Spectroscopy Techniques for pharmaceutical & biopharmaceutical Industries

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lecture 14

Atomic Spectroscopy 2

Hello students, welcome to lecture 14, the last lecture, I discussed about how to solve Schrodinger equation for hydrogen atom. I discussed how to separate between the motion due to centre of mass and motion of electron related to centre of mass. We separated Schrodinger equation into two different part based on small r and capital R and then I went ahead and showed you how to solve the Schrodinger equation which deals with the motion of electrons relative to centre of mass.

We are concerned about motion of electrons and that is why I only discussed the motion of electron and we solved the Schrodinger equation corresponding to the motion electron, I will again start where I left.

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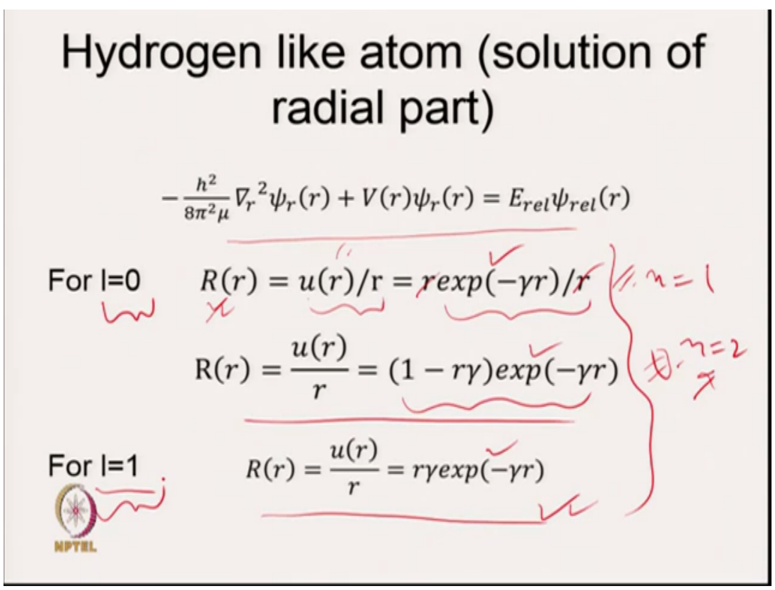

In the last lecture, I showed you when you solve this Schrodinger equation you will get different value of the radial function. The value of radial function will depend on the l value. If l is equal to 0, then I showed you what are the different solutions of the acceptable wave function.

For l is equal to 1, again I showed you how to get a radial wave function. So this is the solution which we obtain when we started with l is equal to 0, this was the first solution. We can also get different solution for the same differential equation and one of them is this. I also told you that the first solution corresponds to your n is equal to 1, whereas next solution belongs to n is equal to 2.

So this is basically wave function associated with the ground state. Whereas this is the wave function associated with your n is equal to 2. So this one is solution for n is equal to 1 and this is the solution for n is equal to 2. Then I went ahead and showed you what will be the differential equation for l is equal to 1 and what will be the solution. I only discussed 1 of the solution and that was given here.

And we can get your, this radial wave function r by using this equation which we assumed before solving the Schrodinger equation and so first solution will be exponential minus gamma r. This r r cancels out. The second solution is simply 1 minus r gamma exponential minus gamma r and this is the second solution for l is equal to 0 and this corresponds to n is equal to 2.

For l is equal to 1, I showed you that if we start with u r is equal to r square gamma exponential minus gamma r, then we will be able to get the answer. One thing you will notice is, all this solutions, has exponential minus gamma r in common. So what now we will try to write this in terms of a general equation which can tell you about the solution of the equation. So one general equation for the solution and since the solution depends on the l value, and so l value and n value. So your, the general solution will have terms corresponding to n and l. So let us see what is the solution?

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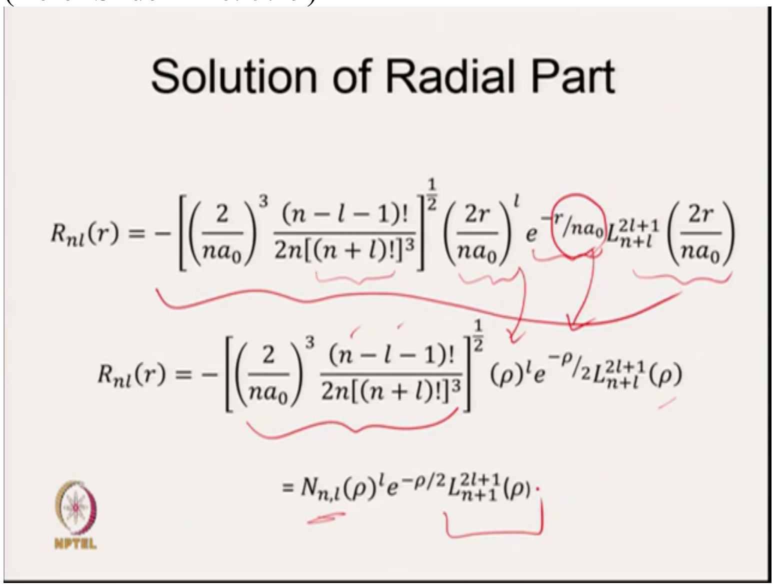

The solution is given here. This is quite big term. but this is the solution and I will show you the solution for how to get l is equal to 0 or l is equal to 1 from this. So it is simply minus sign 2 by n a naught cube. This is l minus n minus 1 factorial divided by 2 n multiplied by n plus l factorial and cube of that and then take a square root of the whole term and then this is your another function of r and this is the exponential term and then there is another function of r. In short, what we can do is 2 r by n a naught.

let us take this as a rho and then you can simply write rho by l and here you can write, in place of r, n by a naught, rho by 2 because you remember rho is 2 r by n a naught and so r divided by n a naught will be equal to rho by 2 and this is again rho. And this is basically known as normalizing factor which certainly depends on n and l and that is what is written here. So this is normalizing factor, rho by l, e minus rho by 2. This is your 1 polynomial.

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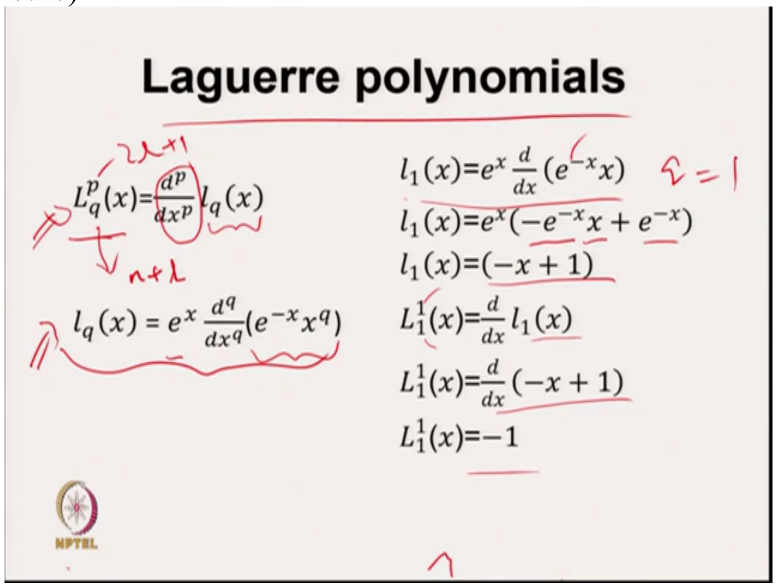

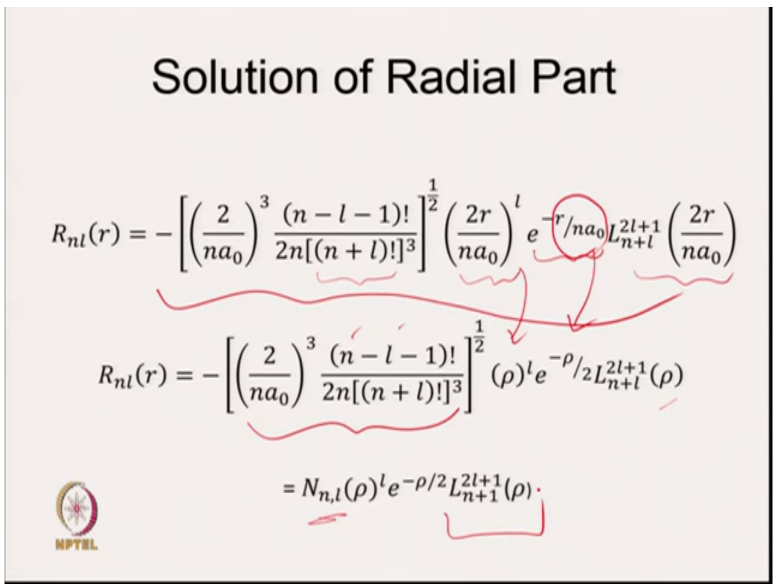

So now I will discuss about this polynomial. This polynomial is called Laguerre polynomial. So this is basically your, this thing, so l and add super strip, this is p and here, subscript is q and if you go back, you can see superscript p is equal to 2 l plus 1 and subscript q is equal to n plus l. So keep that thing in mind. So this is your n plus l, let us go back this Is your 2l plus 1. This Is your 2l plus 1 and this is basically differential with respect to x and there is a power, power of p.

And then this l q x, this is another function. What is this l q x, this, your e x multiplied by d by d x and you can see that this is power q, and e minus x, into x by q. now it looks quite complicated.

It is complicated but if you try to understand then it will not be that difficult. For example, first what I am going to calculate is this quantity. If Q is equal to 1, so this I took Q is equal to 1.

What does that mean is that n plus l is equal to 1 and if you solve this, this is exponential ex and then since q is 1, you will write simply d by dx, e minus x and x power 1. And that is what is your l 1 x. now let us solve this, l 1 x is equal to x d by dx, e minus x into x. So let us first take x constant, and then differentiate exponential minus x. You will get minus exponential minus x.

And then you take this constant and then differentiate with respect to x. So you will get plus e minus x and since this is multiplied by ex, so ex into e minus x is 1. So what you will get is simply 1 minus x, simply 1 minus x. Simply minus x plus 1. now we solve l q x now we will solve this the second one so that is written as l in the superscript you have one in the subscript you have one l 1 1. So this will be equal to d by dx as since p is one and so you have simply d by dx and l 1 x which we just calculated and that is equal to minus x plus 1. So if I differentiate this what I am going to get is minus 1. So l 1 1 x is equal to minus 1 so this is your first polynomial a value of first polynomial

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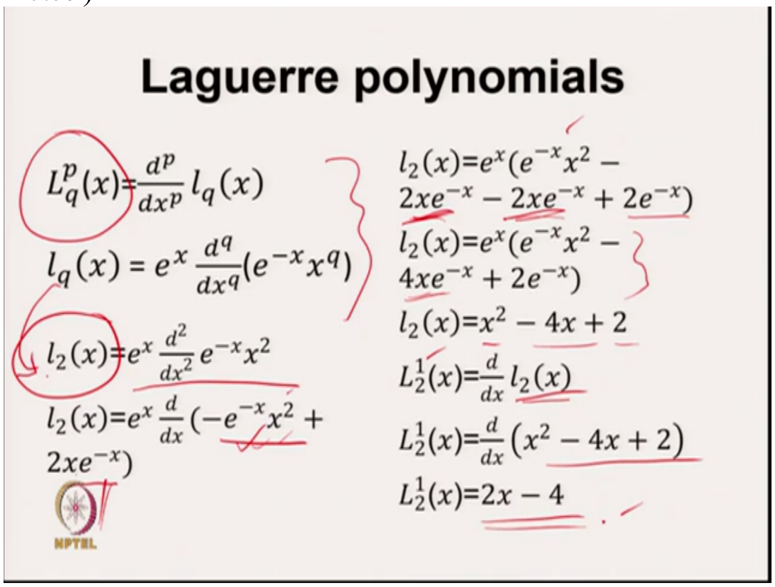

So let us go and see for the second one again same equation I have written here. So that you should not get confused and now what I am going to do is I am going to q is equal to 2, q is equal to 2 and when we do that, this will be equal to e x d 2 by d x square exponential minus x into x square. Now let us differentiate this, if I do for first term, what I will get is minus e minus x into x square, plus 2 x e minus x.

