Introductory Quantum Chemistry

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Lecture - 24
Hydrogen Atom: Finding the Functions theta and phi

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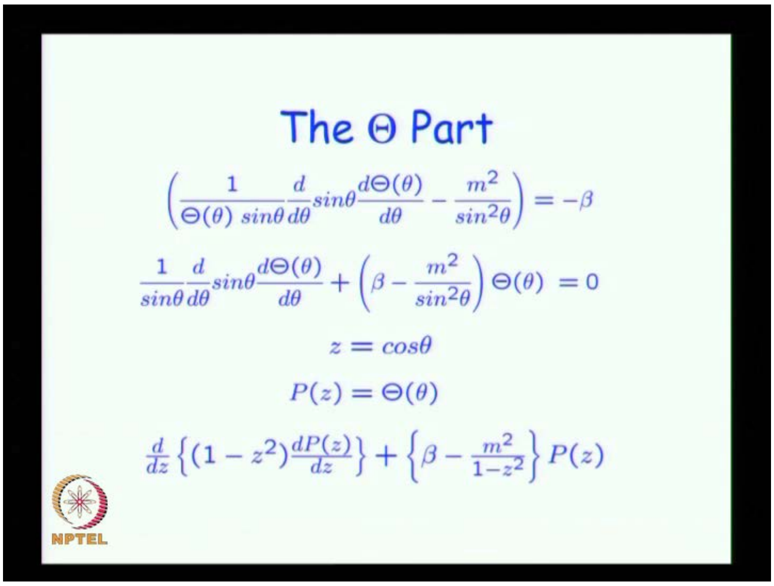

I shall start with where we have left the last time, actually the equation for the theta part. I have shown in the in this slides, this was the equation for theta, we had this constant minus beta which we introduced. And then we rearrange that equation to get this equation, then me made a substitution is a difficult to cos theta and p of z this depend to be equal to vertically theta. And then what happens is that capital p obeys the differential equation that is shown here this equation we discussed all this.

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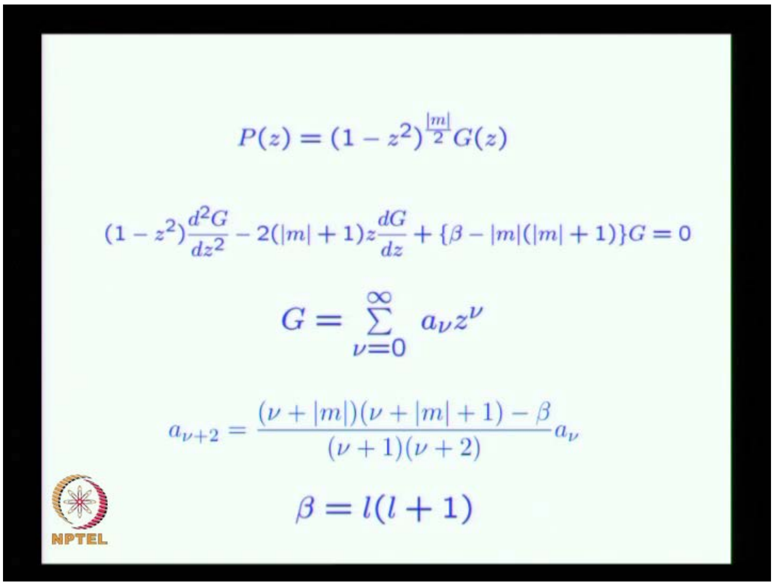

And then the made this substitution p of z this equal to 1 minus z square to the power of absolute value of m by 2 into g of a z. The aim is to find differential equation for capital G and we found this differential equation this is what we have done in the last lecture.

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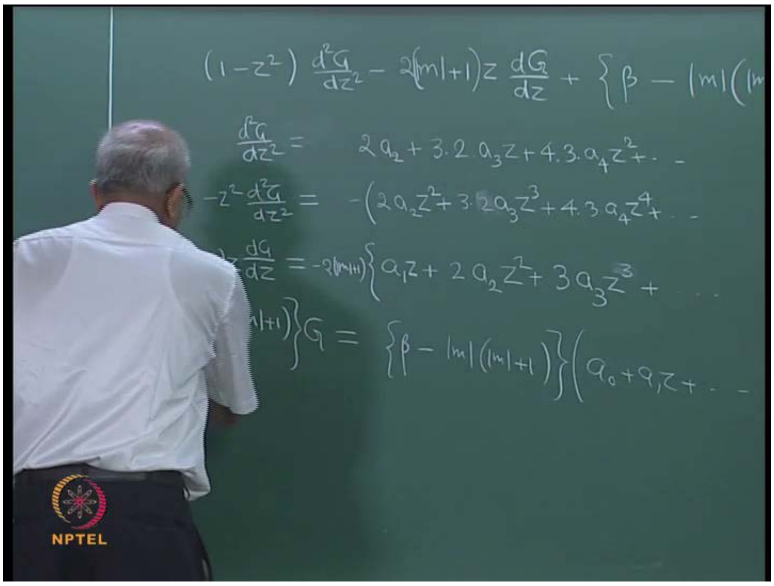

So, I will I will. So, I will starts from this equation. So, the equation says that 1 minus z square. So, this is the differential equation and we want to solve this answer, we will make yourself this idios expansion, which will assume that G may be expanded as a power series. So, G may be written as a 0 plus a 1 z plus a 2 z square plus etcetera.

General term I will use the symbol mu for the general term a mu is z to the power of. So, mu can be 0 or 1 or 2 or anything. So, that is the general term.

So, now let me calculate the first derivative of G d g by d z would be well if you say that this is the you and if you differentiate with respective z. Basically 0 will vanish and you will have the first term as a 1 you will have a 1 plus 2 a 2, yes etcetera from the mu th term you are going to get, mu a mu z to the power of mu minus 1. So, this is the first derivative and I will never write the second derivative, as we can say that I am writing them in order also that I can just add it up to get this result.

