One and Two dimensional NMR Spectroscopy: Concepts and Spectral Analysis

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Lecture 05 - Transitions in coupled spin systems

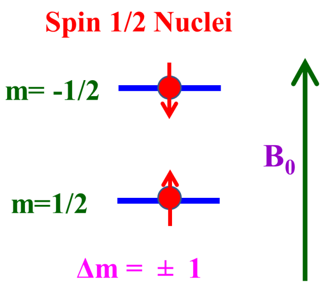
Welcome all of you. In the previous class, we discussed about bulk magnetization. I said what is a bulk magnetization? This concept is essential to understand NMR, because we have to create what is called a coherence. As I told you, we have magnetic moment vectors, which are alpha and beta spin states. Each of the alpha state and beta states oriented in the direction of the magnetic field and in the direction opposite to that of the magnetic field. We resolve them into three components. Due to random phase approximation, I said in the x-y plane, the components along the x-y plane get averaged out. We have only, because of the co-addition, a tiny magnet magnetization, which is like a tiny magnet along plus z and minus z. Due to difference in the population, we get a tiny magnet along the z-axis; that is oriented in the direction of the magnetic field. That is always in the direction of magnetic field, always stationary, or static. For detection of the signal, what we need to do is to perturb the spin system, in the sense from the stationary state, we have to create non equilibrium state. That is what we do by applying a radio frequency pulse in a direction perpendicular to the magnetic field. I said it could be any angle, but the 90 degree brings it to x-y plane from z-axis to x-axis or y-axis, then 180 takes to minus z and then 270 and then 360. You can keep rotating like this.

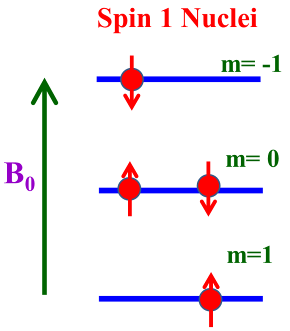
Then, when you apply radio frequency pulse, bring the magnetization to x-axis or y-axis, there is an instantaneous phase coherence. This is what we are going to detect. We detect the coherence and this coherence will not be in the same phase always. With the time, they will start dephasing and it decays. While decaying, simultaneously it grows along the z-axis. Both are exponential functions. One is a decaying function, other is a growth function. Then, we collect the signal decaying in the x-y plane, that is om x-axis or y-axis by putting a receiver. This we collect as a function of time. It is called free induction decay called FID in NMR, the common term FID.

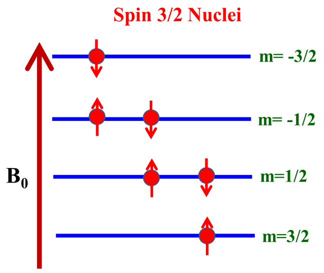
This is a time domain signal. Time and frequency are related to each other by a mathematical operation called Fourier transformation. This Fourier transformation we do for the time domain signal and get the NMR spectrum. There will be lots of frequencies present in that. Different peaks are there. Each peak corresponds to particular frequency. As I said, each of these peaks is not a delta function, it has a natural line width, which comes because of uncertainty principle. It depends upon the duration for which the spin stays in the excited state. Shorter the time stays in the excited state, broader is the peak. This is what I said .

Conventionally, if I take a proton NMR spectrum of molecules containing NH protons or OH protons, they are generally broad because they are attached to nitrogen and oxygen, which are quadrupolar spins. The quadrupolar spins relaxes faster. As a consequence, they do not stay in the exerted state for a longer time. This is what happens and this is what we understood. Now, continuing further, when I say there are transitions, we see the peaks. Peaks are coming because of the transition between different energy states. But, how these transitions are obtained? Is there any rule for it? Let us say, we have different energy states. For spin half we have two energy states. As I go further, I will tell you, if you have two spins, there are four energy states. If you have three, there will be even more. Then, what are the allowed transitions? What is the selection rule? In every molecular spectroscopy technique we have a selection rule.

Similarly, in NMR spectroscopy also, there is what is called as selection rule. Now, what is the selection rule, which allows us to detect the signal? The selection rule tells, each state or energy level has a characteristic magnetic moment, I am sorry, magnetic quantum number called M. And only the transition in which the magnetic quantum number changes by either plus 1 or minus 1 are the allowed in NMR. Anything apart from this plus 1 or minus 1 are not allowed. You understand, the selection rule is, the change in the magnetic quantum number between any two energy states should be either plus 1 or minus 1. They are called allowed transitions in NMR.