In the first term, I have taken x square as constant and the in the second term I have taken e minus x as constant and so I get this whole equation. now l 2 x this l 2 x still has 1, 1 d by dx term, 1 d by dx term. So this is e x from here, this point e x. Now I am differentiating first this term. here, first I took x square as constant and then I differentiated exponential minus x. What I will get is plus e x into x square.

And now what I did is I took e minus x as constant and differentiated x square, so I will get this one. Now come and differentiate this: 2x exponential minus x. So what you are going to get is minus 2 x e minus x, when you differentiate e minus x, and 2 e minus x when you differentiate x keeping e minus x constant and if you see here, these 2 terms are the same. So you get 4 x exponential minus x.

So this is your l 2 x, and if I simplify this, so ex multiplied by e minus x is 1. So you are left with x square and minus 4 x plus 2. So this is your l 2x. So l 2x is equal to x square minus 4 x plus 2. So what you got is this term. So now I want to solve this one l p q. So here, p is taken as 1. So suppose p is 1. So then what you need to do? You need to differentiate this, l 2 x with respect to x. So d by dx into x is basically l 1 2 x and just we solved this. L 2 x is x square minus 4 x plus 2 and if I differentiate this, what I am going to get is 2 x minus 4. So l 12 is equal to 2 x minus 4.

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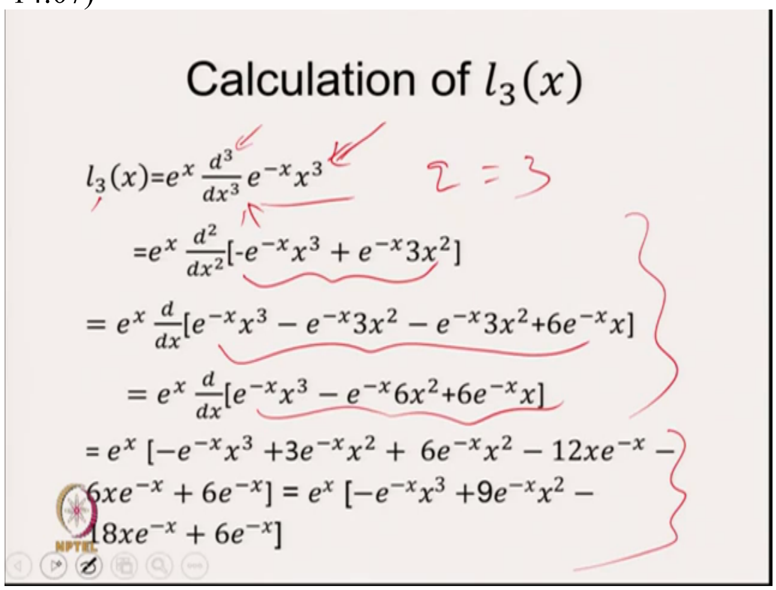

Similarly, we can calculate l 3 x. l3x is ex d3 by dx3 exponential minus x x 3. remember this thing. So this is q, q is equal to 3, and so we put it here. We put it here and then we put it here. now first differential will give this term. The second differential will give you this term and third differential will give you this term. You can do it, it is simple. This is basically differential of u into v type of differential. So this differential is of the type of u and, u into v. So when you do that, you will get this term

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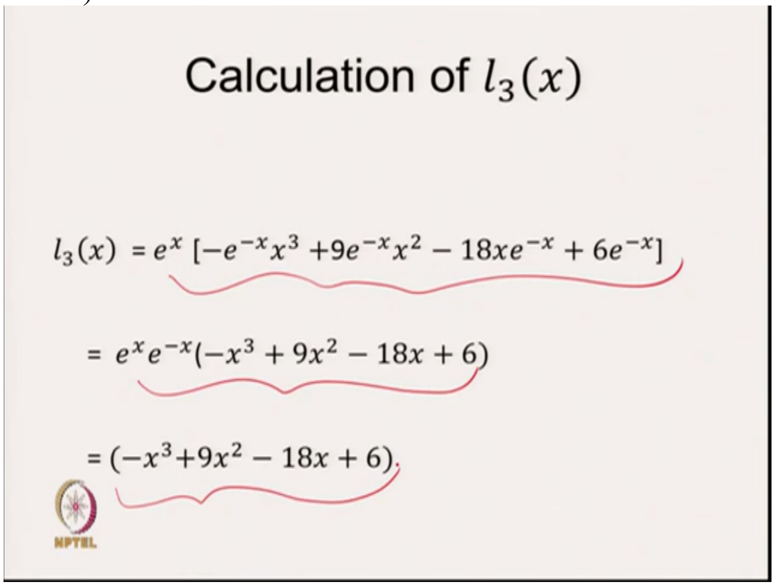

And finally what you are getting is this whole term and if you take e minus x out, then you will get this term and finally l 3 x is this. So l 3 x is minus x cube plus n x square minus 18 x plus 6. This is simple differential. A bit lengthy but it is easy to do. So once I know l 3 x, it is very easy to calculate l 1 3 x or l 2 3 x, so we will see that.

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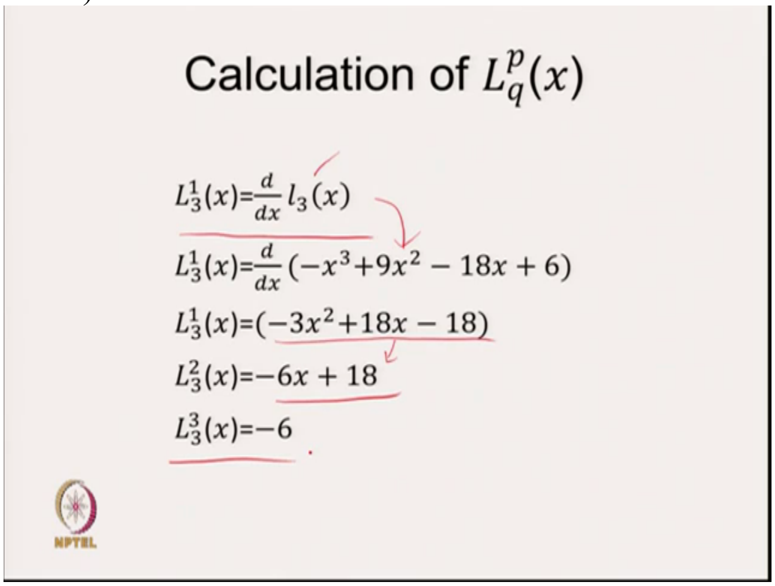

So l 1 3x should be equal to d by dx as l 3 x. In the last page what we saw is that l 3 x is equal to minus x cube plus 9 x square plus 18 x plus 6. So simply the differential, what you will get is minus 3 x square plus 18 x minus 18 and this is l 1 3, we can also get l 2 3. For that, I have to differentiate it again. When I differentiate it again, I will get minus 3 into 2 x square that minus 6 x and 18 from this and you can also get l 3 3 x, which is minus 6. So although, it does not look complicated, it is not that complicated but good thing about this polynomial is, in one polynomial you have all the solution of your radial wave function for hydrogen.

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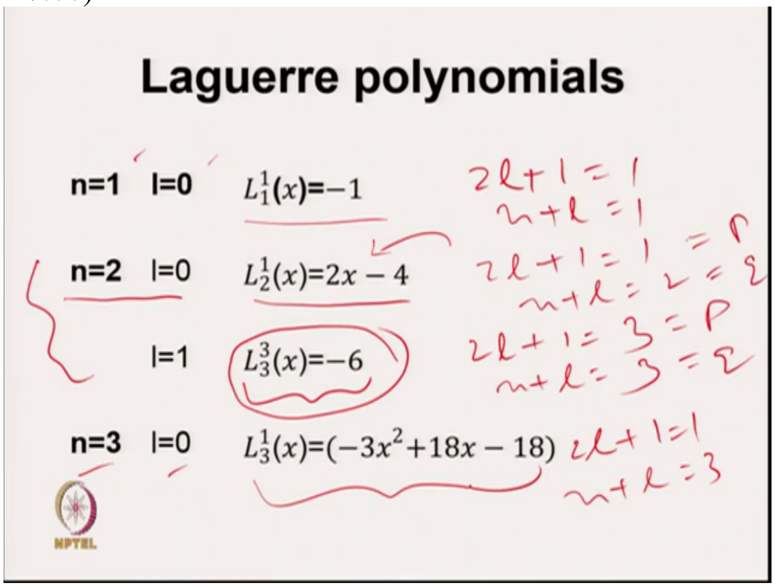

So Laguerre polynomial for n is equal to 1, l is equal to 0 will be given by this. remember 2 l plus 1 is equal to 1 and n plus l is equal to 1. Now if n is equal to 2, l is equal to 0, then what you need is this polynomial. l 1 2 because again 2 l plus 1 is equal to 1 but n plus l will be equal to 2. So this is 1 n plus l is equal to 1, n plus l is equal to 2. So this is your p and this is equal to q. And the Laguerre polynomial for this is 2 x minus 4 which I just showed you how to calculate and again this we will get when n is equal to 2 and l is equal to 1.

So 2 l plus 1 is your 3 and n plus l is 3. This is p and this is q and you have Laguerre polynomial for this thing. Similarly, you can get Laguerre polynomial for n is equal to 3 and l is equal to 0. Here 2 l plus 1 is equal to 1 n plus l is 3. This all I have solved. So just by expressing the solution in one polynomial which is known as Laguerre polynomial, you get solution for each n and l. It looks complicated but it is important to understand these things. So now we know what is the acceptable wave function and what is the wave function for different value of n and l.

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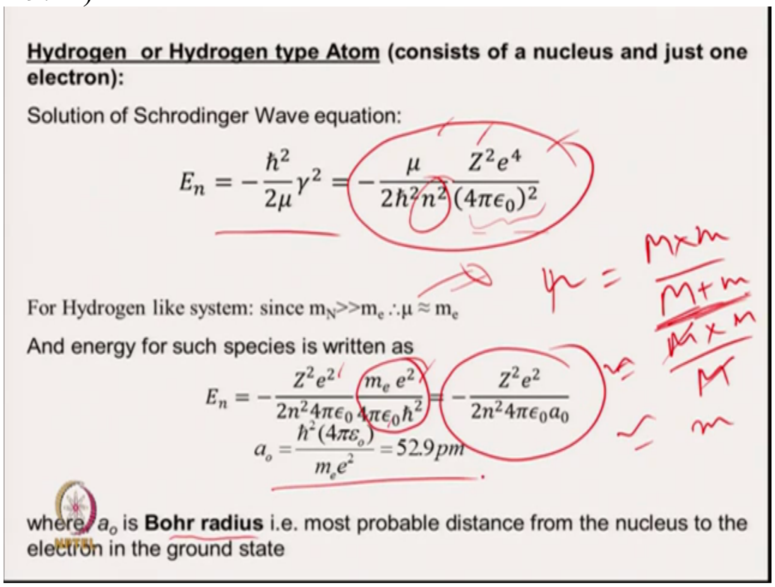

Now we can discuss, what is the energy and in the last lecture, I discussed about how to calculate energy. I showed you when l is equal to 0 and n is equal to 1, what will be the En. And n is equal to 1 and l is equal to 0. I also showed you when l is equal to 0 and n is equal to 2, then what will be the solution. The solution is given by this h cross square by 2 mu, gamma square, and then I proved it that this is the way En looks like, this is reduced mass, Z square e 4 divided by 2 h cross square, n square, Z square e 4, 4 pie epsilon naught square. You see, everything is constant except n. So what does that mean is that En is proportional to 1 by n square for hydrogen atom.

