Advanced NMR Techniques in Solution and Solid-State
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Module-15
Pople Notation, Construction of Spin Hamiltonian
Lecture 15

In the last couple of classes, we have been discussing lot of things. In the first few classes, we discussed a lot about spin physics, basics of NMR, internal interaction parameters, especially the chemical shifts, coupling constants, etc. We discussed varieties of multiplicity patterns in the coupling patterns and then we used those knowledge to analyse one dimensional spectra of varieties of nuclei including proton, carbon, tin, etc.

We got the idea, how to analyse the 1-d spectra, they are all first order spectra, amenable for first order analysis, very simple spectrum, very easy to analyse. The Spectra we chose were simple like that I can see here, there is a peak here, there is a peak, this corresponds to one functional group like CH3; this is for benzene, this is a CH2 like that, that is how we used to interpret.

That is how such type of spectra were chosen, which were easy to analyse. And then also after that, I wanted to introduce Fourier transformation to see how we will get such type of spectrum, different theorems of Fourier transformations, we analysed the spectrum, but you should know how you got it. For that, we introduced Fourier transformation and we discussed a lot about Fourier theorems and everything.

A lot of time was spent on understanding and I explained how they are used, all these theorems are useful in NMR spectroscopy, when you are recording the spectrum; if you understand this theorem carefully, you will know what are the problems, how you can rectify them, while you are doing your experiments. So, mathematical tool, especially the Fourier transformation is very, very important in NMR.

Of course, next thing is I wanted to talk to you about receiver phase and transmitter phase that is the pulse phase, also called transmitter phase. That is what is important when after discussing the Fourier transformation, about imaginary part, real part etcetera. This would have been an apt, but then because of the time shortage, I will come back to you after this thing. But I wanted to bring that at the time when I am using the phase cycling, and product operators.

So, we will delay that and I will come back to that topic later. It does not matter it can be discussed at any time. But today, I am going to start with Quantum mechanical analysis of the coupled spin systems. Remember, in my previous course and basics, I gave a lot of examples about spin system nomenclature. How do you analyse the spin systems, but without getting into quantum mechanical analysis. We analysed, I just briefly discussed and showed you a number of examples, how does the AX spectrum comes, how does the AB spectrum comes, what is the AX spectrum, what is the AB spectrum, what happens when the 3 spins are coupled etc.; a lot of things we discussed. Those are all very much useful, that knowledge is essential to understand these things, at least it is needed.

So, those of you who missed this, again it is mathematical oriented, this course, I mean this part, if you missed something, please refer to that and you will get the point. So, with this, we will start with quantum mechanical analysis of coupled spin systems today.

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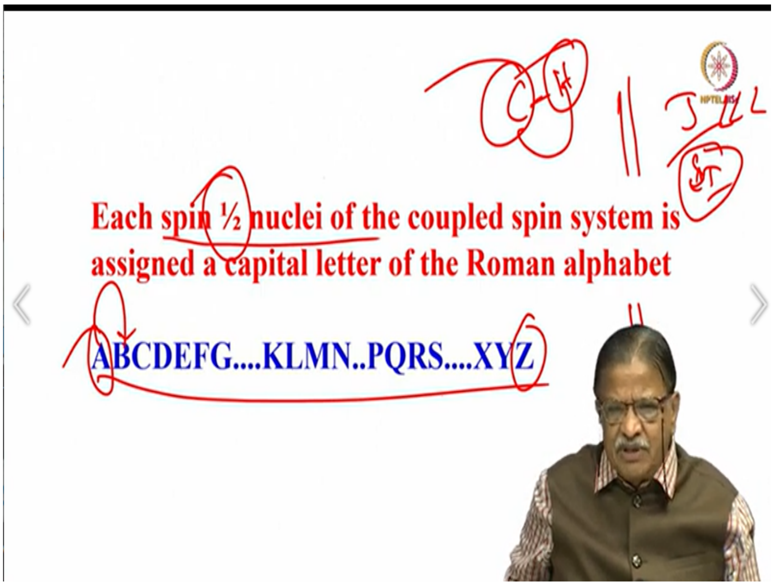

Each spin ½ nuclei of the coupled spin system is assigned a capital letter of the Roman alphabet

ABCDEFG....KLMN..PQRS....XYZ

But first of all, I want to introduce what is called a pople nomenclature. What is pople nomenclature means, if there are n coupled spin system? what is the coupled spin system? If there are many nuclei that are present in the molecules, which are NMR active, they may be coupled to one another. A maybe coupled to B, B may be coupled to C, C may be coupled to D, something else, different protons or different nuclei NMR active nuclei. It could be homonuclear, it could be heteronuclear also. Then there all form a coupled groups of spin system, they are called coupled spin system. If I have spin half coupled nuclei, which form coupled spin system, then each nuclei can be represent spin half nuclei, can be represented by a roman alphabet like this, ABCD up to Z. But then, while referring to that, there is a rule we have to follow.

Let us say I take this carbon coupled to proton, I cannot call this as AB. I have to put the nomenclature depending upon how far they are separated in the chemical shifts. For example, in a 500 megahertz NMR, proton comes at 500 megahertz, carbon comes at 125 megahertz. That means they are far away separated; several megahertz away. But what is the coupling between this and this? Carbon proton coupling is of the order 150 Hertz or less than 200 hertz; sometimes.Where is megahertz, 500 megahertz, 300 megahertz and where is 150 hertz; it is very, very small compared to that chemical shift. That is why such type of system where the chemical shift separation which are much, much larger than the couplings are called weakly coupled spin systems. And for such systems we have to define the letters in such a way; if their chemical shifts are far away separated, A is here, you have to put the X or Y, like that. So, you have to put letter which is far away from the roman alphabet. If on the other hand, the chemical separation is very, small. One is here, and the other is very close to that, and the coupling between them is also comparable. In which case you have to represent by the letters which are closer in the alphabet. That means, if you have the two interacting spins represented by 2 letters, which are closer in the alphabet they are strongly coupled spin systems. It is not possible for you to analyse such spectra in the first order way. They give rise to second order spectra, whereas the chemical shift separation is far away compared to the coupling constant, some 50 times, 100 times difference; you take the ratio of the scalar coupling to chemical shift difference. The ratio if you take, this is very, very large, this value is very, very small, 0.001 like that, such type of spin systems are weakly coupled, they give rise to first order spectra, which are amenable for easy analysis. Straight forward analysis is possible. That is what we analysed, all the spectra which we took as examples. So, now, you know how to put the nomenclature for the coupled spin system; A to X different roman alphabets, depending upon whether they are strongly coupled or weakly coupled. If you have strongly coupled spin system, letters which are closer in the alphabet, for weakly coupled, letters which are far away in the alphabets.

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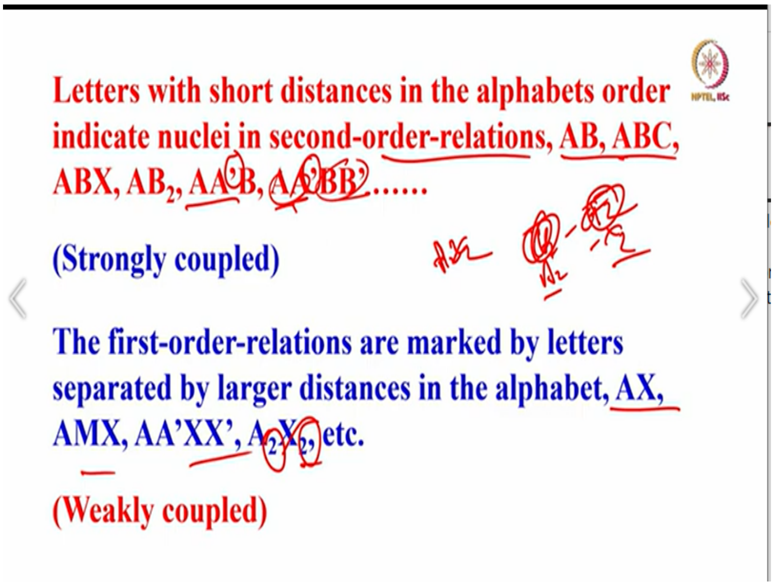

Letters with short distances in the alphabets order indicate nuclei in second-order-relations, AB, ABC, ABX, AB_2, AA'B, AA'BB'……

(Strongly coupled)

The first-order-relations are marked by letters separated by larger distances in the alphabet, AX, AMX, AA'XX', A_2X_2, etc.

