Principles and Applications of Electron Paramagnetic Resonance Spectroscopy
Prof. Ranjan Das
Department of Chemical Sciences
Tata Institute of Fundamental Research, Mumbai

Lecture - 16
How to Analyse First-order EPR Spectra

Hello. Today we are going to learn How to Analyze the First-order EPR Spectra of free radicals. We have seen the first-order EPR spectra come from a Hamiltonian of this kind.

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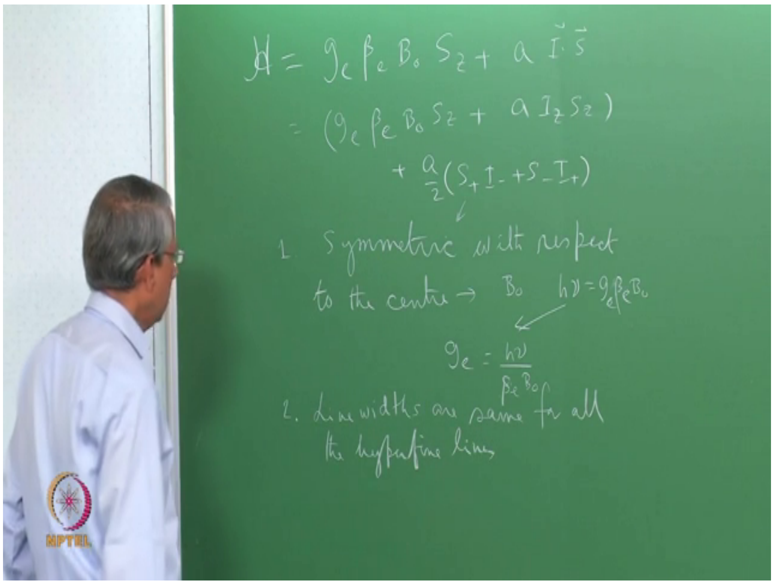

$$\mathcal{H} = g_e \beta_e B_0 S_z + a\,\vec{I}\cdot\vec{S}$$
$$= (g_e \beta_e B_0 S_z + a I_z S_z) + \frac{a}{2}(S_+ I_- + S_- I_+)$$

1. Symmetric with respect to the centre → B_0 $\quad h\nu = g_e \beta_e B_0$

$$g_e = \frac{h\nu}{\beta_e B_0}$$

2. Line widths are same for all the hyperfine lines

Which we have seen for (Refer Time: 00:42) example, this is the electron Zeeman term; this is the hyperfine interaction term and this could be written as plus I z S z plus see here up to first-order calculation this term does not contribute to any energy. So, characteristics of the first-order spectra are that they are symmetric respect to the center and center corresponds to the; if we call a B 0 then g value is given by h nu equal to g e beta I B 0. So, I can get immediately g of electron is h nu by beta e B 0 and the line width are same for all the hyperfine lines.

These are the conditions which are satisfied by the first-order spectra. Now this is true for only one hyperfine nucleus suppose they are more than one, and then this can be easily generalized to write the sum of all the possible.

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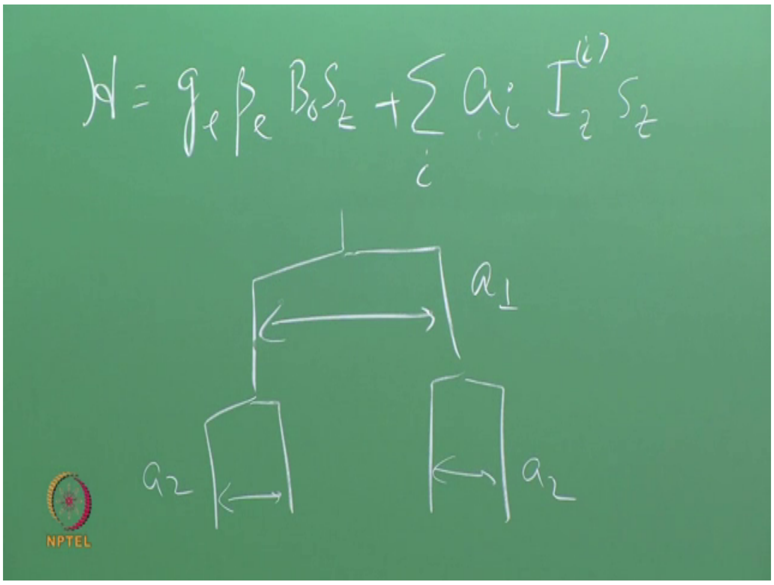

$$\mathcal{H} = g_e \beta_e B_0 S_z + \sum_i a_i I_z^{(i)} S_z$$

Nuclei which are giving rise to the hyperfine splitting plus. So, I have this is the first spectra; spectra comes from this hyperfine splitting constant a. So, if I get various types of nuclei; let us put at I here instead of I here and sum over I. So, I could be the nuclei which are giving rise to splitting.

So, for example, the splitting I have shown many times that this could be split in this fashion and this could be the let us a 1 which is the bigger splitting and have only one spin half nucleus. So, this is split in 2 take for another one; a 2 which is also a 2; this is another spin of nucleus which also causing spitting that way we can analyze the spectrum. So, the analysis involves going the other way round that is start with the given sort pattern of various hyperfine line and try to find out the nuclei which are giving rise to the particular pattern and what do the corresponding coupling constants are. And if we know the frequency of microwave which was used to record the spectrum and a very precise measurement of the of the magnetic field for the center of the spectrum you can measure the g value.

So, we will take some examples now and learn how to analyze such spectra.

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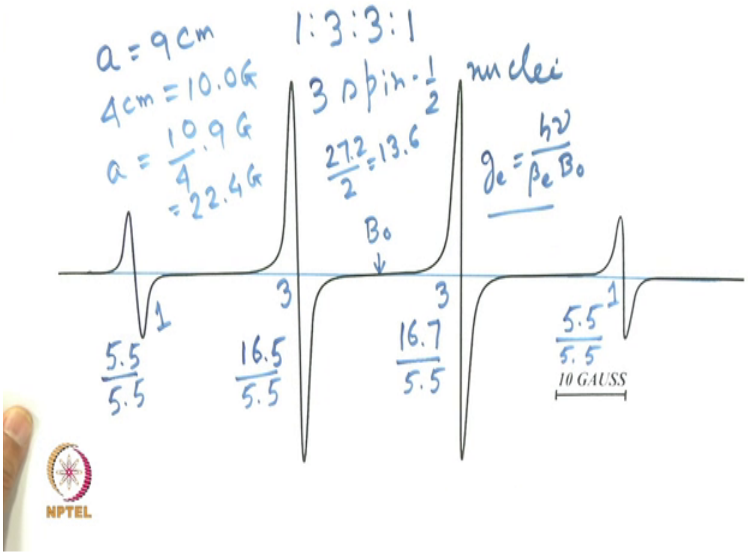

This is a spectrum of a free radical this gives 4 line spectrum to understand what set of radical could give rise to this sort of pattern; let us first find out the hyperfine splitting constant of this now if all the 4 lines are coming from the same equivalent nuclei then the gap must be same. So, let us measure that first, but for measuring that I need to find out where this signals are crossing 0. So, first I draw a line through this 0 signal; this one draw a line here and then make the measurement I have already done that in another copy of the spectrum here it is.

