Basic Quantum Mechanics

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Module No. # 06

Hydrogen Atom and other Two Body Problem

Lecture No. # 02

The Two Body Problem

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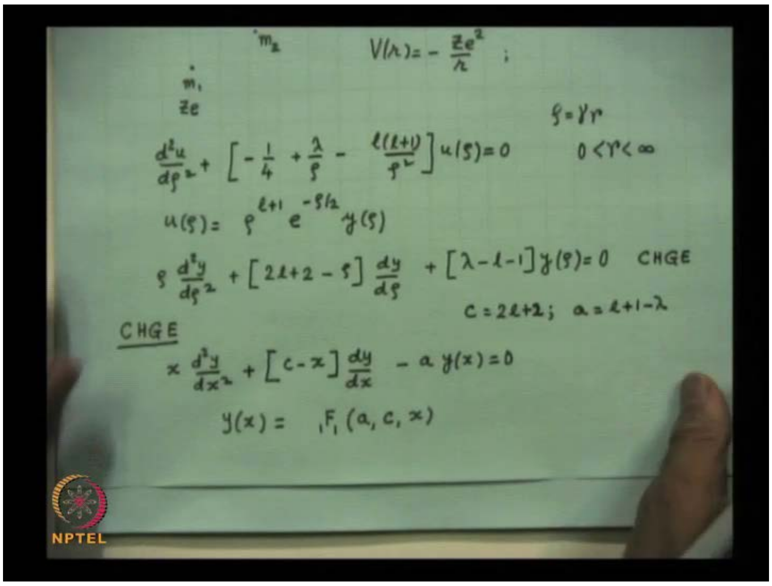

In our previous lecture, we had solved the hydrogen like atom problem, which was the simplest example of a two body problem, and we were considering two particles m 1 and m 2; m 2 would represent usually the electron, m 1 will have a charge of z e, and the potential energy function, was given by minus z e square by r, where z e is the charge of the nucleus. We found that the radial part of the Schrödinger equation, could be written as d 2 u by d rho square plus, since the energy was negative, 1 by 4, plus lambda by rho minus l into l plus 1 by rho square.

Now, we studied the small rho behavior of this equation, and the large rho behavior. That suggested that we should try out a solution of this form, u of rho is equal to rho to the power of l plus 1, minus rho by 2, times y of rho. Now, there is no approximation here, because I have defined y of rho by this equation. Then, we found that if we use this, then y of rho satisfies the following differential equation; rho d 2 y by d rho square plus, 2 l plus 2, minus rho, d y by d rho, plus lambda minus l minus 1, y of rho (Refer Slide Time: 02:37).

Now, if you would recollect some lectures back, we had discussed the confluent hyper geometric equation; confluent hyper geometric equation which was x d 2 y by d x square, plus c minus x, d y by d x, minus a of y of x is equal to 0. So, this tells us, that this equation is also a confluent hyper geometric equation. Of course, the independent variable is rho now, but c is equal to 2 l plus 2, and a, is equal to l plus 1 minus lambda. The well behaved, we have studied this equation in great detail. The well behaved solution of this, y of x at the origin, you must remember that rho was equal to gamma r, and r is the spherical polar coordinate, so r goes from 0 to infinity; not minus infinity to plus infinity.

So, r goes from 0 to infinity. So, y of x was one of the solutions is F 1 1, the well behaved solution is a c x.

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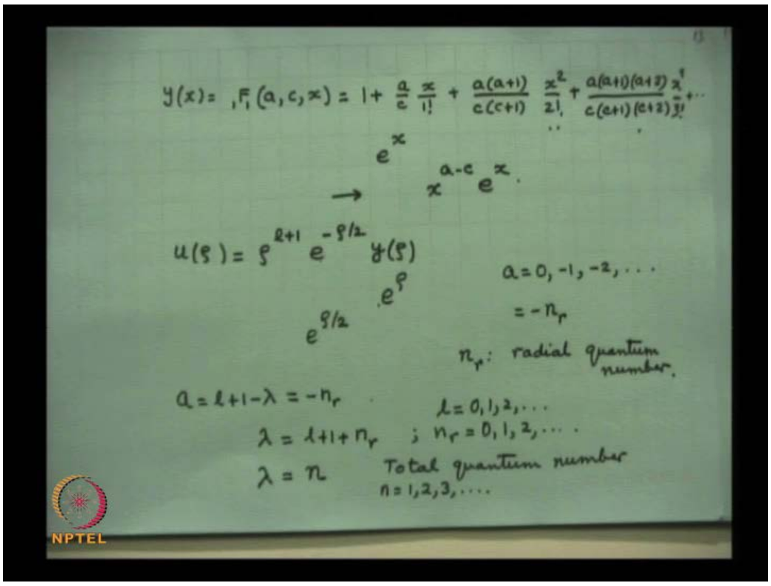

The well behaved solution is y of x is equal to F 1 1. This is the confluent hyper geometric function, and the series representing that, is very easy to remember; one plus a by c, x by 1 factorial, plus a into a plus 1 divided by c into c plus 1, x square by 2 factorial, plus a into a plus 2, plus 1, a plus 2 and so on, c into c plus 1 into c plus 2 etcetera, x cube by factorial three and so on.

Now, assume, as I had disused earlier, if a is equal to c, then this is just the series of e to the power of x. So, although the infinite series is convergent, but it blows up at infinity as e to the power of x. I repeat, although this infinite series is convergent, it blows up, it converges to a very large value for a large values of x.

So, in fact, the asymptotic form of F 1 c, this is x to the power of a minus c into e to the power of x. Now, you may recall that my u of rho function was rho to the power of l plus 1, e to the power of minus rho by 2 y of rho. Now, at large values of rho, this will behave as a to the power of rho. So, this multiplied by this, will become e to the power of rho by 2 and so although the infinite series is convergent, the wave function will blow up and that cannot happen. The wave function can otherwise it will not be normalizable.

