NMR Spectroscopy for Chemists and Biologists
Doctor Ashutosh Kumar
Professor Ramkrishna Hosur
Department of Biosciences and Bioengineering
Indian Institute of Technology, Bombay
Lecture No. 07
Spin-Spin Coupling

Hello, welcome to today's lecture. So we were discussing high resolution NMR spectra of molecules. If you remember in the last class, we had discussed how to make chemical shift field independent

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Because we remember that like if we record chemical shift at different field in terms of frequency or in terms of Hertz the values were changing. So to get rid of that we started looking at the, how to express the chemical shift in ppm value and that ppm value made it independent of field. Then we looked at, that for referencing we need some compound which is inert and does not react with the solvent and the molecule of our interest. And therefore TMS and DSS were obvious choice because their resonance comes quite up field shifted or lower ppm value, they are water, like TMS is highly shielded and that is why it is used as a reference. DSS on the other hand is water soluble and it does not interact with any biomolecules.

And it is used for water soluble compound. So next we looked at the, what are the factors that influence chemical shift and out of those many factors we looked at what ring current can do? So ring current effect we had looked at and ring current is one which causes the downfield

shift or higher ppm value shift of resonance of C-H protons of aromatic compounds. Then we also looked at the contact effect. This is this comes because some unpaired electrons are present and that can shift, chemical shift significantly. Then after that we looked at the chemical shift variation due to different nuclei attached and that all we have summarized in the last class. So now from here we will move forward and we start looking at actually, now the another very, very crucial parameter that is called spin-spin coupling.
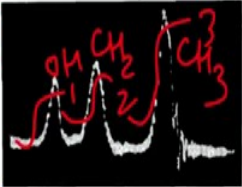
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Or this is also called J-coupling or scalar coupling. So let us start looking each of these parameter together. This is also called J-coupling. Scalar coupling, because this does not depend upon orientation and this is also called as scalar coupling. Now so we had looked at the first chemical shift spectra that were recorded on ethyl alcohol on 40 Mega Hertz and it gave 3 line. The first line corresponds to CH_3, methyl proton, methylene proton and this is for OH proton, so this was for OH, this was CH_2 and this is for CH_3. And the height of each of these peak was like 3 to 2 to 1. That is what we had looked at. So this was the first spectrum recorded by Dharmatti and co-workers and then that actually opened the avenue of NMR in chemistry.

Now in the same year, almost in 50-51, Proctor and Wu discovered one of the very, very important parameter which is called actually the coupling constant. This helps in unambiguous characterization of molecule. So today we will look at how actually it helps in unambiguous characterization of molecule. So what happens that in the high resolution spectrum, actually the one line of methyl proton that we had looked at here is not actually one line.
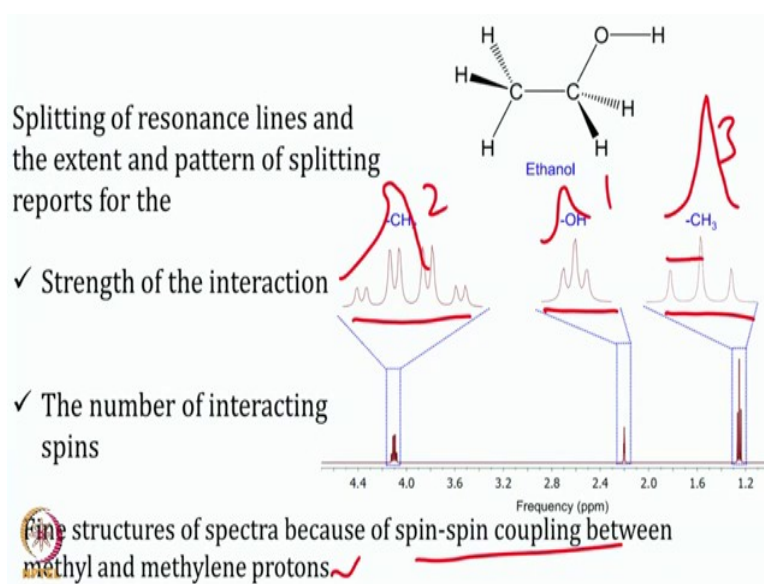
However, it is splitted into three lines and that is what here we see. In case of methylene actually this is also not one line and it is splitted into many lines and similarly OH also splits into many lines. This splitting of this resonance of line and the extent of this splitting, extent of this splitting actually reports for what is the extent of interaction between various spins and how these spins are interacting?

