Advanced NMR Techniques in Solution and Solid-State

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Module-52
DQ and ZQ of coupled spins
Lecture – 52

In the last class, we started introducing a new topic called multiple quantum NMR. These multiple quantum transitions are the ones where the change in the magnetic quantum number between two energy states is anything other than + or – 1, it could be 0, + or – 2, + or – 3 etcetera, anything other than + or – 1. And I also said for such a situation, if I have to see double quantum, two spins should be flipping at a time simultaneously.

If you look at the single quantum, we saw only at any given instant of time, only one spin is flipping from alpha to beta or beta to alpha. Whereas for higher quantum, it is a combination of coherently two spins or three spins into simultaneously flipping. So, this is multiple quantum. And one of the basic conditions for multiple quantum detection, I said all the spins should be part of the coupled spin system. Secondly, the coupling should be reflected in the NMR spectrum. For example, we looked at benzene. It has six protons and each proton experiences three different couplings. Each proton experiences ortho, meta and para couplings of different strengths. But they are not seen in the spectrum, there is no multiplicity; you get only a single peak. Similarly, we saw ethylene and pyrazine molecules, all the protons in these molecules are chemically equivalent.

As a consequence, the couplings are not reflected in the NMR spectrum. So, we cannot do MQT in such systems, since couplings are not getting reflected in the spectrum; that is what I said. And then we found out the barrier to the highest quantum is always the Nth quantum. For any N coupled spin system we can have N + 1 multiple quantum, including zero quantum; that is why it becomes N + 1. So that many quantum you can detect. And we also found out in a N coupled spin system, if N – M spins are simultaneously flipping, then the remaining are passive spins or spectator spins. They indeed give rise to local field at the site of the active spins and causes splittings. Whereas in the case of the N couple spin system, if you go to Nth quantum there are no passive spins. There is no local field generated at the site of the active spins.

As a consequence, local field is only the chemical shifts. So, the Nth quantum of N coupled spins, will resonate at the sum of chemical shifts of all these spins. So, it will be at the sum of the chemical shifts. So, this is what we understood in the last class. We will continue further today and see how chemical shifts and J-couplings evolve in the double quantum and zero quantum excitation of weakly coupled spins; two spin case or three spin case, like that. So, we will continue with that today.

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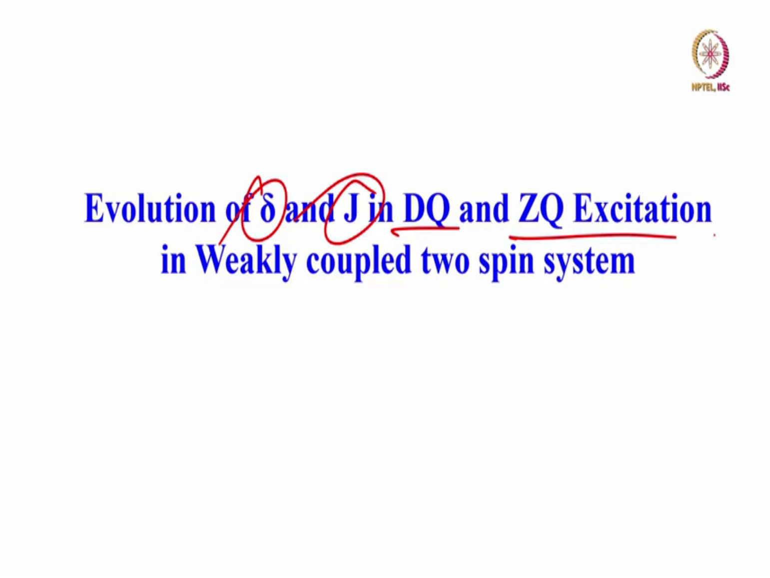

Evolution of δ and J in DQ and ZQ Excitation in Weakly coupled two spin system

And we will start discussing the evolution of chemical shifts and J-couplings in DQ and ZQ excitation of weakly coupled two spin case. Weakly coupled means it could be AX; it has to be AX in the two spin case.

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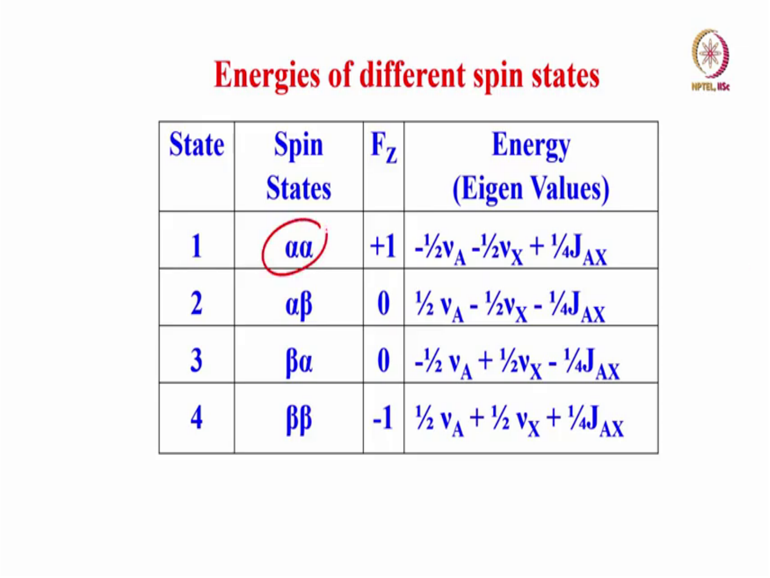

Energies of different spin states

State	Spin States	F_Z	Energy (Eigen Values)
1	$\alpha\alpha$	+1	$-\frac{1}{2}\nu_A - \frac{1}{2}\nu_X + \frac{1}{4}J_{AX}$
2	$\alpha\beta$	0	$\frac{1}{2}\nu_A - \frac{1}{2}\nu_X - \frac{1}{4}J_{AX}$
3	$\beta\alpha$	0	$-\frac{1}{2}\nu_A + \frac{1}{2}\nu_X - \frac{1}{4}J_{AX}$
4	$\beta\beta$	-1	$\frac{1}{2}\nu_A + \frac{1}{2}\nu_X + \frac{1}{4}J_{AX}$

And we have worked out the energies for the different spin states, for two spin case, weakly coupled. Remember, in the quantum mechanical analysis of the coupled spin system, we have worked out what is the energy for alpha alpha, alpha beta, beta alpha and beta beta states. These are the Eigen states we got, the Eigen values for the energy states.

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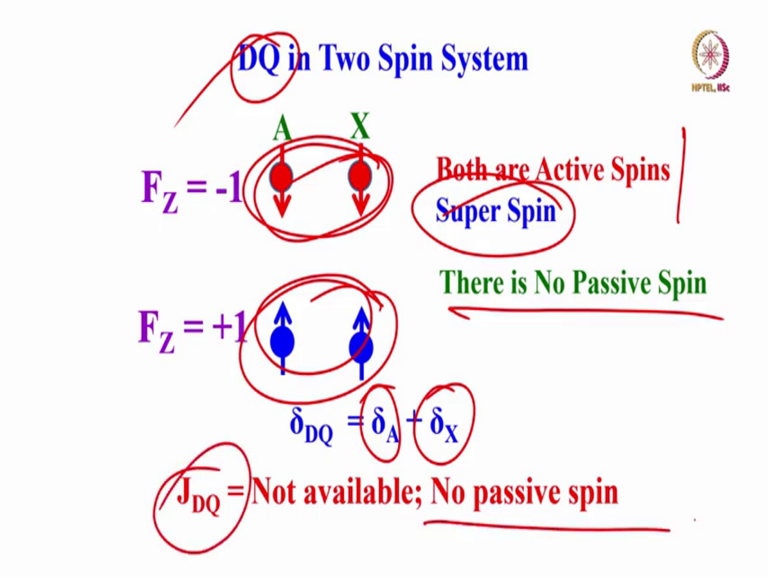

DQ in Two Spin System

$F_Z = -1$

Both are Active Spins

Super Spin

There is No Passive Spin

$F_Z = +1$

$\delta_{DQ} = \delta_A + \delta_X$

J_{DQ} = Not available; No passive spin

So, now, I just wanted to show this so that we will be using this soon. Now, we will go to the double quantum in the two weakly coupled AX spin case. There are only two possibilities for double quantum we can think. This is AX both are here beta beta, here both are alpha alpha. So, the possibilities are this can go like this alpha alpha to beta beta, or beta beta to alpha alpha. This is a transition which is forbidden.

But if we can detect it, there is only one such possibility it is double quantum. So, two spin coupled case, for double quantum, simultaneous flipping of beta beta to alpha alpha spin states takes place, and you get only single peak. Because both are active spins, super spins, two spins together flipping, and there is no passive spin. So, what do you get? As I told you, both the spins flip at the sum of the chemical shifts, the sum of the chemical shifts A and chemical shifts of X. Since J-coupling is not available, there is no splitting and you get only a single peak; no passive spin, no coupling.

