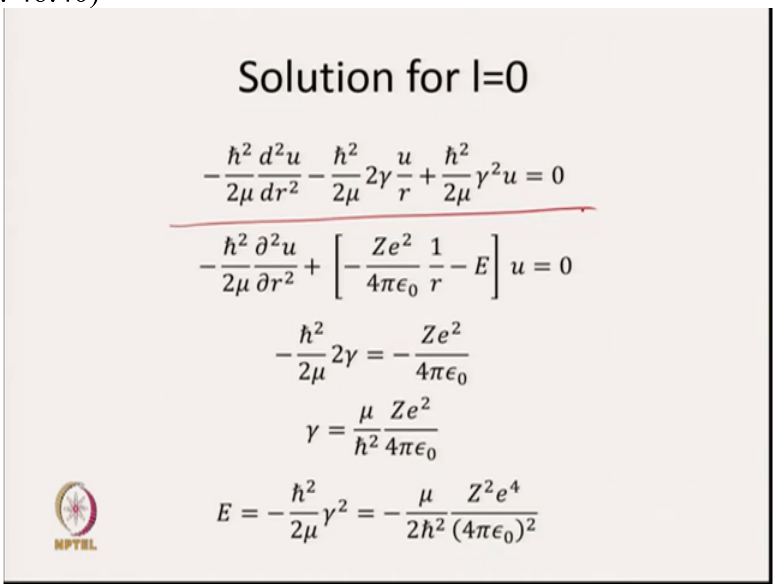

So let us compare the 2 equations. This was the equation which we got right now. So here, I have done, simply I multiplied this whole term by minus h cross square by 2 mu. So you are going to get this equation and now if I compare with the differential equation which I got for l is equal to 0, what I am going to get is. Let us see here, your this whole thing is equal to this whole thing with the minus sign. So minus h cross square by 2 mu into 2 gamma is equal to, or divided by r you could take or leave it, is equal to, minus Ze square by 4 pie epsilon naught.

So you can put r. r r cancels out, so that is all. So this is the first relationship which we got. So from this what you will get is the value of this gamma and gamma is equal to your Z e square by 4 pie epsilon naught minus minus cancels out. So 2 2 cancels out. So mu divided by h cross square, so this is value of gamma. Now the second comparison of this 2 terms will give you e is equal to minus h cross square by 2 mu gamma square and I have already known gamma. So you got the energy term. So this energy term which we have got after solving differential equation for l is equal to 0. So this is not only one solution. I will show you that there are more solution for l is equal to 0. So let us go, what will be the second solution?

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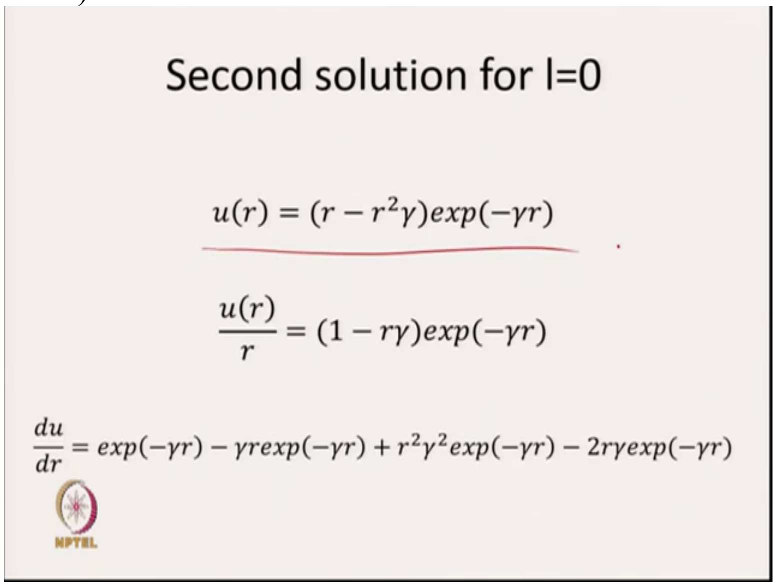

The second solution for l is equal to 0 is obtained when you take ur is equal to r minus r square gamma into exponential minus gamma r. So ur divided by r is equal to 1 minus r gamma exponential minus gamma r. So now let us do, differentiate this with respect to r. What I will get is, first thing you have to differentiate is r exponential minus gamma r. For that, if I differentiate r keeping this constant, then I will get exponential minus gamma r.

