# One and Two Dimensional NMR Spectroscopy for Chemists

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## Lecture - 10
## Selection Rules and Transitions

Welcome back all of you. In the last couple of classes, we discussed a lot of things about fundamentals of NMR including it is historic perspective, concept of spin. And we discussed about spin angular momentum, magnetic moment, magnetic quantum number and the interaction of the nuclear spin or magnetic moment with the external magnetic field. The effect of magnetic field, the linearity of the interaction with the magnetic field. And then we also discussed several things about the sensitivity of detection. And we also arrived at what are the nuclei which give raise to NMR, and how to arrive at the nuclear spin, like whether it is as odd integer or even integer and we applied lots of pulses, we discuss about magnetization, population different ratio, Boltzmann distribution, how to induce resonance and what is bulk magnetization. After introducing the concept of bulk magnetization, how do we tilt the magnetization by any angle we like, the pulse phases, RF phases, signal phases everything we discussed. And last time, we also discussed about, for example free induction decay, T2 and T1 recovery, that is T2 decay where the coherence which is created will get completely decoherence as a function of time, and the growth of magnetization along Z axis to retain thermal equilibrium, all the things were discussed.

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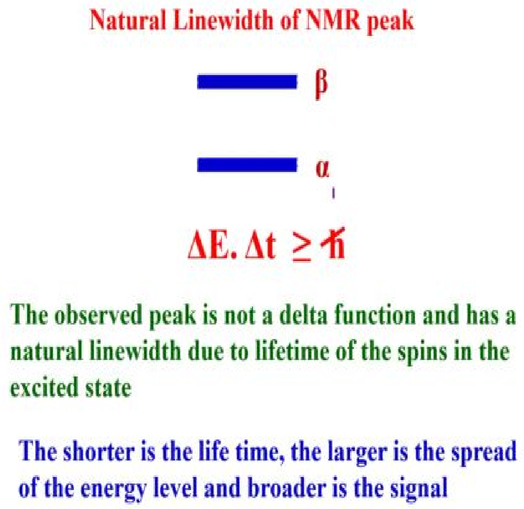

Natural Linewidth of NMR peak

β

α

$\Delta E . \Delta t \geq \hbar$

The observed peak is not a delta function and has a natural linewidth due to lifetime of the spins in the excited state

The shorter is the life time, the larger is the spread of the energy level and broader is the signal

And we also got the free induction decay, we got the signal. That is what, we did theFourier transformation and we knew how to get the NMR spectrum. And one thing I wanted to tell you, when we start discussing about NMR, especially the spectrum after Fourier transformation, we get peaks with certain widths. There will be natural line width for the peak, you will not get delta peak, I am sorry delta peak like this, sharp peak like this. It is not possible to get that.

What is the reason for it? There is a natural line width for this. This is given by this. Due to uncertainty principle delta E into delta t is equal to h cross. We know energy and time are uncertainty pairs. It means the observed peak is not a delta function, and has some natural line width, it is due to the lifetime of the spins in the excited state. That is the important concept you should know.

Now the spins are excited here, what is the lifetime of this spin or Ok, If it comes here and goes back, what is the lifetime of these? If the spins are here they have to be excited to the highest high energy level. So, the observed peak is not a delta function, mainly because of natural line width, depending upon the lifetime of the spins in the excited state. Now, the shorter is the lifetime, the larger is the spread, because delta t becomes smaller and smaller. Energy spread becomes larger and larger, because this is a constant value. So now if it resides in this state for a shorter time, then the spread of this energy becomes even larger, like this, energy state. Then what will happen to the Signal? Signal can be from here to here, here to here, here to here. There are a number of possible transitions you can think of due to spread in the energy level. As a consequence you do not get a delta function of single frequency. You get peaks resonating at various frequencies like this. And you are going to get width like this, this is the width of the peak. It is coming because of uncertainty principle, uncertainty. And the natural line width is coming because of this. Fine, that you cannot do anything. You can get the homogeneity, tune the magnetic field, try to get the best resolution, but beyond the natural line width you cannot do anything. That is inherently present, we have to accept that.