All other transitions apart from plus 1 or minus 1 are called forbidden transitions. Now, consider an example of spin half nucleus. Spin half nucleus has only two energy states. I told you, that is what we have been discussing. This is beta state, this is alpha state, minus half and plus half. Now, a change of the spin state from alpha to beta or vice versa results in a transition. See, what is happening here. Spins from alpha state goes to beta state, spins from beta comes to alpha state. And this is changed here is delta M equal to plus or minus 1. From plus half to minus half, difference is plus 1. From minus half to plus half, difference is minus 1. Both are allowed transitions. So, that is why you will get the signal when the spin goes from here to here or coming from here to here, both are allowed. These are all called single quantum transitions. Every peak in NMR pertains to flipping of a particular spin, where change in the magnetic quantum number between two spin states is either plus 1 or minus 1.

This is the important selection rule in NMR. Please remember, every peak in NMR corresponds to flipping of spin from plus one state to other state where the magnetic quantum number changes by +1 or -1. That is why they are called single quantum transitions. Remember, all the NMR spectrum conventionally what you people see, routinely what you take, each peak is coming because of flipping of the spin where the magnetic quantum member is changing either by plus or minus 1. They are called single quantum transitions. There is one quantum change of energy.That is why it is called single quantum transition. Now, I will consider the example for a single spin half nucleus in a magnetic field. What will happen? For a spin half nucleus, of course, as I already explained to you, there are only two possible spin states. This is the allowed transition.

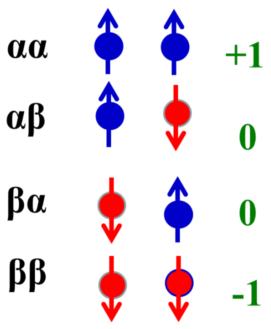
What happens for the nucleus which spin is 1, nuclear spin, for example, some nuclei deuterium has spin 1. As I told you, for I is equal to 1, m changes from minus I to plus I in steps of 1. So, minus 1, 0 and plus 1, three possible spin states are there for spin 1 nuclei. This is m equal to minus 1, you get m equal to 0 and m equal to plus 1. Now, what are the allowed transitions for this spin? Of course, m is equal to minus 1 to 0 or vice versa. That is allowed because the change is only 1. Similarly, m equal to 0 to plus 1. That is also allowed because here also delta m is equal to plus or minus 1. What about transition from this spin state to this spin state? From m equal to minus 1 to plus 1, this corresponds to change in two quantum of energy. Remember, this delta m equal to minus 1 to plus 1 is minus 2, plus 1 to minus 1 is plus 2. This is double quantum, twice the energy compared to the single quantum. As I told you, they are forbidden transitions. You cannot detect. So, this transition is not allowed. From minus 1 to plus 1 transition is not allowed.

Now, let us extend it for the spin 3/2 case. You can consider an example of the nuclear spin, which has spin quantum number 3 by 2. Then, what are the possible energy states for this? We have -3/2, -1/2, 1/2 and 3/2. Same, minus I to plus i in steps of 1, I have taken. Now, these are the possible energy states. What are the allowed transitions here? This to this is allowed. Minus 3 by 2 to minus half or minus half to minus 3 by 2, both are allowed. Either it is plus 1 or minus 1. This is allowed transition. What about this? Minus half to plus half. Of course, we saw that in spin off case, that is also allowed. What about plus half to 3 by 2? The difference is minus 1 and plus 1. That is also allowed. So, there are three possible transitions for a spin 3 by 2 case. If you consider a single nuclear spin, which has 3/2, there are 4 different energy states corresponding to 4 different magnetic quantum numbers, you can expect three transitions like this according to selection rule.

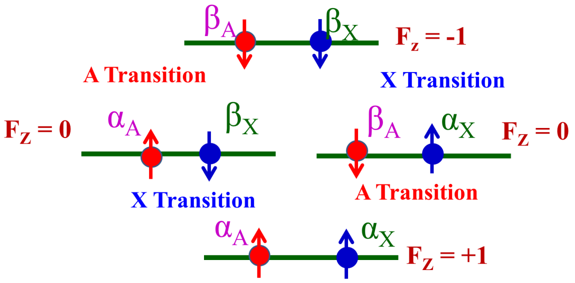
Now we will try to see number of allowed transitions, possible transitions in different coupled spin systems. This is very important, please understand because we have to use this, to understand how to analyze the spectrum, as we go ahead. In this course, we try to analyze lot of proton spectra, NMR spectra of carbon and other varieties of nuclei. So, what is important is to understand how this peak comes. The transition or any peak in NMR is because of the transition between two energy states where delta M is equal to plus or minus 1.