So this actually, this splitting pattern helps us in identifying the final structure of the molecule because the spin-spin coupling between the methyl and methylene proton, actually it tells the neighboring group effect and this is due to something called J-coupling or spin-spin coupling or scalar coupling.

So just to remind you here we should have, if there is no coupling then in case of methyl there was only one peak here and here also there was one peak. And this is also one peak. Now this was 3, 1, 2. Now if you look at here, this OH, it is coming slightly up field shifted than like CH_2 and these spectra was recorded on generally, very like neat alcohol, pure alcohol. So now we move forward and we look at how does this splitting occurs. So what is the reason behind spin-spin coupling or J-coupling?

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So this happens because of interaction of mediated by the electron in the intervening bond. So in a simple term what is happened like we had looked at the chemical shift is because there is a spin and around that there are electronic clouds. Now if you look at, these spins is not in isolation. There is another spin which is near here and that spin can influence the chemical shift or the resonance properties of this spin and that coupling happens via the electrons that are between them. So that is why this is called through bond coupling, so through bond coupling because the two spins are now coupled via electron so in the bond that is intervening here. So a nuclear spin can polarize the electron spin adjacent to the bond orbital here, it can polarize it.

And that polarizes the spin parameter of electron in the same orbital. So that can affect this one. And then what happens, this is through bond so can extend up to 4 to 5 bond but as you go far and far the strength of that effect decreases. Therefore, the J-coupling becomes smaller and smaller as we move far and far. So the strength of the coupling is called coupling constant or J-coupling. So that means how much this spin affects its neighboring spin through bond, it is called J-coupling. And as we say, as we move from one spin to two spin this is quite strong but if you look at the strength of third spin the J-coupling spin decreases because we are moving now far from spin number 1 to 2 to 3. Now what is happening here?
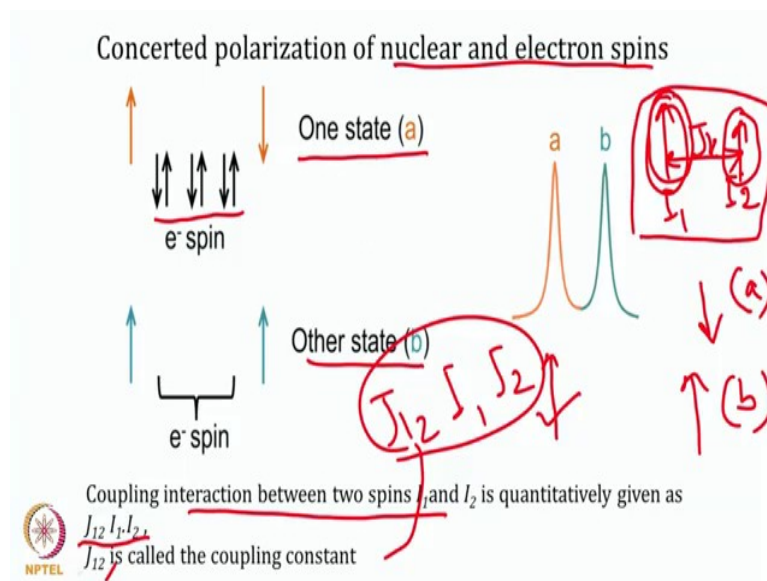
It is a concerted polarization of a nuclear spin and electron spin. So in simple term, suppose we have two spins here, spin and, and there are some electron spin in-between so what is happening? Now if we are concentrating spin number 1, then it is near there is another spin, and that spin can exist into two form, either up form or down form, so spin state a and spin state b. So because of this orientation, now this is our interest spin and this is its neighboring spin. So it has different state, spin state 1, 1 state a and state b. So now this is influencing the electronic spin which is between these two spins and that is here, that is shown here.