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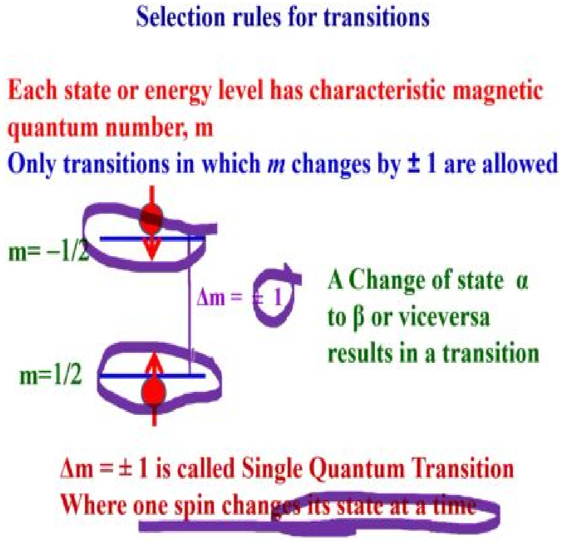

Selection rules for transitions

Each state or energy level has characteristic magnetic quantum number, m

Only transitions in which *m* changes by ± 1 are allowed

A Change of state α to β or viceversa results in a transition

Δm = ± 1 is called Single Quantum Transition

Where one spin changes its state at a time

Now, when I have to detect the transitions. When I get the NMR spectrum, let us say I have a single spin, 1 spin, and I get 1 transition. I have 10 different spins, I will get 10 transitions. What do you mean by getting transitions? Remember we had spin half situation, we have 2 states minus half or plus half. We also discussed the situation of spin by 1, we have minus 1, 0 and plus 1, 3 states. That is what we discussed.

If we go to 3 / 2 spin, we have - 3 / 2, minus half, plus half, plus 3 / 2, four states. Now, what do you mean by observing the peak? Observing the peak is the population difference between 2 energy states, that is what I said. Now, the spins go from here to here, or here to here what is allowed, can it go from here to here and also come back from here to here, is it allowed or the spin can go only from here to here, and come back only from here to here, or if we extend this can this spin go from here to here and come back from here to here? What are the allowed energy levels, between them the spins can undergo transitions? What I mean by transition is the spins can undergo flipping from alpha state to beta state and beta state to alpha state. That is the requirement for observing the signal.

As I said, there are 2 transitions, when the spin goes from alpha state to beta state, or beta state to alpha state, that is from plus half to minus half, or if it comes from minus half to plus half state, we are seeing the signal. One of important conditions to see that transition, when this happens, if there are let us say 100 spins are here, and 99 spins are here. A difference in population of one spin I am detecting.

So, for such a thing to happen, the transition should take place only between the energy levels when m changes by + 1 or - 1. What is m, I already told you m is a magnetic quantum number, which depends upon I, $m_I$, I said it goes from - I to + I. For spin half, there are 2 states, minus half and plus half. Is the transition allowed between them? Look at it, If the goes from plus half to minus half, take the difference it is 1. It also came back, let us say from minus half to plus half it came down, not only it went up but came down. Take the difference, here minus half plus half it is - 1. So, both are allowed transitions. The transition can take place when the spins undergo flipping between 2 energy states whose difference in the magnetic quantum number should be either plus 1 or minus 1.

So if it is m is equal to minus half and m is equal to plus half here, the difference is called delta m, delta m between these 2 energy states. That is the difference in the total magnetic quantum number of 2 energy states. For this energy state magnetic quantum number is minus half, and for this, it is plus half. This difference is what you are going to see, if it is plus 1 or minus 1. Otherwise, transitions are not allowed anything other than this are called forbidden transitions in NMR.

