Advanced NMR Techniques in Solution and Solid State
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Module 6
Scalar Couplings
Lecture - 06

Welcome all of you. In the last class, we discussed about the chemical shifts, precisely, we understood a lot about chemical shifts, how it comes, what are the factors that account for the chemical shifts, how different functional groups affects the chemical shift; how do you measure the chemical shifts, the reference that we are going to use; how do we express chemical shift in PPM; how do you convert PPM to frequency and frequency to PPM? Varieties of these things we understood.

We also understood about the factors that govern the chemical shift. What happened if there is an electro negativity group substituted; how does the chemical shift changes from low field to high field or high field to low field depending upon electronic donating or withdrawing group, you understood the mesomeric effect. And what happened to the shift, because of the benzene ring current, what happened to the protons situated in the plane of the ring. And what happened to the protons seated above and below the plane of the ring, how they are shielded, where they are coming in the spectrum, whether it is shielded or deshielded; all those factors we understood. And we also said the chemical shifts are the fingerprints for a given molecule. The different functional groups where it comes, by and large is well known. And there is a chart available for different nuclei, not only for protons, but for fluorine, carbon, etc. All those things, I did not show but for varieties of nuclei the charts are available.

If you are looking for fluorine, if you want to look for CF3 represent, where it is coming, where it generally resonates, look at the chart, you will get the approximate range; this you can utilize as a guideline and start the analysis. That is how, the chemical shift information can be utilized and we understood a lot about chemical shifts, but there is no time to discuss much more. But today we will introduce another parameter, internal interaction parameter which I said scalar coupling, which we discussed earlier.

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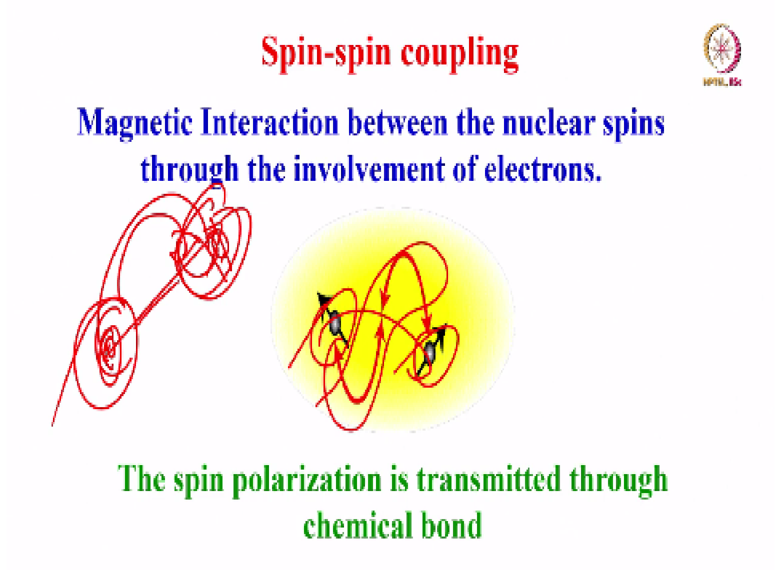

Spin-spin coupling

Magnetic Interaction between the nuclear spins through the involvement of electrons.

The spin polarization is transmitted through chemical bond

The scalar coupling is also called the spin-spin coupling. As the name clearly tells you, the interaction between 2 nuclear spins. Each spin is a tiny magnet, one magnet can interact with another magnet with each other. And this interaction arises due to the involvement of the electron surrounding it. That means, if you consider a C-H proton C-H bond, there is a carbon, this nucleus is surrounded by electrons and this also has a nucleus surrounded by electrons. This electron interacts with this electron and in turn interacts with nucleus. This nuclear spin interacts with this nuclear spin, where the magnetization or spin polarization is transferred from one nuclear spin to another nuclear spin through covalent bond, through the chemical bond. This is an interaction between 2 nuclear spins mediated through covalent bond, and the magnetic interaction is one of the important interaction which is responsible for giving rise to a multiplicity of different functional groups. In the chemicals shift we did not discuss about the multiplicities.

You will see a peak, let us say without any coupling; you get a single peak but once one proton interacts with another proton, then we are going to get the polarization transfer taking place between one proton to other proton. Depending upon the extent of interaction, strength of interaction, we get different multiplicity patterns. That is what we are going to understand today. How this splitting comes, how the multiplicity pattern gets affected.

So, this is the major concept. Remember, the spin-spin coupling arises because of interaction between the two nuclear spin mediated through covalent bond. Without going into more details, let me tell you something about the salient points of the scalar couplings. Scalar couplings are generally represented by J_{IJ}, I and J are the 2 interacting nuclei. Always we discuss about interaction between 2 nuclei, 1 nuclei can interact with many other nuclei. No problem I will show you that now; for any 2 interacting nuclei I and J, the interaction strength that is the scalar coupling is given by JIJ.

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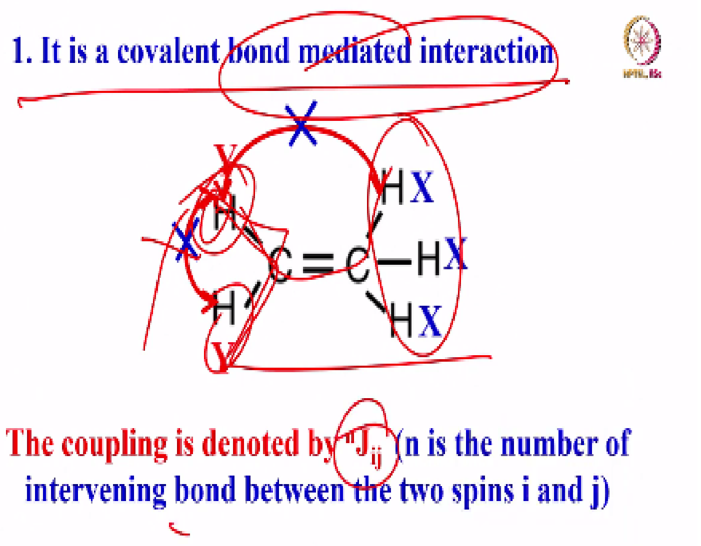

1. It is a covalent bond mediated interaction

The coupling is denoted by ${}^{n}J_{ij}$ (n is the number of intervening bond between the two spins i and j)

Now, these are the few points you should remember. First of all it is a covalent bond mediated interaction; not a through space interaction. Consider a molecule like this, now, this proton can interact with these 2 protons through covalent bond like this. And this proton can interact with any of these protons or all the 3 protons through bond like this; and there is no way it can interact like this. There is no way it can interact like this, that is not possible. This is through space interaction, there is a dipole interaction which is a different thing which we are not discussing. But scalar coupling is always mediated through covalent bond. It is go only through bonds. And J coupling is denoted by ${}^{n}J_{ij}$, where n is the number of intervening bonds between the two spins i and j. For example, in this case, there are 2 intervening bonds. In this case 1, 2 and 3 there are 3 bonds intervening between these i and j.

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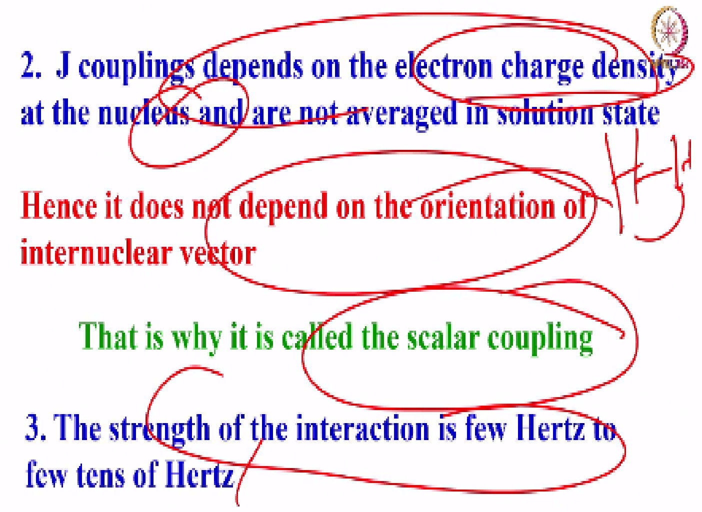

2. J couplings depends on the electron charge density at the nucleus and are not averaged in solution state

Hence it does not depend on the orientation of internuclear vector

That is why it is called the scalar coupling

3. The strength of the interaction is few Hertz to few tens of Hertz

And J coupling depends on the electron charge density at the nucleus and is not averaged out in solution state. Remember, J coupling also depends upon the charge density at the nucleus, but in the solution state, they are not averaged out unlike dipolar couplings. That is why they are not going to depend upon the orientation of internuclear vector. Hence, they are called scalar couplings; because they are not orientation dependent. It does not depend upon the orientation internuclear vector. As a consequence, J coupling is called a scalar coupling, it is just the number and the strength of the interaction always vary from few Hertz to few tens of Hertz. Of course, depending upon the nuclei of your interest. If I consider 2 protons, depending upon the number of bonds, they are separated, the coupling constant can be different; it can be few Hertz to few 10's of Hertz. For hetero nuclei it is even more larger, there are examples in some exotic nuclei, the coupling constant could be very, very large; of the order of thousands of Hertz. It is possible to several 1000s of Hertz; that is also possible. But remember for proton when you are talking, it is few Hertz to few 10's of Hertz.

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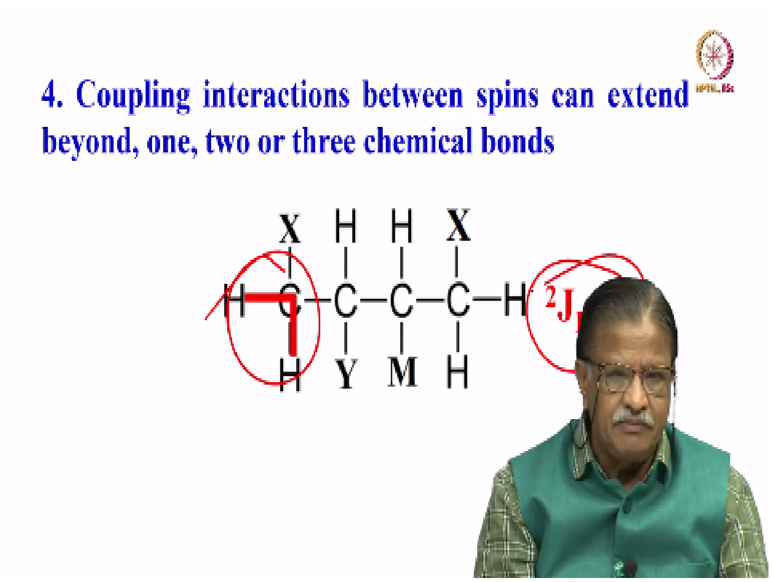

4. Coupling interactions between spins can extend beyond, one, two or three chemical bonds

A coupling interaction between spins can extend between 1 bond, 2 bonds, 3 bonds any number of N bonds; but only thing is as this number of bonds increases, the strength of interaction keeps coming down. Here it is a 2 bond coupling; it is represented as $^2J_{HH}$. This is stronger.

