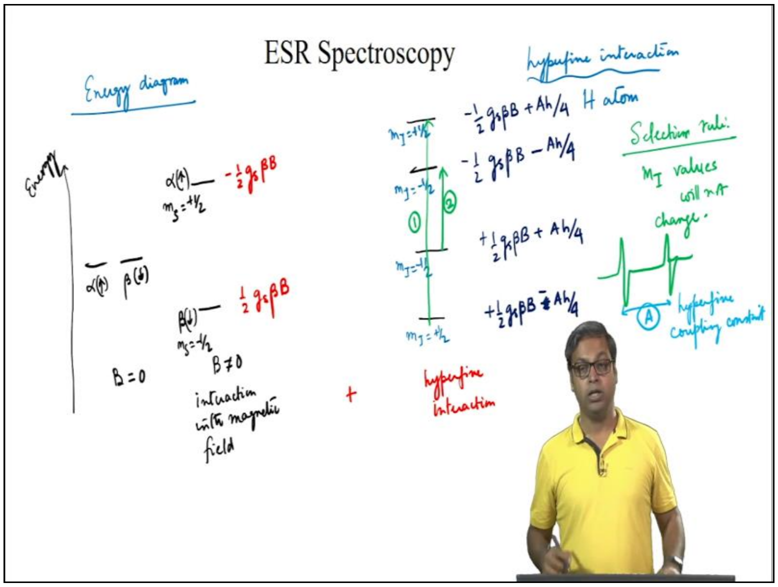
# Fundamentals of Spectroscopy

**Prof. Dr. Sayan Bagchi**
**Physical and Materials Chemistry Division,**
**National Chemical Laboratory - Pune**

**Prof. Dr. Anirban Hazra**
**Department of Chemistry**
**Indian Institute of Science Education and Research – Pune**

## Lecture 55
## ESR Spectroscopy – 3

**(Refer Slide Time: 00:24)**



ESR Spectroscopy

Hello all welcome to the lecture in the last lecture we looked into the hyperfine interactions of the simplest possible system that is for the hydrogen atom. So, let us revisit the energy diagram so as we have seen in the last lecture or vertical axis is the energy axis and when we have no externally applied magnetic field that is B equals 0 we have these two states alpha that is top spin and beta that is down spin.

However when B is not equal 0 then we have interaction with the magnetic field and because of this interaction the degeneracy is lifted and because the degeneracy is lifted we have two levels the lower level is beta the upper level is alpha and in this case m s equals -1/2 this is m s equals +1/2 and if you look into the energies this is 1/2 gs beta B this is -1/2 gs beta B but we can have further interaction that is the interaction of the electron spin with the nuclear spin which is known as the hyperfine interaction.

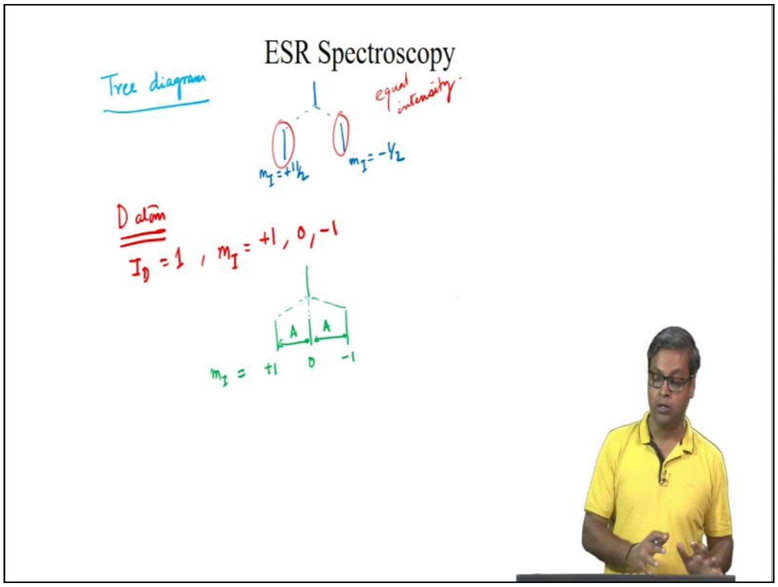
And cause of this hyperfine interaction these energy levels will further split so we will have 4 different energy levels and if we look into the m I values m I here is +1/2 here m I equals -1/2 m I equals -1/2 m I equals +1/2 so we have this interaction with the magnetic field and we have the interaction with the nuclear spin. So, we have this magnetic field interaction plus the hyperfine interaction and if we consider both these interactions the total energy what we get is this is +1/2 gs beta B and this is +A h by 4 actually this is -H by 4 then we have +1/2 gs beta B +A h by 4 this is -1/2 G s beta B +A h by 4 and we have -1/2 gs beta B -A h by 4 so these are the energies for this different levels.

