Advanced NMR Techniques in Solution and Solid-State
Prof. N. Suryaprakash
Professor and Chairman (Retd)
NMR Research Centre
Indian Institute of Science – Bengaluru

Module-17
Quantum Mechanical Analysis of Spin System
Lecture - 17

Welcome back. In the last class, we analyzed Eigen values for 2 weakly coupled spin system for which we assumed one condition, a case where j = 0, the weakly coupled spin system with coupling constant 0, but chemical shifts are well separated because they are weakly coupled. And what we did, we first defined the wave function which has the product functions for 2 weakly coupled cases, we know the product functions are alpha alpha, alpha beta, beta alpha and beta beta and we wrote down the Hamiltonian.

For the Hamiltonian in this case, only we have to consider the Zeeman interaction H0. I defined it as equal to - nu z i into nu a nu I; nu i in this case of 2 spins, nu a and nu x. I consider there are only 2 Zeeman interactions, each spin is interacting with the external magnetic field, there are 2 Zeeman interaction terms only I have to write; and the coupling I assume to be 0. So, I do not have to worry about H1 and used that we solved the secular equation of the determinant; expressed in the form of matrix, and there are 16 elements. But, we showed that only 4 diagonal elements are present there, which are non zero, all the off-diagonal elements are 0. And using these diagonal elements, we could work out what are the frequency of the transitions and we know that 2 of the frequencies are identical and are overlapping for each spin, A spin has 2 transitions which are overlapped. Similarly, X spin has 2 transitions that are overlapped; and they are well separated. So, in weakly coupled 2 spins with J coupling is 0, we get only 2 peaks one is at the chemical shift of X, another at the chemical shift of A; only 2 peaks.

So, now, with that, we will go next and try to understand what happens if we bring in the coupling? in the previous case, where it was assumed to be 0. It may not be 0, let us say the coupling is not 0, how does the spectrum reflect? whether all the elements of the Hamiltonian, are present? or only diagonal elements are only present; what about the off-diagonal elements? are the present in this case? we work it out.

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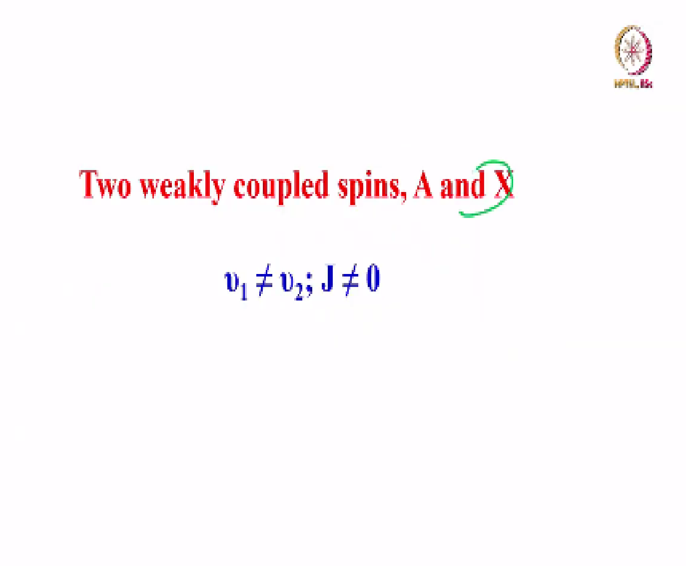

Two weakly coupled spins, A and X

$\upsilon_1 \neq \upsilon_2; J \neq 0$

So, consider a weakly coupled case, A and X. Now, I am going to put the condition nu 1 ≠ nu 2 and J is not equal to 0, this is my condition.