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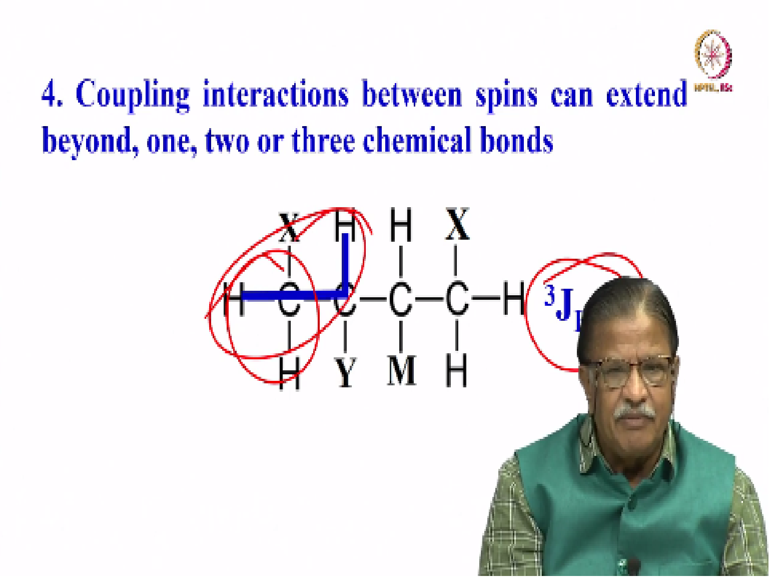

4. Coupling interactions between spins can extend beyond, one, two or three chemical bonds

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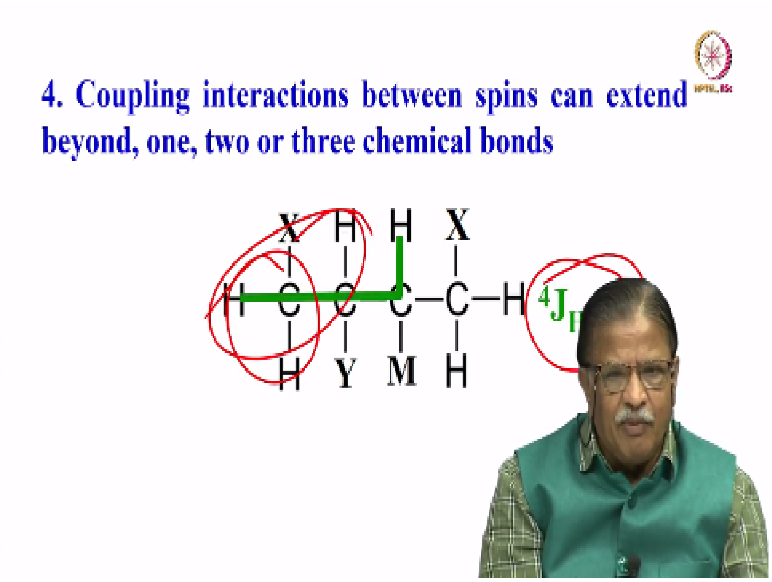

4. Coupling interactions between spins can extend beyond, one, two or three chemical bonds

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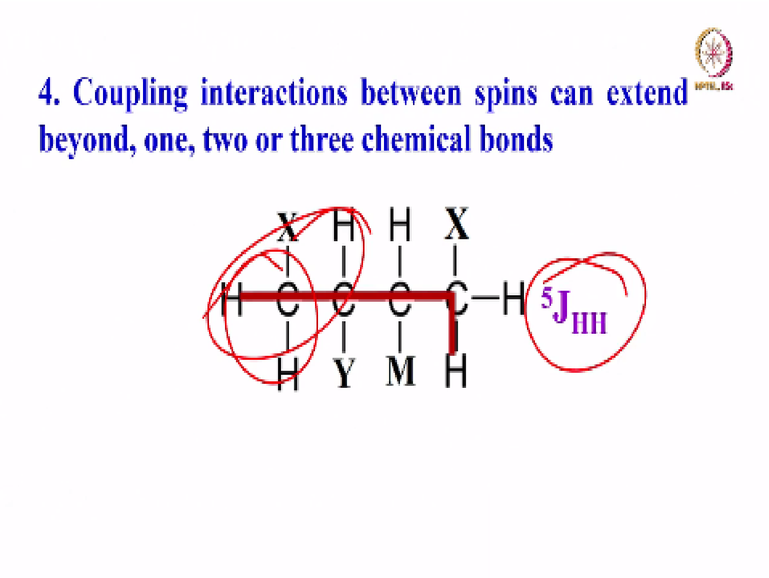

4. Coupling interactions between spins can extend beyond, one, two or three chemical bonds

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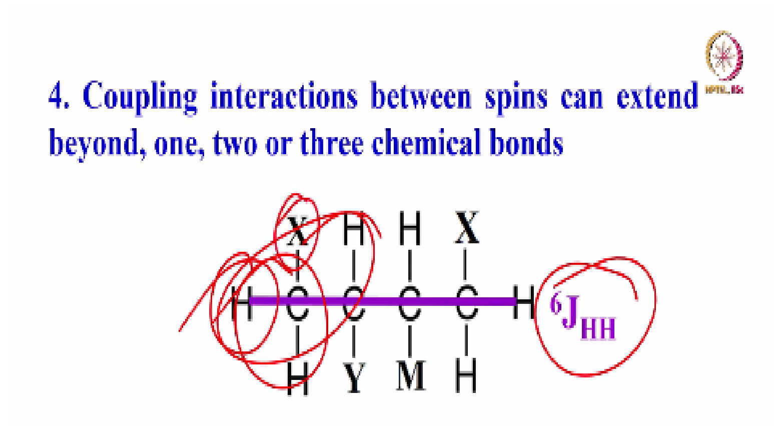

4. Coupling interactions between spins can extend beyond, one, two or three chemical bonds

Go to this one, it is 3 bond coupling, it will be weaker, it is 4 bond coupling, 5 bond coupling these 5JHH, this 6JHH. So, as the number of bonds increases the strength of interaction reduces drastically. But nevertheless, this single proton can experience coupling between varieties of protons, which are separated by several bonds. Also, simultaneously, if it experiences a coupling with this, it does not mean that there is no coupling with this, it can simultaneously experience coupling with all the protons.

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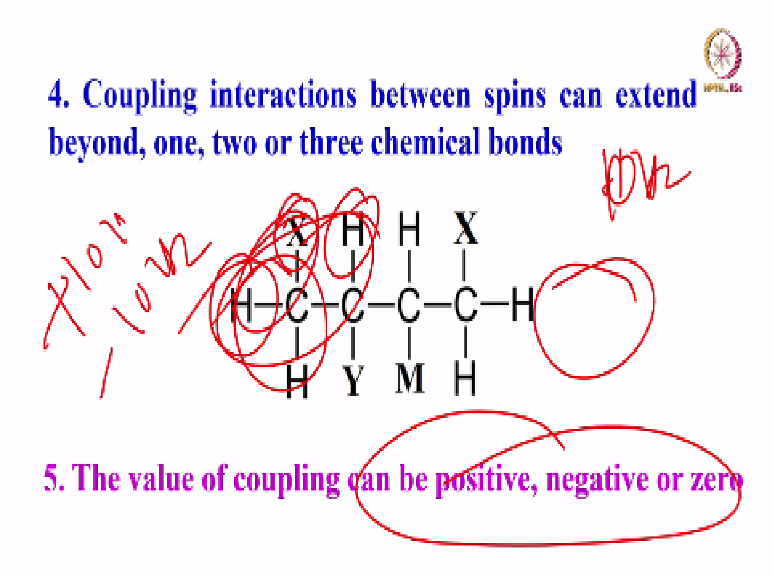

4. Coupling interactions between spins can extend beyond, one, two or three chemical bonds

5. The value of coupling can be positive, negative or zero

Only thing is the strength of interaction is different depending upon how many bonds are separated. And this value of the coupling can be always positive, negative and 0 also. If there is a coupling between this and this, it could be let us say 10 hertz, it could be +10 hertz or -10 hertz or coupling could be 0; also all are possible; it could be positive, negative or zero.

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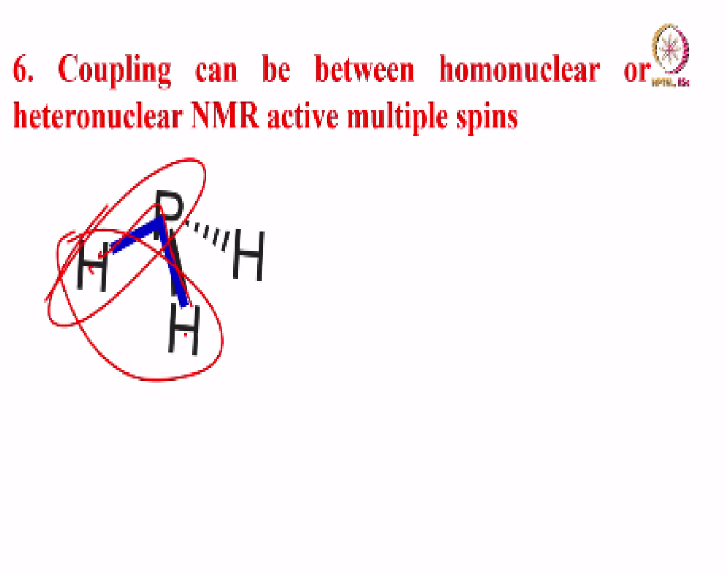

6. Coupling can be between homonuclear or heteronuclear NMR active multiple spins

Strength of interaction can be different. And the coupling can be between homonuclear and heteronuclear. When I am taking this proton that does not mean it should interact with only protons, it will couple with any other nuclei which are present in the molecule. Take for example, this group, an hypothetical group I am taking. Now there can be a coupling between this proton and phosphorus, one bond PH coupling is present. There is also possible coupling between this proton and this proton; two bond PH is also possible.

