Quantum Chemistry of Atoms and Molecules
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Lecture-24
Hydrogen Atom: Schrodinger Equation

We finally begin the discussion that we have been promising from the beginning of this course. We talk about the first atom the atom, hydrogen atom where Schrodinger equation can be solved well you can be solved did I just say that. Let us not say easily so I hope all of us are as happy as this pretty little nucleus here.

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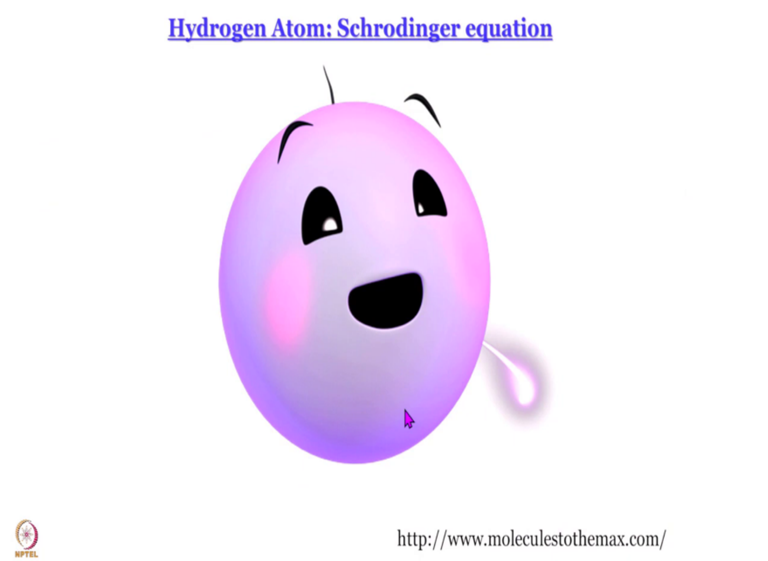

We have got the cartoon from this website and the reason why I put it here is to remind ourselves that in all this discussion of quantum mechanics that we have done. We said at the very beginning that Rutherford model had shortcomings but the experiment was right the experiment form performed by Rutherford students Marsden you might remember we had talked about it in the very first module that experimental result was not wrong.

It said that almost all the mass and all the positive charge of the atom is centralized on this big fat and in this cartoon happy nucleus and the electron goes around it. Now the only thing that we have shed from there is that the electron goes around in circles or the electron goes around in ellipses or we have shed the we have said any pretense of being able to say what kind of trajectory the electron has in the atom that we cannot say right.

But the essential model is that you have a heavy nucleus at the center and in the rest of the atom which is mostly void you have our electron. And this electron wave function is obtained by the Schrodinger equation that is what we are going to discuss over quite a few modules after this. And in all this discussion techniques that we are learnt earlier in free particle, particle in a box, tunneling, a simple harmonic oscillator, rigid rotor everything is going to come handy.

That is why we discussed all these systems before getting into the first real chemical system that is hydrogen atom. So, perhaps this is not even required anymore because we have done so much.

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Recapitulation: Basics of Quantum Mechanics

- Schrödinger equation: Classical wave equation for de Broglie waves
- Eigenvalue equation: $\hat{A}\psi = a\psi$
- Expectation values: $\dfrac{\int \psi^* \hat{A}\psi d\tau}{\int \psi^* \psi d\tau}$
- Boundary conditions: Quantization

But just to recapitulate Schrodinger equation lest we forget is really a classical wave equation for de Broglie waves essentially it is an eigenvalue equation where you have an operator operating on a wave function to give you back the same wave function multiplied by a constant. This wave function is called an eigenfunction of the operator the operator we use in Schrodinger equation is Hamiltonian operator total energy operator.

So the eigenvalue that you get is the value of energy. Expectation value as we have discussed is integral Psi star Psi d tau divided by integral Psi star Psi d tau well if Psi Psi star is normalized as a well behaved wave function would be then denominator would be one anyway. And most important thing is we have learned that quantization does not fall from the sky unlike Bohr model quantization arises naturally when we use boundary conditions.

And we have to use boundary conditions because we are working within the ambit of Born interpretation that these waves are probability waves. Psi Psi star is a probability density right this is what we need to remember and use as we go from here all right.