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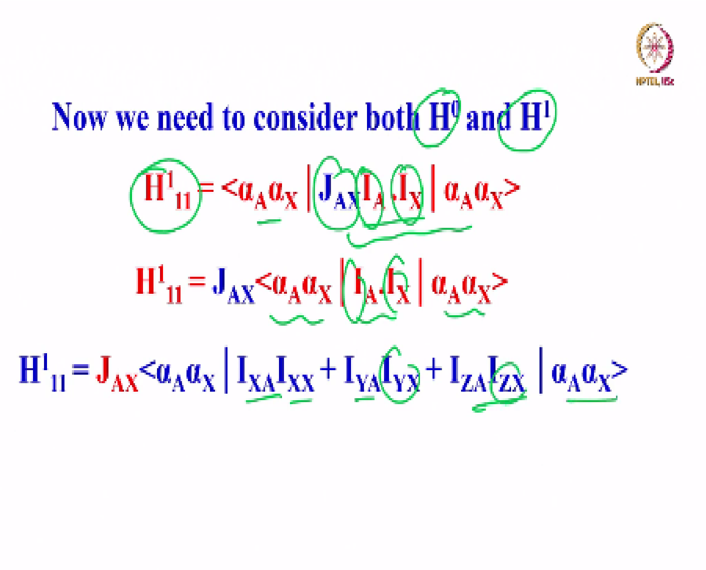

Now we need to consider both H^0 and H^1

$$H^1_{11} = \langle \alpha_A \alpha_X | J_{AX} I_A \cdot I_X | \alpha_A \alpha_X \rangle$$

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$$H^1_{11} = J_{AX} \langle \alpha_A \alpha_X | I_{XA} I_{XX} + I_{YA} I_{YX} + I_{ZA} I_{ZX} | \alpha_A \alpha_X \rangle$$

And I use that; as I told you, you need to consider both H0 and H1 in this case. Of course, H0 we know already; now we have to consider only H11, for H11 is now we have to consider JAX; A and X are interacting, and I know the spin angular momentum of I and X, this is the way J is written, already we have discussed. Now, I consider the first element of the matrix; the diagonal element, first element of the matrix H11, where I am considering only Zeeman J coupling interaction. In which case I write like this alpha A, alpha X which operates in JAX IA IX alpha A alpha X, this is a term I have to evaluate for the J coupling diagonal term. Now, of course, this has added to the H0 term later. Now, similarly H11 now I am going to write; J I can take it out because it is a scalar, just a number, it is just a number, I will take it out then I am going to write alpha A alpha X which is equal to IA IX alpha A alpha X. Now, this I am going to resolve into 3 components. Since both of them are vectors, IA and IX, I can write it as IXA IXX IYA IYX; IZA IZX operating an alpha A alpha X.

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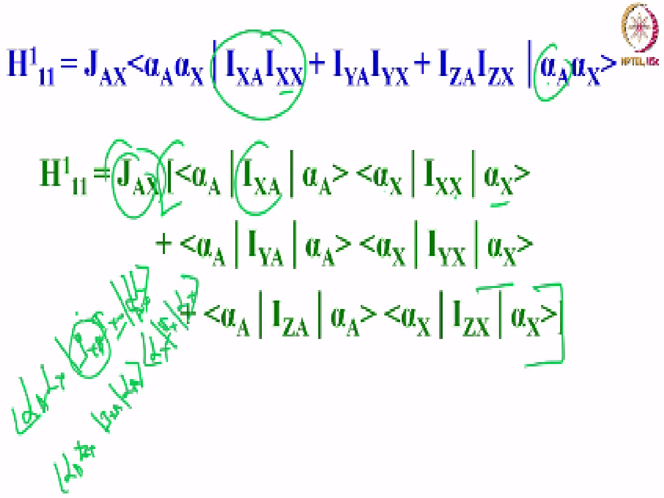

$$H^1_{11} = J_{AX} \langle \alpha_A \alpha_X | I_{XA} I_{XX} + I_{YA} I_{YX} + I_{ZA} I_{ZX} | \alpha_A \alpha_X \rangle$$

$$H^1_{11} = J_{AX} [\langle \alpha_A | I_{XA} | \alpha_A \rangle \langle \alpha_X | I_{XX} | \alpha_X \rangle + \langle \alpha_A | I_{YA} | \alpha_A \rangle \langle \alpha_X | I_{YX} | \alpha_X \rangle + \langle \alpha_A | I_{ZA} | \alpha_A \rangle \langle \alpha_X | I_{ZX} | \alpha_X \rangle]$$

Now, we are going to do one thing, write each of these terms expanded in a comfortable way, like we did for the previous case. So, now I will take JAX always outside, we have to write a square bracket here. Hopefully you are seeing the square bracket. Now alpha A IXA alpha A; I wrote, because I am not dealing with only A spin here. And then of course, when I do that, now what will happen? I also have to consider X; as both are coupled here, I have to consider alpha X operating an IX also with alpha X.

