Basic Quantum Mechanics
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Module No. # 06
Hydrogen Atom and other Two Body Problem
Lecture No. # 03
Two Body Problems: The Hydrogen Atom, The Deuteron, The Diatomic Molecule

We will continue our discussion on the two body problem, in which we will consider two particles which I interacting through a potential energy distribution which depends only on the distance between the two particles; this is known as the central potential problem. And in this for such a case we have a major simplification, the two body problem can be reduced to two one body problems; one describing the uniform translational motion of the center of mass, and the other describing the internal motion of the two body system.

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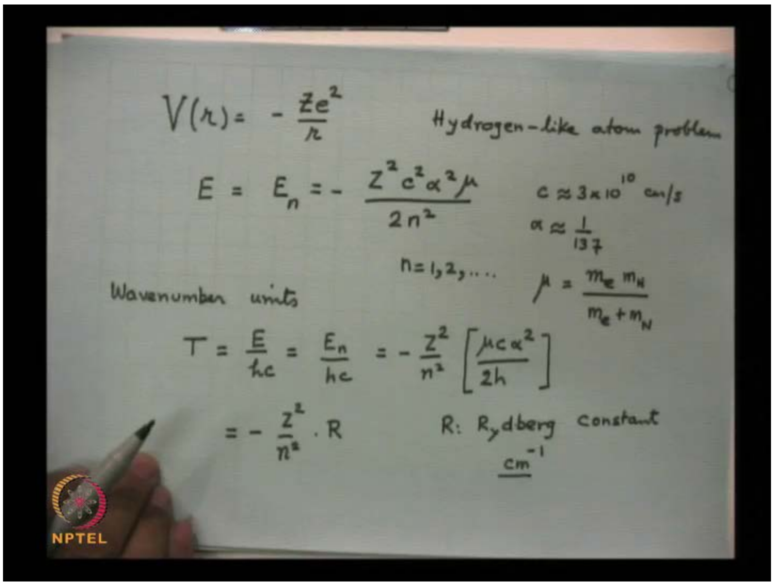

$$V(r) = -\frac{Ze^2}{r}$$

Hydrogen-like atom problem

$$E = E_n = -\frac{Z^2 c^2 \alpha^2 \mu}{2n^2}$$

$c \approx 3 \times 10^{10}$ cm/s

$\alpha \approx \frac{1}{137}$

$n = 1, 2, \ldots$

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

Wavenumber units

$$T = \frac{E}{hc} = \frac{E_n}{hc} = -\frac{Z^2}{n^2}\left[\frac{\mu c \alpha^2}{2h}\right]$$

$$= -\frac{Z^2}{n^2} \cdot R$$

R: Rydberg constant

$\underline{cm^{-1}}$

So, we first we had first considered the hydrogen atom problem or hydrogen like atom problem. In which there are two particle, and the potential energy distribution in the c g s system of units was equal to minus z e square by r; where z e represents the charge of the electron, so this is the hydrogen like atom problem hydrogen like atom problem. Now, we solve the schrodinger equation and we have found that the energy levels. The the bound state corresponds to E equal to E n minus Z square c square alpha square mu by 2 n square, where c is the speed of light in free space, and the see value of c in c g s units is 3 into 10 to the power of 10 centimeter per second.

Alpha is the front structure constant which is about 137 and mu is the reduced mass that is m e m N ; m N is the mass of the nucleus divided by m e plus m N. And n was the total quantum number which can take the values 1, 2, 3, etcetera. Now, we said that usually in spectroscopy we we write the energy levels in wave number units in wave number units, and and we divide we term value for each state is defined as E by h c, where h is the planck's constant and c is the speed of light.

So you will have E n by h c; and this will be equal to minus Z square by n square 1 of the c is will cancel out, so you will have mu c alpha square by h, mu c alpha square by 2 h this quantity is known as the rydberg constant. So we write this as equal to minus Z square by n square into R; where R is known as the R is known as the rydberg constant, after the physicist rydberg and its dimension in c g s units is centimeter to the power of minus 1, so the energy levels are usually in spectroscopy the the energy is measured in wave number units which is centimeter to the power of minus 1, and as I had mentioned that the value of the rydberg constant.

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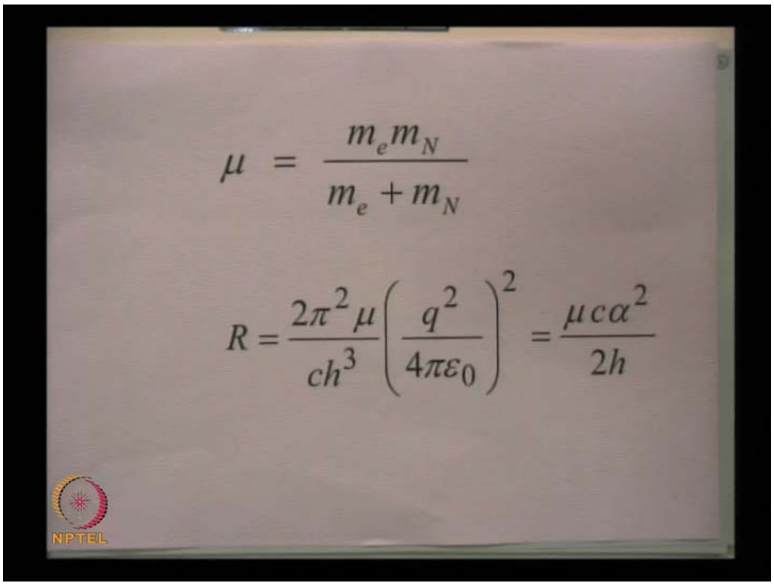

$$\mu = \frac{m_e m_N}{m_e + m_N}$$

$$R = \frac{2\pi^2\mu}{ch^3}\left(\frac{q^2}{4\pi\varepsilon_0}\right)^2 = \frac{\mu c\alpha^2}{2h}$$

As I had mentioned that was equal to 2 mu c alpha square by 2 h and mu is the reduced mass, and since the for different monite mono electron items the mass of the nucleus is slightly different so the rydberg constant is also slightly different.