And now what we see is that we have a selection rule and the selection rule states that that the m I values will not change for a transition to take place. So, the transitions that are allowed is this one and this one so one is between m I values m I that is m I equals +1/2 so this has large energy and the other is m I equals -1/2 which as lower energy. So, we already saw that in the last lecture that the energy gap or the gap between these two lines in the spectrum.

So if we plot these two lines then the gap between these two lines is given by A that is the hyperfine coupling constant. So, this means that we can measure the value of A or the value of hyperfine coupling constant from the experiment and because A can be obtained experimentally that means we can get more things or more important aspects of the molecules or radicals from this ESR spectroscopy.

So, this whatever we have drawn this energy level diagram this lifting of the degeneracy this can also be understood qualitatively using the tree diagram.

**(Refer Slide Time: 06:05)**



ESR Spectroscopy

Tree diagram

equal intensity

$m_I = +1/2$

$m_I = -1/2$

D atom

$I_D = 1$ , $m_I = +1, 0, -1$

A

A

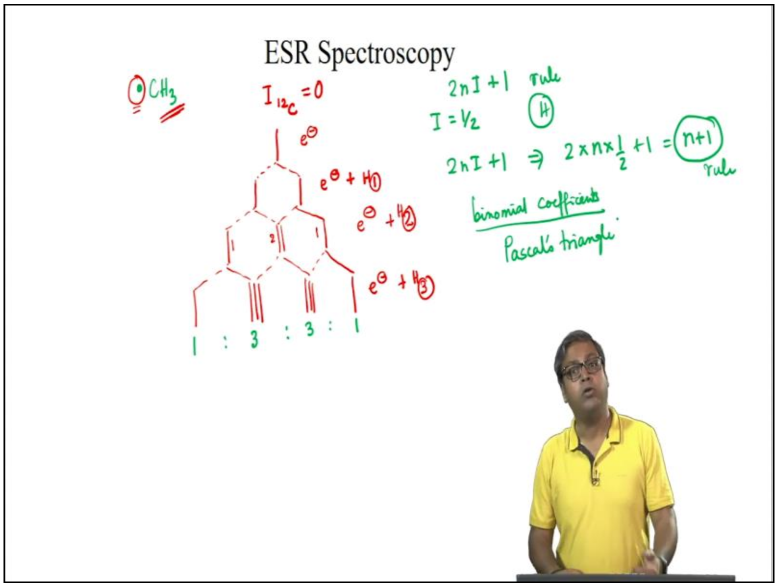
$m_I = +1 \quad 0 \quad -1$

So, let us look into the tree diagram. So, we have already discussed the tree diagram when we are talking about NMR spectroscopy. So, we can think that the line due to the ESR transition will split into two because there is interaction between this m s and m I and this m I can take values of +1/2 and m I can take a value of -1/2. So, that is the reason directly from the tree diagram we can see that we have two lines and these two lines have equal intensity.

So, these two lines one and two they have equal intensity so now instead of the hydrogen atom let us say if we had the D atom or dotronium so let us say we had D atom. So, let us look into the tree diagram now we know that the I value of D is 1 and because I is 1 then m I can take values that is +1, 0 and -1. So, now instead of splitting into two lines we will have three lines that is this line will split into three lines that is +1, 0 and -1 and these are the different values that m I can take.