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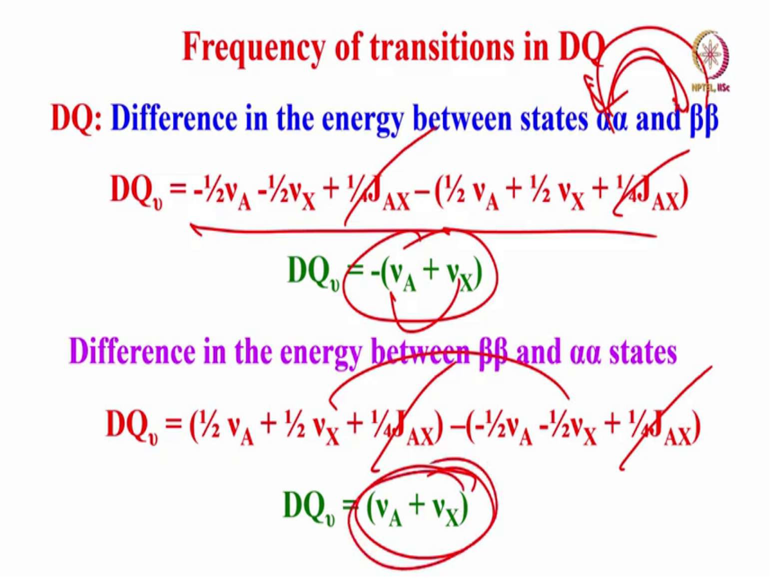

Frequency of transitions in DQ

DQ: Difference in the energy between states αα and ββ

$$DQ_\upsilon = -\frac{1}{2}\nu_A - \frac{1}{2}\nu_X + \cancel{\frac{1}{4}J_{AX}} - \left(\frac{1}{2}\nu_A + \frac{1}{2}\nu_X + \cancel{\frac{1}{4}J_{AX}}\right)$$

$$DQ_\upsilon = -(\nu_A + \nu_X)$$

Difference in the energy between ββ and αα states

$$DQ_\upsilon = \left(\frac{1}{2}\nu_A + \frac{1}{2}\nu_X + \cancel{\frac{1}{4}J_{AX}}\right) - \left(-\frac{1}{2}\nu_A - \frac{1}{2}\nu_X + \cancel{\frac{1}{4}J_{AX}}\right)$$

$$DQ_\upsilon = (\nu_A + \nu_X)$$

So, where do the frequency the double quantum comes? we calculate the energy for a single quantum. Now, find out what is the frequency separation between the energy states alpha alpha and beta beta. This, we take the difference between alpha alpha and beta beta here. Then you calculate this one; it turns out that it comes at; this will anyway get cancelled out; and this will come at the sum of chemical shifts; nu A + nu X.

So, this is where the chemical shift of double quantum come; at the sum of the chemical shifts of two coupled spins, nu A and nu X. What happens? you ask me a question, why are we taking the difference of alpha alpha to beta beta, why not beta beta to alpha alpha? Of course, you can take the reverse of that also; again it comes at the sum of the chemical shifts of two coupled spins A and X, here also JAX gets cancelled out. And then you are going to get at the sum of the chemical shift of A and X together. So, these are the two DQ transitions, where alpha alpha to beta beta and beta beta to alpha alpha transition takes place. That is why I showed you the energy levels and the Eigen values which we calculated for two coupled AX spin system, when we made the quantum mechanical analysis earlier. And we took the simply the difference between alpha alpha to beta beta states and we found out DQ comes at sum of chemical shifts.

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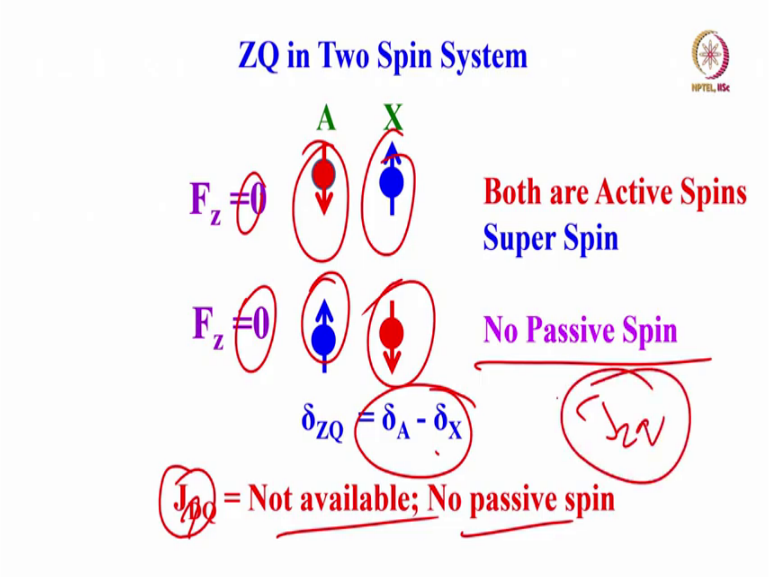

ZQ in Two Spin System

A X

$F_z = 0$

$F_z = 0$

Both are Active Spins

Super Spin

No Passive Spin

$\delta_{ZQ} = \delta_A - \delta_X$

J_{ZQ} = Not available; No passive spin

Now, let us look at the ZQ zero quantum, in two spin case. Now, the same thing is beta alpha and alpha beta. So, Fz is equal to 0, the magnetic quantum number for this state is 0, this is 0. Now, both are active spins and you can allow both of them to flip like that here. Here again no passive spin. But the interesting thing is, you remember zero quantum comes at difference of the chemical shifts. Remember, I told you the double quantum comes at sum of the chemical shifts. The zero quantum comes at difference of the chemical shifts. This is ZQ what is happening is, no passive spin, no splitting is available. So, JZQ is not there at all, no splitting because there is no splitting, because there is no passive spin.

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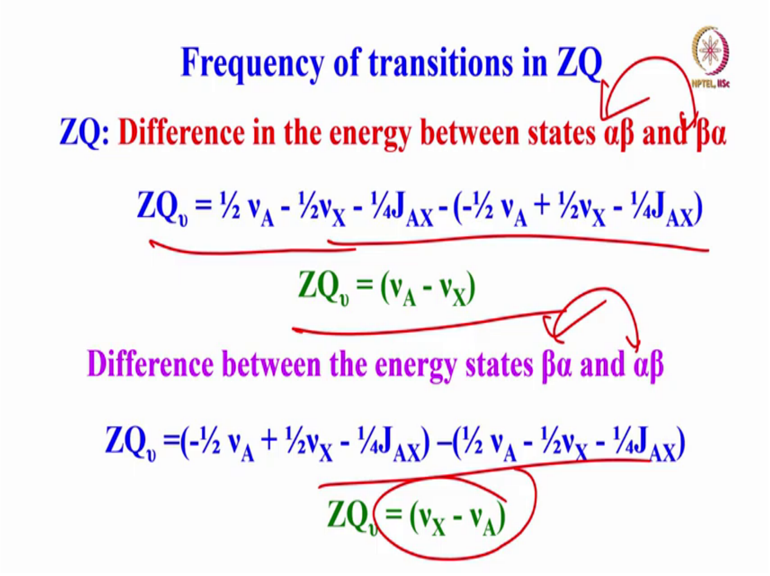

Frequency of transitions in ZQ

ZQ: Difference in the energy between states αβ and βα

$ZQ_\upsilon = \frac{1}{2}\nu_A - \frac{1}{2}\nu_X - \frac{1}{4}J_{AX} - (-\frac{1}{2}\nu_A + \frac{1}{2}\nu_X - \frac{1}{4}J_{AX})$

$ZQ_\upsilon = (\nu_A - \nu_X)$

Difference between the energy states βα and αβ

$ZQ_\upsilon = (-\frac{1}{2}\nu_A + \frac{1}{2}\nu_X - \frac{1}{4}J_{AX}) - (\frac{1}{2}\nu_A - \frac{1}{2}\nu_X - \frac{1}{4}J_{AX})$

$ZQ_\upsilon = (\nu_X - \nu_A)$

We will go to the next one. Now, what is the frequency of ZQ transition. We can work it out here from the energy levels which I have given you. Instead of now alpha alpha and beta beta separation, you take the separation from alpha beta to beta alpha. This is what I gave in the table few slides before. Now, it turns out JQ chemical shift is equal to nu A – nu X. So, zero quantum comes at the difference of the chemical shifts.

Now, why not, you can also take the difference of beta alpha to alpha beta again you do that you find out it is nu X – nu A. So, this is what is going to happen. See the zero quantum always comes at difference of the chemical shields, double quantum always comes at the sum of the chemical shifts. And in the two spins case, in both the cases there is no passive spin. As a consequence, there is no splitting, you get only one peak for DQ and one peak for ZQ.

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MQ Detection in a Three Spin System

Weakly Coupled AMX

So, this is how, you have to understand transitions in higher quantum. Now, let us jump to multiple quantum detection in the 3 spin case. 3 weakly coupled spins, we will consider AMX. Now, how many transitions you can think of in MQ?