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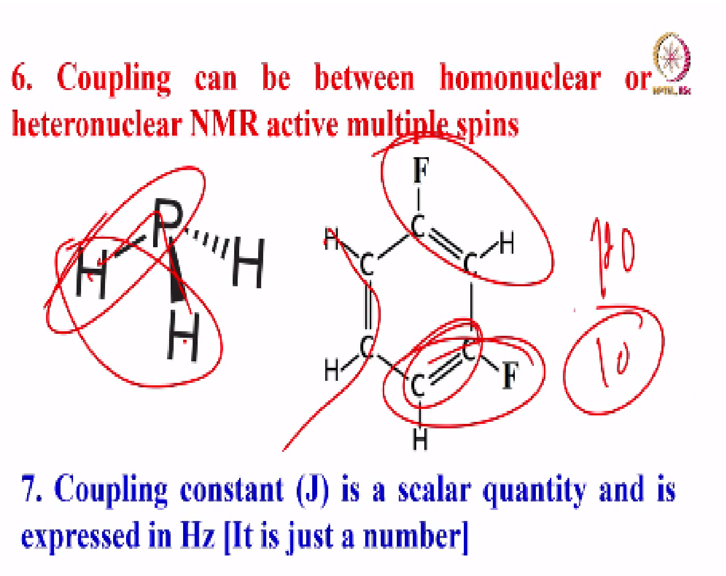

6. Coupling can be between homonuclear or heteronuclear NMR active multiple spins

7. Coupling constant (J) is a scalar quantity and is expressed in Hz [It is just a number]

This coupling is present. You look at this molecule; now I can expect coupling between this present to this proton separated by 3 bonds. Proton to fluorine is possible, carbon to proton is possible, separated by 2 bonds and carbon to carbon 1 bond coupling is possible, carbon to fluorine 2 bond coupling is possible; and fluorine to fluorine 5 bond coupling is possible; and fluorine to proton coupling 3 bond is possible; see varieties of couplings is possible.

It need, not to be homonuclear coupling; it can be between homonuclear spins and also heteronuclear multiple spins. And coupling constant is just a scalar quantity. It is only a magnitude. It is just a number. You do not have to give any unit for it. If I say there is a coupling constant; we just say hertz 10 hertz. But it is a number you should always know it is just Herz. It is expressed in hertz. It is just a number.

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8. The magnitude of the spin-spin coupling between the coupled spins decrease with the increase in the number of bonds. Usual trend, but can be exceptions

$^1J_{HH} > {}^2J_{HH} > {}^3J_{HH} > {}^4J_{HH}$

9. The coupling constants are independent of the applied magnetic field.

10. The splitting patterns are independent of the signs of the coupling constants

The magnitude of the spin-spin coupling between the coupled spin, decrease with increasing the number of bonds. That is what I told you. 1 bond coupling is larger than 2 bond coupling than 3 bond coupling than 4 bond coupling. But it is a general trend. There can be exceptions. You cannot come and say tomorrow okay 2 bond coupling is smaller than 3 bond coupling; it is possible there are many examples like that; many deviations are possible in NMR, but remember this a usual trend.

Usually trend is as the number of intervening bonds increases, the strength of interaction keeps coming down. And the coupling constants are independent of the applied magnetic field, this is a very, very important point, one should remember. Remember I said chemical shifts depend upon the magnetic field; they vary linearly with the magnetic field. Whereas, the coupling constants are independent of the applied magnetic field, you record the spectrum today, in one spectrometer; let us say coupling constants 10 hertz in a 300 megahertz spectrometer. Go and measure it in 500 megahertz, 800 megahertz, 1000 megahertz; no problem the coupling constant remains same, but the chemical shift will be linearly changing, but coupling will not, coupling constant is independent of the applied magnetic field. And the splitting patterns are independent of the sign of the coupling constant; that is another important thing. Let us say I have a coupling; there are 2 lines because of the coupling I am going to see, and measure this coupling as 10 hertz, even if you make -10 hertz, it remains same. Pattern remains same only thing is this line comes here this line comes here, but the pattern will not be different, the splitting patterns are independent of the signs of the coupling constants.

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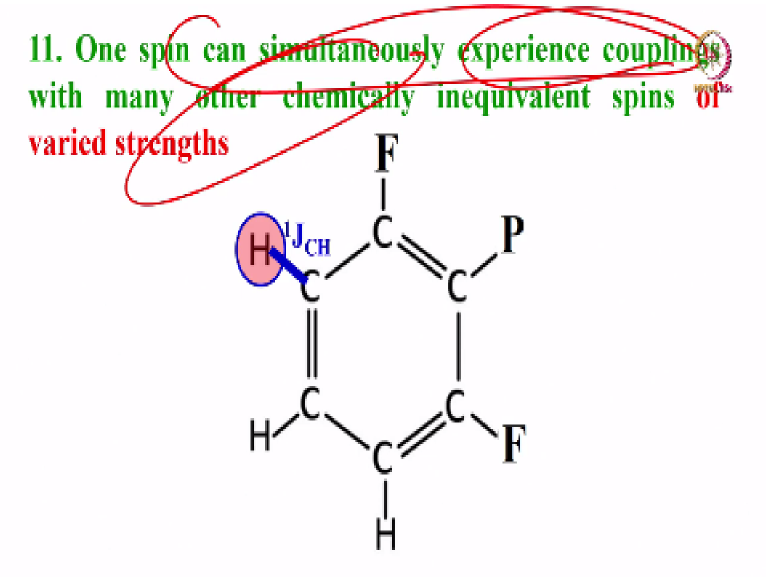

11. One spin can simultaneously experience couplings with many other chemically inequivalent spins of varied strengths

And one spin can simultaneously experience coupling with many other chemical inequivalent protons, or inequivalent spins, not necessarily proton, it could be heteronuclei also. And the couplings can be different strengths. Very interesting point, please understand, very interesting thing is, consider any 1 proton or any 1 spin in a given molecule. Then, that particular spin can simultaneously experience couplings with many other chemical inequivalent spins. Consider let us say proton here this is highlighted in red color. This proton can experience 1 bond coupling with this carbon; 1 bond coupling of CH is quite large.

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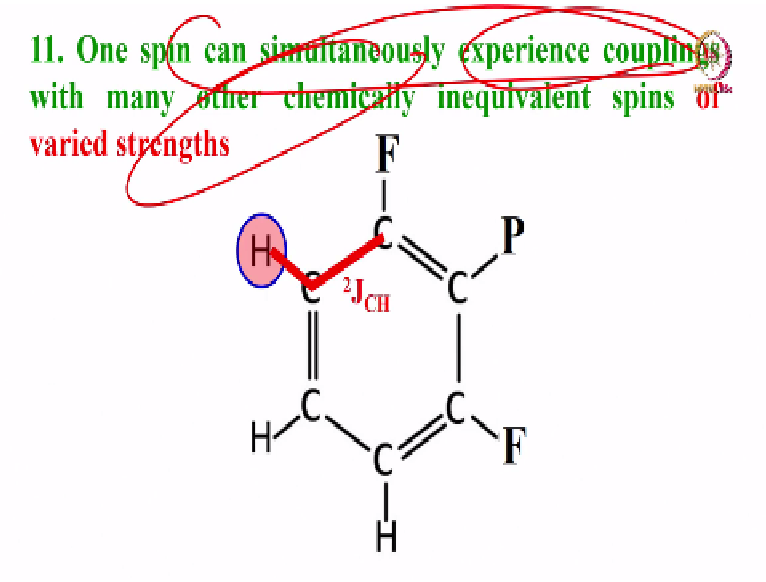

11. One spin can simultaneously experience couplings with many other chemically inequivalent spins of varied strengths

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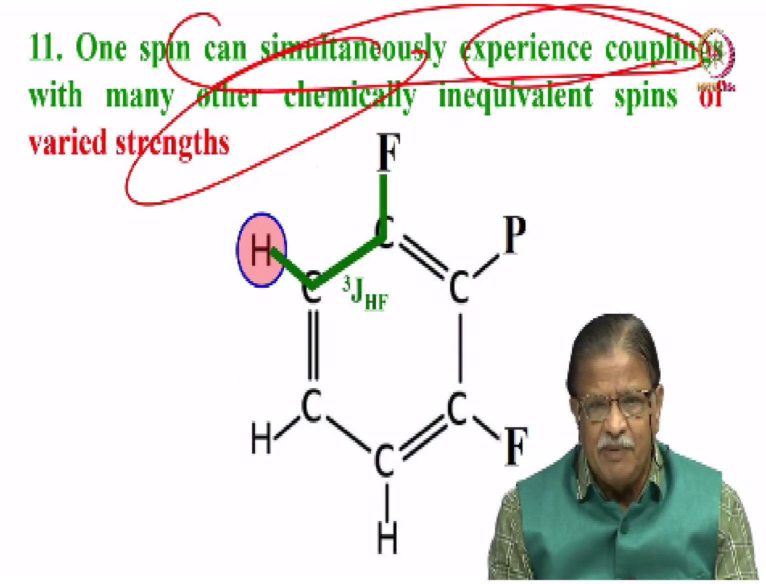

11. One spin can simultaneously experience couplings with many other chemically inequivalent spins of varied strengths

It can experience 2 bond CH coupling which is much, much smaller. It can experience 3 bond coupling with fluorine.

