One and Two dimensional NMR Spectroscopy: Concepts and Spectral Analysis

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Lecture 17: Nomenclature for coupled spins

In the last class, we started discussing about the coupled spin systems and also we introduced what is called Pople nomenclature. Remember, a coupled spin system is the one, where there could be group of protons in a given molecule or group of nuclear spins, which are all NMR active spins and there should be coupling among themselves. It could be homonuclear, it could be heteronuclear, does not matter. So long as there exist couplings among them, they all form the part of the coupled spin system. For example, I have A, B, C, D, 4 spins could be a homonuclear or heteronuclear, does not matter. A is coupled to B, A is coupled to C, A is coupled to D; and B, C, D all are coupled among themselves. One of the couplings could be incidentally zero, the coupling could be 0; does not matter, A, B or A, C coupling could be 0, but then A, D coupling is there A, B coupling could be there. So, that means, they are part of the coupled spin system. One of the coupling could be 0, nevertheless, it becomes part of the coupled spin system. And this coupled spin system can be classified into two types, weakly coupled and strongly coupled. I explained to you what is the difference between weakly coupled and strongly coupled spin systems. Weakly coupled is the one where the chemical separation should be sufficiently larger than the coupling constant. Let us say I have two spins I and J, if the chemical shift of I is delta I and the chemical shift of J is delta J, then delta I minus delta J is sufficiently larger than J_{IJ}. Then it is called weakly coupled spin system. That means, you take the ratio J_{IJ} over delta IJ, it is much much smaller than 1, could be of the order 0.01. Then it is weakly coupled spin system. Or take the reverse of it; delta over J then its value should be sufficiently large, and of the order 50 or even more. Then they are weakly coupled. On the other hand, if the chemical should difference between the two protons I and J is very small compared to that of the J coupling itself, then it is called strongly coupled. The condition is if you take the ratio J over delta; it is almost approximately equal to 1. Then they are strongly coupled. Or take the reverse of that, delta over J that is almost approximately equal to 1 or slightly greater than 1, then they are called strongly coupled. I gave the example of what are weakly coupled and strongly coupled molecules. Measured chemical shifts, measure J couplings both in homonuclear case and heteronuclear case. And of course, heteronuclear case they are always weakly coupled, because the chemical shift separation is of the order of resonating frequency which is of the order of several MHz. As a consequence heteronuclear coupled spin systems are invariably weakly coupled. The strongly coupled system you can think of only in the homonuclear cases. I explained to you the Pople nomenclature. Pople nomenclature is the one, for each spin half nuclei a Roman alphabet is given; and then if it is weakly coupled the farthest letter is given in the alphabet order and the letters which are next to each other or closest to each other are given for strongly coupled.

AX, AMX, AMPX, etc

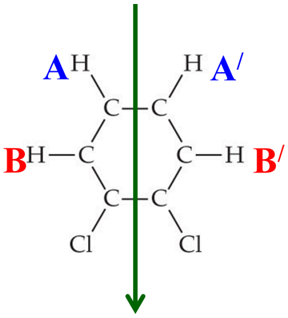
For example, one spin is weakly coupled to another spin, the nomenclature is A and X, A is here, and X is far away that is called weakly coupled. If A is here, next B letter is given, that means the chemical shift separation is much smaller. That is called strongly coupled. So, there could be many many protons coupled. Many can be coupled; they strongly coupled and weakly coupled, we know. AB is strongly coupled; ABC is strongly coupled; ABCD is also strongly coupled. AX is weakly coupled, AMX is weakly coupled 3 spins, AMPX is weakly coupled 4 spins. This what we explained. And now going further you may ask me a question what happens if there are chemical equivalent spins? how do we give the nomenclature for that? what is the Pople nomenclature? Now, we will discuss that today.