So, each term for each of these IXA IXX. Now, I can resolve into 2 terms, but the product terms now, unlike in the previous case, both are products. alpha A and alpha X is a product, alpha A alpha X is a product. So, now I am taking first term, first term is alpha A alpha X, I will take

IXA, IXX alpha alpha AX. So, this I am going to resolve like this, this is the first term alpha A alpha X IXA; of course, remove this one IX alpha XA and then multiply this by again alpha X. Now, IX I will consider; IX alpha X very easily you have to write like that. So, this one you have to do it for all the other terms now, all the terms you have to do.

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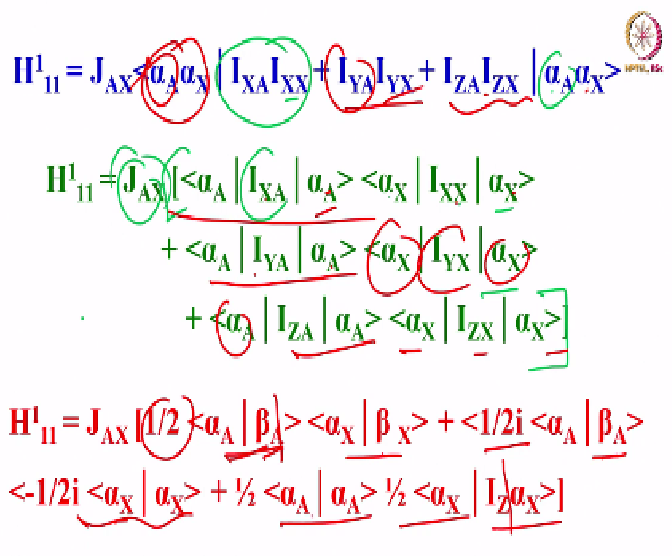

$$H^1_{11} = J_{AX} < \alpha_A \alpha_X | I_{XA} I_{XX} + I_{YA} I_{YX} + I_{ZA} I_{ZX} | \alpha_A \alpha_X >$$

$$H^1_{11} = J_{AX} [< \alpha_A | I_{XA} | \alpha_A > < \alpha_X | I_{XX} | \alpha_X > + < \alpha_A | I_{YA} | \alpha_A > < \alpha_X | I_{YX} | \alpha_X > + < \alpha_A | I_{ZA} | \alpha_A > < \alpha_X | I_{ZX} | \alpha_X >]$$

$$H^1_{11} = J_{AX} [1/2 < \alpha_A | \beta_A > < \alpha_X | \beta_X > + < 1/2i < \alpha_A | \beta_A > < -1/2i < \alpha_X | \alpha_X > + ½ < \alpha_A | \alpha_A > ½ < \alpha_X | I_Z \alpha_X >]$$

So, what we will do is now with all the remaining 2 terms also we will work it out like this, and see what you are going to get. So, now, second term if you take IYA I have to take, the same way alpha A IYA alpha A, I will take this one and this one and alpha X IYX alpha X, I will take alpha A IYX alpha X. Now IZ I will do the same thing; alpha A IZA alpha A alpha X IZX alpha X. All I did is resolved each of these terms to 3 terms first. And again each of these 3 terms I resolved into 2 components which are products one corresponds to spin A other corresponds to spin X. A simple operation, I did nothing great.

Now, we have to find out what is this value? you know that alpha A operating on beta A; first of all you take out what we are going to do now JAX alpha A operating an alpha is half alpha A, I am sorry, here dealing with IX now IX operating alpha A gives beta A; from our previous action of various operators I showed you know.