Certainly, if there are other kind of nucleus, Z will also come into play. For hydrogen like atom, m n is much greater than me and so this mass is simply equal to me. If you remember, mu is equal to m into n by m plus n and since this, m n is, this is basically your m n, this small m is your M e and since this capital M is quite greater than small m, so this will be equal to m, m into n. This is approximately equal. So this is m m cancels out, so this is approximately into to mass of electron.

So what we will do is, we replace mu by m and then I have simply written this as Z square, e square, n square into 4 pie epsilon naught. What we are left is your mu, which is equal to me. Then e has power 4, I have already written it e square. So there will be another e square. 4 pie epsilon naught square, 1 term I have not written here so left is 4 pie epsilon naught into h cross square and this is equal to 1 by a naught, this is equal to 1 by a naught.

Where a naught is called Bohr radius which is basically derived when Bohr proposed his model of atoms. So En is basically equal to minus Z square e square by 2 n square 4 pie epsilon naught a naught and a naught is your 52.9 picometer. This is the probable distance from the nucleus to the electron in the ground state.

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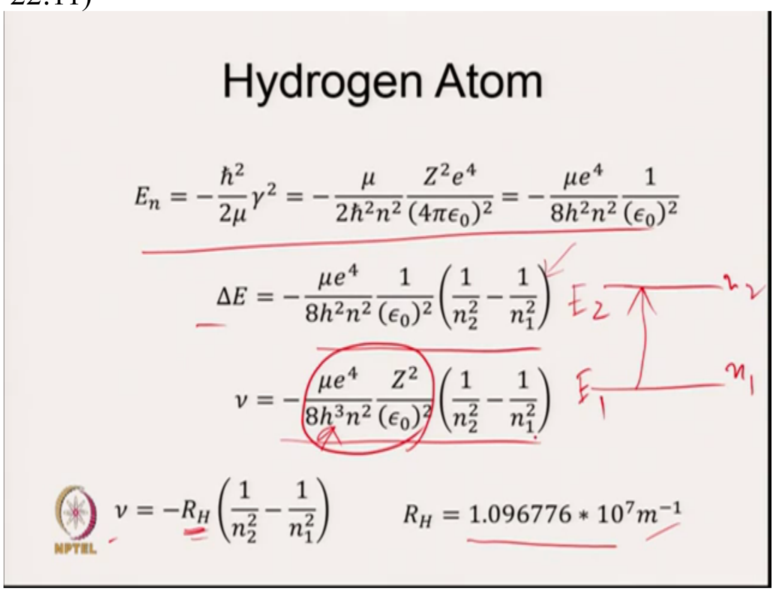

So now let us again think of En. This is you E n, so this is you E n that is we have already discussed. This is simply mu e 4 by 8 h square n square 1 by epsilon naught square. This is same thing which we got in previous slides. Now think of a transition, transition between electronic level in a hydrogen atom. Suppose you are going from n1 to n2 so what will be the frequency of the transition. So frequency of the transition can be calculated by taking a difference between the energies of the 2 levels and divided by h.

So first we will calculate delta e and we will get this one. This other things are constant except n and so, you see this is in brackets and this is your 1 by n 2 is square, so this is going to be n 2. And we started with n 1, so we write 1 by n 1 square and delta e is equal to h mu, divide by h.

When you divide by h, you will get h cube and frequency will be equal to this term and this whole constant is equal to what is known as RH which Rydberg constant.

Rydberg constant has this value in your meter inverse. So it is in meter inverse, so please keep in mind. This is in meter inverse where frequency is in hertz. You need to convert this, so this is basically big number unit and so you need to convert it to frequency unit, then place here. So frequency associated with the transition in hydrogen atom will be given by this equation.

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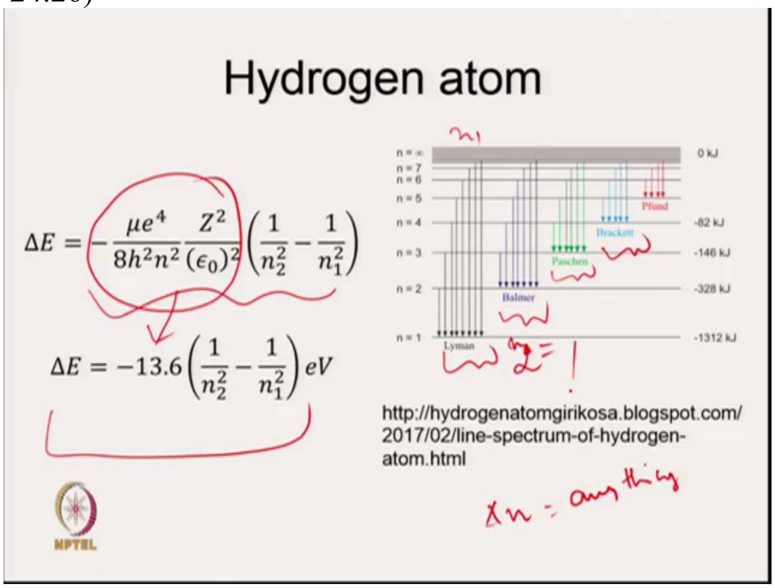

So delta E is equal to this and this whole thing, if you talk about it in energy term, then this will be equal to 13.6 electron volt and so delta E can be calculated using this equation, using this equation. So let us talk about what is known as gross spectrum hydrogen atom. So, for hydrogen atom, delta n, our selection rule is delta n can be anything, anything. We are talking about emission spectra so transition can be between n is equal to 2 to n is equal to 1. It can be from n is equal to 3 to n is equal to 1 and 4 to n is equal to 1.

So this is known as Lyman series. So Lyman series corresponds to transition between your n is equal to higher value, any higher value to n is equal to 1, n is equal to 1. Second one is Balmer series, Balmer series. It corresponds to transition between higher energy levels to n is equal to 2.

Similarly, Paschan series; this corresponds to transition between n is equal to higher energy levels to your n is equal to 3.

Similarly, your Brackett, again this corresponds to your transition between n is equal to infinity to n is equal to 4, n is equal to 7 to n is equal to 4, n is equal to 6 to n is equal to 4. So any higher value transition between any higher value of n is equal to 4. When I say any higher value of n here, what I mean is any value or n 2 should be greater than, greater than your n 1. So here, n 1 is equal to or n 2 is equal to…

So let us see this is n 1 if, so n 1 can be of any higher value and n 2 will be always 1. So this is Lyman series, n 1 is greater than 1, n 2 is equal to 1. In Balmer series, n 1 is higher than 2 and n 2 is 2. In Paschen series, n1 is higher than 3 and n 2 is 3. So similarly, you can talk about other series. So this is your gross spectrum of hydrogen atom.

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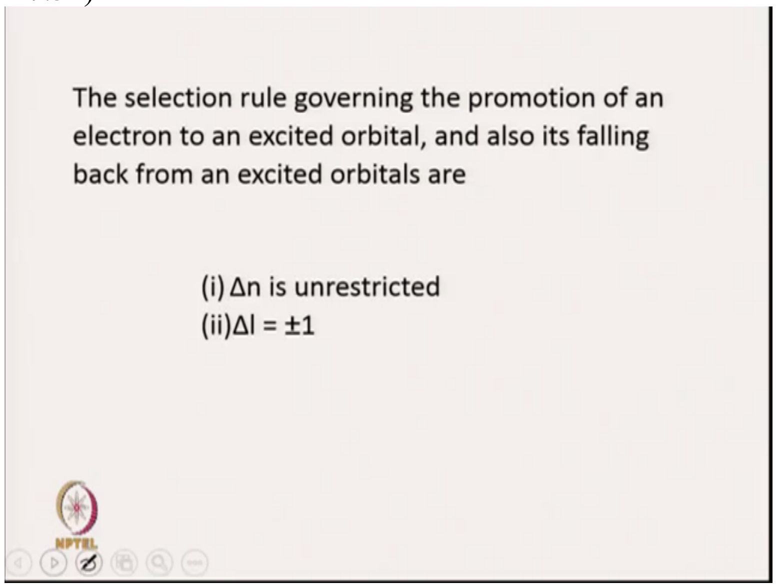

Selection rule already taught to you that selection rule governs the promotion of an electron to an excited orbital and also its falling back from the excited orbitals are these are the 2 selection rules. For gross selection rule, we do not need the second 1. Then we will talk about the fine structure. Then we will see the, what is the importance of second selection rule. So selection rule for electronic transition is that delta n is unrestricted, delta l is plus minus 1.

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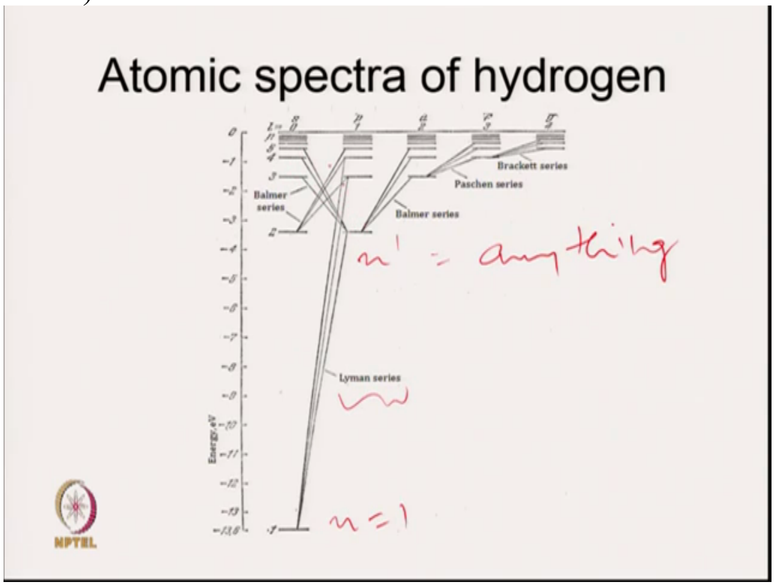

So this is your atomic spectra. So you see, n is equal to 1. This is 1s 2p. So here you see, this is your Lyman series, you can talk about emission, you can talk about absorption both. So, here n is equal to 1 and here you can say n dash can be anything, anything which is greater than 1. In case of absorption, it is n is equal to 1 to n dash is equal to n greater than 1. Whereas in emission, you have your, the transition is happening from n greater than 1 to n is equal 1. Now you see, this transition is also possible. Here you see, what is changing is l value. So here, l is equal to 0; here l is equal to 1.

This is for s electron, this is called p electron. So delta l can be minus 1, delta l can be plus 1, delta l can be plus 1. While delta n can be anything, delta n can be anything. So this is the way to show your gross atomic spectra of hydrogen atom, gross atomic spectra of hydrogen atom.