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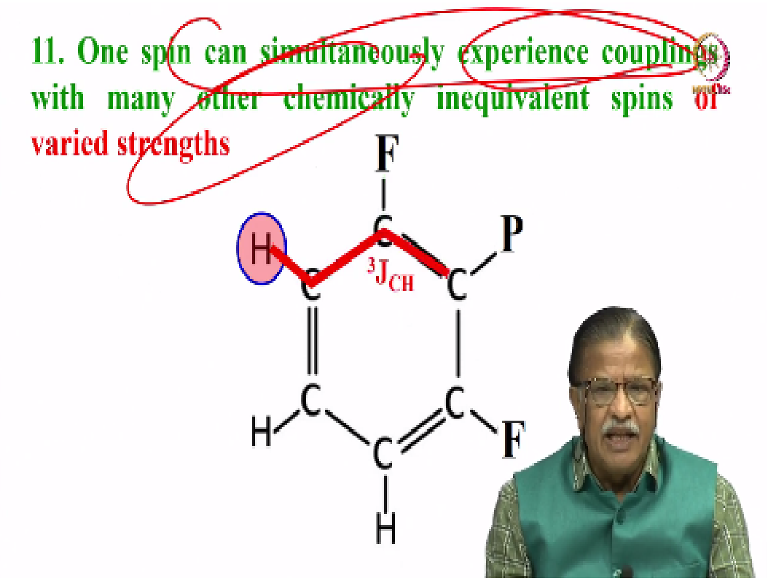

11. One spin can simultaneously experience couplings with many other chemically inequivalent spins of varied strengths

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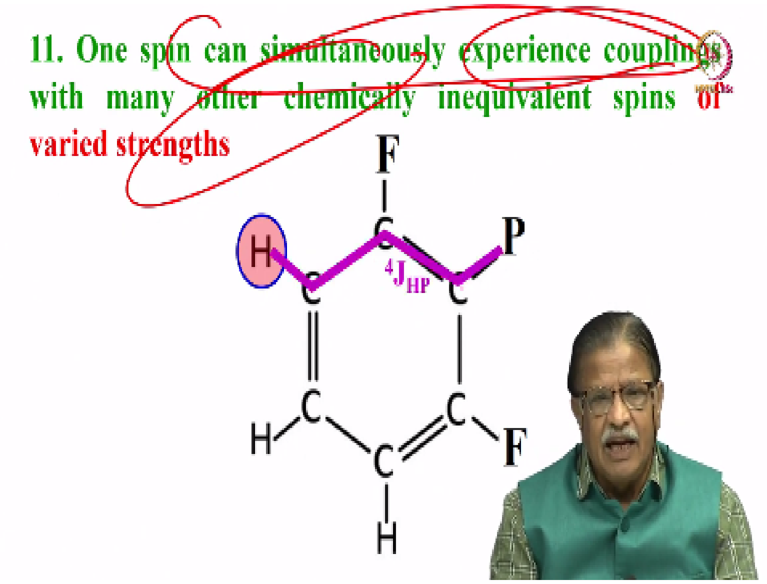

11. One spin can simultaneously experience couplings with many other chemically inequivalent spins of varied strengths

It can experience 3 bond coupling with this carbon. This is much smaller. It can experience 4 bond coupling with phosphorus.

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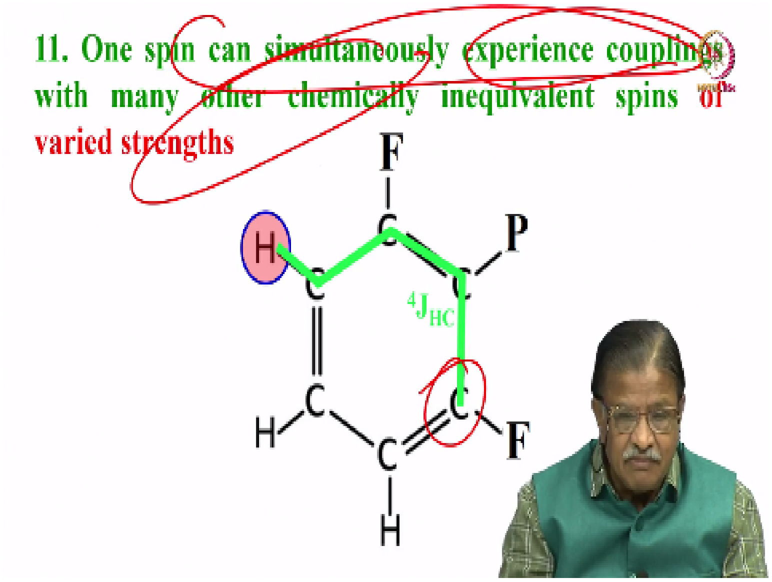

11. One spin can simultaneously experience couplings with many other chemically inequivalent spins of varied strengths

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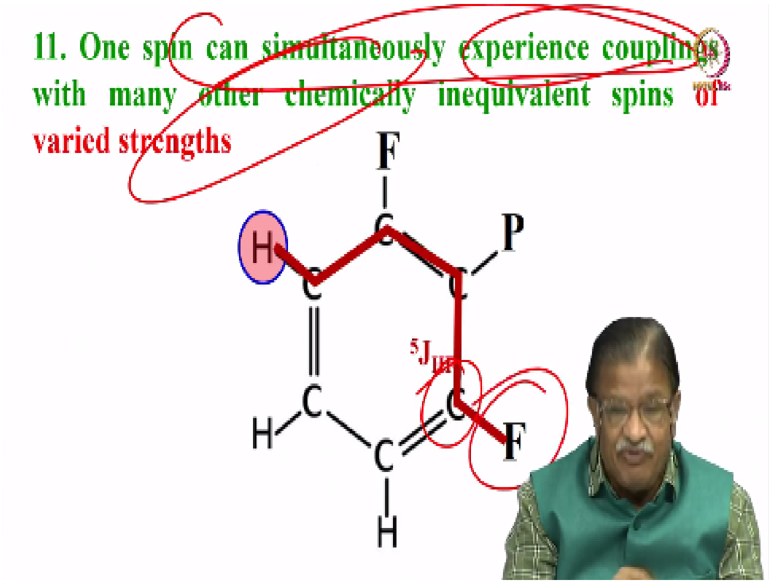

11. One spin can simultaneously experience couplings with many other chemically inequivalent spins of varied strengths

It can experience 4 bond coupling with this carbon. It can experience 5 bond coupling with this fluorine. And it can also experience 3 bond coupling with this proton.

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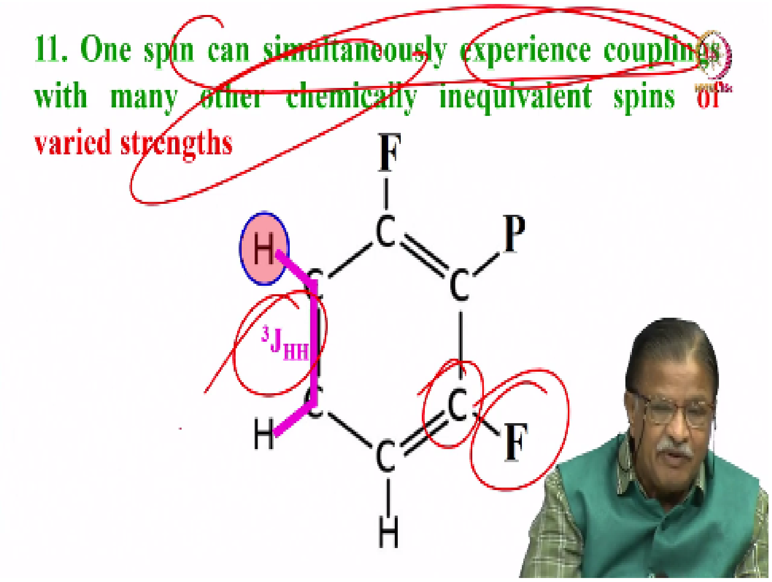

11. One spin can simultaneously experience couplings with many other chemically inequivalent spins of varied strengths

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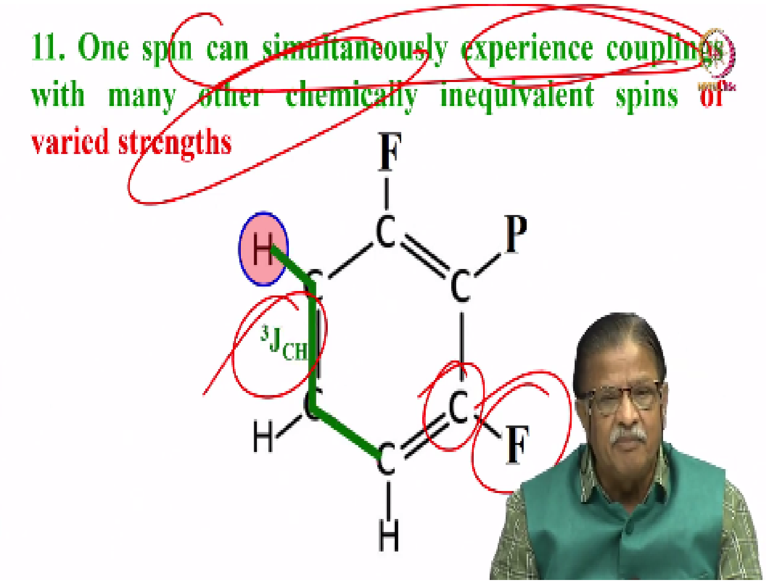

11. One spin can simultaneously experience couplings with many other chemically inequivalent spins of varied strengths

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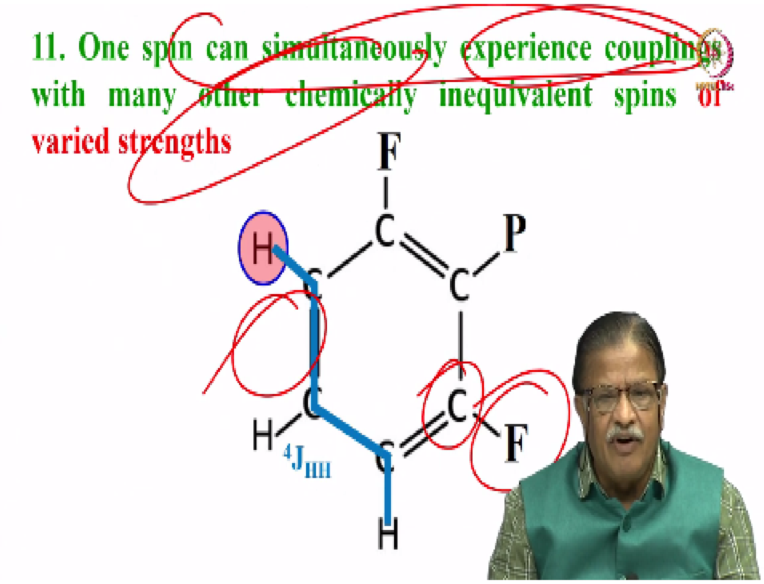

11. One spin can simultaneously experience couplings with many other chemically inequivalent spins of varied strengths

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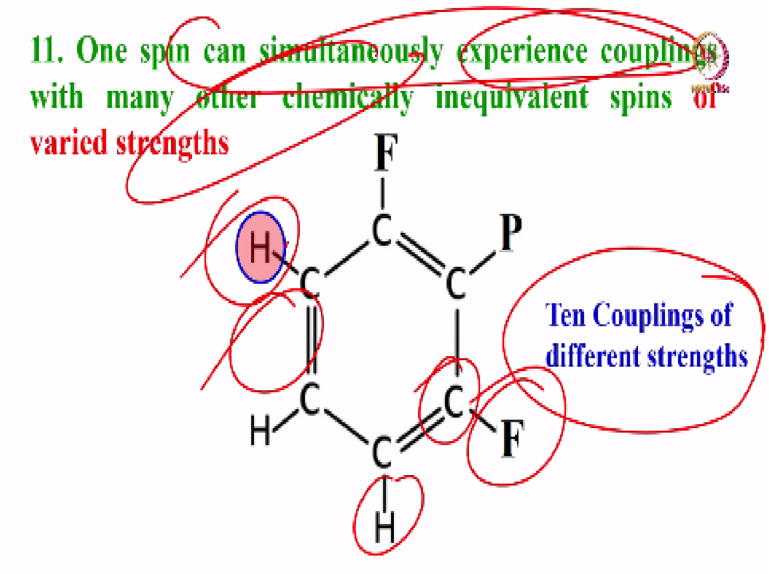

11. One spin can simultaneously experience couplings with many other chemically inequivalent spins of varied strengths

Ten Couplings of different strengths

And it can experience 3 bond coupling with this carbon; and 4 bond coupling with this proton. See varieties; Remember this single proton can experience 10 different types of couplings. Both homo and hetero nuclear. And all these couplings could be differen;t they need not be same, one maybe 10 hertz other maybe 100 hertz; other maybe 500 hertz, no problem, but simultaneously this proton are very particular spin if you consider, if there exists an interaction, it can experience couplings with varieties of spins; simultaneously.