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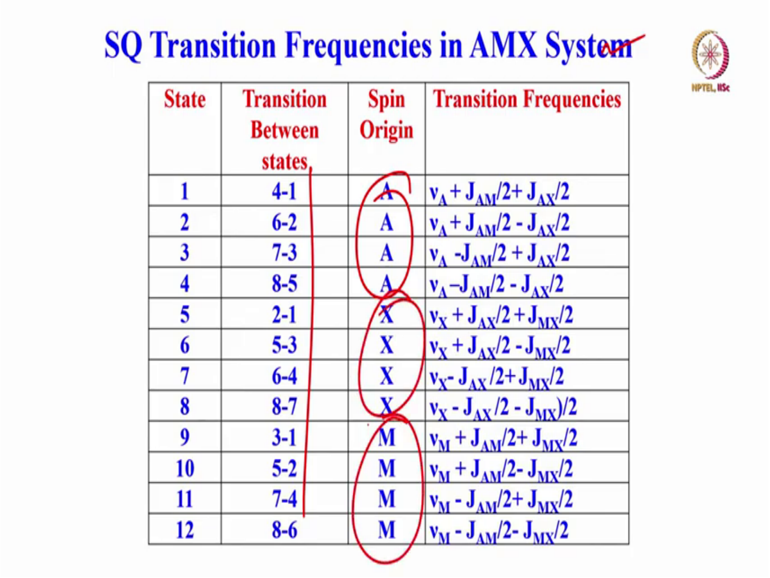

SQ Transition Frequencies in AMX System

State	Transition Between states	Spin Origin	Transition Frequencies
1	4-1	A	$\nu_A + J_{AM}/2 + J_{AX}/2$
2	6-2	A	$\nu_A + J_{AM}/2 - J_{AX}/2$
3	7-3	A	$\nu_A - J_{AM}/2 + J_{AX}/2$
4	8-5	A	$\nu_A - J_{AM}/2 - J_{AX}/2$
5	2-1	X	$\nu_X + J_{AX}/2 + J_{MX}/2$
6	5-3	X	$\nu_X + J_{AX}/2 - J_{MX}/2$
7	6-4	X	$\nu_X - J_{AX}/2 + J_{MX}/2$
8	8-7	X	$\nu_X - J_{AX}/2 - J_{MX})/2$
9	3-1	M	$\nu_M + J_{AM}/2 + J_{MX}/2$
10	5-2	M	$\nu_M + J_{AM}/2 - J_{MX}/2$
11	7-4	M	$\nu_M - J_{AM}/2 + J_{MX}/2$
12	8-6	M	$\nu_M - J_{AM}/2 - J_{MX}/2$

See now, highest quantum. We will look at the energy levels for this also, the single quantum transition frequencies we have worked out. How many are there? There are 4 A transitions, 4 X transition and 4 M transitions, we have worked out already.

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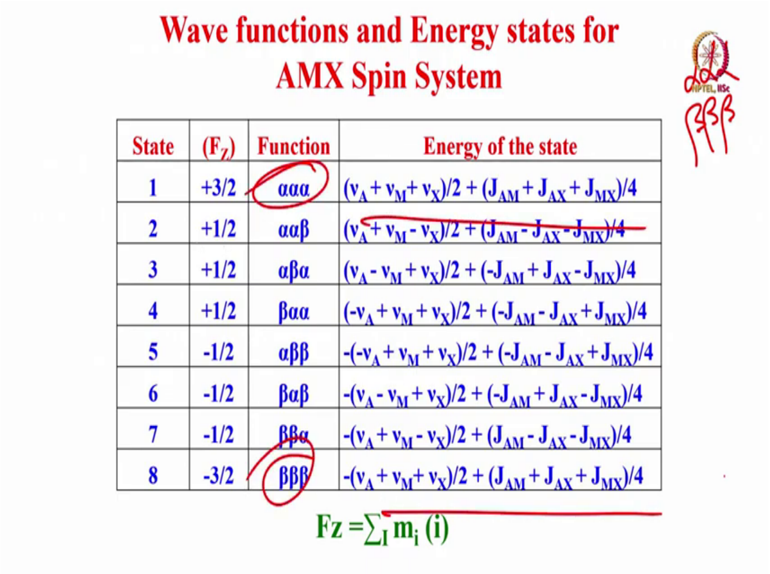

Wave functions and Energy states for AMX Spin System

βββ

State	(F_Z)	Function	Energy of the state
1	+3/2	ααα	$(\nu_A + \nu_M + \nu_X)/2 + (J_{AM} + J_{AX} + J_{MX})/4$
2	+1/2	ααβ	$(\nu_A + \nu_M - \nu_X)/2 + (J_{AM} - J_{AX} - J_{MX})/4$
3	+1/2	αβα	$(\nu_A - \nu_M + \nu_X)/2 + (-J_{AM} + J_{AX} - J_{MX})/4$
4	+1/2	βαα	$(-\nu_A + \nu_M + \nu_X)/2 + (-J_{AM} - J_{AX} + J_{MX})/4$
5	-1/2	αββ	$-(-\nu_A + \nu_M + \nu_X)/2 + (-J_{AM} - J_{AX} + J_{MX})/4$
6	-1/2	βαβ	$-(\nu_A - \nu_M + \nu_X)/2 + (-J_{AM} + J_{AX} - J_{MX})/4$
7	-1/2	ββα	$-(\nu_A + \nu_M - \nu_X)/2 + (J_{AM} - J_{AX} - J_{MX})/4$
8	-3/2	βββ	$-(\nu_A + \nu_M + \nu_X)/2 + (J_{AM} + J_{AX} + J_{MX})/4$

$Fz = \sum_I m_i (i)$

And we also got wave functions and then energy of each of these states we have worked out. And now, we can find out from this what is the third quantum frequency? Because now in this case, 3 spins are coupled. All the 3 spins can flip from beta beta beta to alpha alpha alpha or vice versa. Now, the energy of the alpha alpha alpha state you consider, energy of the beta beta beta state you consider, find out what will happen for the third quantum.

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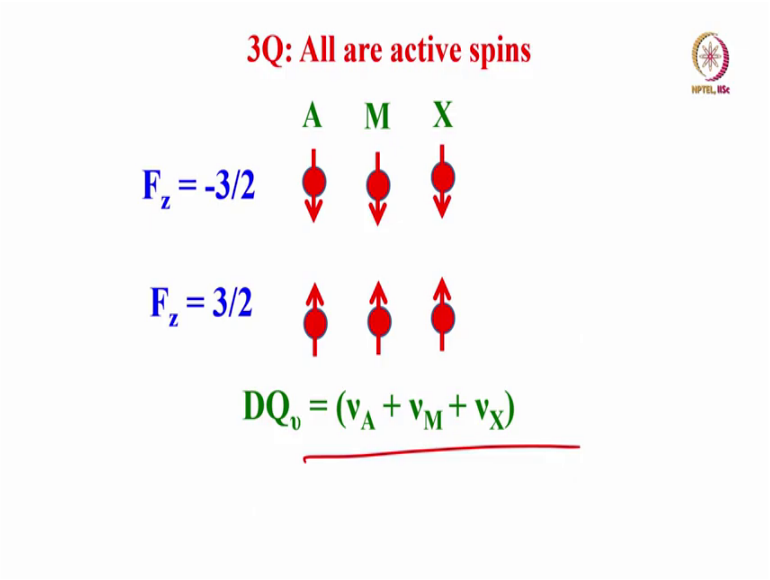

3Q: All are active spins

$F_z = -3/2$

$F_z = 3/2$

$DQ_\upsilon = (\nu_A + \nu_M + \nu_X)$

The third quantum if you find out, you will see that it will come at the sum of the chemical shifts. You look at the energies here, take the difference between this and this, then this term will get cancels out and you get only sum of nu A + nu M + nu X. So that is what is going to happen. Again, I am showing you in the third quantum case, third quantum comes at sum of the chemical shifts of all the 3 spins which are coupled; again no passive spins.