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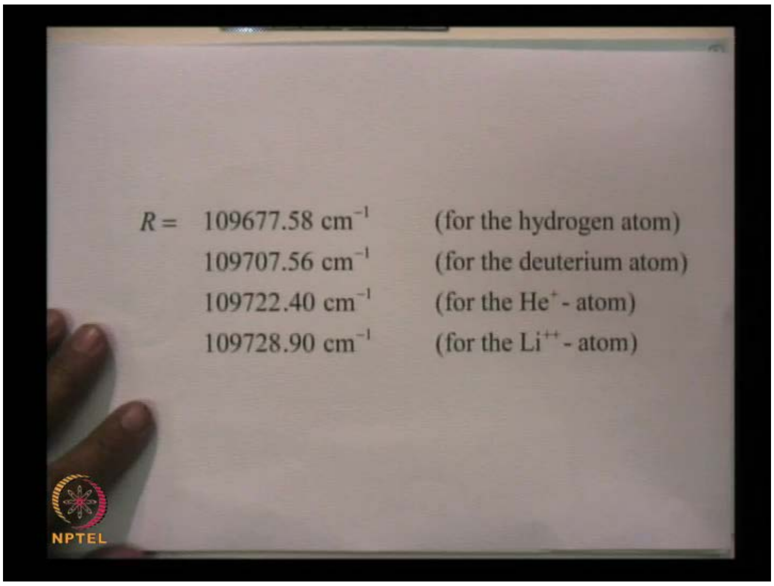

$R =$ 109677.58 cm^{-1} (for the hydrogen atom)

109707.56 cm^{-1} (for the deuterium atom)

109722.40 cm^{-1} (for the He^{+} - atom)

109728.90 cm^{-1} (for the Li^{++} - atom)

In fact we had we had menti 1d that for the hydrogen atom, in which the nucleus consists of just the proton in the case of deuterium atom. The nucleus consists of deuteron 1 neutron and 1 proton for the helium plus atom, the nucleus consists of 2 neutrons and 2 protons. And in each case in each case it is a single electron atom, here Z is equal to 1, this is also Z is equal to 1, this is Z is equal to 2.

And this is 3 protons in the nucleus Z is equal to 3, so because of the fact that in each case the mass of the nucleus is slightly is is different, therefore it leads to slightly different values of the rydberg constant and indeed from the from the fact that the rydberg constant is slightly different for deuterium, it lead to measurement careful measurement of specter lines which were slightly shifted from that of the hydrogen atom. And which eventually led to the discovery of deuterium of heavy water by yuri in the year 1932. Now, this therefore completes the energy level structure, one thing that I missed out in my previous lecture was to give a the the detailed expression for the wave function.

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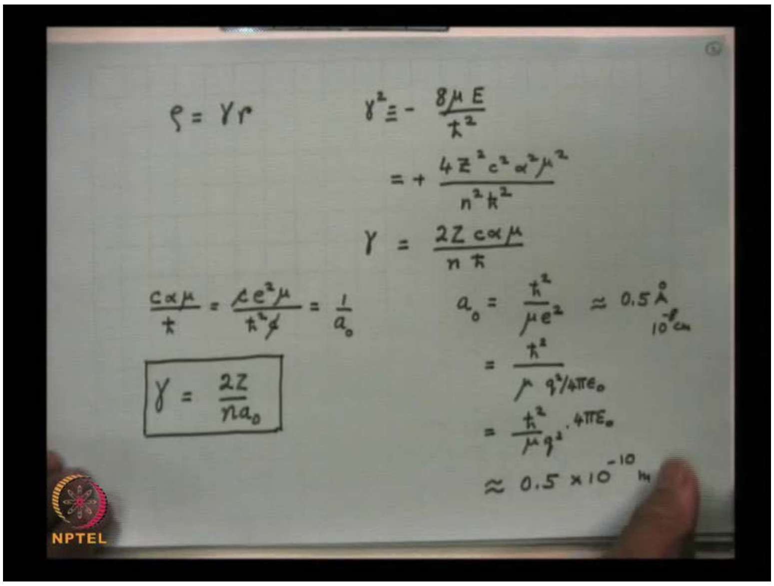

$$\rho = \gamma r$$

$$\gamma^2 \equiv -\frac{8\mu E}{\hbar^2} = +\frac{4Z^2c^2\alpha^2\mu^2}{n^2\hbar^2}$$

$$\gamma = \frac{2Zc\alpha\mu}{n\hbar}$$

$$\frac{c\alpha\mu}{\hbar} = \frac{\cancel{c}e^2\mu}{\hbar^2\cancel{c}} = \frac{1}{a_0}$$

$$\boxed{\gamma = \frac{2Z}{na_0}}$$

$$a_0 = \frac{\hbar^2}{\mu e^2} \approx 0.5\,\overset{\circ}{A} \quad 10^{-8}\,\text{cm}$$

$$= \frac{\hbar^2}{\mu\, q^2/4\pi\epsilon_0} = \frac{\hbar^2}{\mu q^2}\cdot 4\pi\epsilon_0 \approx 0.5\times 10^{-10}\,\text{m}$$

As we know that rho was defined the dimensionless parameter was defined as gamma r, and gamma square was equal to minus 8 mu E by h cross square; this is, this was the definition of the gamma gamma square. Now, E takes negative values as I have just now shown that that the expression for E’s of n is this, and if you now substitute it here then you will get plus 4 z square c square alpha square mu square by n square h cross square, so therefore gamma is equal to 2 Z c alpha mu divided by n h cross.

Now, the quantity c alpha mu by h cross; this is equal to alpha is equal to e square by h cross c, so this becomes c e square mu by h cross square c, and so therefore this becomes sorry h cross c; so this c c cancels out and this is known as the inverse of the bohr radius. So, the bohr radius is defined as h cross square in the c g s system of units m e square, and in the m k s units this is in the c g s units in the m k s units it will be mu q square by 4 pi epsilon naught, so this will be equal to h cross square by mu q square and then the numerator 4 pi epsilon naught. The value of the bohr radius as you must be knowing is about half of an angstrom; angstrom is 10 to the power of minus 8 centimeter or this is equal to about half 0.5 into 10 to the power of minus 10 meter.

So, therefore we have shown that c alpha mu by h cross is 1 over a 0, therefore we get gamma is equal to gamma is equal to 2 Z by n a 0, this it will it is better to remember this particular expression for for the parameter gamma.