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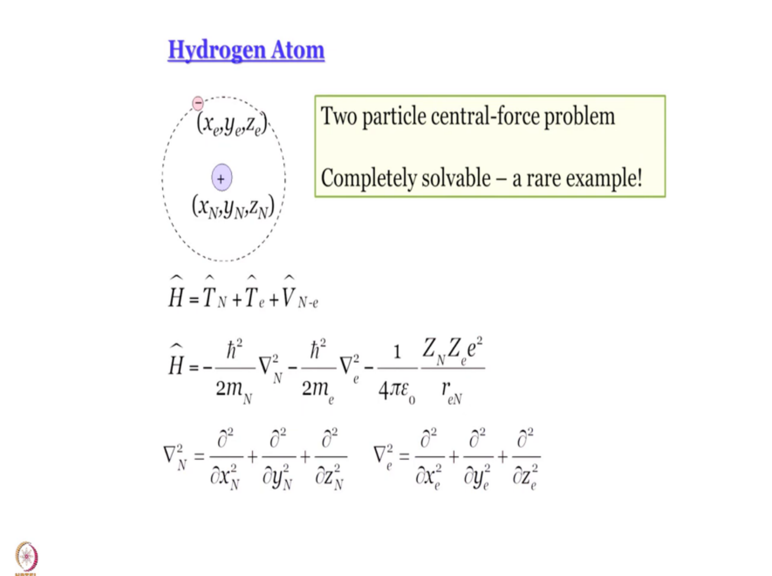

So, the first thing to do is to build the model of hydrogen atom and the model as you said earlier comes from your Marsdenns experiment. There is a nucleus let us say the coordinates of the nucleus are xn and yn and zn and there is an electron xe ye ze this dotted circle is as you can just neglect it for now. So, it is a two particle central force problem well the outer circle is not completely relevant what is it, why am I calling it a central force problem?

Because the electron no matter where the electron is on the circle the potential energy will be the same potential energy is directed towards the center of the circle, the nucleus. So, it is a central force problem and we will see in a couple of minutes how that greatly influences our choice of coordinate system. Alright so we will take baby steps let us try to write the Hamiltonian in the simplest possible form.

The Hamiltonian of course would have three terms first is the kinetic energy operator for the nucleus. Second kinetic energy operator for the electron and finally the potential energy between the nuke the nucleus and the electron that is what your Hamiltonian would look like. So, since we know what the kinetic energy operators are we can expand a little bit instead of T N we can write minus h cross square by 2 m n del n square.

So del n square is the Laplacian for the nucleus instead of T e we can write minus h cross square by 2 m e del e square e for electron minus well we do not always do this because it is just a constant but to keep it in SI unit and we are following Atkin's convention here minus 1 by 4 PI epsilon 0 Z n z e square by r eN what is Z n? Z n is this capital Z remember there is not this small z here. Z n is where ZN e is the nuclear charge e is the fundamental unit of charge Z e into e is the electronic charge of course it is going to be one well minus one and re N is the separation instantaneously separation between the nucleus and the electron.

So that is the Hamiltonian and rest we forget the Laplacian's are essentially del 2 del x 2 plus del 2 del y 2 plus del 2 del x del Z 2 with the appropriate subscript subscript nucleus and for nucleus and e for electron great.

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Hydrogen Atom

$$\hat{H} = -\frac{\hbar^2}{2m_N}\nabla_N^2 - \frac{\hbar^2}{2m_e}\nabla_e^2 - \frac{1}{4\pi\varepsilon_0}\frac{Z_N Z_e e^2}{r_{eN}}$$

$$\hat{H} = -\frac{\hbar^2}{2m_N}\nabla_N^2 - \frac{\hbar^2}{2m_e}\nabla_e^2 - \frac{QZe^2}{r_{eN}}$$

with $Z_N = Z$ $Z_e = 1$ and $\frac{1}{4\pi\varepsilon_0} = Q$

Schrödinger Equation

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

$$\Psi_{Total} = \Psi(x_N, y_N, z_N, x_e, y_e, z_e)$$

So, this is what it is now to simplify the notation a little bit we will write Z instead of Z n and for Z e we are going to write 1 ok. So, we will keep this minus charge explicitly will not write Z n if you wrote Z e equal to minus 1 this minus charge would have become plus charge well this minus sign would have become plus sign. So, we will write Z e equal to 1 and instead of this 1 by 4 PI epsilon 0 we could have written it 1 but let us just write Q for now.

So, with this the Hamiltonian becomes minus h cross square by 2 m N del N square - h cross square by 2 m e del e square – Q Z e square by r eN. Now if this is Hamiltonian what is Schrodinger equation h Psi equal to E Psi so let this h operate on Psi where n is a total I mean Psi of the two the entire atom I do not mean the; so this is still time independent not the time dependent part we got rid of the right time dependent part in one of the early modules.