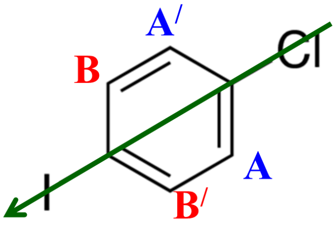
A’A’X, AA’XX’, AA’MXX’

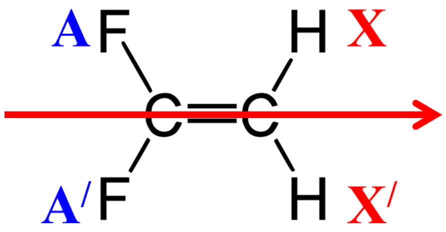
For example, the nomenclature for the weakly coupled spins are given like this. For weakly coupled spins there is a nomenclature which is given by prime notation, It is always used for a chemical equivalent spins. Again in the weakly coupled case AA’X is given; AA’XX’ is given; AA’MXX’ like that. What is this nomenclature? Remember if I take AA’X, AA’, the chemically equivalent spins are strongly coupled AX and A’X are weakly coupled. Hope you understand the logic. AA’X means A and A’ are chemically equivalent spins, between them they are strongly coupled. But each of them is weakly coupled to X spin. IF you consider AA’XX’; Similarly AA’ between them they are strongly coupled, XX’ between them they are strongly coupled. They are chemically equivalent; these two are chemically equivalent and these equivalent, and between A and X, A’ and X, they are weakly coupled.

Similarly, you go further, in AA’MXX’, A and A’; M and M’ are chemically equivalent, X and X’ are chemically equivalent. M is a different spin, a single spin. Now there can be a coupling between A and M; A’ and M, X and M, and M and X’, The coupling between A and X will be there, A’ and X will be there. And between A and M, they are weakly coupled, between X and M they are weakly coupled. This is how for equivalent spins prime is g **A’A’B, AA’BB’, AA’BB’C’**

Same thing if they are strongly coupled, it AA’B; AA’B means A and A’ are chemically equivalent, they are themselves strongly coupled, plus they are coupled to other proton, B, to which both are strongly coupled. AA’BB’ prime means, A and A’ are chemical equivalent, B and B’ are chemical equivalent. Between them, there is that strong coupling, they are strongly coupled. AA’ are strongly coupled because, they are chemically equivalent, there will be a coupling, BB’ are chemical equivalent, there may be a coupling, they are strongly coupled. A and B are strongly coupled, A prime B are strongly coupled like that. Similarly, you can have AA’BB’C. There is no C prime, C is a single independent spin. That means AA’ are chemically equivalent, BB’ are chemically equivalent, Together they are coupled to C. All are strongly coupled. This is the nomenclature used for chemical equivalent spins when they are strongly coupled. So, we can look at a molecule like this, this is ortho dichlorobenzene.



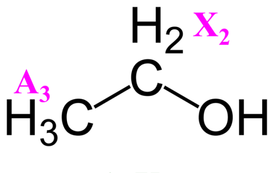




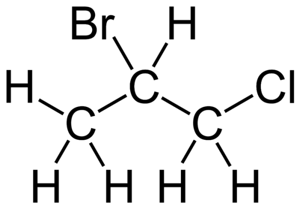
Now, I can put a nomenclature like this. Of course, we have to mention the resonating frequency, because at some frequency at 100 MHz it can be AA’BB’. If you go to 1000 MHz or 1.5 GHz, it can become it can become A2 to X2. The nomenclature changes. ok. So, what I am trying to say is this. In a particular spectrometer, low frequency spectrometer, these two are chemically equivalent they are called AA’; these two are chemically equivalent BB’. It is AA’BB’ spin system. Look at this one this has a different substitution. Again these four protons this is AA’; this is BB’. It is a strongly coupled case. What about this one? There is a symmetry axis. These two protons are equivalent, I call it AA'. These two fluorines are chemically equivalent ,this coupling and this coupling are different. So, I call it AA' XX' spin system. Remember this is AA'XX' spin system. This is AA'BB'. These two are AA' BB' systems. This is AA'XX'. Why XX prime? Becausethey are weakly coupled. I am telling you. Look at it, these are all heteronuclei. Obviously, chemical shift separation is MHz and coupling is so small. So, this is heteronuclear weakly coupled AA'XX' spin system. This is as far as the equivalent spins are concerned.