Consider an example of CHCl3, chloroform. We have only one proton. I am not worried about these two, you know, I will ignore it. No coupling, we will say. Now, if I see protons, single isolated spin, what are the possible energy states? Proton has spin half. So, it has minus half and plus half two energy states. So, there are two energy states. The possible transitions here, that is plus half to minus half, minus half to plus half, both having identical frequency. So, it gives rise to single peak. An isolated spin of nucleus gives a single peak always. If you see the chloroform spectrum, $CHCl_3$ proton NMR spectrum, you will always find a single peak because it has only one isolated spin. It has only two energy states, one transition is allowed, alpha to beta or beta to alpha and gives rise to a single frequency.

Now, consider transitions in two coupled spins. What is a coupled spin? What is a coupling? I will explain that when we go further, may be after one or two classes. Now, consider the situation of two spins. What are the spin combination of orientations of the spins, we can think of? If two spins are there, one can be up, other can be down. Also, this can be up, other can be down. Now, there are various combinations. Both can be up, both can be down and this up, this down or this down, this up. Four possible combinations are there.

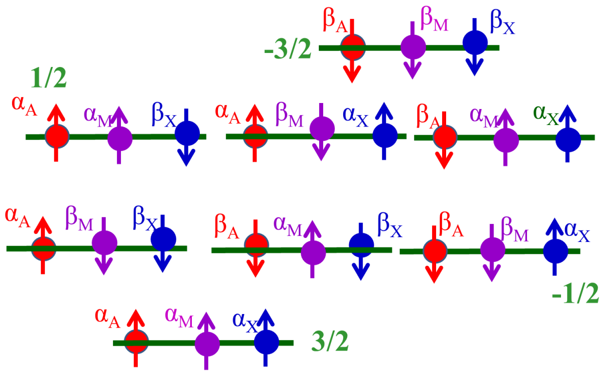


That is what I have written here. Both down, both up. This up, this down, this down, this up. Now, what is the magnetic quantum number of each of these energy states? The magnetic quantum number is just nothing but the sum of the individual magnetic quantum numbers. This is minus half for this spin, minus half for this spin. So, the total magnetic quantum number for this energy state is minus half plus minus half. It is minus 1. Whereas, for this energy state, plus half and minus half, 0. For this energy state, minus half and plus half, 0. What about this state, both are up, plus half, plus half. Then, magnetic quantum number for this energy state is plus 1. So, we know if I have two coupled spins, when two spins are there, four different possible spins orientations are there, four energy states are there. For each energy state, magnetic quantum number you can work out, which is nothing but sum of the individual magnetic quantum number for each energy state. So, this is minus 1, 0, 0, plus 1.



Now, what are the transitions allowed here? We will apply the selection rule. According to the selection rule, if I write like this, from this to this minus 1, say from minus 1 to 0, it is allowed transition. Now, one spin can change its state from beta to alpha. In fact, I can find out which spin is changing, which of the two spins. I call it as A and X spins, two different spins. Now, this corresponds to a transition, because A spin is changing its state from beta to alpha. It is allowed transition, Now, what about this one? Here also, beta spin is changing to alpha and vice versa. Again, A spin; this is again 0 to 1, allowed transition. This is also a transition. What about this one? minus 1 to 0, that is also allowed transition. But notice, here X spin is changing its state from alpha to beta and vice versa. Similarly, this is also allowed, plus 1 to 0. Again, here X spin is changing its state from alpha to beta and vice versa. So, there are four transitions for two coupled spins, two for A and two for X. Easily, I can identify which are the transitions for each spin. You can identify, you can understand this, depending upon which spin is flipping its state from alpha to beta or vice versa.

Now, let us look at energy levels and transitions for three coupled spins. It is little tricky. We have to understand this, because we will try to analyze a spectra of two spin, three spin, four spin, etcetera. First order analysis, second order analysis, everything we will have to do. But now, what are the possible energy states, if I consider three coupled spins? I have identified this as A, M and X, three spins.