Now I am taking r constant and differentiating this term. So r is here and differential of this is gamma exponential minus gamma r with minus sign. So this is for the first term. Now for the second term; r square gamma, first we have taken r square gamma as a constant and we differentiated exponential minus gamma r which will be minus gamma R, minus minus plus, so r square gamma square exponential minus gamma r and then now, you keep exponential minus gamma r constant and you differentiate r square, you are going to get this term. So this is your first differential.

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$$\frac{du}{dr} = exp(-\gamma r) - \gamma r exp(-\gamma r) + r^2\gamma^2 exp(-\gamma r) - 2r\gamma exp(-\gamma r)$$

$$\frac{d^2u}{dr^2} = -\gamma exp(-\gamma r) + \gamma^2 r exp(-\gamma r) - \gamma exp(-\gamma r) + 2r\gamma^2 exp(-\gamma r) - r^2\gamma^3 exp(-\gamma r) - 2\gamma exp(-\gamma r) + 2r\gamma^2 exp(-\gamma r)$$

$$\frac{d^2u}{dr^2} = -r^2\gamma^3 exp(-\gamma r) + 5\gamma^2 r exp(-\gamma r) - 4\gamma exp(-\gamma r)$$

$$\frac{d^2u}{dr^2} = -r^2\gamma^3 exp(-\gamma r) + \gamma^2 r exp(-\gamma r) + 4\gamma^2 r exp(-\gamma r) - 4\gamma exp(-\gamma r)$$

Now you can also do your second differential. If you do second differential for this you are going to get this term. For gamma r exponential, gamma r, this you will get 1. You take r as constant. This you will get when you take exponential minus gamma r as constant. So this is for two terms. Now let us see r square gamma square. So if we take exponential minus gamma r constant, you will get this. If I take r square as constant then I will this.

Now for the third term. So first one when I take exponential minus gamma r as a constant and second I will get when and second I will get when I take r as a constant. So there are 7 terms. But lot of them are common, so you see this one, this one, and so gamma exponential and you see this term. So these 3 are common. So you get minus 4 gamma exponential minus gamma r. Let us look at r square gamma 3. This is one term. So this gives you this term. And then you see gamma square, r gamma square and then r gamma square. 1, 2, 3 to 5, so this one, this one and this one, gives you 5.

5 r gamma square, or gamma square r, exponential minus gamma square and then you can also write this as this 5 have broken into 2 different term. 1 with 1 gamma square R exponential minus gamma r and another 4 gamma r exponential minus gamma r. Why I am doing that? Because now I have to replace this exponential term with u r and see how we can do that.

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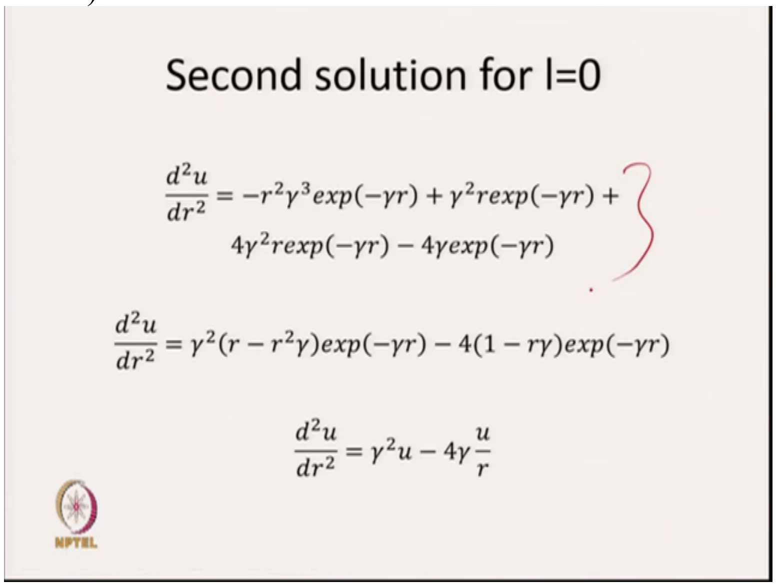

So this is the thing, which I have taken from the last slide and now you see you can take gamma square common. If I take gamma square common, I will get, you see in these 2, if I take gamma square common, you will get r minus r square gamma and exponential minus gamma r and now in this 2, you can take 4 common. So minus 4 if I take. Here you see it is 1. This will be 4 gamma, 4 gamma. 1 minus R gamma exponential minus gamma r and this one is your u and this one is your u by r and so you have this equation, del 2 u by d r square u minus 4 gamma into u by r and now you can see that, this is also a solution.