We only work with time independent part of the wave function what Psi total means it is a wave function of the enter atom nucleus as well as electron. So, this Hamiltonian operating on Psi total gives us E total once again E total means the total energy of nucleus and electron multiplied by Psi total. So, the Psi total I hope is not very difficult to understand is a function of six coordinates xn and yn and Z N x e y e z e it is not enough to specify just the coordinates of electron or just the coordinates of a nucleus you need to know both.

Because you need to understand the interaction between the electron and the nucleus when talking about potential energy, so Psi total is really a function of six coordinates. Two pairs of xyz coordinates one for the nucleus one for the electron.

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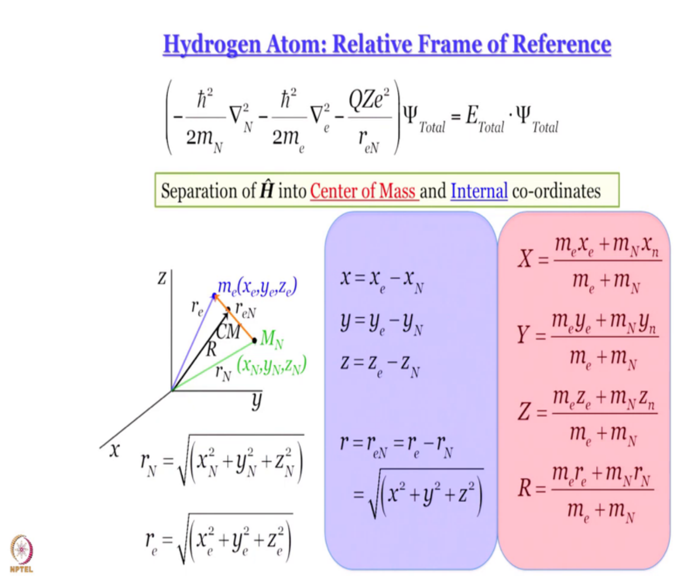

So, next part I will sort of skim through a little bit will not really go through all the math. So, first thing we need to do is we need to separate Hamiltonian into the motion of the center of mass and motion of electron with respect to the nucleus. Let us discuss the physics or the philosophy of it. Maths is little laborious there is no need to get into that at the moment. So, what you are seeing is this your atom consists of a nucleus and an electron.

The electron and nucleus move with respect to each other two body problem and we know how to reduce it to a one body problem by considering reduced mass. Question here I have a heavier body and a lighter body does the reduced mass resemble or is closer to that of the heavier body or the lighter body? Please work out let us say m1 equal to 1000 and m 2 equal to 1, what is reduced mass going to be is it going to be 1001 is it going to be 999 or is it going to be something close to 1. I leave you I leave it to you to figure that out.

When you do it you will see that it is actually closer to 1. So, we reduce this two body problem see it is like the Sun and the earth when we say the art goes about the Sun the Sun also goes about the earth. It is just that since Earth is much lighter than the Sun the effective mass in the system is like that of the earth. So, approximately we can say that Sun is stationary and the earth is going around the Sun.

Similarly here the electron is much, much lighter compared to the nucleus so the reduced mass will be close to the mass of electron and the problem essentially boils down to something with mass that is close to that of the electron going around a stationary nucleus that is what we are going to arrive at eventually. And the other thing is the entire atom is moving if you think of let us say the earth and Sun combined.

Are the only moving about each other the entire solar system is moving the entire galaxy is moving yeah so that motion has to be separated. Unless we separate we will have too many terms and will not be able to solve it. So, we have to separate the Hamiltonian into center of mass and internal coordinate remember it is not enough to do it in terms of nucleus and electron because the internal coordinates has both.

We are talking about potential energy so you need coordinates of nucleus as well in addition to that of the electron. But if you can figure out how the center of mass moves and how electron moves with respect to each other electron moves with respect to the nucleus these are two separate kinds of motion we should be able to separate them. So, let me just show you the definitions and not go through the math.

Let us say this is the position of the electron which has mass m e. This is for nucleus this is the center of mass let us say this diagram is definitely not to scale. So, this is the position vector of the nucleus r N position vector of the electron r e and you know how they are defined the position vector of CM. So, what we do is we define this kind of a system where x is equal to x e - x n, y equal to y e – y N, z equal to z e – z N what is that just think of the x coordinates. So, if this is the x coordinate of the nucleus this is the x coordinate of the electron x e – x N essentially is the separation of the electron and the nucleus in x direction, y ye - yn is the separation between electron and nucleus in the y direction same for z ok.