So, d square G by d z square will be you have to differentiate this a 1 will disappear you will get 2 into a 2 plus 3 into 2 into a 3 z plus 4 into 3 into a 4 z square plus etcetera. And so, what I will do is I will write the term coming from here I would have mu into mu minus 1 a mu is z to the power of mu minus 2. I will also write the term which you has z to the power of mu, what would that be its going to be mu plus 2 into mu plus 1 into a mu plus 2, there is one term in between which I have in written. So, now if you look at this expression is a you need the second derivative, but also need minus z square into the second derivatives or it may just hide that.

Well that will give me minus let me keep the minus sign outside 2 a 2 z square plus 3 into 2 a 3 z cube, this is going to give me mu into mu minus 1 a mu z mu into a to the power of mu. So, that is fine then I need minus 2 times magnitude of m plus 1, let’s a leave me just take this and multiplied by that term, right? So, I am going to multiply by minus 2 into magnitude of m plus 1 into z.

So, this minus 2 into m plus 1 I will keep outside, but this a z that I am going to take inside. So, I will have a z coming here this will become a z square this will become a z cube and that the way I have written this things, you see this will become z to the power of mu that is etcetera. And then the last term last term is; obviously, very simple beta minus magnitude of m into magnitude of m plus 1 into G is equal to beta minus magnitude of m into magnitude of m plus 1, a 0 plus a 1 z plus etcetera a mu is z to the power of mu plus a z.

So, you have to add up all this things and when I add up you see on the left hand side you are going to get just this terms and therefore, those the some of those terms should be equal to 0. And therefore, if you added up all this things what should happen the answer should be equal to 0, but this is the power series in a z and you are saying that this power series z must be equal to 0, for all values a z. That can be valued only if the coefficient of each power of a z must be equal to 0.

And therefore, we can take a general term that that will be the coefficient of a z that to the power of mu and say that that must be equal to 0. So, let us do that. So, if you took the power of a z if you took the coefficient of a z to the power of mu, what are you going to get from here? We are going to get from the first term we are going to get mu plus 2 into mu plus 1 a mu plus, then from this term I will get this term it is going to be minus right that is in the minus on outside mu into mu minus 1.

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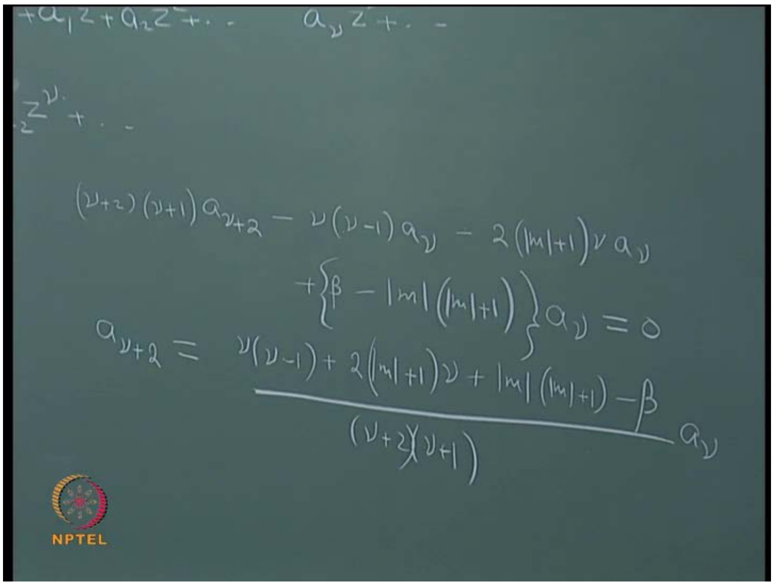

So, it is what I am going to get from there while from here what will I get? I will get there is a minus 2 m plus 1 mu into a mu, would I would not going to go wrong anywhere, this has taken into account. Then from here I am going to get plus beta minus m into m plus 1 into a mu and this should be equal to 0. This is the relationship that I get you will realize that this is the relationship, which is going to give me a mu plus 2 in terms of a mu. So, it is a recursion relation and I can I rearrange this, how will I rearrange this? I shall write this as a mu plus 2 is equal to this terms I will take to the right hand sides.

So, if I took them to the right hand side what will happen I will get mu into mu minus one plus 2 magnitude of m plus 1 into mu plus magnitude of m into magnitude of m plus

1 minus beta divided by mu plus 2 into mu plus 1 into a mu. So, this is the recursion relationship which will determine a mu plus 2 in terms of a mu. So, if you give me a 0, I will be able to calculate a 2 then a four a 6 etcetera and similarly if you give me a 1 I will be able to calculate a 3 a 5 and so on.

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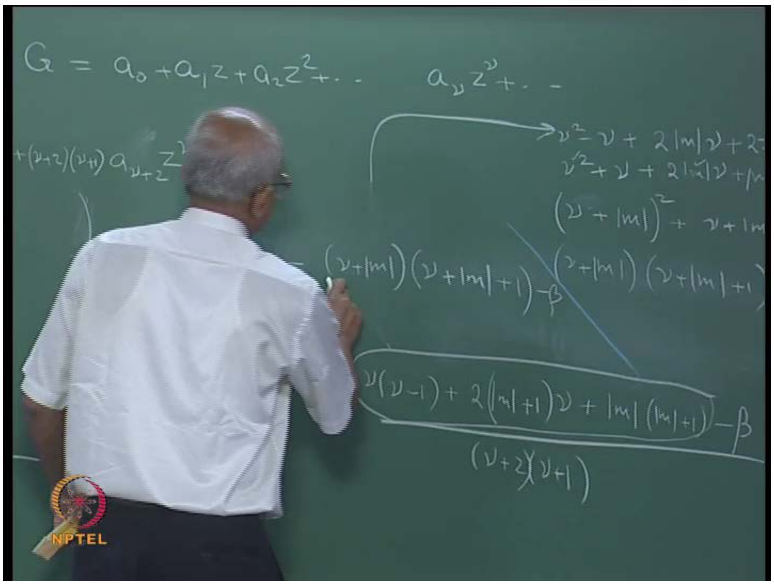

But this numerator I will simplify, well you have mu into mu minus 1, that is actually mu square minus mu this term plus let me just expand this, I am going to get two times m into mu plus 2 mu plus magnitude of m square plus magnitude of m and the just write in this part. The minus beta I am not writing now, and if you simplify this, what is going to happen you are going to get mu square minus mu and 2 mu will combine, I will get plus mu plus 2 magnitude of m mu plus m square plus magnitude of m.