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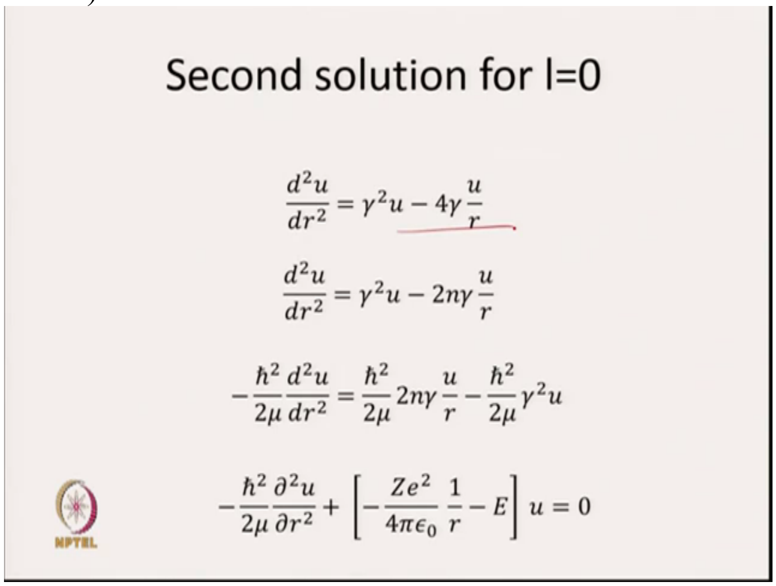

So d 2 u by d r square is this. Gamma square u minus 4 gamma u by r and d2u by d square f r square is equal to gamma square u minus 2 n gamma u by r. So what we have done is; you remember that first solution is basically the solution for the ground state and the second equation, second solution; this is basically solution for the first excited state which is where n is equal to 2. So if I take n is equal to 2, this will be equal to 4 and in that case, we can have this differential equation and I compare with the differential equation which I got for l is equal to 0.

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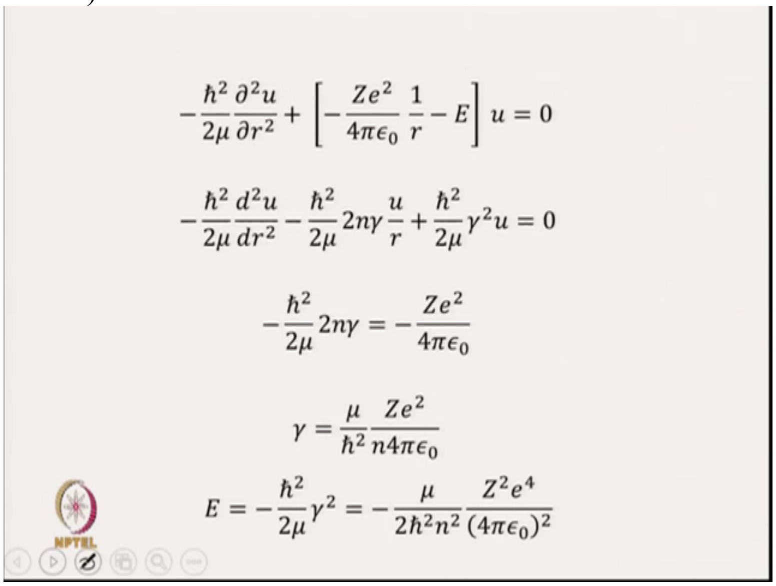

Let us see what we are going to get? We are going to get here you this, make a, these are the 2 equations. We are going to make the comparison. So u by r term, u by r term is this and u by r term is this. Now you can see gamma is equal to this whole thing. So here gamma is almost similar to gamma obtained in the first case, except that there is n here and that n was 1. When we solved, when you proposed the first equation and if I put this gamma to calculate e, what I am going to get is a term which is function of m.