(Weakly coupled)

This is what it is. So, then if they have a second order relationships, in which case, the strongly coupled can be represented as AB, ABC, ABX, AB2, even A2, A3, they are all highly strongly coupled spin systems. For weakly coupled, we can write as AX, AMX, AA'XX', A2X2 like that. Then what are these prime notations? why did we write the prime? The prime are the ones, such nuclei are chemically equivalent, that is very important.

That chemically equivalent nuclei, such nuclei are represented by that AA prime means, A and A prime are 2 spins which are chemically equivalent, but there is a coupling between them. Similarly, there are spins which are chemically equivalent AA prime and BB prime are chemically equivalent, but between them there is a strong coupling, AA prime is strongly coupled, BB prime is strongly coupled. Between AA prime and BB prime, they are strongly coupled.

Then we can represent by prime notation like this, then what is this type of notation, subscripts? They are magnetically equivalent spin system. For example, let us say, I will take CH2CF2 some hypothetical molecule. Fluorine in heteronuclei, which is far away separated resonating frequency is several megahertz away. Then what happens compared to proton? Let us say, I call this as A2, I call this as X2. They are magnetically equivalent spins; F2 let us say. Protons are equivalent; 2 protons are magnetically equivalent, we call it as A2 and this is called as X2, we call the spin system as A2X2. Weakly coupled, but far away separated. Such type of spectra is easily analysable. So, this is how I gave you a brief idea about how to give the nomenclature for the spin system, coupled spin system, more we discussed about the Pople notation in the previous class.

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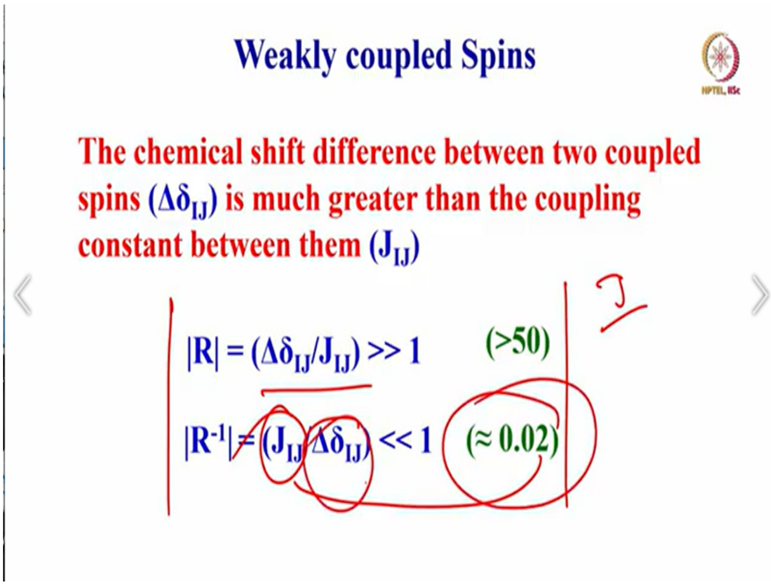

Weakly coupled Spins

The chemical shift difference between two coupled spins ($\Delta\delta_{IJ}$) is much greater than the coupling constant between them (J_{IJ})

$$|R| = (\Delta\delta_{IJ}/J_{IJ}) >> 1 \quad (>50)$$

$$|R^{-1}| = (J_{IJ}/\Delta\delta_{IJ}) << 1 \quad (\approx 0.02)$$

J

All of you can see the previous course and you will understand. Simple term you remember, for understanding we have strongly coupled spin system, you take delta / J or J / delta does not matter, if J / delta is very, very small; like this 0.01 or 0.001 like that. If the J comes in the numerator, chemical shift difference comes in the denominator; if you take this ratio, then if it is very, very small 0.0001 like that. They are called weakly coupled. Also, you can take this one, chemically shift separation divided by coupling, if they are very large, you take the reverse ratio, if it is very large value, more than 50 times; then they are weakly coupled.

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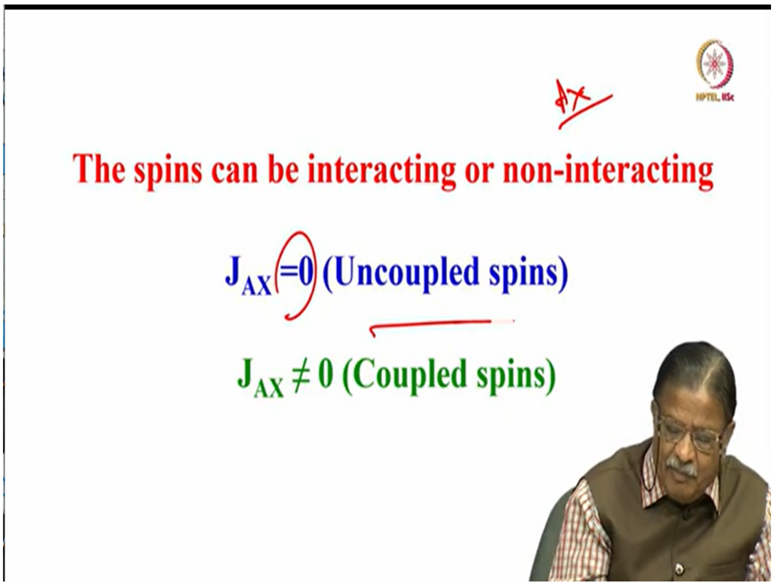

AX

The spins can be interacting or non-interacting

$J_{AX} = 0$ (Uncoupled spins)

$J_{AX} \neq 0$ (Coupled spins)

If I take this strongly and weakly coupled system, they can be weakly coupled or they can be interacting or non-interacting. For example, I have 2 spins, A and X, next to each other, their coupling may be zero or they may have a coupling, coupling is non zero, both are possible. If their coupling is zero they are uncoupled spins, otherwise they are called coupled spins.

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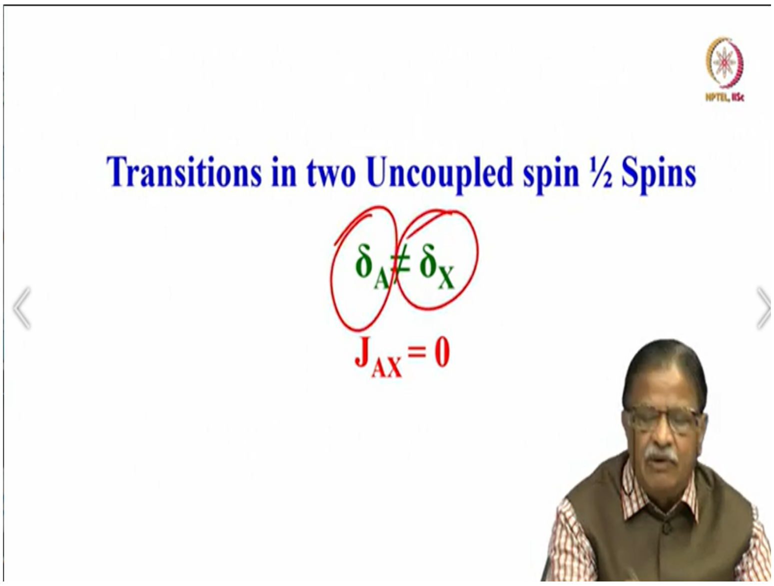

Transitions in two Uncoupled spin ½ Spins

$\delta_A \neq \delta_X$

$J_{AX} = 0$

Now, if consider 2 uncoupled spins, A and X; there is no coupling at all. They are two independent spins, spin half nuclei; that means they are not equivalent. A and X meant they are two different cases, no chemical equivalence or no magnetically equivalence as per my Pople nomenclature. That means chemical shift of A is not equal to chemical shift of X; and if the coupling is 0. What is the type of spectrum we expect?