And then this one and this magnitude of m square you can combine this one, that one and that one you can combine we are going to get mu square plus… Well if you combine you will get mu plus m the whole square plus what are you left with you are left with plus mu plus with magnitude of m and that actually can be written in a in a simple form it is nothing but mu plus m into mu plus m plus 1.

So, therefore the recursion relationship actually simplifies let me just write this once more, it says that a mu plus 2 is equal to mu plus magnitude of m. Maybe I should rub up this patch because I do not need this anymore multiplied by a mu. So, that is the recursion relationship that I get after all this simplifications and therefore, let me just remove this also ultimately this is all that we need. This is a to write the recursion relationship, but then you see the know that if the series goes to infinity, we may run into problems this is exactly the kind of thing that happens with there we argued that you have to terminate the series at the finite power of the variable. Otherwise if it went to infinity then the behavior is unacceptable. So, the same thing happens with this.

And therefore, you have to terminate at a finite of power of z and how will you do that? Well you want to have for example, a 4 non 0, but a 6 you would like it to be equal to 0 and that can be satisfied fully if only if this beta is equal to only if this beta if a this term has to vanish, for a particular value of mu. May be mu is equal to 4 or may be mu is equal to 3 or 2 or 1 or may be 5 or 6 or 7, whatever for some value of mu this has to vanish. And therefore, what is the conclusion the conclusion is that the value of beta is restricted we had introduced it as a it as a constant to define that for the arbitrary value of these constants, we are not going to get an acceptable solution. Acceptable solutions can be obtained only if beta is equal to how much?

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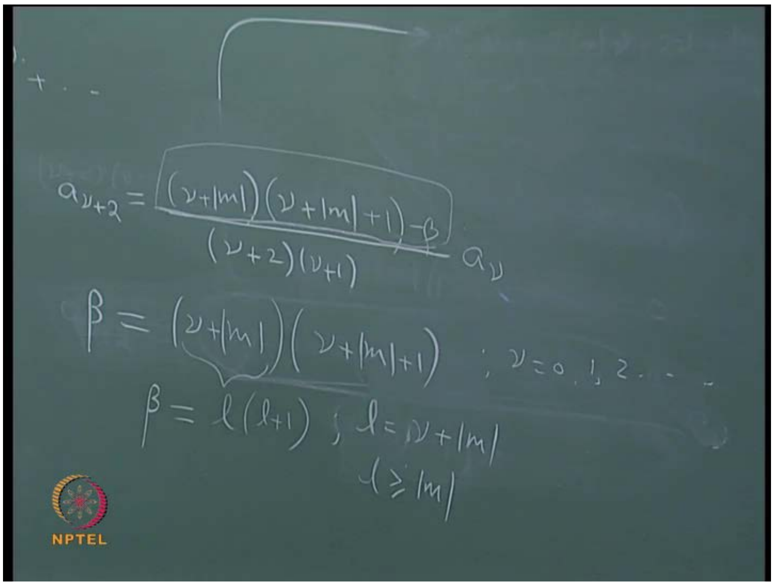

Beta is equal to mu plus m into mu plus m plus 1 only if this is the way it is, but what is the value mu, that you can have mu you can have 0 or you can have 1 or 2 or 3 or any number you like. So, you have the freedom you can choose mu to be equal to 0. So, you say the mu may be 0 or mu may be 1 or two it has to be an integer including the value 0.

I mean if that is the way that is I can introduce a new integer which I will denote by the symbol l going to define l is equal to mu plus magnitude of m right. So, then I will I would be able to write this as beta is equal to l into l plus 1 there, what is l, l actually is defined to be mu plus magnitude of m that is just my definition of l, but with that definition you will realize that with this number l that I am defining, what are the values that it can take? The values that it can take are actually this mu may be 0 or it may be 1 or it may be 2 etcetera.

So, therefore I realize that l itself has to be an integer, but l has to be greater than or equal to the magnitude of m. If I introduce that quantum number a number l by this definition then I am restricted in that the value of l, we look at this expression in this expression, the minimum possible value for mu is 0. So, therefore l has to be greater than or equal to magnitude of m and you would probably realize that this l is nothing but the Azimuthal quantum number that you might be familiar. And m actually is the magnetic quantum number, and if you remember what you have said it in previous classes l and m have to satisfy this condition. And to the next thing is this is already there in my slides.