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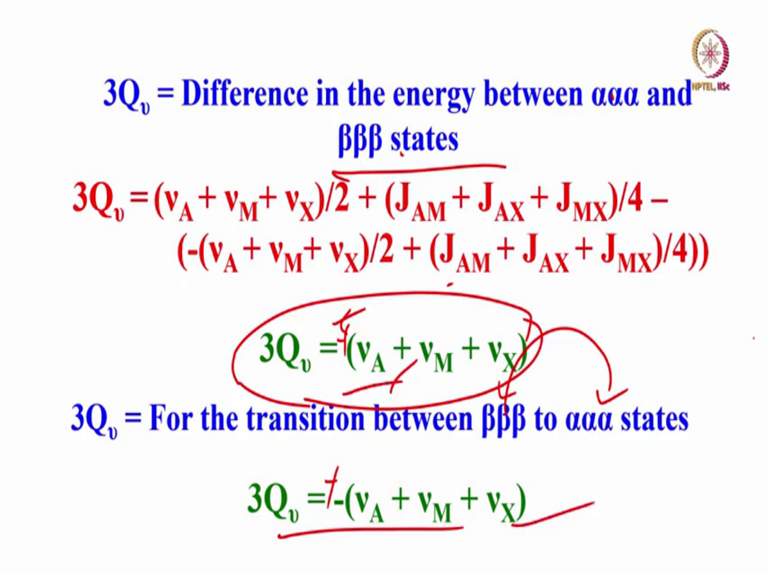

$3Q_\upsilon$ = Difference in the energy between ααα and βββ states

$$3Q_\upsilon = (\nu_A + \nu_M + \nu_X)/2 + (J_{AM} + J_{AX} + J_{MX})/4 - (-(\nu_A + \nu_M + \nu_X)/2 + (J_{AM} + J_{AX} + J_{MX})/4))$$

$$3Q_\upsilon = +(\nu_A + \nu_M + \nu_X)$$

$3Q_\upsilon$ = For the transition between βββ to ααα states

$$3Q_\upsilon = \pm(\nu_A + \nu_M + \nu_X)$$

So, as A consequence, there are no splitting; further splitting. This is the energy difference, I calculated for you already see, see this is the 3Q for this one. From the table which I gave you, I took the energies for the alpha, alpha, alpha state and beta, beta, beta state and took the difference. This is what I am showing you; it is coming at sum of the chemical shifts. So, this is for alpha alpha alpha to beta beta beta transition, you may ask me what happened like in the previous DQ case, what happens if I take this difference. It is same, instead of + here, it is

– that is all. So, both are allowed transitions like p + 1 and p – 1 both are possible; you can detect select the pathway. Fenerally, we always select – 1 pathway, because that is detected. Here also there are two possibilities alpha alpha alpha to beta beta beta and beta beta beta to alpha alpha alpha. So, this is why we have in once case + 3 and in the other case – 3.

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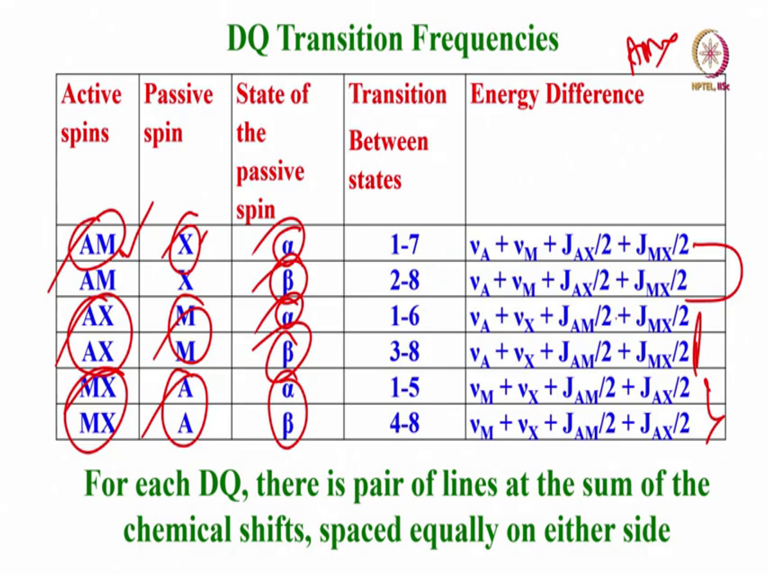

DQ Transition Frequencies

Active spins	Passive spin	State of the passive spin	Transition Between states	Energy Difference
AM	X	α	1-7	$\nu_A + \nu_M + J_{AX}/2 + J_{MX}/2$
AM	X	β	2-8	$\nu_A + \nu_M + J_{AX}/2 + J_{MX}/2$
AX	M	α	1-6	$\nu_A + \nu_X + J_{AM}/2 + J_{MX}/2$
AX	M	β	3-8	$\nu_A + \nu_X + J_{AM}/2 + J_{MX}/2$
MX	A	α	1-5	$\nu_M + \nu_X + J_{AM}/2 + J_{AX}/2$
MX	A	β	4-8	$\nu_M + \nu_X + J_{AM}/2 + J_{AX}/2$

For each DQ, there is pair of lines at the sum of the chemical shifts, spaced equally on either side

So, now, DQ transition frequencies, we will see for 3 coupled case. How many DQ's we can think of; actually there are three possibilities. Now, the 3 coupled case of a A, M and X, I can think of A and M double quantum means out of 3 spins, A and M can be flipping simultaneously and is the X passive spin. And in each case, there are two possible states for passive spin when A and M is simultaneously flipping, X is the passives spin. It can be alpha state or it can be beta state. So, there are two energy states for this. Similarly, for AX double quantum A and X can simultaneously flip, then M is a passive spin, M can be in alpha state M can be in the beta state; again two energy states for this. There is third possibility, there could be MX double quantum, where A is a passive spin. Now, again it can have alpha state and beta state.

So, these are the energy levels for this; energy states. So, now that we have seen the energy differences; for each of them if I consider transitions from 1 to 7, 2 to 8, all those things we can see DQ transition frequency, I have worked it out, you do not have to break your head.

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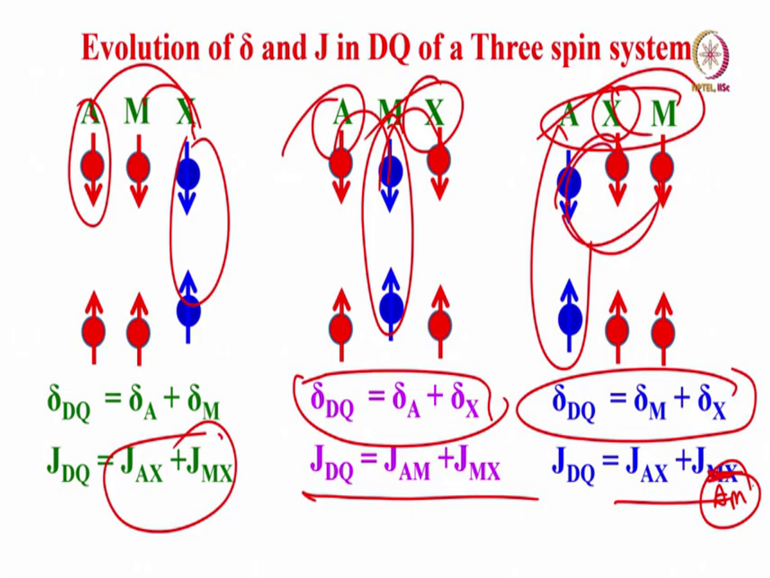

Evolution of δ and J in DQ of a Three spin system

$\delta_{DQ} = \delta_A + \delta_M$

$J_{DQ} = J_{AX} + J_{MX}$

$\delta_{DQ} = \delta_A + \delta_X$

$J_{DQ} = J_{AM} + J_{MX}$

$\delta_{DQ} = \delta_M + \delta_X$

$J_{DQ} = J_{AX} + J_{\cancel{MX}}$ AM

Now, how do DQ comes? This it is simple AM is flipping, X is passive. So then how many peaks we expect? Remember, two spins are flipping, passive spin has alpha and beta spin states. It is split by this. If this is not there, this will be only a single peak. Now, third spin is a passive spin. As a consequence, it comes at the sum of the chemical shifts of A and M, but now we also have a J-coupling.

So, the double quantum line will split into a doublet, it split into two lines. The two lines come because of two orientations, alpha and beta orientations of passive spin X. But now, what is the doublet separation. Remember I have been telling you in the previous course and in this course also. Always at the state of the active spin you get the coupling between the active and passive spins.

Now, there are two active spins. So, you will get the coupling between AX and MX since they are flipping together, you get the sum of JAX + JMX here. That is what is going to happen here. See now, in this case, what is happening is, since this is a passive spin, you are going to get sum of JAX + JMX because simultaneously they are flipping. If they were individually flipping, then you will get AX coupling and MX coupling and only one chemical shift. Now because of the double quantum it comes as the sum of the chemical shifts. So, now again, AX can be double quantum, A and X are flipping and there are M is the passive spin. Then where does it come? It comes at the chemical shift of A and X. That is what happens, it comes at some of the chemicals shift of A and X; but what is the splitting? M is passive spin it will split into a doublet because of JAM coupling and JMX coupling.

That is what happens. So, double quantum of a 3 coupled case, it will be always a doublet because there is one passive spin which splits this double quantum frequency into a doublet of two frequencies, which is the separation given by sum of the coupling between active spins and passive spins. Exactly, you can think of it for XM. Now, X and M are active spins and A is a passive spin.

So, the double quantum will come at sum chemical shift of M and X and the splitting is because of sum of JAX and JAM. So, you please remember, this is the sum of active and passive coupling. So, AX coupling and AM coupling sum, that is what happens.