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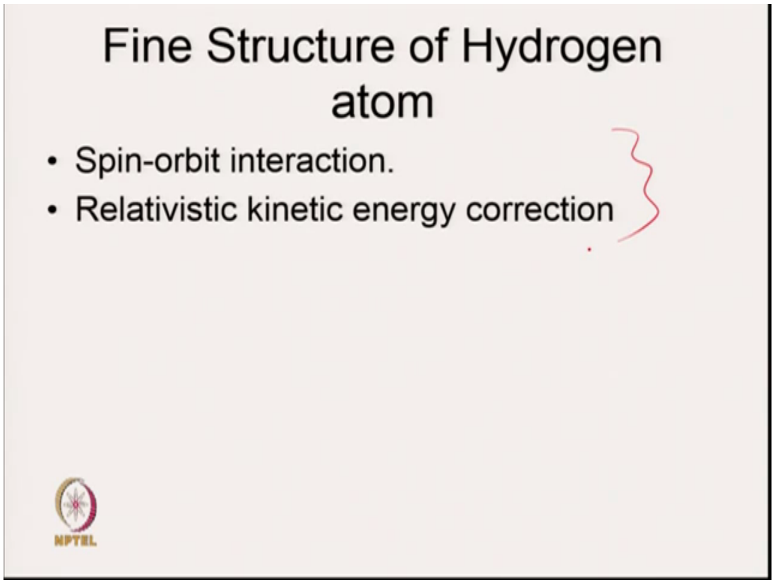

But if you look at the hydrogen spectra, you go to more detail then you see there is splitting of the orbitals and corresponding to that you have a fine structure of hydrogen atom. The fine structure is just due to these 2 thing, spin orbit interaction and relativistic kinetic energy correction. I will not discuss relativistic kinetic energy correction because that is more related to your exact value of energy but I will talk about our spin orbit interaction because that leads to splitting of the energy levels.

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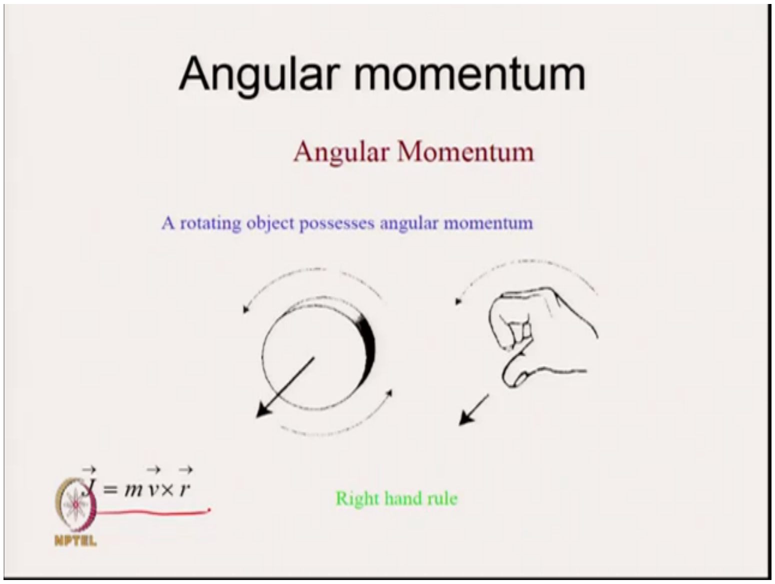

So let us discuss spin orbit interaction, so first let us think of what kind of motion an electron undergo? So an electron undergo rotational motion. Any rotating object possesses angular momentum and your electron is also making rotation, so it must have angular momentum. The way angular momentum is given is this; j is equal to m into v into r. So m is mass. So in this case, it will be mass of electron. v is velocity and r is distance from the centre and the direction you can also know.

The direction is given by right hand rule. So if you see this, if this way your electron is rotating then your angular momentum is in the direction of the thumb. So you see here, it is like this so it is coming up. It will be up, if it is going up from my side, if it is anti clockwise, it is going up. If it is clockwise, it is going down. So the direction of angular momentum will be decided by the direction in which the electron is rotating, electron is rotating.

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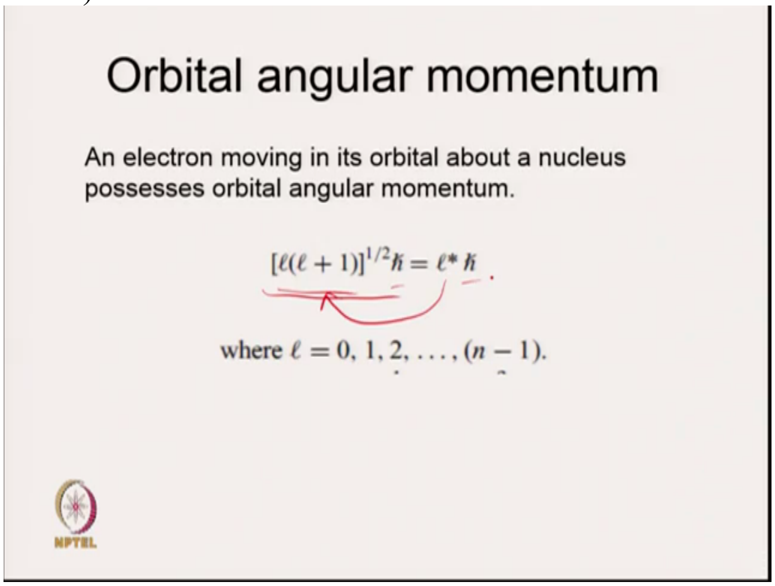

Now if an electron is moving in its orbital about a nucleus. So electron is moving in its orbital about its nucleus and so it will possess orbital angular momentum which will be given by this formula. This we have already discussed in the rotational motion chapter and that is given by l l plus 1, half multiplied by h cross, h cross. So h cross multiplied by square root of l, l plus 1 and this l star denotes l l plus 1 half.

Here, l can take the value n minus 1. So this is your orbital angular momentum and that is because electron is moving around nucleus in its orbital. So these are the allowed direction of electronic angular momentum vector which I discussed earlier. So I am going to leave it.

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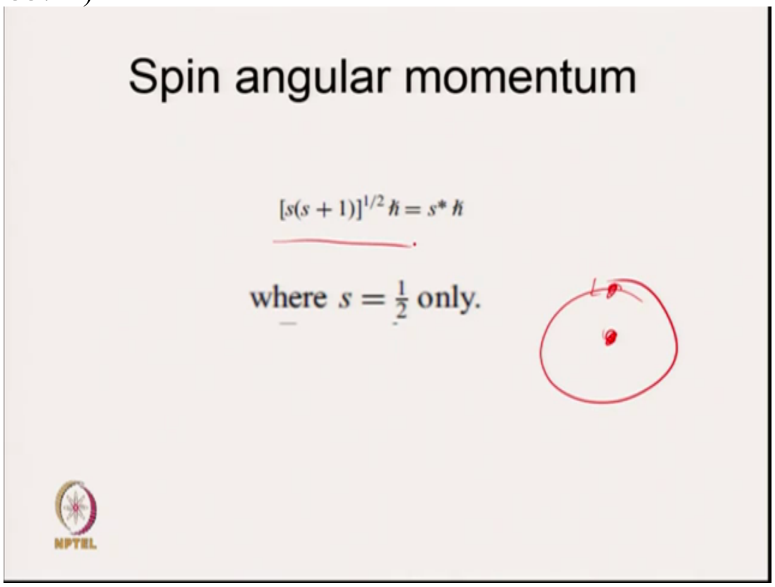

Suppose this is nucleus, and electron is moving around. Electron is at one position, it is also spinning and that spinning gives the electron spin angular momentum. So electron also have the spin angular momentum since it is also going up spin and that is given by S, S plus 1 half into h cross or h cross multiplied by square root of s into S plus 1. Here, s can take half only

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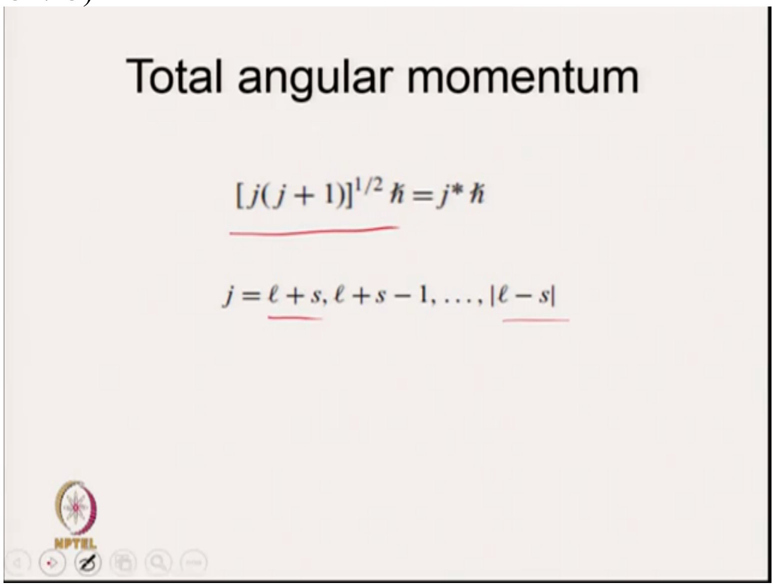

And total angular momentum is basically sum of this 2 angular momentum and it will be given by your, this formula. So j, j plus 1, half, into h cross, where j can have e plus s to l minus s value. This we have already discussed in the rotational motion, but just to refresh with, you know, this angular momentum. I just revised it.

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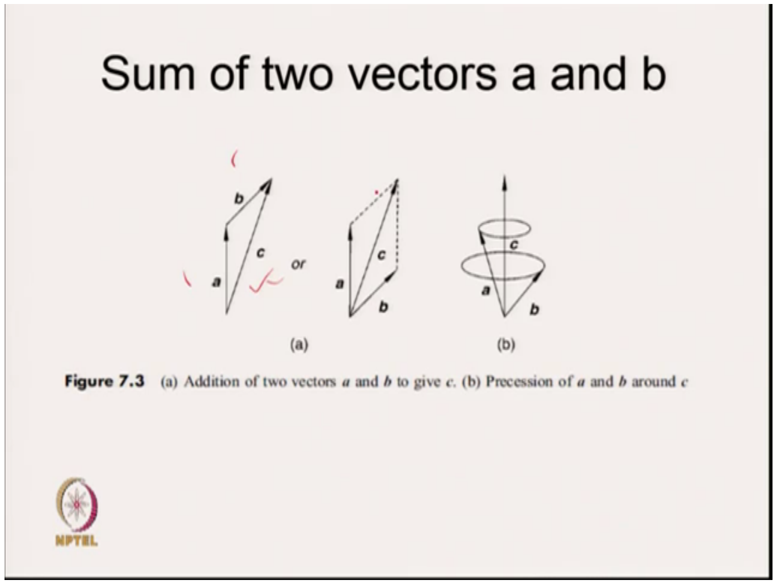

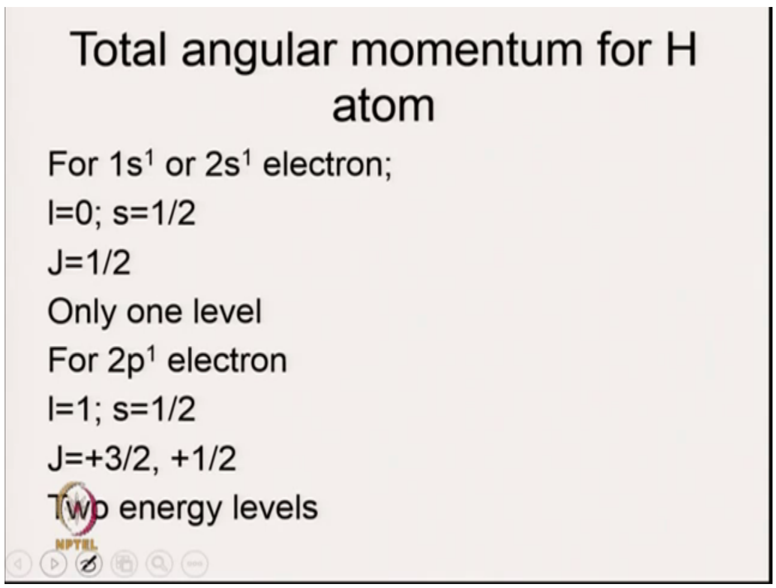

Now sum of 2 vectors, a and b tells you that if there is a and b, this is your vector c and there is, this is another way to look at vector c. So a plus a, gives you vector c. Now let us think about, this is our angular momentum for any electron. Now let us think of angular momentum for any electron in hydrogen atom.