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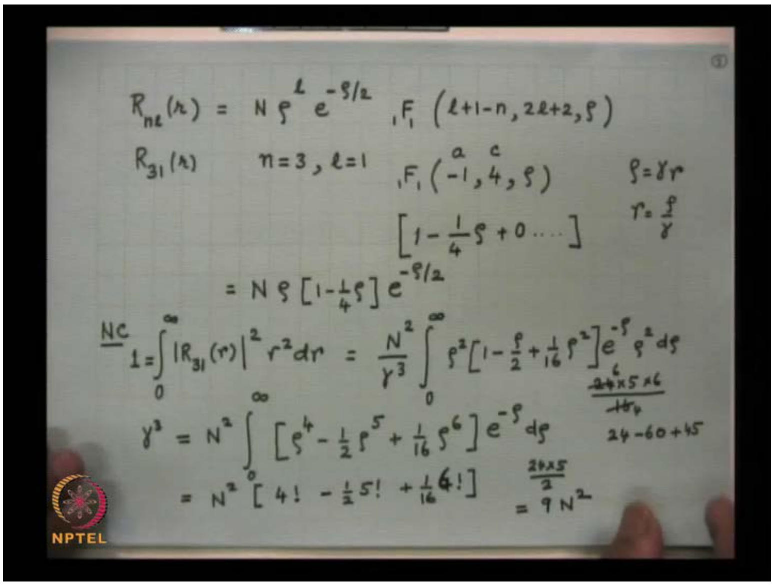

$$R_{n\ell}(r) = N\rho^{\ell} e^{-\rho/2} \, {}_1F_1(\ell+1-n, 2\ell+2, \rho)$$

$$R_{31}(r) \qquad n=3, \ell=1 \qquad {}_1F_1(\overset{a}{-1}, \overset{c}{4}, \rho) \qquad \rho = \gamma r$$

$$\left[1 - \frac{1}{4}\rho + 0 \ldots\right] \qquad r = \frac{\rho}{\gamma}$$

$$= N\rho\left[1 - \frac{1}{4}\rho\right]e^{-\rho/2}$$

$$\underline{NC} \quad 1 = \int_0^\infty |R_{31}(r)|^2 r^2 dr = \frac{N^2}{\gamma^3}\int_0^\infty \rho^2\left[1 - \frac{\rho}{2} + \frac{1}{16}\rho^2\right]e^{-\rho}\rho^2 d\rho \qquad \frac{\overset{6}{\cancel{24}}\times5\times6}{\cancel{16}_4}$$

$$\gamma^3 = N^2\int_0^\infty \left[\rho^4 - \frac{1}{2}\rho^5 + \frac{1}{16}\rho^6\right]e^{-\rho} d\rho \qquad 24-60+45$$

$$= N^2\left[4! - \frac{1}{2}5! + \frac{1}{16}6!\right] \qquad \frac{24\times5}{2}$$

$$= 9N^2$$

Now, I will discuss that we had the radial in my last lecture, we had derived the expression for the radial part of the lecture as N normalization constant rho to the power of l e to the power of minus rho by 2, and it is a very easy formula to remember F 1 1 l plus 1 minus n, 2 l plus 2 into rho this is the confluent hyper geometric function.

And as an example, we will consider we will calculate the R 3 1 of r, so if you want just as an example so n is equal to 3 and l is equal to 1, so this expression becomes F 1 1 l plus 1 that is 2 minus 3 is minus 1 2 l plus 2; that is 2 plus 2 becomes 4 times rho. So as you know this becomes this is the value of a and this is the value of c so the confluent hyper geometric equation as you would remember is 1 plus a by c that is a is minus 1 by 4 into1 factorial which is 1 times rho plus plus a into a plus 1, but a plus 1 is 0 so this and all other terms will be 0, so therefore we will have this as N, l is 1; so this is just rho times 1 minus 1 by 4 rho e to the power of minus rho by 2.

Now, let me normalize these wave function, so we will have the normalization condition is the normalization condition is integral 0 to infinity R 3 1 of r whole square r square dr, so rho is equal to gamma r, so r is equal to rho by gamma, and therefore r square will be rho square by gamma square this will be d rho by gamma.

So there will be a so normalization condition is 1 is equal to so much, so this will be rho cubed divided by gamma cubed. So, if you square this so you will get this is equal to N square by gamma cubed integral from 0 to infinity square of this square of this rho square, and if I square this 1 minus rho by 2 plus 1 over 16 rho square e to the power of minus rho times rho square d rho rho square d rho I have taken the gamma cube outside. So, therefore therefore gamma cubed if I take gamma cubed in this side so N square 0 to infinity, so this is the first term is rho to the power of 4 rho to the power of 4 minus half rho to the power of 5 plus 1 over 16 rho to the power of 6 e to the power of minus rho d rho.

The integrals are very straight forward they can be written in terms of gamma functions, so this is equal to N square brackets gamma of 5 which is 4 factorial minus half of 5 factorial plus 1 over 16 of 7 factorial and that is it. So, if you do the algebra so this is 24 this is 24 and this is 24 into 5 divided by 2 that is minus 60 plus 24 I am sorry this is 6 factorial I am sorry 24 into 5 into 6 divided by 16, so this is 4 6 so 45 so this is just 9, so this is 9 N square 9 N square.

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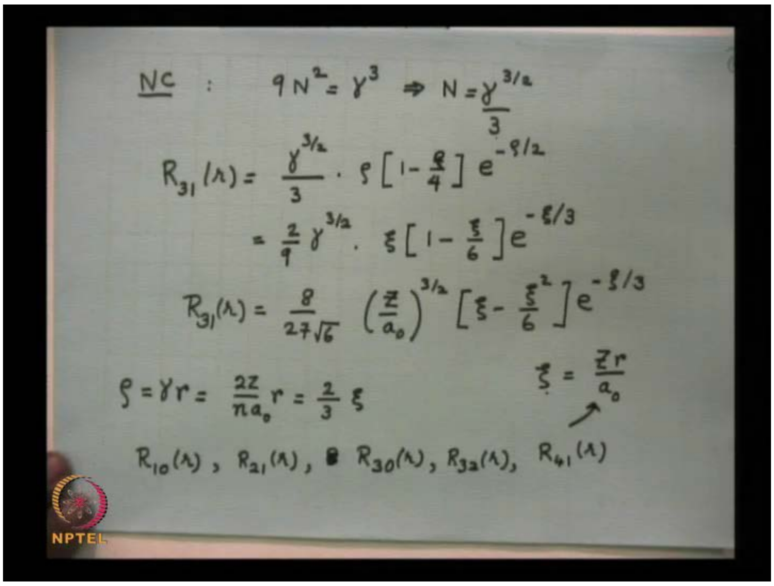

$\underline{NC}$: $9N^2 = \gamma^3 \Rightarrow N = \frac{\gamma^{3/2}}{3}$

$$R_{31}(r) = \frac{\gamma^{3/2}}{3} \cdot \rho \left[1 - \frac{\rho}{4}\right] e^{-\rho/2}$$

$$= \frac{2}{9}\gamma^{3/2} \cdot \xi \left[1 - \frac{\xi}{6}\right] e^{-\xi/3}$$

$$R_{31}(r) = \frac{8}{27\sqrt{6}} \left(\frac{Z}{a_0}\right)^{3/2} \left[\xi - \frac{\xi^2}{6}\right] e^{-\xi/3}$$

$\rho = \gamma r = \frac{2Z}{na_0} r = \frac{2}{3}\xi$ $\qquad \xi = \frac{Zr}{a_0}$

$R_{10}(r)$, $R_{21}(r)$, $R_{30}(r)$, $R_{32}(r)$, $R_{41}(r)$

So, therefore we will have the normalization condition normalization condition will lead to 9 N square is equal to gamma to the power of 3 so this leads us N is equal to gamma raised to the power of 3 by 2 divided by 3.

