Basic Quantum Mechanics

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Module No. # 06

Hydrogen Atom and other Two Body Problem

Lecture No. # 19

The Hydrogen Atom Problem

In our last lecture we had discussed the two particle problem in which there were two masses m one and m two and the potential energy describing their interaction depended only on the distance between the two particles.

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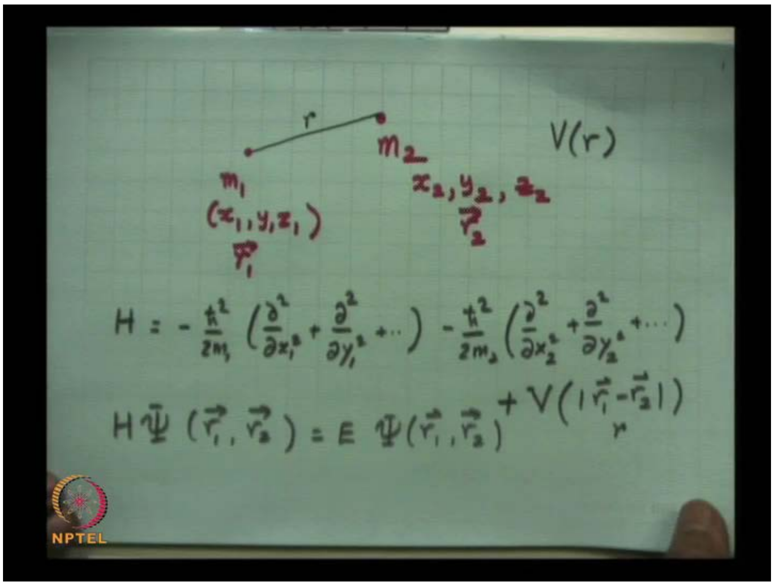

So we considered two particles m one and m two and the coordinates of this point is are x one y one z one and the coordinates of this point of this mass is x two y two and z two. So this is vectorial represented by r one vector and this is by r two vector. And the potential energy describing the interaction between the two particles depends only on the magnitude of the distance only on the magnitude of the distance between the two particles so that is a central force potential that is known as a central potential V of r. So we wrote down the Hamiltonian for the two particles and we said that this is p one square by two m one, so which is h cross square by two m one delta two by delta x one square plus delta two by delta y one square plus delta two by delta z one square minus h cross square by two m two and the coordinates of second particle delta two by delta x two square plus delta two by delta y two square plus delta two by delta z two square plus the potential energy which depends only on the magnitude of r one minus r two and this is represented by small r. So if you want to solve this equation H psi r one r two this is a function therefore of six variables this is equal to E psi of r one r two, then if we assume the separation of variables in which psi of r one r two is a function of r one multiplied by another function of r two then the method of separation of variables will not work. Indeed we introduced we introduced two coordinates one is the centre of mass coordinates m one r one plus m two r two divided by m one plus m two.

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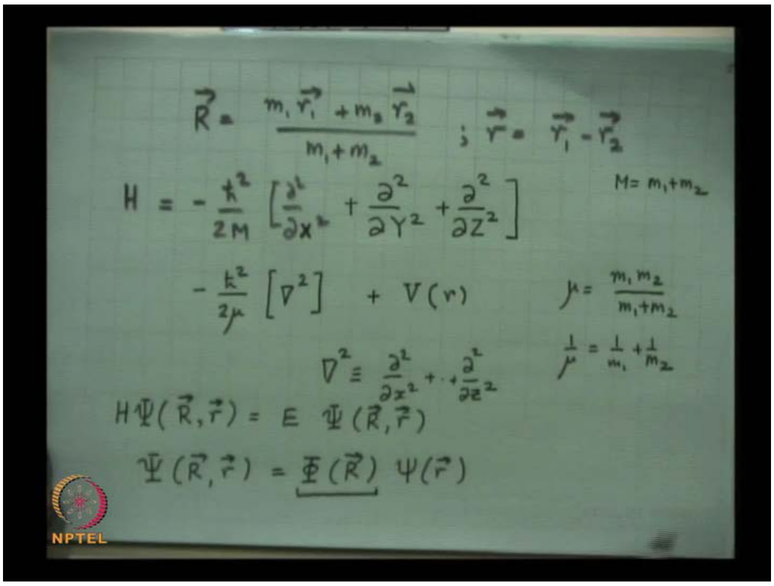

And then the relative coordinate is R is equal to r one minus r two in terms of these coordinates we found that the Hamiltonian operator becomes h cross square by two m where m is equal to m one plus m two delta two by delta capital X square plus sorry plus delta two by delta capital Y square plus delta two by delta Z square.

