One and Two Dimensional NMR Spectroscopy for Chemist
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Lecture - 29
Isotope effect

Welcome back, in the last couple of classes we discussed about scalar couplings, and I gave lot of information about how to arrive at or how to get the information about scalar couplings in a different multiplicity examples, I gave. For example when do you call spin system as doublet of triplet, triplet of quartets, quartet of triplets, triplets of quartet, etc. the various examples we took. At the end of the last class, I also introduced what is called Pople nomenclature. It is a nomenclature used to describe the spin systems to enable the analysis of the NMR spectrum. In that I briefed you about what are strongly coupled spins and what are weakly coupled spins? I distinguished between strongly coupled and weakly coupled spin systems. Of course, in the weakly coupled spin system, I discussed and I said when the chemicals shifts separation between two coupled spins is sufficiently large, compared to the coupling constant, let us say, the ratio chemical shift separation to that of the J coupling when delta delta over J between two coupled spins is sufficiently large, of the order of more than 50, then I told you that such system can be treated as weakly coupled spin systems.

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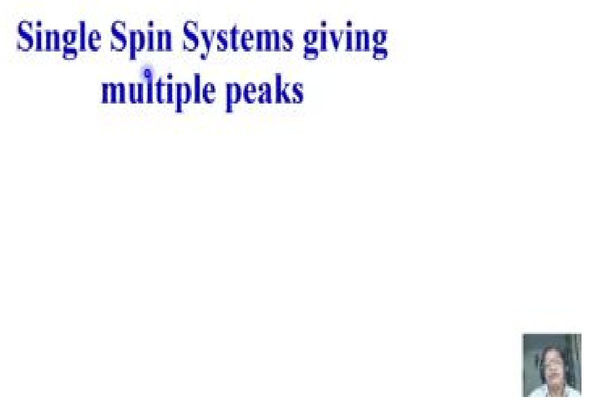

Single Spin Systems giving
multiple peaks

And such weakly coupled spin systems spectra are easy to analyze, the straightforward analysis is possible. Also we call them as first order analysis of the spectrum. Whereas, if you go to the strongly coupled spin system, the condition for which is; the chemical shift separation between two coupled spins is comparable to that of the coupling constant. In other words, if I take the ratio of delta delta, that is the chemical shift separation, to that of the J coupling, that is delta delta over J if you take, then I also said it so happens that it is of the order of 1, and the spin system are strongly coupled and the spectra are not amenable to first order analysis; in the sense, you need to adapt different methods to analyse the spectra

And the intensities are very well described in the weakly coupled spin systems. For example, if I take two weakly two spins, the weakly coupled A and X, we can calculate intensities and show that all of them have equal intensity, but it is not the case with strongly coupled systems. Then I also introduced the notation of Pople for the spin systems, when they are chemically equivalent. What happens, how do you define Pople notation for a chemically equivalent spin? One thing. And I also describe the notation for the groups of chemically equivalent spins present in the molecule. For example, if you have a CH2 group, if you have a CH3 group coupled to some other proton, how do you define this spin nomenclature, and also many examples we discussed. And now we go ahead in analyzing some of the spectra, for example, we start with today single spin systems, which gives multiple peaks.

I gave the example of different spin systems, it can be one spin system, two coupled spin system, three coupled spin systems; and I said what are the possible spin systems you can think of in a single spin. Of course no question of any discussion it has got only one spin, and only 2 energy states alpha and beta. Spins undergo transition between these 2 and then we are going to observe a single peak.

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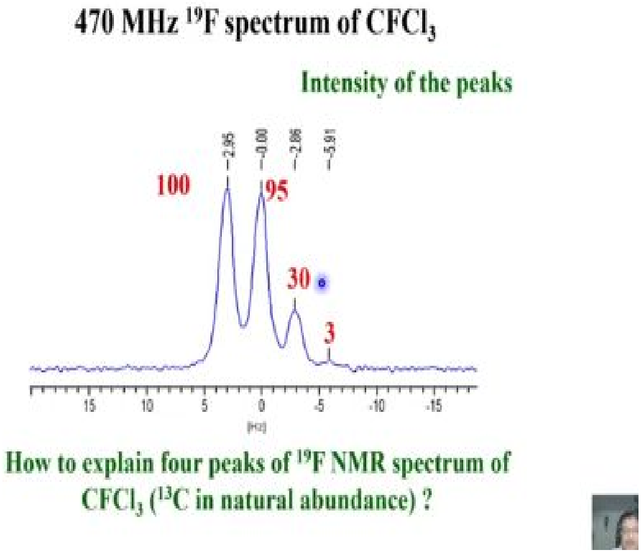

470 MHz ^{19}F spectrum of $CFCl_3$

Intensity of the peaks

How to explain four peaks of ^{19}F NMR spectrum of $CFCl_3$ (^{13}C in natural abundance) ?

And I gave several examples for that molecule like CHCl3, CFCl3 etc. and for 2 coupled spin systems I told you there are three possibilities you can think of weakly coupled AX, 2 spins are weakly coupled, strongly coupled 2 spins; which is AB, and even more strongly coupled with the spins chemicals shifts between 2 spins are exactly same, that is chemicals shifts of A and B overlap and the coupling between them is not seen in the spectrum. That we can call as A2 spin system. So there are three such spin systems possible.

When I go to 3 coupled spin systems, I said there are 10 such spin systems, which I can think of; and all of them can be analyzed very easily in a different way. So there are several ways of analyzing this.

Today let us start with analysis of a single spin system first, which gives multiple peaks. It is something difficult to imagine also. How for example, a single spin containing molecule can give multiple peaks. Last week I was telling you about this. Look at this, this is a simple molecule CFCl3. Now I am looking at the Fluorine 19 NMR spectrum. When I am looking at the Fluorine 19 NMR spectrum, interestingly we got four peaks. Mind you, I wanted to tell you carbon 13 is in its natural abundance in this molecule. That is only 1% of the carbon. Let us say there are two types of Isotopomers. Carbon 12 Isotopomer, which is 99% abundant and carbon 13 Isotopomer is only 1% abundance. So carbon 13 isotopomer we are not considering. We will consider only carbon 12 isotopomer of this molecule; and I also said last time and again repeating chlorine is a quadrapolar spin, which in this work case, I tell you is not coupled to fluorine at all. It does not couple, it may facilitate relaxation that will worry later, but at present in this molecule I am telling you. I am considering a carbon 12 isotopomer and chlorine is not coupled to fluorine.