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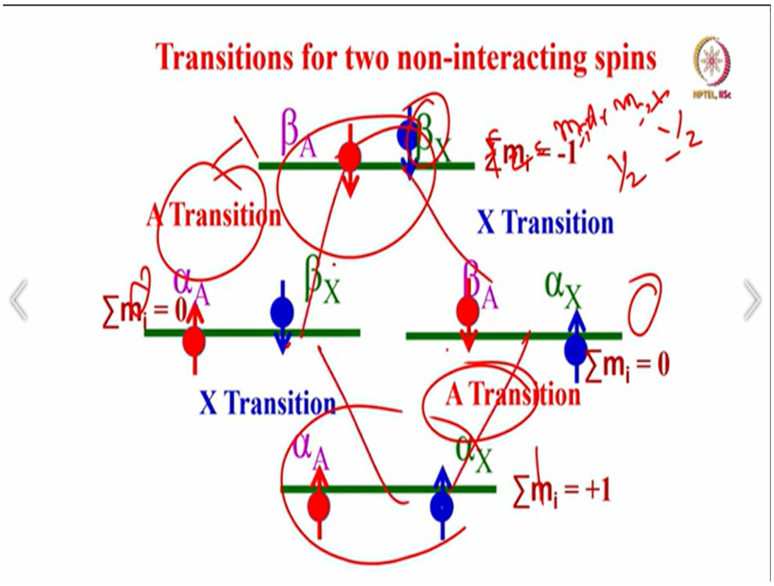

Transitions for two non-interacting spins

β_A β_X $\sum m_i = -1$

$\sum m_i = m_A + m_X$

$-\frac{1}{2}$ $-\frac{1}{2}$

A Transition

X Transition

α_A β_X $\sum m_i = 0$

β_A α_X $\sum m_i = 0$

X Transition

A Transition

α_A α_X $\sum m_i = +1$

Very simple. Let us consider the energy level diagram. When there are 2 spins which are present, either interacting or non-interacting, does not matter. The possible orientations of the magnetic energy states if you consider, both spins can be down like this beta beta, or 1 up 1 down is alpha beta, this down this is up, is beta alpha, both of these are up, it is called alpha alpha. Now, the total magnetic quantum number for each energy said FZ is given by M_i of A plus M_i of X.

What is magnetic quantum number of A for alpha and beta? Alpha is equal to plus half, beta = - half. Now, for in this case both are beta minus half plus minus half is minus 1. Whereas, this is 0; + half and minus half. This is minus half plus half 0; this is plus half plus half is 1. So, now, the transitions are allowed between these two, as per this selection rule. I told you between these transitions, they are allowed transitions. For example, the transition between this to this is allowed, alpha of A can go to beta of A, It start from first one, alpha of A is going to beta of A, here alpha of A is going to beta of A, they are allowed transitions; + 1 to 0, 0 to – 1 both are allowed. Here alpha of X is going to beta of X, it is also allowed, here alpha of X is going to beta of X, that is also allowed, this is X transition. So, this is A transition, this is X transition, but what is the frequency separation? Both are same, we see, there is no separation in the energy levels between this and this, between this and this; they are all same. So, that means, both A transitions have identical frequencies.

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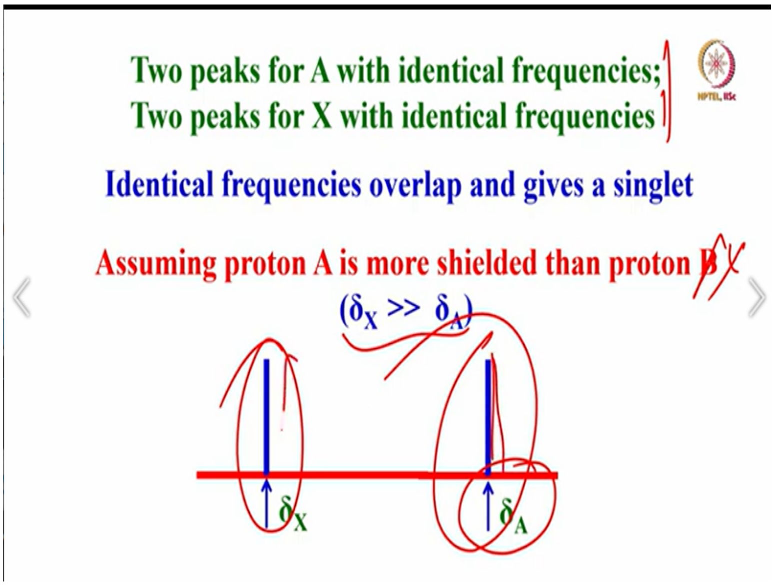

Two peaks for A with identical frequencies;

Two peaks for X with identical frequencies

Identical frequencies overlap and gives a singlet

Assuming proton A is more shielded than proton ~~B~~ X

$(\delta_X \gg \delta_A)$

Both X transitions will have identical frequencies. And we get 2 frequencies for A and 2 frequencies for X, but they are overlapped. As a consequence we get single peak for X; and single peak for A. Which is A, which is X is my nomenclature, depending upon which chemical shift is coming to high field or low field; that is only nomenclature I have given. This is my decision.

In this case, I have assumed that delta A is more shielded, coming to this one then X; I call it as delta X. So, now, there are 2 well separated peaks. Actually, there are 2 peaks overlapped here. So, only we get 2 peaks in uncoupled spin system.

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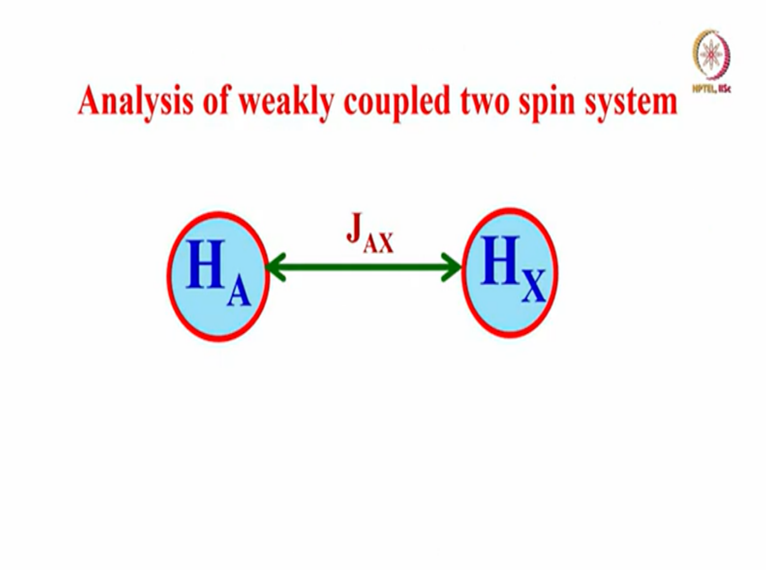

Analysis of weakly coupled two spin system

Now, I consider the example of 2 weakly coupled spin system in which case A is coupled to X.

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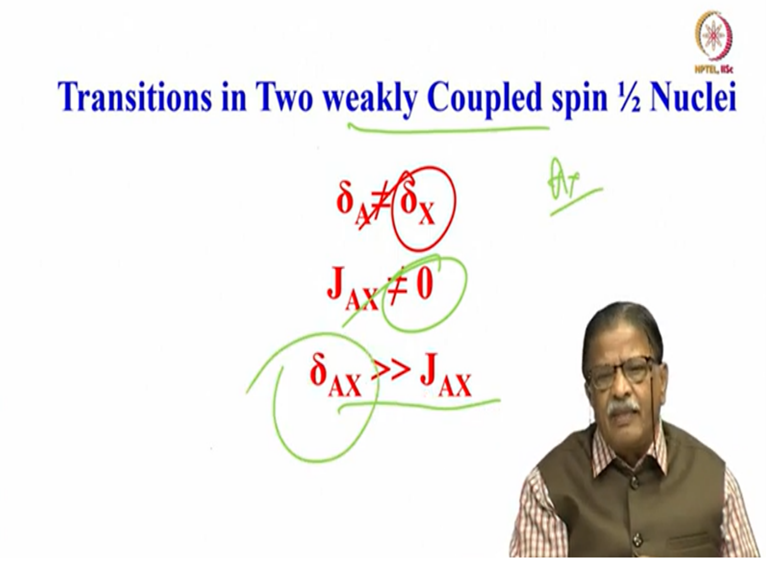

Transitions in Two weakly Coupled spin ½ Nuclei

$\delta_A \neq \delta_X$

$J_{AX} \neq 0$

$\delta_{AX} >> J_{AX}$

Coupling constant is JAX. Since, I said the AX, the chemical shifts are not same, the chemical shift A is not equal to chemical shift of X. And similarly, JAX is also not equal to 0 because, as I said this is non 0 and delta AX is very much larger than JAX; because, I call it as weakly coupled, I told you. Strongly coupled and weakly coupled system are represented by roman alphabets; weakly coupled means, letters which are far away in the alphabet, which

I have taken as A and X here. So, as a consequence, the weakly coupled deltaAX is sufficiently larger than JAX.