These are the X Y Z coordinates of the centre of mass and m is the total mass mass of the centre of mass minus h cross square by two mu and the in terms of the relative coordinates so we will just write del square where del square is equal to defined to be equal to delta two by delta X square plus delta two by delta Y square plus delta two by delta Z square in terms of the relative coordinates. And plus the potential energy function which depends only on the magnitude of r, so if we now substitute if we now try to solve the Schrödinger equation which is now psi which depends on R and small r then we found that the method of separation of variables would work. So if I assume a solution like this psi of R comma r is equal to phi of R and psi of R then the method of separation of variable will work. Here as I had mentioned in my last lecture mu is the reduced mass of the two particles which is given by m one plus m two actually the definition of the reduced mass is one over mu is equal to one over m one plus m one over m two so we can simplify it and obtain this. So this function phi of R we discussed this is the translational motion of the centre of mass free translational motion of the centre of mass. So we solve the equation and we found that capital phi of R was e to the power of I p dot r by h cross.

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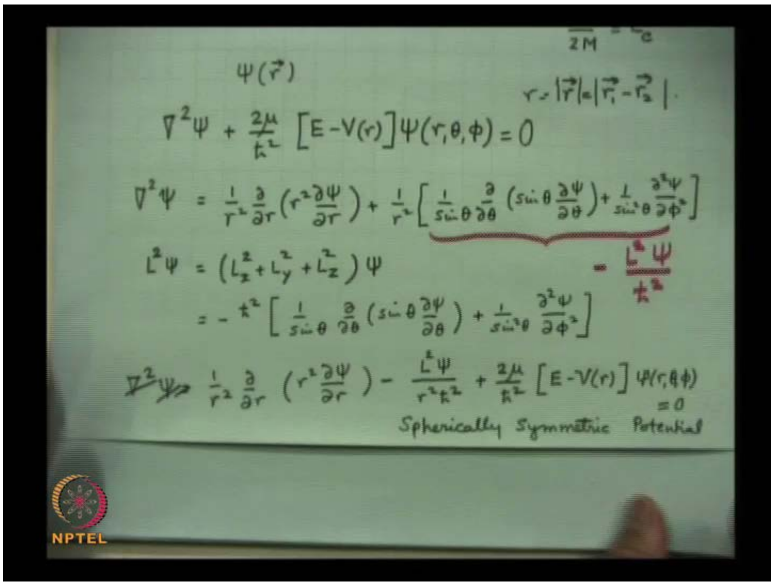

So where p square by two capital M represents the centre of mass energy represents the energy of the centre of mass. And then the the wave function psi of R satisfies the following equation del square of psi plus two mu by h cross square e minus V of r psi which is now a function of r theta phi where small r small theta of small phi are the coordinates corresponding to the corresponding to this to the to the to this vector r is equal to r one minus r two. This is equal to zero therefore we found that a two particle problem can be reduced to two parts one describes the free translational motion of the centre of mass and the other which describes the internal motion of the two particles relative motion of the two particles which satisfies the three dimensional Schrödinger equation with the potential with the spherically symmetric potential energy function. Here we have to replace the mass is the reduced mass of the two particles that is m one m two by m one plus m two this is a rigorously correct solution for any two particle problem and we will apply to this hydrogen atom which consists of a proton and the electron. We will also consider the solution corresponding to the deuteron problem which is the fundamental problem in nuclear physics describing neutron and the proton. And we will also discuss the fundamental problem in molecular spectra namely a molecule consisting of two atoms there also one gets an equation similar to this and we will solve that so the solution of this equation is of extreme importance in atomic physics in nuclear physics and in molecular spectroscopy so we have to carefully understand the solution of this equation. So we will use the spherical polar coordinate system and in which the wave function the the del square operator del del del square operator is given by one by r square this we must remember r square del psi by del r plus one over r square within brackets one over sin theta delta by delta theta sin theta delta psi by delta theta plus one over sin square theta delta two psi by delta phi square. So this is the del square operator and as you may recall that the angular momentum operator the square of the angular momentum operator operating on any wave function psi, so this was as you may recall this is L x square plus L y square plus L z square and we had obtained expressions for L z and similarly, for L x and L y and if I square and add them so this becomes minus h cross square one over sin theta delta theta delta by delta theta sin theta. Delta psi by delta theta plus one over sin square theta delta two psi by delta phi square, so we see that the quantity inside the brackets square brackets are the same therefore this quantity is equal to minus one square psi by h cross. So therefore therefore, del square of psi is equal to one over r square delta by delta r r square delta psi by delta r minus L square psi by r square h cross square. And if I substitute this expression here so del square psi so this equation becomes plus two mu by h cross square E minus V of r psi of r theta phi is equal to zero, so the potential energy function does not depend on theta and phi it only depends on the magnitude of the distance between the two particles such a potential is known as a spherically symmetric potential spherically symmetric potential.