So, this is the line that I have drawn through the 0 signal. So, find out the coupling constant. Now let us measure the gap from this outer most line to the next hyperfine line and further I use this divider; this is the gap between the 2 adjacent lines. Now let us see the same gap is present here also yes this is same as that this is also same as that. So, this gap is same for all the hyperfine lines. That means, the same group of equivalent nuclei are giving rise to these 4 lines. So, what is the coupling constant that is nothing, but this gap now what is the measure of that let us measure this in the scale this is nine centimeter.

So, the coupling constant is nine centimeter and here is the scale of the magnetic field. So, here this length is the 10 Gauss. So, what is the length here 4 centimeter. So, 4 centimeter corresponds to 10 Gauss. So, now, you can easily find out the coupling constant a. So, a corresponds to 10 by 4 into nine Gauss which is 22.4 Gauss. So, we have got the coupling constant determined from these 4 lines.

Next question is what set of nuclei can give rise to this set of relative intensities for that let us measure the intensities of all the 4 lines for the outer most line the height is 5.5 centimeter, I write it here. Next height is similarly for this to this 16.5 centimeter, then the next intensity is may be 16.7 centimeter the last one is again 5.5 centimeter.

So, to normalize all the intensity with intensities with respect to the outer most line, we divide these number by this 5.5 that gives the relative intensities to be let us say this is one 3 this is very nearly equal to 3; this is one. So, we have got the 4 lines with this set of relative intensity 1 3 3 1. Now these can come of course, from a 3 equivalent nuclei with spin half. So, we have got 3 spin half nuclei that is present in the radical without knowing the chemical nature of the radical, it is very difficult to say what precise the radical is, but we can confidently say that radical contents this set of nuclei which are giving rise to this set of hyperfine pattern what is the g value for this spectrum for that I need to find out the center of the spectrum center of the spectrum will be somewhere here; how to find it out again we use the ruler total distance from the middle of this to middle of this is 27.2 centimeter.

So, half of that will be 27.2 divided by 2 this gives 13.6. So, let us find this point here 13.6 corresponds to this place. So, this is my B 0 the center of the magnetic field. So, if I knew the magnetic field axis, I can measure the magnetic field value for this position of the spectrum. And if I know the frequency of the microwave which was used to record the spectrum the g value can be written as g of electron will be h nu by beta I B 0 that is it.

So, we get all the information about the spectrum of course, this is a rather simple spectrum and one may not need all this detailed measurement one can actually see that it is essentially it is 1 is to 3 is to 3 is to 1, but life is not often as simple as this. So, we will take the next example.

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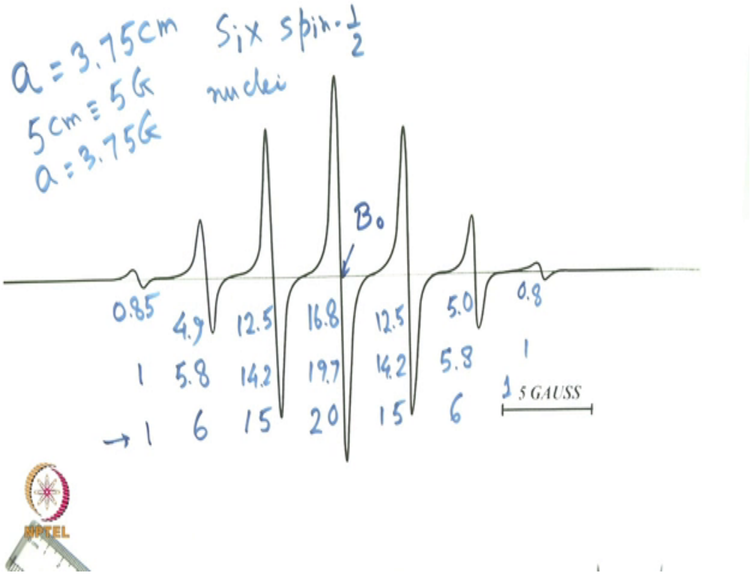

Here, there are 1, 2, 3, 4, 5, 6, 7 lines and let us first measure if the gap is same among them using the divider if the gap between the outer most line and the next line is this and then this gap is same as this one. Let us do it once more yes this is same as that this is same as this; this is same as this; this is same as this and this is same as this ; that means, again all the lines are coming from a group of nuclei which are all equivalent. Similarly, we can measure the coupling constant from this; this is the measure of the coupling constant; what is value this coupling constant is given by this gap which is 3.75 centimeter.

So, here a is equal to 3.75 centimeter what is the scale this or the magnetic field which is given here this 5 Gauss corresponds to this length and that is 5 centimeter. So, 5 Gauss corresponds 5 centimeter. So, naturally this says that coupling constants a is equal to 3.75 Gauss. So, we measure the hyperfine coupling constant the what are the nuclei which are given as this splitting for that we measure the height here this is point eight 5 next one is or nearly 4.9; I do it more carefully 9 to 8 here. And next one is 12.5, then this is 16.8. Now this being a symmetric this also will result to 12.550 and hence here again nearly 0.8.

So, this set of small deviations expected in an experimental spectrum one does not expect to be them to be exactly following the relative values that we expect theoretically. So, small deviations are possible. So, divide all the numbers by its average of this and this and if you do that this values will turn out to be we divide values 8.5; this will be 15.8; 14.2, 19.7; this is 14.2, 5.8 and again nearly 1; ok.

So, now these numbers when I round it. So, that we can get a the values that a Pascal triangle can give either spin half or spin of other nuclei its very obviously that the number that corresponds to which matches very nearly to Pascal triangle corresponding to spin half nuclei is 1, 6, 15, 20, 15, 6 and 1. So, this is nothing, but 6 spin half nuclei can give rise to such relative intensities, we have got 6 spin half nuclei present here in this radical.

So, that is the way you can explain this pattern. Now for this, what is a g value? G value will be again the center of the spectrum. Now, because there are odd numbers of lines the center of the spectrum is precisely here. So, this is my B 0 from this I can calculate the g value if I know the frequency of the microwave and the actual value of the magnetic field here.

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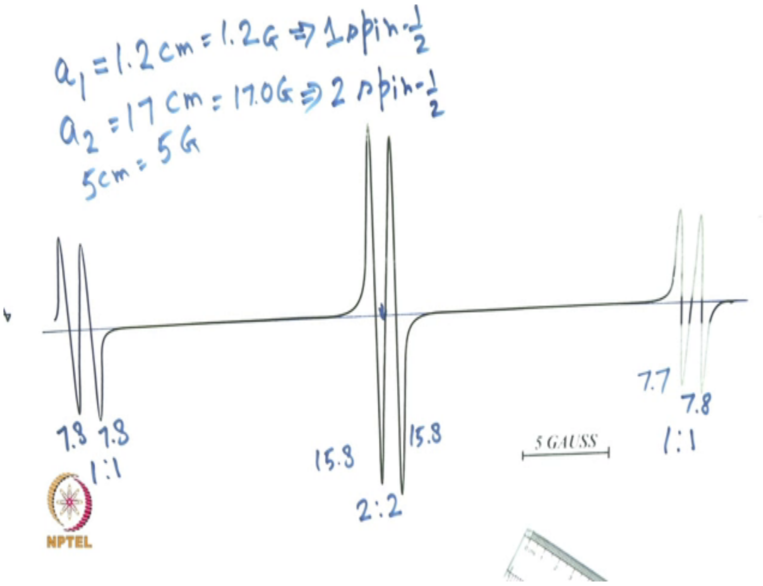

Let us take a little more complicated spectrum now here again we start from the outer most line which is here then measure the gap between that and the adjacent line and this is the gap. Now from you see next line does not fall in line that is between there is no other line adjacent with that; that means, that this line and this line belong to different type of nuclei.