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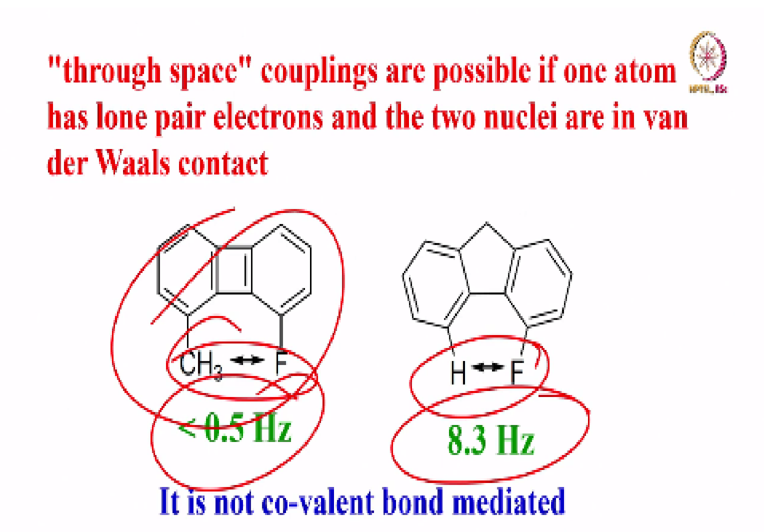

"through space" couplings are possible if one atom has lone pair electrons and the two nuclei are in van der Waals contact

It is not co-valent bond mediated

As I was telling the coupling is always through covalent bond. But there are some typical examples like these molecules, where the through space coupling is possible. It is because if one of the atoms has lone pair electrons, and if the 2 interacting nuclei are very close by, within the Van der Waals radii, then what will happen? You can see the coupling between these 2 directly, without through going to covalent band. This is called through space coupling. These are all exceptions, but it is not covalent band mediated, remember.

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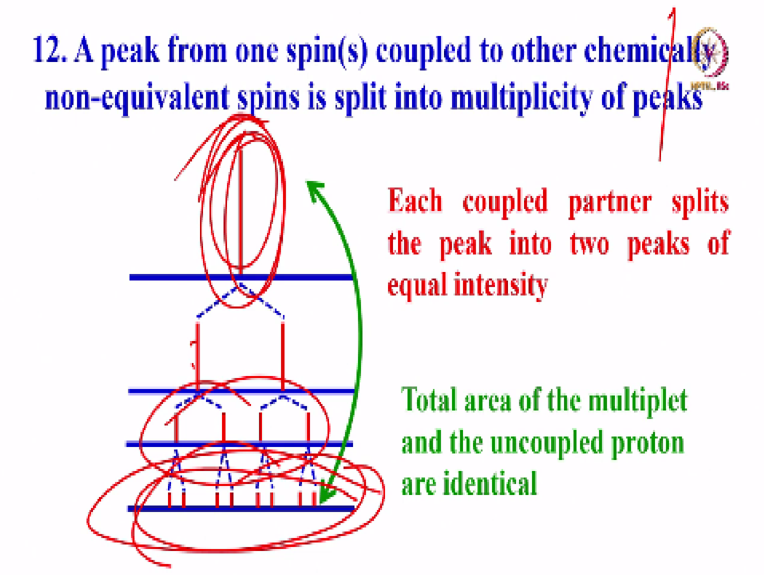

12. A peak from one spin(s) coupled to other chemically non-equivalent spins is split into multiplicity of peaks

Each coupled partner splits the peak into two peaks of equal intensity

Total area of the multiplet and the uncoupled proton are identical

Now, 1 peak from 1 spin coupled to other chemically inequivalent spins is split into multiplicity of peaks. For example, 1 proton is there, it gives rise to a single peak, each coupled partner splits this peak into 2 peaks. Let us take another proton it will become a doublet. One another single proton which if present, makes the single into 2 lines of equal intensity. Now it is coupled to another proton, what will happen? the 2 lines will become further 4 lines, 2, 2 lines of equal intensity; each of these 2 lines will become another 2, 2 lines of equal intensity.

Again if there is another proton, further split into another 2 lines of equal intensity; but remember, the area of this peak, integral area of all these multiplets together are identical. The total area of the multiplets here and the total area of uncoupled proton are identical. There is no difference at all. That is the important point to remember. Only thing is intensity gets distributed when it under goes splitting. It gets divided. 1 will become 2, 2 will become 4, 4 will become 8 like that.

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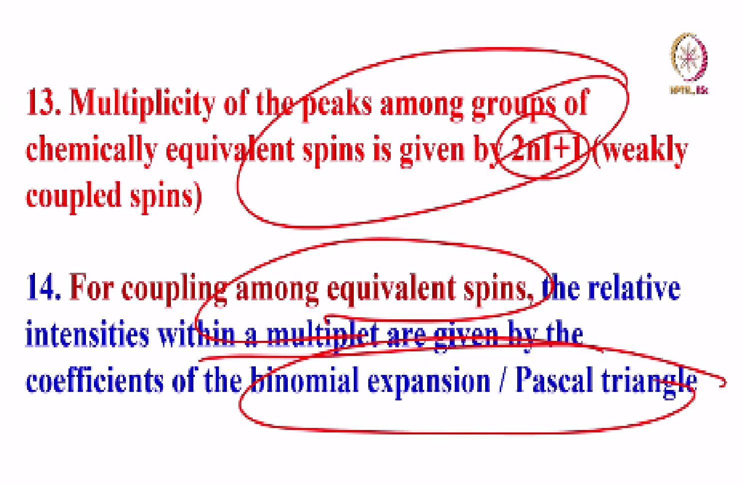

13. Multiplicity of the peaks among groups of chemically equivalent spins is given by 2nI+1 (weakly coupled spins)

14. For coupling among equivalent spins, the relative intensities within a multiplet are given by the coefficients of the binomial expansion / Pascal triangle

And multiplicity of the peaks among the equivalent spins is given by a formula called 2nI + 1, especially for a weakly coupled spin system. I will tell you what is weakly and strongly coupled as we go ahead further. For coupling among non equivalent spins, sorry equivalent spins, the relative intensity within the multiplicity is given by what is called the coefficients of the polynomial expansion or in other words, it is called Pascal triangle, I will show you what is Pascal triangle, when we go ahead further.

So, these are the important salient points of J coupling. Each and every point we can take number of examples and discuss, but this is not the time; I wanted to give you the gist of this. So, you please remember, these are the important points. Now, what happens if there are 2 nuclear spins which are interacting. There is J coupling present with 2 spins. That is what I mean by interaction, through covalent bond. It splits the energy levels. If 1 protons couple other proton, each of them will undergo splitting; energy levels undergo splitting.

In other words, remember, in NMR every interaction is mutual. If proton A is coupled to proton X. proton X is also coupled proton A; the interaction between the spins are mutual in NMR.

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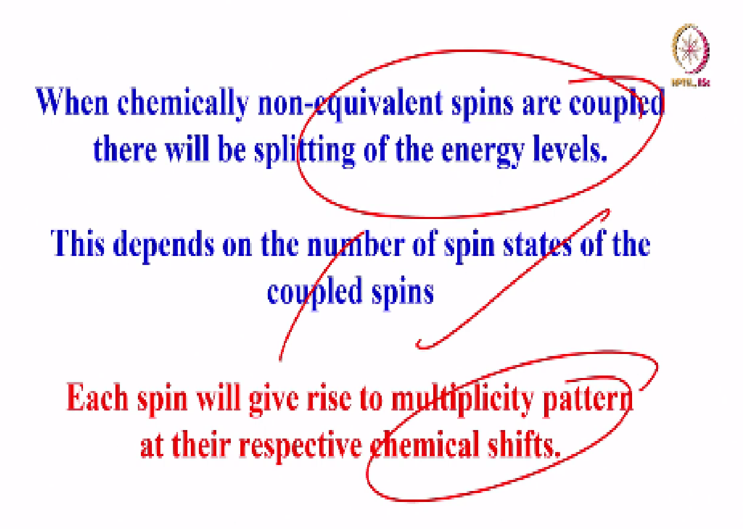

When chemically non-equivalent spins are coupled there will be splitting of the energy levels.

This depends on the number of spin states of the coupled spins

Each spin will give rise to multiplicity pattern at their respective chemical shifts.

Now, we will see the J-split energy levels when chemically non equivalent spins are coupled, there is splitting of the energy levels; this depends upon number of spin states of the coupled spins. I will tell you what is the spin states now, each spin will give rise to multiplicity pattern at the respective chemical shift depending upon the number of spin states available with the coupled spin, very important point you will see that.