Now, there is one more thing that I would like to mention that R 3 1 of r, as I had written was n n is gamma raised to the power of 3 by 2 divided by 3 this is this factor multiplied by rho; now, rho is usually written as is equal to gamma r and as you had as we had derived gamma value was equal to 2 Z by n a 0 into r, so in this particular case in this in this particular case this will be this will be 2 and n is 3 and z pi a 0 into r is denoted by psi.

So this will be multiplied by rho into 1 minus 4 by rho by 4 rho by 4 e to the power of minus rho by 2 so the rho is 2 by 3 psi, so 2 by 9 gamma raised to the power of 3 by 2 into psii into 1 minus rho is equal to 2 by 3 so psi by 6, and rho by 2 will be psi to the power 3. This is usually the radial part of the wave function is recouped and then you substitute for gamma equal to gamma will be 2 Z by n a 0, if you find any substitute that you will get with simple substitution 8 upon 27, I leave the if it is an exercise z by a 0 raised to the power of 3 by 2 psi minus psi square by 6 into e to the power of minus psi by 3, where psi is equal to z r by a 0; and a 0 is the bohr radius, so this is the rigorously correct normalized wave function and it is this form it is in terms of the variable psi that most of the wave functions are written, what I would like to conclude this part of the lecture is by saying that I leave it as an exercise for you to calculate from first principles R 1 0 of r, R 2 1 of r and R 3 sorry R 3 0 of r, R 3 1 of r I have already calculated R 3 2 of r.

And then n is equal to 4, R 4 1 of r etcetera; these are currently state forward to calculate and once you get the hang of calculating this you will find that the use of the confluent hyper geometric function is extremely easy in the calculation of the normalized wave functions. So this concludes the hydrogen atom or hydrogen like atom problem and and we will continue on the two module problem namely that of the deuteron problem.

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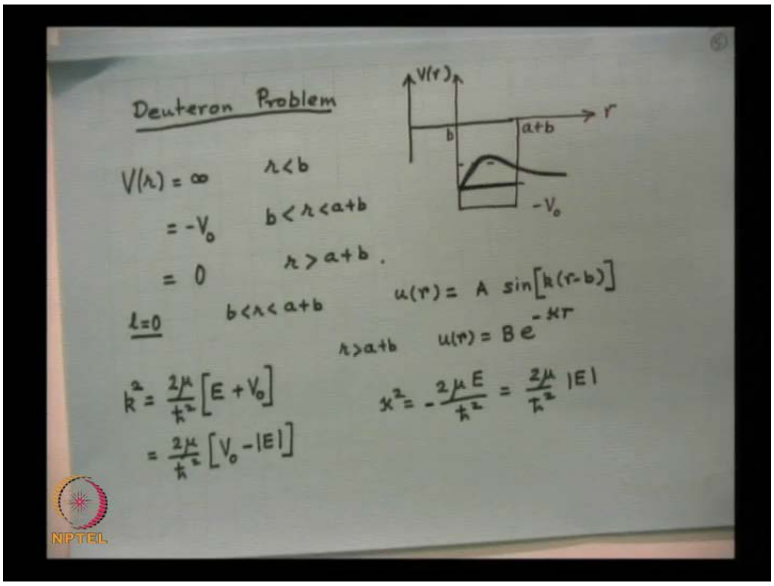

Deuteron Problem

$V(r) = \infty \qquad r < b$

$= -V_0 \qquad b < r < a+b$

$= 0 \qquad r > a+b.$

$l=0 \qquad b < r < a+b \qquad u(r) = A \sin[k(r-b)]$

$r > a+b \qquad u(r) = B e^{-\kappa r}$

$k^2 = \frac{2\mu}{\hbar^2}[E + V_0]$

$= \frac{2\mu}{\hbar^2}[V_0 - |E|]$

$\kappa^2 = -\frac{2\mu E}{\hbar^2} = \frac{2\mu}{\hbar^2}|E|$

In our last lecture we had started on the deuteron problem; in the deuteron problem we have one proton and one neutron which are held together by a potential energy distribution, and we had assumed a very simple model and we had assumed that the potential energy was that this is V of r this is V of r, and the potential energy was infinite at r is equal to b and then it was very deep and equal to minus V 0 and then it was 0, so this coordinate is r.

So this is r is equal to b and this is the point r is equal to a plus b, so therefore we had assumed that the interaction between the neutron and the proton can be described by a spherically symmetric potential, and it is given by V of r is equal to infinity for r less than b is equal to minus V 0 for r less than a plus b b and is equal to 0 for r greater than a plus b. Therefore at r equal to b the wave function must vanish, and we wrote down the radial part of the schrodinger equation and solved it for l equal to 0, and we found that in the region in the region b less than r less than a plus b the solution was the solution of the radial part of the schrodinger equation was A sin of k into r minus b, where k square is equal to 2 mu by h cross square E minus V E minus V but V is equal to V 0, so it is V 0 plus E.

But the we are considering the bound state problems so the energy discrete energy will lie somewhere here, so the energy itself will be negative. So, therefore we write this as 2 mu by h cross square V 0 minus modulus of E, and then we find out modulus of E we will remember that E itself is a negative quantity, then for r greater than a plus b the solutions are exponentially decaying. So u of r we said that will be equal to B into e to the power of minus kappa r and kappa square kappa square was equal to 2 mu E by h cross square with a minus sign; so this is equal to 2 mu by h cross square mod of E, then we made u of r and its derivative continuous at r is equal to a plus b.

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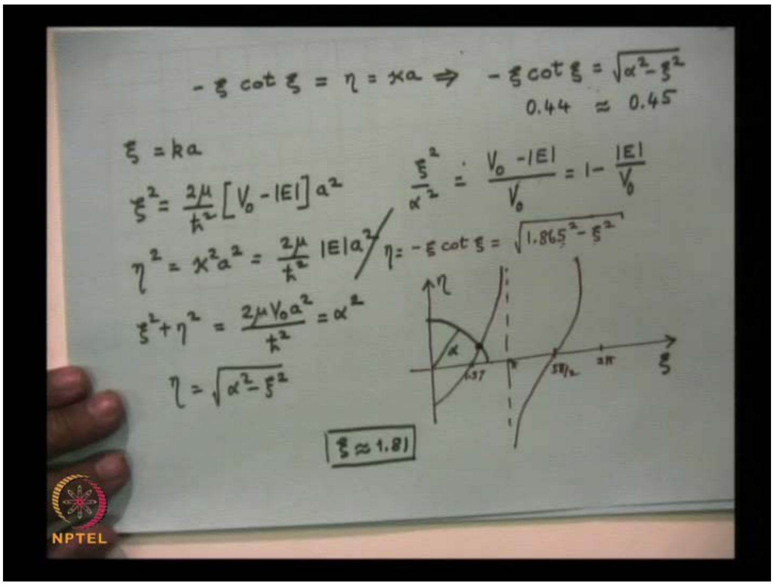