So, the gap between these 2 actually happens to be same as this and same as this. So, that gives the one hyperbolic coupling constant let us call it a 1 whose value is 1.2 centimeter. So, next coupling constant will be between less one of this line to the corresponding line from the other group this too big I cannot measure here. So, we will use the ruler this gives me 0, this is 17 centimeter, see if this is the 17 centimeter, I should expect that between these and the next line should also be 17 centimeter. So, that is exactly what is seen here. So, the between these and that the gap is same as between these and that and that is also the same as between these and these and these and these.

So, 17 centimeter corresponds to another hyperfine coupling constant let us call it a of 2 is 17 centimeter. So, we have got 2 types of nuclei now what do the corresponding coupling constant in have in magnetic field unit this is the scale given here 5 Gauss again 5 Gauss is equal to 5 centimeter. So, 5 centimeter will 5 Gauss. So, this gives therefore, this is correspond to 1.2 Gauss and this corresponds to 17.0 Gauss these are the 2 hyperfine coupling constant.

Now, for this what will be the g value again you have to find the center of the spectrum for that center will be somewhere here it does not fall on any of the hyperfine line. So, we measure the center of the spectrum by measuring the total extent from this to this and then we shall we can measure the center and that will be for here somewhere and you can find out the corresponding g value; how would the relative intensities. So, that we can ascribe this split into certain nuclei now for that this height is found to be the 17.8 centimeter, this is also 17.8, this is 15.8, this is also 15.8, this looks very similar, this is 17.7, this is also somewhere 17.8 or so.

So, we divide by this number the ratio I get is 1 is to 1 here, I get 2 is to 2 here, I can get 1 is to 1. So, from this relative intensity it is very clear that this is a doublet, doublet and doublet that give comes from a 1 spin half nucleus. So, this corresponds to one spin of nucleus and this comes from this relative intensity of 1 is to 2 is to one triplets this comes from 2 spin of nuclei present there.

So, the radical has this set of nuclei again without knowing the chemistry of this formation of radicals it is very difficult to say what precisely the radical is all we can say that the radical has one spin half nucleus and 2 spin 1 nuclei and those 2 nuclei are equivalent.

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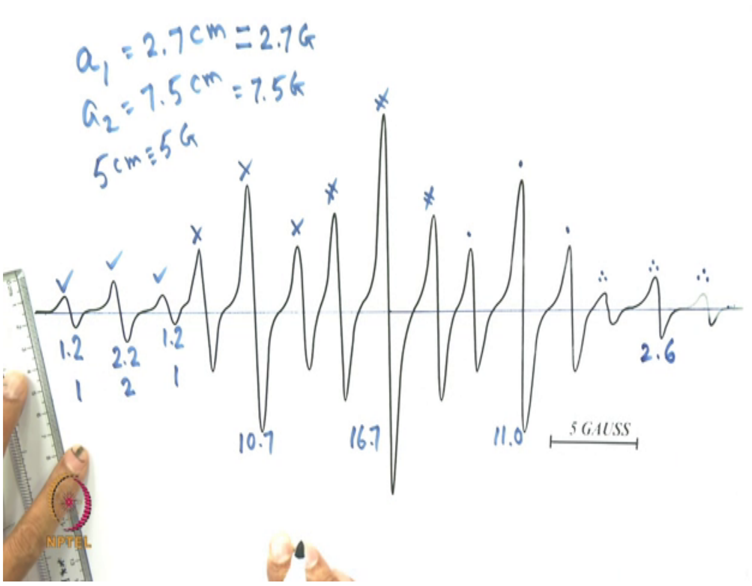

Now, you to a little more complicated spectrum here now things are reasonably routine the so many lines are there. So, we start again from the outer most line and see how many lines belong to one group of equivalent nuclei. So, this is the first gap between the outer most line and the next one.

So, between this gap is same as this gap, but then after that there is no line here this does not fall below in line with this. That means these lines belong to one hyperfine coupling constant this does not belong there. That means this is the beginning of another hyperfine coupling constant. So, if we start from this you see that this gap is actually same as this gap same as this gap and then nothing else is there.

So, this again belong to therefore, same hyperfine coupling constant. So, after that this line is not accountant for. So, again you start from here and is measure the same gap with as earlier. So, these and these again nothing else is there. So, these 3 again belongs to yes give some other symbol here; similarly, it is very obvious that they also belong to this pattern and this belongs to let us say this pattern.

So, I have got this group; this splitting is same for all of them. So, one hyperfine coupling constant therefore, correspond to this gap which is say 2.7 centimeter and next coupling constant will be the distance between this one line of this group to the corresponding line of the next group that is from this to this from that gap is here 7.5 centimeter, we can confirm that by checking that this should be consistently followed by all the lines. So, this is the gap here now between these and then here, yes, it has it matches with that this matches with this; this will also matches or if take the center of this group of line there between this and this, this, this and this.

So, this group they all belong to another coupling constant whose measure is 7.5 centimeter. Now, from the scale again here 5 centimeter is equal to 5 Gauss. So, this gives then this corresponds to 2.7 Gauss this corresponds to 7.5 Gauss here is this splitting constant how would the relative intensities. So, for this we measure this height because we measure actually vertically. So, this is nearly 1.2 centimeter and this is corresponding to 2.2 centimeter; this again corresponds to 1.2 see you see here these are approximately following this part of 1; this to 2 is to 1.

Similarly, this also is 1 is to 2 is to 1; we can quickly check that by without measuring let us say this is the height here. So, between this and this is 2 and this one. So, it 1 is to 2 is to 1; how about the next one again you measure this; this is the height. So, you can here. So, 1 is to 2 is to 1 and same pattern continues: so triplet, triplet, triplet, triplet, triplet. So, what is the relative intensity among these triplets now? So, this for that I measure this compare this height. With let us say this height. So, that height is 10.7.

Similarly, center of this triplet corresponds to 16.7, here 11 this is again. So, here is 2.6 just check here this; what I made a mistake here this is indeed 2.6 here 2.6 here.