So, it can be reduced to a polynomial only if a is 0 or minus 1 or minus 2 etcetera. So, we put this as minus n of r, where n of r is known as the radial quantum number. Radial quantum number therefore, we have, if we recall that we had here in this paper (Refer Slide Time: 07:53) the differential equation that we had obtained was the confluent hyper geometric equation with c is equal to 2 l plus 2 and a is equal to l plus 1 minus lambda.

So, we have now shown that for the solution to be well behaved, a must be 0 or a negative integer or I write that as minus n r. Since, a is equal to l plus 1 minus lambda. So, this is equal to minus n r. Please see this; I take lambda to this side and n r to this side. I get lambda is or is equal to l plus 1 plus n r where n r goes from 0, 1, 2, 3 to infinity, so this is because of l also, if you recollect is equal to 0, 1, 2, 3 etcetera.

This I write is equal to n, which is known as the total quantum number, and n can only take values; n can only take values of 1,2,3,4 etcetera. So, this is my total quantum number, so we have proved that for the wave function to be well behaved that is for the wave function not to blow up at infinity, lambda must be equal to an integer, and if you recall that lambda was equal to 2 mu e square by h cross gamma.

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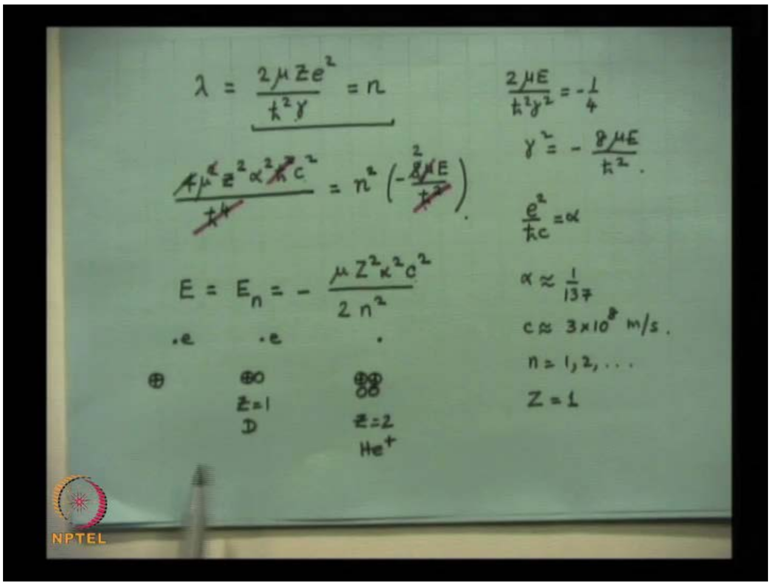

So, we write this down as this. Please, see this lambda was equal to 2 mu z e square by h cross square gamma. This must be equal to n and 2 mu E by h cross square gamma square. We have put equal to minus 1 by 4, so gamma square was equal to minus 8 mu E by h cross square.

So, if I square this, which is very easy, 4 mu square z square E 4. Now, I will do one more simplification, e square by h cross c is equal to alpha. So, this will be e square therefore, alpha square, h cross square, c square divided by, I have square this, so 4 mu square, z square, alpha square, h cross square, c square divided by h cross to the power of 4, n is equal to n square, gamma square, so gamma square is minus 8 mu E by h cross square.

Please see this; we have to do this little carefully. So, h cross square multiplied by h cross square by h cross 4. These two terms we will cancel out. 1 mu will cancel out with 1 mu and 4 divided by 8 is n 2. So, I will get E is equal to E n is equal to minus 4, this becomes two, so 2 n square, mu z square, alpha square c square.

You must check the dimensions. Alpha is a dimensionless parameter, z square is dimensionless, m c square, as you know from Einstein's equation, m c square is the energy. So, this is energy so that is alright.

So, this quantity is, therefore, these are the discrete energy states of the hydrogen atom and it is a remarkable time of the Schrödinger equation. Schrödinger obtained this in his very first paper in 1926. He wrote down the equation; he wrote a series of three papers on and which gave birth to the field of quantum mechanics or wave mechanics and in one of the papers, he introduced the Schrödinger equation and there he solved it for the hydrogen atom problem, and he obtain the discrete Eigen values from the solution of a differential equation. This is considered to be one of the greatest times of quantum mechanics.

From the solution of differential equation, one obtained the energy Eigen values of the hydrogen atom, which compared extremely well with the experimental data; the Balmer series, the Lyman series, the Paschen series. So, here you can see mu is the reduced mass, so as I had mentioned that for the hydrogen atom m e is the electron mass and m p is the proton mass.

So, for the hydrogen atom mu h is equal to, you may write it down if you feel like, m e m p by m e plus m p which is 9.1045 into 10 to the power of minus 31 k g and alpha as we know is about 1 over 137, c is approximately 3 into 10 to the power of 8 meters per second, and n can take values of 1, 2, 3 and for the hydrogen atom z is equal to 1. For the deuterium atom z is equal to 1, because the hydrogen atom is one proton and one electron, the deuterium atom is one proton and one neutron and the electron.

Here, also z is equal to 1 for the deuterium atom, for the helium atom the nucleus consists of the alpha particle, two protons and two neutrons. So, z is equal to 2 for the helium plus simply ionized helium atom has z is equal to 2 and of course, the mass of the nucleus is slightly different so that the reduced mass is different. Therefore, we will have so, these are the energy Eigen values and if you substitute it, substitute the values of mu that I wrote down and alpha that I wrote down and c etcetera and if I assume z to be 1.

