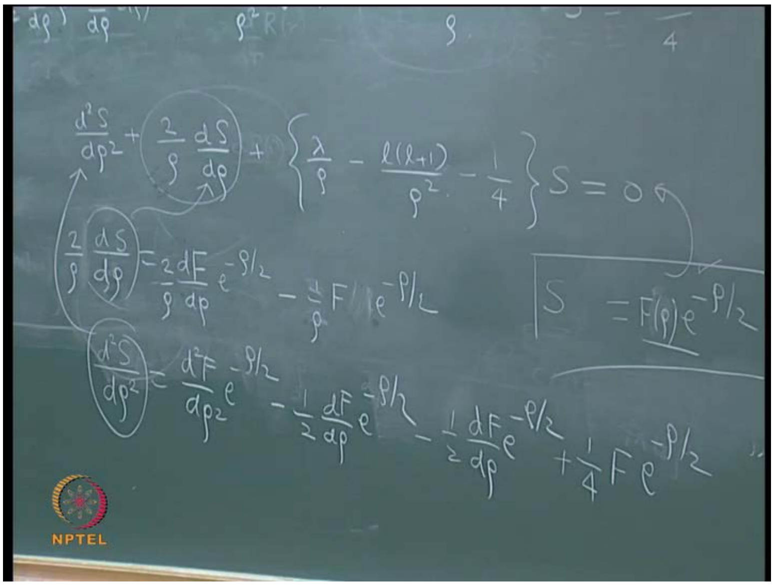
Introductory Quantum Chemistry
Prof. K.L. Sebastian
Department of Inorganic and Physical Chemistry
Indian Institute of Science, Bangalore

Lecture - 25
Introduction to the Course

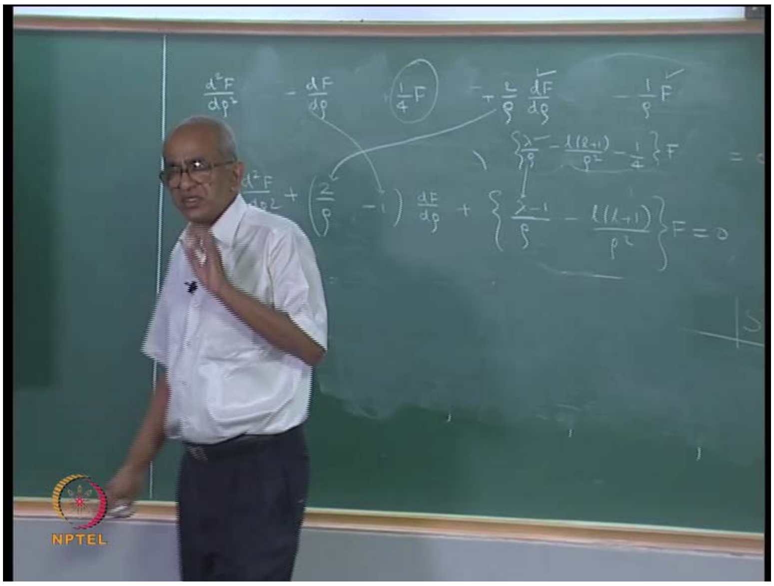
(Refer Slide Time: 00:18)



So, we were discussing this equation and we found that, in the region where rho is extremely large. The differential equation will reduce to that and that has a solution, which has the form e to the power minus rho by 2 with the constant here. But there is valid only in the region, where rho is very large and therefore, we said ok, we would replace that constant with a function and say that the result is a solution of the equation. So, we want to find capital f in such a fashion that, this product actually satisfies that differential equation. So, what I now have to do is, after to take this and put in to the differential equation and find the equation for capital f. So, let me do that, what I will do is first a fall; I will take the derivative of S with respect to rho. Assuming S is given in this expression.