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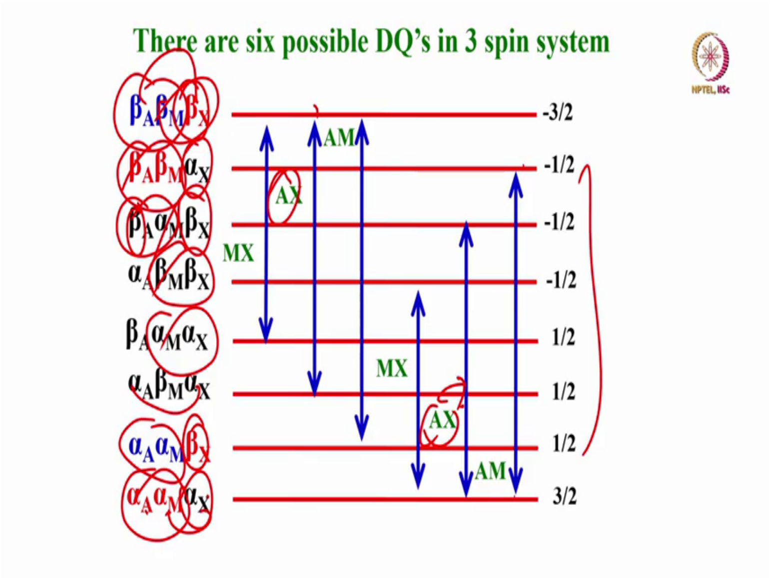

There are six possible DQ's in 3 spin system

So, these are the energy levels, you can look at it, as I said, there is a possibility beta beta can come to alpha alpha, both AM are flipping here, this is possible. This is double quantum and there is another state for this AM here alpha A and alpha M can change to beta A and beta M that is also possible. So, for each DQ, you have two possible transitions one from here to here or from here to here. That is the reason why you get a doublet in the double quantum because passive spin is there in each case in alpha and beta states. This is what is making it split into doublet. If you look at this here, AM doublet, A and M are flipping into alpha A alpha M will flip to beta A and beta M. And similarly, this will be AX, alpha A alpha X is changing to beta A and beta X here, this is AX, for this one. Similarly, this one AX again, here alpha A alpha X is changing to beta A and beta X. Now, what are the other ones, we see MX, here, alpha M alpha X is changing to beta M beta X. Similarly, this one, alpha M alpha X is changing to beta M beta X. So, each double quantum, in the three coupled spin case, has two transitions, where third spin is in its passive state. As a consequence, each double quantum becomes a doublet, because of the third passive spin in alpha and beta states. So, this is what it is.

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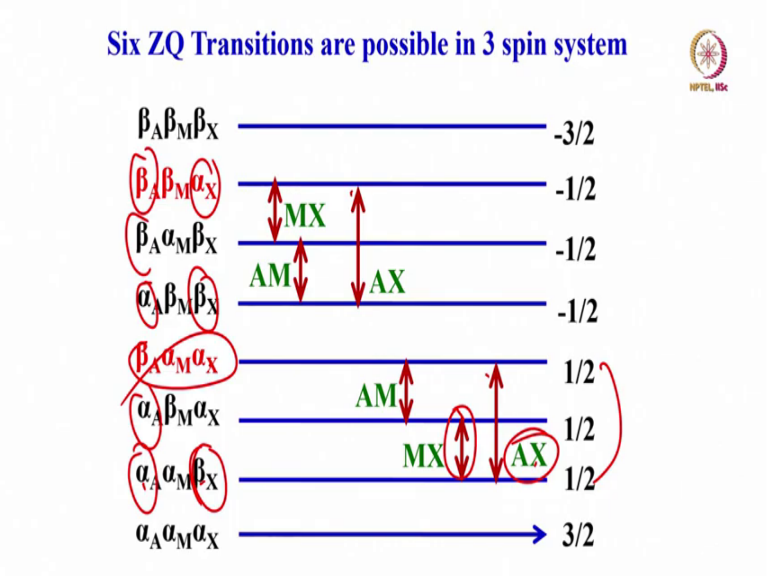

Six ZQ Transitions are possible in 3 spin system

Now, let us understand how the zero quantum evolves in the three coupled spin case, for same AMX, I consider. Now, remember here alpha beta and beta alpha their orientations are opposite here and so it is zero quantum transition, again X is a passive spin. What did I tell you? The zero quantum you get at the difference of the chemical shift. So, you get delta A – delta M. Similarly, J-couplings are also difference, remember one case it is JAX is positive or it JAX – JMX. Of course, you can take other way also. JMX – JAX also; that is also allowed both are possible. So, in the zero quantum, the couplings evolve as the difference. In the double quantum they evolve as sum, but in the zero quantum they evolve as a difference. Same thing you consider AX, M is the passive spin.

So, the chemical shift evolves as delta A – delta X and separation of the doublet because of the passive spin M is JAM – JMX. Exactly, now consider MX, now MX is flipping simultaneously, A is the passive spin, chemical shift is the difference of delta M – delta X and J-coupling, is J-split doublet separation is JAM – JAX, this what it is. So, very simple now. Now we have understood how DQ, ZQ evolves in the two spin case or in the three spin case also.

Again you can think of zero quantum it is plus half to minus of half, half to half. Now, we consider A and X, alpha A beta X it should change to beta A alpha X or it should be this one. It is changing to beta A alpha X; look at it alpha beta is changing to beta alpha. This is AX zero quantum. Similarly, here alpha A beta X is changing to beta A alpha X, this is also AX zero quantum. Similarly, this is the MX zero quantum; alpha M beta M is changing to beta M alpha X. This is MX zero quantum. Similarly, the AM zero quantum. So, again we will have six possibilities here six possible transitions for each double quantum, there are two peaks. Two for zero quantum because the passive spin is splitting this into doublet.

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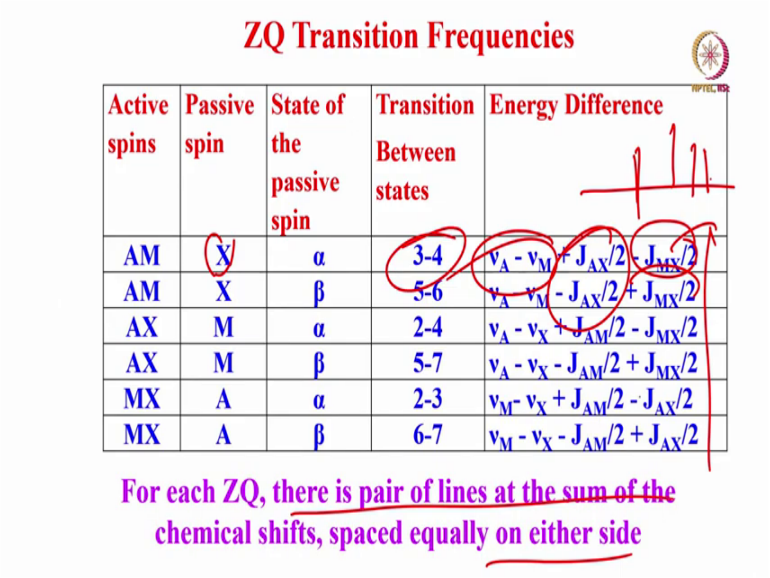

ZQ Transition Frequencies

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AM	X	β	5-6	$\nu_A - \nu_M - J_{AX}/2 + J_{MX}/2$
AX	M	α	2-4	$\nu_A - \nu_X + J_{AM}/2 - J_{MX}/2$
AX	M	β	5-7	$\nu_A - \nu_X - J_{AM}/2 + J_{MX}/2$
MX	A	α	2-3	$\nu_M - \nu_X + J_{AM}/2 - J_{AX}/2$
MX	A	β	6-7	$\nu_M - \nu_X - J_{AM}/2 + J_{AX}/2$

For each ZQ, there is pair of lines at the sum of the chemical shifts, spaced equally on either side

So, what are the ZQ transition frequencies for the AMX; like DQ, we saw; we can work it out for ZQ also. AM and X spin. What are the energy states you find out. Take the difference you will find out for each ZQ there is pair of lines at the sum of the chemical shifts equally placed on either side. That is the important thing. The frequencies of the ZQ if you consider , it is the difference in the chemical shift. But on either side there is one peak one. On the right and left side there are two peaks, one on the right and one on the left. At the same time you also have JAX and one on the left and one on the right, but they will be coming at the difference. So, these are the things which you have to understand for the two frequencies of the doublet in zero quantum.

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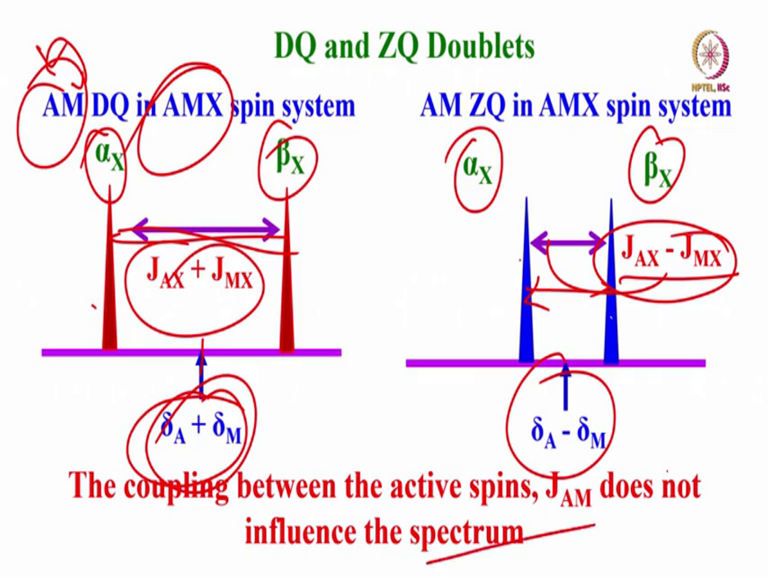

DQ and ZQ Doublets

The coupling between the active spins, J_{AM} does not influence the spectrum

So now, how do you look at it zero quantum and double quantum doublets. I took the simple example of the AM double quantum in AMX case this is the alpha X and beta X, that is X is a passive spin in alpha and beta states. Now, center of this doublet gives rise to sum of the chemical shifts; center this doublet gives rise to sum of the chemical shifts; delta A plus delta M, which are active spins. What is the separation? giving JAX + JMX, X is the passive spin. This is a double quantum of AM in AMX spin system. What about AM zero quantum. Same, this is alpha and this is beta, but now it is the difference JAX – JMX, this is this separation. The center is delta A – delta M; Now see the difference. This is the sum it has a larger separation, double quantum; and zero quantum is the difference with a smaller separation.