And this is this separation is the important parameter when you talk about potential energy this separation is important when you talk about the motion of electron with respect to the nucleus relative motion and this r is r e N so, that is the r e – r N do not forget that the vectors you get when you do the vector addition vector sum you get root over x square + y square + z square. So, these are the internal coordinates.

And these are the center of mass coordinates this is once again very standard techniques of rotational dynamics from classical physics. When you invariably have to separate translation from rotation lots of motions can take place lots of kinds of motion can take place at the same time. But you have to separate each kind of motion otherwise you cannot really formulate your problem. So, capital X capital Y Capital Z denote the position well mass weighted position with coordinates or the center of mass and capital R is also for the center of mass.

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Hydrogen Atom: Relative Frame of Reference

$$\left(-\frac{\hbar^2}{2m_N}\nabla_N^2-\frac{\hbar^2}{2m_e}\nabla_e^2-\frac{QZe^2}{r_{eN}}\right)\Psi_{Total}=E_{Total}\cdot\Psi_{Total}$$

$$\Downarrow$$

$$\left(-\frac{\hbar^2}{2M}\nabla_R^2-\frac{\hbar^2}{2\mu}\nabla_r^2-\frac{QZe^2}{r}\right)\Psi_{Total}=E_{Total}\cdot\Psi_{Total}$$

where $M=m_e+m_N$ and $\mu=\dfrac{m_e m_N}{m_e+m_N}$

Checkout Appendix-1

So what happens is that this Schrodinger equation in terms of electronic and nuclear coordinates can be rewritten in terms of your relative coordinates and center of mass coordinates. So, what we see is how you do it? I will just browse through the appendix one if you are interested in the detail you can go through it, it is not required for this course. But what is important is see the reason why we are two colors of highlights is that the first term is minus h cross square by 2 M capital M.

Remember Capital M is the total mass of the atom minus h cross square by 2 M del capital R square so this would be the kinetic energy term of the center of mass. The second term is minus h cross square by 2 mu what is mu? The reduced mass multiplied by delta small r square. So, the second term is the kinetic energy term of the electron with respect to the nucleus I am repeating this so many times because it is important to understand.

With respect to the nucleus I am not talking about motion of electron in the free space coordinate we are talking about movement of electron with respect to the nucleus does the separation with nucleus increase or decrease does x e – x N increase or decrease y e - y N z e minus z N what happens to those that is what we are dealing with ok. Please remember relative coordinate means how the electron is moving or what is the situation of the electron with respect to the nucleus.

So second term gives us the kinetic energy term in Hamiltonian for the motion of electron with respect to the nucleus third term minus Q Z e square by r, r remember is the separation between electron and nucleus. So, minus QZ e square by r obviously is well it always has been throughout the discussion the potential energy for interaction of electron with the nucleus. So, second and third terms together are in relative coordinates and they talk about the motion of movement of electron with respect to the nucleus.

The first term in a different color highlight is for the movement of the center of mass so Hamiltonian is nicely separated into two parts one for the center of mass one for the electron with respect to the nucleus.

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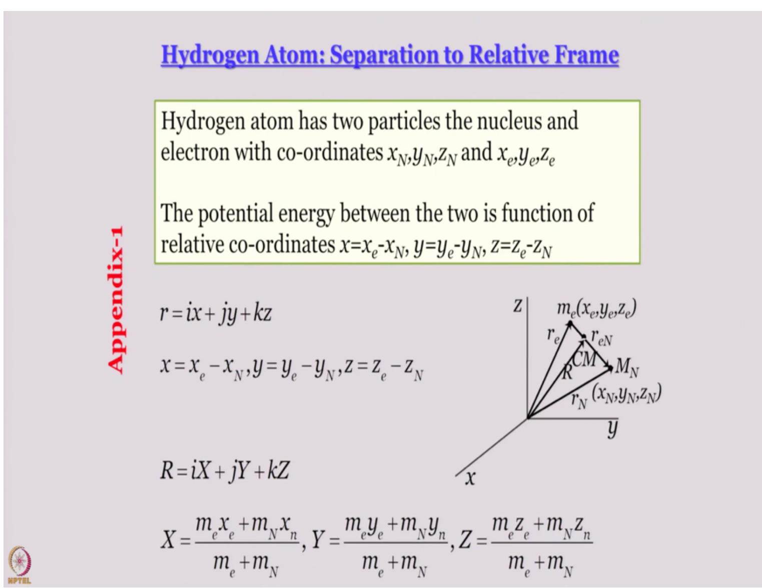