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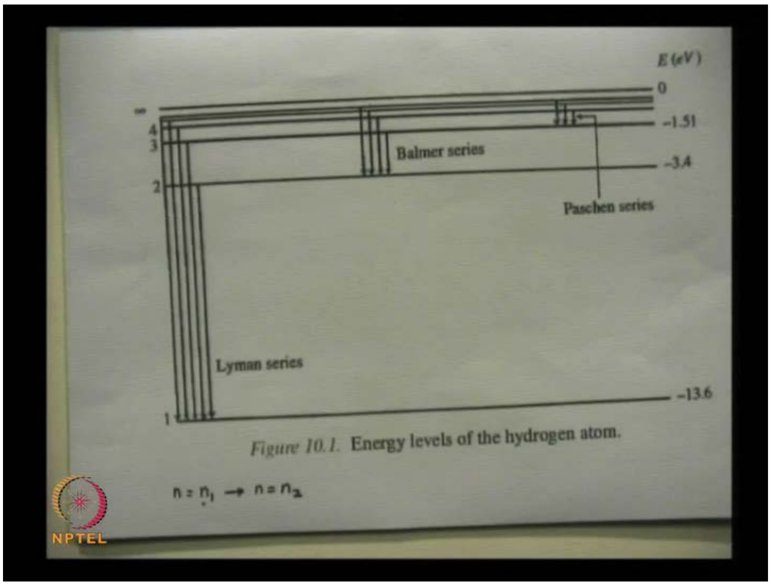

So, you get the lines, energy levels corresponding to the hydrogen atom. So, in a transition say from n is equal to n 1 to n is equal to n 2, when an atom makes a transition characterized by the total quantum number n 1 to a total quantum number n 2, a photon is emitted corresponding to the appropriate frequency or wave length.

So, when n 2 is 1, and n 1 is 2, 3, 4 etcetera, you get what is known as the Lyman series. When n 2 is 2 and n 1 is 3, 4, 5, 6, 7, 8 etcetera you get the Balmer series, and n 2 is equal to 3 and n 1 is 4, 5, 6 etcetera, then you get what is known as the Paschen series. These are the different series in atomic spectra and similarly, you will obtain the series for deuterium atom, the helium single ionized helium atom and the lithium atom.

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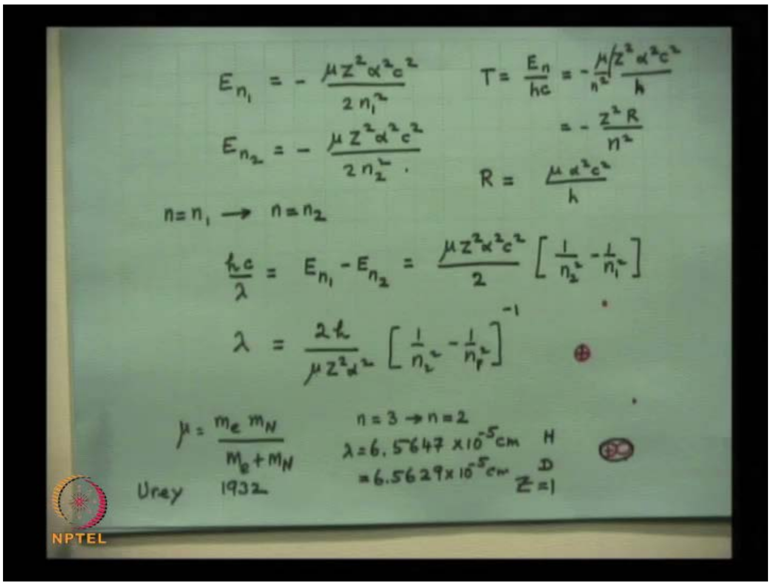

Now, from this we can calculate, if one makes a transition from n 1 to n 2. So, let me write it down that E n 1 is equal to minus mu z square, alpha square, c square by 2 n 1 square and E n 2 is equal to minus mu z square, alpha square c square by 2 n 2 square.

So, if I have a transition from n is equal to n 1 to n is equal to n 2, so you must write down, so the frequency of the wave light emitted will be h mu or h c by lambda is equal to E n 1 minus E n 2. So, this will be minus sign, so this will be mu z square alpha square c square by 2, 1 over n 2 square, minus 1 over n 1 square. So, the wave length of the emitted light will be c and these c will cancel out. So, you get 2 h by mu z square alpha square into 1 over n 2 square minus 1 over n 1 square raise to the power of minus 1.

Now, if I consider two atoms, one is the deuterium atom and the other is the hydrogen atom. As I mentioned, the hydrogen atom consists of one proton and one electron and the deuterium atom consists of one proton and one neutron.

So for both the cases z is equal to 1 but since the mass of the nucleus is larger here. So the reduced mass is m e m n of the nucleus divided by m e plus m n, so because mass of the nucleus is larger here, the reduced mass in the two problems will be slightly different. In fact, what was observed was that in one of the transitions, in n equal to 3 to n equal to 2 transition, which is in the Balmer series, I will leave it as an exercise for you to calculate; the wave length that is emitted was 6.5647. This is the visible regions 10 to the power of minus 5 centimeter and 6.5629 into 10 to the power of minus 5 centimeter, this is for the hydrogen atom and this is for the deuterium atom.

It was Urey, the chemist in 1932, who discovered the presence of another line, in the spectrum of hydrogen. They had similar lines as the hydrogen atom but they were slightly shifted. He measured that carefully and this was in the year 1932 when quantum mechanics was already discovered and he said that this is isotope hydrogen, and he calculated the reduced mass, and from which you can calculate the mass of the deuterium nucleus. Then he said that this must be due to an isotope of hydrogen.