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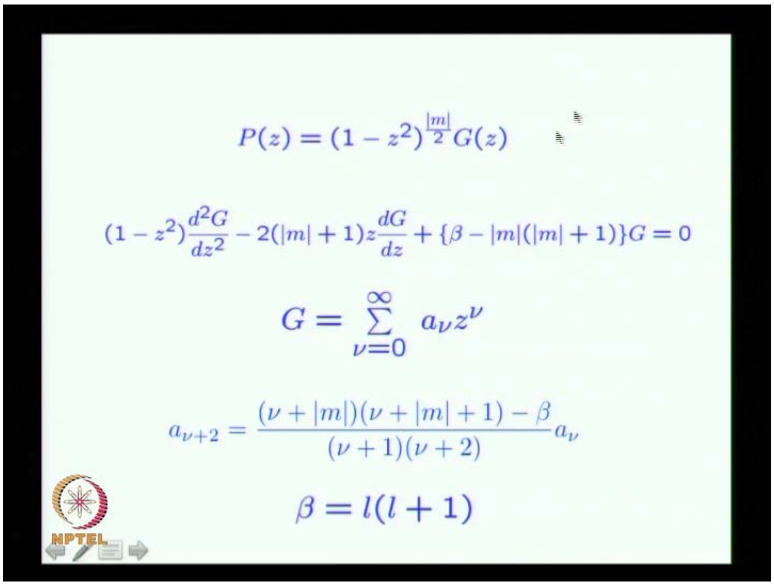

So, this is the recursion relationship which I had written, and then I say beta is equal to l into l plus 1. And then if beta is equal to l into l plus 1 what will happen to my original differential equation.

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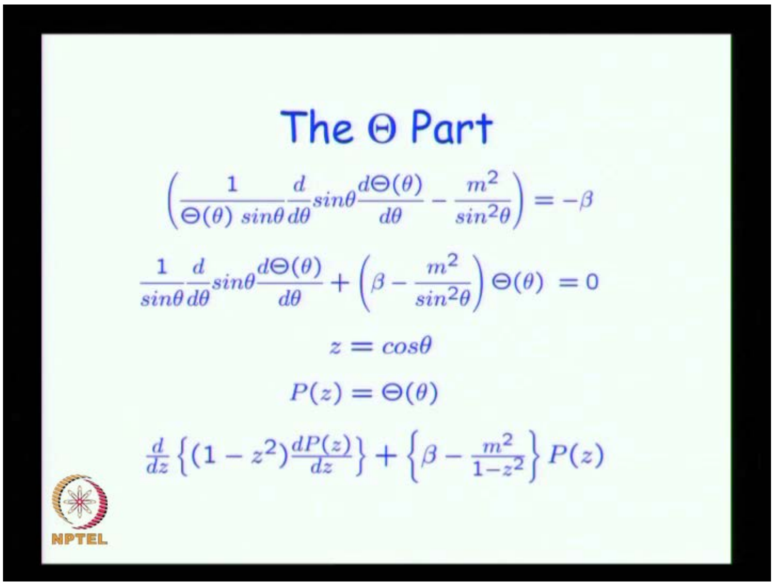

Where is my original differential equation? The original differential equation is this one this is the original differential equation. When we had this differential equation they be all your beta we do not know what it was, but now we find that beta has to be equal to l into l plus 1 then only we will get acceptable solutions. Otherwise we do not get acceptable solutions.

And when beta is equal to l into l plus 1 this function right we can now you can replace this beta with l into l plus 1, where l is an integer greater than or equal to magnitude of m. Then what happens is that this function is very well known it was actually very well known to the mathematicians, this differential equation itself was very well known and they also knew the solutions. And those solutions were known as associated legendary functions.

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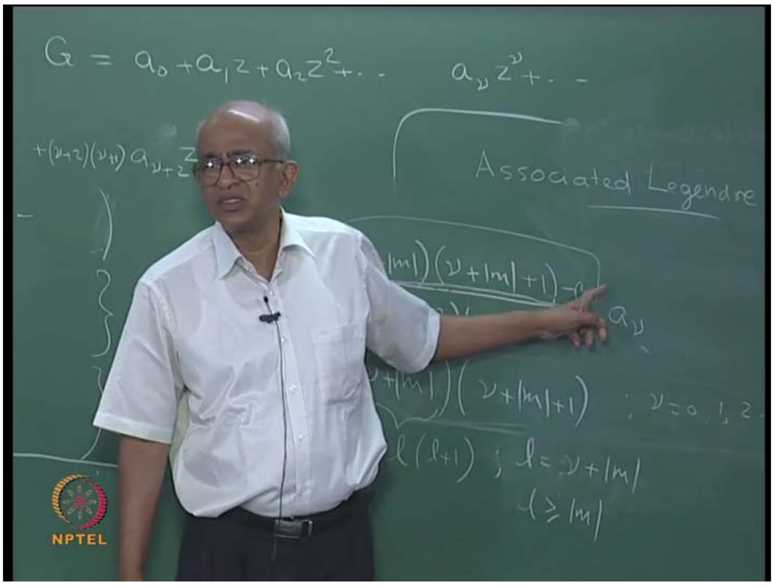

So, this non really associated I mean if I want to find the functions actually all that I need to do is I can use this recursion relationship. I can find the functions if I want, but there is no we will do because you see this is now a differential equation, which is very familiar to the mathematicians we will just take their knowledge, and we will just write down I will give that the details of this function later.

And using those details we will just write wrote the functions rather than actually it as I said it is it is very easy, it is not difficult for me to find what those functions are. All that I need to do is I have to use this recursion relation then I will get everything, but we will not do that because the functions the properties are all very well known. Now, with this let us look at the equation for capital R we will compare to this when we when we look at the full solution.

