

One and Two dimensional NMR Spectroscopy: Concepts and Spectral Analysis

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Lecture 12 Coupling Mechanism

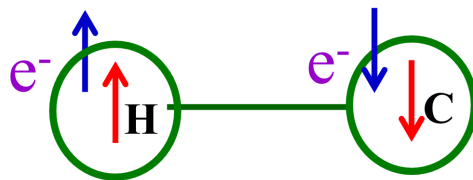
Welcome all of you. In the last class we discussed a lot about scalar coupling, especially I discussed about the multiplicity pattern, how does the spectrum appear when one proton is coupled to another proton. I showed that it is because of the two possible spin states of the coupled spin, one proton will give a doublet. Similarly, other proton will be seeing the spin states, two spin states of the other coupled proton and gives a doublet. When two protons are coupled, I said you will get four lines of equal intensity. This is the way we see the coupling and the total intensity keeps reducing by half each time, depending upon the number of protons it is coupled to. When it is coupled two protons, it will become four lines and intensity comes down by 25 percent for each of them. And we worked out and showed that center of the doublet gives a chemical shift and the separation gives you the J coupling, if you have two coupled spins. Of course, for three coupled spins, multiplicity pattern is the more and more, and there is a way we can calculate j couplings. And I worked out and showed when there are two spins, three spins, four spins are coupled, the number of transitions or the number of peaks that you are going to get at the site of each spin is given by $2^N - 1$. And the total number of peaks in the entire spectrum is given by sum of $N * 2^{N-1}$. That is what we observed.

So, that is what we are going to see the total number of transitions, when we observe a particular spin. We discussed a lot about that, and also we discussed what is called active spin and passive spin. What is active coupling and what is passive coupling? If I have a group of spins, let us say 1, 2 and 3 are coupled. If I am looking at the chemical shift of proton 1, then that is an active spin. And the protons 2 and 3 are passive spins. So, one can couple to 2 and 3, you get 1,2 and 1,3 coupling at the site of proton 1. And the coupling between 2 and 3 passive coupling you will not be seen here.

Similarly, look at proton 2 or 3, let us say proton 3, at the chemical shift of proton 3, you get coupling between 1 and 3 and also 2 and 3. The coupling between 1 and 2 you will not see here, because that is a passive coupling. So, we discussed extensively about active coupling and passive coupling and how we can get this information in homonuclear coupled spins and heteronuclear coupled spins also. I gave one example each, then we know how we get the coupling at the site of a particular spin. Then we

understood clearly what is active coupling and passive coupling. We will continue further today.

Remember in the very first class when I was discussing about the selected features of the scalar coupling, I also said the coupling could be positive, negative or 0. That means, the coupling has a sign. What do you mean by the sign of the scalar coupling? Whether it is positive or negative, you do not know. How do you get the sign of the coupling? When the coupling is 0, it is very simple, you will get only a single peak, no splitting. But if there is a splitting, I measure the separation, but that does not give me the sign of the coupling. How do I know what is the sign of the coupling? How does the spectrum gets affected when the sign of the couplings are different? This is what we will try to understand now, to proceed further. For that we follow what is called a Dirac model.