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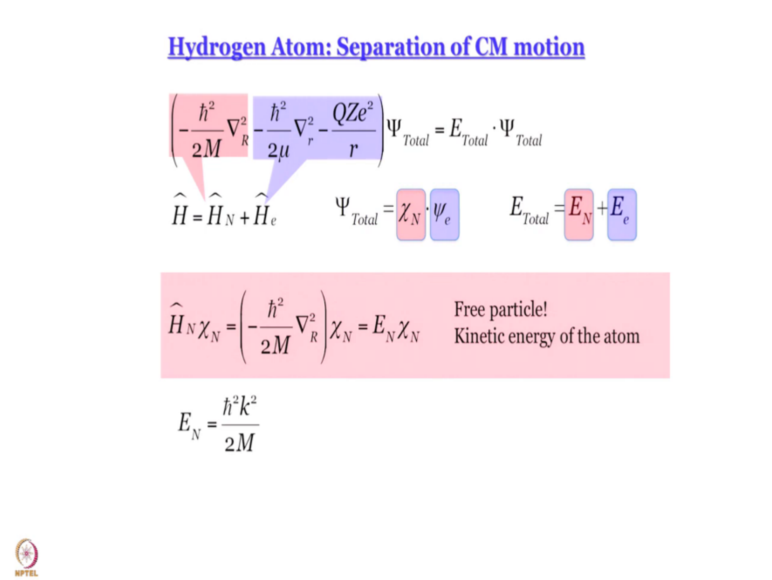

How this is how, so Hamiltonian is solid Hamiltonian can be written as H N + H e. 'N' for nucleus 'E' for electron with respect to nucleus now we have to worry about the wave function. What are we trying to do we are trying to do separation of variables. We are trying to separate the center of mass motion out and forget about it and worry only about the relative motion to do that we can conveniently well we have already said this.

We can conveniently write the Psi total as a product of two wave functions one function in the nuclear coordinates one function in the electronic coordinates relative coordinates this is what we have been doing from the beginning whenever we have a complicated situation. And whenever we are we want to break down a more complex equation into smaller simpler ones. So, now see minus h cross square by 2 m delta r square will operate on Chi N and Psi is going to be constant as far as it is concerned because it is a different coordinate system.

The second one H e will operate only on Psi e as far as it is concerned Chi N is going to be constant. We have once again encountered it as recently as when we wanted to separate theta and Phi for a rigid rotor remember. So, E total also can be written obviously as E N + E E so what we can do is I am not going through the steps of separation of variable because we have done it several times I hope or if you can do it.

If not please post your difficulty on the forum and we will try to address it. So, the first equation we get if you look at this highlight here is H N Chi N that is minus h cross square by 2 M del r square operating on Chi N no potential energy remember we are talking about one hydrogen atom we are not talking about a hydrogen atom that interacts with anything else that equal to E N Chi N only kinetic energy term is there.

So a system which has only kinetic energy term no potential energy potential energy is 0 have you encountered something like that yeah yes we did that is a free particle. A free particle is something that does not care about anything else in the universe does not have any potential energy to any interaction with anything else. So, this is what gives us an idea about how fast the atom as a whole is moving kinetic energy of the atom.

If you go back once again to the Sun-Earth combination it gives us an idea about how the combine of Earth and Sun is moving in space translation and motion and we know the energy do not we, what will be the energy E N, N means for the center of mass energy will be h cross k square divided by 2 M this is what we learned when we talked about the free particle and as we know k can take up any value including 0 yeah.

And this is it can take up any value so this is essentially for translational motion of the atom as well atom behaves as free particle that being said at the moment we do not care right. We have talked about free particles that is done and dusted.

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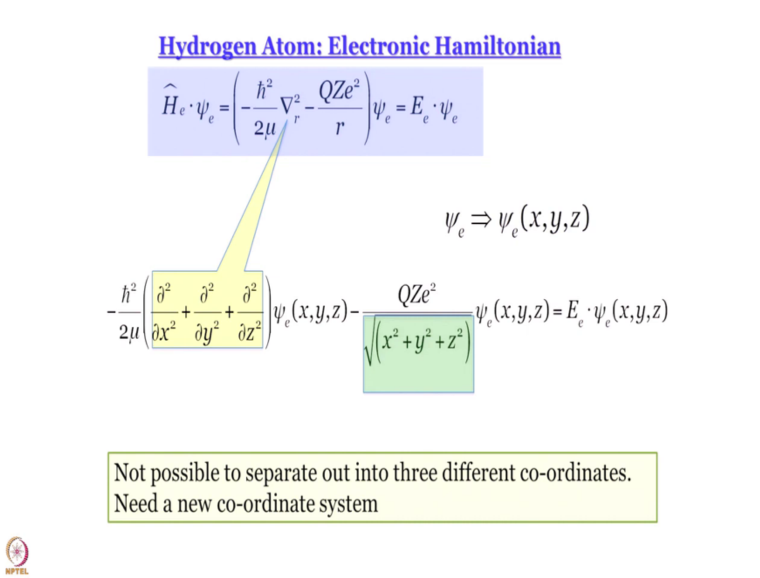