In which case if alpha IX operating in alpha gives as beta; and this of course, similarly IX operating on alpha gives beta; IY operating on alpha gives rise to half of I. Again it is beta similarly, IX so, alpha IX; IX will come here, that will remain same in this case. And now, third term should come here, alpha A alpha A and then half of IX operating on IZX, write all these terms, of course, you are write here. Write all these terms; simply what I did is each of these terms I expanded it in a comfortable way.

So, now, what you are going to see; very simple when IX operating on alpha A gives beta A similarly, IX operating on alpha gives beta and IY gives as to half 1 over 2i beta; IZ operating on alpha gives half alpha. Simply substitute these values.

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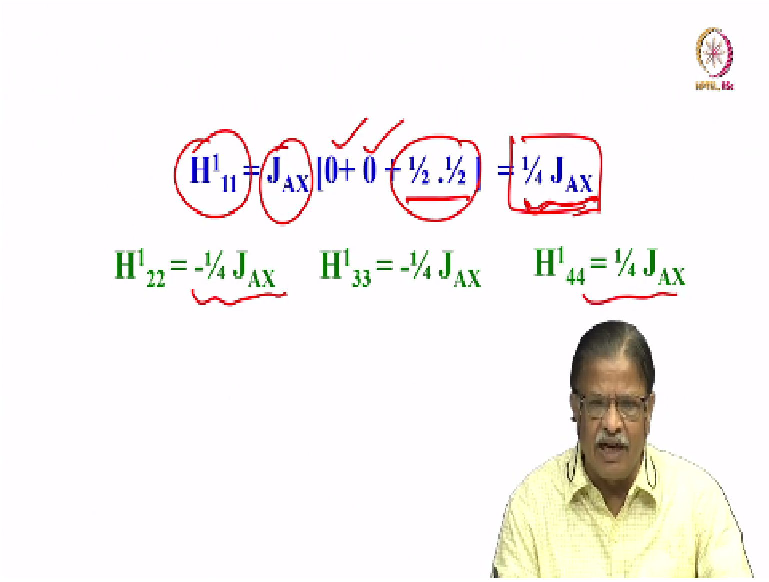

$$H^1_{11} = J_{AX}[0 + \overset{\checkmark}{0} + \underline{\tfrac{1}{2}.\tfrac{1}{2}}] = \boxed{\tfrac{1}{4} J_{AX}}$$

$$H^1_{22} = \underline{-\tfrac{1}{4} J_{AX}} \qquad H^1_{33} = -\tfrac{1}{4} J_{AX} \qquad H^1_{44} = \underline{\tfrac{1}{4} J_{AX}}$$

See what you are going to get. Now, first term becomes 0, second term becomes 0, you can go back and check. Here because now alpha operating on beta is 0. Similarly, second term alpha operating on beta is 0. So, this multiply by this does not matter it is 0. So, now 0 multiplied by this number, here 0 multiplied by this number, it is 0. So, now, we are left with only third term which is half into half; it turns out to be 1/4 into JAX, JAX was a common factor which I took it out.

So, if I workout H11 diagonal element, it turns out to be 1/4 JAX. Very simple, all I did is I just wrote down the Hamiltonian by taking into account the scalar coupling; wrote all the 3 in the form of IXA into IXX, IYA into IYX, IZA into IZX now alpha alpha operating on IXA IXX into alpha alpha; you consider. You know IX operating on alpha gives is to half beta, IY operating on alpha gives rise to 1 over 2i into beta; that are all well known operations. Simply I substitute those number; only thing when IZ operating an alpha gives to half alpha. Similarly IZ operating on X alpha gives rise to half and those terms will survive and we are going to add one forth here. So, finally it turns out to be 1/4 JAX. So, H11 becomes 1/4 JAX. What about H22? you workout it turns out to –1/4 JAX, then H33 also minus one forth JAX, H 4 again becomes one fourth J AX. So, all the 4 diagonal elements in a similar manner you can work out, there is nothing great we have done here. Simply remember this thing here. is again I will repeat.