So, what will be the derivative it is going to be? First I will differentiate F. I am going to get d F by d rho e to the power of minus rho by 2, minus then I will have to differentiate the second term that is going to give me, minus 1 by 2 F of rho e to the power of minus rho by 2. I will need the second derivative. So, I am going to have d square S by d rho square what will that be. So, I will take the second derivative of this will be very quickly write it. So, differentiating that gives me this, then from here minus half gives d F by d rho once more and finally, differentiating this will give me plus 1 by 4 F e to the power of minus rho by two. So, now, it is the question substituting this expression in here and this expression in there and alike the terms together and get the final equation. So, may be what I will do is I will just multiply this term by 2 by rho, this time I should multiply by 2 by rho and put to a rho here and naturally I will get it 2 by rho there and 2 by rho there and. So, I can this will raise 1 by rho. And I am going to add this with that and replace this whole thing. And may be what I do is I should write on top.

(Refer Slide Time: 04:12)



Second derivative of F multiplied by e to the power of minus rho by 2, then here this term and that term are actually identical. So, I can just add them up. Minus d F by d rho e to the power of minus rho by 2, this term has plus 1 by 4. So, that finishes of this term, then I have this term. That finishes of this term and finally; I have this also account for. So, let me arrive to that appear lightly symboled lambda by rho minus l into l plus 1 by rho square minus 1 by 4. About this term S is actually F into e to the power of minus rho by 2. If I have added all these things up, I have to get the answer is 0, correct.

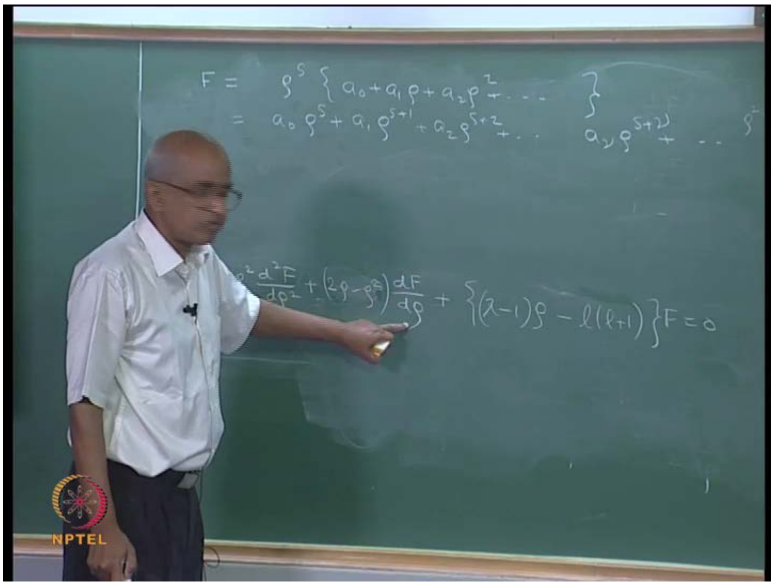
That is how it is, if I substitute all these things appear the again hope there are no mistakes. And if that hope I am going to remove this. May be you should check that, I have not made a mistake. May be what will I do, let me remove this I hope I am not made any mistakes. While the first thing, that you will noticed that e to the power of minus rho by 2 is common everywhere. So, we will just remove that easy for me because, I just have to rub of this.

I am perfectly allowed to do that. And then I should be able to simplify. Can you just tell whether I have anything problematic I suppose not. So, the equation becomes d square F by d rho square first term, plus I have terms involving d F by d rho there is a 2 by rho coming from here, so, this will be here and there is a minus term, which I will put here, so, minus 1. Then what are the other terms that I have left, this term lambda by rho, this I have put here. There is another minus 1 by rho times left. So, I can modify this and say lambda minus 1 by rho. This also I have accounted for, this I have accounted for, this one I have accounted for; there is a plus 1 by 4 and minus 1 by four. So, naturally the 2 will cancel and I will be left with minus l into l plus 1 which is this term, divided by rho square into F. So, I am fine actually. I look at the power point presentation and I see that I have the same equation as the power point presentation therefore; I have not made any mistakes.

But then this has to be a sold subject to one condition. What is the condition? The condition is that, when r becomes very large, small r becoming very large. That means, you are far away from nucleus, then rho will become very large and if rho becomes very large I want the solution to be well behaved. It makes that S has to approach 0; S should approach 0, when rho becomes r or essentially rho becomes infinity. You may say that while it is not obvious then there is c to the power of minus rho by 2, but suppose this F is a function which behaves like e to the power of plus rho then you will; obviously, have a problem and that is actually what happens? That is actually what happens this function F if it goes to infinity and we are going to make use of a series expansion for F. We will find that the series actually may not terminate.