We are only interested at the moment in the electronic part of the Hamiltonian for the rest of the discussion this is what we are going to talk about. Electronic Hamiltonian or on the electronic wave function to give you electronic energy and this is energy of the electron in the field of hydrogen atom. So, H Psi operates on E Psi on sorry H e operates on Psi e to give you E e multiplied by Psi e. This is our hydrogen atom all right.

Now Cartesian coordinates is what we are most comfortable with so we know very well that the Laplacian is written as del del x 2 + del 2 del y 2 + del 2 del z 2 and even if we do that we can perhaps try to write Psi e as product of Psi ex Psi ey Psi ez and try to separate the variables. We would have been successful in doing it if the second term was not there. The second term is QZe minus QZ e square by r and r is square root of x square + y square + z square and that is a problem because this electronic wave function which is a function of x and y and z.

If you try to separate it out in terms of something like Psi e of x multiplied by Psi e of y and x Psi e of z this term in the Schrodinger equation is going to create a problem because you cannot break it down into something in x multiplied by something into y into something into z. How do you do that with square root of x square + y square + z square. So, because of this problematic term it is not possible to separate out the Hamiltonian into three different coordinates.

We cannot proceed further even with hydrogen atom if you want to stick to Cartesian coordinates so we need to use a new coordinate system what will this coordinate system be?

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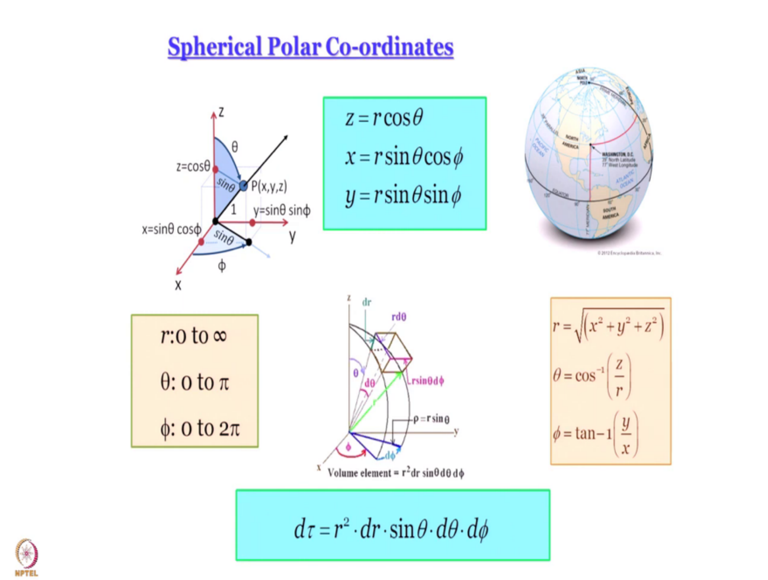

Well it is not really new; we are already familiar with it the coordinate system that we are going to use is spherical polar coordinates and as we know spherical polar coordinates and Cartesian coordinates are interrelated so once we know theta phi and r we can actually work out x y and z without much hassle. Z can be worked out by r cos theta x can be worked out from r sine theta cos Phi so on and so forth.

So if required we can go back to Cartesian coordinates also but it is easier to formulate the problem in spherical polar coordinates why? Because remember what was the problematic part in r formulation? The problematic part was that r in denominator r is square root of x square + y square + z square. So, we said we cannot separate it into something in x something in y something in z.

But here r itself is a coordinate in spherical polar coordinates that is the beauty of it. So, since r itself is a coordinate at least during formulation we do not have to worry about it that is point number one. Point number 2 is it makes perfect sense to formulate this problem in terms of spherical polar coordinates because as we said a little while ago it is a central field problem. The electron is attracted to the nucleus right.

So no matter where it is if you draw an arrow so that is the direction in which the attraction is central field problem. And central field problems are best handled in terms of spherical polar coordinates. So, this is what we are going to use and the next step of course then would be to convert the Laplacian into spherical polar coordinates right. Remember we have already done that when we talked about rigid rotor.