A can have two orientations up and down, M can have two orientations up and down. Similarly, X can have two orientations up and down. These are all alpha states, these are all beta states. So, A can have alpha and beta states, M can have alpha and beta states, X can also have alpha and beta states. Now, all the three when they are interacting, when they are coupled among themselves, how many energy states you can think of, How many possible orientations you can think of? One possibility, all the three can be up, one possibility, all the three can be down, that is also possible. Now, we can think of other combinations, one up, two down and this and this are up, this down. See, varieties of combinatios. Think of two up, one down’ and two up, one down. There are three possible combinations. For example, these two can be up, this can be down, this and this can be up, this can be down, this can be down, these two can be up. So, there are three combinations. Similarly, when two down and one up, again three combinations. So, totally if you have three coupled spins, if you look at the energy levels, there are eight possible energy states. This is only one possible energy state, where all the three are down, minus half, minus half, minus half, all the three are down. Total magnetic quantum number for this energy state is minus 3/2. What about this? Plus half, plus half and plus half, again it is plus 3/2.

Here is the problem, you look at this energy state. Two up, one down, plus half, plus half, minus half. This will become plus half. Same way here, two up, one down, two up, one down, all the three energy states are plus half energy state. Magnetic quantum number is for each of these energy state is plus half, the total magnetic quantum number. Remember, total quantum number, magnetic quantum number is nothing but the sum of the individual quantum number of each of these three. Similarly, here now two down, one up, minus half, minus half, plus half, it is minus half. Similarly, here minus half, minus half, plus half. So, all the three energy state correspond to minus half state. So, there are now three possible orientations you can think of, minus 3 by 2, plus 3 by 2 and minus plus half and minus half. Only eight energy states, but four possible different magnetic quantum numbers are there.

Now, what are the allowed transitions here? I can think of the transition from plus 3 by 2 to half. Here, look X spin is changing from alpha to beta or vice versa. That is allowed transition, plus 3 by 2 to minus plus half is 1. Similarly, half to plus 3 by 2 is minus 1, that is allowed. This is X transition. This is also allowed, half to half. Again, X spin is changing its orientation from alpha to beta. This is also allowed. Again, X is changing from half to minus half. This is also allowed, minus half to minus 3 by 2. Again, X is changing orientation. So, how many transitions we saw for x spin? Four. Four transitions we saw. All these are X transitions.

Now, what about this one? This is allowed. A is changing from beta to alpha. This is allowed, minus 3 by 2 to minus half. You will get minus 1. Similarly, if you go from here to here, you will get plus 1, allowed. What about this one? Plus half to plus 3 by 2, where beta is changing again, beta A is changing to alpha A. This is also A transition. Again, this is the A transition allowed. Half to minus half and another A transition, half to minus half allowed. This is how four A transitions are identified. We saw four x transitions, four A transitions.

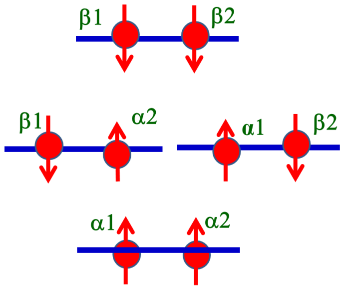
Now, again this is allowed, where M is changing orientation from beta to alpha. This is allowed. Again, M is changing orientation from alpha to beta. Again, this is M transition and this is M transitions. How many we got? Four A transitions, four M transitions and four X transitions. Totally, we have got 12 peaks. When three protons are coupled, or any three spins are coupled, totally we are going to get 12 transitions, 12 peaks.

Remember, when we had two spins, we got four peaks. Two spins are coupled. We worked out in the previous slide. Four transitions are there, two for A and two for X. Now, when three are coupled, we have four for A, four for M and four for X. There are totally 12 transitions. You go to the four spins, it is even more difficult to understand, because they will have a 16 energy states. It is very difficult, but you can work it out. But simple rule is two to the power of n transitions are there. If there are n coupled spins, we have two to the power of n transitions. Here n is equal to, let us say two, two square. That means there are four peaks. Now, take n is equal to three. It is two cube, which is eight peaks. For each of the protons which is coupled, you are going to get, if you look at A, will have, A will have four peaks, M will have four peaks and X will have four peaks. So, 8 energy states totally and total number of transition is given by ${}^{2N}C_{N-1}$. We will work it out when I come to the next one. When I come to the real quantum mechanical analysis, I am going to explain this to you. So, they have eight energy states and then total number of transitions is given by ${}^{2N}C_{N-1}$. Now, flipping of a spin in a coupled spin system, we always see only one spin is fliliping. One spin is flipping for A, M and X transitions. We got four for A, four for M and four for X. Each time only one spin was changing, from alpha to beta or vice versa. Now, we can think of only these are the possibilities. Only one spin is changed from alpha to beta, beta to alpha, whether in the two coupled spin, three coupled spins or ten coupled spin, does not matter. Between two energy states, one spin has to change the orientation from alpha to beta or beta to alpha. Then, we are going to see the transition. This is the selection rule.