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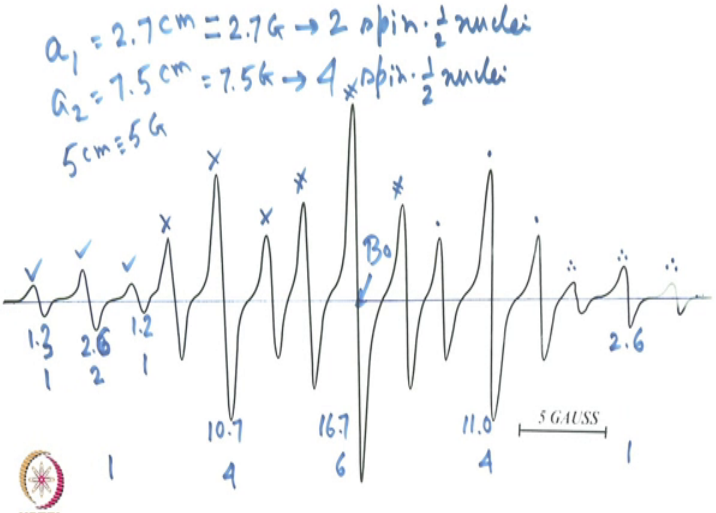

So, this will be also one point more like 4 or so, or from the 3 or so 3 also 3 5. So, any way one is to 2 is to 1 is fine. Now here between this, this, this, this and this the relative intensities turn out to be we divide by 2.6 all over then this becomes 1 4 6 4 1. So, again this pattern is familiar this comes from Pascal triangle of 4 equivalence spin of nuclei.

So, what we I have here that this corresponds to 4 spin half nuclei and this corresponds to 2 spin half nuclei. So, we have figured out all the hyperfine coupling constant that is present here again what will be the g value there will be center of the spectrum for these one; there are odd number of lines. So, this is the center of the spectrum. So, this is your B 0 which can give the g value.

Now, the this is all very well if the spectral very well reserved in all lines are seen with descent signal noise ratio, but practical difficulties are quite common; for example, if there are many hyperfine lines. Usually, the outer most lines intensity becomes very very small often difficult to detect them in their spectrometer then what does one do you see the analysis always there this whether you start from the outer most line. And then keep on finding out the pattern if I do not see the outer most line what does one do. So, there is here is an example which sort of exemplifies that.

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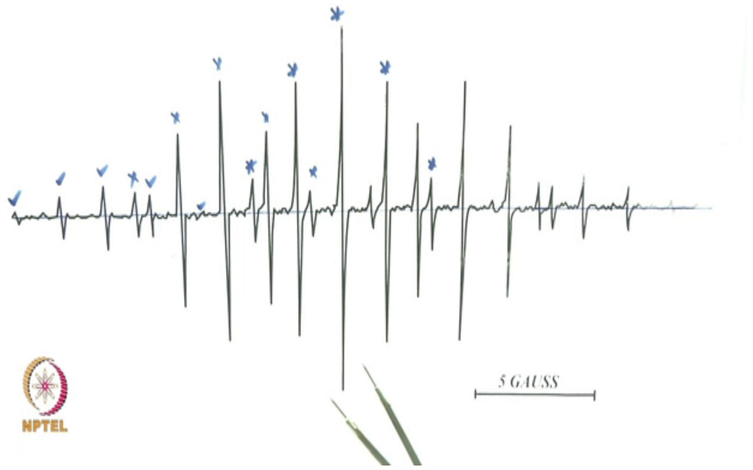

So, here one does not know if these are real line or not it whether so many such lines are lying here difficult to pin point if there is a transition so. In fact, there is a line here I am saying because I know the answer, but if I do not know the answer how does one go about this and analyzing this.

So, if this is the let us say outer most line that I take it to be true. So, using the our prescription that we first measure the gap and then see the next line which is here and then after that there is no more line. So, these 3 line corresponds to one group of hyperfine line this, this and this, this one does not belong to that; so, it possible that this may be a triplet, but we will check the later from the intensities. So, we now start from the next one which is not part of the previous group; so, this is the line here. So, see this is the gap or the hyperfine coupling constant. So, we start from here we measure the same. So, you see this of course, matching with this; so, this and this and this, this and this.

So, now we have got 5 lines; now we earlier for this group has 3 lines. So, let us mark them as this, this, this, this and this just let us check once again this, this, this and they are same. So, I got 5 groups of line. So, something probably is wrong here that is something is missing here to be absolute sure that something is missing let us look at the next group of lines which are not part of this hyperfine line. So, that is here.

So, we start from this again find out the lines which are the same coupling constant at these or these that is starting from here this one here these; these and these again you see there are 5 lines . So, let us put some sort of this set of sign here. So, see this pattern is present here it is natural that there must be line for these 3 groups of 3 lines also it cannot be just 3 there will be 5 lines. So, I start from here go back and see that looks like there is a line which is hidden here. Similarly that could be line here even if I do not see it I how to assume that it is indeed there, but buried in the noise level. So, I have a line here and here similarly other side also that there could be a line which is here, here and somewhere and not same there.

So, that way one goes about and analyzing the spectrum and even if we do not see the outermost line one has to make intelligent guess and find out where those little lines which are buried inside the noise level are hidden and then from this pattern one can completely analyze the spectrum and get all the possible hyperfine coupling constant, we have just now seen how to analyze first-order EPR spectra which are recorded on this paper and use this 2 important tools one is this my divider and other one is this ruler this may sound old fashion because nowadays almost all EPR spectrometers are interface with computers and one really gets specter printed on paper, but they are available in electronic form and one can allies on the computer.

So, we are going to quickly have a look how one goes about using computer programs to analyze the spectra , but the principle that we have learnt using this technique of measuring this; this height and the gap here there remains the same. So, it is the same principles which are used in the computer which only helps us presumably do it somewhat faster, but not necessarily easier. So, you have to still measure the coupling constant a to measure the height. And then find out the number of nuclear which are present there everything remains the same also sometimes the lines of various adjacent hyperfine components may be overlapping. So, it may become difficult to measure using this ruler and divider. So, then the computer program may be able to help us do a somewhat more accurate job.

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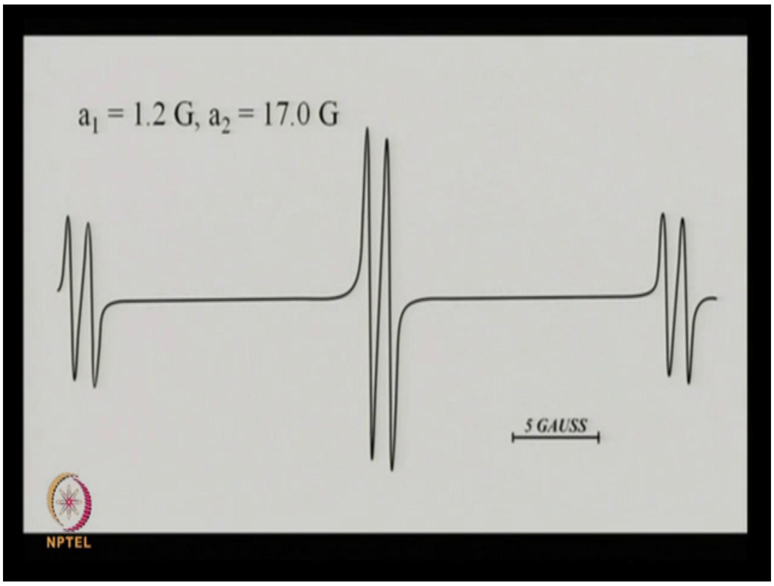

Let us see how that is done; we have seen this spectrum earlier it has got 2 coupling constant a 1 1.2 Gauss and a 2 17.0 Gauss, we measured these values using our ruler and divider technique if you see very carefully the height of these is not matching with this height here this is slightly lower than this one. On the other hand bottom of the; this is slightly lower than this one same is true for all the lines it means that there is a partial overlap of the intensity coming from this line with the line here same is true here also the part of the signal correspond to this hyperfine line is overlapping with the signal from this hyperfine line that is why this sort of unequal heights are appearing here.