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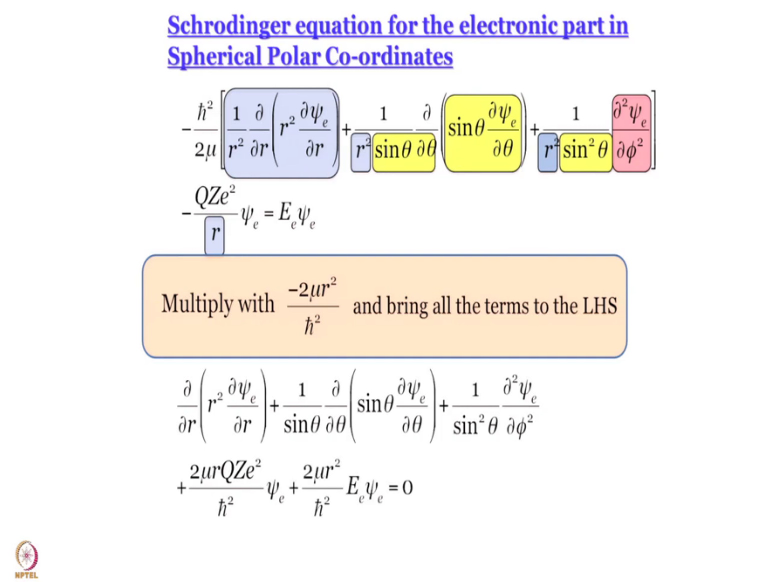

At least we pretended to do it what we said at that time is this here is the kinetic energy of in spherical coordinates and we showed you some appendix 2 remember appendix 2 it was called appendix 2 because originally it was here in this presentation. I lifted it and took it there. So, anyway axiomatically we take the kinetic energy operator in spherical coordinates multiply it by well this Laplacian, so multiply it by minus h cross square by 2 mu and to get the Hamiltonian we add minus QZ e square by r.

To get Schrodinger equation for the electronic part in spherical polar coordinates we make this Hamiltonian in spherical polar coordinates operate on Psi e to give us E into Psi. Now all this is in r all this is in theta all this is in Phi. What is the next thing to do? The next thing to do is to separate this into three equations one in r, one in theta, one in Phi. To do that again I will go through this a little quickly because we have done it many times.

But please do it yourself and make sure that everybody is on the same page. To start the separation we multiply with minus 2 mu r square divided by h cross why because I have this minus h cross square by 2 mu on this side and here we have r square multiplied by sine theta d Phi so if we do this then at least a little bit of cleaning up is there. The first term becomes del del r this one del del r multiply by del bel r operating on r square del Psi e del r.

The second term becomes well now this r square is gone 1 by sine theta del del theta operating on sine theta del Psi e del theta. What about the third term, we get 1 by sine square theta del 2 del Psi e del Phi 2. So, in the third term only there is a little bit of mixture of theta and Phi. The first time is only in terms of r second term is only terms of theta. Last term is only in terms of r and then what we do is we bring the term mean energy to the left hand side as well.

So all this is in r what does that mean before going further what it means perhaps is that the energy will depend only on r and nothing else it will not depend on theta and Phi. Of course it is a little premature to say this because we are still not separating the wave function into r theta Phi components but I hope it is not very difficult for you to understand that that is where we will inevitably be headed anyway.

So that is interesting and that takes us back to Rutherford's model. Remember in Rutherfod's model energy would depend only on the separation right what he called the radius of the orbit or Bohr's model. In Bohr actually worked out something where expression of energy was there and there was something in 1 by r squared right. So, now it appears that we will reach somewhere similar after all this sophisticated treatment. This is in theta and Phi.

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Separation of variables

$$\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi_e}{\partial r}\right)+\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi_e}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2\psi_e}{\partial\phi^2}$$

$$+\frac{2\mu rQZe^2}{\hbar^2}\psi_e+\frac{2\mu r^2}{\hbar^2}E_e\psi_e=0$$

$$\psi_e(r,\theta,\phi)\Rightarrow R(r)\cdot\Theta(\theta)\cdot\Phi(\phi)$$

$$\psi_e\Rightarrow R\cdot\Theta\cdot\Phi$$

$$\frac{\partial}{\partial r}\left(r^2\frac{\partial(R\cdot\Theta\cdot\Phi)}{\partial r}\right)+\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial(R\cdot\Theta\cdot\Phi)}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2(R\cdot\Theta\cdot\Phi)}{\partial\phi^2}$$

$$+\frac{2\mu rQZe^2}{\hbar^2}(R\cdot\Theta\cdot\Phi)+\frac{2\mu r^2}{\hbar^2}E_e(R\cdot\Theta\cdot\Phi)=0$$

So what we have is we have one part in r one part in theta and Phi. So, we can take them to different sites if we write the wave function as capital R which is a function of R capital theta which is a function of theta capital Phi which is a function of Phi and for the rest of the module we just write it as capital R into capital theta into capital Phi. So, you know how to do the separation I will not say all that we just do the separation do the differentiation.