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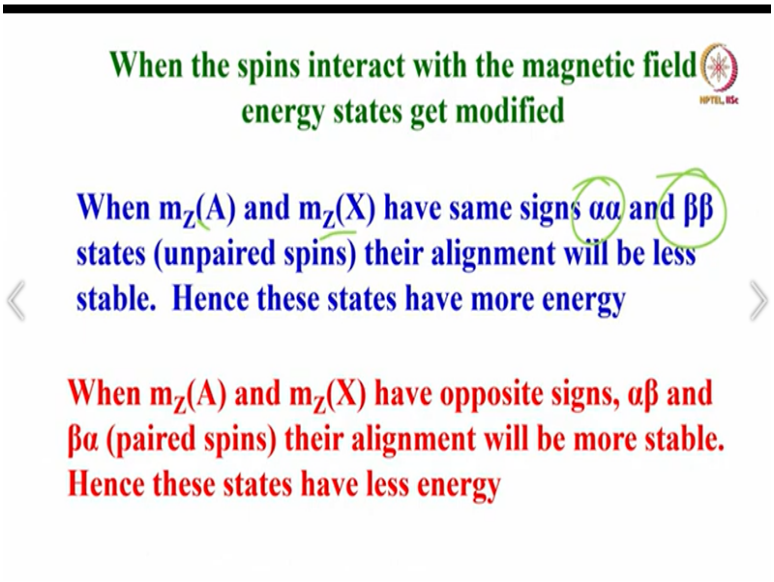

When the spins interact with the magnetic field energy states get modified

When $m_Z(A)$ and $m_Z(X)$ have same signs αα and ββ states (unpaired spins) their alignment will be less stable. Hence these states have more energy

When $m_Z(A)$ and $m_Z(X)$ have opposite signs, αβ and βα (paired spins) their alignment will be more stable. Hence these states have less energy

Now, when the spins interact with each other, how does the energy level get modified accordingly we get the transitions. For example, mZ of A and mZ of X you take, both are alpha alpha states, what is going to happen? They are unpaired spins and what is going to happen and in this case, the energy is unstable. They are a bit unstable, they require more energy to get themselves paired up like this.

Similarly, if I take alpha beta and beta alpha they are paired spins, one is plus half or other minus half; they are paired. Here both are plus half, plus half, minus half, minus half; they are not paired, they are unpaired. These have more energy, these have less energy.

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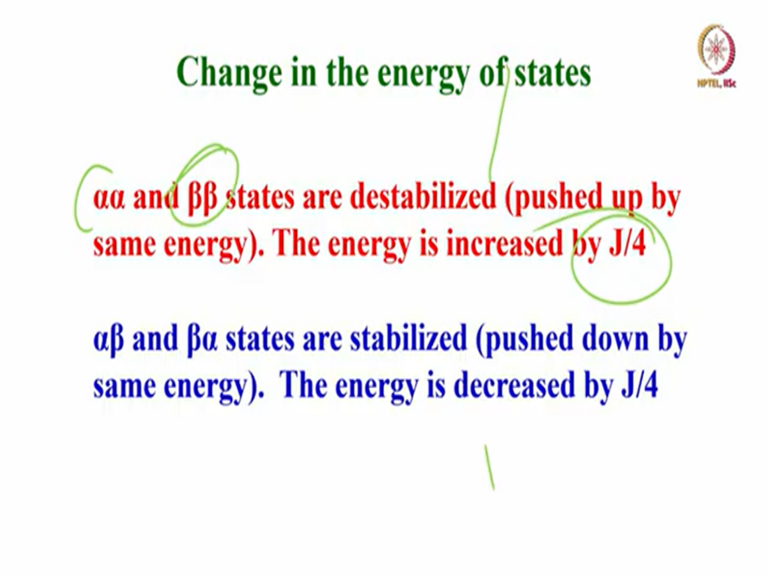

Change in the energy of states

αα and ββ states are destabilized (pushed up by same energy). The energy is increased by J/4

αβ and βα states are stabilized (pushed down by same energy). The energy is decreased by J/4

As a consequence, what happens? alpha, alpha and beta beta states get destabilized; and goes up by J/4. I will show you the diagram now. Whereas alpha beta and beta alpha are stabilized the push it down by the same energy, this will go up, push it up, this will come down by the same amount of energy.

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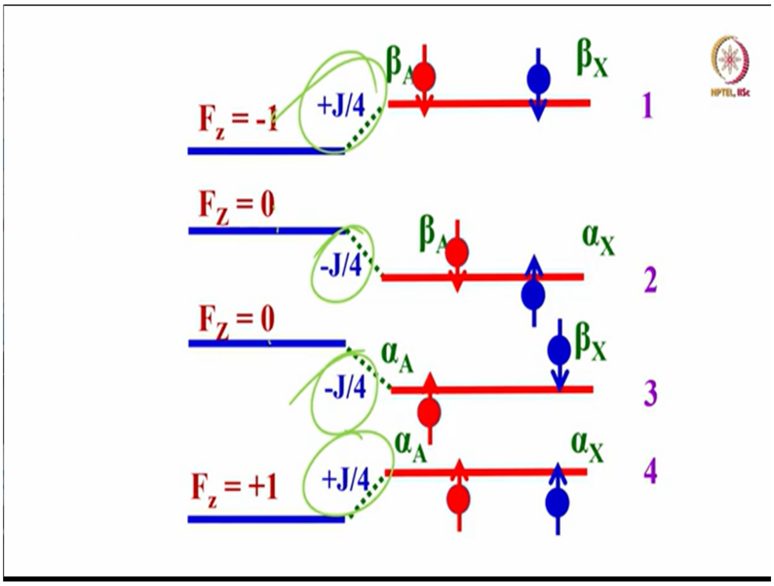

And now, if I have the energy level like this, without any interaction, without any coupling between 2 spins A and X. There are 4 energy states like this. Now, alpha, alpha, if I consider or beta, beta both of them are destabilizing goes up by J/4, + J/4. Now alpha beta and beta alpha get destabilized by - J/4. Now, same allowed transitions -1 to 0; +1 to 0 this to this, this to this. There are 4 allowed transitions you can see that all, this is allowed A to A and this is also allowed A to A, this is allowed X to X. It is also allowed transition X to X. Now, frequencies are not identical; in the earlier case when there is no coupling; they were identical frequencies they were overlapping, but now in one case the energy level separation is larger, and in other case energy level separation is smaller. That means the frequencies are not same.

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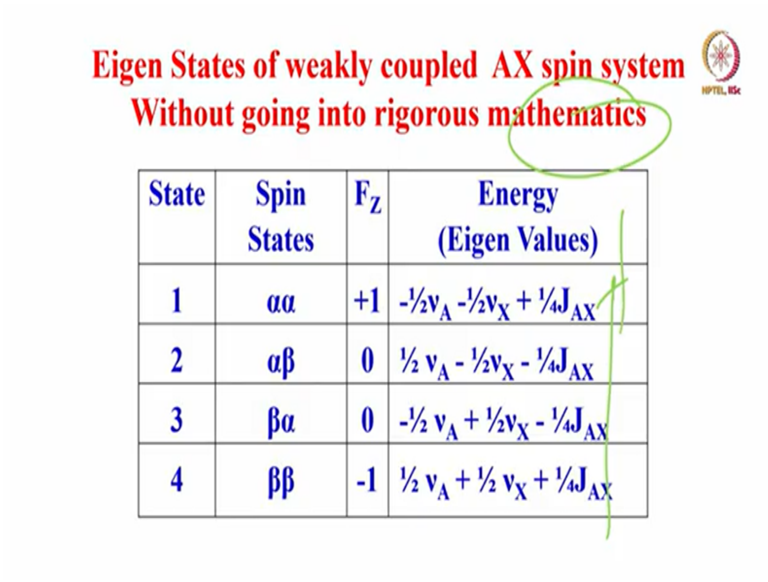

Eigen States of weakly coupled AX spin system
Without going into rigorous mathematics

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

As a consequence, what will happen if we calculate the energies of these states? For spin states alpha alpha, we have one energy; for spin state beta alpha and alpha beta, you can calculate the energies like this. And without going into the rigorous mathematics, I wrote earlier in the previous course. Today we will go into the mathematics and try to understand how we got these things. These are the energy states we call it the Eigen values. So, 4 spin states, 4 Eigen values are there.