Then how many peaks I must expect. Logically if you look at this molecule there is only 1 isolated fluorine, which is not coupled to anything. That means I must get only single peak for the fluorine spectrum of this molecule.

Interestingly we are seeing four peaks. This is with 100% intensity, this is 95% intensity, this is 30% intensity; there is another small peak here, if I enlarge the intensity scale, you will see, it is 3% intensity. And I want to repeat this is a real spectrum. Do not get confused, there is no impurity or anything, It is the real spectrum. Now the question is how, when you are looking at a single fluorine, which is present here, can give rise to 4 such peaks; and now the question is we have to understand this.

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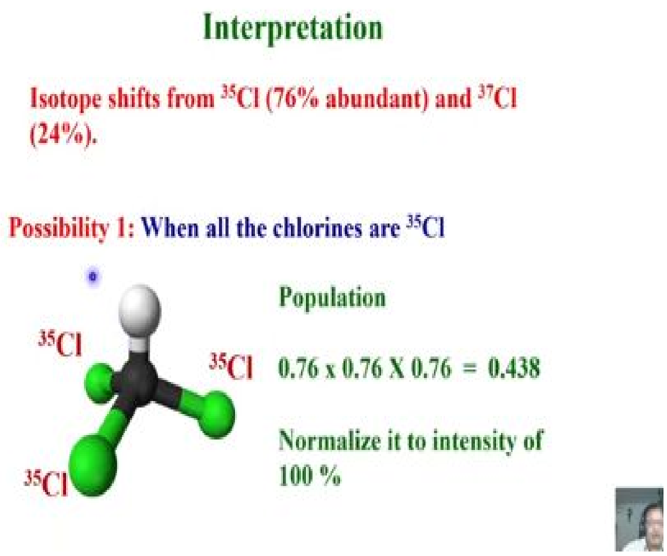

Interpretation

Isotope shifts from ^{35}Cl (76% abundant) and ^{37}Cl (24%).

Possibility 1: When all the chlorines are ^{35}Cl

Population

$0.76 \times 0.76 \times 0.76 = 0.438$

Normalize it to intensity of 100 %

So what I am going to do is, this is called isotope shift in NMR spectrum. We will take an example of this molecule and interpret the spectrum. We will go ahead further and in the next one or two subsequent classes, I will discuss more about the chemical shifts, I will come to that point later. But for this example, we will analyze the CFCl3 spectrum and find out why we are seeing four peaks.

Now the thing is, first before the interpretation we shall understand isotopes of chlorine. Chlorine has two isotopes one is chlorine 35, which is 76% abundant; other is chlorine 37, which is 24% abundant. Understand, what I am telling. Now we have to discuss about isotope shifts; as a consequence we have to find out the number of isotopes of chlorine. I said there are two types of chlorine; isotopomers; one is 35 and other is 37, one has 76% abundance other has 24% abundance.

Now let us consider the possibilities of isotopomers present in this molecule. This is my CFCl3 molecule, this is fluorine, and there are 3 chlorines present here. Let us consider the situation, what is the possibility of population of an isotopomer, where chlorine 35 is present in all the chlorines. All chlorines are isotopes of chlorine 35. Understand thing very
clearly what I am telling you. Let us say that all the chlorine 35 are isotopes of chlorine 35. Then what is the percentage of population; or the probability of population you can expect. Now in this case all are 35, let us say we the understand it, it is 76% abundant; 76% of it.

I took 0.76 for this chlorine, 0.76 for this chlorine and 0.76 for this chlorine. Multiply all the three, I get 0.438. This is the population when all the chlorines are in 35 isotopomers in this molecule. So if I say I have only 1 molecule of CFCl3, one type of istotopomer, where all the chlorines are in 35 isotopomer position; in which I will get 0.438. I will normalize this to the intensity 100%. Understand, only all chlorines are 35 isotopomers, in this molecule, ie. you have an isotopomer of CFCl3 with all the chlorines in 35, then we must get only 1 peak. I normalize this for intensity of 100%.

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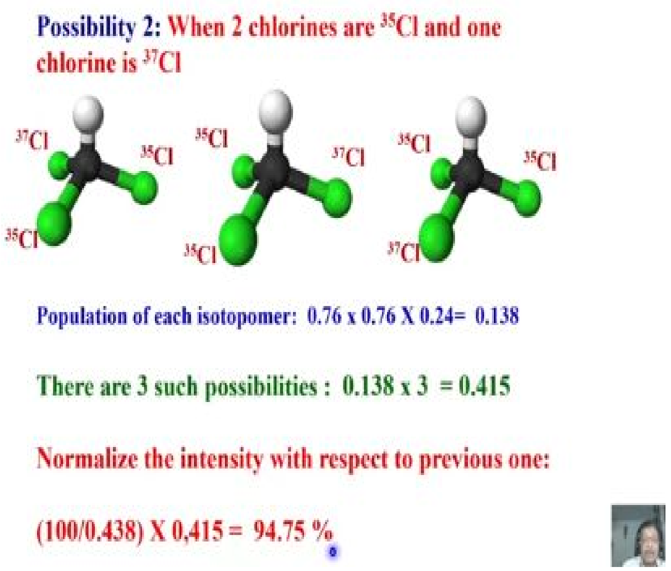

Possibility 2: **When 2 chlorines are ^{35}Cl and one chlorine is ^{37}Cl**

Population of each isotopomer: 0.76 x 0.76 X 0.24= 0.138

There are 3 such possibilities : 0.138 x 3 = 0.415

Normalize the intensity with respect to previous one:

(100/0.438) X 0,415 = 94.75 %

Now what is a possibility 2? There is other possibility we can think of; when two chlorine are 35 and 1 chlorine is 37 isotopomer, it is possible, right? Look at this one; now this chlorine can be 37, this can be 35, this can be 35. But remember there are 3 such possibilities. Now I said this was 37 this can also be 37 and this can also be 37; and I am sorry there is, no okay, it is fine and this can be 37 and this can be 35. Another possibility is this is 37 and these two are 35, there are 3 possibilities I can think of.