What is the nomenclature of chemically equivalent spins? when I have group of spins like CH2 and CH3. IN CH2 group there are 2 protons, which are chemically equivalent. Here 3 protons which are equivalent. It could be chemically equivalent or magnetically equivalent, does not matter, there are equivalent groups. Then what nomenclature we have to give in such spin systems? What is the nomenclature we have to use when there are equivalent protons? Remember when they are chemically equivalent we gave prime notation when there are equivalent groups we use a subscript like this. That means if I say AB2, that means there are 2 protons which are chemically equivalent. In A2B2 there are 2 protons which are chemically equivalent, 2 groups are there. It may be a CH2 group, this is like CH3 group may be there. So, for strongly coupled spins and when chemically equivalent spins are present, we use the nomenclature with a subscript. The subscript number refers to number of equivalent protons. For example, if I say AB2 there are 2 protons which are chemically equivalent; there is a group of protons which are chemically equivalent; here CH2 group may be there. There are 3 protons which are chemically equivalent the subscripts refers to number of chemically equivalent protons; and A and B letter tells you they are strongly coupled. So, in A2B2 there are 2 protons which are chemically equivalent here; 2 protons which are chemically equivalent. Between them there is a strongly coupling. That is the nomenclature you should understand. The nomenclature what we are going to give here is AB3; A and B are strongly coupled, but in B there are 3 equivalent protons, that is why subscript 3.

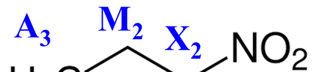
The same thing we can do for weakly coupled. I can call it AX2; A2X2; A2M2X2; AX2. There are 2 protons here which are chemically equivalent, thus there is a subscript 2, and A and X are weakly coupled. Similarly, A2X2; here 2 protons are chemically equivalent, here 2 protons are equivalent, but A and X are weakly coupled. That is the nomenclature. Same thing for 3 different protons are coupled here. These 2 are equivalent here; 2 are equivalent here ; and 2 are equivalent here. A and M are weakly coupled, M and X are weakly coupled, and A and X are weakly coupled. So, this is nomenclature we use.