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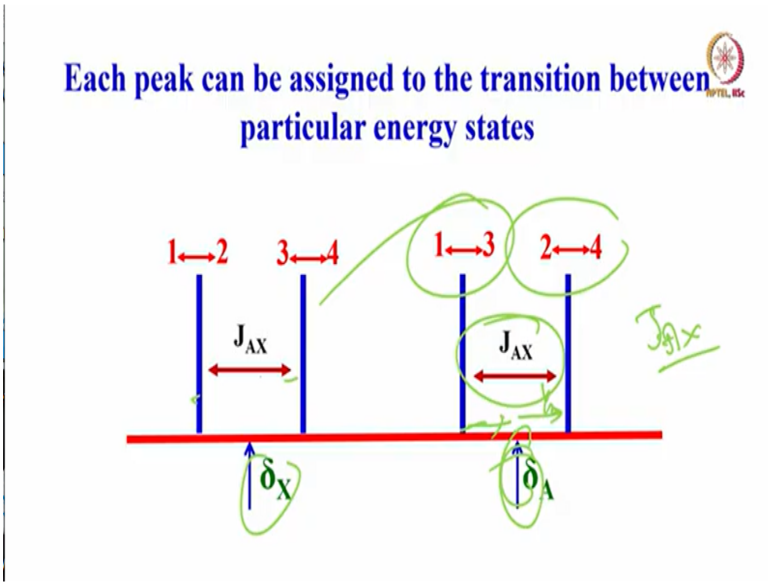
Each peak can be assigned to the transition between particular energy states



Using this you can get the frequency of the transitions, you can find out what are the transitions, you can assign the peaks for each of the transitions, like this. So, now, if you go to the chemical shift of A, at the site of A, you have 1 peak towards the right, shifted by certain frequency, 1 peak towards the left, shifted by the same frequency. So, now, this is delta A, this is increased by half of JAX, this is decreased by half of JAX. You understand? So, this is what is going to happen and you get 2 peaks, because the energy levels or frequency of transitions are different. And this separation is called interaction strength, coupling constant, scalar coupling constant JAX. Identically you see that in the X spin case also. This A, this X spin, same, we get 2 lines. Separation is JAX. 4 peaks you got, and you got 4 energy levels. This is all for the beginners who did not come to my last class, I wanted to brief you.

Now, how did we get this one? I gave only the table, but how did you get this? The rigorous mathematic is there, through which we can understand. So, today, we will try to understand the quantum mechanical treatment of AX spin system, 2 spins coupled.

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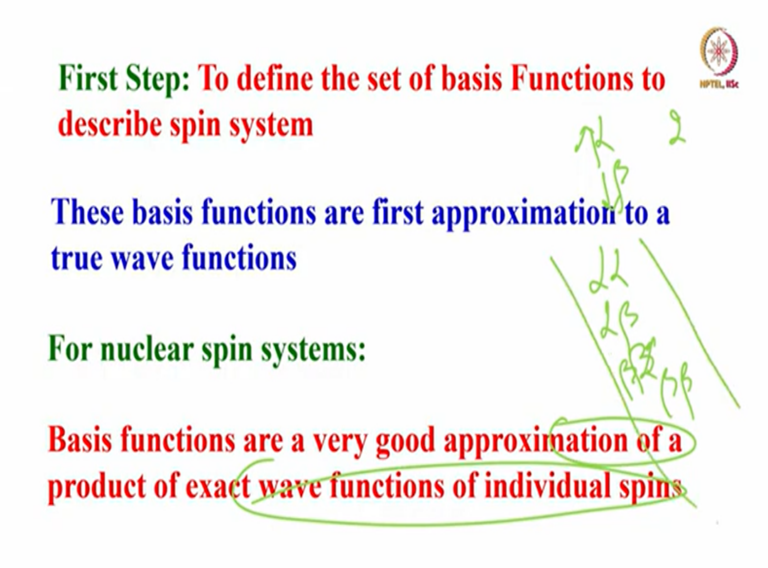

First Step: To define the set of basis Functions to describe spin system

These basis functions are first approximation to a true wave functions

For nuclear spin systems:

Basis functions are a very good approximation of a product of exact wave functions of individual spins

For example, if I have to do the quantum mechanical analysis, the first step is as to define the basis set. Set of basis functions to describe the spin system. I have a spin system, I have to decide what are the basis functions, set of basis functions. I should define; that is the first step. And second step once I know this basis function, then I have to build the Hamiltonian. Now, what are these basis functions for this spin system? And then we start with basis functions, when you start with the analysis in quantum mechanics. To the first approximation, these basis functions are the true wave functions, there is not much difference. Basically, we start like that. The first approximation what we do for the basis functions, they are nothing but the true wave functions, close to true wave functions.

And for the nuclear spin system, which you are dealing with. Nuclear spins in NMR what we are dealing with, the basis functions are to a very good approximation, they are nothing but product functions of the exact wave function of the individual spins. What it means is, I have the wave functions of the individual spins, what are the exact wave functions of the individual spins, if I take one spin, one is alpha, other is beta, there are 2 possibilities.

Now, the basis function if I were to take 2 spins coupled, which I showed you in the case of A and X, we have alpha alpha, alpha beta, beta alpha and beta beta. What does it mean? Here, the combinations, the basis set what I have chosen are nothing but to a very good approximation nothing but the exact wave function of the individual spins. So, for 2 individual spins there are 4 possible combinations of these wave functions. They are nothing but the product functions, the product of the basis functions which you have to choose.

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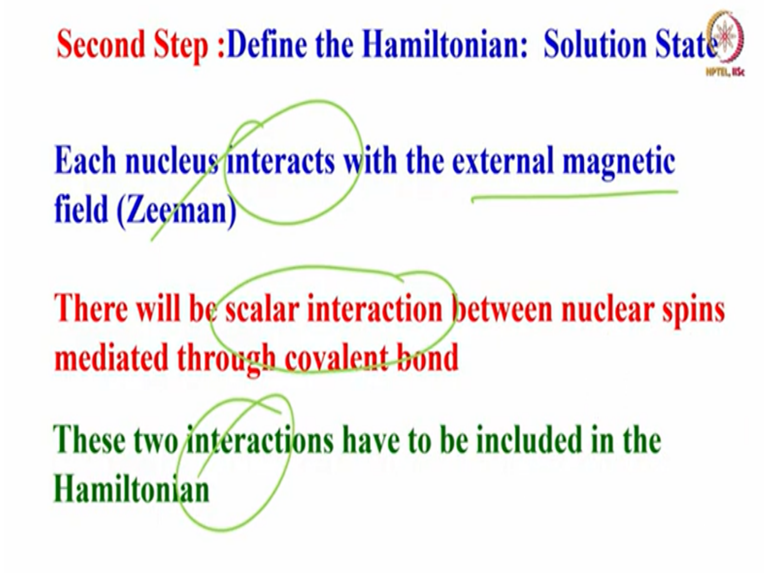

Second Step :Define the Hamiltonian: Solution State

Each nucleus interacts with the external magnetic field (Zeeman)

There will be scalar interaction between nuclear spins mediated through covalent bond

These two interactions have to be included in the Hamiltonian

Once you know what are the product functions. So, in the second step what you have to do is you have to define the Hamiltonian. Of course, Hamiltonian of these nuclear spin interactions if you want to define, then it is different for the solution state and it is different for the solid-state. In the solid-state there are different types of interactions coming, since we are not dealing with a solid state right now, we will not worry about it. We will concentrate only on the solution state Hamiltonian.