Think of a possibility when 2 chlorines are 35, and only one chlorine is 37; there are 3 such possibilities any one of them can be 37 other two can be 35. So there are 3 such possibilities. Now consider the population in such a case; when one chlorine is 37 you can find out what are the possibilities? What is the percentage of abundance I found out. I said chlorine 35 is 76, chlorine 37 is 24. Now in this case 35 is 76% abundant, then you will put 0.76. 0.76 for two chlorines which are 35, and 0.24, 24% abundance of chlorine which is 37. So, this is the population for any one of these isotopomers. Multiply all these things I find it is 0.138. Simply plug in these number into calculator and you will get it as 0.138. But this is for one of the isotopomers. But we have 3 such possibilities. So multiply this by 3 intensity tells whatever we 0.415. Now compare with intensity with the original first possibility, where all were 35. Now, normalize this other one, it is 100 by 0.438 into 0.415. This turns out to be close to 95%. It is a simple arithmetic; You do not have to do anything. Now for all the 3 possibilities of the isotopomers of two chlorines are in 35 and one chlorine is 37, the population if you calculate it turns out to be 95 % population, possibility of that.

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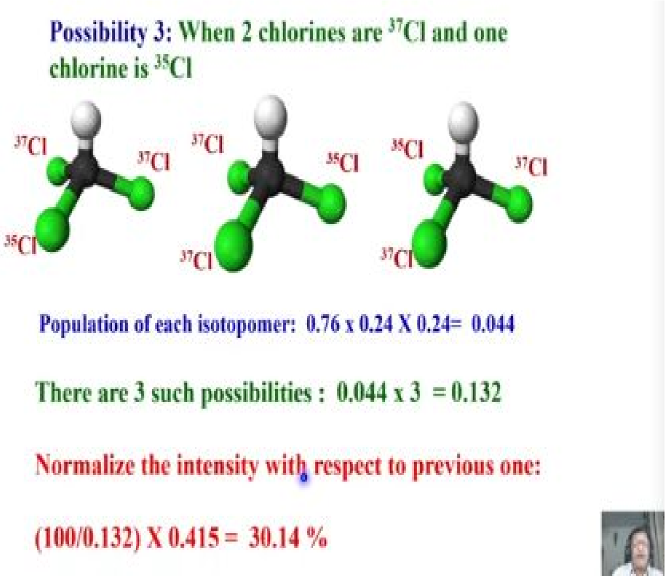

Possibility 3: When 2 chlorines are ^{37}Cl and one chlorine is ^{35}Cl

Population of each isotopomer: 0.76 x 0.24 X 0.24= 0.044

There are 3 such possibilities : 0.044 x 3 = 0.132

Normalize the intensity with respect to previous one:

(100/0.132) X 0.415 = 30.14 %

Is there any other possibility we can think of for isotopomers? Yes, now two chlorines could be 37 and one chlorine is 35, that is possible, this is 37, this is 37, it is 35 true, these two are 37 this is 35, these two are 37 and this is 35. So now calculate the population for this. Now one is chlorine 35, it is 76%. Put 0.7,6 other is chlorine 37, it is 24%. There are two such chlorines; 0.24 into 0.24. Now you multiply. What did you get? 0.044, it is simple arithmetic.

This is for one type of isotope isotopomer, one possibility. Now there is 3 such possibilities; multiply by 3 we get it 0.132. Now normalize the intensity of this, with respect to the first one, where all chlorines were 35. I took that as a standard for 100% right? the population with intensity is 100%. Now to normalize this 100 divided by 0.132 into this first normalized factor; it turns out to be 30%. Very interesting.

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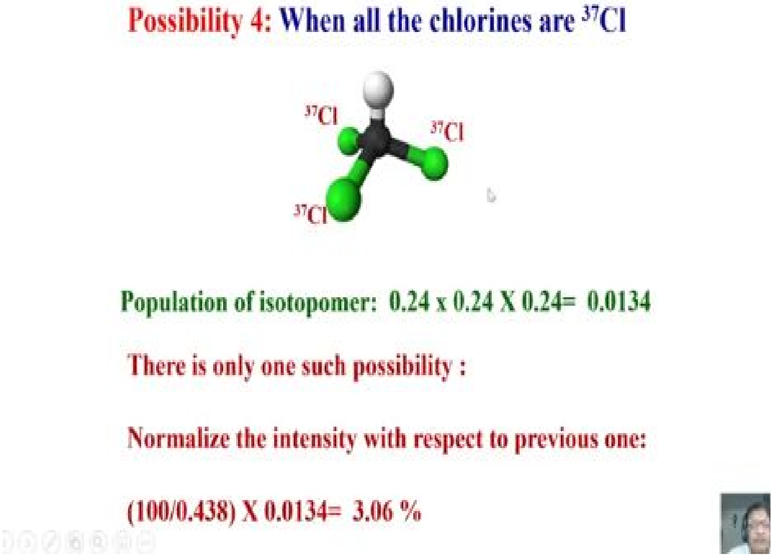

Possibility 4: When all the chlorines are ^{37}Cl

Population of isotopomer: 0.24 x 0.24 X 0.24= 0.0134

There is only one such possibility :

Normalize the intensity with respect to previous one:

(100/0.438) X 0.0134= 3.06 %

Now what is the last possibility we can think of? When all the chlorines are 37 How many possibilities are there? only one type of isotopomer is possible in that, all the chlorines are 37. All are same and actually there is no need to consider this, this and this. Now when all the chlorines are 37, this is the only one possibility; and we calculate the population of all of them. 0.24 into 0.24 into 0.24; it turns or to be 0.0134. Normalize this with the situation 1; where all the chlorines were 35, what is the percentage you are going to get? We get 3%. Now understood everything; there are 4 different types of isotopomers are possible here, when only one possibility where all the chlorines are 35, which I took as a standard 100% intensity. Second when when chlorine is 35, I am sorry 2 chlorines are 35 1 is 37. We got 95% intensity; population is 95%.

Third, when 1 chlorine is 35, 2 are 37, then again 3 such possibilities, when we normalized the intensity, we obtained it as 30%.