It may go to, go and contain infinite number of times. And if it contains infinite number of times this F will behave like e to the power of rho. I am not going to prove this, but I am telling you this is the way and therefore, we have to be very careful. So, now, I have to solve this equation and how I am going to solve this equation? The procedure is going to be at the series expansion. So, what is the series expansion that I am going to adopt?

(Refer Slide Time: 10:31)



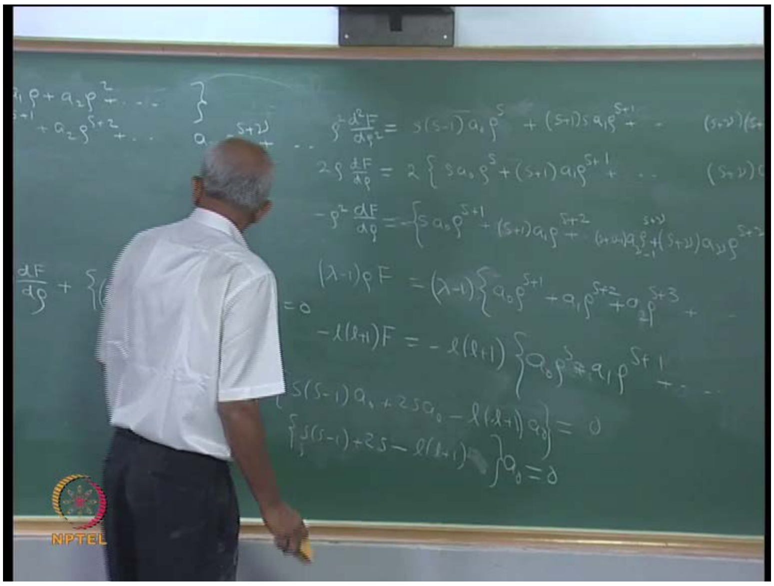
I am going to say that, this F may be written as a power series in rho. a 0 plus rho a 1 plus etc, but there is not what exactly what I will do, I will think of a more general power series. Where I will say that it may be of the form rho to the power of S. S is in undetermined h, into a 0 plus a 1 rho plus a 2 rho square etcetera. You will agree when I say that this is a little bit more general then what we were doing earlier because, if we put S is equal to 0, you will get the original there earlier kind of things that we were doing. And the reason why we do this is actually?

If you look at the potential you see, you have 1 by rho square, 1 by rho sittings in different places. So, when rho approaches 0 what will happen? These times you would except will be have diverging and to cancel that divergences kind of thing we would discuss, this is the basic reason. But anyway this is what we will do and therefore, what will happen? I will write this as a 0, I can take this inside rho to the power of S plus a 1 rho to the power of S plus 1 plus a 2 rho to the power of S plus 2 plus etcetera a nu rho to the power of S plus 1.

This is what we will write, and this differential equation itself what I will do is I will multiply throughout by rho square. So, that I do not have any division by rho. And if I multiply throughout by rho square, what will be the result? I will get rho square d square F by d rho square plus if you multiply this, the answer is going to be 2 minus rho into rho. So, maybe I will write this, as 2 rho minus rho square plus lambda minus 1 into rho minus 1 into l plus 1 into F is equal to 0.

So, this is the equation that I should now solve. That means, I will need d F by d rho first of all, what will that the, shall we have to go on differentiating this, we will get S into a 0 rho to the power of S minus 1 as the first term, plus a 1 well S plus 1 into a 1 rho to the power of S this is the simple differentiation. And what with the general term you will get S plus mu a nu rho to the power of S plus nu minus, correct. One differentiation I have done, let may carry out the second differentiation. The second differentiation is going to be fairly simple and straight forward S into S minus 1 a 0 with p d s, that is the second derivative. Right. So, but you need see, I will need rho square into d square F by d rho square. But let me, straight away multiply by rho square here. And that will you see, that it will remove minus 2, here it will become plus 1 correct. And here again it will remove this minus 2 that is it. So, rho square into second derivative will be giving me that. Then I will need this term, 2 rho into d F by d rho.