Now, if n nuclei are present interacting with each other, each nucleus interacts with the external magnetic field. I have 2 spins A and X; A can interact with Zeeman magnetic field, Zeeman interaction A can be there, X can also have as Zeeman interaction. There are n number of spins, each of them can individually interact with the magnetic field, each of them can have a zeeman interaction.

And in addition to that, there is also a scalar interaction between the nuclear spins. Let us take the example of 2 spins, A and X. A can interact with the magnetic field then there is Zeeman interaction; X can interact with the magnetic field, there is Zeeman interaction. Between A and X there is a scalar coupling, mediated through covalent bond. There are 3 types of interactions if I have 2 spins. Two chemical shifts, that is Zeeman interactions or the interaction the magnetic moment of individual spins with the external magnetic field, and other is scalar coupling. Both are present. These 2 interactions you have to consider and then build the Hamiltonian to carry out the analysis.

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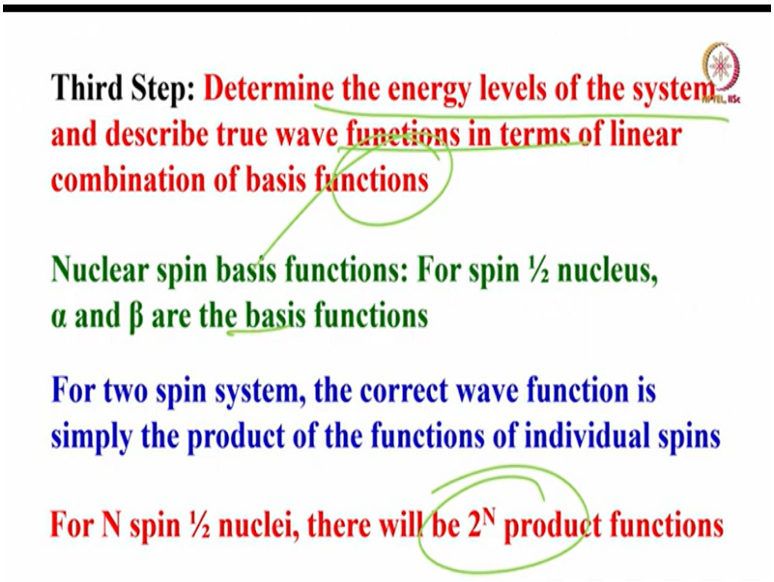

Third Step: Determine the energy levels of the system and describe true wave functions in terms of linear combination of basis functions

Nuclear spin basis functions: For spin ½ nucleus, α and β are the basis functions

For two spin system, the correct wave function is simply the product of the functions of individual spins

For N spin ½ nuclei, there will be 2^N product functions

That is what we have to do. Once you build the set of basis functions, we have to build the Hamiltonian, what is the next step, third step is to determine the energy levels of the spin system and describe through wave functions, in terms of the linear combination of the basis functions. Here that is what I already explained to you; for the nuclear spin basis functions are for a spin half nucleus are alpha and beta. Now, if I have to consider 2 spins, what is the correct wave function? The correct wave function is the product of the functions of individual spins. That is what I said, if I have 2 spins, the product functions are alpha alpha, alpha beta, beta alpha and beta beta. So, this is the especially for a nuclear spin basis function, it is very easy, basis function alpha and beta you would consider; they are nothing but the product function. That is the correct wave function.

So, if N nuclear spins interacting, I took the example of 2 spins, 2 spins interacting with each other, we have 4 possible spin states, 4 possible basis functions, wave functions we got; alpha alpha, alpha beta, beta alpha, beta beta. Instead of 4 let us say, instead of 2, let us say 3 nuclear spins are interacting, how many you can think of? Each of them will have alpha and beta spin states. So, various permutation combinations you can think of, then it is 2 cube 8, 8 product functions will be there, if you go to 4 spin, 16 will be there. So, the general formula is for N coupled spins there are 2 to the power of N product functions. You understand? For N spin half nuclei, if they are coupled among themselves, there will be 2 to the power of N product functions.

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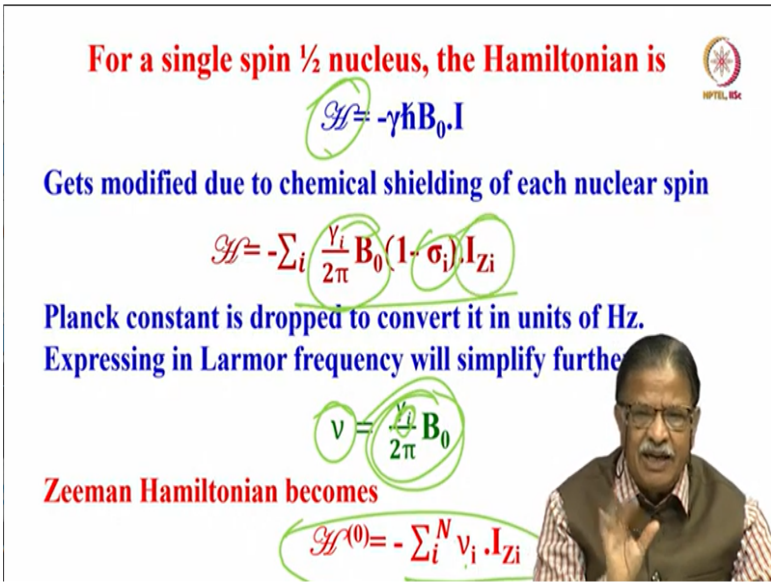

For a single spin ½ nucleus, the Hamiltonian is

$$\mathcal{H} = -\gamma\hbar B_0 . I$$

Gets modified due to chemical shielding of each nuclear spin

$$\mathcal{H} = -\sum_i \frac{\gamma_i}{2\pi} B_0 (1-\sigma_i) . I_{Zi}$$

Planck constant is dropped to convert it in units of Hz.

Expressing in Larmor frequency will simplify furthe

$$\nu = \frac{\gamma_i}{2\pi} B_0$$

Zeeman Hamiltonian becomes

$$\mathcal{H}^{(0)} = -\sum_i^N \nu_i . I_{Zi}$$

Now, we will consider a single spin half nucleus, only one nucleus; let us not bring in J coupling at the moment. When there is 1 spin there is no J coupling, the Hamiltonian is given by minus gamma h cross B naught into I. What is this? This is nothing but Zeeman interaction. So, this already we have been discussing, right in the first class. So, this one gets modified, because of the chemical shielding of the nuclear spin. I told you the Zeeman interaction is there and then because the internal interaction, shielding effect will be there; then this Hamiltonian gets modified. How it gets modified? It is like this. So, if I consider this one, I consider this as, I write like this gamma over 2 pi into B naught into I Zi that we know the resonating condition. Now, this modification term what we have put is 1 - sigma i which is due to chemical shielding, screening constant we discussed.

So, now the Hamiltonian without taking into account for a scalar coupling gets modified because of the chemical shift like this. So, this is the Hamiltonian only considering interaction of the nuclear spin with the magnetic field, taking into account the chemical shielding. Now, what I will do is, the Planck concept here is dropped. Why did I drop it? to convert this in terms of Hertz, very easy.

So, you know in future we go ahead every time to have this gamma and go 2 pi, getting this 2 pi term is a little messy. To avoid that we remove the gamma, or these things. So, Planck constant term we write it as gamma i over 2 pi into B naught, i is the nuclei of your interest; there could be N number of nucleus. So, Zeeman Hamiltonian can now be written as h of 0, this, I call it as H0.

For scalar coupling, I put different number; for H0 is only direct interaction of the nuclear spin with the magnetic field, taking into account the chemical shielding; this is written as i = 1 to N nu i IZi. This is what Zeeman Hamiltonian, we have written. Because I have written nu is equal to gamma over 2 pi into B naught, gamma over 2 pi B naught I remove that and put as nu, express in terms of Hertz; frequency units as Larmor frequency. Then it will become nu i I Zi, that is all, very simple. I have not done anything. If there are N interacting spins, I sum it over N to i because they are all individually each of them are interacting.