Let me give you one more example like this. And also one more thing you should understand in this case, what is happening is, if there are a number of spins, only the change in the quantum of energy between the states is only 1. It is a single quantum energy change, plus half to minus half or minus half to plus half. The change in the energy is only 1 quantum, only 1 spin is changing its state. It is called single quantum transition. A transition with one spin changes it is state from alpha to beta or beta to alpha, if not one spin, even 2 spins or 3 spins does not matter, but the total magnetic quantum number of this state and this state you find out, and the change in the magnetic quantum number between these 2 states, should be always plus 1 or minus 1. That means when the magnetic quantum number changes by plus 1 or minus 1, it is called single quantum transition.

Please understand, the magnetic quantum number changes between 2 energy states, either plus 1 or minus 1, it can be single spin or multiple spin, no problem, multiple spins also can undergo transition. But total change in the magnetic quantum number between 2 energy states must be either + 1 or – 1, they are called single quantum transitions.

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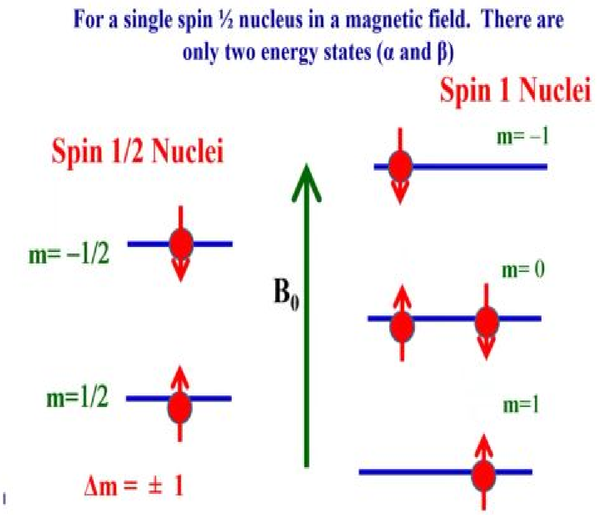

For a single spin ½ nucleus in a magnetic field. There are only two energy states (α and β)

This we just now we understood for spin half nuclei, this is the allowed transition because delta m is equal to plus 1 or minus 1.

Now, my question is, let us look at spin 1 nuclei. There are 3 possible energy states, m equal to minus 1, 0 and plus 1. Now, what are the allowed transitions here? Remember, minus 1 to 0 is it allowed, difference is minus 1, 0 to minus 1 is also allowed, difference is 1, 0 to 1 is allowed, difference is minus 1, 1 to 0 is also allowed ,difference is 1.

What about the transition between here to here, minus 1 to plus 1; if we take the difference, it is 2, plus 2 or minus 2, it is double quantum. It requires 2 quantum of energy, not single quantum. In all these changes here, when the magnetic quantum number changes where plus 1 or minus 1 there is 1 quantum of change in the energy. But here 2 quantum of energy, that is not allowed, only single quantum is detected, they are the allowed transitions.

So now let us see what are the allowed transitions in the spin 1 system, this is allowed, this is also allowed. What are the other things allowed here? Nothing there are only 2 possible transitions allowed in the spin 1 nuclei.

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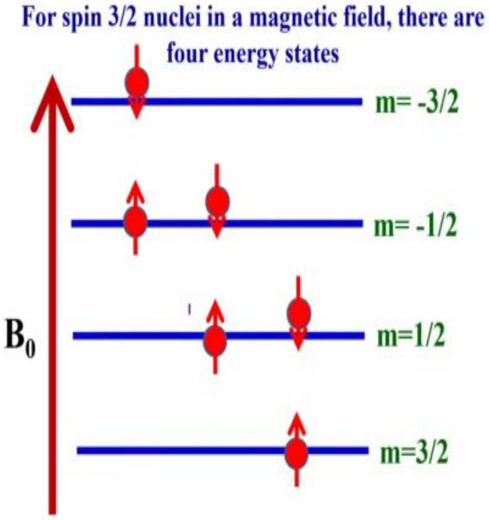
For spin 3/2 nuclei in a magnetic field, there are four energy states