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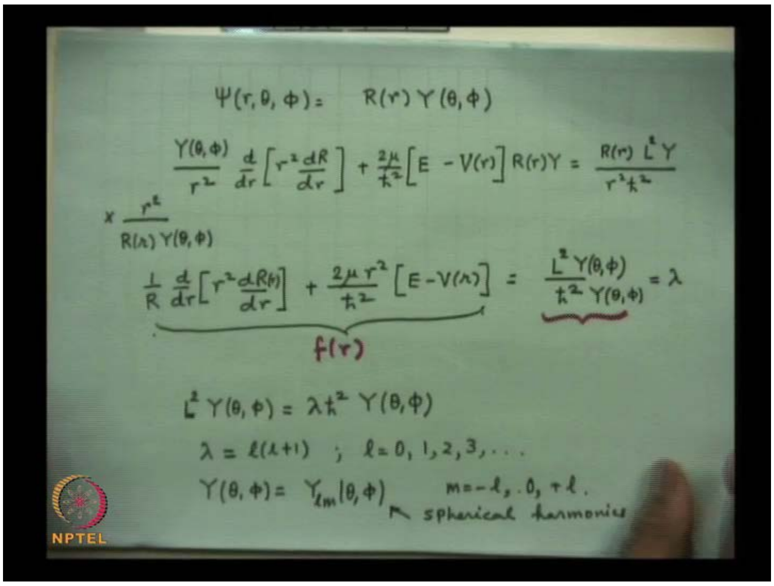

Now the solution of this equation is fairly straight forward so what we do is that we use the method of separation of variables and we write this as psi or r theta phi is equal to a function of r times a function of theta phi so if I substitute this in this equation then Y, I can take outside so I get Y theta phi you see this divided by r square and since this is a function of r only so this becomes a total differential d by dR r square dR by dR. What I will do is take this to the other side of the equation so you will get plus two mu by h cross square E minus V of r R of r Y theta phi is equal to one square which depends only on theta and phi one square depends only on theta n phi so I can take the R of r outside L square Y divided by r square h cross square.

Now the variables are still not separated out this has r theta and phi and this has r theta and phi this also has however if I multiply the whole equation by r square divided by R of r and Y theta of I then the first term will become Y Y will cancel out so will r square will also cancel out so it will be 1 over R d dr multiplied by r square dR by dr and then plus two mu r square by h cross square because I multiplied by r square and I have divided by r times Y, so this two times cancel out so I will have E minus V of r this will be equal to the r square will cancel out r Y will cancel out L square Y by h cross so L square involves only theta and phi. Y involves only theta and phi and r involves r is a function of r only so the variables are indeed separated out this is a function of r only and this is a function of theta only so a function of r cannot be equal to a function of theta unless both of them this has to be divided by Y this has to be divided by Y so this is Y.

So divided by y theta phi so this must be equal to a constant, so the left hand side is the function of r the right hand side is a function of theta and phi and we say that the method of separation of variables has worked and a function of r can be equal to a function of theta on phi only if both of them are equal to a constant. So therefore so therefore, if I write this I will get L square Y of theta phi is equal to lambda h cross square Y theta phi.

Now this is the equation determining the Eigen values and Eigen functions of the operator L square and we have found found that the values of lambda the Eigen values of the operator L square is equal to l into l plus one where l would be zero one two three etcetera only then only for these values of one this equation will have a well behaved solution. And Y theta phi are spherical harmonics Y l m theta phi and for each value of m for each value of l sorry m will go from minus l to plus l including zero, so these we have discussed in our last lecture these are the spherical harmonics.

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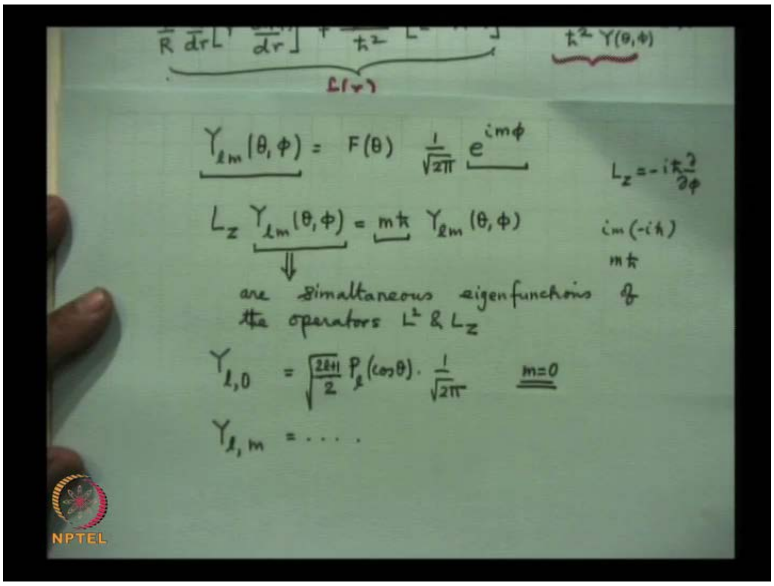

And we had shown that and we had shown for example, y m l theta phi this is a function of theta times the phi dependence was of the form of root two pi e to the power of i m phi F. So therefore, Y l m theta phi are simultaneous Eigen functions of L square as well as L z, so L z Y l m theta phi L z it may recall the which we had first derived from first principles minus i h cross delta by delta phi so this is equal to m h cross Y l m theta phi because the phi dependence is of the order of is of the form of e to the power of i m phi and if I differentiate with respect t phi I will get i m and if I multiply by minus i h cross as it is here so then you will get m h cross these are the Eigen values. So Y l m theta phi are simultaneous simultaneous Eigen functions this you you all must remember of the operators L square and L z and as we had discussed we are also shown that for Y l for m equal to zero, so this is under root of two pi and these are proportional to P l of cos theta so the normalization constant was 2l plus one divided by two. So these this is for m equal to zero for arbitrary value of l and m the spherical harmonics are little complicated and we will discuss this little later may be about six seven lectures later, so Y theta phi so this this term gives me an Eigen value equation and we have shown that lambda must be equal to l into l plus one. And therefore, let me write down the so lambda is equal to lambda is equal to l into l plus one.