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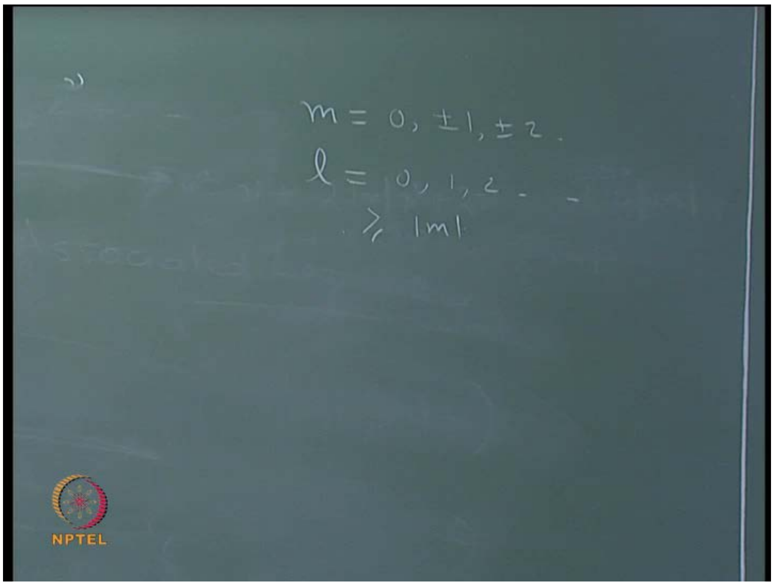

So, till now we have got two quantum numbers, the first was m, m can take the values 0 plus or minus 1 plus or minus 2 etcetera. We found another quantum number this first one was obtained when we try to solve the equation for capital 5, then we try when we solve the equation for capital theta, we found the next quantum number l it may taken the value 0 1 2 3 etcetera. But it has to satisfy the condition that it has to be greater than or equal to m, this are the things that we have found. And now we will look at the equation for capital R, which we have written down earlier. So, I will just look at my slides.

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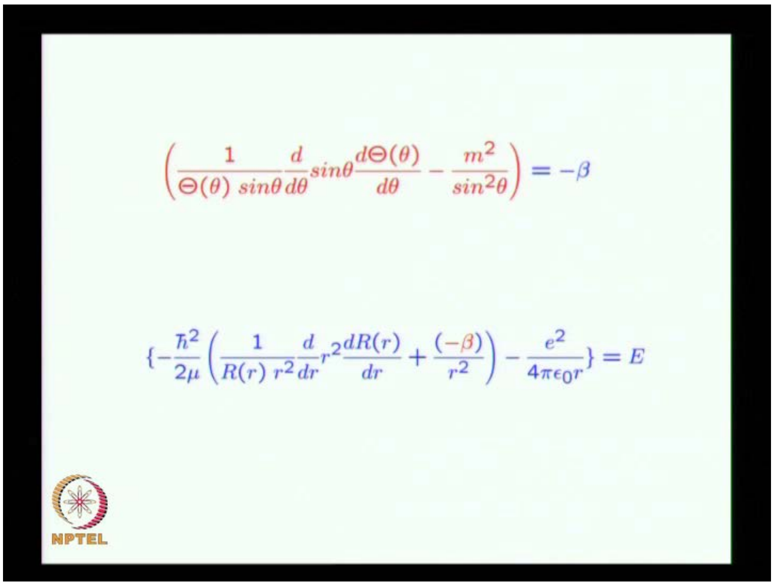

This is the equation for capital R, how does it read it's actually minus h cross square by 2 mu.

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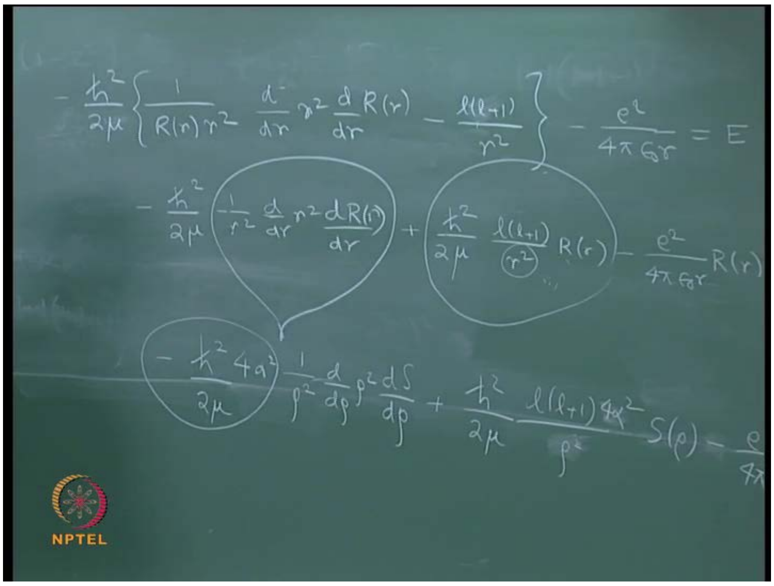

1 by capital R of R, this was the equation which we obtained by using the method of separation of variable and in this equation we would now replace beta because we have found that beta is stickled you can have to live the values of the half l into l plus one. So, we will put l into l plus 1 here, and I subtract in the earlier versions of the equation I had actually multiplied by capital R. So, I will do that and then what will happen is that I should get minus h cross square by 2 mu 1 by R square d by d R, r square d capital R by d R first term next term will be plus we will look at this .

So, please keep a close watch because if I make a mistake then I will run in to difficulty. Now, if you look at this equation see, what are the term that are occurring in this equation here is the total energy of electron remember E is the total energy, what is this term? This term is the potential energy because of this interaction with the nucleus minus e square by 4 pie epsilon 0 r, this term is what this is coming from kinetic energy for radial motion.

Remember this equation actually is a Schrodinger equation, which describes the radial motion how the distance of the electron varies from the nucleus. That is what this equation describes and this is defiantly coming from kinetic energy, but now we have an additional term here, what is this term look at the term. So, what is happening is that, that the electron is moving around the nucleus again, therefore is it as not just radial motion it also has angular motion. We have got rid of angular motion, but what does happen there is an additional term appearing here right and this is actually coming from the angular motion this term this is extra term that is coming. And look at that that is actually appearing as if it is a potential energy because its similar to this term by this the occurrence the way it obtains is similar.

So, it is actually occurring as a potential energy now why does it do this and in fact, why is it that there is a 1 by R square sitting here. Actually I if I look at the problem some classical mechanics also exactly the same kind of the things will happen. So, what is happening is that when the electron is moving around the nucleus, you should remember that the potential depends only upon the distance. So, it does not matter where the in which direction the electron is whether, it is in this direction or in that direction if the distance from the nucleus is the same then the then the potential energy is the same.