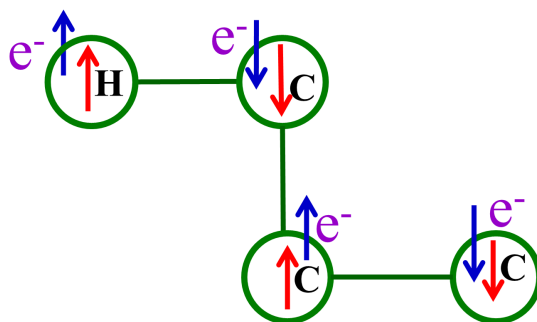


If I consider protons or let us say a C-H bond, carbon has a nucleus and surrounded by electrons. The proton has a nucleus surrounded by electrons. And there is an interweaving covalent bond. And the most stable orientation of the magnetic moments of proton and electron in a given molecule is, consider the carbon atom or the proton hydrogen. The most stable orientation for nuclear spin and the electron spin are when they are anti parallel to each other. When they are orientated anti parallel, it is a stable state. This is how it is. Since the electron has a negative magnetic moment, we all know, then the stable state is not parallel orientation, but anti parallel orientation, it is a parallel orientation like this. In principle, this is a stable state, this is proton, this is electron. Since electron is a negative magnetic moment, the stable state is this one. Proton and electron both have a similar orientation, same orientation. The magnetic moment of proton and that of the electron, if the alignment is in the same direction, then it is stable state. This is how it is. You have to understand the Dirac model.

Consider the example of one bond coupling between carbon and proton. The nuclear spin is orientation like this. As I said, electron has to be oriented parallel to it to become a stable state, not anti parallel, because electron has negative magnetic moment I said. Then because electron is oriented like this, in a chemical bond it ensures that other electron orients opposite to this for its stable state. Of course, you can understand Fermi rule and everything later. And this electron in turn ensures that this is opposite because of stable state, then only it is energetically stable. So, if I have $^1J_{CH}$, but only one bond between carbon and proton, then if I start with the proton spin oriented like this, it will

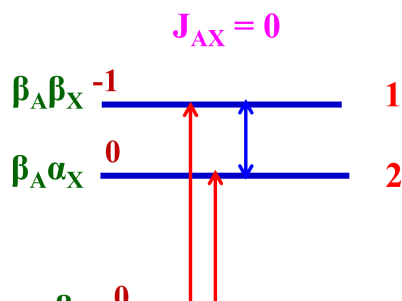
ensure such that through the electron, other spin oriented opposite to this. That means, this is a lower energy state, when both of them are oriented opposite to each other, it is stable state. It is a lower energy state. That is a situation where coupling is positive. Coupling is positive means it is a stable state, lower energy state. So, that means, if I consider one bond carbon and proton coupling, it must be always positive because of this Dirac model. We can understand. So, one bond carbon proton coupling is always positive.

You may ask me a question, what happens if the proton orientation is like this? There are two possible orientation. I took alpha. What happens if the proton orientation beta is taken? Similarly, this electron will become like this and this electron will become like this and then again this will be like this. So, it is depending upon which orientation of spin you are considering alpha and beta, correspondingly you can work out the orientation of the other coupled spin. If both are anti-parallel to each other, it is a lower energy state and that will be a positive J coupling. So, the sign of the coupling is positive. That is the reason why $^1J_{CH}$ is positive.



Then what about two bond couplings of carbon proton? I mean 2 bond carbon proton, and 3 bond carbon proton? Again one bond coupling we know, extend it for another bond. It so happens, if you extend the same logic, then these two are like this. Higher energy state you will have, that means, you are going to get a negative J_{CH} . You go further, it is going to be positive. So, depending upon how the spins are oriented, one bond coupling $^1J_{CH}$ is positive, $^2J_{CH}$ is negative, $^3J_{CH}$ is positive. You can work it out simply by extending this Dirac model. I worked out only for J_{CH} , but you do not think it will work out for everything. Consider carbon fluorine one bond, one bond carbon fluorine coupling is always negative. You can work out in a different way. Now, if I know the coupling could be positive, negative or 0, how does it get reflected in the NMR spectrum?