A_3X_2

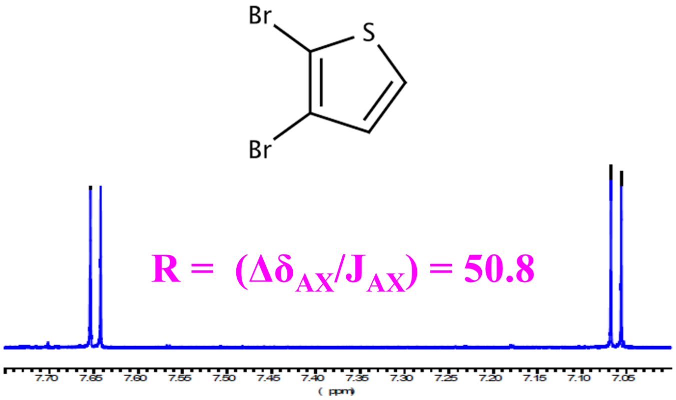


A_3MX_2

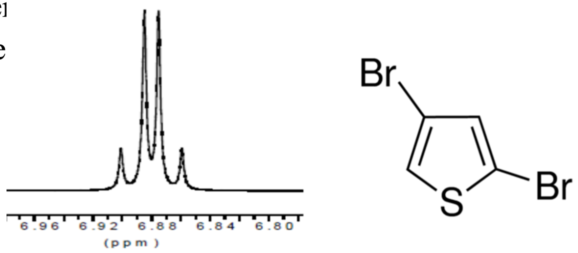


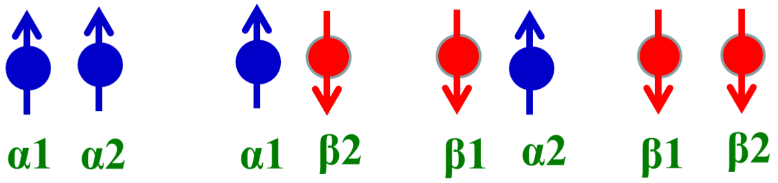
Here is an example. Look at a molecule like this. Here there are 3 protons which are chemically equivalent; 2 protons which are equivalent; CH3 and CH2 groups. It is a simple classic example of ethyl alcohol. What is the nomenclature for this spin system? A3X2. I am not worried about OH group. This? is called A3X2 spin system.

What about this molecule? we have a CH3 group here, CH2 group here; and a CH group here. Of course 3 protons are there, this subscript is 3; this subscript is 2, and subscript is 1. You call this as A3MX2 spin system. It is an A3MX2 spin system. What about this molecule? there is CH3 group, we have a CH2 here ,we have CH2 here. This is assuming they are far away separated, they are weakly coupled. I call it as A3M2X2 spin system.



We will take example as how we look at the spectrum of some of the molecules. Here is a molecule, I consider 2 protons which are homo nuclear weakly coupled spin system. Why I say they are weakly coupled? Measure this separation; I have given you chemical shift of one of the protons, let us say A; the other is X. One is 3830 chemical shift in frequency, and the other is 3530. The difference is almost 300 Hz, and the coupling measured is 5 or 5.77. What is the ratio 300 divided by 5. The chemical shift delta delta difference over J coupling is almost 60. That means it is a weakly coupled spin system. Delta delta difference, if you measure the difference, this is already calculated and look at this intensity, they are of equal intensity, almost of equal intensity. And the chemical shift separation is so large, very easy to analyze this is AX spin system. All I have to do is go to the center of this doublet I get chemical shift of this; go to the center of this doublet I get chemical shift of this proton. If this is A, this is X. I get delta A here I get delta X here. I can get the chemical shift I measure this separation this gives you J_{AX}. I measure this separation exactlyI get J_{AX} because interactions are mutual, it is a straight forward analysis. This is called first order analysis. So the first order analysis is possible in weakly coupled case. I can get J couplings and chemical shifts by just looking at the spectrum, by simple analysis. And look at it all the lines are of equal intensity, whereas look at this molecule, he d. Look at this peak here two central lines are nes, which are of weaker intensity. And also look at it it is tilted like this. This is called a roof effect. And if I measure the chemical shift separation between these two, see actually there is a small change in the chemical shift and this chemical shift depends between 1 and 2 and 2 3 and 4 if you consider there are four different peaks, four chemical shift frequencies have been written. All the four frequencies for all the four peaks are here. What you can do is measure the separation between these two lines this is about 688.7 okay, make it 688. Whereas, this separation if you measure, this to this, the average is 687. You see the difference is very small. Okay, here it is written JAB, Already here the chemical shift operation is about two hertz, you have worked out chemical shift difference between any of these two peaks if we consider, I do not know which is A and which is B, I cannot say. I cannot say what is chemical shift A and chemical shift B here. Somehow let us say I measure the separation between these two lines; and these two lines; and this is delta AB is delta υAB or delta delta AB is 1.9 or 2 Hertz. Whereas, the coupling is quite large about 3 hertz. If you take the ratio this is much smaller. See this is not 0.01 or 0.001 like that to be weakly coupled. This ratio tells me, these two protons are strongly coupled. And in the case of roof effect always what happens? the some lines will be of equal intensity; and then this tells me this is coupled in this direction; if this is weak intensity this tells me it is coupled in this direction; see this intensity is larger than this. So it is coupled here, this intensity is smaller than this. This is coupled this way. So the direction of tilting, the direction in which the intensity is changing tells you which proton is coupled to which proton. This proton is coupled to this, this is coupled to this. It is called roof effect and roof effect is a dominant phenomena you will see in strongly coupled spins. And in the weakly coupled spins intensities are equal. The roof effect will not be seen. The roof effect is seen in the strongly coupled spins. Take for example this molecule 2,3 dibromothoephene; at 100 MHz, this is the spectrum you are going to get, But you can see this and this are far away