Now, what about the spin 3 / 2 it will take, what are the possible energy states? What are the possible magnetic quantum numbers? 3 / 2, minus half, plus half and plus 3 / 2. Now look at it, what are the allowed things; minus 3 / 2 to minus half is allowed. Take the difference it is 1 either way also possible, minus -1 / 2 if you go to -3/2, that is also allowed. what about between these two states, of course it is allowed because we know in the spin half case, plus half or minus half are the 2 energy states, we know it is allowed. what about plus 3 / 2 into half that is also allowed. But what about transition from here to here, there is change of 2 quantum of energy. It is called double quantum, that is not allowed, not at all. What about from here to here? If we take the difference from here to here, it is 3 quantum of energy. It is triple quantum definitely forbidden. So, this one is a double quantum transition, where 2 quantum of energy is involved, here triple quantum, 3 quantum of energy is involved. They are not allowed, only single quantum transition, where the change in the magnetic quantum number is either plus 1 or minus 1 are allowed. In this case, also only 3 transitions are allowed that is what we observed.

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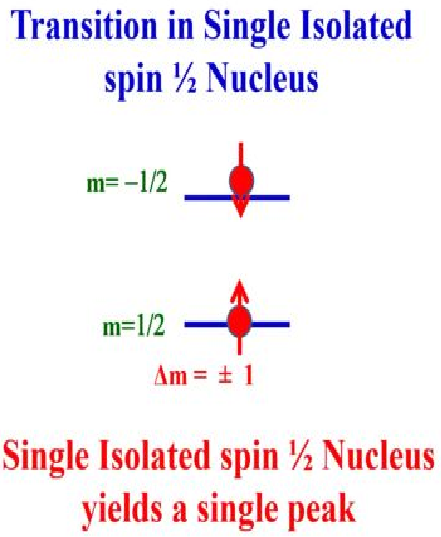

Transition in Single Isolated spin ½ Nucleus

Single Isolated spin ½ Nucleus yields a single peak

So, now let us understand, what we observe in isolated spins and coupled spins. Coupled spins we will discuss little later, when we introduce spin-spin coupling, scalar coupling. At the moment, I will just simply tell you for uncoupled spins, what are the energy levels? What are the allowed transitions? That we will discuss. Of course, you can always think of one isolated spin 1, spin half nuclei, one spin.

Which is the example for that? Think of chloroform CHCl3, if I take CHCL3. Now only one proton is there. If I want to detect, of course do not worry this is the natural abundance, I do not expect this to interact, at the moment we will not consider that. We will see only one proton and this will not interact with chlorine also. So, how many energy levels you can think of? only 1 proton is there, and spin of nuclei, there are only 2 possible energy states.

This is like this, it can be treated like an isolated spin half nucleus. Although it is in a molecule, at the moment we will ignore the interaction with carbon 13 and also their interaction with chlorine 35, in which case we say this is an isolated spin half nucleus. The number of allowed transition is only 1. So, if you go and take the spectrum of chloroform, in NMR how many peaks you should get? Only 1 peak, that is what happens. That is what you observe. Nothing else you we will see. OK. A single spin, isolated spin, gives a single peak.

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## Energy levels Separation for
## Homo and Heteronuclear spins

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Now, let us consider the energy level diagram for homo and heteronuclear spins and see how many transitions are allowed in each of the cases. how we detect the transition? It is a very important thing, so that for future classes to understand, this is a requirement.

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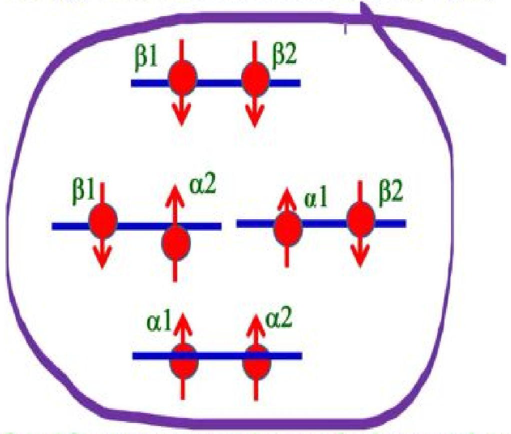
### Energy States of Two Homonuclear Spins