So then the coupling interaction between these spins I_1 and I_2 each quantitatively given by spin interaction which is called J_{12}, I_1 and I_2. So this is the coupling strength, where J_{12} is a coupling constant. So in a simple term if there is a spin here and if there is another spin here, now this spin is affecting the resonance frequency of this, because spin number 2 here, I2 and I_1, so this is I_1 and this is I_2, so the interaction occurring between them because of this coupling is J_{12}. So now the resonance frequency of I_1 is affected by I_2 and vice versa. And that is called spin-spin coupling or the scalar coupling.

So let us define two spins like A and X. Now as we see is that if these two spins are close by and they are connected by bond then there is a there is a coupling between them which is called J-coupling. Now then what happens, energy of spin A and now actually it has two Zeeman states. So like here spin A, I_A, then it has two Zeeman spin, alpha state and beta state. Now depends upon, this state depends upon whether the X spin is in alpha state or beta state. So I_A, this state depends on whether the X spin is in α state or X spin is in β state. That affects the resonance frequency of this.

And this coupling can be positive, so because of that what will happen between these two states, now there are two spins as we discussed, spin A and say spin X. Now spin A has two

states, α and β state. And similarly X spin has α and β state. So now because of this, there are four state can be possible. αα, αβ, βα and $\beta\beta$. What it means, in terms of vector, so here is α state and this is β state. Here is also α state and β state. So it can be up up both spin, up down, down up and down down. That is all we were discussing.

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So because of this the all states that we were discussing, it can exist here, αα, αβ, βα and $\beta\beta$ state. And these states will have different energy. So because now A spin is not in isolation, it is coupled with B spin, therefore this different energy will be. So coupling between them is positive if the energy of alpha state of spin A increases. That means if the energy changes here. And if it increases and increases for X spin that is in α state, and it decreases if X spin is in β state.

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So what we are saying, the energies of spin A and B can change so suppose here, here is the energy of A spin. It can decrease or increase depending upon if the X spin is in α state or β state. It can increase or decrease.

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Let us have two $I=1/2$ spins say A and X

There is a J-coupling between A and X
then energy of spin A in any of its two Zeeman states α and β
depends upon whether the **spin X is in the α or the β state**

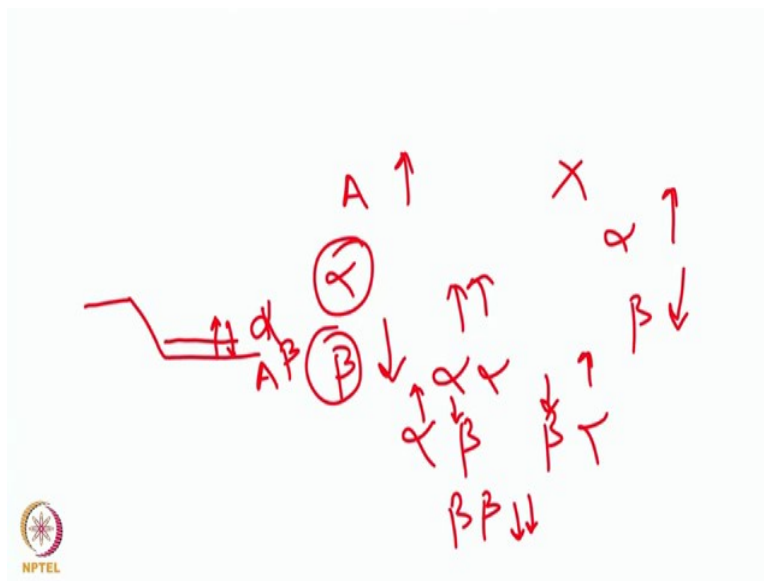Spin configurations $\alpha\alpha$, $\alpha\beta$, $\beta\alpha$, and $\beta\beta$ will have different energies