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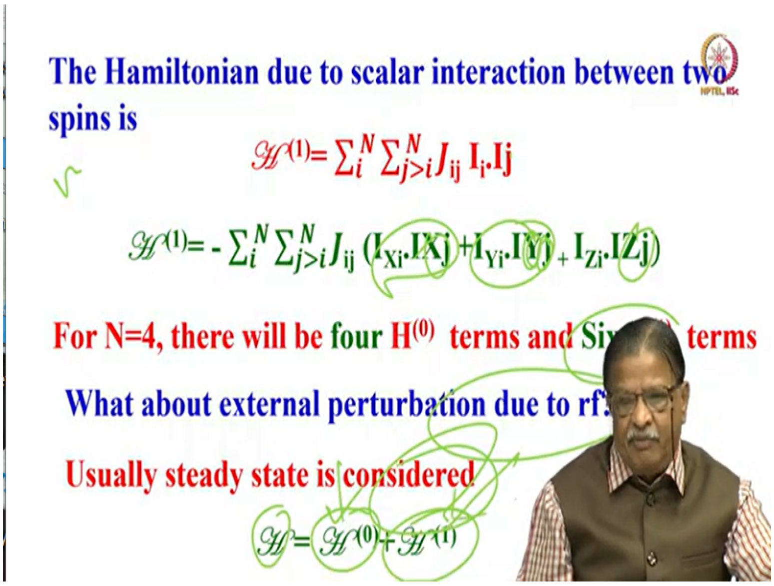

The Hamiltonian due to scalar interaction between two spins is

$$\mathscr{H}^{(1)} = \sum_i^N \sum_{j>i}^N J_{ij}\, I_i . Ij$$

$$\mathscr{H}^{(1)} = - \sum_i^N \sum_{j>i}^N J_{ij}\, (I_{Xi} . IXj + I_{Yi} . IYj + I_{Zi} . IZj)$$

For N=4, there will be four $H^{(0)}$ terms and Si terms

What about external perturbation due to rf

Usually steady state is considered

$$\mathscr{H} = \mathscr{H}^{(0)} + \mathscr{H}^{(1)}$$

Now, if there is a scalar coupling, now I bring another nuclei and if it is interacting also in addition to that, what is happening? We will write Zeeman Hamiltonian plus we also bring in the interaction between nuclear spin I and j. I and j are interacting and coupling constant is Jij. This is scalar interaction Hamiltonian, depending upon number of spins I can take 1 to N.

This is N + 1 to other number you can take if you want ,i = 1 to N and the M you can put N - 1 to J; some number you can write, so that you will get all possible combinations of that.

And of course, NMR interaction is mutual, J12 is also equal to J21 both are same. So, you have to consider only J 12, you do not have to consider the J coupling of 12. You do not have to consider 21. So, it does not matter. So, this is simple way you can represent this Hamiltonian. So, this is J coupling Hamiltonian taking into account interaction between the 2 nuclear spins. Now, this Ii and Ij we can resolve into 3 components X, Y and Z. This is a vector, so I resolved into Xi and Xj and then Yi and Yj; it is a product.

So, Xi of course, this should have been y and j should have been subscript, but by mistake I did not put, but do not worry; the subscript like Xi, it should be Xj should be subscript Yj and Zj, all the 3 should be subscripts. It is only the nomenclature that is all. So, now, this Hamiltonian is expanded into 3 components, Jij Ii.Ij. I wrote in terms of the X, Y, Z components of the vector. Now, for example N = 4, there will be 4 H0 terms. I say 4 nuclear spins are interacting. How many H0 terms are there? each nuclear spin have a separate Zeeman interaction there are 4 H0 terms, that is why I wrote nu i I Zi. So, nu1 I Z1, nu2 I Z2 like that, therefore 4 Hamiltonian terms are there for H0. But for this one, there are 6, because, for 4 nuclei you can consider as 12, 13, 14, 23, 24, 34. There are various combinations you can think of, there are 6 H1 terms here. So, it is very simple; consider 4 interacting spins, the Hamiltonian becomes so complex, there will be 4 H0 terms and 6 H1 terms.

Now, you may ask me a question, what about radio frequency pulse you are applying. Are you not perturbating the system, is there no interaction with rf. External interaction is there like Zeeman interaction we discussed. External interaction there are things; one is the Zeeman; other is rf, rf also has an interaction. But we will ignore it. Right now, external perturbation we do not consider because we are considering only the steady state.

We will not bother about it at the moment for calculations. So, the basically the total Hamiltonian can be written as H = H0 + H1. H0 is a Zeeman Hamiltonian, H1 is the scalar coupling Hamiltonian. These 2 are can be individually considered.

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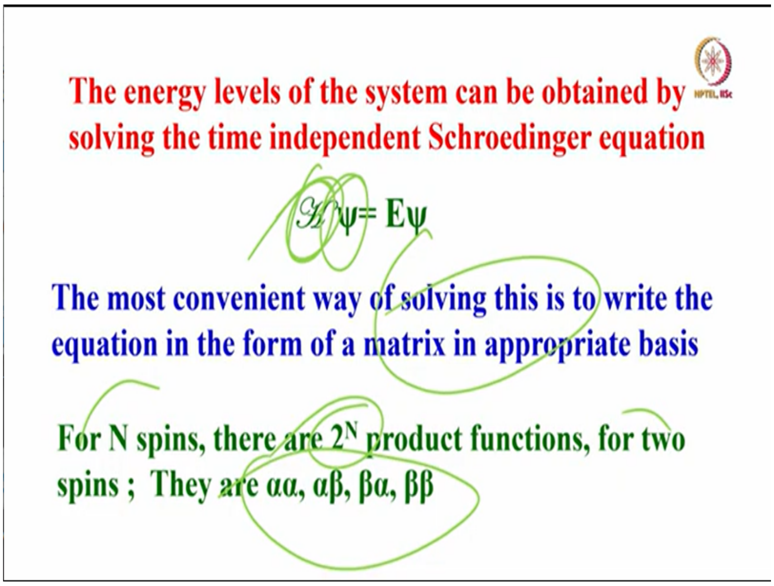

The energy levels of the system can be obtained by solving the time independent Schroedinger equation

$$\mathscr{H}\psi = E\psi$$

The most convenient way of solving this is to write the equation in the form of a matrix in appropriate basis

For N spins, there are 2^N product functions, for two spins ; They are αα, αβ, βα, ββ

So, what you do is you have built the Hamiltonian, you know the wave functions, the energy levels of the system you have to compute now. What you will do? in simple basic quantum mechanics you will have studied, you have to solve this time independent Schrodinger equation that it is H psi = E psi. We try to solve the time independent Schrodinger equation. Then you write this; solve it, and you are going to get Eigen values and Eigen functions everything; that is the basic thing.

So, understood what we have to do, for quantum mechanical analysis, you have to build the Hamiltonian first; find the wave functions, which are nothing but the product functions for the nuclear spins to the first approximation, but there are also true wave functions, built the Hamiltonian. One Hamiltonian is Zeeman interaction of each individual nuclear spins, other is coupling among nuclear spins. So, all these things together, you have to consider a total Hamiltonian and then solve this equation. So, time independent Schrodinger equation and for that, you need to solve it in a matrix form. You have to write it in the matrix representation and then solve it. So, for N spins, remember there are 2 to the power of N product functions. And for 2 spins that are only 4 product functions. That is what we discussed. For N spins, 2 to the power of N product functions are there. For 3 spins 2 cube, for 4 spins 2 to the power of 4. For 2 spins, we are dealing with only 2 spins, because if you want to make the quantum mechanical analysis 3 spins, 4 spins it will take almost the entire course. You will take the pages and pages hundreds and hundreds of pages and start working out everything; it will take an almost half a year for you to solve all those things; even if you go to 4 or 5 interacting spins. So, right now, I will tell you the method of solving this by solving the Hamiltonian by taking only 2 spins, where there are 4 possible product functions.