αβ and βα states are nearly same for homonuclear spin system

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Now if I consider the energy states of 2 homonuclear spins, remember, I have considered 2 homonuclear spins. There are possibilities like this for 2 homonuclear spins are like this, I have 2 protons, this proton and this proton can interact, because there are 2 tiny magnets. They can interact, they need not interact, does not matter either of them is possible. When they interact, there is an interaction energy. You know what is the interaction strength? I will tell you what that, coupling everything later. There could be interaction, there may not be interaction. Now consider both the possibilities, let us see what happens. Now, if you have 2 spins, what are the possible orientations of these spins? Whether it is coupled or uncoupled does not matter, whether they are interacting or not, let us say only 1 spin is there, only 1 spin, which is spin half nuclei, it can have 2 orientations, plus half and minus half. I have to take another spin, another proton,  2 orientations again, plus half and minus half. Now I will take both of them together. What are the combinations you can think of? Both can be up, both can be down, or this up, this down or this up, this down.

Only 4 possibilities, let us find out what happens if both are down, when it is down this is spin minus half orientation, this is spin minus half.  the total magnetic quantum number for this energy state is sum of these 2. Please understand, the total magnetic quantum number for this energy state, if you take, it is the sum of the individual magnetic moments.

What is the individual magnetic moment of this spin, in this state? Minus half, this is minus half. So, what is the total magnetic momentum of this energy state minus half, plus minus half, this is minus 1. What about this state? This is minus half this plus half. So, what is the total magnetic moment of this energy state, 0, minus half plus half if you take some of these is also 0. This total magnetic moment of any energy state ,if you want you have to take magnetic state each of the spin, what is it magnetic moment is it plus half or minus half, and then take the sum. That is all. Now, we do the same thing here.  This is plus half, this is minus half. So, if you take the sum it is 0. So, this is the state where the total magnetic moment is 0, what about this one plus half and plus half, the sum is 1. So now there are 4 possible energy states, corresponding to first 4 possible orientations.

The magnetic moment of each energy state if you calculate, they are minus 1, 0, 0 and plus 1. But remember one thing, I have written, alpha and beta states and have put as nearly same for homonuclear spin. I use the one nearly same, although plus half and minus half is 0, minus half plus half is 0, but if you go very deep into the NMR theory. It is not exactly equal, there is small difference could be there that we will not worry, but for your level, for the level of understanding at the moment it is OK.

Without going into the detailed advanced NMR, we will say both the energies are equal and I have written energy states as nearly equal. although small difference I have given do not worry about it. So, this is the energy state for the homonuclear spins. 4 energy states, we write like this.

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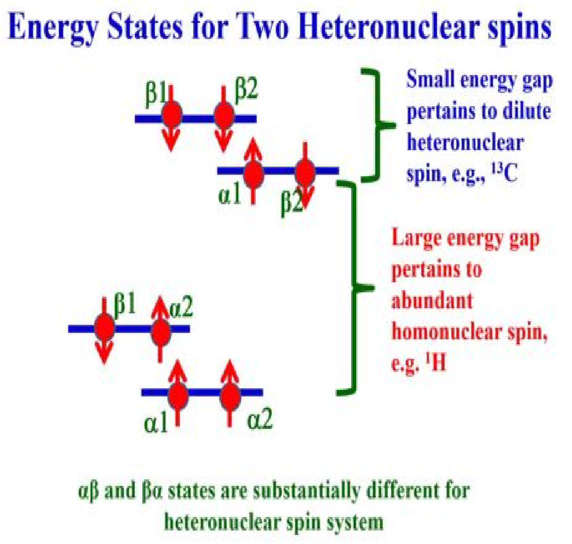

What about the energy states for 2 heteronuclear spins? Like one is proton, other is carbon. How does it work? Look at this. These are the energy states I have written. Now, these 2 have one energy separation, look at this and that is exactly equal to this. Look at this energy separation, this is exactly equal to this energy separation.That means 2 energy separations are same in one case and 2 energy separations, these 2 energy separations are same in other case. Why did I write like that? Remember, I am considering 2 heteronuclei one is proton, hydrogen OK. one is proton, another is carbon 13. What is it gamma of carbon 13? Gamma of carbon 13 is one fourth of that of proton. What do you understand from the concepts we have so far discussed? If the gamma is one fourth less, the energy separation is one fourth less. Right?