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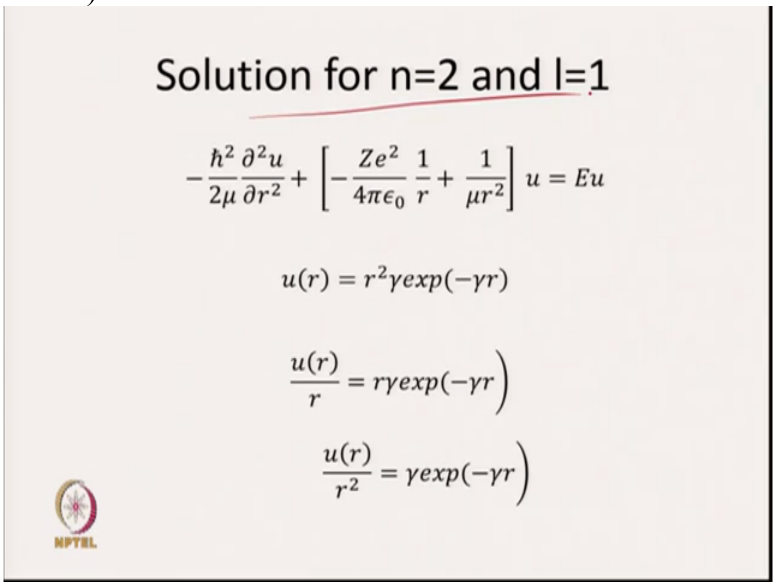

Now this we have done for l is equal to 0. Now we will look at what is the solution for L is equal to 2 and l is equal to 1 or maybe just a solution for l is equal to 1. So when we put L is equal to 1, this is the differential equation which we are going to get and again we know this and solution can be given by this function, ur is r square gamma exponential minus gamma r. So ur by r is r gamma exponential minus gamma r ur by r exponential square is gamma exponential minus gamma r.

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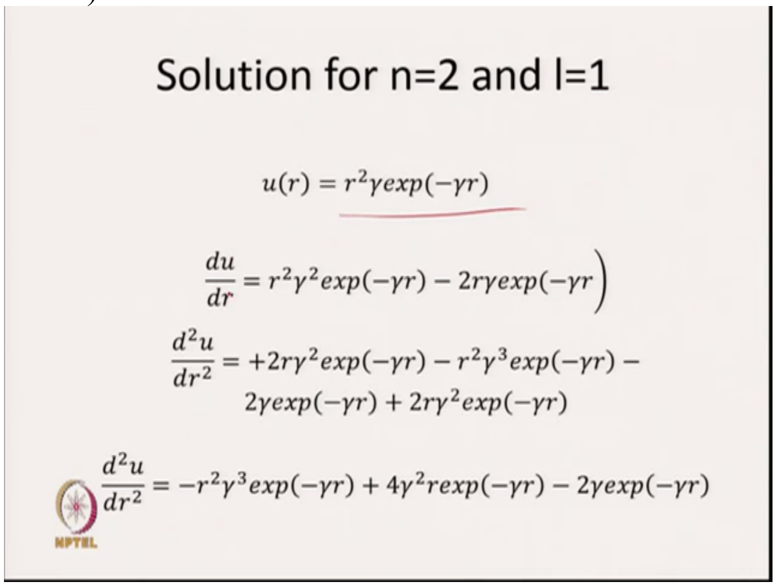

So let us see, what will be the first differential. So this is R square gamma exponential minus gamma r. If you take differential of u with respect to r. So here r square is constant, what you will get is gamma square exponential minus gamma r and then here, what you are going to get is minus 2 gamma r exponential minus gamma r and there is one problem here, and there should be minus here and there should be plus here.

So R square gamma square, yes. So this should be minus, this should be plus. d 2 u by dr square will be what? 2 r gamma square exponential minus gamma r. So first we are doing for r square. So let us take this. So 2 r gamma square exponential minus gamma r. Now we will take r square constant, so minus r square gamma square into minus gamma. So minus minus plus.

So this will be plus r square gamma exponential minus gamma r Now let us do the differential of this. So first we will do differential with respect to r, then we will get this one and if you do differential of this with respect to exponential gamma r then we will get minus 2 r gamma square exponential minus gamma r. So this is minus 2 r gamma square.

So this is minus 4 r gamma square. And this is your R square gamma 3 plus exponential minus gamma r. And this is plus 2 gamma exponential minus gamma. So same thing I have written, because there are 2 terms here which are the same