So, it is through spectroscopy that the heavy water or heavy hydrogen was discovered. So, you have here for example, the Rydberg constant, you see the energy in spectroscopy is usually measured in centimeter inverse. So, we write this as a term value is equal to E n by h c. If I divide by h c, you will get minus mu z square alpha square c square by n square divided by h.

So, this the dimension of this is centimeter inverse, and this quantity is known as the Rydberg constant that is minus z square R divided by n square. So, where R is known as the Rydberg constant, which is equal to mu alpha square c square by h.

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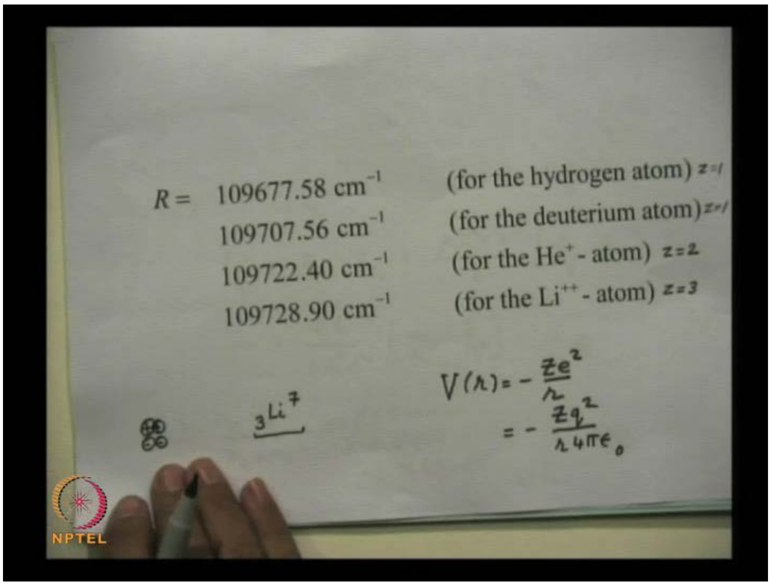

Because of the slight difference in the reduced mass the value of the Rydberg constant is slightly different. For the Rydberg constant is 1096 you may write it down if you feel like 109677.58 centimeter inverse for the hydrogen atom, 109707.56 centimeter inverse for the deuterium atom. Both of them are z is equal to 1. This is z is equal to 2 for the helium plus atom and this is doubly ionized lithium atom in which this is z is equal to 3.

Here for the example, for the helium plus atom you have two protons and two neutrons and because of two protons the nuclear helium atom consists of two electrons. If you take one electron out then you will have the helium plus atom.

Similarly, for 3 lithium 7 you have three protons and four neutrons. In this, one of the isotopes of three protons and so the mass number is seven, the atomic number is three. So, the for the neutral lithium atom, you will have three electrons, if you take two of them, you ionize two of them, then you will obtain a single electron atom but, z is equal to 3. Since, the mass is much heavier now the reduced mass is slightly larger and which results in a slightly different value of the Rydberg constant.

So, we have now obtained the solution of the Schrödinger equation, and the Eigen values spectrum correspond to the single electron atom, in which the potential energy function is given by minus z e square by r in the CGS system of units, and in the MKS system of units all that I have to do is replace e square by q square by 4 pi epsilon naught and that is it. And q is the charge of the electron in coulombs and z is the charge of the nucleus, so that completes the energy Eigen values spectrum of a one electron atom.

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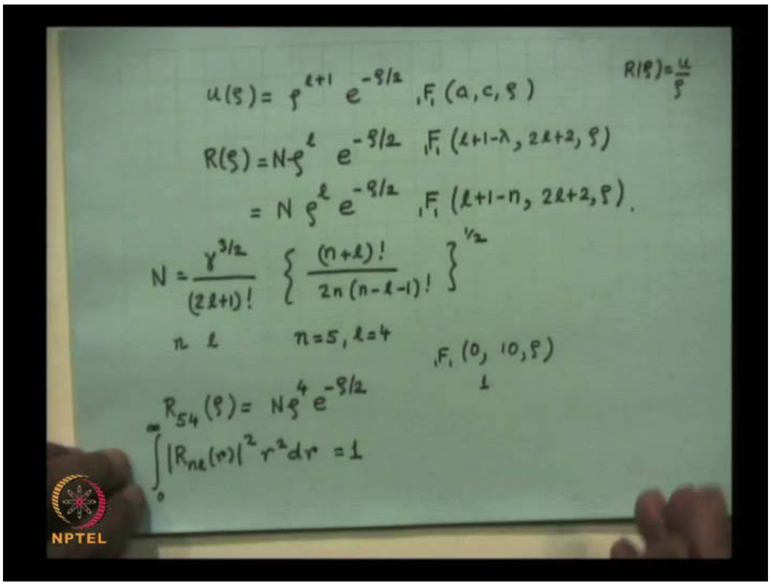

Now, we go back to the to the radial part of the Schrödinger equation and we have u of rho as rho to the power of l plus 1, e to the power of minus rho by 2, F 1 1 of a c rho and a was equal to l plus 1 minus lambda, c was equal to 2 l plus 2 and this is rho. You may recall that R of r or R of rho was equal to u of rho by rho.

So, the radial part of the wave function was equal to rho to the, multiplied by a normalization constant N, rho to the power of l, e to the power of minus rho by 2. This is the rigorously correct wave function for the hydrogen atom. How would I determine?

These functions are so, lambda was put equal to n, so let me write it down. This is the normalization constant, rho to the power of e l minus rho 2 F 1 1, l plus 1 minus n, 2 l plus 2 into rho, and the normalization constant is that is equal to that is very difficult to obtain, little cumbersome, I would not say, 2 l plus 1 factorial multiplied by n plus l factorial divided by 2 n into n minus l minus 1 factorial. The hyper geometric functions are much easier to handle than the associated Laguerre polynomials, which is motioned in most of the books.