So, what we did is, the same in the homonuclear case what you observed, we wrote for four energy levels. But remember here, I wrote the energy separation for heteronuclear spin, that is carbon 13. This separation is 4 times smaller than this separation. This is another energy separation for this, this is 4 times smaller than this. Now, why I wrote like this, what is this one? This is simple.

To understand this one, we will look at the transitions later, but at the moment you understand, I consider this as beta state of spin 1, this is beta state of spin 2. Let us consider 1 as proton and 2 as carbon 13. That is what we consider. Now, the transition from this to this is allowed; minus 1 and 0 this is allowed, plus 1 and 0 this is allowed, plus 1 and 0 this is allowed, plus 1 and 0 this is allowed. So there are 4 transitions allowed because the magnetic quantum number of these energy states are; minus 1, 0, 0, plus 1. Similar to homonuclear case, this what you got.

Can I allow this transition? Yes it is allowed. In this transition which nuclei is changing the state? Look at it. I said 1 is proton and 2 is carbon, the carbon, no I am sorry it should be different, because carbon I made smaller here. 1 is carbon 2 is proton, because I have written this energy state smaller. So, we will consider this to be carbon energy. So, 1 is carbon 2 is proton.

In this case, proton is changing its state from beta to alpha, one single quantum, it is allowed, but the state of carbon is remaining same. This transition corresponds to proton, understand, the transition takes place between these 2 states, this has to be for proton because proton is changing its state from alpha to beta and vice versa. What about this transition? It is also allowed 1 and 0, but here again proton is changing its state from alpha to beta. These 2 are proton transitions, the energy separation is larger, has a larger intensity peak like this.

We will go to the next one, this transition is allowed, what is getting changed in this case, it is between - 1 and 0. Which spin is changing the state on this? 1 is carbon, see carbon one is changing from alpha to beta and beta to alpha. This is allowed, and what about proton state here? it remains unaltered.

What about this one? Here also, alpha of carbon is changing to beta and vice versa, but proton states remain unaltered. So, these 2 correspond to carbon transitions. And these 2 correspond to proton transitions. And I said this separation is larger, the intensity is larger. I will say this is larger and this is only one fourth intensity, this is for carbon. That is why I wrote the energy states like this. Proton has highest intensity, 4 times more than that of the carbon. This is heteronuclear energy state, small gap is for heteronuclear dilute spin, with less gamma. This large gap is for proton with abundant gamma, that is it.

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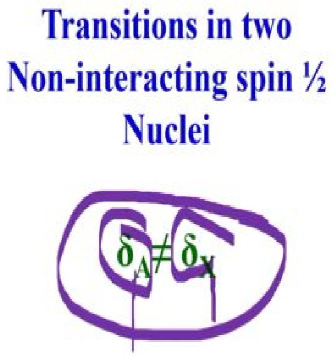

## Transitions in two Non-interacting spin ½ Nuclei

$\delta_A \neq \delta_X$

Now, we look at the transitions in 2 non-interacting spins. That means the same 2 spins we will consider whether it is homonuclear or heteronuclear, does not matter. There is no interaction between these 2, they are simply isolated spins. Nevertheless, we consider a situation one has a chemical shift A, which I will discuss later, OK. Instead of chemical shift, I will be using the word frequency. So one comes at a frequency A, other comes at frequency X, we will say that because I have not introduced chemical shift yet, that I am going to talk in the next class. So one comes at frequency A, one comes at frequency X, you assume like that.