I just do one maybe when you differentiate with respect to R capital theta capital Phi are not functions of R so they come out and you're left with del capital R del r only.

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Separation of variables

$$(\Theta\cdot\Phi)\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right)+(R\cdot\Phi)\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta}{\partial\theta}\right)+(R\cdot\Theta)\frac{1}{\sin^2\theta}\frac{\partial^2\Phi}{\partial\phi^2}$$

$$+\frac{2\mu rQZe^2}{\hbar^2}(R\cdot\Theta\cdot\Phi)+\frac{2\mu r^2}{\hbar^2}E_e(R\cdot\Theta\cdot\Phi)=0$$

Multiply with $\frac{1}{R\cdot\Theta\cdot\Phi}$

$$\frac{1}{R}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right)+\frac{1}{\Theta}\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta}{\partial\theta}\right)+\frac{1}{\Phi}\frac{1}{\sin^2\theta}\frac{\partial^2\Phi}{\partial\phi^2}$$

$$+\frac{2\mu rQZe^2}{\hbar^2}+\frac{2\mu r^2}{\hbar^2}E_e=0$$

Similarly these functions come out and now this is what you get how do you get the terms together just multiply with 1 by capital R capital theta capital Phi like what we have done for rigid rotor. And then you get on the left hand side one by capital R del del R operating on R square del R del r plus 1 by capital theta into 1 by sine theta del del theta operating on sine theta del capital theta del theta + 1 by capital Phi 1 by sine square theta del 2 capital Phi del Phi 2 plus 2 mu R QZ e square by h cross square + 2 mu r square by h cross square E e equal to 0. E means electronic energy.

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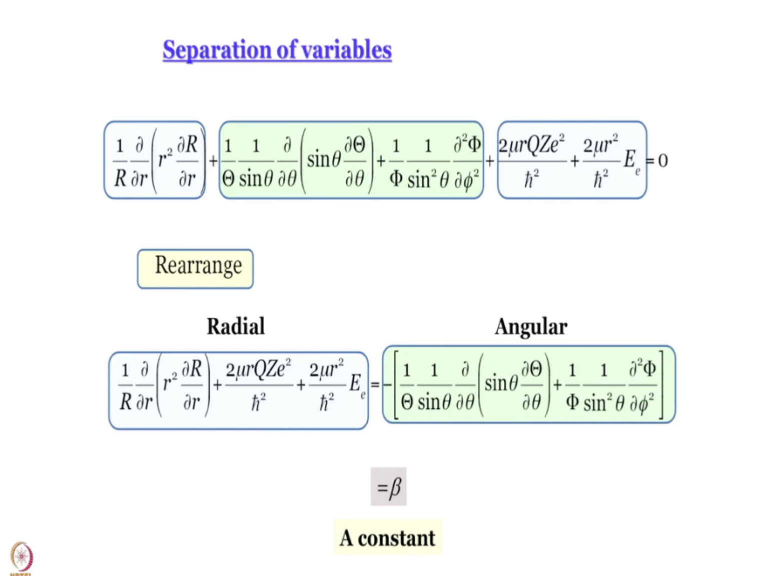

So, just rearrange it a little bit take everything in are together on one Psi take everything in theta and Phi on one Psi you get 1 upon rearrangement you get this. So, left hand side is entirely in terms of the radius R so you call it the radial part right hand side is only in terms of theta and Phi angles we call it angular part. So, as usual we equate it to an constant beta because otherwise something that is function of R but not Theta Phi cannot be equal to something that is function of theta and Phi but not R they have to be constant. So this beta is a constant that links radial and angular parts.

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Separation of variables

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

Radial equation

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

Angular equation

So we have been able to separate Schrodinger equation into a radial equation and an angular equation and the angular equation is familiar with to us. We have encountered it when we talked about rigid rotor remember. So, we know how to separate the angular equation into its component as well. So, that is what we are going to do in the next module and we are going to recapitulate what we have done in a rigid rotor and we will see how the quantum numbers emerge nicely from using boundary conditions in the subsequent discussion.