In both the case AM double quantum and AM zero quantum; X is the passive spin. So, you will understand the splitting pattern, whether it is DQ or ZQ depending upon, that you will know the separation is sum of the couplings or difference of the couplings. And you may ask me a question what happens to the coupling between A and M. They are active spins; together both of them are active. Their splitting will not be reflected in the spectrum. That will not influence the spectrum.

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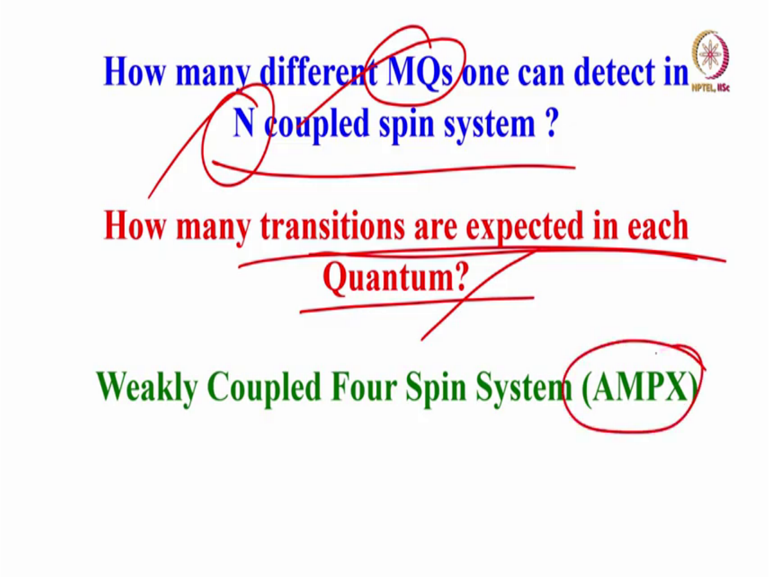

How many different MQs one can detect in N coupled spin system ?

How many transitions are expected in each Quantum?

Weakly Coupled Four Spin System (AMPX)

Now you can ask me a question; fine, we understood DQ ZQ two spin three spin etc. Now, I have an unknown N couple spin system, N could be any number, large number 3, 4, 5, 8 like that how many different multiple quantum I can get in the N coupled spin system? And how many transitions I can expect in each quantum? That question we have to answer, because in the double quantum of two spin you get only one peak, triple quantum of three spin will get only one peak. Similarly, we understood double quantum or 3 spins you will get two two peaks for each quantum, for each double quantum. So, all those things you understood, we will generalize the formula for the different MQs of N coupled spin system. How many transitions are expected in each Quantum. We will take the example of 4 spins AMPX, weakly coupled four spin.

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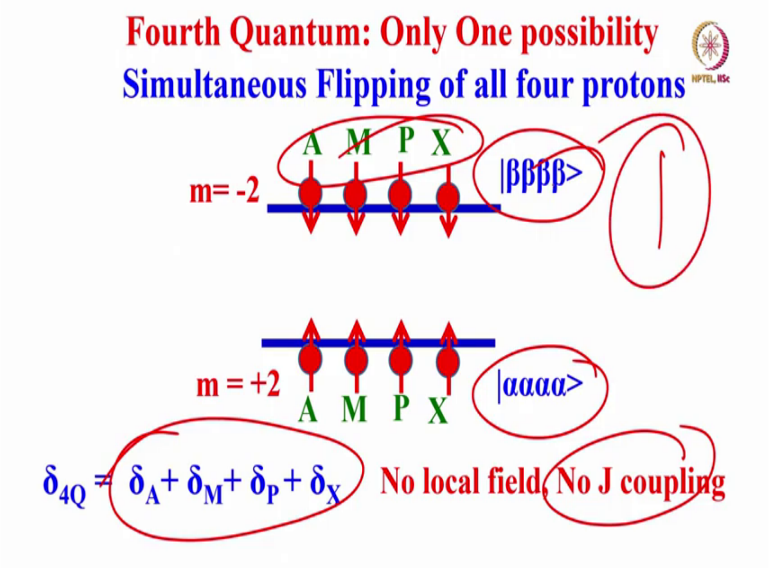

Fourth Quantum: Only One possibility

Simultaneous Flipping of all four protons

$\delta_{4Q} = \delta_A + \delta_M + \delta_P + \delta_X$ No local field, No J coupling

What is the 4th quantum? All the 4 spins AMPX are changing from beta beta beta beta to alpha alpha alpha alpha, state like this. This is the 4th quantum, where does it come? It comes at the sum of the chemicals shifts of A,M,P and X is done. So, no local field, no J coupling fourth quantum of four coupled spin is a single peak, which we understood.

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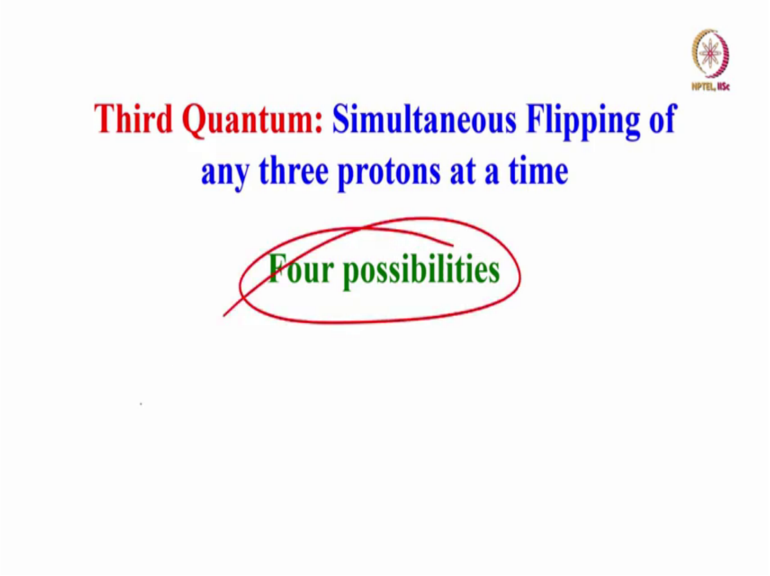

Third Quantum: Simultaneous Flipping of any three protons at a time

Four possibilities

Now, we will go to third quantum; how many possibilities are there? In the third quantum any 3 protons can simultaneously flip among the 4, any 3 protons can flip. How many possibilities are there? There are 4 possibilities.

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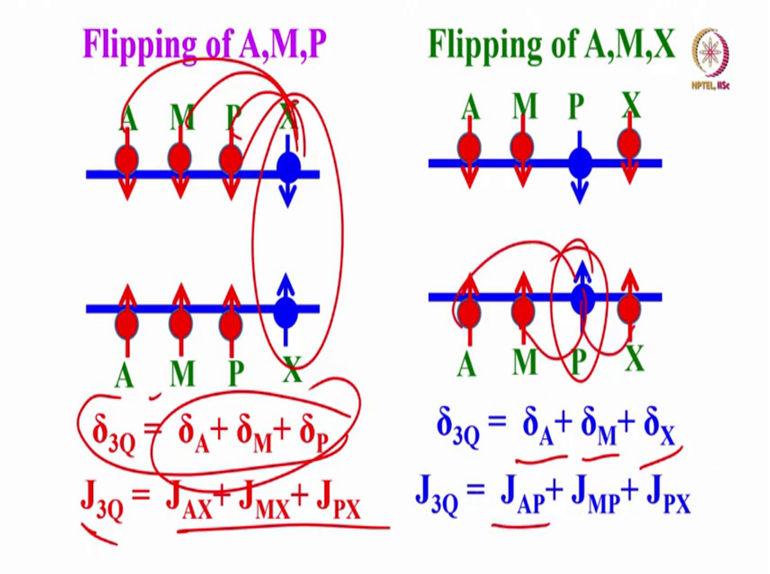

Flipping of A,M,P

$\delta_{3Q} = \delta_A + \delta_M + \delta_P$

$J_{3Q} = J_{AX} + J_{MX} + J_{PX}$

Flipping of A,M,X

$\delta_{3Q} = \delta_A + \delta_M + \delta_X$

$J_{3Q} = J_{AP} + J_{MP} + J_{PX}$

Look at this one, these 3 can flip, X is the passive spin, then chemical shift of 3Q is the chemical shifts of A, M and P and separation is the sum of JAX, JMX and JPX that this separation. Again it is a doublet, because only one passive spin is there. Now, there is a possibility A, M and X can flip, instead of AMP, now P is a passive spin. So, what is the chemical shift? It is delta A + delta M + delta is X, sum of all the spins which are flipping. Chemical shifts of all the three spins which are undergoing flipping from alpha to beta states, the passive spin is p. So, what is the doublet separation JAP,+JMP+JXP.