So suppose I consider, 1 s 1 electron of 2 s 1 electron. So what will be the l? l value is 0 and s value is half. And if you calculate J value, it will be equal to plus half. So only one value of J is allowed and thus it will have 1 energy level. For 2 p 1 electron, l is equal to 1, and s is equal to half. l is equal to 1, since p orbital equals to 1 and s is equal to half. So j can have 2 values, plus 3 by 2 and plus 1 by 2.

And so you will have 2 energy levels. So this is to know how many or a particular energy level is split into how many energy levels if there is a coupling between your l and j spin orbit coupling. So for 2p1 electron, there will be splitting into 2 energy levels or 2 p level is basically a split into 2 energy levels. One corresponding to J is 3 by 2 and other corresponding to J is half. Now let us think of how to get the energy associated with these levels, energy associated with these levels.

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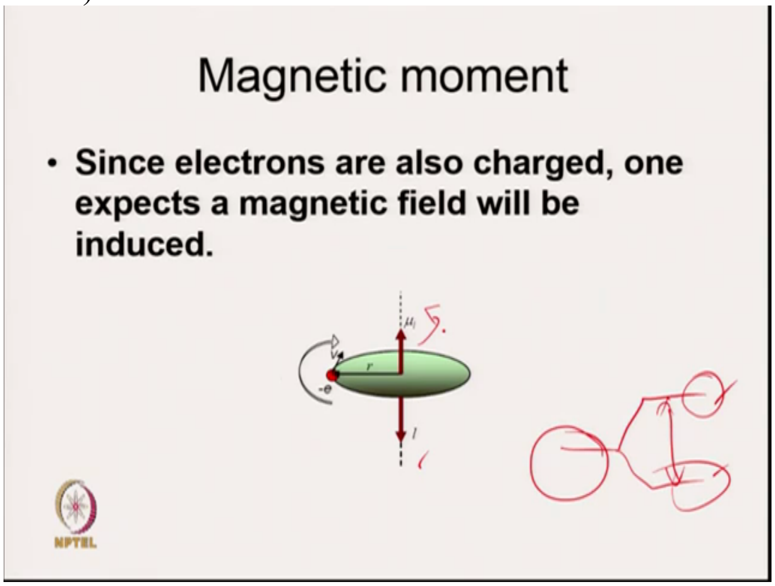

Because you see 2 p orbital is like this and we know that it splits into 2. So the question is now, I know the energy of 2 p level, it will depend on it. but I do not know the energy of these 2 levels and unless we know the energy of these 2 levels, I cannot calculate what will be the delta e, what will be the delta e. So now look at the fine spectrum of the hydrogen atom. So first thing is to calculate the energy of this 2 levels which are initially degenerate but they split because of spin orbit coupling.

Now first, we need to understand the magnetic moment. Electrons are charged and so when they will rotate, they will also induce magnetic field. So not only, we are talking about your angular momentum, anything which is rotating will have angular momentum. But the things which are rotating with charge, has charge, then you expect them to induce magnetic field with them.

And the magnetic field is just opposite to or what is called as magnetic moment direction will be opposite to your direction of angular momentum. So for example, just I told you how to get the direction for angular momentum, so you see electron is moving like this, so if you do that, right hand rule, and so you see this is going down and that is what is shown here. So angular momentum direction is this and then magnetic moment direction will be this and I will tell you how. But first let us calculate the magnetic moment. So first thing is, since electrons are also charged one would expect a magnetic field will be induced.

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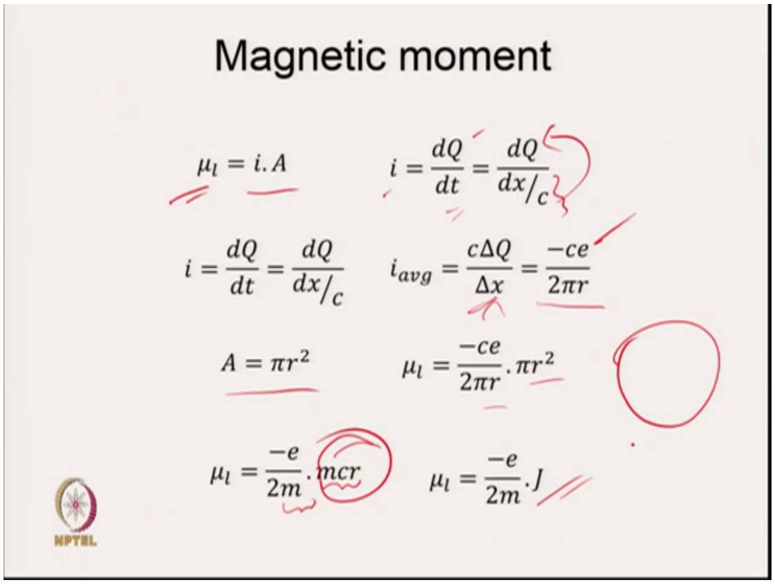

So let us calculate magnetic moment. Magnetic moment is given by this sign and l shows you that it is because of the movement in orbit, movement in orbit not due to spin and this is equal to i into A, where i is current and A is area.

This is the way magnetic moment is calculated. And what is i, i is dQ by dt, change in charge with respect to time and what is dt? Time is distance by velocity. So this is your dx by c. So I will be written as dq by t, dq by dx by c and if I want to calculate i average, current average; then I will simply write c into delta q by delta x, c into delta q by delta x and delta q is e, which is charge of the electron by 2 pie r.

So this delta x is 2 pie r, which is perimeter of a circle. And A we know, a should be equal to pie r square. For a circle, area is equal pie r square and so mu l, magnetic moment, orbital magnetic moment will be equal to minus ce 2 pie r into phi r square. Pie pie cancels out, 1 r cancels out, so what I will get is minus e by 2 m and then m c r. So what we did is, I multiplied numerator by m and denominator by n. So we have minus e into m c r divided by 2m. And this, m c r is equal to your j or orbital angular moment l and you can say here l. let us write l. So this is your angular orbital moment. So magnetic moment and angular orbital moments are related, and they are related by this equation.

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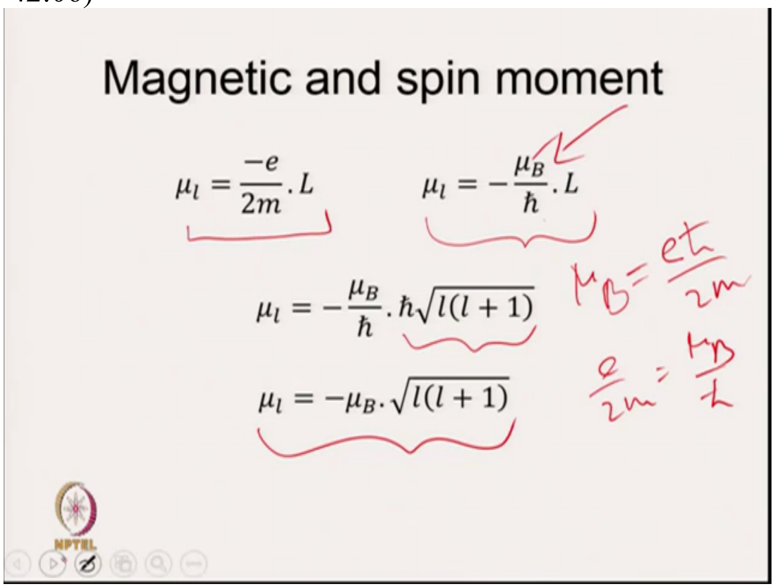

So this is your mu l is minus e by 2 m into l. So there is another way to write this, mu l is minus mu v by h cross. This is called Bohr magnet. So mu b is equal to, if you see that mu b is equal to your e h cross by 2m and so e by 2m can be written as e by 2m will be mu b by h cross and that is what I have done here. So mu l can be written in terms of mu B. So this is equal to minus mu B by h cross into l and we know l is equal to h cross square root of l l plus 1 and this h cross h cross cancels out, so this mu l is equal to minus mu B into square root of l l plus 1. This is your magnetic moment due to orbital movement or electron movement in orbit.

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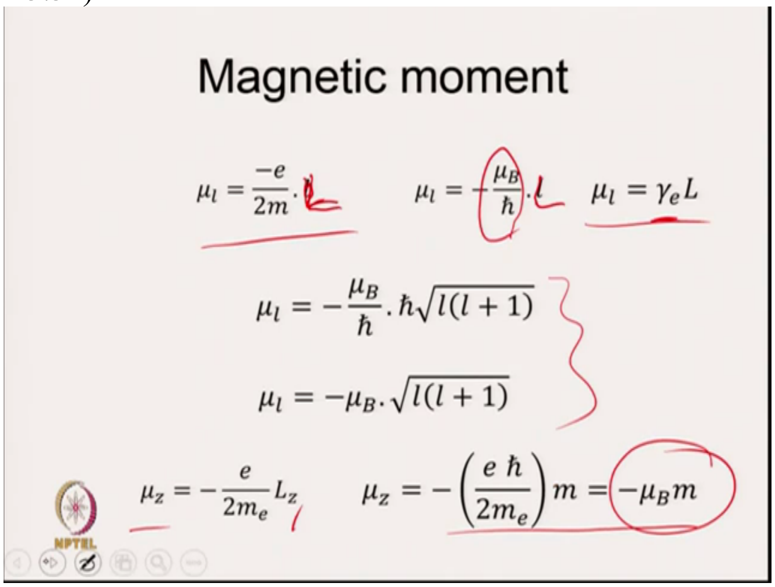

So that is what we derive mu l is minus e into l, so let us write this l, this is l, this is the angular orbital moment and this whole thing can be written as gyromagnetic ratio of electrons. So magnetic moment can also be written in this term. This already we discussed how to write mu l in different notations mu j can also be written. In that case, l will be replaced by l z and mu z can also be, and l z we know is equal to m h cross. So here we have written in terms of m h cross and mu z will be given by minus mu B m. So this is about magnetic moment due to orbital, orbital magnetic moment.