The last possibility we can think of; all the chlorines are 37, only one such possibility and the normalized intensity with respect to the first one, it is 3%

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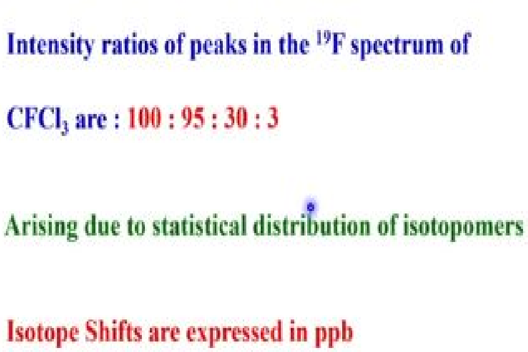

Intensity ratios of peaks in the ^{19}F spectrum of

$CFCl_3$ are : 100 : 95 : 30 : 3

Arising due to statistical distribution of isotopomers

Isotope Shifts are expressed in ppb

So the intensity ratios of peaks in the 19F spectrum are 100, 95, 30, 3. So you understand. now you should find that 95, 30 and 3 arising due to the statistical distribution of isotopomers. Generally isotopic shifts are expressed in parts per billion.

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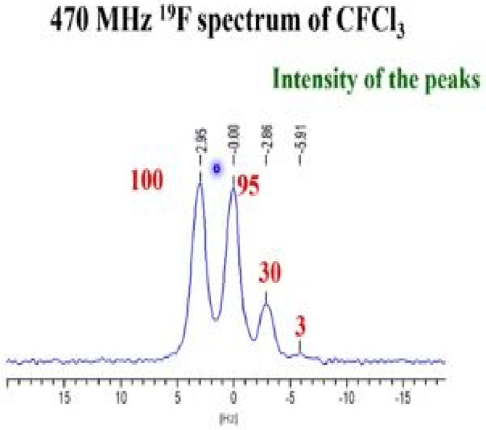
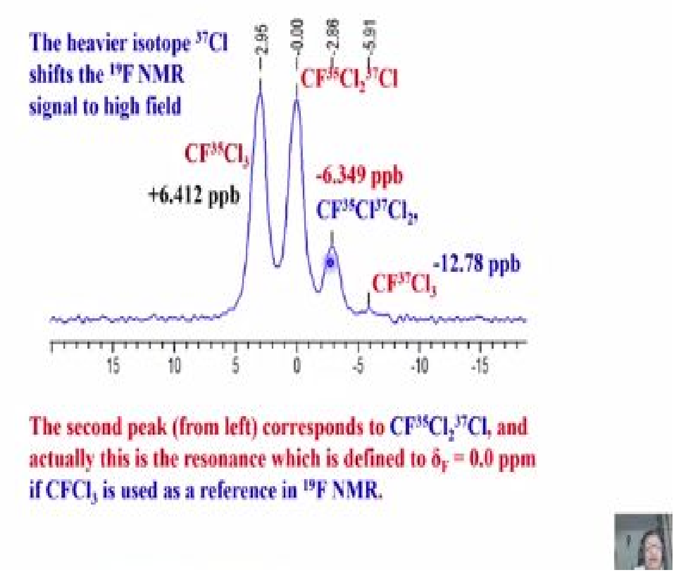


470 MHz ^{19}F spectrum of $CFCl_3$

Intensity of the peaks

You understood this. Now we will go back to the original spectrum, which I showed you, this is the CFCl3 spectrum and we had worked out the intensity this is 100% and this has to be the peak coming when all the chlorines are 35; only 1 possibility; this comes because when 2 chlorines are 35 and one chlorine is 37, there are 3 such possibilities; the intensity when you calculated as

95% population for these isotopomers; this one where one chlorine is 35; two chlorines are 37, and 3 such possibilities and when you calculate the populations and intensities it turns out to be 30. Now, this is the last possibility where all the chlorines are 37 only one such possibility we got 3% intensity. Very beautifully we can understand this spectrum. Remember a single spin system gave you multiple peaks. This you do not get confused, the interpretation is because it is due to isotopic effect, and you find out the difference between these two. What is the difference it is only when all 3 are 35 here. Only one is 37 isotope and the effects of the chemicals shift here; take out the difference, it is very small. And take the difference between this and this, and this and this we can find out. What is the effect of different isotopomers on the chemicals shift? how much it is shifted due to isotopic substitution and this is due to isotopic effect. Okay, very clear now. **(Refer Slide Time: 19:32)**



The heavier isotope ^{37}Cl shifts the ^{19}F NMR signal to high field

The second peak (from left) corresponds to $CF^{35}Cl_2{}^{37}Cl$, and actually this is the resonance which is defined to $\delta_F = 0.0$ ppm if $CFCl_3$ is used as a reference in ^{19}F NMR.

Now, if you calculate this, I can tell you one interesting thing is happening. The heavy isotope always shifts the fluorine signal to the high field. Heavy isotopomer generally shifts be the peak to the high field. So now you take the difference in the chemical shift between this and this. It has shifted by 6.412 ppb. I took this as a reference CFCl3 and if you take this one, this is +6.412, when I take the other possibility it moved this side, it is -6.4, approximately 6.4.

And take this one because now there are all the 3 are fluorine 37, it has shifted by 12.78 ppb. See generally this is the peak which we always use as a reference in fluorine. That is why we took this as 0, we have fluorine 35 is 2 and only 1 fluorine 37 isotopomer; with respect to this how much peak has shifted you can calculate and find out the positions of the others, because the isotopic substitution is always expressed in power square.