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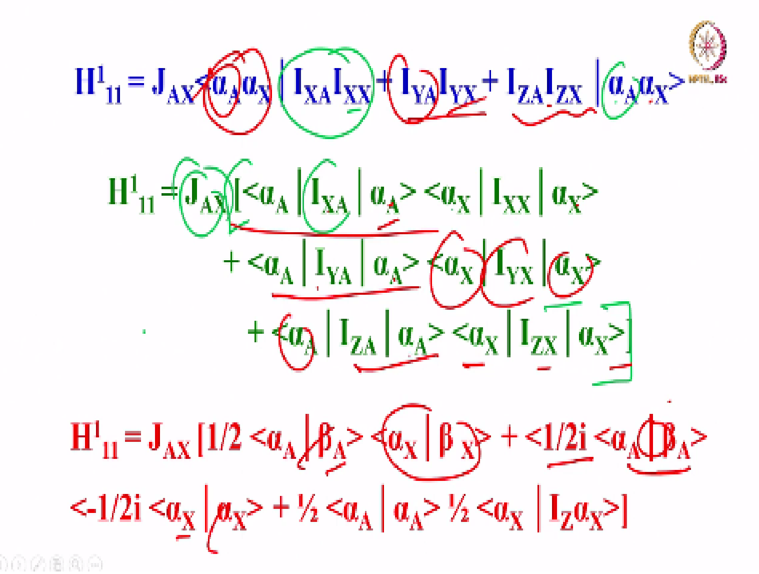

$$H^1_{11} = J_{AX} \langle \alpha_A \alpha_X | I_{XA} I_{XX} + I_{YA} I_{YX} + I_{ZA} I_{ZX} | \alpha_A \alpha_X \rangle$$

$$H^1_{11} = J_{AX} [\langle \alpha_A | I_{XA} | \alpha_A \rangle \langle \alpha_X | I_{XX} | \alpha_X \rangle + \langle \alpha_A | I_{YA} | \alpha_A \rangle \langle \alpha_X | I_{YX} | \alpha_X \rangle + \langle \alpha_A | I_{ZA} | \alpha_A \rangle \langle \alpha_X | I_{ZX} | \alpha_X \rangle]$$

$$H^1_{11} = J_{AX} [1/2 \langle \alpha_A | \beta_A \rangle \langle \alpha_X | \beta_X \rangle + \langle 1/2i \langle \alpha_A | \beta_A \rangle \langle -1/2i \langle \alpha_X | \alpha_X \rangle + ½ \langle \alpha_A | \alpha_A \rangle ½ \langle \alpha_X | I_Z \alpha_X \rangle]$$

What I did is simply I wrote like this, we expanded everything. See, now, I expanded the first term, first term alpha IX operating an alpha gives rise to beta; see this is like this. So, now, when you write like that, this will become 0. Similarly, you can expand this one; then this alpha operating on this will become alpha beta because IY operating an alpha gives as to 1 over 2i beta A this will become 0. So, this term will go, this term will go, only if we consider the last term IZ operating on alpha gives half alpha, IZ operating on alpha gives half alpha, both for A and X we will get half into half, we are going to get one fourth.

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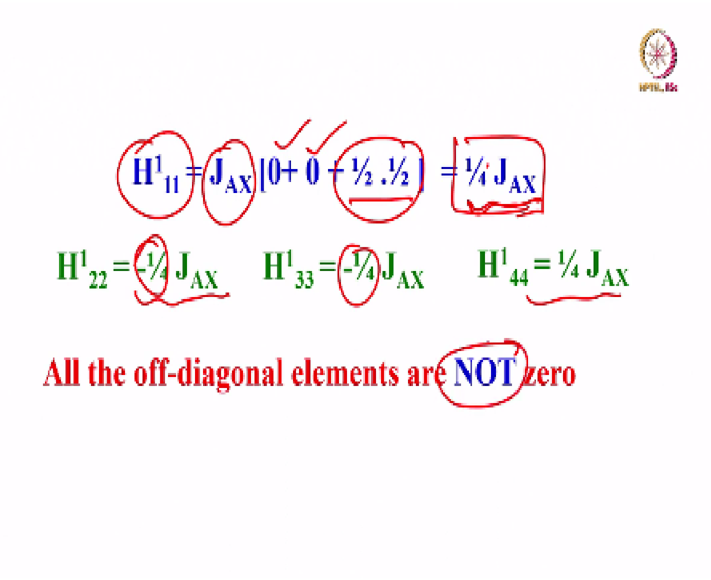

$$H^1_{11} = J_{AX}[0 + 0 + \tfrac{1}{2}.\tfrac{1}{2}] = \tfrac{1}{4}J_{AX}$$

$$H^1_{22} = -\tfrac{1}{4}J_{AX} \qquad H^1_{33} = -\tfrac{1}{4}J_{AX} \qquad H^1_{44} = \tfrac{1}{4}J_{AX}$$