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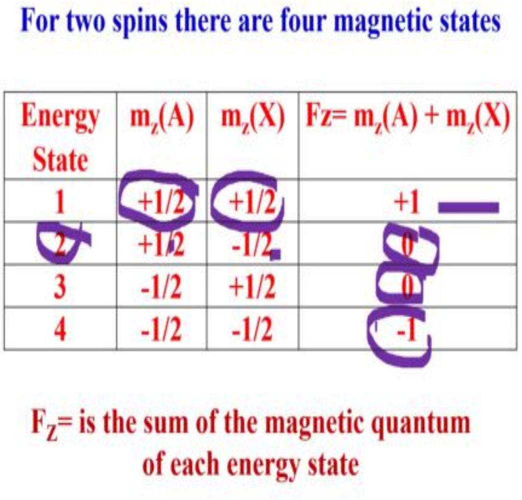

## For two spins there are four magnetic states

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

$F_Z$= is the sum of the magnetic quantum of each energy state

Now find out what are the 4 magnetic states for this? What is the total magnetic moment of each of these energy states? first is plus half and plus half, both are alpha, alpha states, it is plus 1, second energy state plus half and minus half, it is 0, minus half, plus half, it is 0, minus half and minus half, minus 1. These are the only possible magnetic states. We arrived at simply taking the sum of each individual magnetic moments of the particular state, that is all we did.

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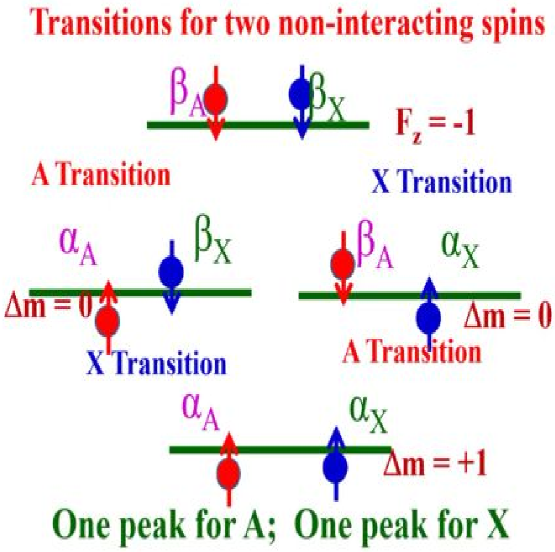

Transitions for two non-interacting spins

One peak for A; One peak for X

We wrote energy levels, we knew that, we have taken the example of homonuclear, we already discussed. Now let us look at the allowed transitions. This is allowed. I said it is 1 spin, that correspond to A, it is undergoing transition, homonuclear if I take, 2 protons, I do not care which is which, I call one as A, other as X, that is all. These correspond to one of the transitions for a particular proton. I labeled it as A, it is A transition

What about this? here also, alpha of A is changing to beta of A. Similarly, here, alpha A is changing beta A and vice versa. What is this transition? That is also A transition. Now, what are the other transitions allowed? Use your selection rule, what you have understood just now, it is allowed, minus 1 to 0 allowed, the difference is 1, minus 1 or plus 1 both are allowed.

So, here the state of proton remains unaltered, it remain same, but the state of X is changing from alpha to beta. What is this transition then? It is X transition. what is allowed now? One more is allowed, this is also allowed. Again the state of proton is remaining unaltered, the state of X is getting to changed from alpha to beta. What is this transition? X transition. So, how many X transitions we got? 2. How many A transitions we got? 2.

In a 2 spin system which are non-interacting, we have got 4 spins, I am sorry, 4 transitions, 4 peaks we get, but remember, this is energy separation, this energy separation, this and this. This is same as this, and this is same as this. That means, A transitions, although there are 2 peaks, the frequencies are same, because this energy separation is same, what will happen then, both A transitions will overlap and give raise to a single peak, It is like 2 peaks, one over the other, overlap.

What about the X, X also, this and this, the same frequency, because the energy separation is same. Here also there are 2 peaks, overlapping one over the other, there are 2 peaks.