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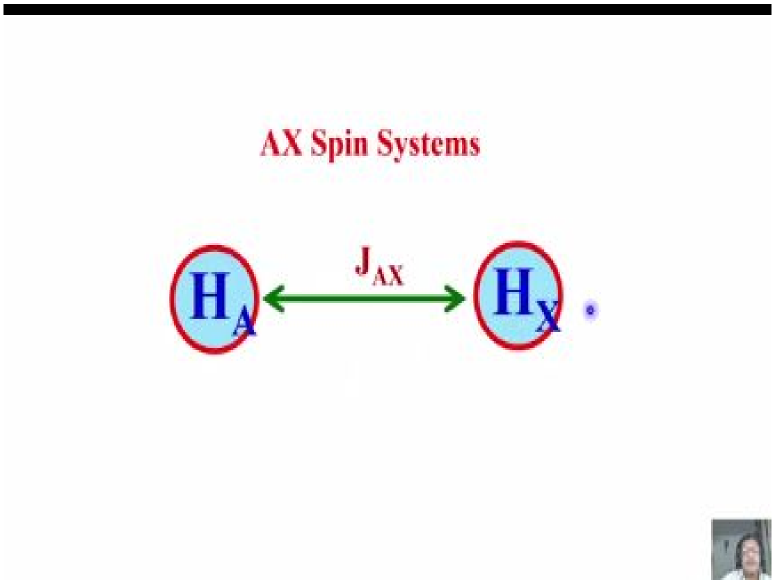

AX Spin Systems

So you can start discussing all these things later, when the isotope effects are discussed. I come to this more detail later. But at the moment, I just wanted to tell you, sometimes when you look for a single spin system where only one proton or one fluorine is there. You expect only one peak; however, sometimes it so happens you may get 3 to 4 peaks. I wanted to bring to your attention do not get confused, it is not because of any other reason. It is only because of isotope effects.

Now consider next possibility of spin systems when two nuclear spins are coupled. What are the possibilities? First we will consider AX spin systems. That is A is here, X is far off in the alphabet, you know, that means when it is far away, it is weakly coupled spin system. This is A and this is X. And the coupling between them is JAX. Coupling between A and X is JAX.

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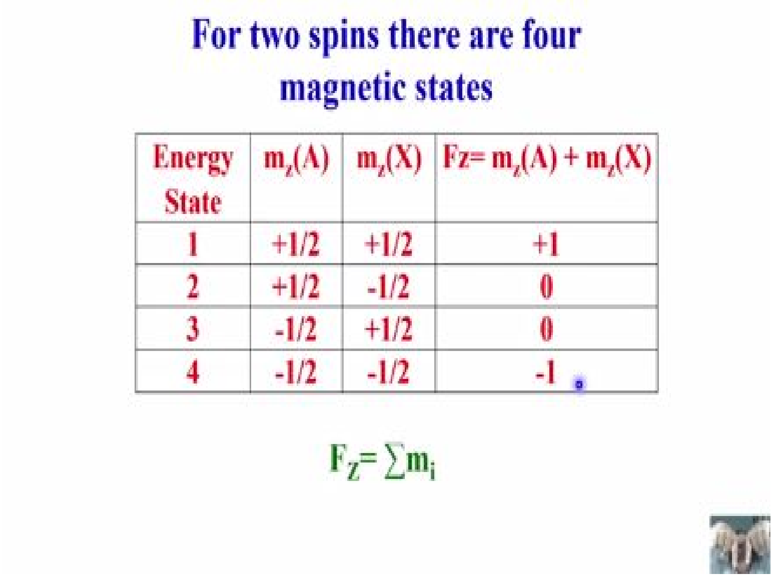

For two spins there are four magnetic states

Energy State	$m_z(A)$	$m_z(X)$	$Fz= m_z(A) + m_z(X)$
1	+1/2	+1/2	+1
2	+1/2	-1/2	0
3	-1/2	+1/2	0
4	-1/2	-1/2	-1

$$F_Z = \sum m_i$$

Now, what are the two possible spin states for this? Remember we worked out. The allowed transitions, possible transitions in two weakly coupled spin system, we also worked out what is the magnetic quantum number for each of the spin states; and then each possible orientation of each spin, and then for each energy state we worked out the total magnetic quantum number for the state; where two spins are in alpha alpha state it is +1. It is alpha beta it is 0. Beta alpha it is 0 because it is minus half and plus half, and for beta beta the energy state, it is -1. Remember, I do not have to go into the details. I discussed this earlier there are only 4 energy states for this corresponding to 4 different possible orientations of this nuclear spins. When both states and alpha alpha it is +1 and this is the alpha, this is beta. plus half and minus half, the total magnetic quantum number of the energy state is 0. In this situation it is beta alpha, also 0 and the last possibility, beta beta both are down, it is -1.

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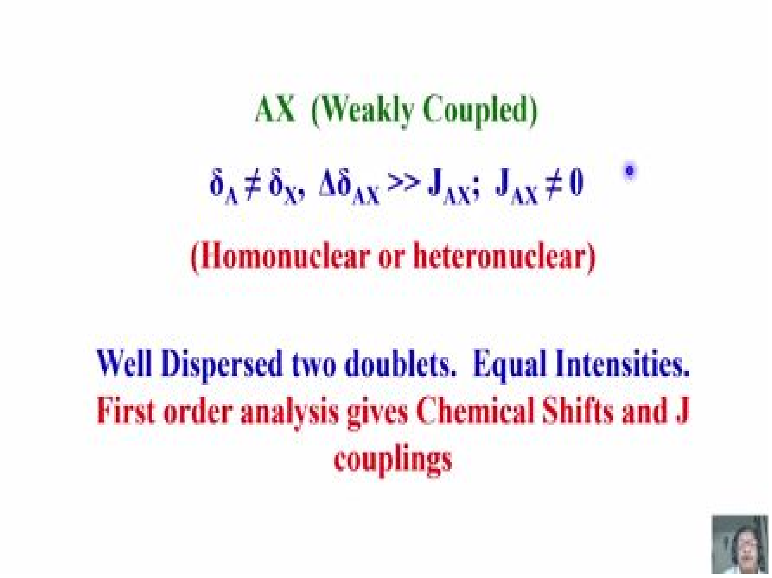

AX (Weakly Coupled)

$\delta_A \neq \delta_X$, $\Delta\delta_{AX} >> J_{AX}$; $J_{AX} \neq 0$

(Homonuclear or heteronuclear)

Well Dispersed two doublets. Equal Intensities.
First order analysis gives Chemical Shifts and J couplings

And now I will put one important condition, not a condition it is true, it can happen. In weakly coupled case, delta A is not equal to delta X, it should be true because, chemical shifts have to be far away separated. So, the A and X chemical shifts are not equal. Secondly, the delta delta of AX, chemical shift difference between A and X, has to sufficiently large. Remember one of the conditions of weakly coupled spin system.