Coupling is **positive** if the energy of the α state of A spin increases for the X spin in the α state and decreases for the X spin in the β state

The energy of the β state of A spin will increase if the X spin is in the β state and will decrease if the X spin is in the α state

Now that is what we call couple is positive. However, the energy of β state of spin A will increase if the X spin is in the β state. So if X spin is in β state then it will increase and it will decrease if X spin is in α state. So that actually changes. So that is what, now we can understood.

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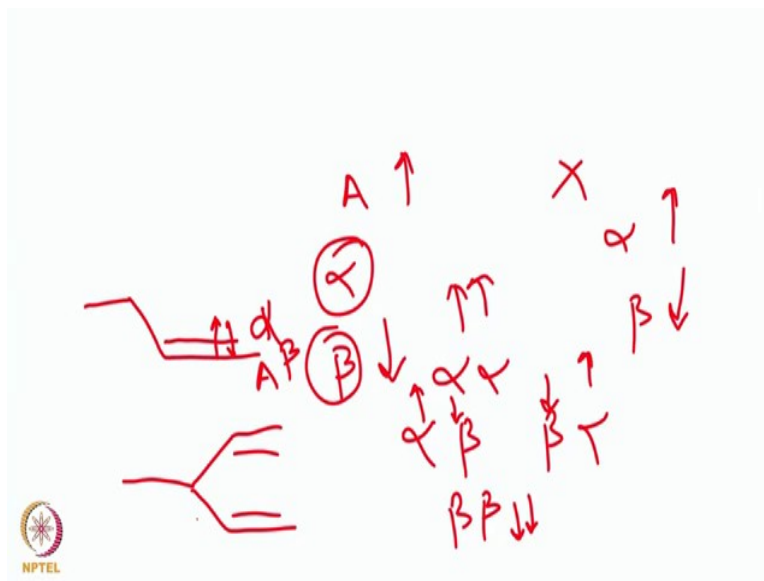
So instead of now two energy here, it can be depending upon whether what is the state of B and we can have four states here depending upon whether B is in α state or β state.

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Energy level representation of a two spin (A and X) spin ½ system

when A is coupled with X, two transitions, $\alpha_A\alpha_X \rightarrow \beta_A\alpha_X$ and $\alpha_A\beta_X \rightarrow \beta_A\beta_X$ are possible.