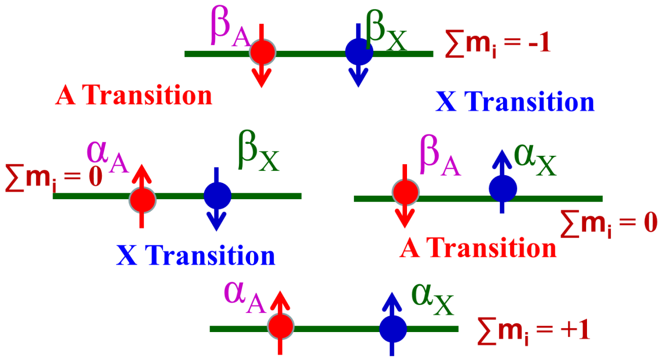


separated in chemical shift; but you see the intensities are not equal; there is a roof effect in this direction. That means it is more close to AB than AX. The chemical shift separation if you see, you can say what is the chemical shift of this, the chemical shift of this more like an AX, but if you look at the intensity pattern there is an AB character, this has a minute AB character in the AX spin system. So it could be AB, because of the intensity. If you look at the chemical shift it could be AX. So it is the AX with the AB character, minute AB string is there in that. So in the spectrum because intensities are not equal, you have to calculate it, because it is a strongly coupled case. With this now we will take the examples of transitions you see in two coupled spins case. How do we get the transitions? how do you measure the frequencies in the coupled spins. This is the real analysis we have to start. Part of it is already discussed when I was explaining to you about the chemical shifts and J couplings between the two spins. I explained to you about the transitions we get in two coupled spins.

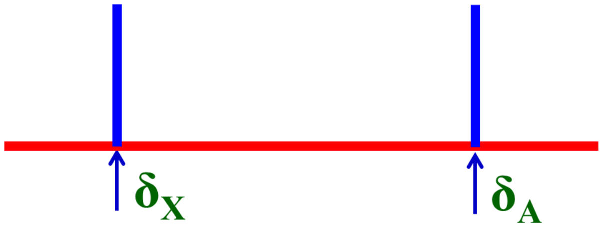
Each spin sees the other spin states of the other spin. There will be four possible spin states when two protons are coupled. Or two spins are coupled which I explained to you; alpha alpha, beta beta, both are down, both are up alpha alpha, one up one down alpha beta, beta alpha. We already explained this and the magnetic energy states of each of them are different. The magnetic energies are different. There are four different energy states. The small difference in the energies are there and then we can get the total magnetic quantum number for each of the energy states.