Now, let us suppose that I want to find out, you give me any value of n, and any value of l, so let me find out for n. n is equal to 5 and l is equal to 4, so you can now see that l plus 1 minus n. so this function will be F 1 1will be 0, 2 l plus 2 will be 10 into rho, but if a is 0 this is 1. I can immediately write down within a multiplicative constant R 54 by of rho, is equal to some normalization constant, rho to the power of 4, e to the power of minus rho by 2. If you do not want to remember this cumbersome formula, then you can immediately determine the normalization constant by saying that R n l of r mod square, this is the normalization constant, r square dr, from 0 to infinity must be equal to 1.

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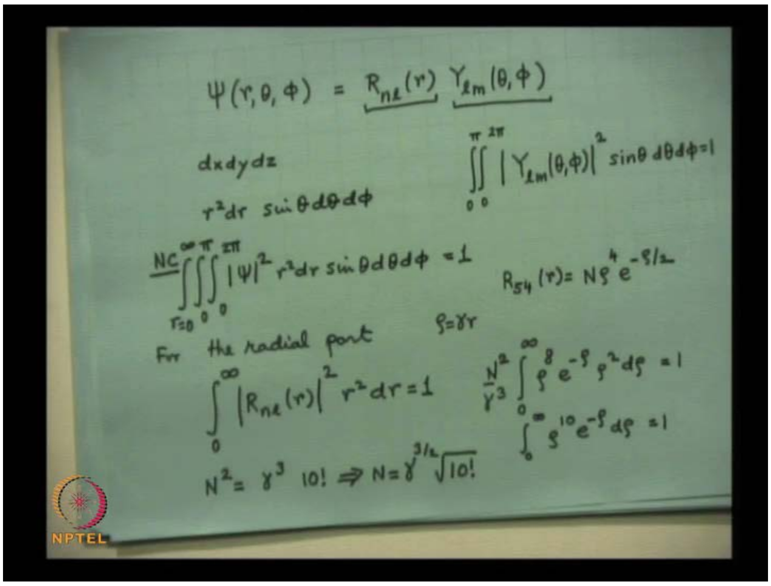

So, you see the complete wave function, psi of r theta phi is equal to R n l of r, Y l m of theta phi. This you must remember. This is normalized. So, in the in cartesian system of coordinates the volume element is dxdydz. In the spherical polar coordinates, the volume element is r square dr sin theta d theta d phi, so the normalization condition is mod psi square. This whole volume element r square dr sin theta d theta d phi triple integral r was from 0 to infinity, theta goes from 0 to pi, and phi goes from 0 to 2 pi, this must be equal to 1. This is the normalization condition.

So, if I take the r part outside and the theta part outside, so the normalization condition for the spherical harmonic is this theta going from 0 to pi, and phi going from 0 to 2 pi, then modulus of Y l m theta phi square sin theta d theta d phi is equal to 1. This is the normalization condition for the spherical harmonics and for the radial part, therefore, for the radial part you will have integral 0 to infinity R n l mod square, actually they are all real, r square dr is equal to 1 this is r and not rho (Refer Slide Time: 32:51).

So, we had here for example, R 54 of r, I hope I have done it correctly, so R 54 of r is equal to N rho to the power of 4 e to the power of minus rho by 2. So, rho is equal to gamma r, so we can see if I multiply by gamma cubed, then I have a one over gamma cubed N square, rho to the power of 8, this is R n l, e to the power of minus rho and then rho square d rho, from 0 to infinity.

So, this is 0 to infinity, rho to the power of 10, e to the power of minus rho d rho, is equal to 1. So, this is 10 factorial, so N square is equal to gamma cubed into 10 factorial, or N will be gamma to the power of 3 by 2 square root of 10 factorial. So, if you want to do or if you want to calculate any radial part of the wave function then it is really very simple.

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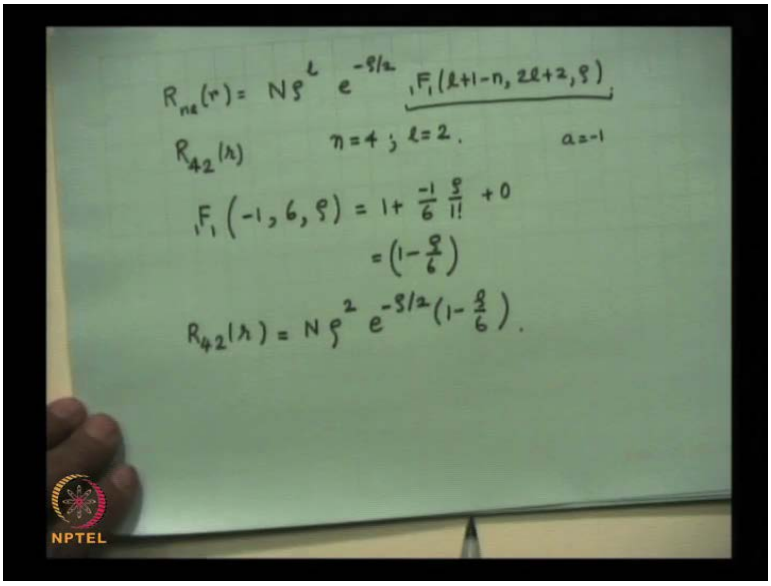

Let me give you another example. So, as I have said R n l of r is equal to N rho to the power of l, e to the power of minus rho by 2, F 1 1 l plus 1, minus n, 2 l plus 2, rho. Now, let me calculate for R 42 of r, just an example. So, n is four and l is 2, so let me first calculate what is this function.