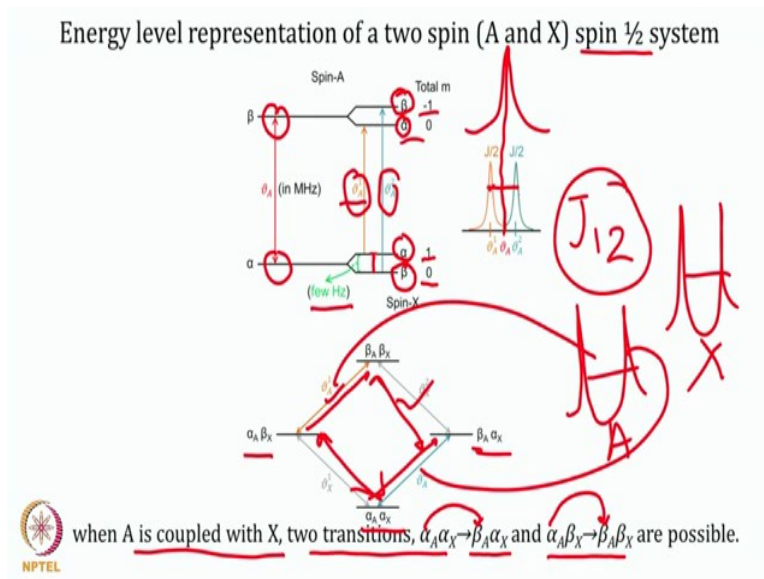So that is what it is shown here. So again I will repeat it. So say, spin A has two energy level, one for α state, one for β state. Now depending upon what is the orientation of spin X, if it is β state or α state, so here if you look at this energy level is changing. If it is β state, the energy is decreasing. If it is in α state, energy is increasing. And the separation between two states is only few Hertz. Similarly, here also the energy of β state also has changed depending upon whether X is in beta state or alpha state. So there are four energy level now created,
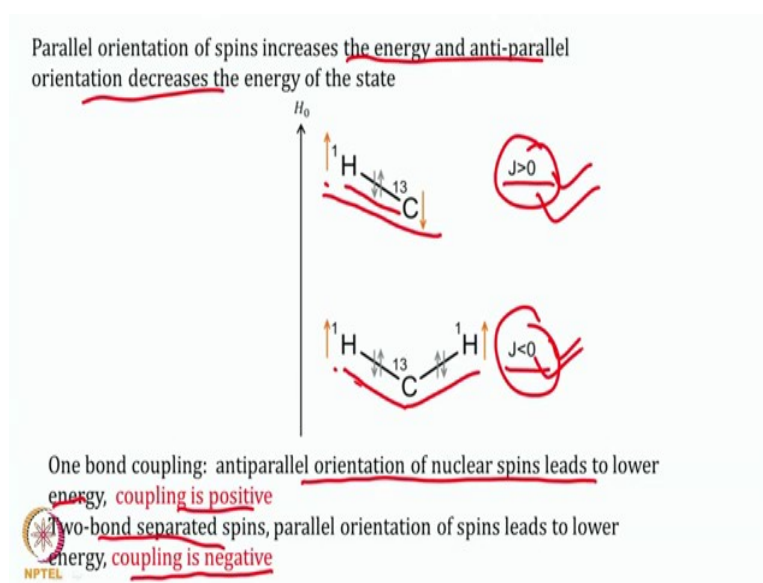
depending upon whether the X spin is in β state or α state, so we can call this as a, like $\alpha\beta$ state as a 0, $\alpha\alpha$ state as a 1, here $\beta\alpha$ state as a 0, and $\beta\beta$ state as -1.

So now the resonance for the spin A will have two lines, one will be δ_{1A}, so this is first line and this would be second line. Therefore, the now, earlier which was only one line here, centered at the δ_A, now it will be splitted into two line. And that separation between these two line will be J_{12} or J-coupling between these two states. So if we look at the energy level diagram so if $\alpha\alpha$ is, $\alpha\alpha$ state, that is α_A, α_X is this, $\alpha\beta$ is this, $\beta\alpha$ is this, $\beta\beta$ is this.

So now we have four energy states, one coming from here, if the first spin is changing its state that is α is going to β and here also if α is going to β, here again we have the energy state. So now spin A we have two lines, one corresponds to this and another corresponds to this. Similarly, it will happen also for β and that will be given by these two lines here.

So if A is coupled with X, X has split A into two line, similarly if A is ½I and X is also ½I spin as we said , so X will be also split into two lines. So these are for A spin, this is for X spin. So now that is the final structure. So now when A is coupled with X the transition will be called α_{AX}, β_{AX}. So this is here, if you look at, A is splitting. Similarly, here again A is splitting. And that is what this and this line corresponds to, this and this line corresponds to.

Parallel orientation of spins increases the energy and anti-parallel orientation decreases the energy of the state

One bond coupling: antiparallel orientation of nuclear spins leads to lower energy, coupling is positive

Two-bond separated spins, parallel orientation of spins leads to lower energy, coupling is negative

So, now as you have seen parallel orientation of these spins increases the energy states and antiparallel will decrease the energy states. So here if you look at, now we are looking at the coupling between this H-C and here it is coupled via C. So if they are antiparallel here, if the parallel orientation of spin increases the energy, where as antiparallel decreases the energy. So here J will be positive and here will be negative.