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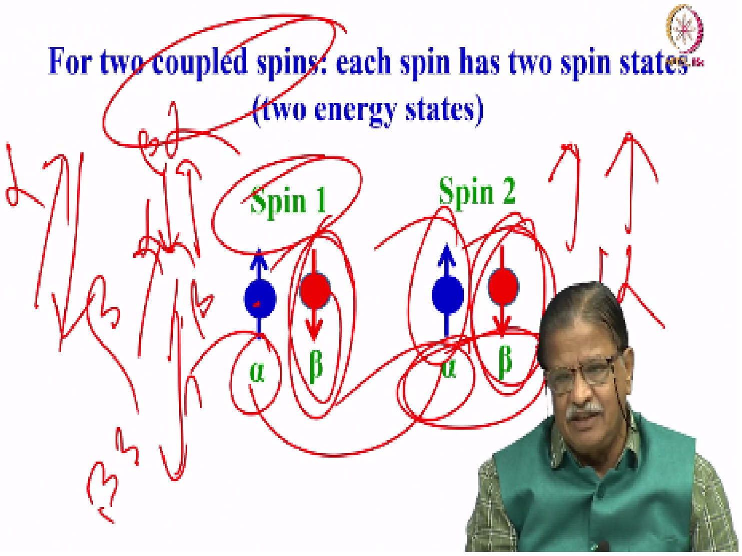
For two coupled spins: each spin has two spin states (two energy states)

Now, look at this one, there are 2 coupled spins I will take as an example. If there are 2 coupled spins, how many possible spin states we can think of? please remember in the very first class I told you that there are 2 spin states for a spin 1/2 nuclei; alpha and beta. One corresponds to the direction of the field, other in the direction opposite to the field; this is alpha and this is beta. That is what we discussed. Now, there are 2 spins. Whether it is coupled or uncoupled, let us look at the situation, what are the various combinations of these interactions you could think of.

Now, spin 1 can be in alpha position and beta position; spin 2 can be in alpha and beta position. Now, you have to take the combinations. Combination will be like this; alpha can interact with alpha, that can be alpha alpha orientation, when this spin is up, this can also be up when this spin is up, this can be down; when this is down, this can be up; when this is down this also can be down. So, 4 such possibilities are there. When both are up we call it as alpha alpha, when both are down, we call it beta beta. When one up and one down is called alpha beta; when this is down this is up, we call it as beta alpha. Like these 4 different combinations we can think of; That means each spin will see other spin in 2 different energy states. And this causes a splitting of the energy states. It is splitting of the energy levels and as a consequence you see the multiplicity of transitions.

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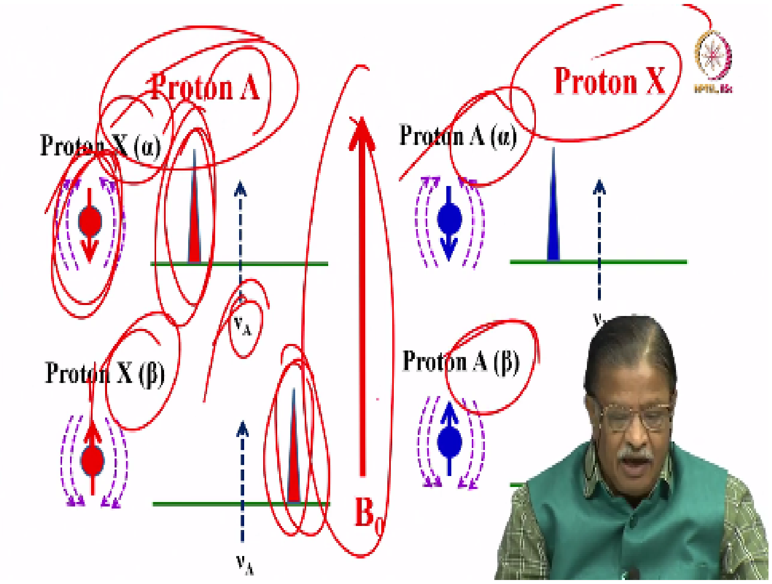
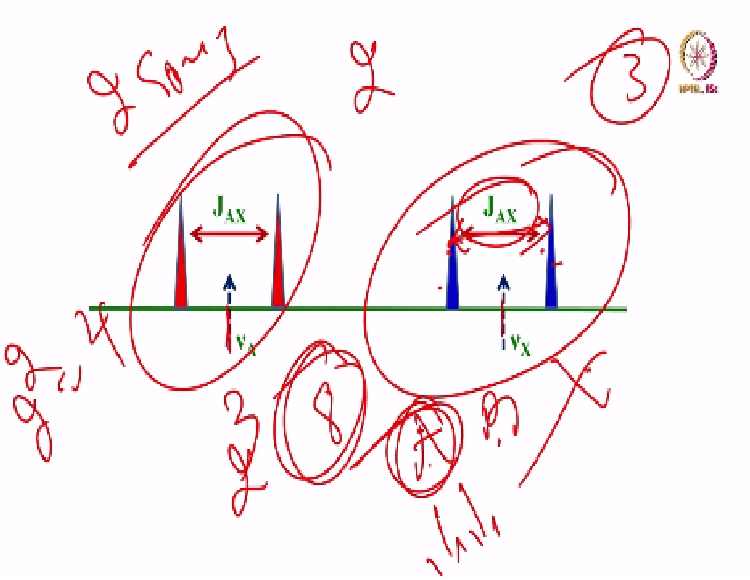


Look at this one. Now consider the proton A, I consider 2 protons A and X coupled to each other. Now they are put it in a magnetic field B_0. The proton A, can see proton X in alpha position, remember proton A is coupled to proton X. You can see proton X in alpha position; then it gives rise to a frequency which goes down field, it is because the orientation of the X spin is alpha. It orients like this. As a consequence, we are going to get a peak in the down field with respect to the original chemical position of the proton A. Now, it can also see proton X in beta position. In beta state you will see. That will be orientatation like this, then it will also see another energy state, because of that, it resonates at higher field; it comes here. Together proton A sees proton X in alpha and beta states. As a consequence, it has 2 peaks; 2 resonance frequencies, because it sees 2 energy states. The magnetic field experienced by this proton A are 2 different things; 1 B_0 + small value or V_0 - some value. So, there are 2 magnetic fields seen as a consequence, you get 2 peaks. This is because of 2 different orientations of the coupled spin. Now you may ask me a question, what happenes to proton X? identically, proton X also behaves like that; the proton X sees proton A in alpha and proton A in beta. As a consequence again you see 2 peaks here. **(Refer Slide Time: 20:03)**



Essentially it means when the 2 spins are coupled, you will get 4 peaks; 2 for A, 2 for X. At the centre is what is called the chemical shift of A here, chemical shift of X here. Which is A and which is X is my nomenclature; you can interchange also, no problem. The centre this doublet gives you a chemical shift of one nucleus, the centre of this gives you chemical shift of other nucleus. And the separation between this multiplicity pattern gives us the what is called coupling constant, this is called J coupling.

Now, I am considering 2 spins and they give rise to that, each of them will become a doublet and the separation is J coupling. Now, you might ask me why 2, if I take 3 what will happen? when there are 2 you got 4; this is 2 square is 4. When there are 3 spins let us say, what will happen? you will consider 2 cube that will be 8; 8 transitions you can think of. So, 8 possible energy states, 8 possible energy states. You can find out how many transitions are allowed based on the selection rule. Or in simple words I tell you, If proton A, M and X are there, this proton A will see this in alpha and beta positions, becomes a doublet; then it will see this in alpha and beta positions, becomes doublet of doublet. So, A will give raise to 4 peaks. Similarly, M will give 4 peaks, similarly, the X will give 4 peaks. This is how you can understand how the multiplicity comes; it depends upon number of spin states available for the coupled spins. So, now, we will understand the multiplicity of the NMR spectrum, how it comes in different situations.

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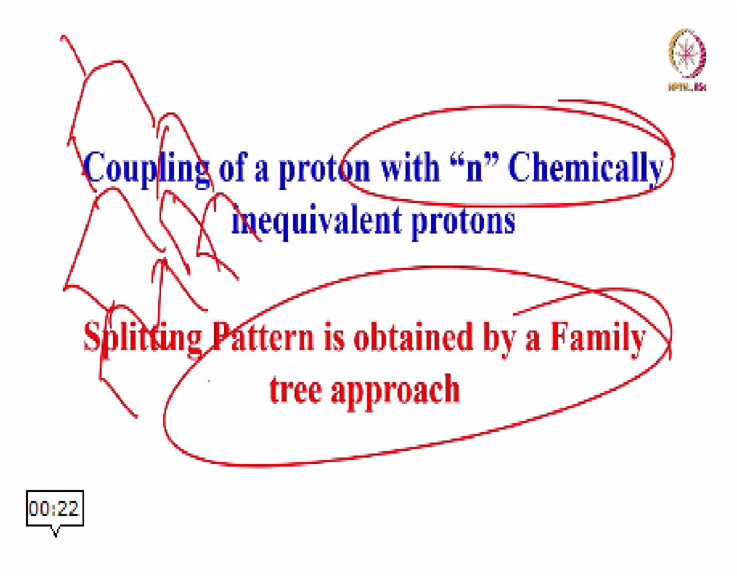

Coupling of a proton with "n" Chemically inequivalent protons

Splitting Pattern is obtained by a Family tree approach

Simple rule; the coupling of a proton with n chemically inequivalent protons, if there are n chemically inequivalent protons, the splitting pattern is easily obtained via family tree approach. What is a family tree approach; very simple 1 will become 2; then 2 will become 4, 4 will become 8; like this it keeps multiplying. This is called a family tree approach; like fission reaction in a nuclear reaction.

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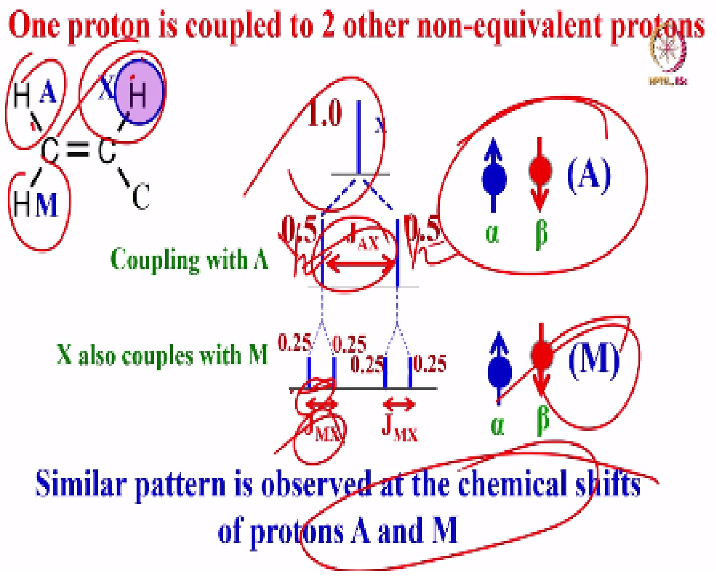

One proton is coupled to 2 other non-equivalent protons

Similar pattern is observed at the chemical shifts of protons A and M

So, now, we will understand this. Let us say 1 proton is coupled to other non equivalent protons, how it will affect. I am considering a situation; 1 proton is coupled to 2 other non equivalent protons. Remember, I consider a hypothetical case; look at proton X. This is a hypothetical molecule. Now, this can couple to proton A and proton M simultaneously; both are possible. What are the coupling strengths? they are different, we do not care, but there is a coupling. Now, let us start with proton X without any coupling. Assume there is no coupling between this and this Then how many peaks you expect? Only 1 because coupling strength is 0. Now, I bring in the coupling; let us say intensity is 1 for this. I bring in the coupling of this X with A. A can have 2 orientations alpha and beta; as a consequence, this will become a doublet. Now, what is the intensity, 1 will become half and half; 0.5 and 0.5 and the separation is the interaction strength between A and X. that is J_{AX} and intensity reduced to half, half.