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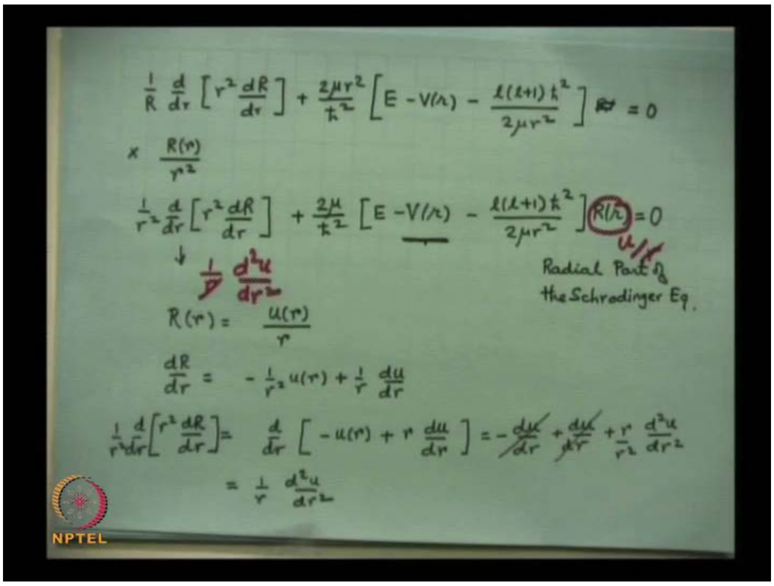

So let me write the radial part of the equation so, this is one over R d dr into r square dR by dr plus two mu r square by h cross square E minus V of r and I take l into l plus one on the left hand side so it will be minus l into l plus one and since I have taken inside the brackets, so I must multiply by h cross square divided by divide by two mu r square R of r sorry this is equal to zero.

The next step is I multiply by R of r divided by r square of r so, this becomes this becomes one over r square d dr r square dR by dr plus two mu by h cross square E minus V of r minus l into l plus one h cross square by two mu r square R of r equal to zero, so this equation is known as the radial part of this of the Schrodinger equation this is an extremely important equation and we should all remember this is known as the radial part of the Schrodinger equation. So if we solve this equation we will obtain the Eigen values in the problem please notice that we have still not specified V of r, so we have carried out an important simplification for any central force potential that is if we consider two particles and if the potential energy describing these the interaction between the two particle depends only on the distance then the three dimensional Schrodinger equation can always be simplified in terms of only one variable. So we do not have to solve in each case the three dimensional Schrodinger equation we just have to solve one equation involving the the radial coordinate r so this is the major simplification which is possible only when the potential is spherically symmetric that is V depends only on r, there is another simplification possible if I substitute define a new variable which is u of r by r that is I u of r is defined as r times R of r. So this is the definition so this equation represents the definition of u of r then simplification occurs because dR by dr if I differentiate this this becomes minus one over r square u of r plus one over r d u by d r in this there is an r square termed here so if I multiplied this by r square dR by dr please leave some space here so if I multiply by r square it becomes minus u of r plus r times du by dr. Then I must differentiate this with respect to r, so I differentiate this so I differentiate this with respect to r so this will become minus du by dr plus du by dr because the differential coefficient of r with respect to r is unity plus r d t u by dr square and you can see this term cancels out with this term. So if I divide by r square so we get r square so divide by r square so we get one over r d t u by dr square so this term this term becomes one over r d two u by dr square and here this term will become u of r by r so the r r cancels out and we finally, obtain I hope you understand so, let me do this once again so you have one over r d two u by dr square.

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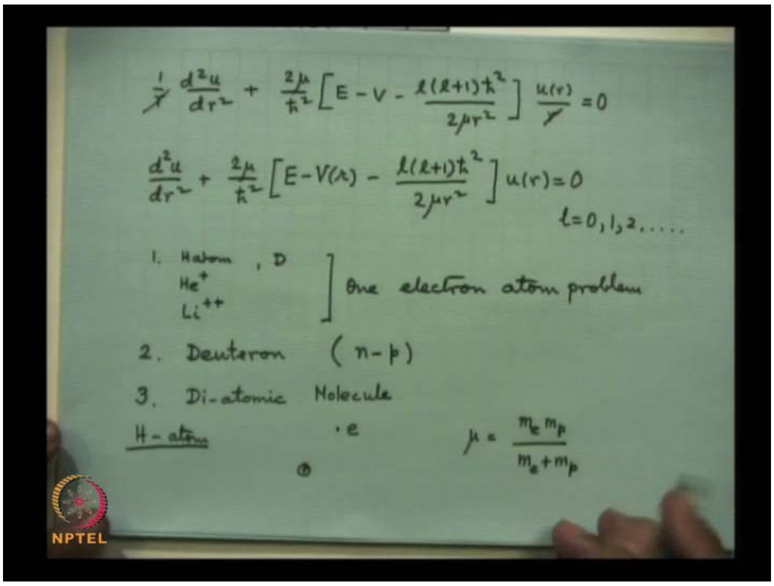