(Refer Slide Time: 16:27)



So, let me write that 2 rho into d F by d rho would be how much? Yes I have to take this expression, which is d F by d rho multiplied by 2 rho. So, I will leave the 2 outside and write this as S into a 0 rho to the power of S plus this will give me S plus nu a nu rho to the power of S plus nu that gives general. Great, all that they have done is take this equation multiplied by 2 rho and throughout is that is all nothing more. And then of course, I will have to evaluate this term, minus rho square into d F by d rho. So, I will when I have d F by d rho written here. So, I will just put a minus rho square here; that means, I will have a negative sign sitting outside and I will have a rho into multiplied by rho square. So, this will become S minus 1 plus 2 which actually becomes S plus 2 sorry S plus 1, then this will become S plus 2. And this term will become S plus nu plus 1 plus etcetera, right.

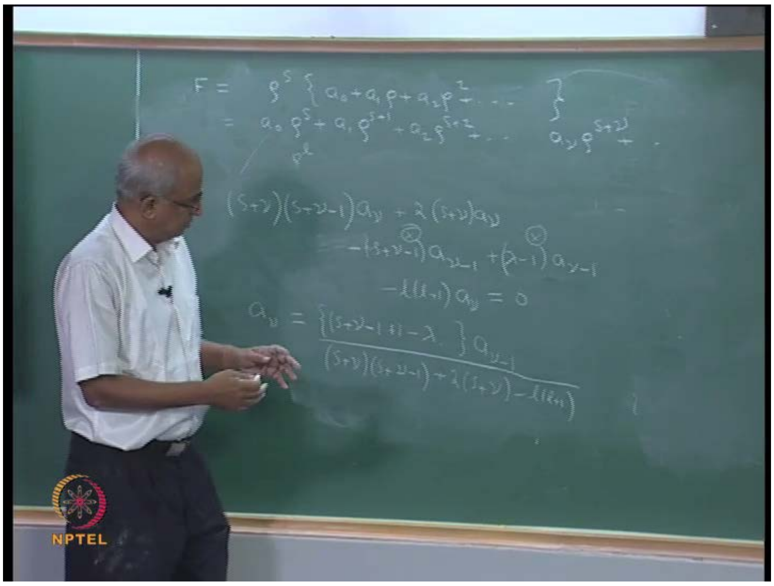
And if this is the way, it is may be, because you see eventually what I will do this; I will look for coefficient of S to the power of sorry rho to the power of S plus nu. That is what I am going to do eventually. Then I will say that coefficient should be equal to 0. So therefore, may be what I should do is, I will write one more term here, which will contain rho to the power of S plus nu because, that is more convenient for me. So, write it straight away. That term will be rho to the power of S plus nu multiplied by a nu minus 1 into S plus nu minus 1. Hope it is clear, because I did not have much space there; that is the term that will contain rho power of S plus nu. And then from here, I am going to get lambda minus 1 into rho into F, right. Lambda minus 1 into rho into F is what I have I to write and that is going to be equal to how much, going to be a 0 rho to the power of S plus 1, right. Lambda minus 1 is there then rho into F. So, F is written somewhere F it is written here. So, I will use that and I will get a 0 rho to the power of the S plus 1 plus a 1 rho to the power of the S plus 2 plus a 3 rho to the power of S plus 3 it is that, correct. I suppose it is plus etcetera.

I will have a clearer term rho to the power of S plus nu. What will that be correct, I know I made a mistake, right? Where it is? This is the mistake, a 2 rho to the power of S plus two. So, if I wanted to write the coefficient of rho to the power of S plus nu. It is going to be a nu minus 1, correct that is it. And the last term is minus l into l plus 1 F is equal to minus l into l plus 1 into a 0 plus a 1 that is fairly simple. So, we have to add up all these things and say that the result is equal to 0 that is all. But then you again realize that, it is a power series. In power series, rho you are going to say that it is to be identical equal to 0 for all values of rho. If that is to be satisfied the coefficient of each power of rho must be equal to 0. So, let us actually look at the coefficient of rho to the power of S. What is the coefficient of rho to the power of S? Just to illustrate take the coefficient of rho to the power of S, you will see that from here.