Now, simultaneously it can also experience coupling with M, M is again in alpha and beta states. Again it will become each peak half, half. Now, what is the intensity? 0.25, 0.25, 0.25, 0.25 and the separation gives you couplings between A, I am sorry M and X, this is J_{MX} coupling. Now, you might ask me a question what happens if I look at A and M not X. It is exactly the same phenomena. Now A can experience coupling with the X; and M in 2 different spins states for each of them. For A will also give 4 lines, similarly M also will give 4 lines. Similar pattern is seen at the chemical shifts of protons A and M.

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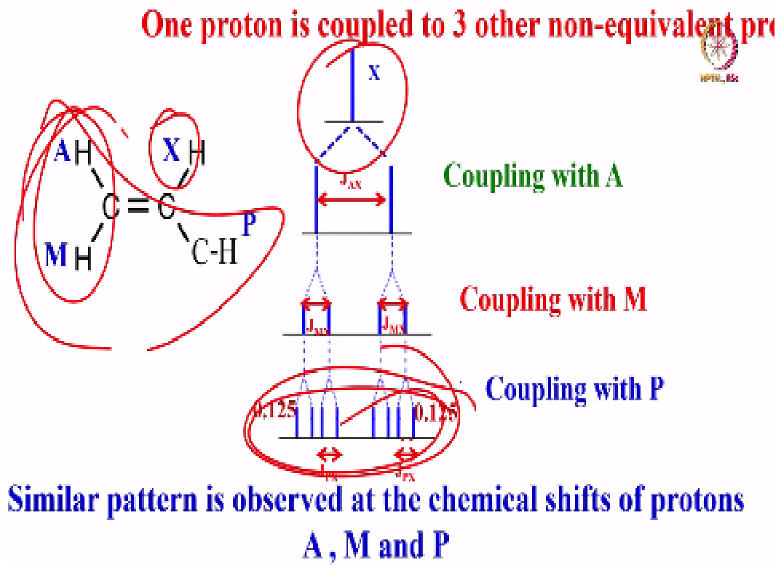
One proton is coupled to 3 other non-equivalent pro

Coupling with A

Coupling with M

Coupling with P

Similar pattern is observed at the chemical shifts of protons A , M and P

Now 1 proton is coupled to 3 other protons, let us say what is going to happen? Look at this. This is proton X, proton X in coupled to proton A. Up to this we already understood. We are going to get 2 lines again 2 lines, 0.25, 0.25 intensity. Now I am bringing in third proton coupling with P what will happen, each of them will further split into 2 lines. So, we are going to get 8 lines. Earlier, when one was coupled to 2 protons, you got 4 lines. Now when the one is coupled to 3 protons are going to get 8 lines. And what is the intensity, now further reduced by 0.125, 0.125, 0.125 and 0.125.

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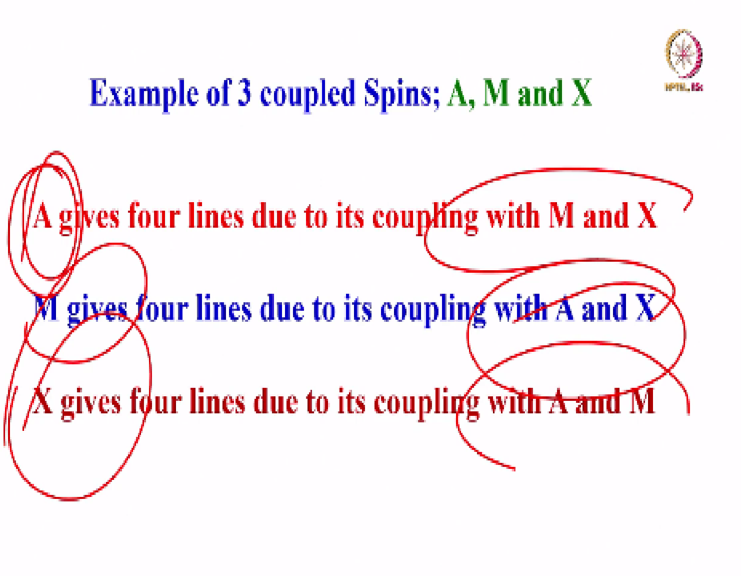

Example of 3 coupled Spins; A, M and X

A gives four lines due to its coupling with M and X

M gives four lines due to its coupling with A and X

X gives four lines due to its coupling with A and M

So, this is the example of 3 coupled spins A M and X, A gives 4 peaks, because of its coupling with M and X, M gives 4 peaks because of coupling with A and X, X gives 4 peaks because of its coupling with A and M. Remember, the spin you are observing is coupled to remaining 2 spins. Now we are observing M it coupled to remaining 2 spins, A and X. Now you are observing X, it is it coupled to remaining 2, A and M. And each time you have got 4 lines.

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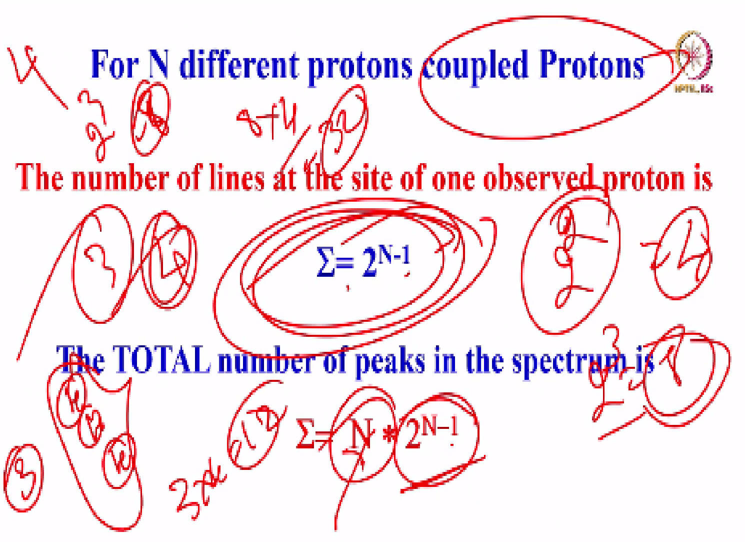

For N different protons coupled Protons

The number of lines at the site of one observed proton is

$$\Sigma = 2^{N-1}$$

The TOTAL number of peaks in the spectrum is

$$\Sigma = N * 2^{N-1}$$

So, totally you got 12 lines. So, for N different protons in there coupled different other protons, the total number of lines at the site of the observed proton is 2 to the power of n - 1. Now for example, 3 spins case 3 spins, 2 to the power 3 - 1, that is 2, 2 square. So, it is going to 4. That is what we observed. For each proton at the site chemical shift position we got 4 peaks. So, if there are 4 couples, what will happen? 2 the power of 4 – 1, it is going as 2 cube.

So, at the respective the chemical shift position of each proton, you are going to get 8 lines. So, now there are 4 protons coupled, 8 into 4, there are 32 lines here, 3 protons are coupled with four lines, 3 into 4 there are 12 lines. That is how it goes. So, the number of peaks you will see at the site of one observable proton, when it is coupled to N another protons is given by 2 to the power of N - 1. And the total number of peaks for the entire spectrum is given by N protons, you get the N into 2 to the power N - 1 number of peaks.

So that means for 3 spins, each spin will give 4 lines; that is 4 lines, 4 lines, 4 lines. Now, according to this formula, 3 into 4, you must get 12, that is exactly what you are seeing. You get all lines, if you go to 4 spins coupled to each other, you say 2 to the power of 3, 8 peaks you get for each of the protons, 8 into 4, you get 32 peaks. So, using the family tree approach, you can calculate, you will see there will be 32 peaks. This is how you identify the number of peaks you are going to get in the chemically inequivalent protons that are present, when they are coupled among themselves.

Now I will tell you something about what is called active and passive couplings. This is something very important you must understand, we always use this jargon in NMR, called active spin, passive spin, etcetera. Similarly, we talk about active couplingx and passive couplings. What is an active and what is the passive coupling? we will see here?

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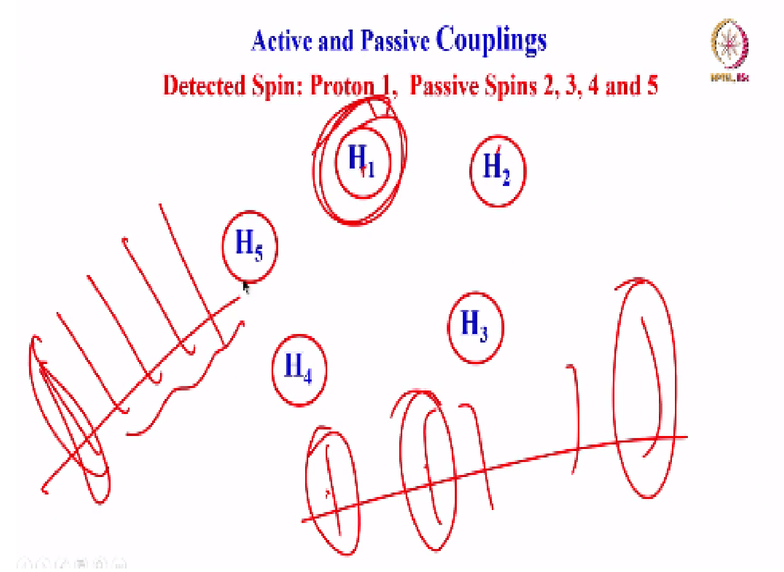

Active and Passive Couplings

Detected Spin: Proton 1, Passive Spins 2, 3, 4 and 5

Look at this one. Let us say I have 5 protons; 1 2 3 4 5. I circled here they are all coupled among each other; among themselves. Now I am going to detect proton 1. That means there are 5 different chemical shifts, I am detecting. Let us say proton which comes here; it is a coupled spin system. A spin system is one where every spin is coupled among themselves. Now I am looking at this the proton; the one I am observing is called an active spin. Remember this is an active spin. When I look at this chemical shift, this is an active spin.