Let us take the example of two protons coupled and three possible situations, when the coupling between them is 0, positive and negative, all the three examples we will take. I have two protons coupled among them since day 1, there are four possible spin states,

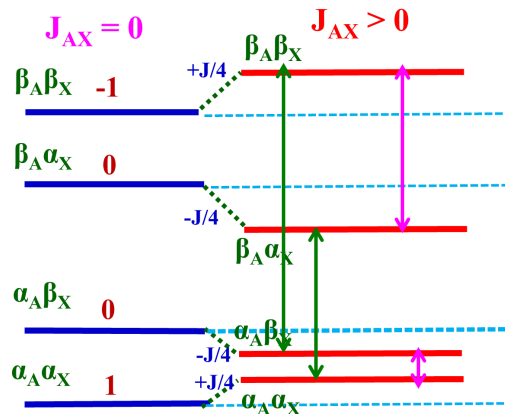


that is alpha alpha, both are up, beta beta both are down, this up and this down, alpha beta, this down, this up, it is beta alpha. Both are, there are four possible spin states we can understand. We will consider a situation, coupling between A and X is 0.

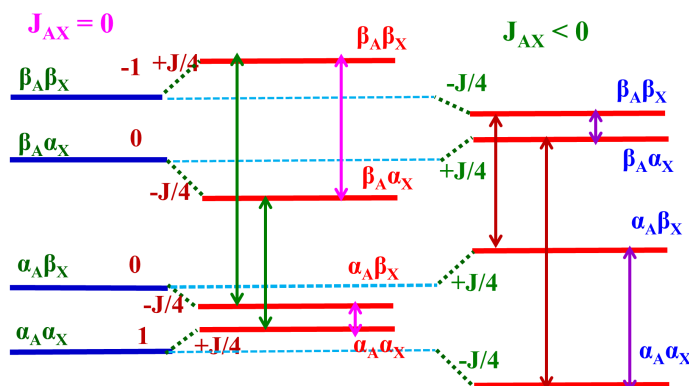
Of course, we have four possible energy states. The energy states are different, because the orientations are different. So, now I am writing like this. This is beta beta, its total magnetic quantum number is minus 1, and this is 0, this is 0, alpha alpha is 1. This we knew already, we have discussed how to calculate this one. This is a half, the total magnetic quantum number for this energy state is sum of these two, it will become 1. This is minus 1, this is 0, 0. And I have numbered these energy states as 1, 2, 3, 4 for my case of understanding. So, this is what it is. Let us see now, how we are going to see the spectrum. The transition between 1 and 3 is allowed. You see minus 1 to 0 allowed transition. Here, which spin is flipping, A is flipping. So, this is A transition. What about this one? Here also A is flipping, 2 to 4 is also allowed transition. This is A transition, What about this one, 1 to 2? This is allowed, where X spin is changing its orientation from alpha to beta. Similarly, here also 3 to 4 is allowed. Again, it is X transition because X spin is changing from alpha to beta and vice versa. But remember, this frequency is same. This energy separation is identical and this energy separation is identical. Look at this energy separation, this is larger, this is smaller. That means this is higher frequency, this is lower frequency. But these two higher frequency peaks overlap and gives rise to a single peak. These two will be identical frequency overlap and gives a single peak. So, that means, then we will get two transitions, one for A and one for X. In reality, there are four peaks, two of A are overlapped, two of X are overlapped. Two transitions each for A and X, when they overlap, it appears as if it is one-one line. This is the situation when the coupling between A and X is 0. This is a simple example, when coupling is 0. This is what we have been discussing, when the coupling is 0, we get only one peak each.

Now, consider a situation, J_{AX} is non-zero or take it as positive. Whatever it is non-zero, positive or negative, we will worry later. Now, the situation is the total magnetic

quantum number of m_Z , if they have a same sign like alpha alpha, both are half, half or beta beta negative, minus half minus half, they are called unpaired. Both are like this. Pairing is only when they are opposite to each other. They are unpaired states, unpaired spins. That means, their alignment will be less stable. They are not stable because they are unpaired. Pairing means lower energy, unpaired means higher energy. So, alpha, alpha and beta beta states are less stable. So, these have more energy. These two states will have higher energy. As a consequence, what will happen? Alpha alpha and beta beta states, energy levels gets destabilized and pushes up. How much it pushes up the energy state? By what is called $J/4$.