And with such a problem what happens is that the angular momentum, we would come to angular momentum later, but the angular momentum actually is a constant of motion. That means, that the electron would move only in such a fashion that the angular momentum that is not change. So, if the angular momentum does not change you say what suppose the electron is moving in this direction and suppose somehow it comes close to the nucleus, the value of the angular momentum has to be the same. So, how can it do that?

I mean from a large distance if it comes closer if the angular momentum is still to have the same value then the electron should move much faster right. So, if the angular momentum, I hope you remember the definition this a product of the mass into the distance into the velocity. So, if the distance decreases, the velocity has to increase. So, if the electron is close to the nucleus, it will be moving very fast. Therefore what will happen is that the energy of angular motion will change as you approach nucleus.

And because the electron will move much faster near the nucleus, what would you expect then you will actually the energy do to the angular motion will increase very fast, and that exactly is what is happening with this term right. So, this is a this term is coming from the angular motion and because of the fact that the angular momentum is concaved the electron is constrained to move faster, as it approaches the nucleus. And therefore, its kinetic energy for angular due to angular motion will increase. So, this is actually that term and now let me try to solve this equation if you look at this equation you would realize that there are many, many constants I want to get rid of all of them and as per as possible. So, we will make a substitution, what is the substitution that we will make?

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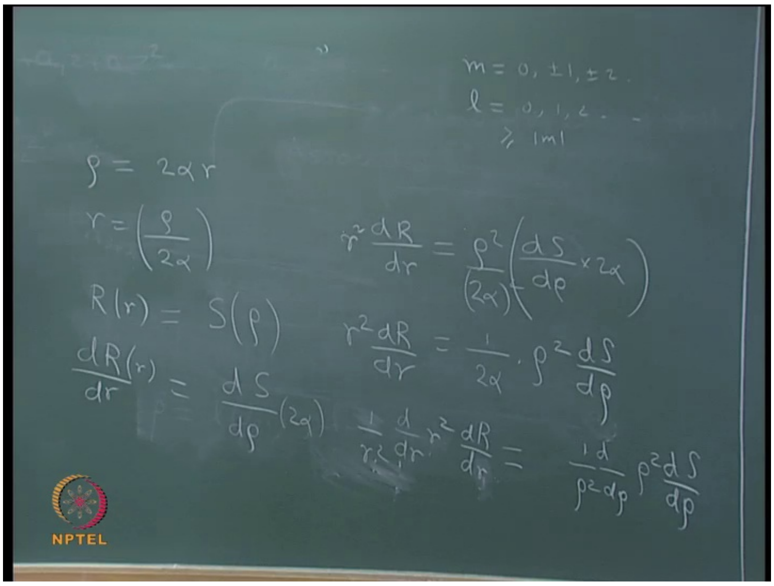

We will say that we have a mu variable which have denote by the symbol rho and say that that is equal to two alpha times r, alpha is yet to be defined. So, therefore, you can say r is equal to rho divided by 2 alpha. So, where ever r is occurring I am going to put rho by 2 alpha and this capital R actually is a function of small r and that will be equal to function of a rho, which I will denote as S. So, S is defined to be equal to R, but S is the function which is the function of rho. So, if you if you think of d R by d small r that will be equal to d S divided by what? R is rho by 2 alpha. So, therefore, actually you will get d rho into a 2 alpha.

So, d capital R by d R may be written as d S by d rho 2 alpha and so, you can do exactly the same thing I mean with all the terms see here and what would be the result, I hope I can just write the mu set of terms to mu, what happen to R square I am going to get 2 alpha the whole square divided by rho square 1. While d by d R will give me what another 2 alpha in the numerator, this R square will give me may be I will work it out that will be better. So, this is what this then d capital R by d R multiplied by R square is equal to d S by d rho into 2 alpha R square will be rho square by 2 alpha the whole square.

So, that this will be actually equal to 1 by 2 alpha rho square d S by d rho, we can find the relationship between R square d R by d small r at cross square d S by d rho and that is the relationship, but here let the remove this probably easy to do it this way and. So, have to now calculate d R d by d R in to 1 by R square and what would that be?

This is the term that occurs and you can easily work this out, I mean just write the answer I think that is the answer, I think you can easily verify this. If you just did this substitution R is equal to rho by 2 alpha what will that happen is that you will get just a 4 alpha square there. And therefore, this object will become 4 alpha square and you have this minus h cross square by 2 mu, then you have plus h cross square by 2 mu, l into l plus 1 divided by R while this R square like to replace with rho. So, I will get rho square into 2 alpha or 4 alpha square into capital R is nothing but S. This R also I should replace with rho by 2 alpha.

So, this is what we are going to get, I am yet to define my alpha, but has we have done previously what we will do is you will define alpha in such a fashion that equation looks as simple as possible. So, the next thing that I will do is I will divide throughout by this term, divide throughout by that term then what is the result?