This is the hyper geometric function is l plus 1 minus n, that is 2 plus 1 that is 3 minus 4 that is minus 1, and 2 l plus 2 that is equal to c is equal to 4 plus 6 into rho, and this is 1 plus a by c, that is minus 1 by 6, into rho by factorial 1, then a is minus 1.

So, a into a plus 1, so that is 0. So, this will be just one minus rho by 6. So, R 42 of r, will be equal to n, l is two, this is E to the power of minus rho by 2 minus rho by 6. Confluent hyper geometric equations function gives you very readily the complete radial part of the wave function, provided you, of course, you must be given the values of n and l.

So, this completes the analysis of the hydrogen like atom spectrum. What I would like to do or before that let me summarize.

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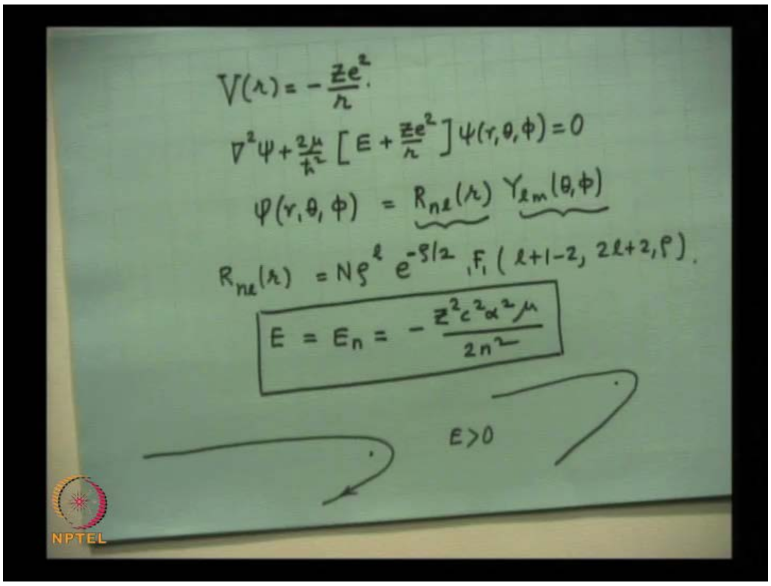

Let me summarize therefore, you will have V of r for a minus z square by r and the wave function will be one describing the translational motion of the total hydrogen atom or hydrogen like atom. The total motion of the center of mass as a free particle and the internal motion, for that we have to solve the in terms of the radial coordinate, 2 mu by h cross square, E minus V of r, that is plus z e square by r, psi of r theta phi and then psi of r theta phi was equal to R n l of r, Y l n of theta phi. These are the spherical harmonics and this is the radial part of the wave function, and the radial part of the wave function is R n l of r is equal to n rho to the power of l, e to the power of minus rho by 2, F 1 1, l plus 1 minus 2, 2 l plus 2 into rho, and we have already discussed.

Finally, the energy Eigen values are E is equal to E n minus z square, c square, alpha square mu by 2 n square. These are the energy eigen values of the hydrogen like atom problem and we discussed that that you can use this formula to calculate to obtain the spectra associated with the hydrogen like hydrogen atom, deuterium atom, simply ionized helium atom, doubly ionized lithium atom and so on.

There is one thing that I would like to mention that we have considered the negative energy states. Now, the positive energy states is if I have a proton sitting here, and an electron comes from very distance and get scattered. So, those are the E greater than 0 states. So, even in planetary motion, you can have a object, which comes near the sun and gets scattered and then there is earth, which is bound to be sun, which is rotating in a orbit. So, even in the hydrogen atom, in both the cases we have inverse square law.

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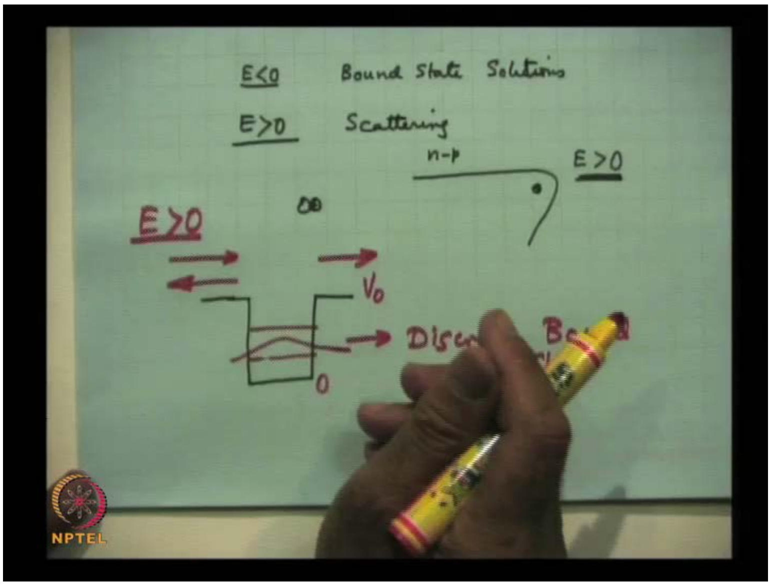

In quantum mechanics also, there are two types of solutions. One corresponds to E less than 0, so those are the bound state solution and for E greater than 0, those are the scattering state, for any problem, scattering solutions. Even in the neutron, proton problem, you have a bound state problem, in which the neutron and proton are held together and you find the discrete energy states.

On the other hand, you can have a neutron proton scattering problem, which is one of the most important problems in quantum mechanics, that you have a neutron beam coming in here, and getting scattered by the proton. So, this is known as the neutron proton scattering. So, those correspond to the continue solutions, E greater than 0.

In one dimensional quantum mechanics, you had remembered, that we had the potential well problem. Now, in this potential well problem, there are two types of solutions. Let us suppose 0 and V 0, for E lying between 0 and V 0, they are bound state solutions, where the particle is confined within the well, where your wave functions which are exponentially decaying here.