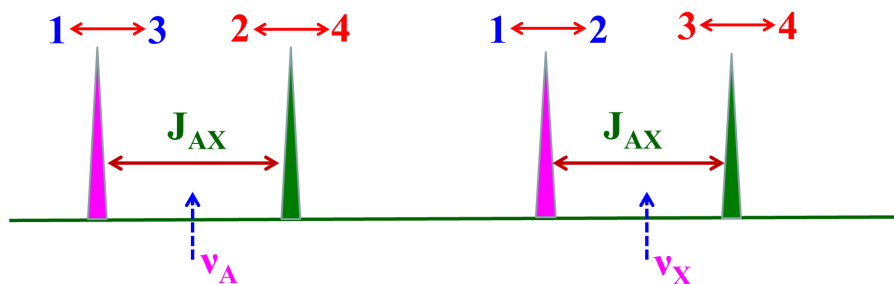


I will show you by picture. Please remember, when we consider the alpha alpha and beta beta states, the energy states are pushed up by $J/4$, this is the energy state, it pushes up by $J/4$ and this will be energy state now. Similarly, if it is beta beta, it pushed up by $J/4$. This is the situation we are going to get for the unpaired states, unpaired spin. Now, we consider situation where they are paired, alpha beta and beta alpha, they are paired spins. Their alignment will be more stable. So, they have less energy. Then obviously, if you consider the states alpha beta and beta alpha, they get stabilized and then their energy comes down, they are push down, their energy is decreased by $J/4$. So, if this is the state for alpha beta or beta alpha, instead of going up, they come down by $J/4$. In other case, this is alpha alpha and beta beta, this went up by $J/4$. That is how the energy states get destabilized in the earlier case. When it is stabilized, energy state comes down by $J/4$. When it is destabilized, it goes up by $J/4$. And now, let us see the energy level diagram. Consider the situation J_{ax} is non zero.



As I said, J_{AX} is positive, greater than 0. Then what is going to happen is, just now I explained to you, beta beta states are pushed up by J by 4. Similarly, alpha alpha state is pushed up by J by 4. Beta alpha states come down by J by 4. This also comes down by J by 4. There is a shifting. Energy states are destabilized and destabilized because of un-pairing of the nuclear spins. Now, let us calculate the frequency of the transitions. Again, 1, 2, 3, 4, energy states if I write.

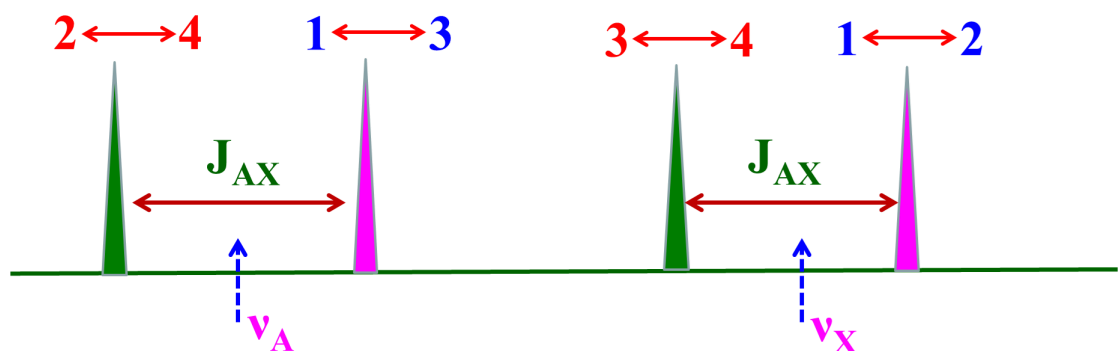
1 to 3 is allowed. That is A transition. This is also allowed, 2 to 4. And this is allowed, 1 to 2. That is X and this is X. Now, what is happening? This has more energy, higher frequency. This is compared to this, it is less energy, lower frequency. We have two lines, one at higher frequency, other at lower frequency. Similarly, X has one higher frequency and one lower frequency. There are two peaks. So, this is what we saw, when the two spins are coupled, we get two lines each. And now, you can see the frequency of one of them is larger than the other one. That is why one moves to higher frequency, other moves to lower frequency, exactly here for the X also. So, this is how we can understand because of four energy states. When there is a coupling, there is stabilization and destabilization of paired and unpaired spins. As a consequence we get four transitions. And I told you, transition 1 to 3 is A, 2 to 4 is A. Transition 1 to 2 is X, 3 to 4 is X. This are the four lines pattern you expect when the J_{AX} is greater than 0. This separation gives you coupling, this center of them gives you chemical shift of A and X. This is an example of the spectrum for two coupled spins A and X.