You will have rho to the power of S into S minus 1 into a 0 right. And then from here, what will you get 2 S a 0, there is no rho to the power of S in any of these times, it is only here. And from here, what are you going to get? We are not going to get, rho to the power of S because, it starts with rho to the power of S plus 1. It also starts with rho to the power of S plus 1 right. What about this one, you do get rho to the power of S here and that is going to be minus l into l plus 1 into a 0 and this must be equal to what? This is the coefficient of rho to the power of S, but it is written the term containing rho to the power of S is shown here. So, that is actually the coefficient and the coefficient has to be equal to 0, correct. So, you look at this equation, what does it tell you? It tells you that S into S minus 1 a 0, well a 0 you would realize is common. So, I am going to take it out.

I am going to get S into S minus 1 plus 2 S minus l into l plus 1 a 0 is equal to sorry; a 0 have taken out that is equal to zero. So, if this is to be satisfied. In fact, is not a recursion relationship, because is a recursive relationship will determine a 0 or may be a n plus 1 in terms of may be a n or nu plus 2 in times of a nu. So, this is not a recursion relationship, but you realize that this equation definitely should be satisfied and if this is to be satisfied again what is the conclusion? You can have a 0 is equal to 0, we will see that there is not acceptable. You will see that in a minute and therefore, the only possibility is that your S, see I have not determined S was something that I had introduced. Your S has to satisfy the condition, that S into S minus 1 plus 2 S minus l into l plus 1 must be equal to 0.

(Refer Slide Time: 24:44)



So, let me rewrite that condition. It says that S into S minus 1 plus 2 S that is nothing, but S square plus S correct, minus l into l plus 1 must be equal to 0 right. So, S has to satisfy this condition. So, S into S minus 1 plus 2 S, you expand it you are going to get S square plus S. So, this is just like quadratic equation in S, you can solve it.

Because you want to find S which will satisfy this condition and you will find that there are two solutions. One is actually S is equal to l and the other is actually minus of l plus 1. You can verify this, when if you say that, this is a quadratic equation S and solve it you will get two solutions. One is S is equal to l and the other is S is equal to minus l minus 1. And then what will happen? Suppose you look at the solutions and going to again claim that, this is 1 that is acceptable, while this is not acceptable, why do I make that claim. Look at the power series, your power series actually for F starts with a 0 rho to the power of S, if you had rho to the power of l here you remember, what is l? l may be 0 or it may be 1 or it may be 2 or it may be 3, 4 etcetera. So, then the series, then this is very well define rho to the power of l, suppose you are very close to the nucleus where rho is very small, when rho to the power of 0, rho to the power of 1 or rho power of 2 they are all very well behaved functions.

On the other hand, if you had S is equal to minus l plus 1. What will happen is that? This will become a 0 rho to the power of minus l plus 1 right. And l is 0 or may l is 1 or l is 2 what will happen if l is 0 you will have rho to the power of minus 1 here, if l is 1 you will have rho to the power of minus 2 and so on. And what will happen, when rho becomes very small? That is when you approaching the nucleus, this solution will actually divert to infinity right.

Because when you are very close to the nucleus you will have rho to the power of minus 1, rho to the power of minus 2 or some function of that form and therefore, we rule out this solution, only this is acceptable. So, we have now determined the value of S has to be equal to l and remember l is an integer, which may also take the value 0. And then let us look at the recursion relationship that we will get how we will get the recursion relationship? You have to say that the coefficient of rho to the power of S plus nu must be equal to 0. So, you have to collect together terms which will involve rho to the power of s plus nu, so let us do that.