So, there could be more problems of overlap and then our ruler and divider technique may not be giving very accurate estimate of the coupling constant for that we need to go to a computer program and try to analyze the spectrum using the program.

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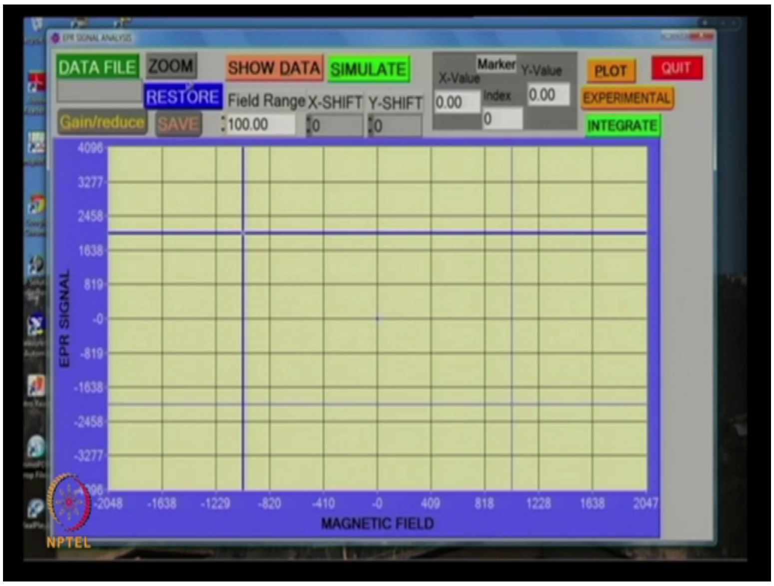

Field Range 100.00
X-SHIFT 0
Y-SHIFT 0
X-Value 0.00
Y-Value 0.00
Index 0

Now, here is a computer program which will help us analyze the spectrum most commercial EPR spectrometer vendors provide their own software one can find similar software in the in internet also this particular one is made a in our own laboratory, but nevertheless by and large all this programs look very similar in their operation.

So, to show how this work one could initially calculate a spectrum by giving some known hyperfine coupling constant let us say a 1 coupling constant is 1.2 Gauss I can enter these values here.

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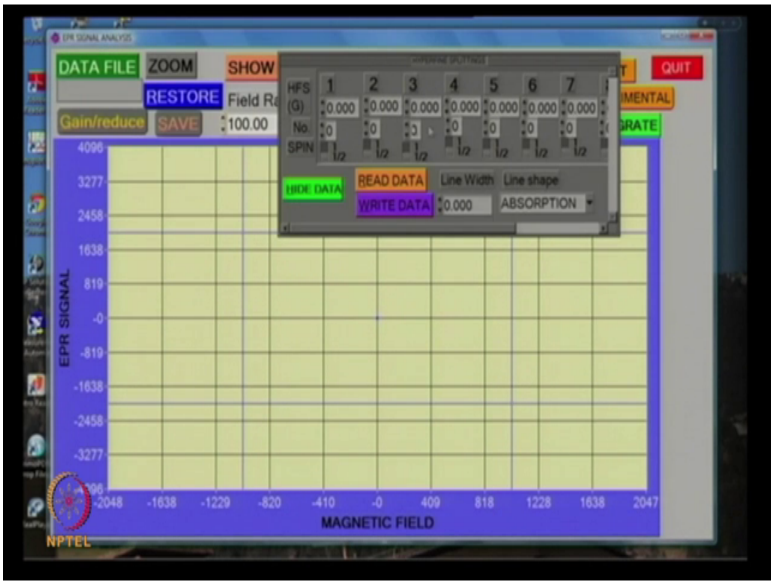

Here one can enter various coupling constants and their nuclear spin half of; this will be spin of one or half a number of such nuclei and their coupling constant.

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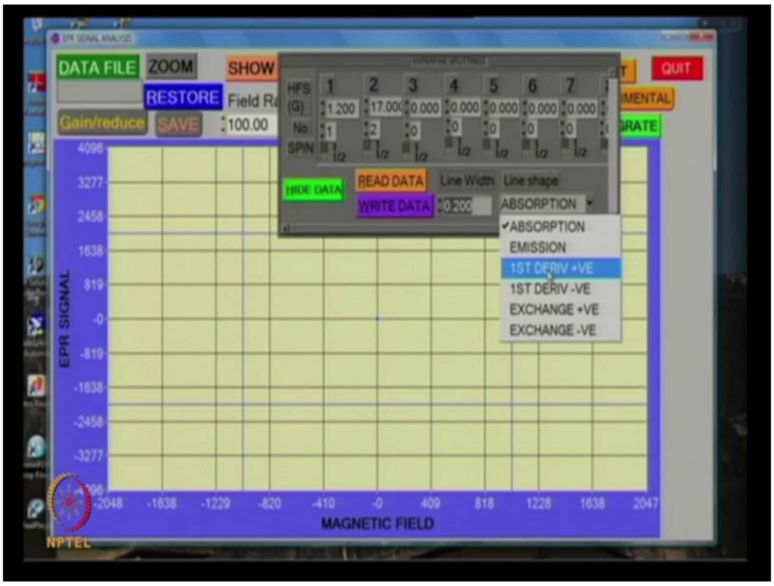

Let us give the value let us say 1.2 Gauss. And I have a splitting of nucleus of spin half and number of such nuclei is only 1. Another coupling constant is 17.0 Gauss and there are 2 of them and again spin half let us give some line width of 0.2 Gauss and the spectrums would like first derivative keep it here let us simulate the spectrum and the experimental range of the magnetic fields can let us keep it at 50 Gauss.

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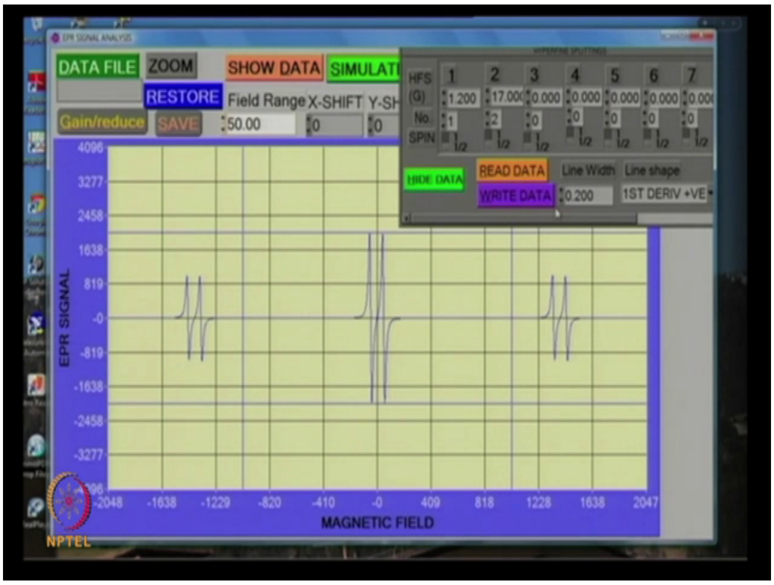

Field Range: 50.00
X-SHIFT: 0
Y-SH: 0

	1	2	3	4	5	6	7
HFS (G)	1.200	17.000	0.000	0.000	0.000	0.000	0.000
No.	1	2	0	0	0	0	0
SPIN	1/2	1/2	1/2	1/2	1/2	1/2	1/2

Line Width: 0.200
Line shape: 1ST DERIV +VE

Now, simulate it that is the way it looks like doublet, doublet, doublet and overall triplet is present here which is similar to what we saw earlier.