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

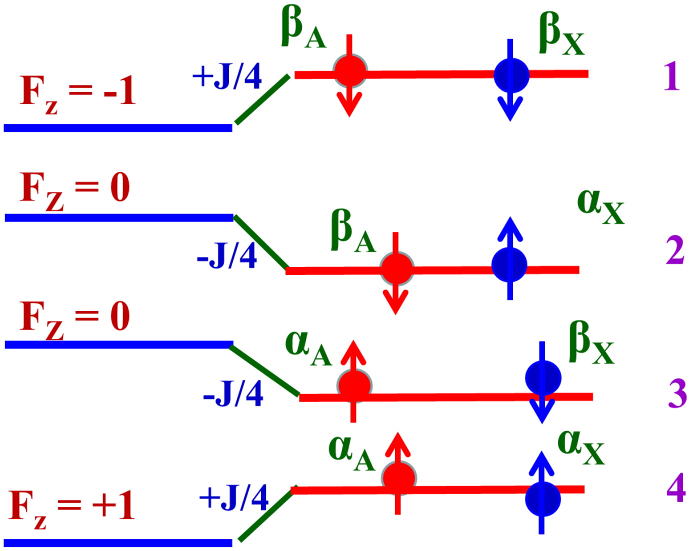
The total magnetic quantum number is the sum of mzA and mzX. That is what we have been discussing. I did not write explicitly mathematically, I did not work out, but I told you when both are alpha alpha states, plus half and plus half, the total quantum magnetic quantum number of that energy state is plus one. One is plus half other is minus half, the total magnetic quantum number of that energy state is zero, because it is a sum of mzA and mzX. For two spins mzA and mzX individually when you write, for the particular state the sum is mzA plus mzX. So as a consequence that is zero. Finally here plus half minus half; zero minus half minus half, minus one. The FZ is the sum of the magnetic quantum numbers of each energy state. The spins can be both interacting and non-interacting, that is what I said. If they are interacting means coupling is non-zero, when there is no interaction coupling is zero. Still they can be coupled spins but coupling can be zero and if it is non-zero it is different. Of course we call them as uncoupled spins when the coupling is zero. The transition in the two uncoupled spins if I consider.



Let us understand how do we get the transitions into coupled spins. Of course the chemical shifts are different, delta A is not equal to delta X, and coupling I made it zero. This is my condition. I have put to understand the transition that we see in two uncoupled spin half nuclei. Of course this we worked out βA and βX are the two spins which are having orientation minus half minus half; This alpha A and alpha X, plus half plus half orientation; plus half minus half; minus half plus half orientation. The magnetic quantum number FZ is mzA plus mzX which you worked out, minus one, plus one, zero, and zero. The selection rule we apply that I have already discussed. When I explained I took this example this transition is allowed minus one to zero transition where alpha spin is flipping alpha to beta beta to alpha, that is allowed, A transition. This also allowed alpha A to beta A is flipping from zero to plus one, that is A transition. This is zero to plus one is allowed, zero to minus one is also allowed. Here alpha X spin is changing, from alpha to beta, X transition. This is also allowed where alpha to beta of X is flipping, X transition. So two peaks for A with identical frequency and two peaks for for X with identical frequencies are there. But identical frequencies overlap.



Remember there are two frequencies here, both are of identical frequencyfor A, identical frequency for X. Both the transitions have same frequency. That means there is a overlap of the frequencies. As a consequence if there is no coupling each of them, A will give a single line, X will give a single line. That is what we understood. A will give a single line X will give a single line. We assume chemical shift of one of them is larger than the other one. Whichever is larger or whichever is smaller that is our assumption. I assumed here chemical shift of X is more than that than that of A. So X comes here; A comes here. And this is the chemical shift of A, this is the X chemical shift. Remember both are of equal intensity, but appears as a single line. But there are two lines overlapped, there are two transitions for A two transitions for X. They are overlapped and gives rise to single peak. This is the spectrum of two protons or two spins which are not coupled. That mean or in other words JAX is 0.