Let us go further. This is what we understood for AX positive, J coupling positive, What will happen to the energy states when the coupling is negative? Reverse will happen. What will happen? When the coupling is negative, the unpaired states gets destabilized, the paired states get stabilized. This is what happens. Beta beta comes down and beta

alpha goes up. Exactly here, alpha beta goes up and alpha alpha comes down. Here what happened you see? Beta beta and alpha alpha both were going up and these two are coming down. Here these two are going up and these two are coming down because the coupling is negative. Everything gets reversed. Let us see the transitions now. This is 1-3 transitions. If I take 1-3 for four energy states that is for A and this is again A transition. See the difference now. What did you observe? Higher energy, the energy separation larger, higher frequency. Higher frequency was this. Now higher frequency was between 1 and 3. Now it is between 2 and 4. See the difference and lower frequency was between 2 and 4. Now lower frequency became from 1 and 3. The lines got interchanged. Higher frequency and lower frequency transitions get interchanged for A. Exactly for X spin also, this is 1-2 transition and this is 3-4. See earlier 1-2 was larger frequency, larger energy separation and 3-4 was smaller. But now 1-2 is smaller and 3-4 is larger. What did you understand? The transition in the previous case I showed you here in the previous slide. This is for 1-3, this is for 2-4, this is for higher frequency, this is for lower frequency. From the energy separation I can say that for A this is again higher frequency and lower frequency for X. But what happened in this case is everything get reversed. So when the coupling is negative, the larger separation that is higher frequency and the lower separation that is lower frequency are now interchanged. The frequency of the two transitions get interchanged.

What happens to the appearance spectrum? This was earlier 1-3 and this was 2-4. Now you see this became 2-4, this became 1 and 3 transition. Earlier this was 1 and 2, now it became 3 and 4 and the earlier this was 3-4 transition, now it become 1-2 transition. What happened? The peaks from here to here got interchanged. Let us look at the color here. In the color spectrum I wrote here some color. You see this, let us say magenta color was left higher frequency and the other one was green color was there lower frequency in both the case. But in this case again what happens? You see magenta became lower frequency, green became higher frequency, exact here also. The lines got interchanged.



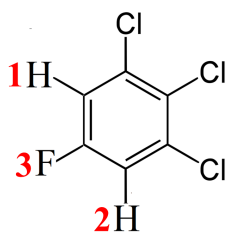
Transition from 1-2 became 3-4, 3-4 became 1-2. Similarly 2-4 became 1-3, 1-3 became 2-4. This is exactly what happened. So can you see the difference if I do not tell you this, and if I give you only the spectrum of two-two lines, you will not know whether J sign is positive or negative. What does it mean? The splitting patterns are independent of the signs of the coupling constant. So that means one dimensional NMR spectrum does not give signs of the couplings.