Now, we can see the effect of line width on the spectrum. See here I have used a line width of 0.2 Gauss let us increase it.

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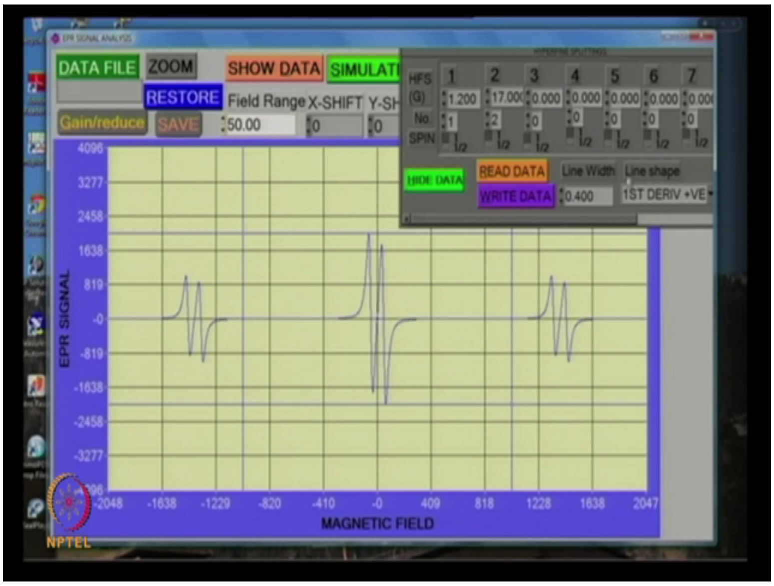

Field Range: 50.00
X-SHIFT: 0
Y-SH: 0

	1	2	3	4	5	6	7
HFS (G)	1.200	17.000	0.000	0.000	0.000	0.000	0.000
No.	1	2	0	0	0	0	0
SPIN	1/2	1/2	1/2	1/2	1/2	1/2	1/2

Line Width: 0.400
Line shape: 1ST DERIV +VE

So let us say 0.4 Gauss and again simulate this. So, see now these 2 heights are not same as here. So, that means, that when the line width has become bigger there is partial overlap of the 2 hyperfine lines.

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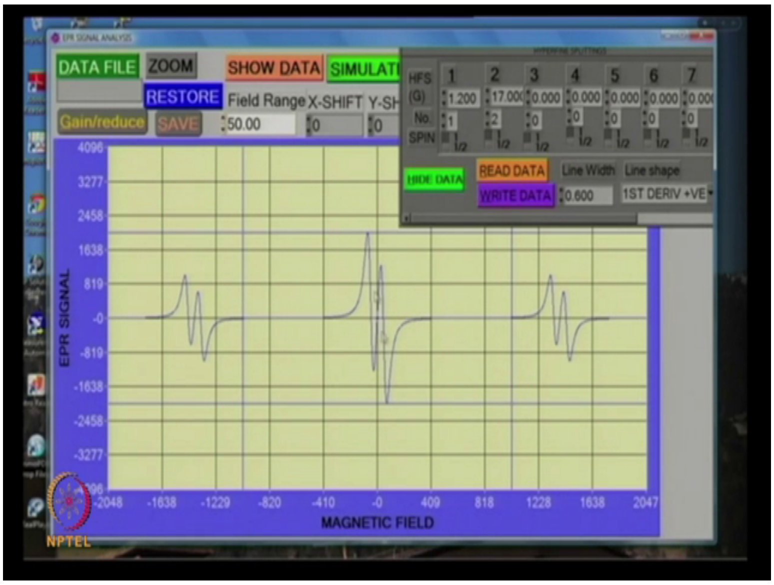

Field Range 50.00
X-SHIFT 0
Y-SH 0

	1	2	3	4	5	6	7
HFS (G)	1.200	17.000	0.000	0.000	0.000	0.000	0.000
No.	1	2	0	0	0	0	0
SPIN	1/2	1/2	1/2	1/2	1/2	1/2	1/2

Line Width 0.600
Line shape 1ST DERIV +VE

If increase further there is a 0.6 Gauss again simulate it say how it is becoming a unequal in their heights.

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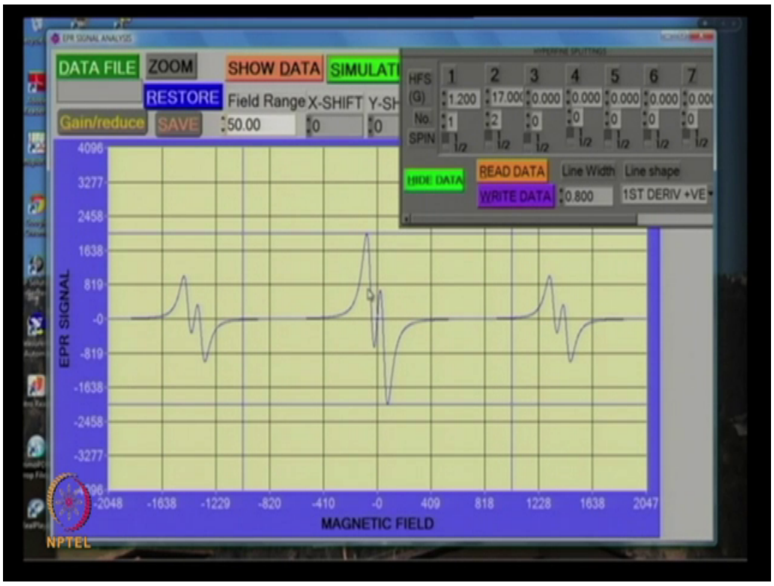

Field Range 50.00
X-SHIFT 0
Y-SH 0

	1	2	3	4	5	6	7
HFS (G)	1.200	17.000	0.000	0.000	0.000	0.000	0.000
No.	1	2	0	0	0	0	0
SPIN	1/2	1/2	1/2	1/2	1/2	1/2	1/2

Line Width 0.800
Line shape 1ST DERIV +VE

Further broadening simulate that is the way it comes out to be. So, things can be pretty complicated in the sense that ruler and divider technique may not give the values accurately if there are more than one nuclei giving similar splitting and in such broad lines then it may become almost impossible to make some measurement.

So, to see that how the line width effects the number of hyperfine lines and the appearance let us consider a case of only let us 4 spin half nuclei and the hyperfine coupling constant is less give a value of 2 Gauss to start with and width is kept very small let us simulate this one right and remove this nuclei.