$$-\xi \cot \xi = \eta = \kappa a \Rightarrow -\xi \cot \xi = \sqrt{\alpha^2 - \xi^2}$$

$$0.44 \approx 0.45$$

$$\xi = ka$$

$$\xi^2 = \frac{2\mu}{\hbar^2}\left[V_0 - |E|\right] a^2$$

$$\frac{\xi^2}{\alpha^2} = \frac{V_0 - |E|}{V_0} = 1 - \frac{|E|}{V_0}$$

$$\eta^2 = \kappa^2 a^2 = \frac{2\mu}{\hbar^2} |E| a^2$$

$$\eta = -\xi \cot \xi = \sqrt{1.865^2 - \xi^2}$$

$$\xi^2 + \eta^2 = \frac{2\mu V_0 a^2}{\hbar^2} = \alpha^2$$

$$\eta = \sqrt{\alpha^2 - \xi^2}$$

$$\boxed{\xi \approx 1.81}$$

And similar to the one dimensional equation, we found we arrived at the following transcendental equations psi cot psi is equal to eta; which was equal to kappa a, where psi is was equal to k a. And so therefore psi square will be equal to k square a square, so 2 mu by h cross square V 0 minus mod of E a square, and eta square was equal to kappa square a square; so this will be equal to 2 mu by h cross square these are all dimensionless quantities.

So, if you add them up psi square plus eta square so this term will cancel out with this term, so we will get 2 mu V 0 a square by h cross square; so this is a dimensionless number alpha square. So my eta is equal to under root of alpha square minus psi square, so this equation becomes the following transcendental equation psi cot psi is equal to under root of alpha square minus psi square, for a given system that is for a given value of the reduced mass. The potential energy depth the range of the potential, and of course planck’s constant is a constant the value of alpha is known, so far a known value of alpha we have to solve the transcendental equation, and obtain the value of psi once we obtain the value of psi we can calculate the value of E.

For example, if I if I divide psi square by alpha square if I divide psi alpha square psi square by alpha square, so please see this you will have 2 mu by h cross square V 0 minus E a square divided by 2 mu V 0 a square by h cross; so this will be V 0 minus mod E divided by V 0, so this will be 1 minus mod E by V 0. Now, let me calculate let me consider a simple example simple profile, and calculate the value of alpha; and the value of alpha is under root of 2 mu V 0 a square by h cross square let me do this on the next page.

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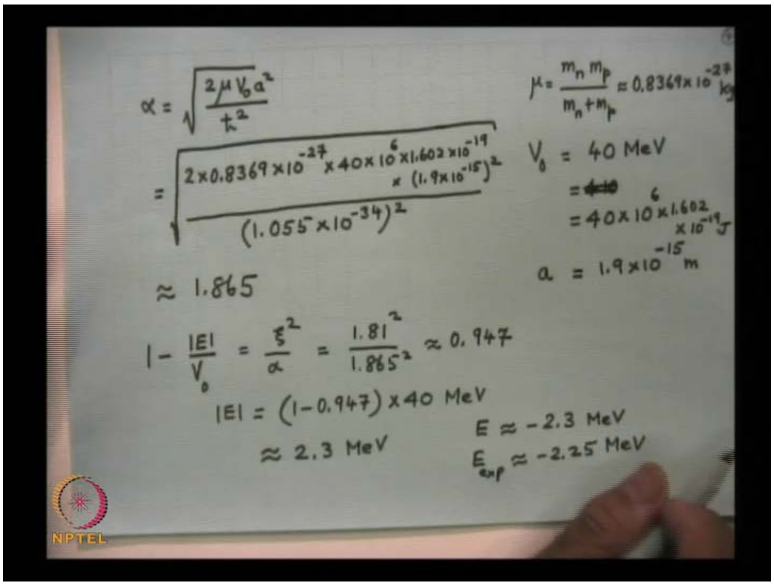

$$\alpha = \sqrt{\frac{2\mu V_0 a^2}{\hbar^2}}$$

$$= \sqrt{\frac{2\times 0.8369\times 10^{-27}\times 40\times 10^{6}\times 1.602\times 10^{-19}\times (1.9\times 10^{-15})^2}{(1.055\times 10^{-34})^2}}$$

$$\approx 1.865$$

$$\mu = \frac{m_n m_p}{m_n + m_p} \approx 0.8369\times 10^{-27}\ \text{kg}$$

$$V_0 = 40\ \text{MeV}$$

$$= \cancel{40\times 10}$$

$$= 40\times 10^{6}\times 1.602\times 10^{-19}\ \text{J}$$

$$a = 1.9\times 10^{-15}\ \text{m}$$

$$1 - \frac{|E|}{V_0} = \frac{\xi^2}{\alpha} = \frac{1.81^2}{1.865^2} \approx 0.947$$

$$|E| = (1 - 0.947)\times 40\ \text{MeV}$$

$$\approx 2.3\ \text{MeV}$$

$$E \approx -2.3\ \text{MeV}$$

$$E_{exp} \approx -2.25\ \text{MeV}$$

So you will have alpha is equal to under root of 2 mu V 0 a square by h cross square, we consider the neutron proton problem, and therefore mu is equal to mass of the neutron, mass of the proton divided by mass of the neutron plus mass of the proton. If you substitute the values of this then you will get about 0.8369 into 10 to the power of minus 27 k g in in case system of units. I assume V 0 the depth of the potential is equal to 40 M e V, so this is equal to 40 sorry I am sorry 40 into 10 to the power of 6 electron volts multiplied by 1.602 into 10 to the power of minus 19 this is the joules. And we assume a is equal to about 1.9 Fermi's 10 this is a typical value 10 to the power of minus 15 meter this is the range of the potential.

So, let me substitute it here so you will get alpha is equal to 2 into 0.8369 into 10 to the power of minus 27 this is the reduced mass of the neutron. And the proton V 0 value is 40 into 10 to the power of 640 M e V into 1.602 into 10 to the power of minus 19 multiplied by in the denominator a square 1.9 into 10 to the power of minus 15 square the whole thing under the root divided by divided by h cross square and the h cross square is 1.055 into 10 to the power of minus 34 whole square.