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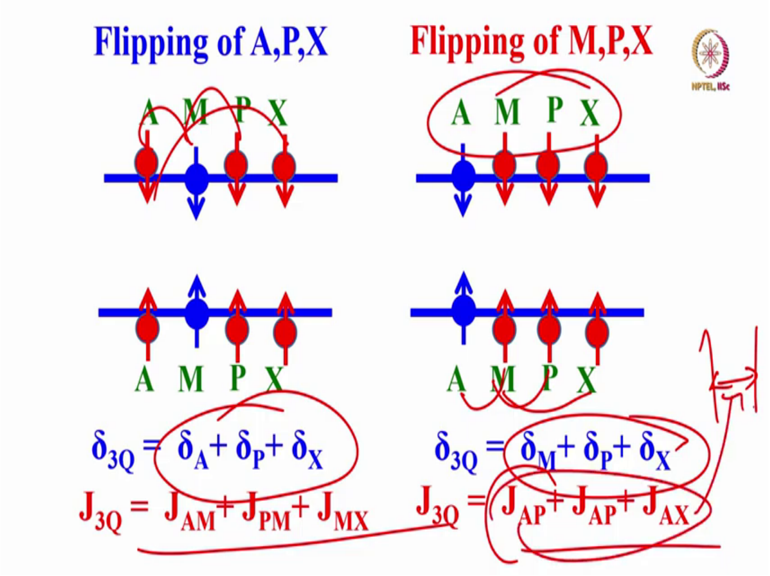

Flipping of A,P,X

Flipping of M,P,X

$\delta_{3Q} = \delta_A + \delta_P + \delta_X$

$J_{3Q} = J_{AM} + J_{PM} + J_{MX}$

$\delta_{3Q} = \delta_M + \delta_P + \delta_X$

$J_{3Q} = J_{AP} + J_{AP} + J_{AX}$

Now, there is a possibility APX can flip and the M is passive spin. So, now, 3Q chemical shift is delta A + delta P + delta X; and what is a coupling; you must know by now. It is JAM+JPM+JMX, all the three are there. Sum of these, all the three together will split into a doublet.

Similarly, now, you go to AMPX now, MPX can flip A is a passive spin. So, it comes as some of delta M + delta P + delta X. And triple quantum separation is sum of JAP+JAM+JAX; that is a doublet separation. You measure the separation, that corresponds to this one.

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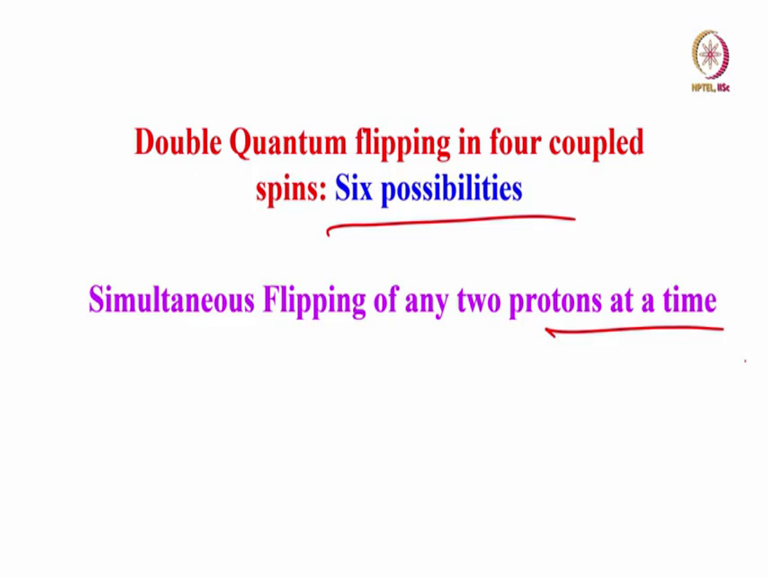

Double Quantum flipping in four coupled spins: Six possibilities

Simultaneous Flipping of any two protons at a time

So now, we understood triple quantum if you are four couples spin system. Similarly,, we can go double quantum, how many possibilities you can think of six possibilities. Simultaneous flipping of any two products at a time. Here, we considered simultaneous flipping of any 3 protons at a time.

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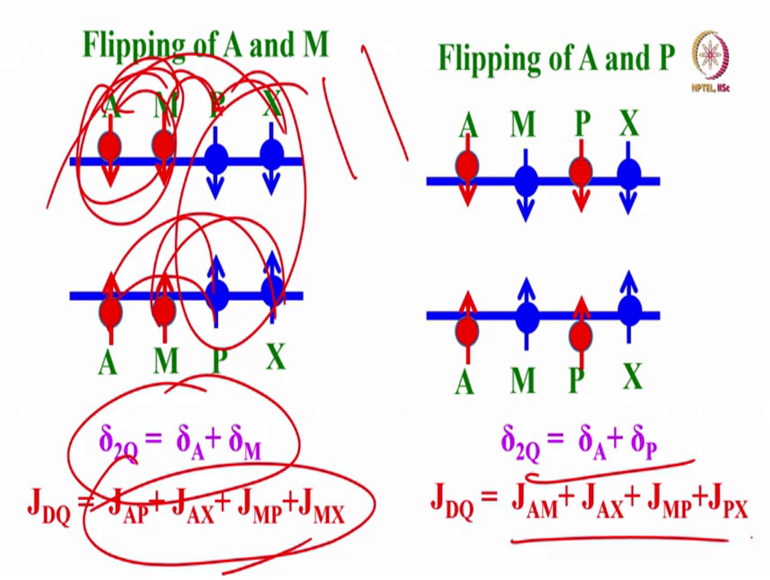

Flipping of A and M

$\delta_{2Q} = \delta_A + \delta_M$

$J_{DQ} = J_{AP} + J_{AX} + J_{MP} + J_{MX}$

Flipping of A and P

$\delta_{2Q} = \delta_A + \delta_P$

$J_{DQ} = J_{AM} + J_{AX} + J_{MP} + J_{PX}$

Now, we can consider double quantum like this; two can flip. Now, very interesting case. Where does the chemical shift come? double quantum comes at the sum of chemical shift A and M. These are the active spins. Now, tell me what is the J-coupling? what is the separation? Separation is sum of JAP + JAX and JMP + JMX. Now, these two are the active spin there are two passive spins.

So, it should be some of the coupling between active spins and passive spins. Now, A can couple to P, A can couple to X. Similarly, M can couple to P and M can couple to X. So, this doublet separation is; in principle it is not a doublet, with the couplings are different, you will get multiplet; you will get in fact more peaks. We will see that, if chemical shifts are not equivalent, or if they are inequivalent, so many possibilities you could think of. But nevertheless, we are going to get, if you consider a doublet, whose separation corresponds to this sum. Similarly, this can flip simultaneously and this is the splitting chemical shift is sum of the A and P and this DQ.

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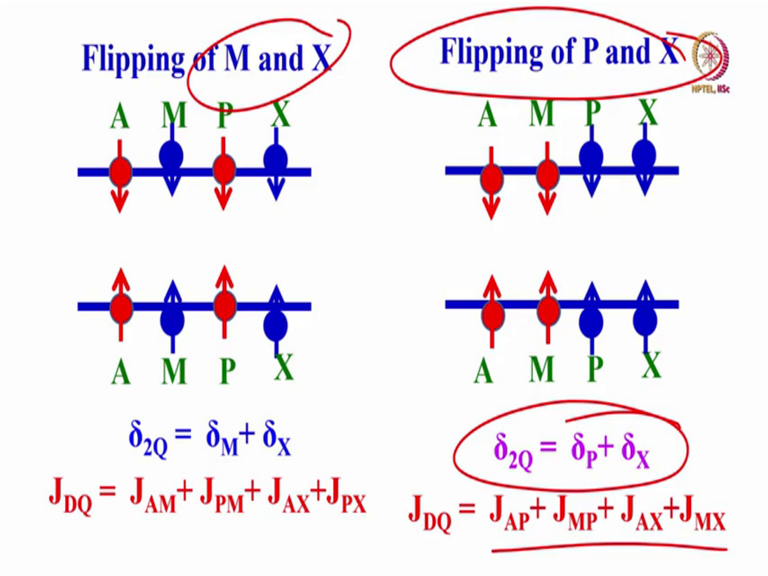

Flipping of M and X

$\delta_{2Q} = \delta_M + \delta_X$

$J_{DQ} = J_{AM} + J_{PM} + J_{AX} + J_{PX}$

Flipping of P and X

$\delta_{2Q} = \delta_P + \delta_X$

$J_{DQ} = J_{AP} + J_{MP} + J_{AX} + J_{MX}$

So, similarly, we can have flipping of A and P, and M and P all those things you can think of. So, there are varieties of possibilities you can think of; all six possibilities are there. Please understand, now, if it comes to flipping of P and X, M and X, A and P, A and M, A and X, all possibilities you could think of, you will know what are the chemical shifts; they come at sum of the chemical shifts. And couplings are the sum of the couplings between active spins and the passive spins. That comes as a sum.