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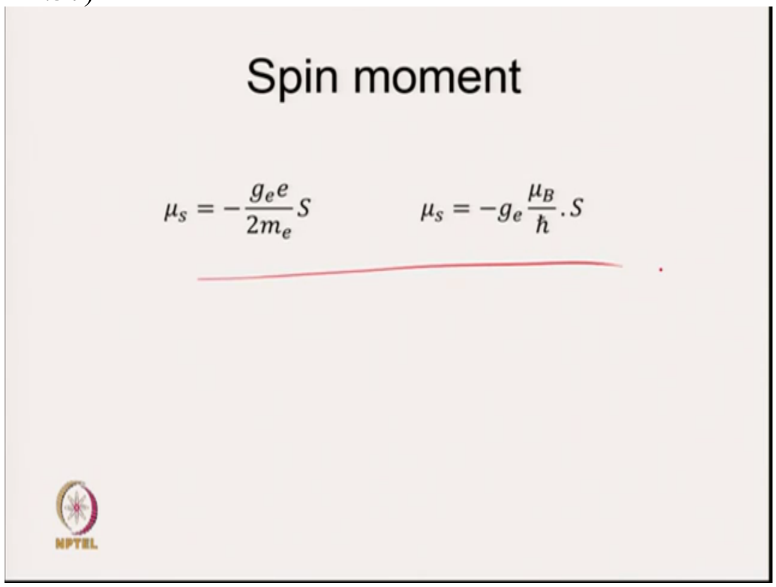

Similarly, we can write the spin moment, same way. Only thing now we have considering spinning of electron rather than its movement in orbital around the nucleus. So spin moment can also be written like this.

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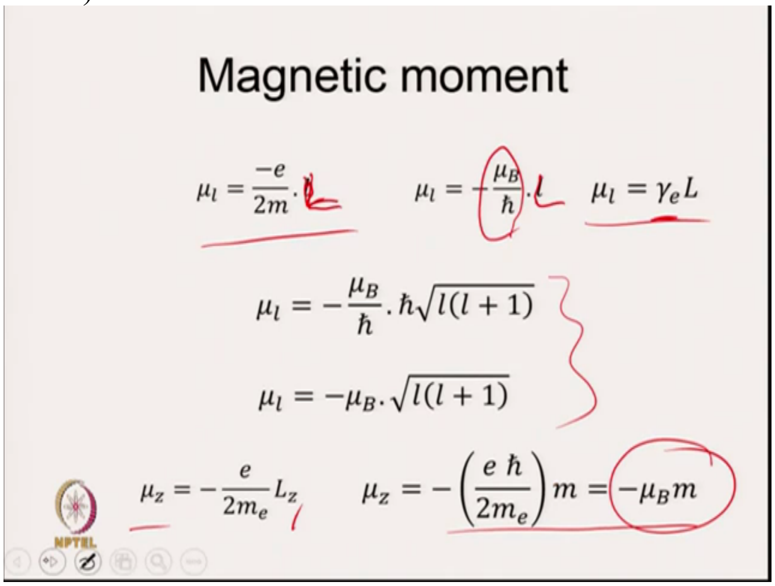

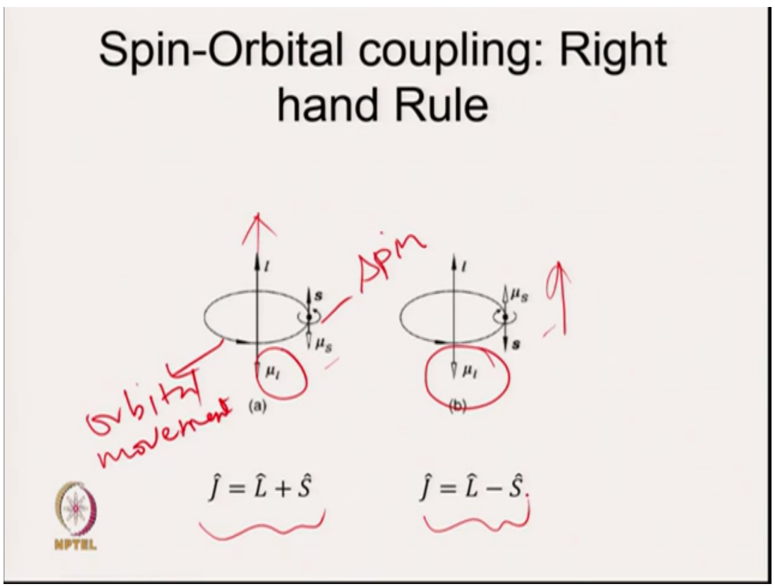

Now let us think about, spin orbital coupling and I already told you how to know the direction of angular momentum and magnetic moment. So you see, this is your spin moment, spin, spinning, and this is orbital, orbital movement, orbital rotation. Now you see this, this is going anti clockwise. So applying right hand rule, the direction of the right hand rule will be up.

And so direction of magnetic moment will be down. So let us see why this direction is down or just opposite to your angular orbital momentum. Now this is your equation, if you go, this this is your equation. You see there is a minus sign. So what will be the direction of l? The direction of magnetic momentum will be opposite to it, opposite to it and that is what is shown here.

Now look to the spinning of the electron and that is also in same direction and so mu S is going to be in same direction and so J is equal to L plus S. Now take the opposite case. Electron is moving in the orbital in the anti clockwise fashion that is spinning is in clockwise direction. In that case, mu l will be down and the direction of mu S will be up and so your J will be L minus S and that is why we split it.

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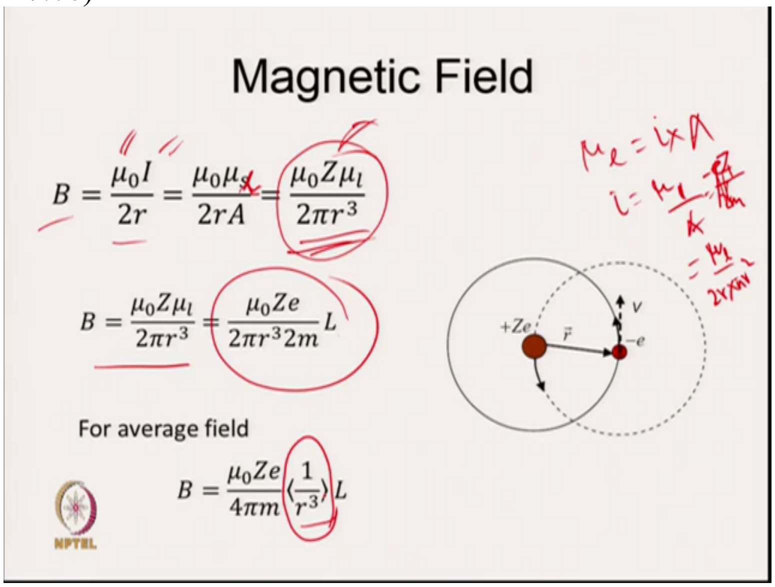

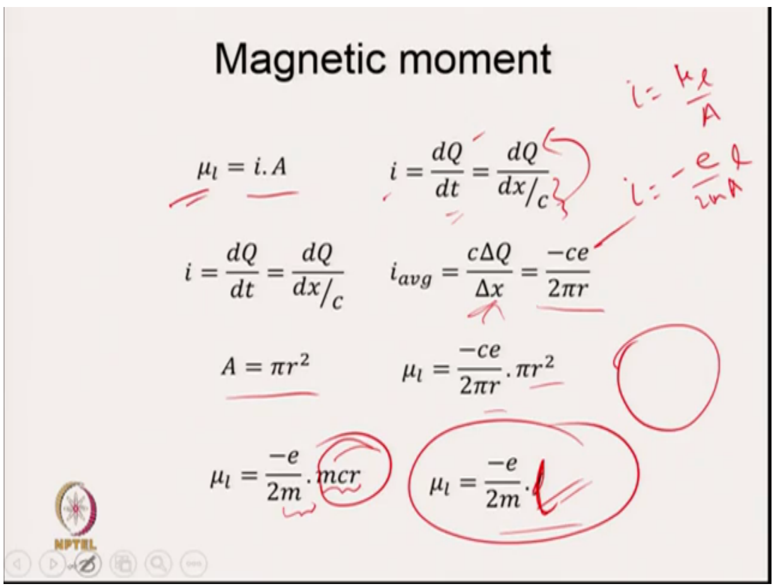

Now let us go and calculate what will be the energy? So let us see, there is your, here is your electron moving and here is your nucleus. Now what I am doing is that I take a reference where electron is static and centre of mass is moving. From the Ampere's law, we know that if this happens that will result into a magnetic field and that magnetic field will be given by b. So b is equal to mu naught, where this mu naught is your permittivity, permittivity of the medium into I, I is current divided by 2r.

R is the radius or distance between the nucleus and electron. So this is from the Ampere's law. I just, we calculated, so let us just see what is the I. So if I go here, here we see, current is equal to mu l by A. And mu l is this. So I will be mu l by A and mu l is, and I is equal to minus e by 2mA in to l. So remember this, minus e by 2mA into l. now go and see here. I is equal to, let me write; this is mu l. So please change this.

So mu 0, mu l by A. So I showed you that your mu l is equal to I into A. Let us write I,. I is equal to mu l by A. mv is equal 2r into pie r square. So 2 pie r cube, so this is your 2 pie r cube and Z I introduced because here you have not only F charge e, it is z into e, that is why I introduced z. So this is your B; mu naught z, mu l by 2 pie r cube and if you remember, mu l, it is e by 2m l. So you have this expression. So mu naught z e by 2 pie r cube 2m into l and for average field, you just take 1 by 2m out and you just have to take average of 1 by r cube. So this is your magnetic field, magnetic field due to your orbital motion.

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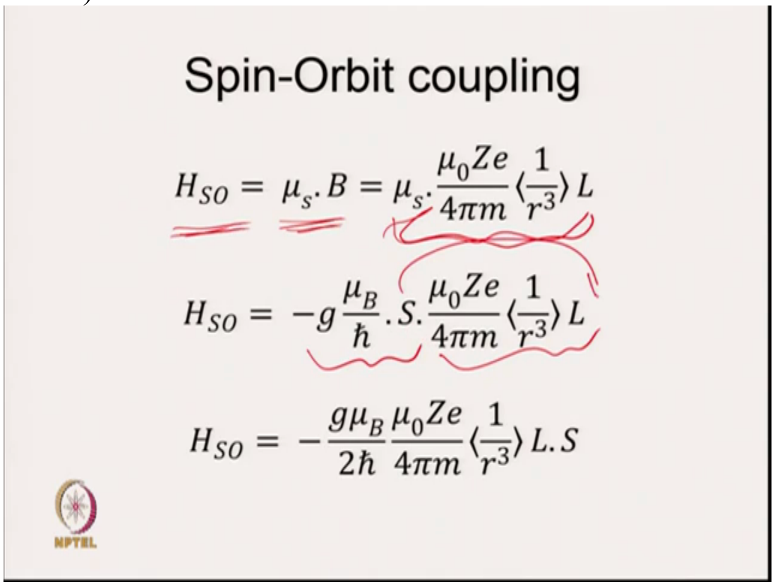

Now let us think about spin orbit coupling. So how to write the Hamiltonian for spin orbital coupling and for that you have to calculate; this Hamiltonian will be given by mu S. So this is, so remember this is due to spin, magnetic moment due to spin into B and this, already we calculated B, we already calculated. This is mu naught Ze by 4 pie m, 1 by r cube l and into mu s and mu s, we have expressed this. This term and you have this quantity and now if you simplify, you take s this side, then you have l into s, and all constants, l into s, and all constants. So this is your Hamiltonian for spin orbital coupling. This is Hamiltonian for spin orbital coupling.