So, if you do this very simple calculation then this comes out to be approximately 1.865 alpha is 1.865, so far the neutron proton problem these are this is an approximate calculation so alpha is about 1.865. So, we go back to this transcendental equation so we have the where you have calculated the value of value of alpha, so the transcendental equation becomes minus psi cot psi is equal to under root of 1.865 whole square minus psi square. So, I plot as we had done at psi equal to 0, this goes to infinity this goes to 0 so the product tends to a finite number, and the first 0 occurs at pi by 2; pi by 2 is about 1.5 7, so it is something like this and it becomes infinity at psi cot psi becomes infinity as we had discussed earlier and so on, so this is 3 pi by 2 and then it goes again to infinity at 2 pi.

Now, this is pi this is 3 so the radius is 1.865 so we have to draw so it would be on the right side of this so, if I sort that arc of a circle so it will be somewhat between 1.75 and 5 so it will be something like this this radius is alpha. And in this case alpha is 1.865 so this is the point so this is the horizontal axis is psi, so this is eta is equal to so much so this is my eta so at this value of psi will be between 1.57 and 3.1, if you do this then it will come out to be psi will come out to be 1.81.

Remember when you do the numerical calculation, this psi is measured in radians so 1.81 times cotangent of 1.81, if you calculate that then this becomes about plus 0.44 and this becomes if you 1.865 whole square minus 1.81 whole square comes out to be about 0.45 something like that they are approximately equal, so for this value of psi for this value this is the method for solving the transcendental equation for this value of psi the left hand side becomes equal to right hand side, and so therefore that is the root of the problem that is the Eigen value that is the Eigen value.

So, therefore you will have from this equation 1 minus mod E by V 0 is psi square by alpha square. So, let me write it down so let me write it down here that 1 minus mod E by V 0 we had derived this earlier is equal to psi square by alpha square psi square we found that is about 1.81 square, and this is 1.865 square. So, if you divide this then you will find that this is about 0.947. And you take E by V 0 is equal to 1 minus 0.947 and into 40 M e V and this comes out to be about 2.3 M e V about.

So the binding energy of the deuteron according to our simple analysis simple model comes out to be 2.3 M e V, and the actual experimental value the experimental value is minus 2.25 I think, is one thing I would like you to understand at least for the l is equal to 0 case which we have been considering there is only one bound state there is one bound state. So, therefore you will have here here only one bound state which is deep inside it this is the bound state the wave function goes to 0, here and it is exponentially decaying here so this is the ground state wave function corresponding to the hydrogen atom corresponding to the deuterium deuteron problem.

So we have solved the fundamental problem in nuclear physics, what is this simplest atom in atomic physics; that is the hydrogen atom or hydrogen like atom like atom which consists of only one electron. So, we have solved that hydrogen atom problem and the the fundamental problem in nuclear physics is the deuteron problem; the deuteron the hydrogen nucleus consists of just one proton and the deuterium nucleus consists of one proton and one neutron. So, we have found that if we assume a a potential energy hardcore potential energy distribution like this, and if we assume V 0 to be about 40 M e V, and the range of the nuclear force is about 2 Fermi is about 2 Fermi then one gets a binding energy of the form of the order of the value which is observed by the experiment, so we have solved the we have solved also the deuteron problem.

We next consider this was the this was the second example, first example was the hydrogen like atom problem this is the second example. And now we will consider the third example third most fundamental problem in molecular spectroscopy the simplest molecule is a diatomic molecule like hydrogen chloride which consists of one hydrogen atom and one chlorine atom; these molecules these molecules in the first approximation can be assumed to be something like a dumbbell they can undergo vibrations which we to vibrational energy of the diatomic molecule, and they can rotate also with an uniform, the centre of mass will move in a straight line in a in a a chamber, but you can have rotational motion and vibrational motion.

The rotational motion gives rise to what is known as the rotational spectra, and the vibrational motion gives rise to the vibrational spectra and by carefully measuring the spectral lines, one can find out the the inter atomic distance between the molecules what is the force constant describing these small vibrations.

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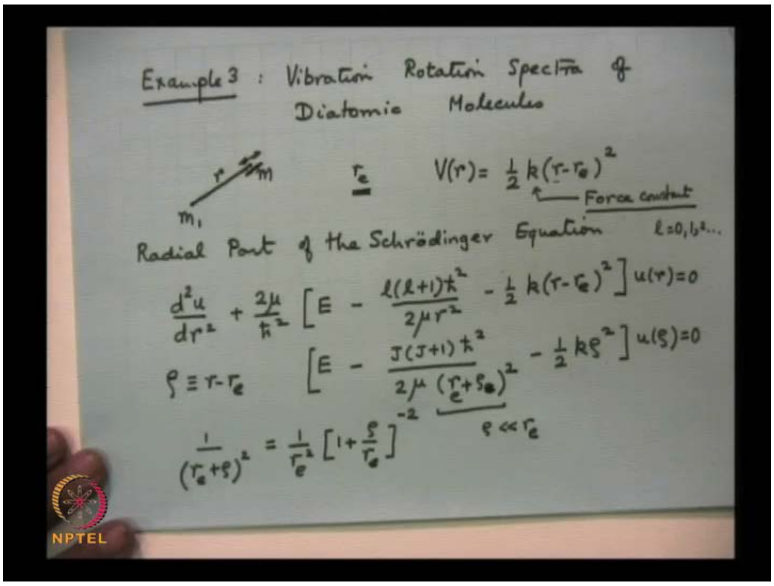

Example 3 : Vibration Rotation Spectra of Diatomic Molecules

r_e

$V(r) = \frac{1}{2} k (r - r_e)^2$

Force constant

Radial Part of the Schrödinger Equation $l = 0, 1, 2 \ldots$

$$\frac{d^2u}{dr^2} + \frac{2\mu}{\hbar^2}\left[E - \frac{l(l+1)\hbar^2}{2\mu r^2} - \frac{1}{2} k (r - r_e)^2\right] u(r) = 0$$

$$\rho \equiv r - r_e \qquad \left[E - \frac{J(J+1)\hbar^2}{2\mu \underbrace{(r_e + \rho)^2}_{\rho \ll r_e}} - \frac{1}{2} k \rho^2\right] u(\rho) = 0$$

$$\frac{1}{(r_e + \rho)^2} = \frac{1}{r_e^2}\left[1 + \frac{\rho}{r_e}\right]^{-2}$$

So, so the our third example that we will be considering is the vibration rotation spectra of of diatomic diatomic means the molecule have two atoms. Let the mass of the two atoms be m 1 and m 2, and this is the distance r and the we assume a hook slot type of force so that there is an equilibrium distance r e, and if you displace it in any direction then there is a restoring force which tries to bring it back to this equilibrium thing.

So, such a hook slot type of force in which the force is proportional to the displacement from the equilibrium separation is described like in a harmonic oscillator is described by a potential energy distribution, which is half k r minus r e whole square if the distance between the two molecules is r e then this is 0, if you displace it one way or the other then it will lead to a restoring force and the corresponding potential energy distribution is given by this.