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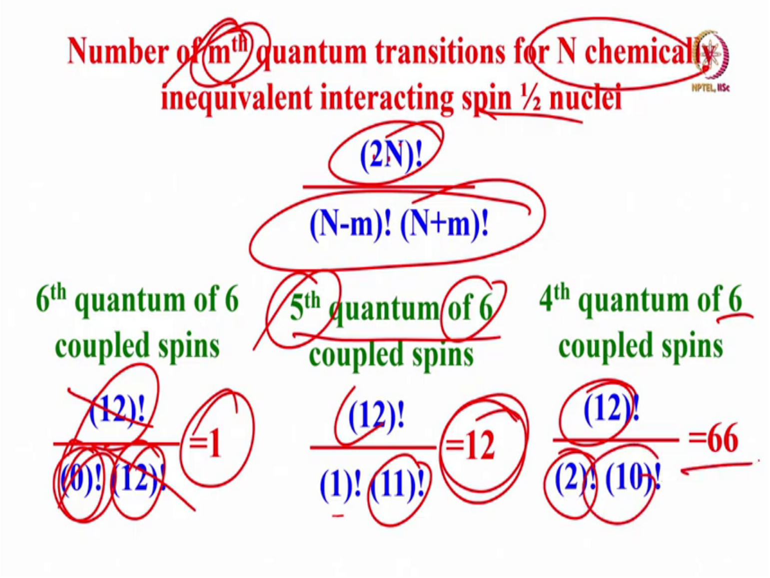

Number of m^{th} quantum transitions for N chemically inequivalent interacting spin ½ nuclei

$$\frac{(2N)!}{(N-m)!\,(N+m)!}$$

6^{th} quantum of 6 coupled spins

$$\frac{(12)!}{(0)!\,(12)!}=1$$

5^{th} quantum of 6 coupled spins

$$\frac{(12)!}{(1)!\,(11)!}=12$$

4^{th} quantum of 6 coupled spins

$$\frac{(12)!}{(2)!\,(10)!}=66$$

So, now, it can give raise to a general formula for this. Number of mth quantum transitions for N chemically inequivalent interacting spins. Understand my statement. Now, the number for any mth quantum, how many transitions we can get? If there are N couple spins, we can get m quantum for spin 1/2 nuclei. And that is going to be a general formula to 2N factorial over N – m factorial into N + m factorial.

That means, you go to a 6th quantum. 6th quantum of 6 coupled spins, how many peaks you expect? N is 6, it is 12 factorial, 2 into N, 12 factorial; N – m is 0 factorial; N + m is 12 factorial. So, this will cancel out and 0 factorial is 1, so, we get 1. So, it is correct right, 6 quantum of 6 coupled spins will give only one peak. Similarly, you got fifth quantum of 6 coupled spins; here it is N into 2 is 12, 12 factorial N – m is 1; N + m is 11. So, we are going to get 12 peaks, if all the spins are chemically inequivalent you are going to get 12 peaks, because there are six such possibilities. You can think, of each of them can be doublet. Remember, 5th quantum of six coupled spins, any five can flip at a time. So, each time another leftover spin is a passive spin, it is splits this into a doublet. So, there are six such possibilities, six possible double quantum, hence we are going to get 12 transitions.

Similarly, 4th quantum you will get, if you take it, this is 12 factorial over 2 factorial 10 factorial, you get 66 peaks. So, you can find out, how many peaks are there for each quantum.
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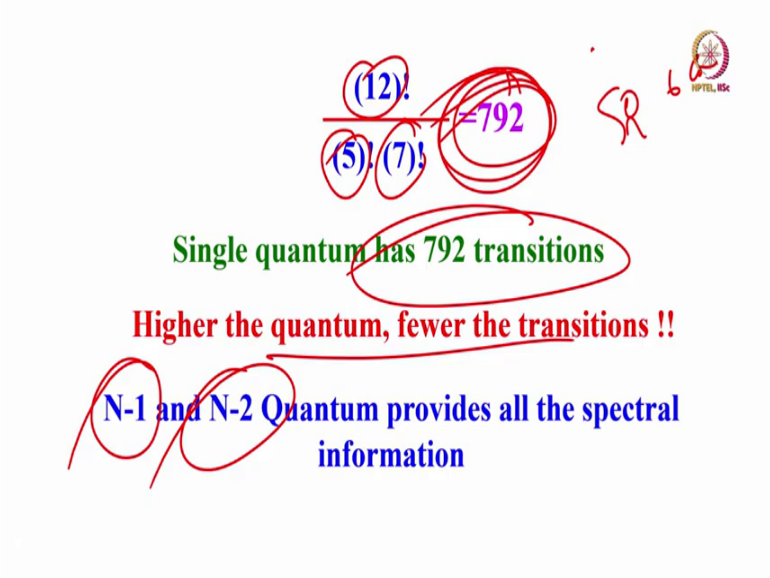

$$\frac{(12)!}{(5)!\,(7)!} = 792$$

SR 6

Single quantum has 792 transitions

Higher the quantum, fewer the transitions !!

N-1 and N-2 Quantum provides all the spectral information

So, if you come to single quantum let us say, how many peaks are there? Single quantum; see this is 2 into N 16, N is 1. So, N – m is 5 and N + m is 7. So, you calculate, it turns out to be 792. The single quantum transitions in 6 coupled spins are 792. There are 792 transitions in six coupled spins case, it is for a single quantum. Six coupled spins, gives us 792 transitions theoretically. All you may not be able to detect, some may be very weak in intensity, some has negligible intensity. But what I am trying to say is, there is the reduction in the transitions as you go to higher and higher Quantum. So, what did you understand from this exercise. As you go to higher and higher quantum, here we saw, you get fewer and fewer transitions. If you go to the highest quantum, you will have only one. N – 1 quantum gives few transitions. And N – 2 quantum is fewer transitions; only when it comes to single quantum more transitions are there. So, higher the quantum, fewer the transitions. And in general, all I need to know is N – 1 and N – 2 quantum spectrum. If I can analyze that I can get the complete spectral information, you understand. See for example of 792 lines, the spectrum I have to take and analyze 792 transitions to get this information for the sixth coupled spin case.

On the other hand, I can go to this one fourth quantum is 66. And fifth quantum is 12 lines. If I can analyze this spectrum and this spectrum, I get complete spectral information. That makes my life quite simple. I do not have to go to single quantum spectrum analysis at all. So, what I am trying to say is, OK, the time is getting up I am going to stop here, what I wanted to say is highest the quantum gives a single peak for N coupled case.

As you keep on reducing the quantum from N to N – 1, N – 2, N – 3; the number of transitions keeps on increasing. If you come to single quantum you have lot of transitions.

That means single quantum transitions are highly redundant, you do not need that many transition to get the spectral information. And I took the example of evolution of DQ and ZQ in two coupled spins and three coupled spins, we saw what are the possibilities.

In the two coupled spins case double quantum comes at sum of the chemical shifts and there is no passive spin. So, no splitting, you get only single peak. Whereas the zero quantum comes at difference of the chemical shifts. Again there is no passive spin and no splitting, it will give a single peak. We went to the three spins case, the third quantum gives a single peak.

Whereas in the three spins, if we go to double quantum, there are three possibilities. Consider AMX. The AM double quantum, MX double quantum and AX double quantum; all the three are possible. And each time, third spin, left over spin is the passive spin. So, both the spins will flip simultaneously to alpha and beta. But the X spin is sitting idle, passive spin that has alpha and beta spin states. As a consequence, each double quantum of these three coupled spins case will be a doublet. Where does the doublet come? At the sum of the chemical shifts of the active spins. And the separation corresponds to sum of the J couplings between the active spins and the passive spin. That is important thing. So, similarly, you understood what happens if you go to the zero quantum. Zero quantum also again, several possibilities are there; AM zero quantum, MX zero quantum and AX zero quantum. Each time again, left over spin is the passive spin and it splits the peak into a doublet. And here, the doublet comes at the difference of the chemical shifts; and doublet separation pertains to difference in the couplings between active spins and passive spin. This what we understood and we even went to the extent of understanding how many peaks are possible?

How many peaks one can detect in the mth the quantum of N coupled spins by taking the example of six coupled spins. So, we understand that as you go to higher and higher quantum there are fewer transitions, you can reduce the redundancy. That is the important point I wanted to tell you. So, we stop here with this. Will continue in the next class. And we will go into some few applications and try to see how we can utilize MQT and how we detect MQT and few applications. I stop here. Thank you.