All the off-diagonal elements are NOT zero

Similarly, you wrote for H 22, H 33 and H 44. please remember all the 4 diagonal elements when you work for a weakly coupled spin system, especially when taking scalar coupling in account each of these term turns out to be 1 over 4 into JAX in 2 case 22 and 33 were negative and 11 and 44 are positive. All the off-diagonal elements are not zero in this case, remember. In the earlier case, when J coupling was equal to 0, I showed that H of 23 is 0 or 12 I took and showed it is 0.

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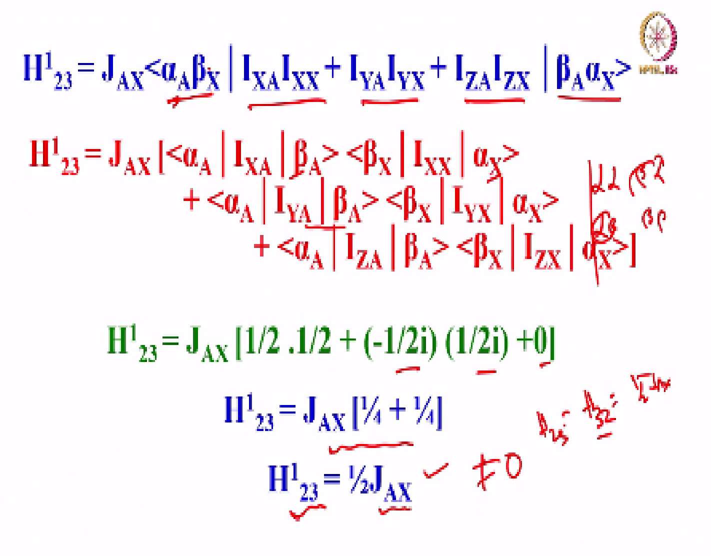

$$H^1_{23} = J_{AX}\langle\alpha_A\beta_X \mid I_{XA}I_{XX} + I_{YA}I_{YX} + I_{ZA}I_{ZX} \mid \beta_A\alpha_X\rangle$$

$$H^1_{23} = J_{AX}[\langle\alpha_A \mid I_{XA} \mid \beta_A\rangle\langle\beta_X \mid I_{XX} \mid \alpha_X\rangle + \langle\alpha_A \mid I_{YA} \mid \beta_A\rangle\langle\beta_X \mid I_{YX} \mid \alpha_X\rangle + \langle\alpha_A \mid I_{ZA} \mid \beta_A\rangle\langle\beta_X \mid I_{ZX} \mid \alpha_X\rangle]$$

$\alpha\alpha$ $\beta\beta$

$\beta\alpha$

$$H^1_{23} = J_{AX}[1/2\,.1/2 + (-1/2i)(1/2i) + 0]$$

$$H^1_{23} = J_{AX}[\tfrac{1}{4} + \tfrac{1}{4}]$$

$$H^1_{23} = \tfrac{1}{2}J_{AX} \checkmark \neq 0$$

$H_{23} = H_{32} = \frac{1}{2}J_{AX}$

Whereas in this case, it is not 0 we can work it out. I am taking 23, just one of the off-diagonal elements you write like this alpha A beta X, IXA IXX, plus IYA IYX plus IZA IZX and beta alpha. See alpha beta and beta alpha I am considering they are off-diagonal elements. So, if you consider the matrix alpha alpha, alpha beta, here beta alpha, beta beta it goes like this. So, now I am considering alpha beta operating on beta alpha, so, this is a term I am considering. So, now, I consider that, H23 I expand like this very easily; alpha beta IXA IXX beta alpha you consider.