So you write down one over r d two u by dr square plus two mu by h cross square E minus V minus l into l plus one h cross square by two mu r square. This is the due to the one square operator or the orbital angular momentum multiplied by r of r r of r is u of r divided by r so this this is what I tried to say this r and this r cancel out and we get a very simplified equation that d two u by dr square plus two mu by h cross square e minus v of r minus l into l plus one h cross square by two mu r square multiplied by u of r is equal to zero. This is also known as the radial part of the Schrodinger equation and this you must remember this one and one is equal to zero, one, two, three etcetera. We will solve this equation for hydrogen atom problem actually for hydrogen like atom so that for helium plus atom for the deuterium atom problem for the lithium doubly ionized which consists of one electron. So essentially for all one electron atom problem and we will all solve for the deuteron problem that is two particles like neutron and proton and we will all solve the same equation for a diatomic molecule like hydrogen chloride diatomic molecule and we will get what is known what are known as the rotational and vibrational spectrum of the diatomic molecules. So let me first consider the simplest of the atoms namely the hydrogen atom as we all know hydrogen atom consists of an electron and a proton the electron proton is about 1836 times heavier than the electron so the reduced mass of the hydrogen atom will be m e m p divided by m e plus m p.

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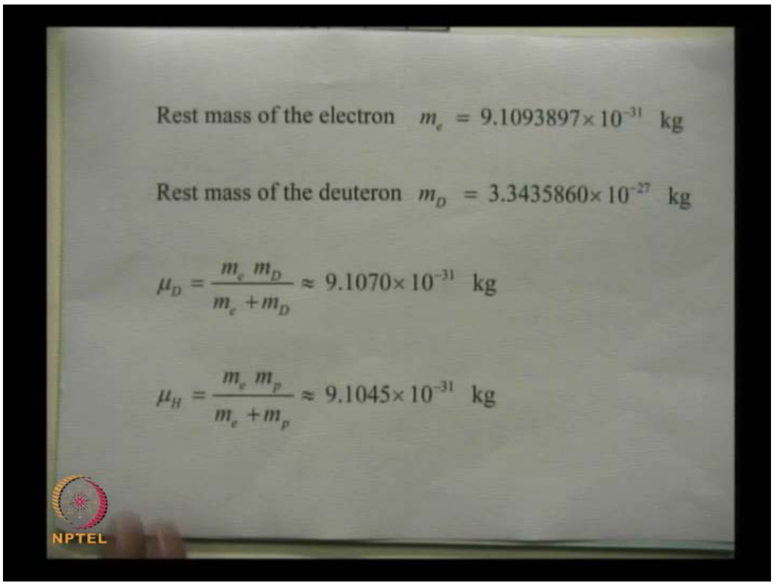

So you have here I have written down in any book including in our book so have given the accurate values of the rest mass of the electrons which is 9.10939897 into ten to the power of minus thirty one k g.

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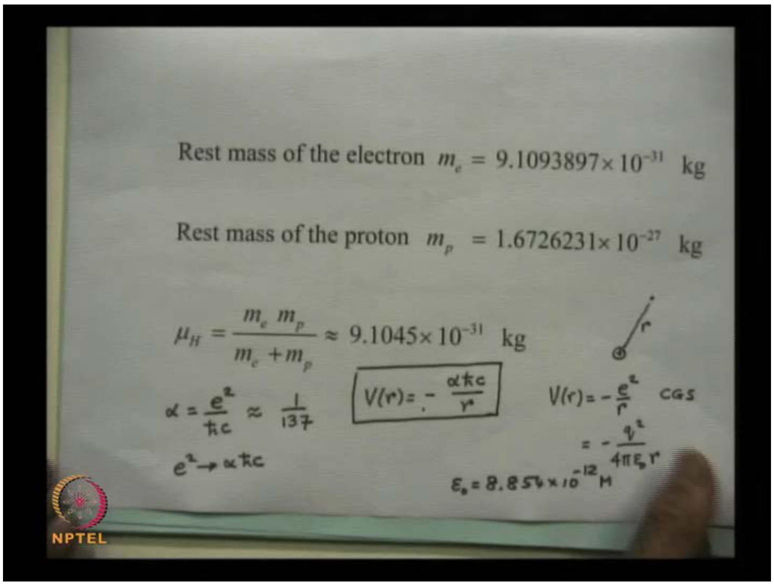

Sorry this is for the deuteron cell this is for the proton the rest mass of the proton is 1.6726231 so the rest mass corresponding to the hydrogen atom is m e m p divided by m e plus m p is 9.1045 into ten to the power of minus thirty one kilograms if we if we solve this if we consider the deuteron atom so the this is the rest mass of the deuteron deuterium which consists of a proton and a neutron so much. So you have the deuteron deuterium atom which consists of a proton and a neutron and a single electron this is the nucleus this is the nucleus so the analysis of the deuterium atom is the same as that of the hydrogen atom except now the the rest mass of the deuteron deuteron the nucleus is now slightly more. So we will first consider the hydrogen atom problem in which the hydrogen atom consists of as I mentioned the electron and the proton and the reduced mass is given by 9.045 into ten to the power minus thirty one k g and the potential energy describing this interaction is given by in the CGS system of units we knew the CGS system of units this is given by the V of r is equal to minus e square by r in the CGS system.