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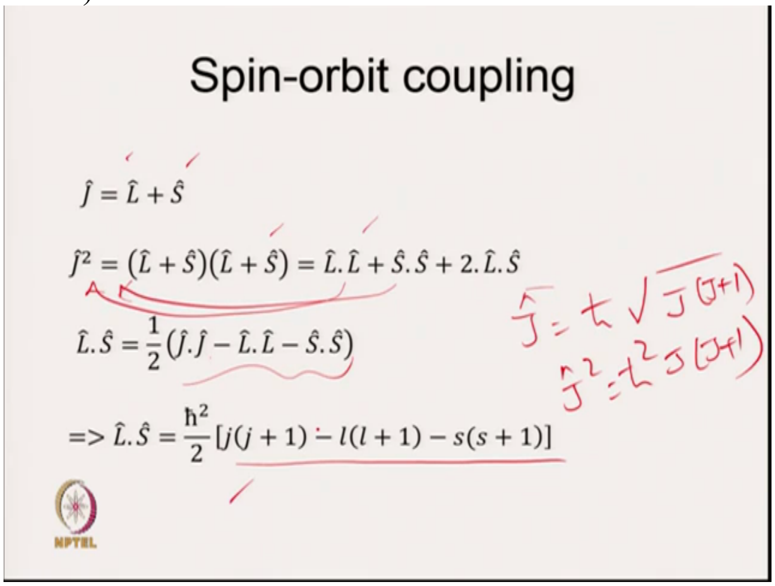

Now let us calculate l into s. We know that J is equal to L plus S. So J square will be L plus S into L plus S. This will give you L dot L, S dot S, plus 2 dot s dot l. So L dot s will be half of your J square into J minus; so let us take this side, these 2, so L S is equal J square minus L minus s dot s divided by 2. This is what is written here. So l dot S is equal to h cross square by 2, j j plus 1, l l plus 1, minus s s plus 1. We know that j is equal to h cross j j plus 1. So j square is h cross j j plus 1. That is what is written here. So now we have calculated l dot s.

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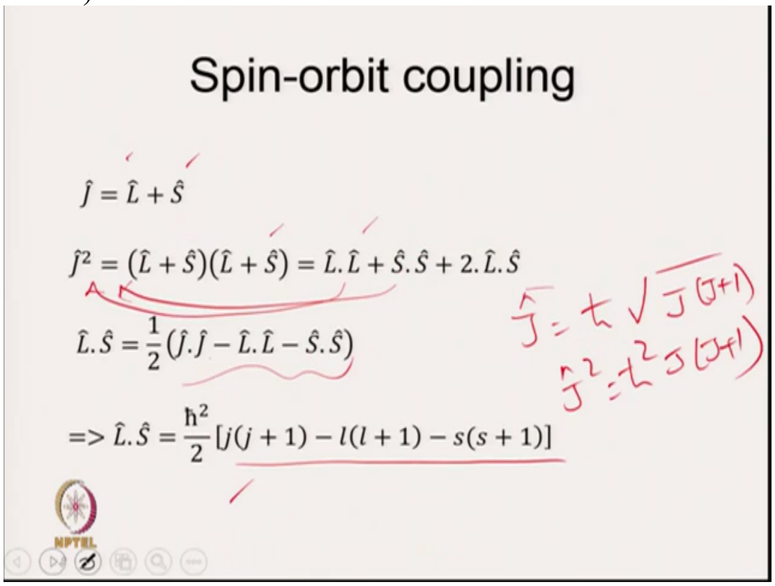

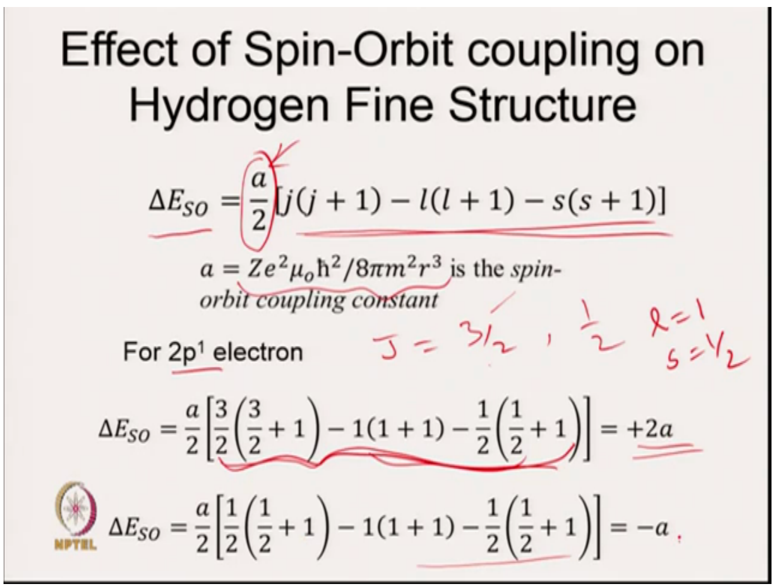

So we can now calculate delta E. Effect of spin orbit coupling on hydrogen fine structure. So when there is coupling, you get a fine structure. So delta e s o is given by a by 2 and a is constant, j j plus 1, minus l l plus 1 minus s s plus 1 and a is equal to this whole value, which is basically given here.

Remember this whole value is your a. So this you can say is some constant a into l into s. So that is all. So A divided by 2 and then this. So a is basically the constant there, so this constant is, if you look at this, this constant is a by h cross square and if I multiply by, a by h cross square into h cross square by 2. So this is your a by 2.

A by 2, j j plus 1, minus l l plus 1, minus s s plus 1 and A will be here, and now you can calculate what will be the delta e for 2p electron. So for 2 p 1 electron, j can be equal to 3 by 2 electron or half what we saw and when j is equal to 3 by 2, if you calculate j j plus 1, minus l l plus 1, minus s s plus 1, you will do this calculation and then what you will be get is get is plus 2a. So 3 by 2, 3 by 2 plus 1, here since 2 p is equal to 1, so l is equal to 1 and s is equal to half. So this is going to be same only thing is that j is changing, and j is basically 3 by 2 or half. And that is why you get 2 values of delta e s o; plus 2a and minus a.

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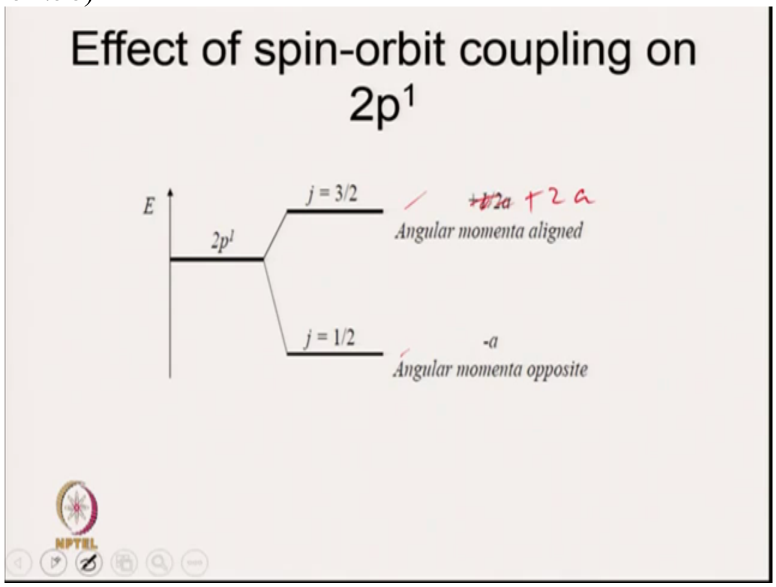

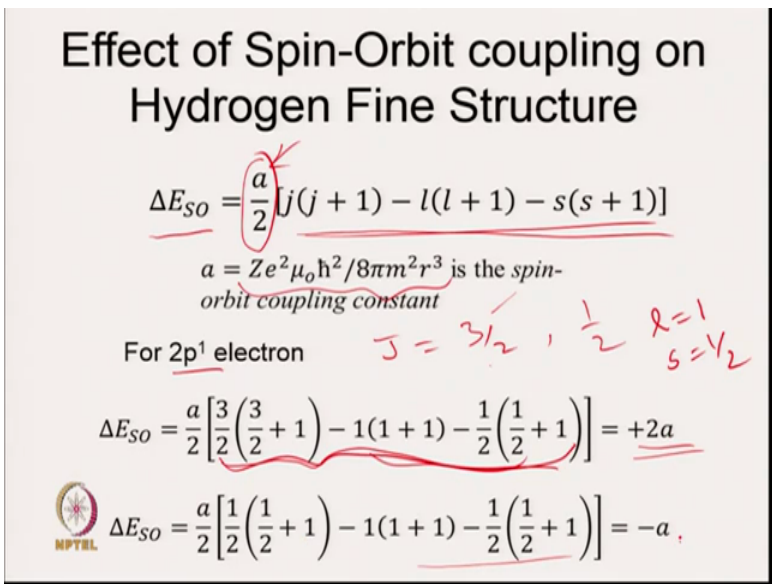

And so now you know the effect of spin orbit coupling on 2p1 electron. So 2p1 will be split into 2 energy levels. This will have, if you have, j will be equal to 3 by 2, then you will have energy, so you see e is plus 2a, it is wrong, it plus 2a. And this will be minus a. This is your energy level

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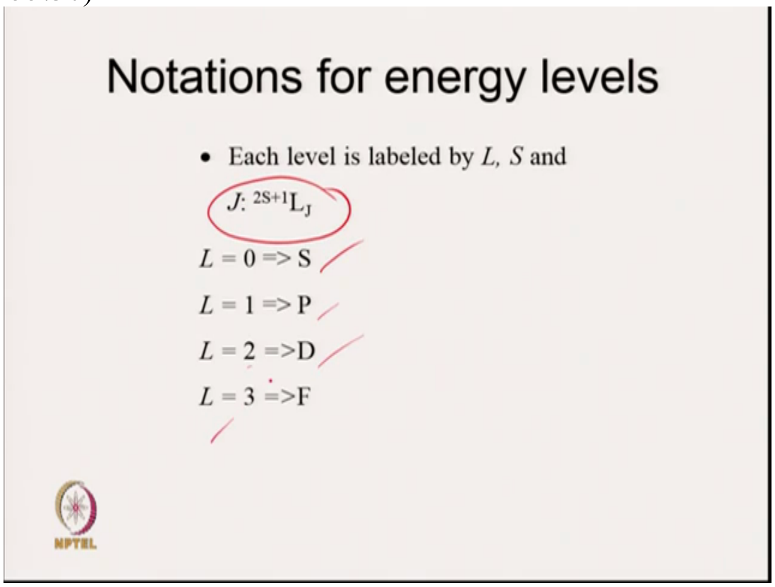

Now how to denote this energy levels? So just we saw that if electron is in 2p level, it will split into, the energy level will split into 2, the question is how to level it? Generally, we level it, the rule which follow is for levelling is 2S plus 1 LJ. So if l is equal to 0, it gives value S. If l is equal to 1, give value p. If l is equal to 2, then level it as d, if l is equal to 3, level it as f. Again, selection rule I already told you, so I am not going to discuss. Only thing that you know is that delta n can be anything, and delta l is plus minus 1.