Again resolved into 2 parts here alpha IXA operating on beta, beta IXA operating on alpha X, IXA operates on alpha X here. Similarly, this term second term we consider. Now consider A, A X and X ; alpha A operating on IYA and again here I consider beta A, I take beta X IYX. Now, second term is alpha X, take the third one alpha A first term IZA, first term is B A and second term B X, he has second term is IZX and second term is alpha X.

Simply I resolved the terms in a comfortable way for analysis. But you can find out here; these terms turns out to be half, this turns out to be half. Whereas, the second term if I consider here this term -1 over 2i into 1 over 2i and the last term turns out to be 0. Very easy using those action of different types of operators how on different wave functions, I showed that they use the table and simply substitute these values; and you will find out these turns out to be JAX into 1/4 + 1/4 it will become 1 over 2 JAX.

So, off-diagonal elements in this case is not 0, this is not 0. Whereas, in the case when j = 0 off-diagonal term was 0, here it is not when the J coupling is nonzero. This is what is going to happen, I consider a H23 then it is turn out to be 1 over JAX. But remember I told you matrix is symmetric. So, H23 it can also be called as H32, so that was another diagonal element you already know; this is also equal to half JAX, it is clear? So, 2 off-diagonal elements are nonzero here because one I calculated, and because of symmetry I know the other one.

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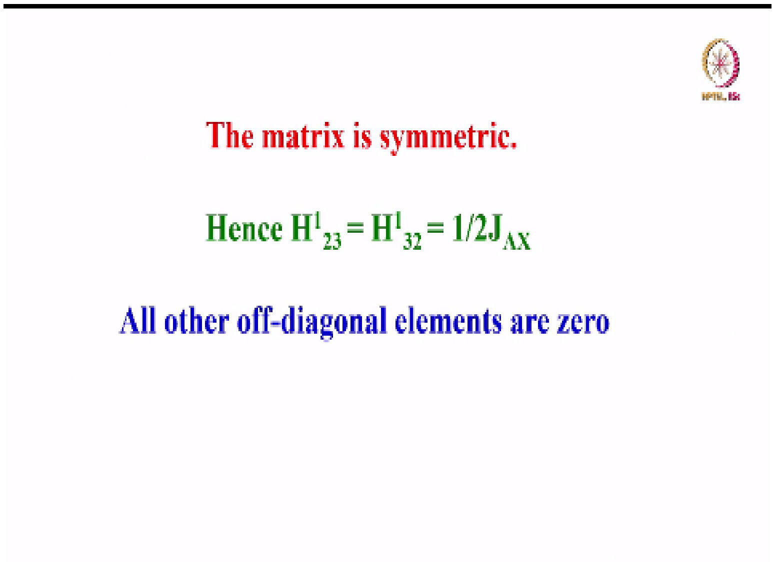

The matrix is symmetric.

Hence $H^1_{23} = H^1_{32} = 1/2 J_{AX}$

All other off-diagonal elements are zero

Now what about other off-diagonal elements? I do not want to work it out, it is very, very simple. Go and find out yourself, all the off-diagonal elements are 0. Remember, in this case, very simple, this thing I did here.

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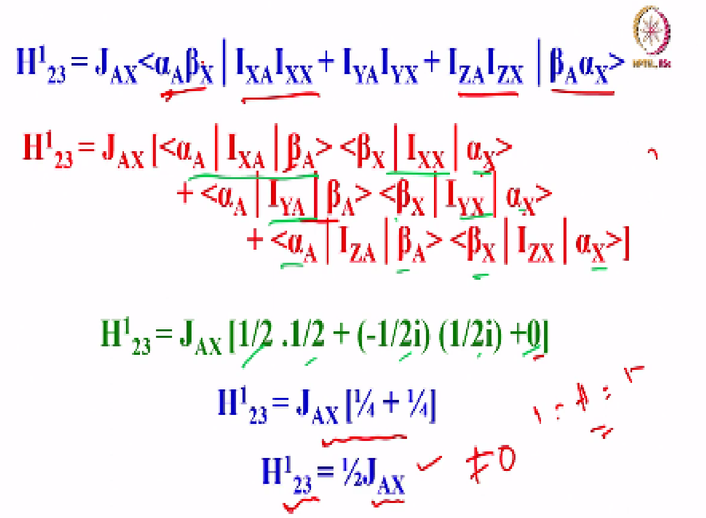