So if I give you the NMR spectrum, I will measure the coupling, but you will not say, you cannot say whether it is positive or negative because the spectrum remains invariant with the change in the sign of the couplings. This is what I wanted to tell you. So I hope you understood about the sign of the coupling, how the sign of the coupling matters in the spectrum. It is due to the stabilization and destabilization of the energy levels, but as for the real spectrum is concerned, you will not see the difference. You will not see the effect of it at all. All right, hope it is clear for you. With this, I will introduce one more term which is essential for observing the NMR spectrum and multiplicity of the NMR spectrum. That is called magnetic equivalence. We will discuss what is magnetic equivalence. Remember I told you chemical equivalence earlier before discussing the J coupling. I said in the chemical equivalence, there is a symmetry operation. Symmetry operation ensure that the particular protons will have identical chemical environment and they give rise to a single peak. There is no separate peaks. They come at the same chemical shift. But I did not say about the coupling at that time. There could be coupling between them. There may not be coupling. Both are possible and when we bring in the coupling, in addition to chemical equivalence, we introduced another term called magnetic equivalence. That is what I am going to introduce now. Look at it. magnetically equivalent nuclei means not only they have the same chemical shifts and they should have identical scalar coupling to all other coupled spins.

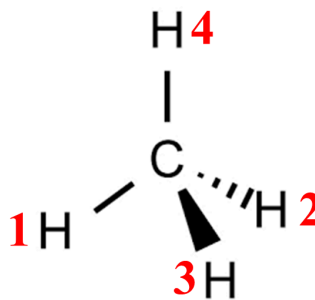
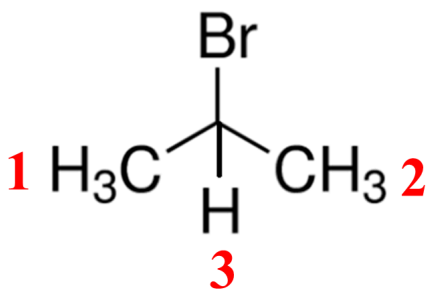
Very interesting. Remember, not only chemical shift should be same, the coupling strength to the remaining coupled protons to which it is coupled to, are all should be identical. They should not be different. I will show you that with an example. For example, I have three protons. When I say all the three protons are magnetically equivalent in a molecule, what does it mean? The chemical shift of one, δ_1 , chemical shift of two, δ_2 and chemical shift of three, δ_3 , all the three should be identical. That means they should be chemically equivalent. In addition to that, there may be a coupling. J_{12} is there, coupling between one and two, coupling between two and three is there and coupling between one and three is also there. All the three are there. So, that means all the three couplings should be equal, not only they are present, they should be equal. Not only chemical shift should be identical, even coupling should be identical. Then these three protons, one, two and three are called magnetically

equivalent spins. You understood the magnetically equivalent spins? Now, you can understand the statement. All magnetically equivalent nuclei are invariably chemically equivalent because of the chemical shift should be identical, and at the same time, we have brought in another condition J coupling being identical. So, that means all magnetically equivalent nuclei must be invariably chemically equivalent. But what about the reverse? Converse is not true. All chemically equivalent spins need not be magnetically equivalent, because couplings can be different. Only when the couplings are same, they are magnetically equivalent. So, this is the important point. Please remember, I stress it again. All magnetically equivalent spins are chemically equivalent, but all chemically equivalent spins are not magnetically equivalent.

Let us look at the example here. I am taking the example of one molecule.



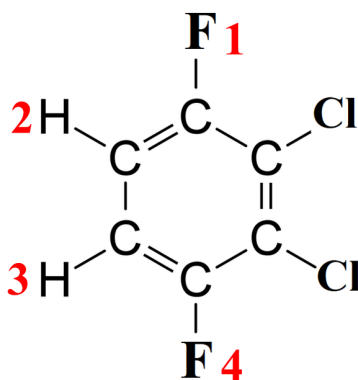
Is there a symmetry axis for this? Of course, there is a symmetry axis here, because of that, this proton and this proton are chemically equivalent. Chemical shift is same. δ_1 equal to δ_2 . Chemical shifts are same. They are chemically equivalent. Now, the fluorine is there. There can be a coupling between proton one and two and there can be a coupling between two and three. It is possible. In which case, J_{13} is also equal to J_{23} in this molecule because there is a symmetry axis. Not only chemical shifts are same. δ_1 is equal to δ_2 . J coupling J_{13} is also equal to J_{23} . That means, two protons are magnetically equivalent. It satisfies the condition. Not only the chemical shifts are there, not only are chemically equivalent, they are also magnetically equivalent because the couplings are same. So, this is the condition for magnetic equivalence. This is one example.