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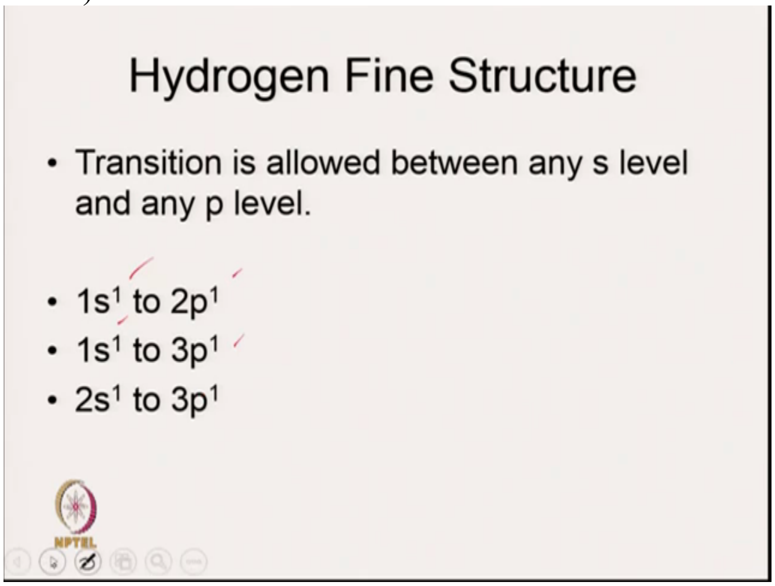

So what does that mean is, the transition is allowed between 1s1 to 2p1, 1s1 to 3p1 also because delta n, there is no condition. And then you can have 2s1 to 3p1, 2s to 3p1. All this kind of transition is allowed. Now let us see, if we have electron in 1s or 3s.

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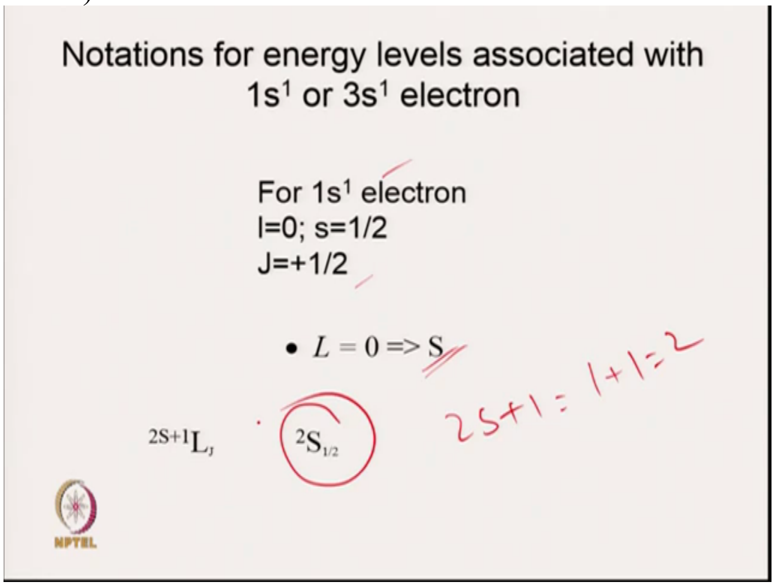

So for 1s1 electrons, l is equal to 0, s is equal to half and so j will be half. There is only 1 value of j. And since l is equal to 0, so it will correspond to, it will be given level s. And 2s plus 1 is equal to 2s plus half, 1 plus 1 is equal to 2. So there is 2 here. And j is equal to plus half, 2s half. So there only one level which will be levelled as 2s half. If you have electrons in 2p level, then l is equal to 1, s is equal to half. So any P level, l is equal to 1, s is equal to half.

And j will have 2 different values; plus 3 by 2 and plus half. And since l is equal to 1, that corresponds to level p. And 2s plus 1 will be 2s plus 1 again will be 2. And j is, j has 2 values, so j will have 2 energy levels. So y energy level is levelled as 2p 3 by 2 and another energy level will be given by 2p half.

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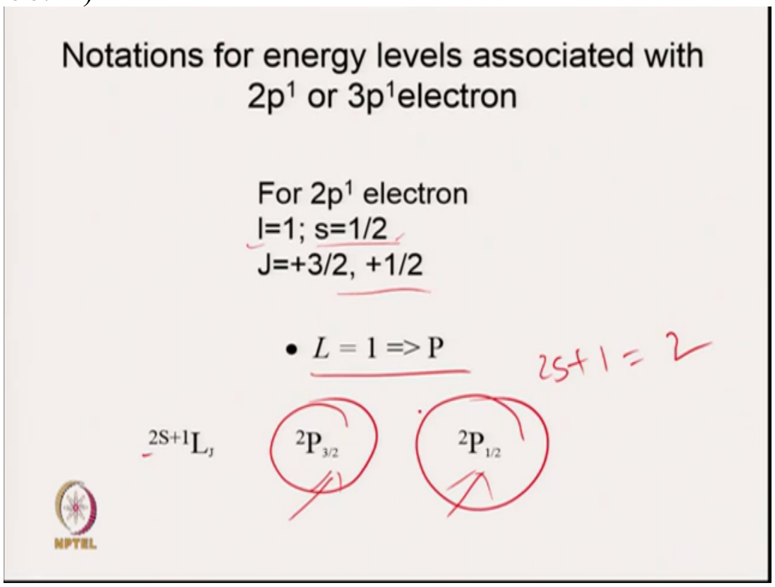

Notation for energy levels associated with 3d1 or 4d1 electron; here we are talking about d electron. For 3d1 electron, l is equal to 2, and if you have 1 electron s is equal to half, and your j value will be plus 5 by 2, 3 by 2. l is equal to 2, corresponds to level d. And then you have these 2 energy levels. Leveling of these 2 electron levels will be 2d 5 by 2 and 2d 3 by 2. Since j has 2 values, it mean that the energy level will be split into 2 different energy levels. 3d energy level will be split into 2 different energy levels. What will be the name? The name 2d 5 by 2 and 2d 3 by 2.

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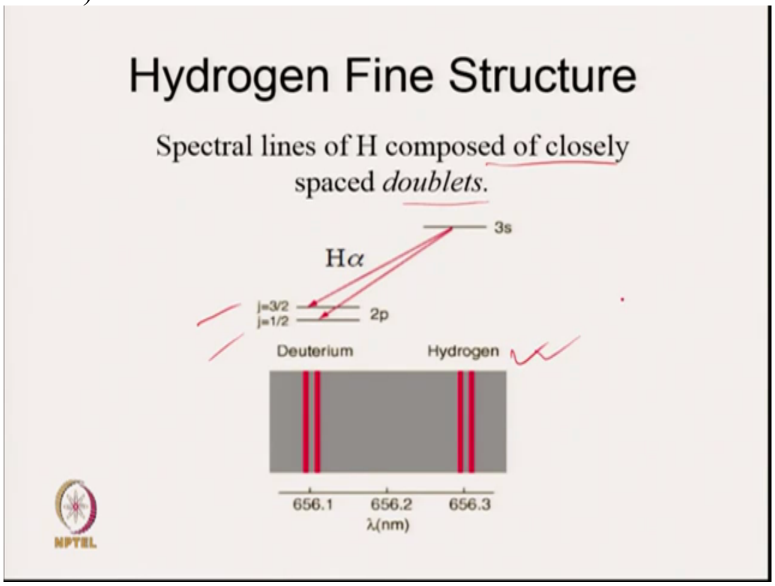

So now look at the spectral line of hydrogen atom. here, we are discussing about fine structure. It will be composed of closely spaced doublets. For example, if you are going from 3s to 2p; I told you for 3s, there will be no splitting. For 2p, there will be 2 energy levels because of spin orbit coupling, 2p level will not be degenerate, it will be split into 2 energy levels given be j is equal to 3 by 2 and j is equal to half and that corresponds to 2 different line in the hydrogen spectra.

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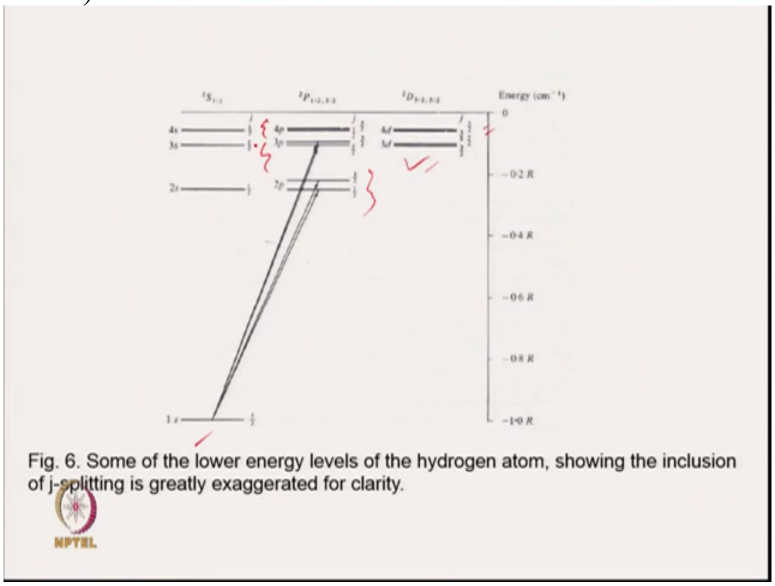

Fig. 6. Some of the lower energy levels of the hydrogen atom, showing the inclusion of j-splitting is greatly exaggerated for clarity.

In totality, what you will see that you have, suppose you have 2s, this is 1s, this is 2p is split in split into 2, 3p is split in split into 2, 4p is split in split into 2. Similarly, 2d is split in split into 2, 3, 4dp is split in split into 2. The splitting, the gap between the split energy level will be higher for 2p, lower for 3p and much lower for 4p.

If you go this side, the splitting will be much smaller for 3d in comparison to 3p or 3p. but if you go up, the gap between 4d will be smaller than the gap between 4d and this all transition are possible; 1s to 2p, 1s to 3p - that is what we talked. We cannot go from 1s to 3d, because then the delta l will be plus 2. That is not allowed, delta l will be plus 2 is not allowed. Delta l is plus minus 1 is allowed. So it can go to 2p to 3s, 2p to 3s. This is your finer, or fine kind of spectrum of hydrogen kind of atoms.

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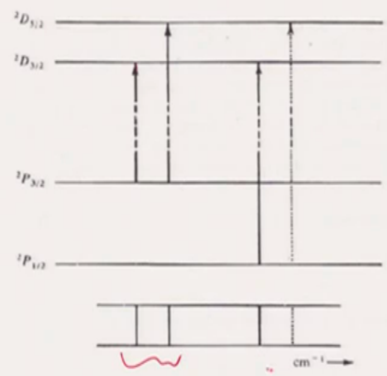

The compound doublet spectrum arising as the result of transition between ^2P and ^2D levels in the hydrogen atom.

So now you see, this is, what we are showing is compound doublet spectrum arising as a result of transition between 2p and 2d levels in the hydrogen atom. So before that, I discussed transition from S to p level. Now I am seeing the transition between the p level and d level.

Now you see here 2p 3 by 2 to 2d 3 by 2, 2p 3 by 2 to 2d 5 by 2. That is possible and 2p have to 2d 3 by 2, and 2p have to 2d 5 by 2 and so there will be doublet here, there will be doublet here. So this is the transition between p to d levels which will result into double doublet, result into double doublet. So this is the way to understand fine structure of hydrogen atom. So today, I discussed the fine structure of hydrogen atom.

I am not going to discuss your relativistic effect because it is your bit higher, higher in thinking and it is not required for this course. But I hope that you are able to understand how the splitting takes place when spin orbit coupling happens, spin orbit coupling happens. So thank you very much for listening. These are the different books that I am taking notes from. So Alberty, book from Alberty, book from Peter Atkins, and then fundamental of molecular spectroscopy from banwal and mccath. Thank you very much.