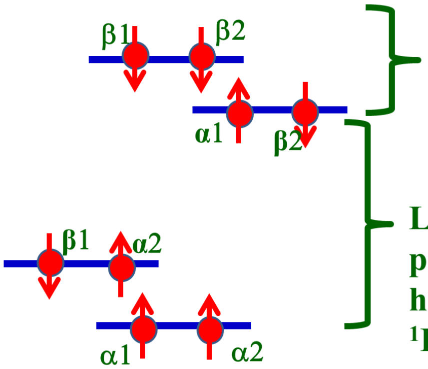
Now, we can also consider another possibility. It is something different. This is called combination transitions. So far, we worked out four transitions each for A, M and X. Is there any other thing which we can think of? Look at this possibility. This is half to half allowed. What is happening here? All the three spins are changing alpha to beta, beta to alpha. See, beta A becoming alpha A, alpha M is becoming beta M, alpha X is becoming beta X. Here all are changing, but still the change in the total quantum number is minus half to plus half only. It is still one only allowed single quantum. Remember in the previous slide, I said only one spin is changing at any time to give a transition. But these are all examples called combination transitions, where multiple spins can flip at a time, but still maintaining the condition, the change in the magnetic quantum number between two energy states is either plus 1 or minus 1. These are called combination transitions. Here, this is allowed. This is also allowed. These are also allowed. These are the three transitions which are allowed. Again, all the three spins are flipping at a time, but still delta m is always plus 1 or minus 1. So, a single spin or multiple spins can flip at any given instant of time provided the delta m equal to plus or minus 1 should be maintained. They are called allowed transitions and in each of these transition, energy change is a single quantum and that is why they are called single quantum transitions. All the conventional NMR, what you people are seeing is called single quantum NMR. That is what I have been telling you.

Now, let us look at the little bit of details into energy level separation for HOMO and HETERO nuclear spins. We saw four energy states for two coupled spins for HOMO nuclear spins. I did not say whether HOMO or HETRO nuclear spins in the previous slide. Now, I will explicitly tell what happens if it they are HOMO nuclear spins, what happens if they are HETERO nuclear spins. HOMO nuclear spins means like both protons, both could be fluorine, both could be phosphorus, does not matter. HETERO means one is proton, other may be carbon, nitrogen, phosphorus, fluorine, etcetera. In these two states, in these two conditions, when you have HOMO nuclear spins or HETRO nuclear spins, how the energy transition comes, these are the energy states.

For HOMO nuclear case, you see the four energy states, but you see this is how it comes. In the HOMO nuclear case alpha-beta and beta-alpha states where magnetic quantum number is 0. Both the states have nearly same energy. There is small difference, minute difference, do not worry, but we can say practically they are equal.



Whereas, if you want to look at the energy states for two HETERO nuclear spins, it is something different.



Small energy gap pertains to dilute heteronuclear spin, e.g., ^{13}C

Large energy gap pertains to abundant homonuclear spin, e.g. ^{1}H

Look at it, alpha, beta states have substantially different energy. This also has m equal to 0, this also has m equal to 0, but nevertheless they are not of the same energy. Energy separation is quite large between alpha-beta and beta-alpha spin states. This is one alpha, alpha, and see this is beta, beta, this is alpha, beta and beta alpha. There is enormous separation between alpha-beta and beta-alpha states.

This small energy gap here correspond to dilute spins. For example, carbon-13, nitrogen-15, etcetera. They have low gamma. I told you, gamma difference is more, your energy separation is very small, 4 times smaller gamma. This I explained to you in one of the classes previously. Proton energy separation is this much and carbon has 4 times less gamma, energy separation is 4 times smaller. Similarly, when you take a heteronuclear spin, this has lower energy separation because these have larger energy separation because they are different spin, may be abundant spins like proton or fluorine or phosphorus. This is how the energy states will appear especially for heteronuclear spin system. This large energy gap is for abundant homonuclear spins like proton, fluorine, phosphorus, etcetera. So, alpha, beta and beta alpha states are substantially different for heteronuclear spin system. But what are the allowed transitions? Again same, there is no difference. This corresponds to a transition; corresponds to let us say beta to alpha, which is heteronuclear spin, here beta to alpha heteronuclear spin. Here alpha to beta; in this case alpha beta for one of them, alpha beta for other one, you can see. See, this is what happens. You can see alpha to beta 2 is changing here, alpha to beta 2 is changing here. Here beta 1 to alpha 1, here alpha 1 to beta 1. These transitions correspond to heteronuclear spin and these larger transitions correspond to homonuclear spins. As a consequence, this peak is 4 times smaller in intensity than this one. If I take this as the carbon 13; the carbon 13 intensity is 4 times smaller than proton because the energy gap is 4 times smaller.