Since the potential energy distribution depends only is assumed to depend only on the distance between the two particles, once again the two particle problem can be reduced to a one particle problem. And the radial part of the Schrodinger equation the radial part of the Schrodinger equation can be written as many people put two dots overo

Schrodinger this is an in Schrodinger was an Austrian physicist. And so you will have d 2 u by dr square plus 2 mu by h cross square E minus l into l plus 1 h cross square by 2 mu r square minus half this is the potential energy term minus r e whole square; this is the Schrodinger equation describing two atoms which are held together by a hook slot type of force such that potential energy is k times half k r minus, this k is known as the force constant force constant.

Now, let me look at this term so we will what we will do is in order to solve this equation we will introduce a variable rho which is defined to be equal to r minus r e this is not the same rho as we had discussed in the hydrogen atom problem, this has the dimensions of length so these becomes, so this term becomes E minus. In spectroscopy the angular momentum quantum number is written as J it is just a convention, so as we all known one is equal to 0, 1, 2 etcetera. So, we will just replace l by J so J into J plus 1 h cross square by 2 mu r square r square is r plus rho e r square r e plus rho sorry r e plus rho whole square I am sorry r e plus rho whole square, and this second term the last term will become half k rho square u of rho, this quantity can be written as 1 over r e plus rho whole square, I can write this as if I take r e outside r e square 1 plus rho by r e raised to the power of minus 2.

Now, please see that rho r e represents the equilibrium distance and r e represents sorry r e represents the equilibrium distance and rho represents the small vibrations around the equilibrium position, so therefore the quantity rho is much much smaller than r e for small vibrations let me mention this once again.

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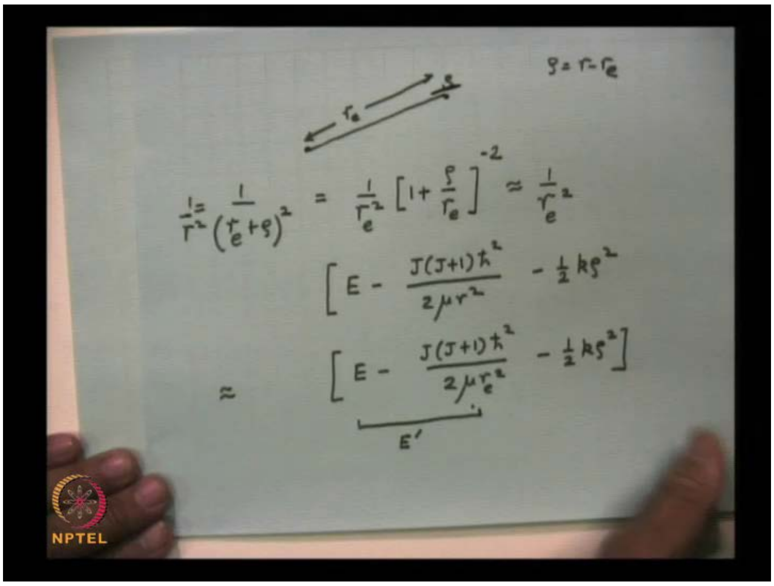

$\rho = r - r_e$

$$\frac{1}{r^2} = \frac{1}{(r_e+\rho)^2} = \frac{1}{r_e^2}\left[1+\frac{\rho}{r_e}\right]^{-2} \approx \frac{1}{r_e^2}$$

$$\left[E - \frac{J(J+1)\hbar^2}{2\mu r^2} - \frac{1}{2}k\rho^2\right.$$

$$\approx \left[\underbrace{E - \frac{J(J+1)\hbar^2}{2\mu r_e^2}}_{E'} - \frac{1}{2}k\rho^2\right]$$

That I consider two atoms this is the equilibrium position r e, now this is the double the the atoms will vibrate about their equilibrium position this atom and this atom also, but this distance which I define as rho because rho is equal to r minus r e but rho itself is very small compared if there are small vibrations, this distance is very small compared to r e, so therefore when I write 1 over r plus r e plus rho whole square this is 1 over r square this is 1 over r square.

So, I take r e outside r e outside and you will get 1 plus rho over r e raised to the power of minus 2, I can actually make a binomial expansion and I can still obtain the solutions and one can show that the effect of this term is very, very small. So as a first approximation if rho is very small I replace this by 1 over r e square which is a constant, so therefore the the the term inside the square brackets was E minus J into J plus 1 h cross square by 2 mu r square, so this will be approximately equal to E minus J into J plus 1 h cross square by 2 mu r e square, and then you have this term half k rho square minus half k rho square so this is just a constant, now this is does not vary with rho so I represent this by E prime.

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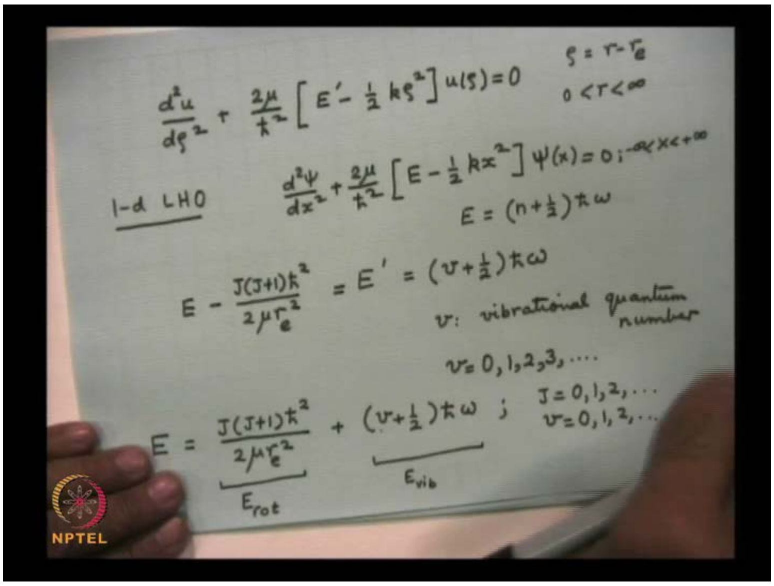

$$\frac{d^2u}{d\rho^2} + \frac{2\mu}{\hbar^2}\left[E' - \frac{1}{2}k\rho^2\right]u(\rho) = 0 \qquad \rho = r - r_e \qquad 0 < r < \infty$$