You can take the example of this molecule. What is this molecule? There is a symmetry. There are two CH₃. So, this CH₃ chemical shift and this CH₃ chemical shifts are same. They are chemically equivalent. But what about the coupling between this proton and this CH₃ and this proton and this CH₃? What is the coupling between 13 and 23? J₁₃ is again equal to J₂₃. That means, these two methyl protons are magnetically equivalent.

Consider this classic example of methane. This methane has four protons. Very interestingly, all the four protons 1, 2, 3 and 4, they are chemically equivalent. They come at the same chemical shift. Whatever is the coupling, there are several couplings, 1, 2 coupling, 1, 3, 1, 4, 2, 3, 2, 4, 3, 4. All the couplings are present, but all of them are equal, identical coupling. So, the methane is a classic example of all the four protons which are magnetically equivalent. This is an example. All the six couplings are same. All the four chemical shifts are same.

But we can come across some funny situations also. We can come across magnetic equivalence with multiple couplings. Look at this molecule.

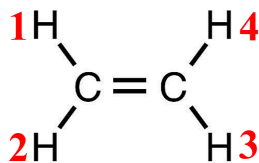


This is 1, 4, difluoro, di chlorobenzene, whatever that name. We have two protons and two fluorines. Consider the chemical shift of fluorine. 1 and 4, they are same. Consider the chemical shift of protons. 2 and 3, they are same. What is the coupling 1, 2? It is equal to 3, 4. What is the coupling 1, 3? It is equal to 2, 4. That means, each proton experiences two couplings, 1, 2 and 2, 4. This proton experiences two couplings 3, 4 and 1, 3. Each proton experiences two couplings. Similarly, each fluorine experiences two couplings. This fluorine experiences two couplings, and the interesting thing is coupling 3, 4 is not equal to coupling 2, 4. They are different. But each proton experiences two different couplings. Each fluorine experiences two different couplings. That means, two protons are magnetically equivalent and two fluorines are also magnetically equivalent.

Go to the example of benzene. We all know benzene has six protons. Let us look at six

protons. All the six protons of benzene come at the same chemical shift. All of them have the same frequency, identical frequency. All are equal. At the same time, each proton can experience three different couplings. Consider this proton 1. It can have an ortho coupling. It can have a meta coupling and it can have a para coupling. Each proton experiences three different types of couplings. But couplings are identical. For example, this is what we said for proton 1. Go to the proton 2. This has ortho coupling. This has meta coupling. This has para coupling. So, each proton experiences three different couplings of identical strengths, because these ortho meta para couplings are not identical in benzene. The ortho coupling is 8.5 hertz. meta coupling is 1.5 Hz. para coupling is 0.5 Hz, approximately. They are different strengths. So, but nevertheless, it gives a single peak in the NMR. That means, all protons are chemically equivalent. At the same time, in spite of multiple couplings present, all the protons experience the same type of couplings. So, it is magnetically equivalent spin with multiple couplings.

This is another example. Ethylene. All the four protons are chemically equivalent. But 1, 2 coupling is different from 1, 3, different from 2, 4 or 1, 4.



Similarly, this coupling, this coupling and this coupling are different. Consider this. This, this and this couplings are different. So, all these examples I am giving you. Ethylene also is a classic example of magnetically equivalent spins with three different couplings. Benzene is also an example of magnetically equivalent spin with three different couplings.