So, they are tightly confined here. They are localized and the energy Eigen values are discrete. So, these are known as the discrete bound states; discrete bound states, and then we will have E greater than 0 solutions. These are the scattering stage, and therefore will continue, all possible values of energy are allowed and therefore, you will have this and incident beam coming in, part of it is reflected and part of it is transmitted.

So, we will have two types of solutions, in the hydrogen atom problem or what we will be going to discuss is the neutron proton problem. We will just now confine ourselves to the negative energy solutions in which you have what are known as the bound states.

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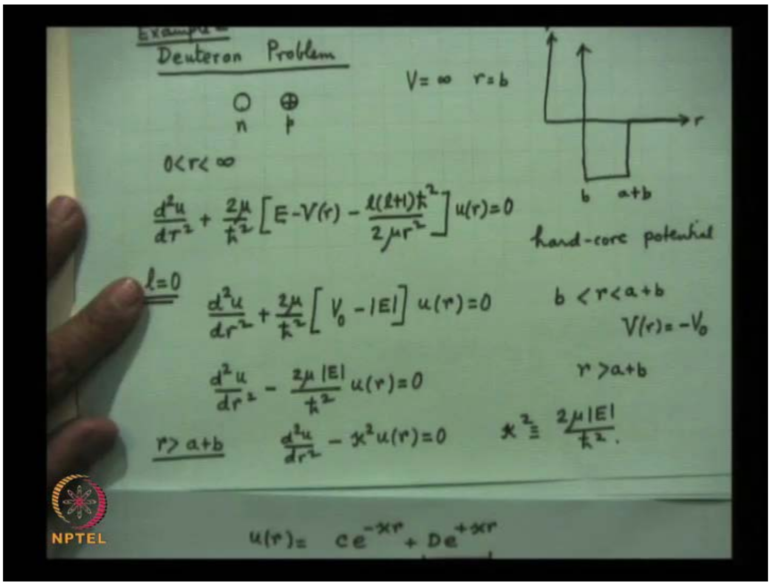

Now, let me just start and then we will continue with that in our next lecture. We considered the deuteron problem. This is the fundamental problem in nuclear physics. The deuteron problem in which you have a neutron and proton, now, scattering experiment suggest that because neutron is an uncharged particle, we have no interaction beyond a certain distance. So, there is a model, in which you have V is equal to infinity at r is equal to b, something like this, this is the potential as a function of r, so at r is equal to b, is an infinite potential and then it is minus b 0 from r equal to b to a plus b, and then it is 0 beyond this. This is known as the hardcore potential; hardcore potential, in which the neutron and the proton cannot be closer than the distance b.

So, let me write down the radial part of the Schrödinger equation. So, d 2 u by d r square plus 2 mu by h cross's square, E minus V of r, minus l into l plus 1, h cross square by 2 mu r square, u of r is equal to 0. I assume consider the l equal to 0 problem, just to make life simple, and then you have, you must always remember r goes from 0 to infinity, not minus infinity to plus infinity.

We will consider once again the negative energy states of the problem and so E is negative and l is 0. This we consider as example two, the deuteron problem, so you have d 2 u by dr square plus 2 mu by h cross square. E is negative, so I write this down as V of r is equal to V 0, minus V 0, so V 0 minus mod of E. I hope you understand. u of r is equal to 0, this is for r less than a plus b, less than b. In this region V of r is assumed to be minus V 0, minus V 0.

For r greater than a plus b, you will have V of r is 0, this term is 0, but E is assumed to be negative. These are the bound state problems, so d 2 u by dr square minus 2 mu mod E by h cross square of u of r is equal to 0. So, this is for r greater than a plus b. So, in the region r greater than a plus b, I write this as d 2 u by dr square minus kappa square u of r is equal to 0, where kappa square is defined to be equal to 2 mu mod E by h cross's square.

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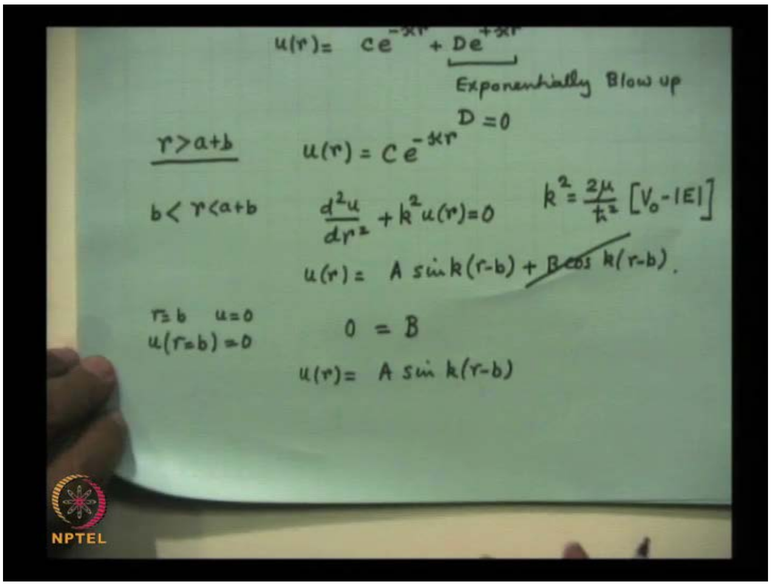

So, as we all know, this has two particular solutions. So, the solution may be u of r will be say c e to the power of minus kappa r plus D into e to the power of plus kappa r. This will exponentially blow up and therefore, the wave function will not be normalizable. So, you must choose D is equal to 0, so in the region r greater than a plus b, the wave function will be u of r is equal to C e to the power of minus kappa r.