So in case of one bond coupling like here one bond coupling the antiparallel orientation of nuclear spin leads to lower energy and that coupling is called positive. Whereas two bond separated spin like here, two bond, one bond here, one bond here, two bond separated spin, the parallel orientation of the spins leads to lowering of the energy and this coupling is called negative. So we can have the value of J positive and negative. So now depending upon how the orientation of each spins the value is also changing.

But one thing to remember, this J-coupling is field independent. Chemical shift was field dependent when we expressed that in ppm value it become field independent. J-coupling, invariably it is field independent. So positive and negative sign depends on the orientation but does not depend upon which field we are recording. This is a constant value.
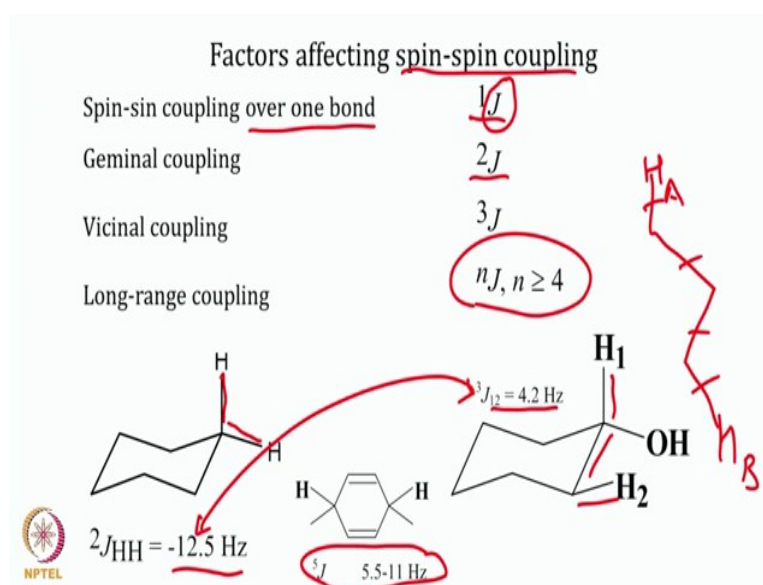
So what are the factors that influence the spin-spin coupling or J-coupling? So first as we see the closeness of two spins dictates what will be the strength of bond, because these spins are coupled via a bond and in bond there are electron. So spin-spin coupling for one bond is denoted by ^1J, like here J is the scalar coupling and 1 denotes the 1 bond value. Now the geminal coupling which is say is two bonds, so here the two bonds are called here like one bond here and one bond. So these are two bond coupling. Now vicinal coupling is called three bond coupling. So if you look at one bond, two bond and three bond coupling. Similarly, long range can be like more than 4 bond coupling.

So depending upon 1 bond, 2 bond, 3 bond, 4 bond coupling so H here and H here will be 4 bond coupling if it is connected like this. Or 1, 2, 3, 4, so that is more than, this is called long range coupling. So if you look as the distance is increasing, the strength of the coupling will decrease, because this is connected through bond. So as for an example if you look at two bond coupling and we are saying this is *-12.5*, 3 bond coupling is *4.2*. However, depending upon how they are oriented, if long range coupling like 5 bond is *5.5* to *11* Hertz. But if you compare 2 to 3, actually as we move further the coupling constant strength is decreasing.