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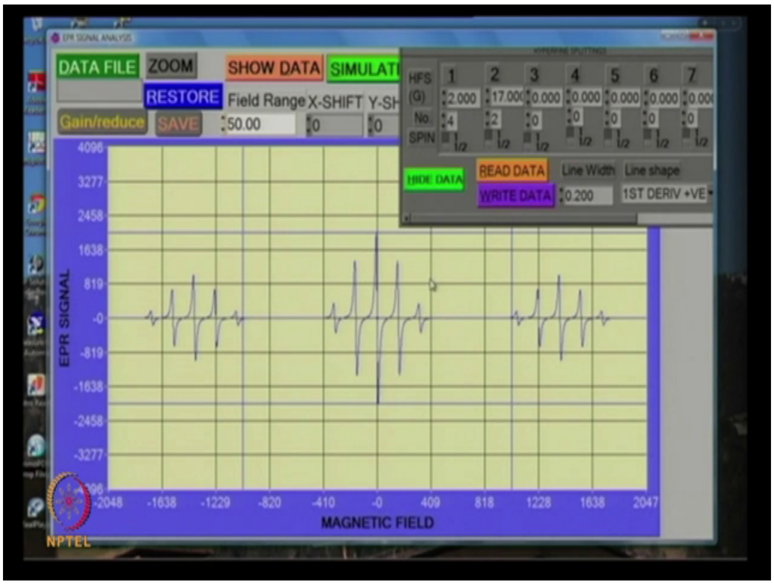


Field Range 50.00, X-SHIFT 0, Y-SH 0

HFS (G): 1: 2.000, 2: 17.000, 3: 0.000, 4: 0.000, 5: 0.000, 6: 0.000, 7: 0.000

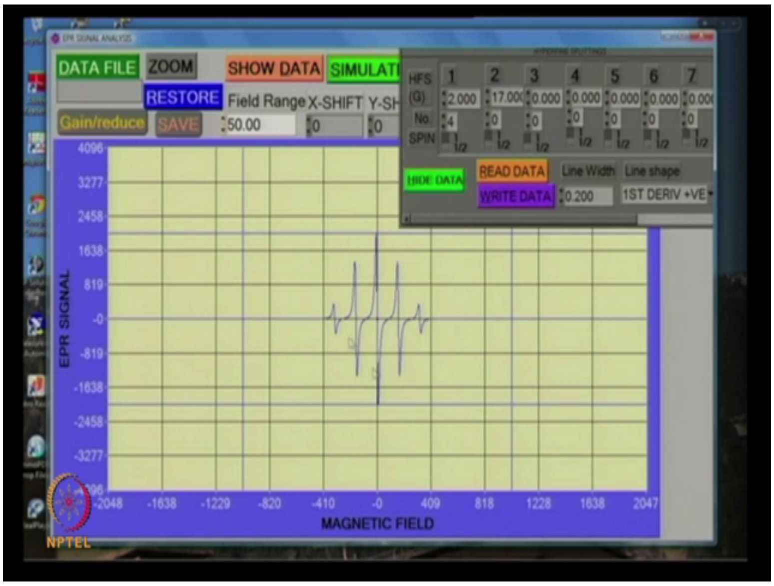
No.: 1: 4, 2: 2, 3: 0, 4: 0, 5: 0, 6: 0, 7: 0

SPIN: 1/2

Line Width 0.200, Line shape 1ST DERIV +VE

So, simulate this one.

(Refer Slide Time: 42:16)



Field Range 50.00, X-SHIFT 0, Y-SH 0

HFS (G): 1: 2.000, 2: 17.000, 3: 0.000, 4: 0.000, 5: 0.000, 6: 0.000, 7: 0.000

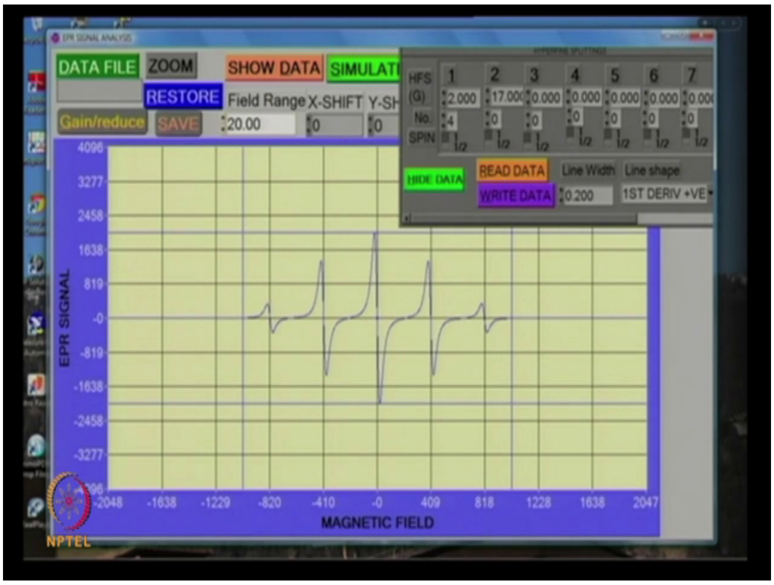
No.: 1: 4, 2: 0, 3: 0, 4: 0, 5: 0, 6: 0, 7: 0

SPIN: 1/2

Line Width 0.200, Line shape 1ST DERIV +VE

So, 5 line spectrum and they are following the usual 1 4 6 4 1 type of intensity ratios. Now, one could expand the spectrum by working at a small or scan range it is make it 20.

(Refer Slide Time: 42:32)



Field Range 20.00
X-SHIFT 0
Y-SH 0

HFS	1	2	3	4	5	6	7
(G)	2.000	17.00	0.000	0.000	0.000	0.000	0.00
No.	4	0	0	0	0	0	0
SPIN	1/2	1/2	1/2	1/2	1/2	1/2	1/2

Line Width 0.200
Line shape 1ST DERIV +VE

Total range becomes twenty Gauss let us simulate that is how it looks like. So, it looks so cleaner.

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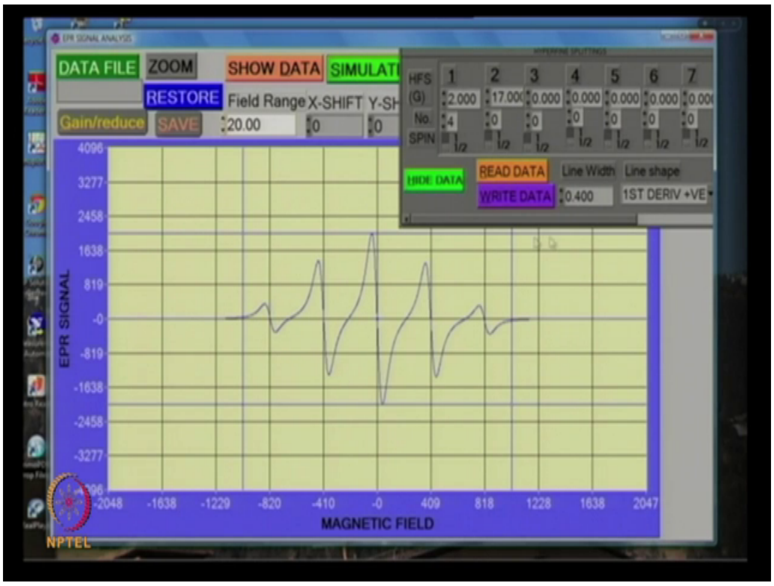

Field Range 20.00
X-SHIFT 0
Y-SH 0

HFS	1	2	3	4	5	6	7
(G)	2.000	17.00	0.000	0.000	0.000	0.000	0.00
No.	4	0	0	0	0	0	0
SPIN	1/2	1/2	1/2	1/2	1/2	1/2	1/2

Line Width 0.400
Line shape 1ST DERIV +VE

Now if I keep increasing the line width see how it changes 0.6 Gauss see already they start showing distortion.