And the spacing between any two consecutive line will be given by A and so now we can see that instead of hydrogen atom if we take D so instead of two lines we will get three lines. So, now let us look into another radical.

**(Refer Slide Time: 08:41)**



ESR Spectroscopy

$\dot{C}H_3$

$I_{^{12}C} = 0$

2nI + 1 rule

$I = 1/2$ (H)

$2nI + 1 \Rightarrow 2 \times n \times \frac{1}{2} + 1 = \boxed{n+1}$ rule

binomial coefficients

Pascal's triangle

So, let us look into something known as the methyl radical or the CH3 dot. So, in this case this unpaired electron will interact with 3 protons it will not interact with the carbon nucleus because the I value for the 12 carbon is 0 and because I is 0 then there is no interaction possible between this free electron and the carbon nucleus however let me tell you here that if instead of 12 carbon if we had 13 carbon where I is not equal to 0 then we need to consider also the interaction of this free electron with or the unpaired electron with the carbon nucleus.

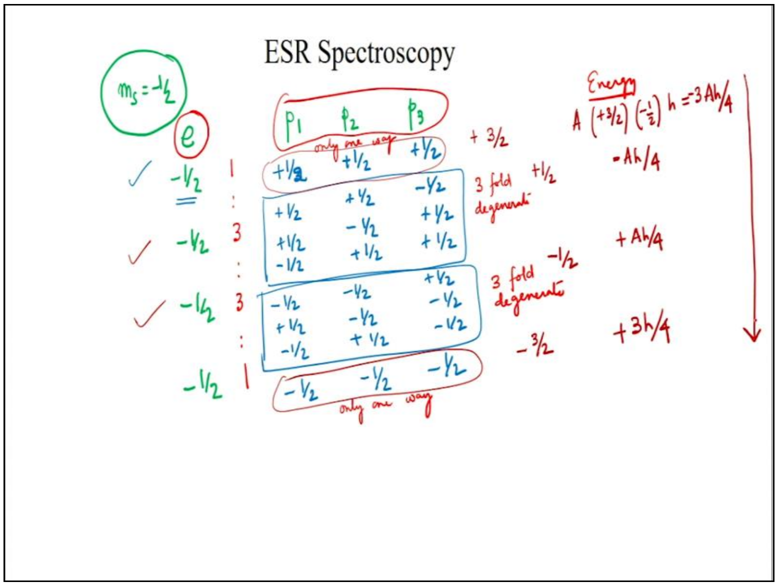
So, now let us consider first the tree diagram so we will consider only the interaction of these unpaired electrons with the three protons because we have 12 C. So, let us say this is my electron so this will split so this is my electron +H1 and this will further split because now I am considering the interaction with electron plus the second hydrogen atom. So, this is ratio of 1 is to 2 is to 1 however there are 3 protons so we are talking about 3 interactions so we have electron plus the hydrogen that is the third hydrogen.

So this will further split so we will have 3 here we will have 3 here so what we finally have is a ratio of 1 is to 3 is to 3 is to 1. So, these 1 and 3 are the binomial coefficients. So, we can see from the tree diagram that if we have a methyl radical we will have 4 ESR lines and their intensities will be in the ratio of 1 is to 3 is to 3 is to 1 and all these observations are consistent with the 2 n I +1 rule.

So here I equals 1/2 for a proton and because I equals 1/2 we can write 2 n I +1 that means 2 times n times 1/2 +1 that means for this case as you have seen before we have the n +1 rule. So, we can say it will obey the n +1 rule for the number of lines and because we have 3 protons 3 +1 equals 4. So, these observations are consistent with the n +1 rule and the intensity ratios is consistent with the binomial coefficients.

So we will write the binomial coefficients which we can obtain from the Pascal's triangle so these binomial coefficients will dictate the intensity ratio. On the other hand we can also understand these coefficients in a different way.