In the MKS system of units it will be minus q square by four pi epsilon naught r where q is the charge of the electron measured in coulomb's and epsilon zero is the dielectric permittivity of free space so as we all know that epsilon zero is equal to 8.854 into ten to the power of minus twelve MKS units so just for the sake of convenience we will use the CGS system of units however if we there is a dimensionless constant which is known as the fine structure constant alpha which is given by e square by h cross c. This value is approximately equal to one over thirty seven, so if I replace e square by alpha h cross c then that formula is valid both in the MKS system of units as well as in the CGS system of units if I write V of r as equal to minus alpha h cross c by r then this formula is valid more in the MKS system of units as well as in the CGS system of units. So let me write down the we can use this formula or this formula it does not matter so our objective is to solve this equation our objective is to solve this radial part of the Schrodinger equation with V of I given by minus e square by r or actually if we consider an atom whose nucleus has charge z e then it will be minus z e square by r.

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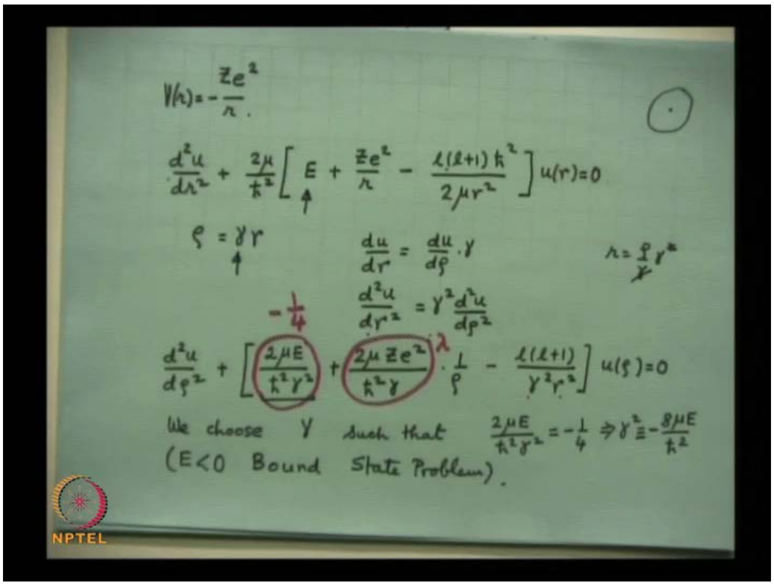

So we will assume that that let us suppose the nucleus has a charge z e so the potential energy given minus z e square by r, so you will have d two u by dr square plus two mu by h cross square you may solve for the bound states for which e is negative for which e is negative and when the when you have proton and electron the total energy of the hydrogen atom is negative so those are the bound states of the problem. So the the energy E will be negative so e minus V of r so this will be plus z e square by r minus l into l plus one h cross square by two mu r square u of r is equal to zero. Now let me write in terms of a dimensionless units so that it becomes looks little simpler so we define a coordinator rho which is equal to gamma r we still do not know the value of gamma and we will choose gamma appropriately. So we will have du just as we did in our harmonic oscillator problem du by dr is equal to du by d rho into d rho by dr so that is gamma so if I differentiate this again so we will have d two u by dr square is equal to gamma square d two u by du square so I substitute it here and then divide the whole expression by gamma gamma square so you get you see this I substitute for d two u by dr square here and write gamma square d two u by dl. So write d two u by d rho square plus if I take two mu by h cross square outside two mu e by h cross square gamma square plus two mu z e square by h cross square please see this r is rho by gamma r is rho by gamma and then I had divided by gamma square this will be gamma square in the denominator so one gamma one gamma will cancel out so this will be gamma times one by rho.

And you please see this two mu by h cross square will cancel out so this will be l into l plus one and I had divided by gamma square, so this will be gamma square r square so this will be rho square I still had not choose have not chosen the value of gamma just as we did in our harmonic oscillator problem. We choose gamma we choose gamma such that you know e is negative so this quantity is minus one by four so two mu by h cross square gamma square is equal to minus one by four therefore, this implies that gamma square is minus eight mu E by h cross square this is the definition of gamma I am assuming E to be negative bound state problems E is less than zero which corresponds to the bound state problem. So I choose gamma square is equal to eight mu by h cross so that here this factor I will replace by minus one by four I write this I define this as lambda and this quantity is rho square gamma square r square is rho square so that the this equation simplifies to the following.