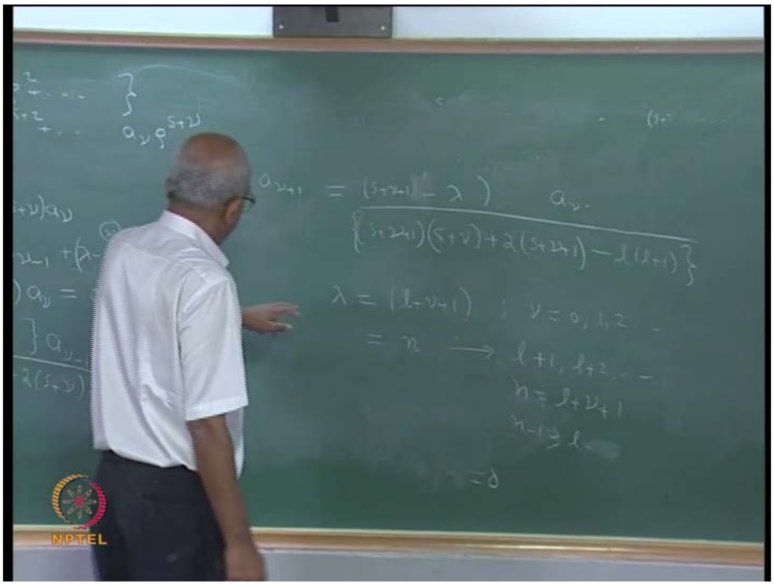
Well here again, I have to be very careful, from here I will get one term. So, that is this term, here again I will get one term s plus nu in to a nu, but there is 2 sitting outside. So, I have to remember that. So, I have taken this term, I have taken this term in to account now, after take this term in to account, now what is that s plus nu minus 1. That is ok, this one is minus correct, thank you otherwise I would have been in difficult.

There is a minus sign and here I am going to get plus lambda minus 1, what is the general term a nu minus 1 and from the last one, minus l in to l plus 1 a nu what is the term, yeah I think that is minus l in to l plus 1 into a nu and that must be equal to 0 correct. So, I will rearrange and write it as a recursion relationship, which says that a nu must be expressible in terms of a nu minus 1. Now, here things are little bit different earlier it was always a nu plus 2 is expressed in terms of a nu that is how it was, but in this case a nu plus 1 is expressed in terms of a nu over a nu is expressed in terms of a nu minus 1 ok.

So, what is the expression? The expression is actually, well I can just write this I suppose, this is the recursion relation. All that I have done is, I have taken this term and that term to the right hand side, these two terms because, they are depended a nu minus 1, I have taken to the right hand side and rearranged and I will get this equation. Well what I will do is normally, you see we express in the previous cases we had expressed a nu plus 2 in terms of a nu, so we well do similar things here, we will express a nu plus 1 in terms of a nu what is the relation. All that you need to do is, where ever nu is occurring you just replace with the nu plus 1, before I do that actually you will see that, this minus 1 and the plus 1, I could have cancelled.

So, with that let me replace nu with nu plus 1, I am going to get S plus nu plus 1, no there is S plus nu plus 1 minus lambda divided by S plus nu plus 1 in to S plus nu plus 2 times of S plus nu plus 1 minus l into l this is what will happen. So, a nu plus 1 is determined in terms of a nu Correct.

(Refer Slide Time: 33:15)