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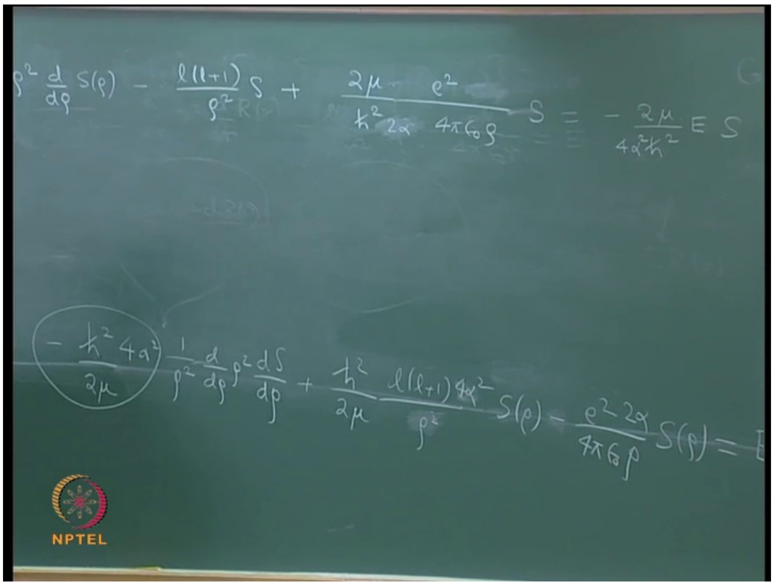

We will get 1 by rho square d by d rho rho square that be my first term, this term will become minus l into l plus 1 divided by rho square into S correct me I make mistake. This will become minus l, l into l plus 1 by rho square into S the next term will become plus. And on the right hand side, you are going to get minus 2 mu divided by h cross square into E is that all 4 alpha square right into S.

So, this is crucial I mean I have put in all the factors otherwise I will into difficulties, any term that I have missed out? I mean there are minus simplification that I can make there is a 2 alpha here there is a 4 alpha square. So, let may remove this 2 alpha and the write this as two alpha. And what I am going to do is there are so many things here. So, what I will do is this number. See I have introduced the variable, I introduce the parameter alpha and what did you find I can define it in any fashion with that I like, but what I want to do is I want to define it in such a fashion that the equation very simple.

So, therefore I am going to define this to be equal to one and I can always depend alpha in such a fashion that this is equal to 1. So, what will be the definition of alpha? It says that minus 2 mu e divided by alpha square h cross square is equal to 1, or it says that alpha square must be equal to something, what is that something?

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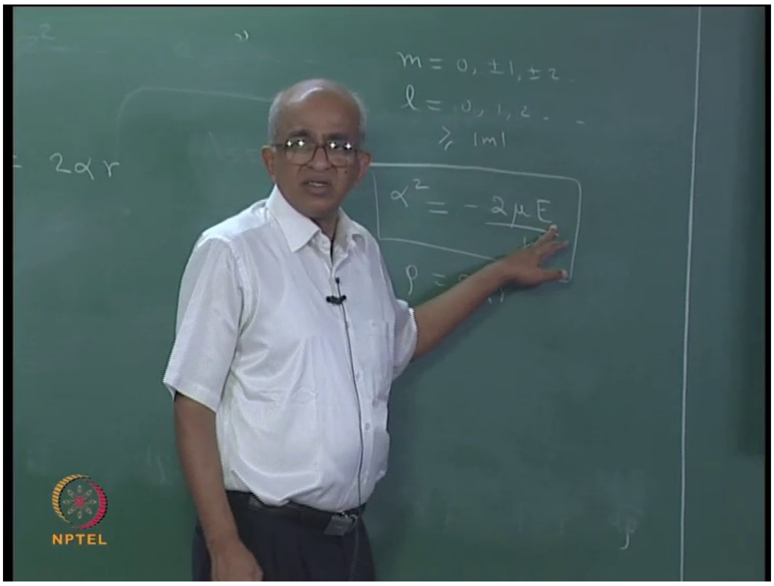

Alpha square must be equal to equal to minus 2 mu e divided by h cross square and this rho of course, is actually defined to be equal 2 alpha. Now, you may say this is a rather strange definition because the way it is depend which there is a negative sign occurring right.

So, alpha square you would have expected to be something real. So, it may appear that alpha if you defined this the alpha it may turn out to be imaginary, but what is going to happen is this you have the nucleus, you have the electron. And if the electron is far away from the nucleus there is no interaction. And the energy of the system will be let us I we will take it to be 0 and if I bring the electron close to the nucleus what would I expect I would expect that if there is a bound state for the system, the energy of the system between less than 0 less than generally that the system would have at infinity.

So, if you say that the electron is in the vicinity of the nucleus, I would expect that the total energy if it is bound to the nucleus I would expect that the total energy of the system will be less than 0 and therefore, I expect that this E is negative. So, if E is negative everything is fine alpha is real, but this also implies that I am only looking at the bound states of the system, stays it is for which the energy total energy is less than 0. If you are living at this at states, which have E greater than 0 then you may have to modified this statement.

So, we are actually we are putting the condition that let us look at the only solutions whose energy is negative. And then alpha is guaranteed to be real and I would not have any problem. So, this with this, what will happen to the equation if this is equal to one I hope I have not made any mistakes and this will be equal to equal to one. So, I will have 1 by 4 here and if I looked at the right hand side what is going to happen, I have all this constants, but the constants are occurring only in one part they are not occurring anywhere else expect of course, l into l plus 1, but l is a quantum number which can take different values.

So, what I will do is I will define this 2 mu e square divided by what? 4 pie epsilon 0 into h cross square into 2 alpha, let me just denote by the symbol lambda because I do not want to writing this again and again fine, and if you did that what will happen this part I can just remove and put lambda. So, now ever location you will agree that it look much nicer than earlier, and this is the differential equation that I have to solve, let me rewrite this equation in a slightly modified fashion, I will carry out this differentiation.