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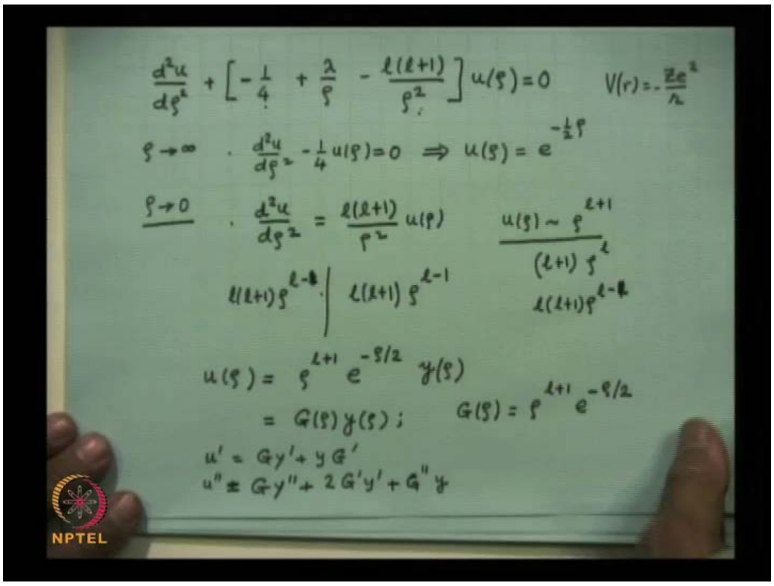

So the above equation becomes d two u by d rho square plus minus one by four plus lambda by rho minus l into l plus one by rho square u of rho is equal to zero. Where where gamma square is so much and also we have lambda is defined to equal to two mu z e square by h cross square gamma, gamma is this we will calculate it explicitly later. So this is the radial part of the Schrodinger equation to which it had simplified for the hydrogen like atom problem in which the potential energy function the charge of the nucleus is z e and therefore, the potential energy function is r. R is the distance between the nucleus which is assumed to be a point and the electron. Now I want to solve this equation and such equation as we had done for the harmonic oscillator problem we look for solutions both for rho tending to zero and rho tending to infinity. Now let us take the simple case so as rho tends to infinity this term and this term becomes divisible. So I can neglect this so d two u by d rho square minus one by four u of rho is equal to zero, so the solution is u of rho becomes e to the power of either plus half rho or minus half rho we will choose the minus sign because plus half will blow up at infinity then as rho tends to zero this term is very important. Because this goes to infinity fastest then this is a constant they say this is fastest so as rho tends to infinity sorry this is d two u by d rho square. So the radial part of the Schrodinger equation becomes if we neglect the other two terms is equal to l into l plus one by rho square. Now the solution which is well behaved at rho equal to one as you can see is rho to the power of l plus one because if I substitute this if I differentiate this twice if I differentiate it once I will get eleven plus one rho to the power of l and if I differentiate it again then I get l into l plus one rho to the power of l minus two. So my left hand side becomes l into l plus one rho to the power of l minus two and the right hand side becomes l into l plus one this is rho to the power of one plus sorry this is l minus one I am sorry so rho to the power of l plus one minus two so this will be rho to the power of one minus one so this is the solution to which it tends to as rho tends to zero. So these two limiting forms suggest that we try out a solution like this u of rho is equal to rho to the power of l plus one e to the power of minus rho by two into y of rho and I write this down as G of rho times y of rho where G of rho is identically equal to rho to the power of l plus one minus e to the power of minus rho by two. I hope this is clear now if I differentiate it once. So you will get u prime will be G y prime plus y G prime if I differentiate this again you will get you will get G y double prime plus y prime G prime y prime G prime from here two g prime y prime plus G double prime y therefore, we will have that u of rho if it is G of rho y of rho then u double prime of rho if I differentiate this equation twice.

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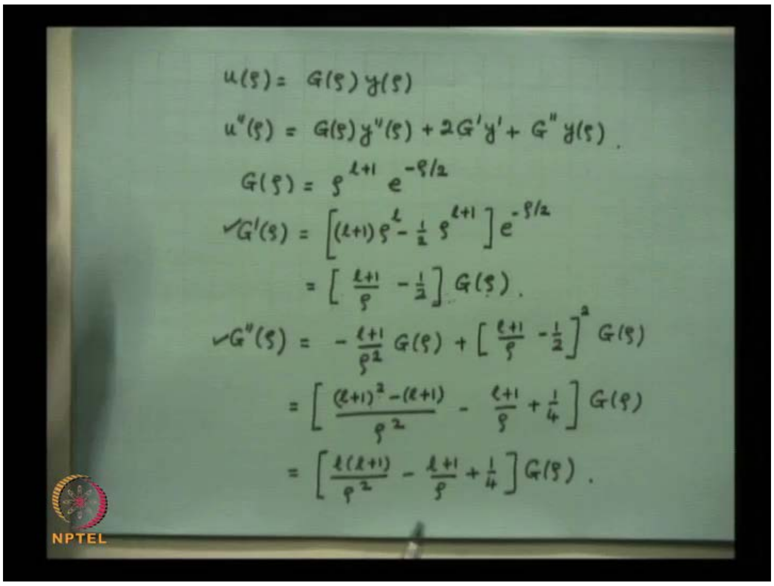

So it will be G of rho y double prime of rho plus two G prime y prime plus G double prime y of rho, where G of rho is equal to rho to the power of l plus one e to the power of minus rho by two.