In the region of b, for r lying between a plus b and b, this we write as d 2 u by d r square plus k square, u of r is equal to 0, so where k square is equal to 2 mu by h cross square V 0 minus mod E.

The solutions are very simple; A sin k r, so I write this as r minus b plus b cos of k r minus b. Just, I have introduced this B for the sake of simplicity. Now, at r is equal to b there is an infinite potential, so the wave function has to go to 0, because the inter particle distance cannot be less than b and that is what this potential physically implies. This is known as the hardcore potential where the neutron and the proton cannot… This is one of the models and no one really knows the exact potential energy distribution between the neutron and the proton.

This is a simple model which is quite accurate that for distances between the neutron and the proton cannot be less than b, so at r equal to b, the wave function must be 0. So, at r equal to b the wave function is 0 so u at r equal to b must be 0. So, if I put r equal to b, this term goes 0. So, 0 is equal to, this is cos of 0 so that b cos of 0 is one, so this term b is 0.

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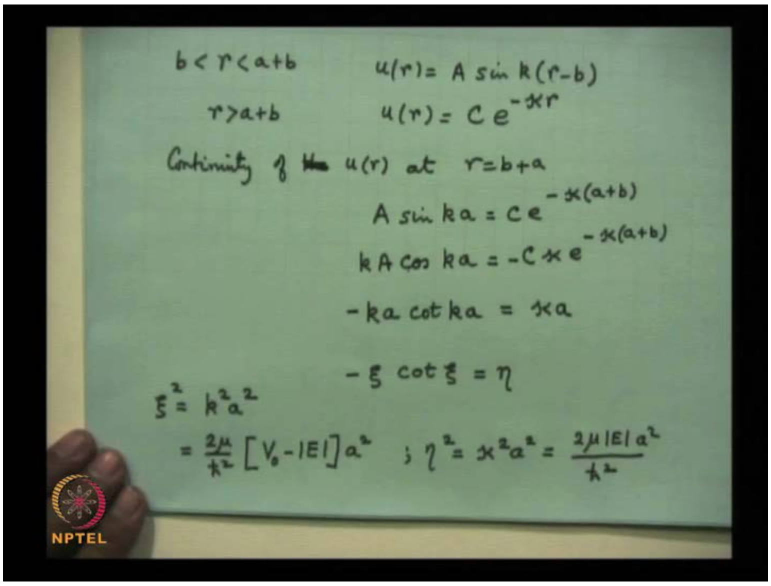

You had u of r is equal to A sin k of r minus b. Therefore, we will have for r less than a plus b, less than b, u of r is a sin k r minus b, for r greater than a plus b, u of r will be c into e to the power of minus kappa r.

We must have the wave continuity of the wave function of u of r at r is equal to b, will give me a r is equal to b plus a, continuity at r equal to a plus b will give me A sin k a, is equal to c into e to the power of minus kappa a plus b.

Similarly, if I take the derivative continuity of u prime of r, so this will be k a cos k r minus b and at r equal to a plus b, it will be cos k a minus c kappa e to the power of minus kappa a plus b. so, if I divide this equation this equation by this equation, I will get minus k a cot k a is equal to kappa. So, if I multiply both sides by a, so I will get something like this.

So, this is an equation which is similar to what we are encountered earlier. So, minus psi cot psi is equal to eta, where xi square is equal to k square a square, and this is equal to 2 mu by h cross square V 0 minus mod E multiplied by a square and eta square is equal to kappa square, a square, and that is equal to 2 mu mod E a square by h cross square and if I add these two equations then I will get…

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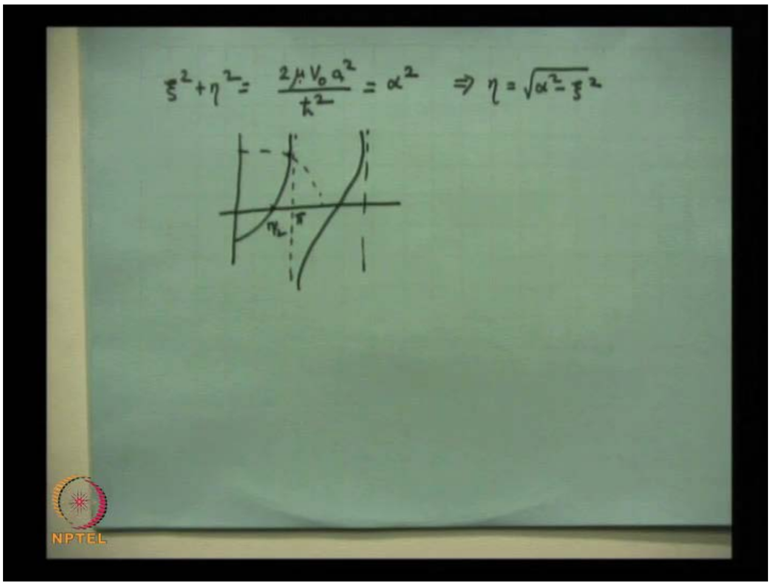

If I add these two equations xi square plus eta square, then you can see mod eta cancels out, so you get 2 mu V 0 a square by h cross square. This I put equal to alpha square and for a given potential, for a given reduced mass, for a given radius, and of course, Planck's constant is a constant, so therefore, this gives me that eta is equal to under root of alpha square root minus xi square. Therefore, this term will be just the similar thing that we had experience in our one dimensional case.

So, for a given value of alpha, we have to solve this transcendental equation and obtain the discrete eigen value, so minus xi cot xi, we have something like this. This is a pi that it will become infinite, and this is pi by 2, and then you will have something like this, and the right hand side will be the quadrant of a circle, and the points of intersection, will give me the eigen values.

We will specifically consider a profile which closely corresponds to the deuteron problem and then we will solve this equation and obtain the Eigen values of the problem. Thank you.

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