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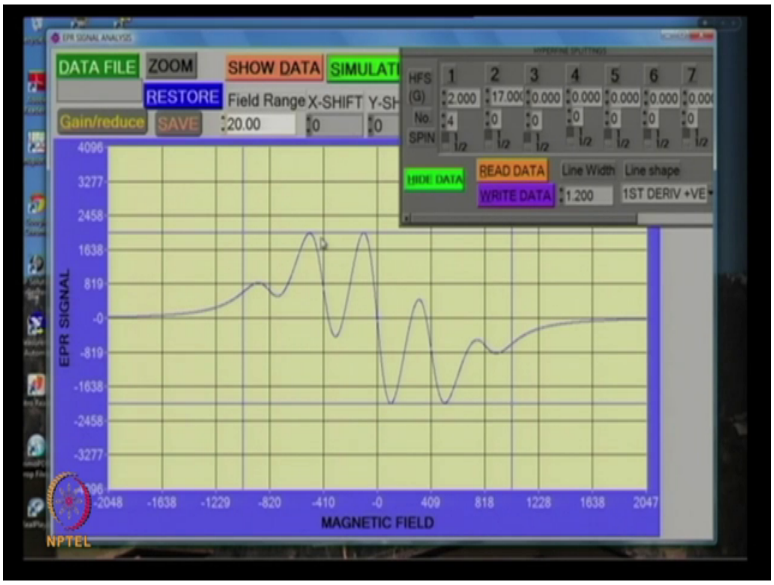

Field Range 20.00 X-SHIFT 0 Y-SH 0

HFS	1	2	3	4	5	6	7
(G)	2.000	17.00	0.000	0.000	0.000	0.000	0.00
No.	4	0	0	0	0	0	0
SPIN	1/2	1/2	1/2	1/2	1/2	1/2	1/2

Line Width 1.200 Line shape 1ST DERIV +VE

Is it not so; that means that here it will be very difficult to measure the line width and the coupling constant accurately.

So, we need to use the; this simulation program to compare with our experimental spectrum and get an accurate estimate of the hyperfine coupling constant and line width.

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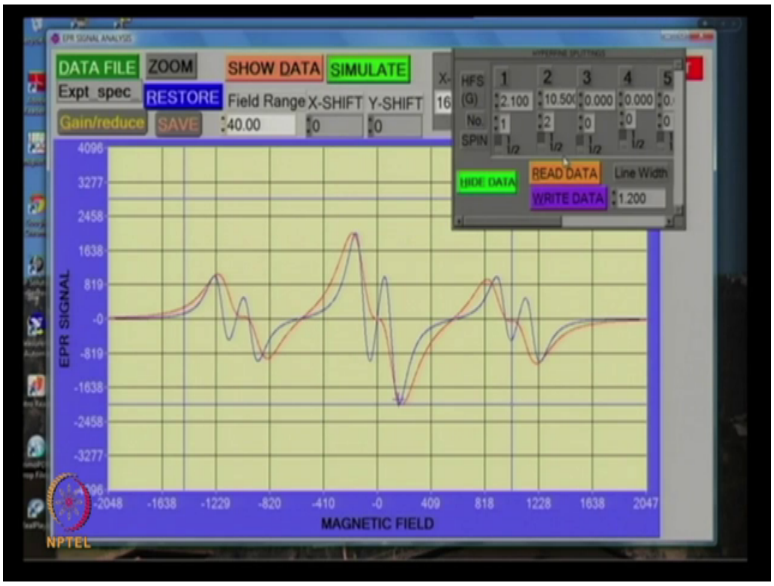

Expt_spec

Field Range 40.00 X-SHIFT 0 Y-SHIFT 0

HFS	1	2	3	4	5
(G)	2.100	10.50	0.000	0.000	0.
No.	1	2	0	0	0
SPIN	1/2	1/2	1/2	1/2	

Line Width 1.200

So, to do that we first load our experimental spectrum from which has been recorded earlier and this is here for this the total scan range was kept at 40 Gauss; let us say using this cursor I can place this anywhere we like and I can measure the height of this peak and the valley from there, this I can get the intensity and the distance from this to this in the horizontal axis will give me the separation using.

So, that way I can find out the approximate value of the hyperfine coupling constant and let us say from this I have got an approximate value of which are entered in the data. So, let us say one value is 2.1 Gauss and there is only one half nucleus of spin half and other is let us say 9.5 and there are 2 nuclei of this kind and this is derivative signal; let us start with the narrow line width. So, with this I can calculate the spectrum and that is the simulation one. So, this simulates this one of course, it does not look anywhere near the observed spectrum, but what we could do is that we can; obviously, change the line width and see how it approaches the experimental spectrum point 4 Gauss simulate again point 6 Gauss here increasing looking keep increasing line width increased one Gauss another 1.2 Gauss.

So, it is sort of sort of not quite similar, but trying to become now let us watch here that this rate graph is the rate race is the experimental spectrum when blue is the simulated one. So, these peaks are not coming near to this observed peak here; that means, our values of the hyperfine coupling constants are not quite right. So, this has to go away from here this has to has to go away from there. So, this guest values need to be modified let us make it this increase this coupling constant see what happens.

Now, at least these positions are right. So, you may have made a some progress some improvement in the coupling constant now still this is not matching with this. So, this is not matching with this one. So, maybe we need to increase this coupling constant.

It is 2.2; let us say then see what happens here does not look quite right at all. So, may we should increase the line width further little bit more alright. So, it is trying to be similar to the experimental spectrum, but now what has happened this blue the simulated spectrum shows a line which is further away from the observed one; this is also further way from observed one same is true here also; that means, the big coupling constant has become more than what is supposed to be.

So, let us reduce this may be what was the value earlier 9.5; let us go back to nine point eight let us simulate it ya. Now, it is coming closer to that there little bit more 9 10 may be 10 here. So, this are almost matching the line positions here now may be the width is not yet sufficient increase the width trying to become similar to that further not bad, but now you see this has gone away from this the blue line is more than the red line. So, I need to optimize another coupling constant let us say how about this one a 2 0.1; it is improving may be in the same direction let us continue 0, ya not bad.

So, almost all features are reproduced except this little bit differences one can see between red and blue. So, may be the line width is a too much reduce it further; it has disappeared no it has not disappeared they are actually overlapping to. So, that let us deliberately shift one spectrum here you see show the experimental spectrum has move out. So, it means that now I have got the perfect matching between the red experimental spectrum and the blue which was calculated here let us go back and bring all the shift back to the previous value ya.

So, these are now shift has become 0. So, I have got perfect matching of course, it was a contrived example the because this red spectrum though I am calling it in a experimental spectrum it is actually calculated. So, I can get the exact matching these are the values now I can report for this the coupling constant for first nucleus was 2 Gauss with the one number of spin half nucleus set coupling constant of 10 Gauss was for the second group of 2 nuclei of spin half and line width was 2 Gauss and gives me perfect matching.

So, this is the way to go about analyzing the EPR spectrum using a computer.