Let me differentiate this so G prime of rho because I need G prime and G double prime so G prime of rho is equal to l plus one multiplied multiplied by rho to the power of one into e to the power of minus one rho by two which I will take outside and if I differentiate this so this will become minus rho to the power of one plus one divided by two half sin because it is multiplied by e to the power of minus rho by two. So if I rho to the power of one plus one if I take outside so you get one plus one divided by rho minus half rho to the power of one plus one multiplied by this so that is G of four, so G double prime of rho if I differentiate this again the differential coefficient of this term will be minus one plus one by rho square multiplied by G of rho plus eleven by rho minus half times G prime of rho.

But G prime of rho is this times G of rho so this will be square of G of rho I hope this is clear so as I have differentiated this once so first I differentiate this term so this will be minus one over rho square and then I differentiate this G prime of rho so this will be G prime of rho is l plus one by rho minus half into G of rho so this becomes square so this becomes please see this. So this is l plus one whole square l plus one whole square by rho square minus l plus one divided by rho square and the square of this is or if I multiply this square of this then this will be twenty one plus one by rho and then plus one by four G of rho so if we take one plus one whole square outside bracket so one plus one minus one so that is l. So this becomes l into l plus 1 by rho square minus one plus by rho plus one by four G now I have the expression for G prime of rho I have the expression for G double prime of rho therefore, u double prime is a little laborious algebra but, fairly straight forward that you will have u double prime will be equal to as we have said that G y double prime plus 2 G prime y prime plus G double prime y.

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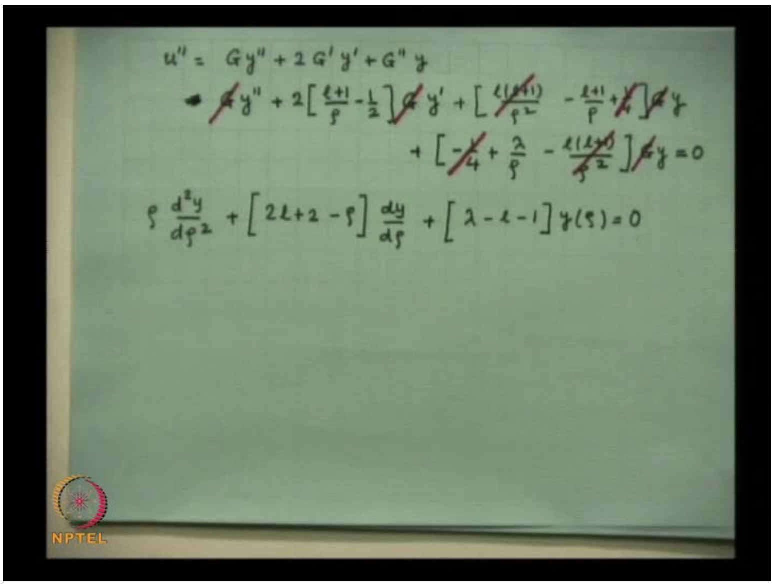

So this will be first of all the first term will be G y double prime plus two G prime G prime will be 2 l plus one by rho minus half times G into y prime and plus G double prime plus G double prime is equal to l into l plus one by rho square minus l plus one by rho plus one by four into G of rho times y. This is u double prime and if I recollect the radial part of the Schrodinger equation had these three terms d two u by d rho square plus within brackets minus one by four plus lambda by rho minus lambda l into l plus one by rho square, so I will put it here so my radial part of the Schrodinger equation becomes plus within brackets minus one by four plus lambda by rho minus l into l plus one by rho square times u. U is G times square so the G cancels out everywhere and if you carefully see this minus five by four cancels out with this minus one by four these are rigorously correct solutions this term cancels out with this term so if I multiply by so the G is also cancel out G cancels out from here here here here so we will have if I multiply this with rho so I get rho d two by d rho square plus if I take two inside 2 l plus 2 2 l plus two minus rho because I had multiplied by rho. dy by d rho plus, I have here I have multiplied by rho so this rho cancels out lambda minus l minus one y of rho is equal to zero. Now this is the equation if you recall that this is very similar to the confluent hyper geometric equation that we had written down earlier before we finish this class we I would like to mention that we had obtained asymptotic forms for u of rho for rho tending to infinity as e to the power of minus half rho. For rho tending to zero as rho to the power of one plus one, so these two helped us to write the solution in this form but, this is a rigorously correct solution rigorously correct solution there is no approximation here so y of rho is defined by this equation and y of rho now satisfies this particular equation. So if I am able to solve this equation then I would have obtained a rigorously correct solution of the Schrodinger equation of the radial part of the Schrodinger equation for the hydrogen atom problem or for the hydrogen like atom problem so these are all rigorously correct solutions I want to emphasize that thank you.