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So there are range of coupling constant. So a homonuclear coupling are generally small compared to heteronuclear, so proton-proton like two bond coupling is generally 5 to 20 Hertz, whereas 1 bond coupling in heteronuclear system like ^{13}C and proton it is quite a bit, 100 to 250 Hertz. For nitrogen proton coupling here, it is 80 to 100 Hertz. And then phosphorus proton coupling is typically around 7 to 12 Hertz. Now here if you take 3 bond coupling this decreases, 4 bond coupling further can decrease the proton proton coupling. However, this is called homonuclear coupling and these will be called heteronuclear coupling because that is between proton and proton and here our X nuclei like ^{13}C, ^{15}N and phosphorus are there.

Till now we have understood that there is one parameter which is important is chemical shift. The another parameter is important, coupling constant. Coupling constant is coming because of another spin coupled to the spin of our choice and this coupling is happening via electronic bond. And as we move further the strength can decrease but this splitting, the splitting caused because of this J-coupling or scalar coupling. So now these two parameters, chemical shift value and J-coupling, these two are very important parameter because these are required for high resolution NMR spectrum analysis for any molecule, even small molecule or bigger molecule.

Analysis of NMR spectra of molecules

Two Important parameters of a molecule:

➤ Chemical Shift (δ-Values) : Particular Nuclei ✓

➤ Coupling constant (J-Values) : Interaction between those Nuclei

Basic Analysis is done on the basis of 1st order analysis

: Certain Basic rule

More complex one requires Quantum mechanical calculations

Now as we looked at the chemical shift value is for a particular nuclei. So that gives the particular resonance frequency for a nuclei. And this is denoted by delta value. So that is chemical shift value. The coupling constant actually determines the interaction between those nuclei. So particular spin will have a chemical shift and another spin will have another chemical shift and how strongly they are coupled or how strongly or weakly they are interacting, that is given by J value. So the basic analysis for any molecule requires these two parameters, their chemical shift value and the coupling constant between these two.

If you know these value one can identify the molecule. So this basic analysis of any molecule is done by using these two parameters and this is called first order analysis. And there are certain basic rule to understand what is what is required first order analysis. And then that I am going to come in a minute. But for more complex analysis of these spin-spin coupling you require even more complex formalism and that we will look at later at the course which is called quantum mechanical calculation for, if the spins are too strongly coupled. So now we move to first order analysis. It is the simplest analysis of the molecules. So before we move ahead, we define some of the spins nomenclature.

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And spins are generally defined in terms of upper case of the alphabet like A, B and C. Now a spin will be called *AB* system or *AX* system depending on what kind of chemical shift they have. If their chemical shift is quite close, then they will be they will be called AB system because in alphabet *A* and *B* are close. If their chemical shift is far then they will be called *AX* system if you look at the alphabet, *A* and *X* is quite apart.

So *AX* system these two spin have a resonance frequency that are widely separated, like something say here. This will be *A* and *X*. And on the same magnet, *AB* system will be something like *A* and *B*. Now, so *ABX* system will be like, say *A B* and *X* here, because *A* and *B* are quite close, and *X* is far from them. That is called *ABX* system. Now, so *AB* are fairly close in relation to the, in comparison to *X*. There is another parameter which, which is determined here is called coupling constant. So the coupling between them is called J_{AB} and coupling between them will be called J_{AX}.

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So now here *AX* system because their chemical shift is quite far, *AX* system or *AMX* system or *AMQX* system because they are like separated in the alphabet, these will be called weakly coupled system whereas *AB* system or *ABC* system will be called as strongly coupled system. So what is happening here? *A* and *X*, their chemical shift quite far and the separation between say

$$\delta_A - \delta_X > J_{AX}$$

And this is consideration to define that, as a weakly system whereas

$$\delta_A - \delta_B \approx J_{AB}$$

and this will be called strongly coupled system. So if you look at strongly coupled or weakly coupled system are not reflection of strength of the coupling constant alone, however it is the consideration of the chemical shift. So how far the chemical shift is in comparison to the coupling constant, that determines whether the systems are weakly coupled systems or strongly coupled system. So typically heteronuclear system are weakly coupled system and many of the homonuclear system are strongly coupled system, not all but they are in homonuclear system, we have a strongly coupled system.