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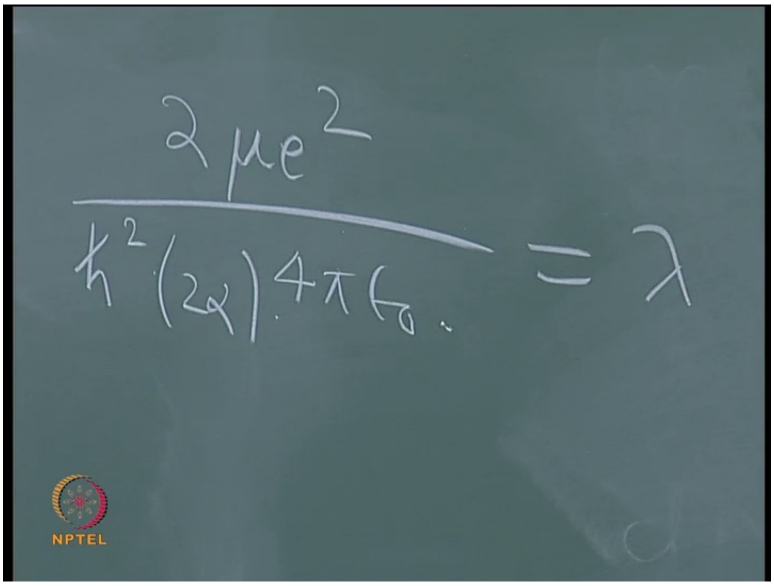

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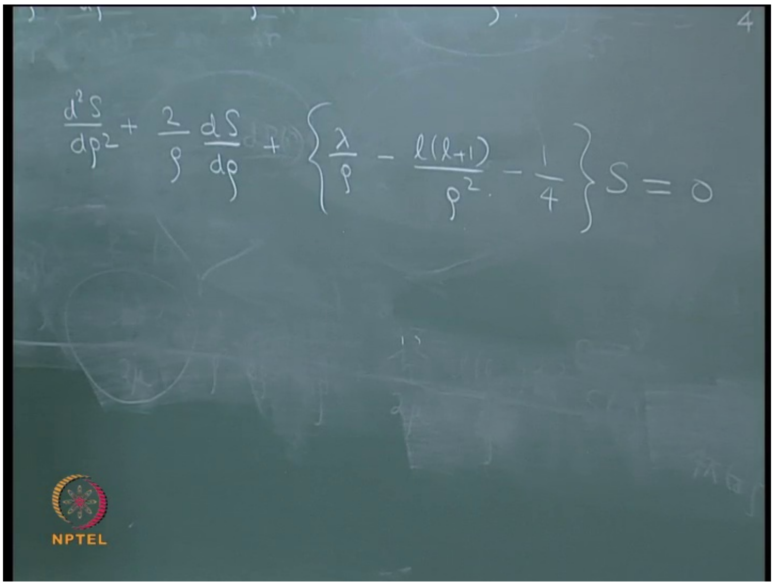

And if I carried out the differentiation what is going to happen is I shall have d square s by d rho square, simple thing to carry out the differentiation. So, let me just write it this is this are the two terms that will come from here, I will take this term to the left hand side. So, what I will get is plus lambda by rho minus l into l plus 1 by rho square minus 1 by 4 into S is equal to 0. So, this is the differential equation that we have to solve, let me check whether this is I think I have it in my slide.

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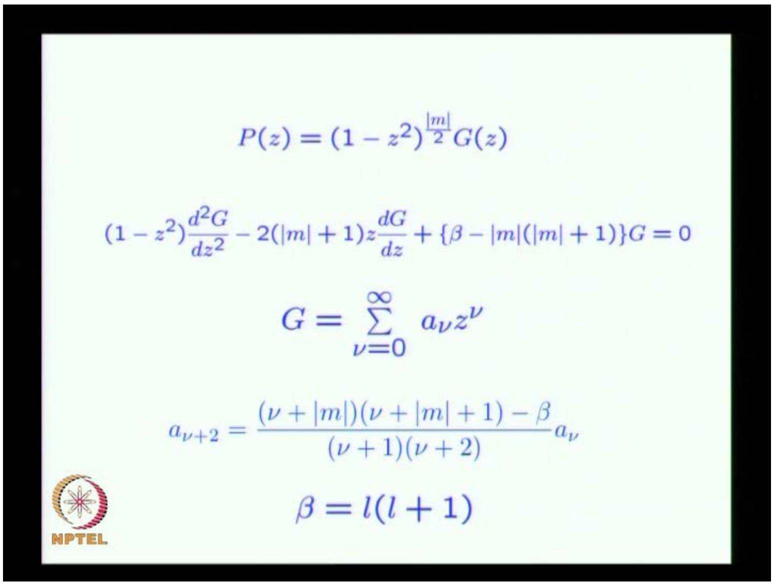

So, you will see that agree well this is the equation in a slightly different form that it does not matter. So, this is the equation that the now have to solve, and now again I mean how do I solve this equation, the answer is simple I first try to find an the asymptotic solution. What do I mean by asymptotic solution? This is the solution that will be valid in may be large values of rho, if rho is large you can ask what will happen to this differential equation. If rho is extremely large you would expect that this term can be neglected this term also can be neglected, and perhaps this term also can be neglected.

And therefore you would expect that the differential equation may perhaps reduce to d square S by d rho square minus 1 by 4, S is equal to 0 right this will be the form of the differential equation, which is valid this is what I would expect. And so, this is a simple differential equation d S square by rho, rho square is equal to 1 by 4 S what is the solution of that equation? The solution will be any constant into perhaps e to the power of minus rho by 2 as you can easily see thus if we took the second derivative of that function, you will see there it satisfies this equation. Not only that that also any constant B into e to the power of plus rho by 2 will satisfy the equation.

And there by immediately what will be the same this second solution which is e to the power of plus rho by 2 cannot be acceptable because when the value of R becomes very large R is my distance of the electron from the nucleus, R becomes very large naturally rho will become very large. And if rho becomes very large my solution the second solution will become very large it will go infinity and so it will not give me an acceptable solution. So, therefore, the only possibility is to have this as the solution.

So, I have found the asymptotic solution, the asymptotic solution should have this particular form, at this is only an asymptotic solution it is not valid for small values of rho and how will I make it satisfy, the equation for the small values of rho. And that is something that we will do, we will say that instead of this a I will have constant sorry I would have to have a constant f of rho. And I will discuss what to do with this function in the next lecture.

Thank you for listening.