So, these are all examples of classical examples of chemically and magnetically equivalent spins with multiple couplings. Not only there are multiple couplings, sometimes there can be single coupling also. But the important point you should remember is all magnetically equivalent spins are chemically equivalent and the converse is not true. And all these magnetically equivalent spins, if you take the NMR spectrum, they give rise to a single peak. For example, this ethylene gives rise to a single peak in NMR. Similarly, benzene gives rise to a single peak in NMR, although there are three couplings. Methane, there are different couplings. Five or six couplings are there, but all of them are identical. All proton chemical shifts are identical and gives a single peak in NMR. So, this is the concept of magnetic equivalence. So, since the time is getting over, I am going to stop here.

But what we discussed today, I would just like to summarize in couple of sentences. See, we started discussing about the multiplicity pattern yesterday and today, we wanted to talk about relative signs of the coupling. As I said, the coupling could be positive, negative or 0. How does this sign of the coupling is affecting the NMR spectrum? When the coupling is 0, we took the example of two coupled spins, four possible energy states. In the four possible energy state, beta, beta, alpha, alpha, alpha, beta, beta, alpha, there are four possible transitions, two for A, two for X, two A transitions will overlap, two X transitions will overlap and gives rise to only two peaks. Chemical shifts are different, that is when the coupling is 0. I said when the coupling is present, not only present, if it is positive, what will happen? Alpha, alpha and beta, beta are unpaired spins. Their energy states get destabilized. As a consequence, they are pushed up by $J/4$.

So, energy gets changed by $J/4$. Whereas, alpha, beta and beta, alpha states are paired spins. Their energy states are pushed down by $J/4$. Now, we calculate the frequencies. Again, transitions which are allowed for A transitions and X transitions, we found out. One of the A transitions has higher frequency and other one has lower frequency. So, that is how we get a doublet when there is a coupling. Similarly, X spin has one higher frequency, X has one lower frequency. So, they are again two lines with A and two lines for X and this separation gave me J_{AX} , but I do not know whether it is positive or negative. But I know AX coupling give 4 transitions,, when 2 spins are coupled, we get 4 peaks. That is fine. We also understood what happens if the coupling is negative. Then, reverse will happen. Alpha, alpha states instead of pushing up, they get stabilized comes down. Similarly, beta, beta comes down. Whereas, alpha, beta, beta, alpha state pushes up. The states get reversed. Calculate the energies, calculate the frequency again. Now, same 1, 3 transition which was higher frequency now became lower frequency and 2, 4 transition which has lower frequency became higher frequency because of large energy separation. So, same thing is true with X-spin. So, that means, the two-two lines which were like this get reversed like this. It was like this, became like this. So, one dimensional NMR spectrum if you take, you will not know the effect of coupling at all. That is appearance of this spectrum remains invariant. It remains invariant with the change in the sign of the coupling. This is what we understood.

And also, I introduced about magnetic equivalence. Magnetic equivalence is the situation where not only spins should be chemically equivalent. That means, chemical shift should be same. Each spin should be having the identical coupling strength with other protons which it is coupled to. I took the example of methane. One proton is coupled to remaining three protons of the same coupling strength. All the four protons of the methane has the same chemical shift. So, it is a perfect example of magnetic equivalence. Other examples is benzene and ethylene we took. Each of them have multiple couplings. Multiple couplings, benzene has three couplings. Again, ethylene has three different couplings. But, each of the protons of benzene has three-three couplings,

identical three couplings. Couplings are same. Each of them experience ortho, meta para couplings. Similarly, in ethylene, each proton experience three couplings of identical strengths. These are also example of magnetic equivalence with multiple couplings. This is what we discussed today and further lot more we have to understand about the interpretation of NMR spectrum. We will continue with that in the next class. I am going to stop it here. Thank you very much.