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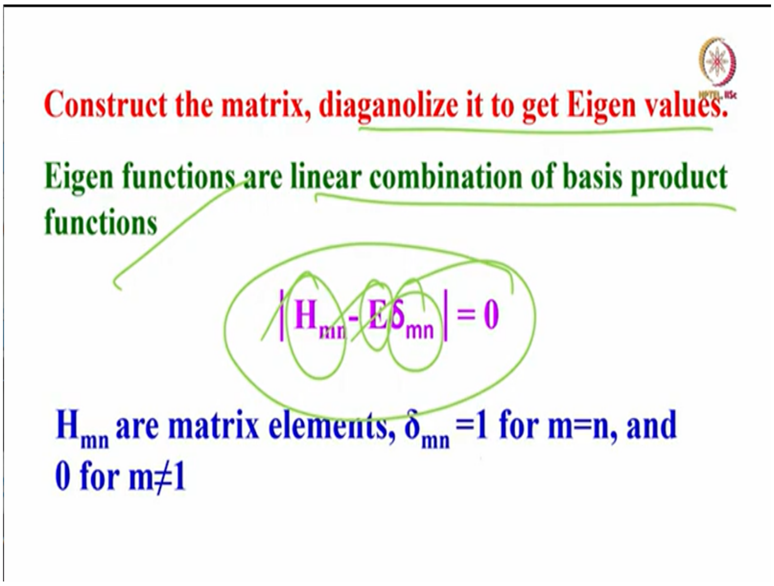

Construct the matrix, diaganolize it to get Eigen values.

Eigen functions are linear combination of basis product functions

$$|H_{mn} - E\delta_{mn}| = 0$$

H_{mn} are matrix elements, δ_{mn} =1 for m=n, and 0 for m≠1

So, what we have to do is to construct the matrix, diaganolize matrix to get the Eigen values and Eigen functions of the linear combination of the basis product functions. And basically, you have to write the Hamiltonian like this, I am sorry this a matrix like this; Hmn - E delta mn = 0, Hmn are the each individual elements of the matrix and delta mn is the kronecker delta. For m = n this is 1; otherwise it is 0. And then each energy Eigen values we have to work out. So, Hmn are the matrix elements and for this is equal to 1 for m = n, and 0 for m is not equal to 1.

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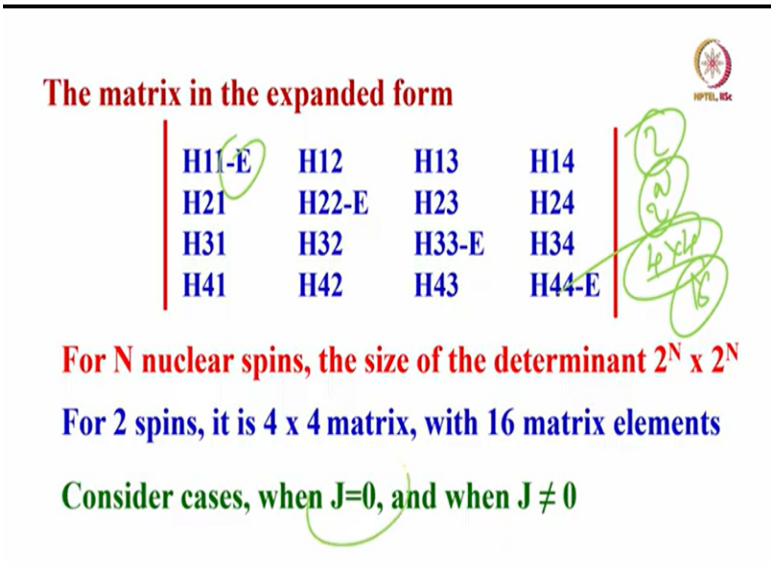

The matrix in the expanded form

$$\begin{vmatrix} H11-E & H12 & H13 & H14 \\ H21 & H22-E & H23 & H24 \\ H31 & H32 & H33-E & H34 \\ H41 & H42 & H43 & H44-E \end{vmatrix}$$

For N nuclear spins, the size of the determinant 2^N x 2^N

For 2 spins, it is 4 x 4 matrix, with 16 matrix elements

Consider cases, when J=0, and when J ≠ 0

So, matrix is you have to write in the expanded form is like this, for nuclear spin system. For 2 spins, I wrote H11 element, H12, H13 like this, and then of course, the same thing what is shown below, you have to solve this equation, and then represent in the matrix form; it is a 4 by 4 matrix, because there are 2 spins, 2 to the power N product functions. So, it is a 4 into 4, matrix there are 16 elements here.

If now nuclear spins N becomes larger and larger; imagine you take 3 spins, there are 8. That is 2 cube 8, 8 into 8, 64 elements of the matrix. That is why I said beyond to spin quantum mechanic analysis if you want to do manually it is very difficult. For 2 spins, it is 4 by 4 for N spin it will become larger. So, now we what we will do is we start analysing the 2 spins case quantum mechanically considering only 2 examples; 2 cases, the case A and X can be coupled to each with the coupling constant 0; or with the coupling constant non 0.

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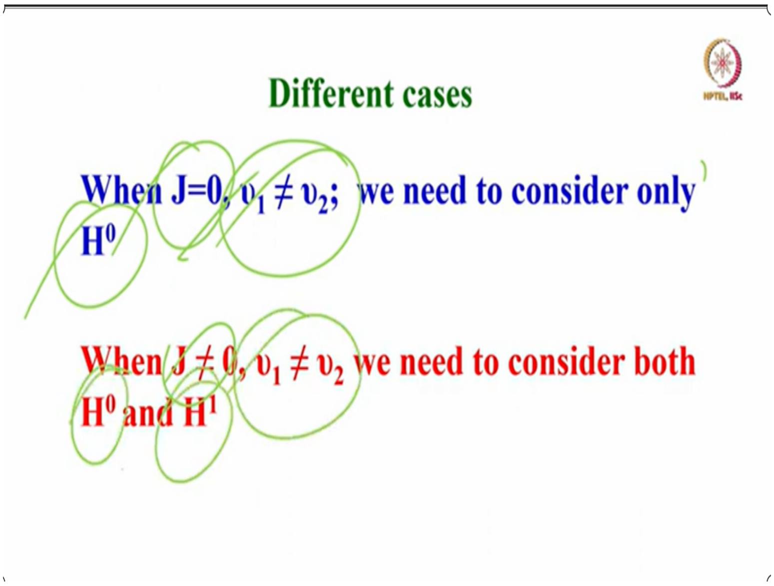

Different cases

When J=0, $\upsilon_1 \neq \upsilon_2$; we need to consider only H^0

When $J \neq 0$, $\upsilon_1 \neq \upsilon_2$ we need to consider both H^0 and H^1

We have to consider these 2 different cases; when J = 0 chemical should nu 1 is not equal to nu 2. We need to consider in this case only H0 because J coupling is 0. You do not have to consider at all. I told you, when J is not equal to 0, nu 1 is not equal to nu 2, you have to consider both H0 and H1 and then start building the Hamiltonian. So, now the time is up.

What I am going to do is in the next class we will take 2 examples of 2 coupled spins. Work out both the cases; J is equal to 0 and J is equal to non 0, and get the Eigen values and find out the transition frequencies and see how the spectrum comes. This is basically what is done for all other coupled spin systems; and we take the example for strongly coupled spin system for AB also and A2 also.

For AB we will work out, for A2 we do not work out, you know it is again a lengthy process will be there. Once you know AX and once you know AB, the rest of the things is easy. And for higher spins it is enormous amount of laborious work. We do not do that. And then I will just show you diagrammatically how the energy levels come; because some of the stalwarts have already done it and given us the charts, we can utilize that.

And beyond 3 or 4 spins it is humanly impossible, you need to use the computers to simulate and then diagonalise the matrix and get the Eigen values and Eigen functions etc. So, I am going to stop it here for today. So, we have understood something today; I started introducing you the quantum mechanical analysis of the coupled spin systems, I introduced Pople notation, what is strongly coupled, what is weakly coupled spin system, their notations and I told you how we have to build the Hamiltonian, for the coupled spin system to analyse.

And first of all, take H0, H1 etcetera. H0 is the Zeeman interaction, it is the interaction of the magnetic moment of the nuclear spins with the external magnetic field; it is Zeeman Hamiltonian which is equal to minus nu I Zi. For N spins you have N number of terms, then for H1 is interacting term which is scalar coupling term, which nuclear spins themselves can interact due to scalar coupling, then you have to build it as H1 that is J ij, Ij dot Ij which we remove the X and Y component; it will become IZi, IZj. Of course, we can work out and show that later. And then I showed you for 2 spins. We take the example. There are 4 possible product functions. And then we can build the Hamiltonian and start analysing for both the cases. So, we will do that in the next class. Thank you. I am going to stop it here.