1-d LHO

$$\frac{d^2\psi}{dx^2} + \frac{2\mu}{\hbar^2}\left[E - \frac{1}{2}kx^2\right]\psi(x) = 0 ; -\infty < x < +\infty$$

$$E = (n + \tfrac{1}{2})\hbar\omega$$

$$E - \frac{J(J+1)\hbar^2}{2\mu r_e^2} = E' = (v + \tfrac{1}{2})\hbar\omega$$

v: vibrational quantum number

$v = 0, 1, 2, 3, \ldots$

$$E = \underbrace{\frac{J(J+1)\hbar^2}{2\mu r_e^2}}_{E_{rot}} + \underbrace{(v + \tfrac{1}{2})\hbar\omega}_{E_{vib}} ; \quad J = 0, 1, 2, \ldots \quad v = 0, 1, 2, \ldots$$

So the Schrodinger equation becomes I am sorry the radial part of the Schrodinger equation becomes d 2 u by d rho square plus 2 mu by h cross square E prime minus half k rho square u of rho is equal to 0. Now, if I compare this if you recall when we solved the one dimensional linear harmonic oscillatory problem one-dimensional linear harmonic oscillatory problem, then we had d 2 psi by dX square plus 2 mu by h cross square E minus half k X square u psi of X is equal to 0, so it is almost identical it is identical. And therefore and we had obtained E the energy Eigen values of the problem as n plus half h cross omega, here we will obtain we will write E prime where n is equal to 0, 1, 2, 3 etcetera, here E prime we will write instead of n the vibrational quantum number V plus half h cross omega V plus half h cross omega where V is known as the vibrational quantum number and V takes the values 0, 1, 2, 3, 4 etcetera.

So, if you recollect that the E prime which we had written down E prime, this was equal to E minus J into J plus 1 h cross square by 2 mu r e square; so this was equal to E minus J into J plus 1 h cross square by 2 mu r e square. So, the energy of the diatomic molecule will be represented as E as the rotational energy because of its angular momentum 2 mu r E square plus the vibrational energy, here J is equal to 0, 1, 2, 3 and V is equal to 0, 1, 2 this is the vibrational quantum number V and J is the rotational quantum number and we call this some some books write this as E rotational energy. And this is as the vibrational energy E r, E rot and E vib; so these are the very 2 this is an very important expression that we have derived, the energy of a diatomic molecule consists of a rotational part and a vibrational part.

Now, before we go further I would like to mention one thing that here in the when we solved the one dimensional linear harmonic oscillatory problem, X was between plus infinity and minus infinity you may remember that rho was equal to r minus r e, rho is the spherical polar coordinate so r goes from 0 to infinity.

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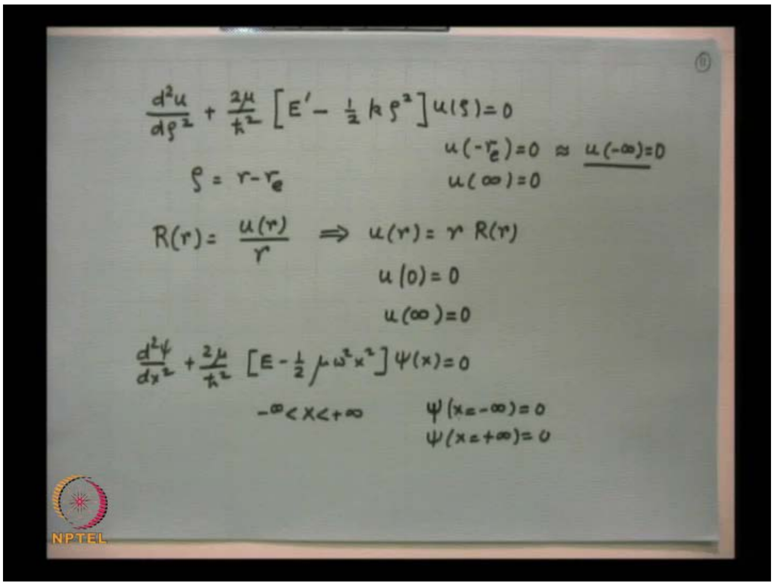

$$\frac{d^2u}{d\rho^2} + \frac{2\mu}{\hbar^2}\left[E' - \frac{1}{2}k\rho^2\right]u(\rho) = 0$$

$$u(-r_e) = 0 \approx \underline{u(-\infty) = 0}$$

$$\rho = r - r_e \qquad u(\infty) = 0$$

$$R(r) = \frac{u(r)}{r} \Rightarrow u(r) = r\,R(r)$$

$$u(0) = 0$$

$$u(\infty) = 0$$

$$\frac{d^2\psi}{dx^2} + \frac{2\mu}{\hbar^2}\left[E - \frac{1}{2}\mu\omega^2x^2\right]\psi(x) = 0$$

$$-\infty < X < +\infty \qquad \psi(x = -\infty) = 0$$

$$\psi(x = +\infty) = 0$$

So, let me write this down again we have d 2 u by d rho square plus 2 mu by h cross square E prime minus minus half k rho square u of rho is equal to 0, so rho is equal to r minus r e. And if you remember that the radial part of the wave function was given by R of r is equal to u of r by r, and so therefore for R of r to be finite at r equal to 0, so therefore from this equation I can write down u of r is equal to r, R of r.

So, therefore at r equal to 0 this is 0, so u of 0 is equal to 0. And of course at infinity it is 0, so r equal 0 means rho equal to minus rho e, so the boundary conditions are u at minus r e must be 0 and u at infinity must be 0. Now, and in the one-dimensional case as I mentioned d 2 psi by dX square plus in the one-dimensional harmonic oscillator case E minus half mu omega square X square psi of X is equal to 0, X goes from plus infinity to plus minus infinity, so u so the psi at X is equal to minus infinity must be 0 and psi at X is equal to plus infinity must be 0.

So, here u of plus infinity is 0 but u not at r equal to minus rho equal to minus infinity but rho is equal to minus rho e, but since the values of rho for which the vibrations occur are much smaller than r e. This is approximately equivalent to u of minus infinity equal to 0, so therefore in this approximation and which is really a very valid approximation the the the energy spectrum (Refer Slide Time: 46:33) the energy levels corresponding to the diatomic molecule is given by this particular expression, this is an extremely important expression and I would like all of you to remember this.

And in my next lecture we will discuss the consequences of this equation, observe the rotational vibrational rotational spectra of diatomic molecules like carbon monoxide, carbon oxide and carbon monoxide, C and O, hydrogen chloride, hydrogen bromide and and many other diatomic. The entire field of diatomic molecular spectroscopy can be understood by this particular equation of course, there are corrections to that that we had made little approximations here and there but otherwise more or less the rotational vibrational spectra of diatomic molecule.

So we have done really the the fundamental problem in atomic physics namely the hydrogen like atom problem the fundamental problem in nuclear physics. The deuteron problem and the fundamental problem in molecular spectra namely the diatomic molecular problem, so in our next lecture we will discuss the consequences of this equation. Thank you.