**(Refer Slide Time: 13:07)**



ESR Spectroscopy

So, now let us look into this different way so we can think that all the protons in the methyl radical they are equivalent that means as this protons are equivalent the value of A that is the hyperfine coupling constant will be the same for all the protons and thus we just consider the interaction of let us say m s equals -1/2 let us take this example m s equals -1/2 with all the three protons. So, let us put the electron here and so the value of m s is -1/2 you will understand why I wrote this 4, –1/2’s.

And now let us put the protons let us put proton 1 then proton 2 and then proton three 3. So, these protons the m I values can be either +1/2 or -1/2. So, we can have one combination where both are all three in not both but all three are +1/2. So, if we have all three +1/2 there is only one way we can have this that is plus, plus and plus. On the other hand let us say if we have 2 +1/2's and one -1/2 then we can write this as +1/2, +1/2, -1/2 but we can combine this these protons which are indistinguishable and in a different way we can write +1/2, -1/2, +1/2 or we can also write -1/2, +1/2, +1/2.

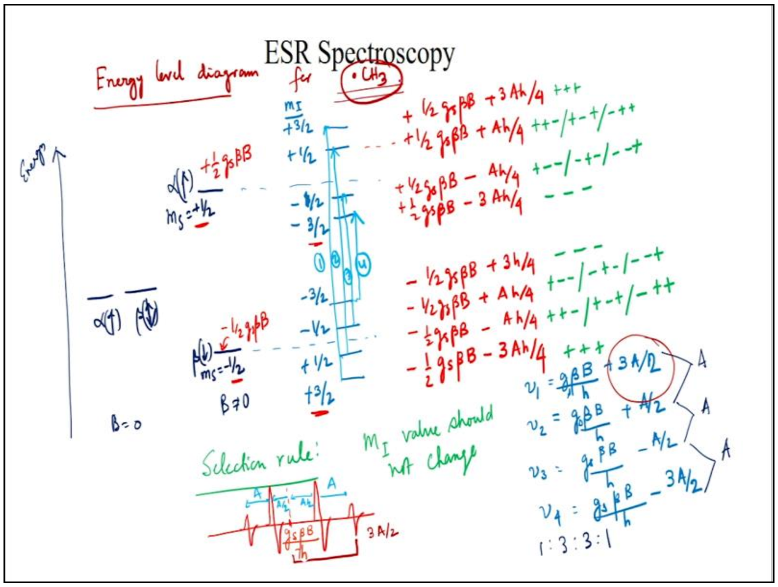
So you can see we can write the plus-plus combination in three different ways in other words we can write this is 3/4 D generate. Now let us consider the other that is minus minus plus so we can write this as -1/2, -1/2, +1/2 or +1/2, -1/2, -1/2 or we can write -1/2, +1/2, -1/2 so you can see these three cases are indistinguishable and again this is a case where this is three fold degenerate. And the 4th case is when we have all three m I values are minus. So, you have -1/2, -1/2 and -1/2 but again like three pluses, three minuses can be written in only one way or there is only one possibility to write this minus, minus and minus.

So, we can see that there are 4 different ways it can interact and all these 4 different ways are not equivalent. In one case we have one way to write this actually in two ways we have that and in two other ways there are three fold degenerate. So, we can think the ratio is 1 is to 3 is to 3 is to 1 because we are considering the interaction of this electron spin with the protons. So, now we know that we can look into a different way to find this 1 is to 3 is to 3 is to 1.

Now let us look into the energy so the question is how can we get the energy. So, now let us look how can we get the energy. So, in the first case here the energy is -1/2 and for these three protons all we need to do is we need to sum this up. So, if I sum this up what I get is +3 by 2 so the energy is A times +3 by 2 times -1/2 times h so this is 3 A h by 4. Now if I sum up the second case then we have two pluses and one minus.