This delta by J has to be greater than 50. That is what I said, at least of that order that is one condition. Secondly, JAX is non-zero, if JAX is zero, it will become a different type of spin system. I will tell you that later, and this AX can be both homonuclear spins and heteronuclear spins. Two spins could be homonuclear and two spins can be heteronuclear. So in this case in the AX, we also discussed earlier when two spins are weakly coupled, well dispersed doublets will be there.

One doublet for A, one doublet for X, very easily you will see two peaks for each of them. And equal intensity, remember, there is no intensity anomaly here. All of them are equal intensity, we put it as a ratio 1 : 1 : 1 : 1. So there are two weakly coupled spins, it will give rise to 4 peaks of equal intensities, and you do one thing, the analysis will become very easy. There are two peaks here and two peaks here.

Center of this doublet gives you chemical shift of one of them; center of this doublet gives you chemical shift of other one; and a separation between this doublet will give you J couplings. So this is called first order analysis. If you want to, if you can analyze this spectrum simply without going into much mathematics or computation, this is a first order analysis; where you can directly extract the chemical shifts and coupling information.

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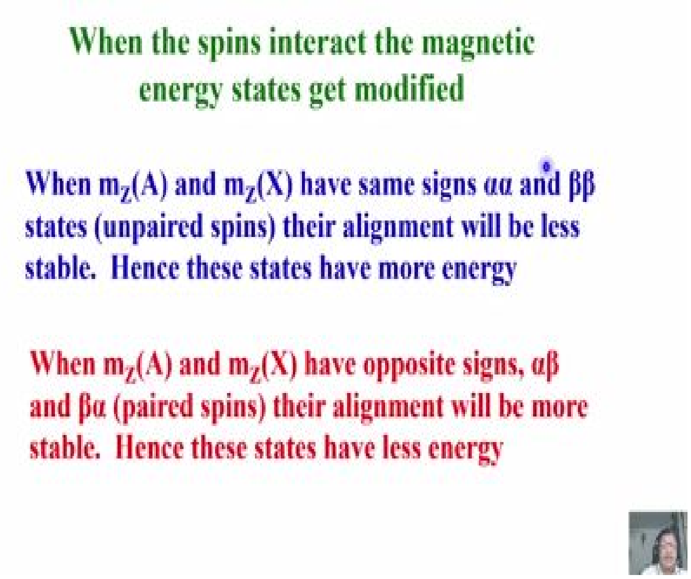

When the spins interact the magnetic energy states get modified

When $m_Z(A)$ and $m_Z(X)$ have same signs $\alpha\alpha$ and $\beta\beta$ states (unpaired spins) their alignment will be less stable. Hence these states have more energy

When $m_Z(A)$ and $m_Z(X)$ have opposite signs, $\alpha\beta$ and $\beta\alpha$ (paired spins) their alignment will be more stable. Hence these states have less energy

Now of course, how it comes I already explained to you. I do not have to go to this in detail and alpha alpha, beta beta states or unpaired spins get destabilized, and actually in that case they have more energy. In the other case when alpha beta beta alpha states their paired spins, and they will be more stable. As a consequence, I said the energy level gets destabilized and we could arrive at the possible transitions.

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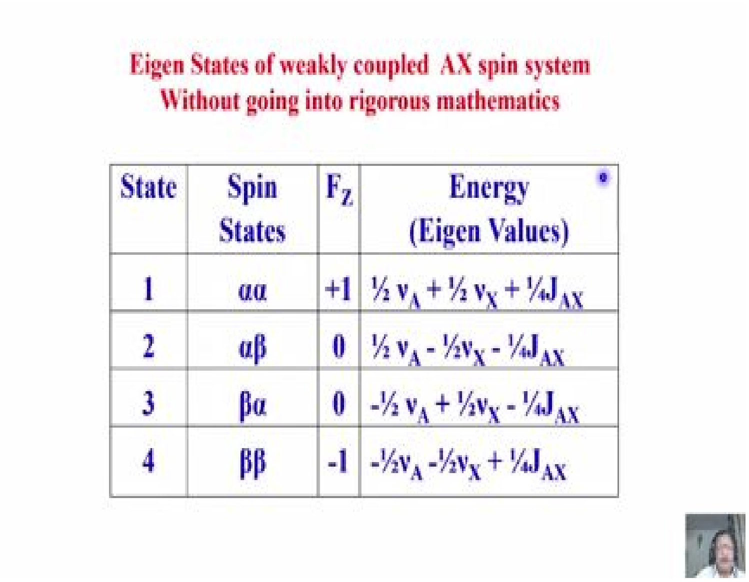

Eigen States of weakly coupled AX spin system
Without going into rigorous mathematics

State	Spin States	F_Z	Energy (Eigen Values)
1	αα	+1	$\frac{1}{2}\nu_A + \frac{1}{2}\nu_X + \frac{1}{4}J_{AX}$
2	αβ	0	$\frac{1}{2}\nu_A - \frac{1}{2}\nu_X - \frac{1}{4}J_{AX}$
3	βα	0	$-\frac{1}{2}\nu_A + \frac{1}{2}\nu_X - \frac{1}{4}J_{AX}$
4	ββ	-1	$-\frac{1}{2}\nu_A - \frac{1}{2}\nu_X + \frac{1}{4}J_{AX}$

So now we can easily work out also. Remember alpha alpha and beta beta states destabilized, the energy levels will be shift by J /4. Alpha beta and beta alpha states are destabilized and the energy is decreased by J/4. So all the 4 possible transitions you understood. You worked out last time, remember? But I did not give you the frequencies and how do you get frequencies from this thing. I only showed you four possible transitions, where we identified 2 for A and 2 for X. I am going tell little bit more in this. I will give you more information and the energy Eigen values. These are called Eigen. These are all the Eigen states, and Eigen values of these things you can find out. The Eigen functions are nothing but the product functions. Eigen states are magnetic quantum states. The total magnetic quantum number of these states are 1, 0, 0, -1 and we have Eigen values, or the energy of each of the states we consider.