Let us consider the example of two spin half nuclei where coupling is there, that means J AX is nonzero and chemical shift is not same. They are not equivalent spins; chemical shifts are different, the coupling is nonzero. And I assume the chemical shift difference between A and X is sufficiently larger than JAX. Why did I assume? I assumed because I consider weakly coupled spins. Remember the nomenclature which we discussed so two weakly coupled, the nomenclature is AX. So the chemical shift separation between A and X is sufficiently larger than the coupling constant. That is a weakly coupled case and I have considered the example of two weakly coupled spin half nuclei. In this case we have to understand little bit more about what happens to the energy states when the spins interact. Remember in one of the cases, I also explained to you the energy levels gets modified because mzA and mzX, when they have the same signs, alpha alpha and beta states, the states they are called unpaired states, they are unpaired spins, their alignment is less stable because they are unpaired. They have more energy. If I consider mzA and mzX they have same signs. Thus alpha alpha and beta beta have more energy. If I consider alpha and alpha beta beta they are destabilized ,the energies will be pushed up by J/4 because they are unstable, they are less stable; not unstable I would say less stable, they are destabilized; and the energy will be pushed up by J/4. What about other spin state?s consider alpha beta and beta alpha they have plus half and minus half, they are paired when they are paired their alignment is more stable. Like spins are always you know are destabilized, more energy. These have less energy because they are stable. They are paired, so alpha beta and beta alpha are paired states. Then what will happen? the energy will be pushed down. What is the energy? how much energy is pushed down compared to alpha alpha and beta beta ?they are pushed up by J/4; here they are paired state they are push down by J/4. You understand the difference. If you consider the energy states, alpha alpha and beta beta are pushed up because they are unpaired states, and unpaired spins. Whereas alpha beta and beta alpha energy states are pushed down as they are decreased by J/4. So this is what happens. In the earlier case both the energy states were identical. There was no pushing up there was no stabilization or destabilization because coupling was 0. Now the coupling I have assumed, there exists a coupling between A and X spins. Now this state beta beta is pushed up by J/4 alpha alpha is pushed up by J/4. Whereas beta alpha and alpha beta are pushed down by J/4. See energy states are now not same, they are different. Butt remember what is the energy if you can calculate the transition between different states, I consider 1 2 and 3 4 energy states. We will find out what is the transition 1 3. It is allowed where A is flipping. And 2 4 is allowed again A is flipping. But look at this frequency separation compared to this frequency separation. This frequency is larger because delta E separation is larger compared to this. That means they are not of the identical frequencies. In the previous example when they were uncoupled, the frequencies were same. But here the frequencies are different. One has a larger frequency and the other as a smaller frequency. The larger frequency you see is different and smaller frequency is different, because one is pushed up by J/4 other is pushed down by J/4. Similarly for X spin 1 2 and 3 4 transitions are allowed. This is allowed see 1 2 frequency is larger because of energy larger separation larger and 3 4 frequency smaller compared to 1 2. So X spin also has two frequencies X spin has two frequencies; one is larger frequency other is smaller frequency. Yes two frequencies, one is larger, other is smaller. And how much it is? Tthat you can work out you can calculate mathematically, which I am not going to do that, because this has been already discussed in one of my previous course. Without going into rigorous mathematics I tell you four energy states alpha alpha; alpha beta and beta alpha and beta beta are like this.

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**	**$\frac{1}{2}\nu - \frac{1}{2}\nu - \frac{1}{4}J$**