So this is +1/2 so it will be A h by 4 so there is a minus sign here there is a minus sign here but in this particular case the third case we have minus, minus, plus so this means we have the total is -1/2 that means the energy will be +A h by 4 and in this last case is minus, minus, minus so the sum is -3 by 2 so the energy will be +3 h by 4 and you can see the energy is increasing from top to bottom.

**(Refer Slide Time: 19:37)**



So, now let us look into the energy level diagram that we have already drawn for the hydrogen atom but now we will look into the energy level diagram for the methyl radical. So, the first part we know that we have this energy axis that is my vertical axis and when P equals 0 there are two states alpha and beta which are degenerate. But when we not equal to 0 then we have interaction with the magnetic field and due to this interaction the degeneracy is lifted and now we have better so beta is down-spin.

So beta will be of lower energy alpha will be of higher energy so alpha means m s equals +1/2 and here m s equals -1/2. So, now if we want to consider all the three interactions at one go and final and that way obtain the final splitting we can write this as there are 4 energy levels. So, two are up and tore down similarly we will have 4 energy levels here two are up and two are down. So, the values of m I if I write it this will be +3 by 2, +1/2, -1/2, -3 by 2.

And in this case it will be -3 by 2, -1/2, +1/2 and +3 by 2. So, now let us put the energies together so this is -1/2 gs beta B for this state and this is +1/2 gs beta B. And so now when we have this 8 different states if I put down energies we have -1/2 gs beta B and then we have – 1/2 times +3 by 2 that that is -3 A h by 4 then -1/2 gs beta B -A h by 4 then we can write -1/2 g s beta B +A h by 4 and this is -1/2 g s beta B +3 h by 4.

And for this alpha state interaction you can write this is +1/2 g s beta B and then we have plus times minus so this is -3aA h by 4 this is +1/2 gs beta B then -A h by 4 for this case we have +1/2 gs beta B +A h by 4 and here we have +1/2 g s beta B +3 A h by 4. And now because we have already seen it we can write this as +++ this is ++- which can be written as +-+ or -++ nd this is +-- which can be written as -+- or --+ and here is ---.

Similarly this is --- this is +++ and then we have +-- so we can write is -+- --+ and this is ++- so this is +-+ -++ so we can see now you have this 8 different levels. Now we think about the selection rule and the selection rule says the m I value should not change and because they m I value should not change let us draw the possible transitions. So, one is +3 by 2, 2 +3 by 2, one is +1/2 one is - 1/2 other is -3 /2 to -3/2. So, we have 4 transitions, so we can write this as 1, 2, 3 and 4 because we have 4 transitions and we see that the starting point we have either it is single fold degenerate that means there is only one possibility or there is 3 fold degeneracy.

So this 4 transitions we can see should be and if you look into the energy difference we can see that 1 and 4 the intensity should be 1 and for 2 and 3 the intensity should be 3. So, we have 1 is to 3 is to 3 is to 1 so now we have 4 lines. So, now let us look into the frequencies of these 4 lines so we can write that nu 1 is g beta B +3 A by 2, so this is g beta B by h. Similarly nu 2 is g beta so this is g s beta B by h +A by 2.

Then we have nu 3 which is g s beta B by h -A by 2 and nu for that is gs beta B by h -3 divided by 2. So, now if we take any two consecutive line let us say these two lines then the gap between the energies of these two lines is A, here again this is A and here again this is A and we can see the ratio is 1 is to 3 is to 3 is to 1. So, now if you really want to plot it like we did it for the hydrogen atom here this is let us say g s beta B divided by h so this is the middle point.

So, we will have 4 peaks so one peak here one peak here then one peak here and one peak here. So, if you look into the distances this is A by 2 this is A by 2 this is A this is A in other words if we take from the midpoint to one of those extreme peaks this is 3A by 2 and that is what we get here. So, we have extensively looked into the energy level diagram and to try to understand the ESR spectrum of the CH3 radical.

So this brings us to the end of this lecture. So, in the next lecture we would discuss what information we can obtain from this ESR spectrum.