So if I look at the ^{13}C chemical shift, like ^{13}C chemical shift and proton chemical shift so here on 600 Megahertz this will be near to 600 Megahertz, chemical shift and this chemical shift will be near to 150 Megahertz. However, the coupling constant between them will be around, say 150 Hertz. So this separation between the chemical shift is quite far from the strength of

coupling constant and these will be weakly coupled system. This cannot be the case for the homonuclear system. Here it can be, like equal as we were saying here or almost equal. These will be strongly coupled system. So first order analysis or simplistic analysis are generally done for weakly coupled system, not for strongly coupled system. For those we need a quantum mechanical calculation to understand.

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Now one more concept I will explain and that, this is called chemically equivalent and magnetically equivalent nuclei. Now a group of nuclei we can define as magnetically equivalent if all of them have a same chemical shift and each of them has a same coupling constant to every other nuclei outside that group. So these will be called magnetically equivalent nuclei.

So similarly like here, A to X, now A here, if you look at here, we have a 3 kind of proton, this proton and this proton will have same chemical shift. And they have the same coupling constant with X. So this will be called magnetically equivalent nuclei. So that is why this system can be written as A_2X that means A_2 are equivalent but that are different from X, that is why A_2X.

So spin coupling between these magnetically equivalent nuclei does not appear in the spectrum. That means the A_2; there the spin coupling between them will not appear in the spectrum whereas the coupling constant between this A and X and this will be appear. So these they are not magnetically equivalent to X. However, among themselves they are magnetically equivalent.

Now look at the another system and here we define as another type of nuclei which is called chemically equivalent nuclei or isochronous. So chemically equivalent nuclei will not be magnetically equivalent if they have a different coupling constant to other nuclei in the molecule. So like, if I look at here, here look at this molecule. The once of this substitution is NO2 and another is OH. Now here the H^X and $H^{X'}$, here H^A and $H^{A'}$, so these are actually chemically equivalent but not magnetically equivalent. So there will be coupling constant between these.
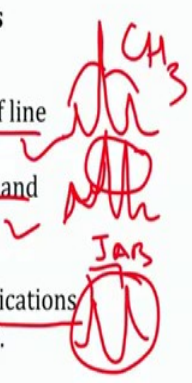
They are not magnetically and there will be coupling constant between them. So they are not magnetically equivalent. They are chemically equivalent. Like, similarly if you look at here, here H^A and H^B they, they are not magnetically equivalent, neither they are chemically equivalent, so there will become coupling constant exist between them. If I look at these nuclei, so fluorine and proton, their resonance frequency is quite, quite close. So they are also, they will be coupled and there will be coupling constant between them and they can be also for different chemical, like they will be not magnetically equivalent neither chemically equivalent.

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So now these all will be important in interpretation of multiplet structure of a compound. Multiplet pattern, so when we do analysis, the multiplet pattern of different groups of line will be different. And that will be also dictated by the relative intensity of individual group like as we see, different group like CH_3 was like this and CH_2 was even more complicated. So CH_2 like it was splitted into four, so that we will look at how this splitting comes from. And intensity, how it changes the intensity so that again is very important when we are interpreting the multiplet structure.

And measurement of coupling constant, what I mean by measurement of coupling constant is this, measuring J_{AB}, from the splitting of individual group is important because that helps in identification of group having same coupling constant. So here this measurement is there. So all these parameters we are going to discuss in detail, the intensity, the pattern as well as the strength. And that helps us in analyzing the first order spectrum of the molecule.

So that I am going to discuss in the next class. How to do the multiplet analysis of different groups and what is the basis of different intensity in the group and how we can measure or how we identify the coupling constant to identify the groups are similar or different, and that all comes under first order of analysis. So if you have any question for today's lecture you are welcome to ask and we will try to respond each and every point that we have discussed for today. Look forward for your attendance in the next class, thank you very much.