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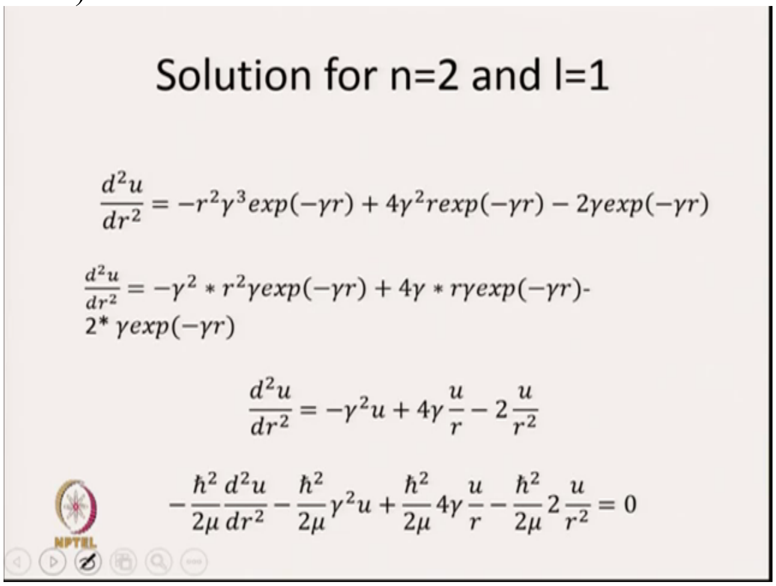

Now del 2 u by del r square is equal to, you just simply write down as r square gamma 3 plus. So here Change the sign plus, this will be in minus. This will be plus. So here, we are again writing same thing. So gamma square into only thing what I am trying to write is this is your u. So and this is your u by r, so you write like this. So plus, this is your minus, and this is your plus. So del 2 u by del r square is plus gamma square u minus 4 gamma u by r and plus 2 u by r square and if you bring that here, this side, so you the and multiply by H cross square by 2 mu minus h.

So this is first term. This is plus multiplied by minus. If you bring it this side, what you will get is square mu square u. And then h cross square by 2 mu 4 gamma u by r minus h cross square by 2 mu by r square is equal to 0.

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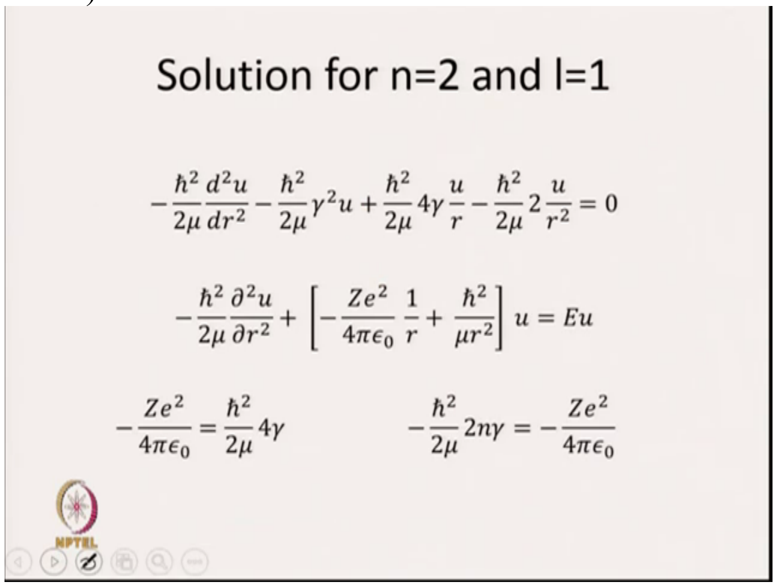

Let us see the equation, sign is okay. Gamma square mu minus, so minus is here, so this should be plus. This should be plus. This should be minus. So here, this should be minus h cross square by 2 mu. So here, minus minus plus. So here minus and this will be plus. So this is equal to 0.

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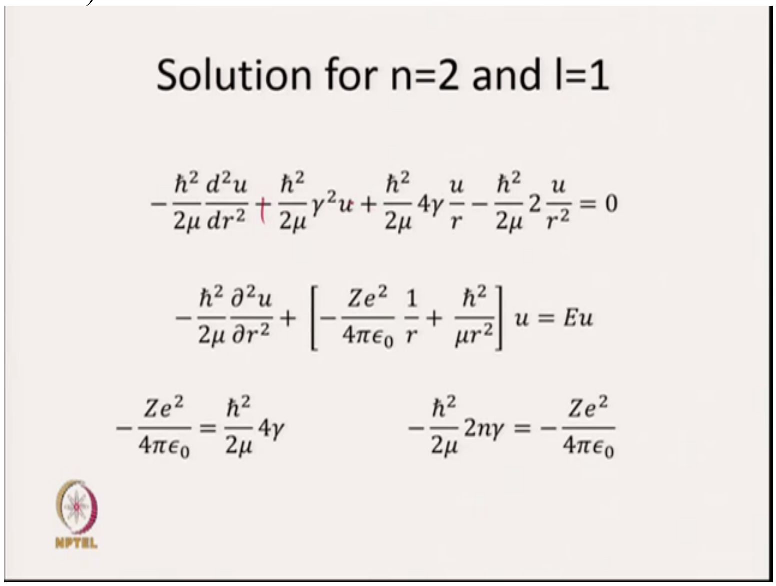