You can calculate eigenvalues. **$\frac{1}{2}\nu_A + \frac{1}{2}\nu_X + \frac{1}{4}J_{AX}$** for this one; **$\frac{1}{2}\nu_A - \frac{1}{2}\nu_X - \frac{1}{4}J_{AX}$** for this one; **$-\frac{1}{2}\nu_A + \frac{1}{2}\nu_X - \frac{1}{4}J_{AX}$** and **$-\frac{1}{2}\nu_A - \frac{1}{2}\nu_X + \frac{1}{4}J_{AX}$.** Very easily you can calculate quantum mechanically. You can work out the Eigenvalues and then the difference in the eigenvalues gives you the frequencies. For example 1 and 2 if you calculate here, go back here 1 and 2, you take this 1 and 2 and calculate the difference. If you take the diff this number is by mistake cut and paste while I made a mistake it is not this 1 and 2 this is different. And if you calculate that difference then this will turn out to be **($\nu_X + \frac{1}{2} J_{AX}$),** so that means for the x-pin there are two transitions. One is +1/2 J_{AX} other is -1/2 J_{AX}. There are two frequencies for the x-spin. Similarly you can calculate for 1 3 and 2 4 one is +1/2J_{AX} with respect to υA other is -1/2JAX with respect to υa. One gives chemical shift of A plus half of 2J_{AX} other is chemical shift of a minus half of 2J_{AX}. So essentially what happened, if you calculate mathematically, quantum mechanically you have to write down the Hamiltonian diagonalize the Hamiltonian, calculate the eigenvalues get the frequencies and get the difference of the frequencies by applying your selection rules. You can see that proton A will give 2 peaks, one is shifted up from delta A by the +1/2J_{AX} other is shifted by delta a -1/2J_{AX}. Similarly proton X will give 2 peaks. One is shifted from chemical shift of X by +1/2J_{AX} other is shifted from chemical shift of X by -1/2J_{AX}. That means proton A will give 2 peaks from the center moved by same value from the center on either side. Same way with delta X there are two peaks from the center one moved by +1/2J_{AX} other is more by -1/2J_{AX}. You get four peaks for two coupled spin system, maximum of four peaks. Okay, two for A and two for X. The centre of this doublet gives me chemical shift of A; the center of this doublet gives me chemical shift of X. And as I showed you they moved just exactly by plus J/2 and minus J/2 from the centre, if you take the difference we get J_{AX}. Similarly you take the difference you get J_{AX} So, when two protons are coupled the chemical shift of one of the doublet gives a chemical shift of A, the centre of the other doublet gives you chemical shift of a X, and that their separation always gives you J_{AX}. Whether you take this separation or this separation the separation gives you J_{AX}. So that is what I said. The two coupled spins gives maximum four peaks. For N couple spins like this we can calculate. I will come to that later. Today the time is up, I am going to stop it. What I am going to tell you is in this class what we discussed, we understood more about the Pople nomenclature for the equivalent spins, the chemically equivalent spins and when there are group of spins, for example CH2 groups; CH3 groups like that. When there are spins that are chemically equivalent then we use a subscript notation. For chemically equivalent I said we use prime notation. Again prime notation can be used for weakly coupled and strongly coupled. For example weakly coupled we can use AA'XX' ; for strongly coupled we can use AA'BB' ; and for equivalent spins we can say A2'B2'; or AA'BB'. Whereas in the weakly coupled case you can say A2X2, A2'X2' like that. Varieties of nomenclatures we can use, and I took the example of two spins with J coupling 0 and J coupling nonzero. And I wrote down the energy states for alpha alpha, beta beta, alpha beta, and beta alpha It is nothing but the total magnetic quantum number. It is nothing Fz which is mzA + mzX. For beta beta it is minus 1, for alpha alpha it is plus 1, for alpha beta it is 0, for beta alpha it is 0. And for Jax 0 we get two transitions. of identical frequencies for A, which overlap. Similarly two frequencies for X that are identical and overlapped. We get two singlets only. Whereas if there is are J couplin, the alpha alpha and beta beta spins are unpaired. As a consequence that these states are stabilized; and these energies are pushed up by J/4, when there is an interaction. Whereas alpha beta and beta alpha are paired spins. Their energies are more stabilized; pushed down by J/4. Now if we calculate the frequencies; in the coupled case, we found out we will have two frequencies, one pushed by +J/2 other by -J/2. That means from the center you have one peak which is moved by J/2 and the one peak which is moved by J/ 2. One is moved to the left and the other is moved to the right. The separation gives you J. Similarly for X spin from the center of the doublet one peak is moved by J/2 to the left and the other is moved by J/2 to the right. And the difference gives you J_{AX} . The center of this doublet gives you chemical shift. Like this for two coupled spins, we showed there are only four possible transitions, okay. Two for A and two for X. We discuss later what happens when we have more coupled spins, how many peaks we get, etc in the next class. I am going to stop here. We will discuss more things in the next class. Thank you very much