There four states are identified as 1, 2, 3 and 4. For state 1, if you go into quantum mechanical analysis, we have to write down the full hamiltonian. Total hamiltonian is hamiltonian of the Zeeman part and hamiltonian for JIJ part, spin spin coupling and work out for all the four 4 product functions, you will get the 4X4 matrix. And then very easily you can work out what are the energie,s and you can calculate the Eigen values and these are the Eigen values of 4 energy states. But the frequency is nothing but the difference in Eigen states. We will find out what are these frequencies. So I have worked out here for alpha alpha state what you are going to get, it is half nu A, plus half nu X, plus 1 /4 JAX, this is the energy or Eigen value for this alpha alpha state. And this is for the alpha beta state where energy for this state is half nu A, minus half nu X, minus 1/ 4 JAX.

Remember, always it so happens one of the energy states will move from the chemical shift position, we have observed one peak goes to the left and 1 peak goes to the right, by a fraction of J. Half of J will move to the right, half of J, one peak will move to the left. How it comes. It is because when you work out, this Eigen values and look at the transitions and calculate each of the transition frequencies, you can find out these things.

So similarly beta beta, beta alpha is worked out and this is the energy state for the beta beta, So these are the four energy Eigen values. Now remember, we know what are the possible transitions, for example alpha alpha this and consider as A first one, second is X. Right? First is A, second is X. AX, AX, AX, same order I will take. And now I have written like this what is the transition between 1 and 2, A has not changed it is in spin state. It remains of alpha whereas X has changed from alpha to beta. Take the difference of these two, when I take the difference, this will get cancelled out. These half νX plus half νX when I take the difference, it will become nu X and 1 fourth JAX, minus of minus, so it will be half JAX. So, this is te chemical shift of X, one peak is moved from the chemical shift X spin by +1/2 JX. So this is the chemical shift of X spin. One peak is more to the right by half of JAX.

Now what is other possibilities you can think of? This possibility 3 and 4. The A spin is not changing at all, it remains in beta state. Here A spin is changing from alpha to beta, if I take the transition. Well again now find out the difference between these two you will find out that the frequency is such that, it is νX minus of 1/2 JAX. So from these 4 energy states. What you should do is find out the allowed transitions, which spin is flipping from alpha to beta and beta to alpha. This one, 1 to 2 corresponds to X transition. 3 to 4 corresponds to X transition. This is simple arithmetic to find out the difference of these thing, you will find from the chemical shift of νX, one peak has moved to the right by half of J. One peak is moved to the left by half of J. So it is split into a doublet, the central peak will not be there. So now without coupling there was one peak. Now, because of the coupling it is split into two, where one move to the right by half of JAX, one move to the left by half of JAX.

So totally the separation of this if you measure, it is JAX. Same way now we look at 1 and 3 where A spin is changing its state, but alpha of X remains alpha. Now 2 and 4 if you take again A spin is changing state from alpha to beta, but X spin is remaining same. Understood the logic now.

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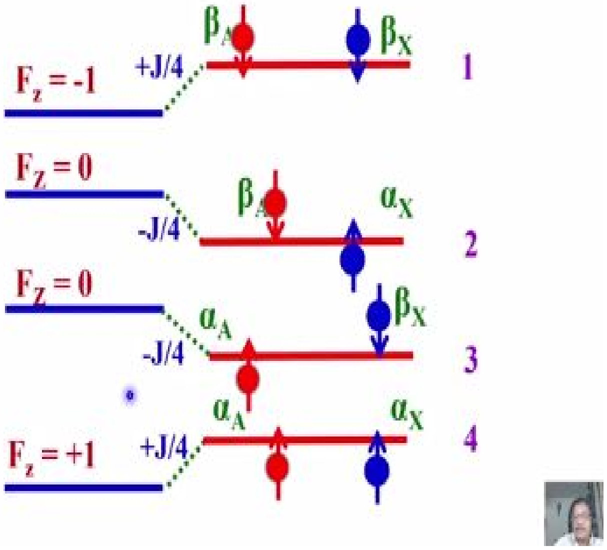

So that way we can now work out all the possible transitions like this. I do not have to go to this. I described this in one of the classes.

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Difference in the Eigen values of the states can be used to calculate the transition frequencies

Difference in eigen values between states 1 and 2

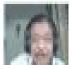
$$(\tfrac{1}{2}\nu_A + \tfrac{1}{2}\nu_X + \tfrac{1}{4}J_{AX}) - (\tfrac{1}{2}\nu_A - \tfrac{1}{2}\nu_X - \tfrac{1}{4}J_{AX})$$

$$= (\nu_X + \tfrac{1}{2}J_{AX})$$

Difference in eigen values between states 1 and 2

$$(-\tfrac{1}{2}\nu_A + \tfrac{1}{2}\nu_X - \tfrac{1}{4}J_{AX}) - (-\tfrac{1}{2}\nu_A - \tfrac{1}{2}\nu_X + \tfrac{1}{4}J_{AX})$$

$$= (\nu_X - \tfrac{1}{2}J_{AX})$$



Now the difference in the Eigen values is worked out like this. I took the difference in the values between first state and second state. This is νX plus half JAX and the difference between this is 3 and 4. Now, this is 1 and 2. I am sorry this is 3 and 4. Then it turns out to be νX minus half JAX. Understand? I took the Eigen values. I gave the list of all the four possible Eigen values for each state, first and two if we take the difference you get this; and 3 and 4 here you will get this thing.

So that means these were identified as X transitions. So from the chemical shift of the X spin, it is one peak at half of JAX, there is another peak, at half of JAX, so minus half of JAX, we will doublet centered at chemical shift of X and whose separation corresponds to JAX.