So in the essential you see one peak for A and one peak for X, that is all. You understood! So, how many peaks we got? Totally 4 peaks, 2 for A and 2 for X, because of the energy is same, they are non interacting spins, if they were interacting, it would have been different. You would have got 4 peaks, but since they are non interacting, there is a overlap of transitions and you get only 2 peaks, that is all.

Let us take an example; I have a molecule. 10 different protons are there, 10 different hydrogens are there. None of them are interacting with each other. How many peaks we expect? 10 peaks, because each of them, we consider as an isolated spin.

If you consider the possibility of spin orientations, you have to write, OK., 10 may be difficult, take 3. You have to take alpha, alpha, alpha, beta, beta, beta, it is like two up, one down, etc. all combinations you have to see, then you find out what are the allowed transitions. If there are no interactions, you will find out, if there are 3 spins you could get only 3 peaks because for each of them get 4 peaks, they overlap. So, in non interactive spins, there may be n number of spins present in the molecule. If none of them are interacting among themselves, then you get 1 peak for each of these spins and this can be treated like n isolated spins. You understand, this is what happens if the spins are not coupled or interacting. Now, basically in NMR, that situation is very rare. All the spins generally will interact. Maybe we if they are far away this coupling is low, interactions will be low.

But generally they interact. then you will not get 2 peaks which are overlapped, You get 2 separate peaks like this; that is what we are going to discuss when you go to scalar coupling discussion, etc. But you please understand now, in this 2 non interacting spin case, there are 2 frequencies for A and X and the 4 peaks are there; 2, 2 will overlap, and you get only 2 peaks like this; one for A and one for X.

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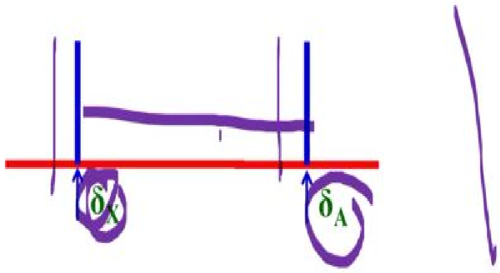
Assuming $\delta_X >> \delta_A$



I am assuming here frequency of X is larger than that of A. I am not talking anything about chemical shift for you, the symbol used for chemical shift is called delta. Right now I dont worry about it, this what I say, the frequency of X is larger than A. So I get 2 peaks like this. If I take 2 non interacting spins, put in the NMR magnet, take the spectrum, you get two peaks like this; you understood.

So when it interacts, the spectrum becomes very complex, and why they get separated like this. Why instead why can't both these come at the same frequency. All those things we discuss. That come under a topic called chemical shift, and when these are interacting what will happen? there is a coupling and there is a further splitting of the energy levels, this comes in a topic called scalar coupling.

All these things together give NMR spectrum, a beautiful spectrum with more multiplicity, more complexity, more dispersion, etc. So, we analyze all those things in the subsequent classes, from next class onwards and then by the end of this course, you should be in a position to analyze all NMR spectra of various nuclei. I will take examples and discuss all of them with you. So, that is it for now.

And in all these several classes, previous classes, this was the conceptual understanding of varieties of things we discussed. And most important thing is what happens to spin? What is the sensitivity? What is the interaction? And what is this coherence? What is saturation? What happens to the coherence? What happens to the longitudinal magnetization?

Number of things, we discussed, I tell you in the last about 8 or 10 classes. Please go back and read, NMR is huge ocean and what I have given you is a tip of an iceberg, there are a lot of things to understand. But this one is the basic requirement for you to understand at least fundamentals of NMR, so that you will be comfortable enough to analyze the spectrum and interpret, at least this much.

Please, I do not only rely on what I have been talking, what I have given is some concepts, some ideas, which is only a very small percentage. Lot of information you have to get from the literature. Please go to books and journals and you will understand much more. So I will stop here. From next class onwards will go to other topics like chemical shift, coupling, interpretation of multiplicity, and varieties of nuclei, lot of other topics. After 1D, then we go to 2D, there are lot more things to cover in the remaining classes of this course. Okay, thank you. I will stop here for the day.