This is what a little bit of information which I wanted to tell you especially when you want to understand heteronuclear spin state. So, with this little bit of introduction to NMR spectroscopy conceptual understanding we have completed. But what I wanted to summarize today is what we discussed in this class. We discussed about the selection rules. Selection rules is the one where the change in the total magnetic quantum number between two energy states should be either plus 1 or minus 1. We took the example of spin half case. In spin half case, there are two possible orientations; plus half and minus half, alpha state and beta state. A transition between both of them are allowed alpha to beta, beta to alpha because the difference if you take between these two energy state is either plus 1 or minus 1. They are allowed transitions. Whereas, consider the spin one case, we have minus 1, 0 and plus 1, three energy states are there. In three energy states, again minus 1 to 0 is allowed, 0 to plus 1 is allowed. They are possible transitions because the difference is plus 1 or minus 1. Minus 1 to plus 1 is not allowed, it is double quantum, not allowed. That is a forbidden transition. Go to spin 3 by 2 case, minus 3 by 2, minus half, plus half and plus 3 by 2. Now, minus half to plus, minus 3 by 2 to minus half is allowed, minus half to plus half is allowed, plus half to plus 3 by 2 is allowed. Other things are not allowed because that will be different. These are all single quantum transitions. Anything other than that is different from plus 1 or minus 1. Delta m is not plus or minus 1, it is more than or less than that. They are not allowed. Similarly, we try to understand what happens if you have a combined spin system like coupled spin system like two spins. We have possible combinations for four different energy states; two for n coupled spins. We have 2 to the power of n energy states and ${}^{2N}C_{N-1}$ transitions, which we discussed, but the energy states are 2 to the power of n. For two coupled spins, there are four energy states. For three coupled spins, there are eight energy states. And what are the possible spin states we worked out for two spins, alpha alpha, beta beta, alpha alpha beta, beta alpha. Similarly, for three spins, alpha alpha alpha, beta beta, beta and all possible combinations we can work out. There are only four possible magnetic quantum numbers. They are minus 3 by 2, minus half, plus half and plus 3 by 2. So, that means, what are the allowed transitions we can find out. We understood there are four allowed transitions for A, four for M and four for X for three coupled spins, and for two spins, two for A and two for X.

For three coupled spin, at any given instant of time, only one spin is changing its orientation from alpha to beta or beta to alpha. And I also showed you in the three coupled case, there are possibilities where combination of spins can also flip over. Three spins from plus half to minus half, plus half to minus half. Here all the three spins can simultaneously switch over, that is allowed. All the three will change from alpha to beta, beta to alpha. Each spin was changing either from alpha to beta or beta to alpha, but simultaneously they are flipping. But still maintaining the total change in the magnetic quantum number between energy states is either plus 1 or minus 1. That is they are called combination transitions, that is also allowed. And then we also saw what is the energy level separation for a two spin homonuclear case and heteronuclear case.

In the homonuclear case, alpha-beta and beta-alpha energy states are nearly equal. Whereas, in the heteronuclear case, alpha-beta and beta-alpha states are substantially different. And for heteronuclear case with gamma being smaller, energy separation is smaller. For homonuclear case, for homonuclear energy states separation are quite larger. As a consequence, if you consider heteronuclear spin case, energy of transition of proton is much larger in intensity compared to other heteronuclear spin. For example, if you take proton and carbon, proton intensity is quite large, carbon is four times smaller than that, one-fourth of that intensity because of gamma.

This we can understand by looking at the energy level diagram. So, with this, I have summarized what we discussed today. So, basically in the last two, three classes and till today, we discussed lot of things about fundamental concepts of NMR spectroscopy. This concept you have to understand. It is very, very important. So, I discussed a lot of things and explained many things and in the next classes, we start understanding more about NMR parameters like chemical shifts, coupling constants, etcetera. But till today, only the basic fundamental concepts of NMR have been discussed. I am going to stop it here today and we will continue with the remaining topics from next class. Thank you very much.