So let us sign change it, this is minus, this is plus and then you compare with this. If you compare with this, then what you are going to get it is, this is u term, then your minus Ze square 4 pie epsilon naught is equal to, you see, this is minus h cross square by 2 mu 4 gamma and now here you see that h cross square by 2 mu 2 n gamma is equal to minus Ze square by 4 pie epsilon naught. So I am writing same thing but minus sign, this is minus sign, this is right.

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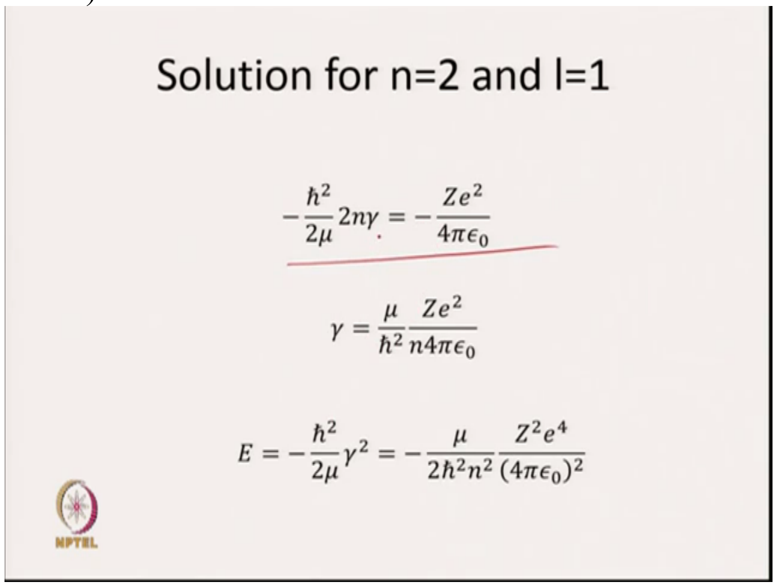

So this is one equation and this is from this, you can get this gamma in terms of and then e is equal to… if you remember then e is equal to, where is e? So this is minus e, so e will be equal to minus h cross square by 2 mu gamma square and so you will get this equation. What you will notice is the energy in all these 3 solution does not depend on value of h. It only depends on value of n and this is one of the very important thing about the energy of different electronic levels of hydrogen atom.

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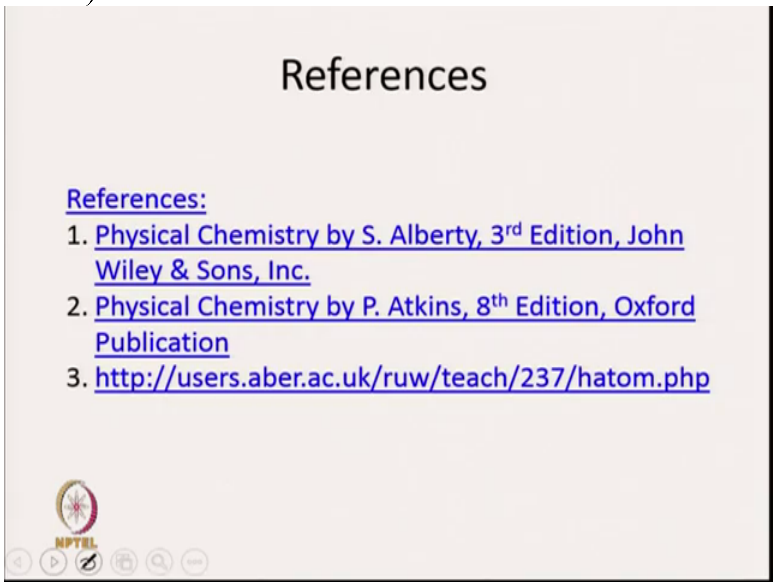

So I discussed today, how to calculate energy of hydrogen atom or hydrogen like atoms. The next class we will discuss if there are more than one electron, then how to calculate the energy of different energy levels and then after that we will go different to look at the atomic spectra of other elements and thank you very much for listening.