When I look at this, this is an active spin. Then what are passive spins? all the remaining spins which you are not observing are passive spins. So, there are, let us say, 5 protons here. I am observing this, this is in active spin, the remaining 4 are passive spins. So, in this case, now one is a proton which I am observing, this is an active spin and remaining 4 protons are called passive spins. So, now we will see what has happens in this case here.

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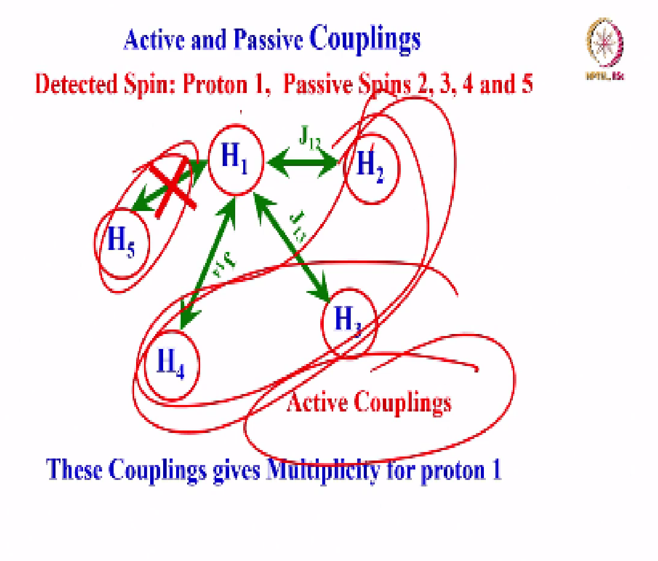

Now when I am looking at the proton spin, it can couple. See this proton spin, can couple to proton 2 with the coupling constant J12, it can coupled to 3, j13, it can coupled to 4 it can coupled to 5. It need not coupled to 5, no problem. Coupling of 0 does not matter. But all these are called active couplings, because you are looking at the active spin, which is coupled to passive spins. They are called active couplings, active spin coupled to passive spins are called active couplings. Now, these couplings give the multiplicity for proton 1.

Now we can understand this is coupled to this, become a doublet, doublet of doublet, doublet of doublet of doublet because of this, it will become 2 lines, 4 lines and 8 lines, this coupling is zero, it does not matter, I do not care, but nevertheless, this proton coupled to 3 remaining protons, which are called active couplings.

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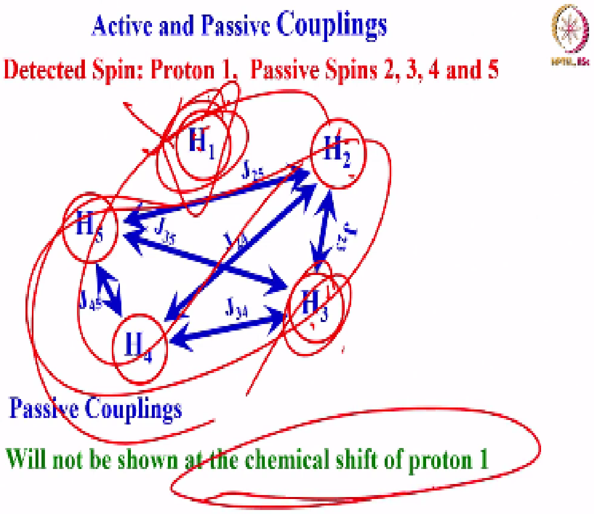

Active and Passive Couplings

Detected Spin: Proton 1, Passive Spins 2, 3, 4 and 5

Passive Couplings

Will not be shown at the chemical shift of proton 1

Now, another thing; what about this coupling? See, we also see other protons which are active here. See, for example, this coupling is also present. proton 2 forms the part of the coupled spin system, this can be coupled to this, this can coupled with this, this can be coupled to this. All other couplings are present. Now, these are called passive couplings, these are couplings among the other spins other than spin of my interest, these are called passive couplings, these passive couplings are not seen at the active site.

At this proton site, you only see the coupling between active and passive spins, but not among the passive spins. Remember, what is active and passive coupling, active coupling is the one which are going to be seen. The coupling between active spin and passive spins are seen and the coupling among the passive spins are called passive couplings are not going to be seen here. On the other end, let me consider this one I want to see proton 3 and this is the active proton, the active spin. Then the coupling to this is active coupling; other than this these are passive that is not seen here.

This is the difference between active couplings and passive couplings; and the passive coupling will not be shown at the chemical shift position of this proton which you are observing now.

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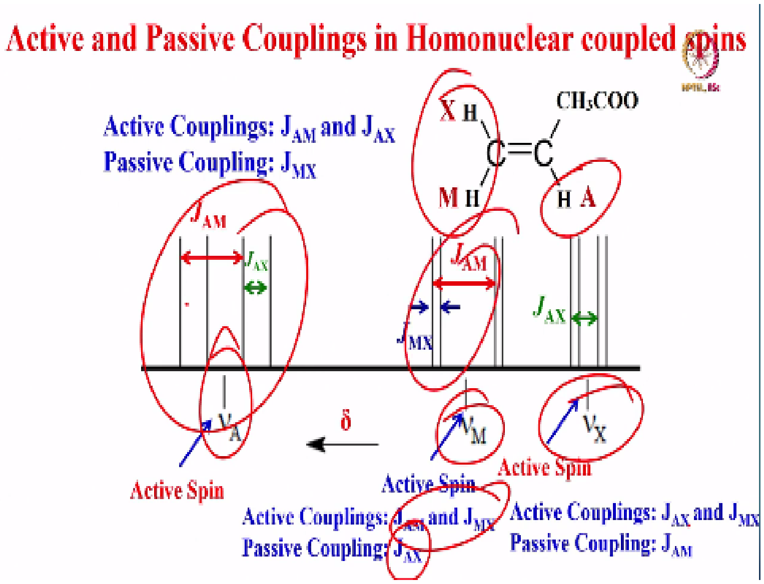

Active and Passive Couplings in Homonuclear coupled spins

Active Couplings: J_{AM} and J_{AX}
Passive Coupling: J_{MX}

Active Couplings: J_{AM} and J_{MX}
Passive Coupling: J_{AX}

Active Couplings: J_{AX} and J_{MX}
Passive Coupling: J_{AM}

So, active and passive couplings in homonuclear case, I will take a simple example like this. I consider 3 spin case, 3 protons are coupled. I call it A, M and X. Now, when I am looking at the A, A is an active spin. When A is active, these 2 are passive. Correct? So, A we will be coupled to M and X. So, AX and MX are the active couplings, that is JAX and JMX. The JAM is the passive coupling.

Similarly, look at this one, M is an active spin now, when M is active spin, AM and MX are the active couplings and passive coupling is AX. Similarly, here we are observing this X, X is active spin and couplings are AX and MX they are active couplings. Passive coupling is AM that is not seen here, you cannot get AM here, you cannot get AX here, you cannot get MX coupling here. So, active couplings are seen at the site of the chemical shift of the proton which we are observing, you see active coupling. Passive coupling will not be seen. For that you have to go to chemically shift position of the different protons.

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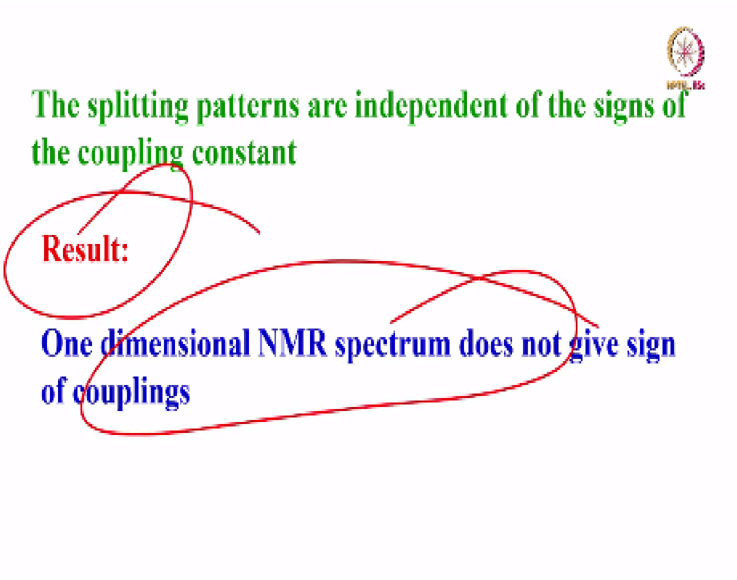

The splitting patterns are independent of the signs of the coupling constant

Result:

One dimensional NMR spectrum does not give sign of couplings

The splitting patterns are independent of the signs of the coupling constants, that means it does not change, whether the coupling is positive or negative it does not change the pattern of the spectrum at all. As a consequence, important point, remember, one dimensional NMR spectrum does not give the sign of the couplings, you do not know, just by looking at the spectrum, whether the coupling is positive or negative, that information is not available at all. So, you understood, what is active coupling and passive coupling like that.

So, I think now time is up. I will stop here. And we talk more about the couplings later. But today, I am going to stop here. But what did we do today, we started with another interaction parameter called coupling constant. And we understood various salient features of the coupling constant, what will happen to the coupling, how do you represent the coupling it is a scalar. It is just a number represented by Hertz, it could be homonuclear or heteronuclear, 1 proton gets simultaneously coupled with other spins. And when it interacts with number of protons, there is a multiplicity which depends upon the number of spin states of the other protons. As a consequence, what is going to happen? the multiplicity pattern changes. So, the multiplicity pattern if you interpret you know the coupling constants, and what you are going to see the proton is an active spin. And you are going to detect the coupling between the active and passive spins, which are reflected at the site of the active spin. Passive coupling cannot be seen here for that you have to go to the chemical shift position of other proton.

So, varieties of things we understood; how the mechanism of splitting arises based on the orientation the spin states of the coupled spin also we saw, taking an example of the 2 spins. And we know for the chemically inequivalent spins if there are N protons coupled among themselves, the number of peaks you are going to see at the chemical shift position of one of the protons is given by 2 to the power of N - 1.

And the total number of peaks you see in the NMR entire NMR spectrum of that molecule they are weakly coupled, I will tell you what about too strong and weakly coupled later, is given by N into 2 to the power of N - 1. These are the things we understood today. We will stop here and come back later. Next class, we will continue further more interesting phenomena about the multiplicity pattern, the patterns we are going to get how we can get different multiplicities, the different patterns in the NMR spectrum. Thank you.