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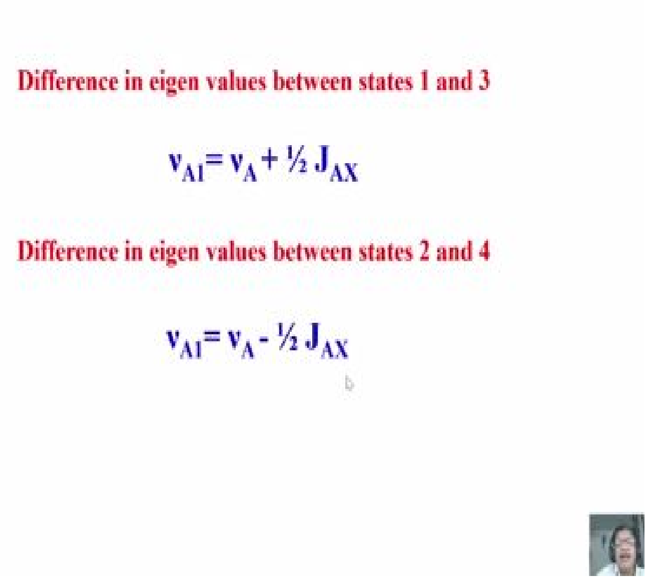

Difference in eigen values between states 1 and 3

$$\nu_{A1} = \nu_A + \frac{1}{2} J_{AX}$$

Difference in eigen values between states 2 and 4

$$\nu_{A1} = \nu_A - \frac{1}{2} J_{AX}$$

Same way you can do that for 1 and 3 and 2 and 4. Now you will get the frequency for A and one peak is shifted from the chemical shift of A by half JAX to the one side and other peak is shifted from the chemical shift of A by half JAX on the other side. So, that means each of these nuclear spins split into doublets and you get doublets of equal intensity separated by JAX. This is what I wanted to say.

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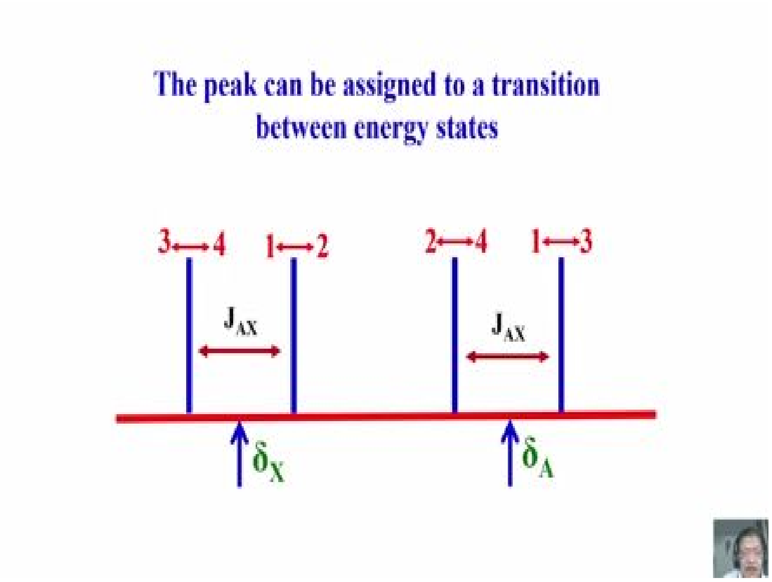

The peak can be assigned to a transition between energy states

This is what we observed 1, 2, and 3,4 transitions correspond to X with this separation; 2, 4 and 1, 3 transitions correspond to A with this separation. Always this center of the doublets is the chemical shift of A here. This center of the doublet is the chemical shift of X. So now analysis of the two coupled spin system A and X which are very well separated, weakly coupled very easy to interpret. It gives four lines of equal intensity; get the center you get chemical shift of this. Get this center you get the chemical shift of this. Simply measure one of these separations you will get JAX.

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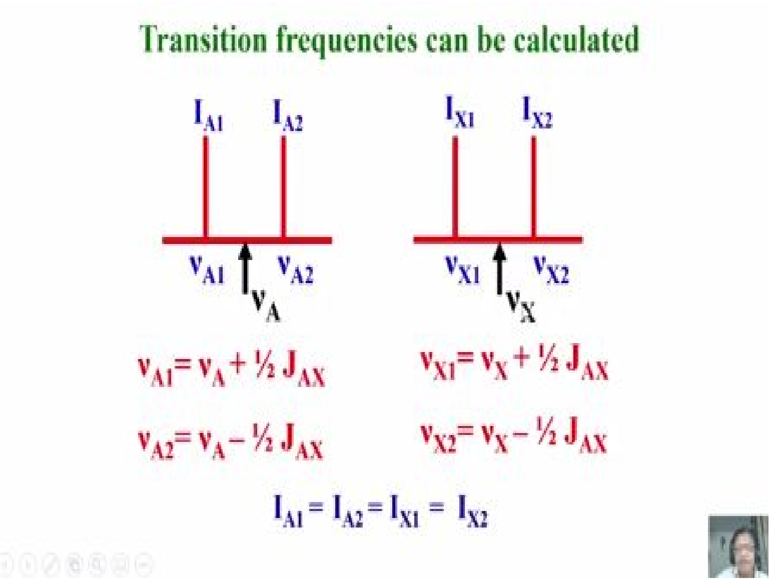

Transition frequencies can be calculated

$\nu_{A1} = \nu_A + \frac{1}{2} J_{AX}$ $\nu_{X1} = \nu_X + \frac{1}{2} J_{AX}$

$\nu_{A2} = \nu_A - \frac{1}{2} J_{AX}$ $\nu_{X2} = \nu_X - \frac{1}{2} J_{AX}$

$I_{A1} = I_{A2} = I_{X1} = I_{X2}$

And you can also calculate the transition intensities. The transition intensities in this case, for all of them are IA1, IA2, IX1, IX2. These are the intensities for each of the transitions. But without working more with the details, again we can do quantum mechanical calculations, I am telling you all, intensity of A1and A2, intensity of X1 to X2 are same. So the intensity ratio 1 : 1 : 1 : 1.

The summary of AX spin system is such that, when two spins are coupled, weakly coupled. There are four transitions 2 for A, 2 for X, it is called AX spin system in the Pople nomenclature, separation of any of these doublets will give you J coupling. Centre of each doublet gives you chemical shifts. You got the point how to analyze the AX spin system? and all of them are equal intensities. It is a very important thing you should remember. Very easy to analyze 2 spin spectrum, you can give to workout. The detail quantum mechanical calculations you can make. But it is a cumbersome work it takes lot of time. I am giving you just some idea as how to analyze. So what you will do. So will stop today and then continue tomorrow with the analysis of one or two strongly coupled case like AB, A2 spin and an example of 3 spins weakly coupled before we start the analysis of some other spectra.