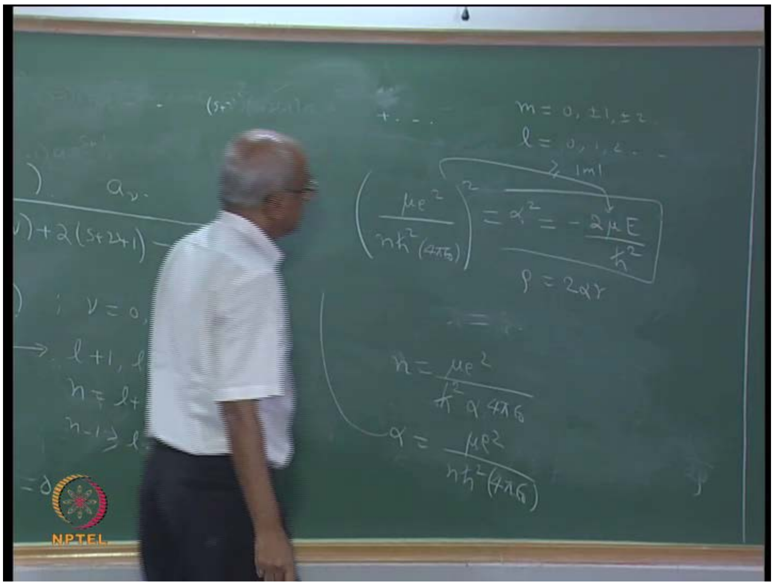


And now, you will realize why a 0 cannot be 0, because if a 0 is 0, this recursion relationship implies that a 1 must be 0. If a 1 is 0, then a 2 will be 0, then a 3 will be 0 so, the entire power series will become 0 and there is not acceptable. Because the wave function is identically vanished. So, it cannot have a 0 equal to 0 which is what I have said earlier. And now again you have the problem what is the problem. The problem is that the series if should not go to infinity, because if it went to infinity your wave function will not be acceptable. For some value nu what should happen is that a nu plus 1 must be equal to 0, for some value of nu may be a nu is equal to 4, a 4 is non zero, but a 5 has to be 0. So, what is the procedure is the wave out. So, wave out has to say that lambda must be equal to, if lambda is equal to S plus nu plus 1. This is absolutely no problem for some nu ok.

So, what is going to happen is lambda must be equal to S plus nu plus 1 and what are the values that nu can take, you can have a solution that where you could put nu equal to 0. You say that lambda is equal to S plus nu plus 1, but could put nu equal to 0; lambda is equal to S plus 1 that is one possibility. So, next possibility is that lambda is equal to S plus, put nu equal to 1, S plus 2, then S plus 3, S plus 4 etcetera. But what is S? We have already found S. S is actually equal to l. S is equal to our quantum number l. So, therefore, now I will replace S with l right. So, we find that lambda must be equal to l plus nu plus 1, what are the values that you can assign to nu. nu may be taking the value 0, 1, 2, 3, etcetera, any one of these values is possible you are going to get absolute solution. Now, is it this combination difficult to write so, what I will do is I will introduce a number; I will refer to as n, what is n? n is equal to l plus nu plus 1. So, then what are the different values for n that you may assign you may assign well n can take the values, while nu can have the minimum values 0.

So, minimum value of nu is equal to 0 means n may can take the value l plus 1 right. So, l plus 2 plus etcetera correct. Or you can say that, this number n if I introduce this n minus 1, what is the definition of n. n is equal to l plus nu plus 1, which implies that n minus 1 is equal to l plus nu. And nu can take the value 0, 1, 2, 3, etcetera, so therefore, you have the condition that n minus 1 has to be greater than or equal to l right. If I correct, because n minus 1 is equal to l plus nu and nu can take the values 0, 1, 2, 3, etcetera. And this n is actually nothing, but your principle quantum number. It is what you will find, if number that we have introduced is actually principle quantum number, but what have we found? We found that lambda must be equal to n. What is the minimum possible value of n? It is one; obviously right, because l may be 0, nu also may be 0, but then you have a 1 here, minimum possible value is 1. Next possible value is 2; next possible value is 3 and so on. And further we found that lambda is equal to n had a definition of lambda unfortunately that has been rubbed of…

(Refer Slide Time: 38:38)



So, I will have to depend upon your notes or my notes, to write the value of lambda. lambda was defined be nu e square divided by 4 pi epsilon 0, what else we had h cross square, anything more? alpha right. So, this was the definition of lambda and lambda we now say, lambda has the value, it is equal to n. Where n is an integer which may take the value 1, 2, 3, 4, etcetera. And therefore, what will happen you are led to the conclusion that alpha must be equal to Mu e square divided by take alpha here, unknown to the other side by n h cross square 4 pi epsilon 0 right, alpha must be equal to that. And now, alpha is related to the energy. What is the relationship? alpha square must be equal to that. So therefore, what I will do is I will take this expression for alpha and put it there and say that I do not have solution for arbitrary values of alpha, but only for these values of alpha.

I have solution only for these values of alpha, but alpha is related to the energy. So, therefore, what is the conclusion? The conclusion is that only for certain values of energy, would I get acceptable solution. And what are those values of e how will I find that instead of this alpha I will put that expression and solve for e. What is the expression that you will get? So, you are going to get this equal to Mu e square divided by n h cross square 4 pi epsilon 0, this is just alpha, you have to take the square and say that the square is equal to that much and solve for e. I will write that in next lecture, but you will see that the e that you obtain is nothing, but the expression that bore had obtained. The expression that you will get is just the expression that bore had obtained in this series, which assumed that there are only certain orbits that were allowed. So, exactly the same result you will get by solving the Schrodinger equation, so will continue in the afternoon.

Thank you for listening.