$$H^1_{23} = J_{AX} \langle \alpha_A \beta_X | I_{XA} I_{XX} + I_{YA} I_{YX} + I_{ZA} I_{ZX} | \beta_A \alpha_X \rangle$$

$$\begin{aligned} H^1_{23} = J_{AX} [&\langle \alpha_A | I_{XA} | \beta_A \rangle \langle \beta_X | I_{XX} | \alpha_X \rangle \\ &+ \langle \alpha_A | I_{YA} | \beta_A \rangle \langle \beta_X | I_{YX} | \alpha_X \rangle \\ &+ \langle \alpha_A | I_{ZA} | \beta_A \rangle \langle \beta_X | I_{ZX} | \alpha_X \rangle] \end{aligned}$$

$$H^1_{23} = J_{AX} [1/2 . 1/2 + (-1/2i)(1/2i) + 0]$$

$$H^1_{23} = J_{AX} [1/4 + 1/4]$$

$$H^1_{23} = 1/2 J_{AX} \quad \checkmark \quad \neq 0$$

I explained to you already, see this is a thing which you should remember how we work it out. I will consider a different thing, so that you will be able to judge it. Now, I resolved into 2 things alpha A IX beta; beta X IX alpha X, this is the first term, second term, IY term, again alpha beta IYX alpha beta, IZ term alpha beta, beta alpha; And with the usual action of the operators, we know that this will become half half, this will become –1 over 2i into 1 over 2i and this I the last term is 0. And it turns out to be 1 / 4 + 1 / 4 = half JAX, this is what it is.

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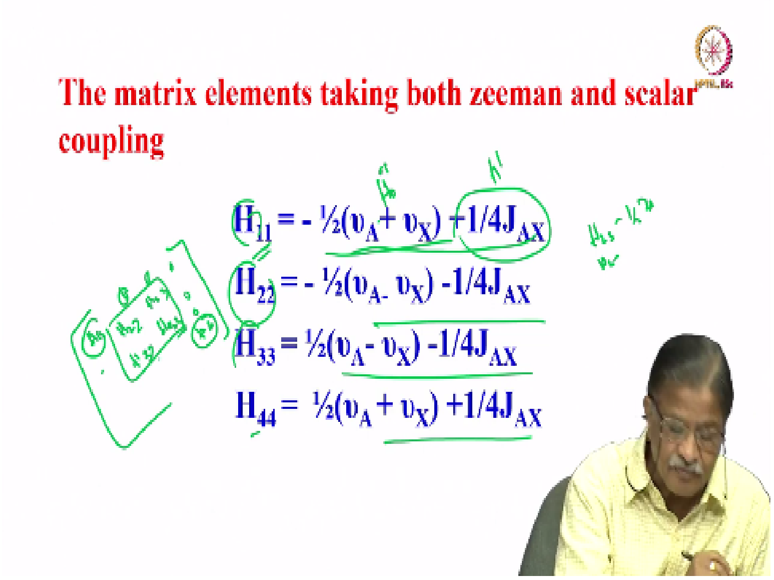

The matrix elements taking both zeeman and scalar coupling

$$H_{11} = -\tfrac{1}{2}(\upsilon_A + \upsilon_X) + 1/4 J_{AX}$$

$$H_{22} = -\tfrac{1}{2}(\upsilon_A - \upsilon_X) - 1/4 J_{AX}$$

$$H_{33} = \tfrac{1}{2}(\upsilon_A - \upsilon_X) - 1/4 J_{AX}$$

$$H_{44} = \tfrac{1}{2}(\upsilon_A + \upsilon_X) + 1/4 J_{AX}$$

And all other off-diagonal elements, I said are 0. Now, you can construct the matrix element taking into account H0, H0 I did not work out. But remember in the last class I worked out, I am just simply borrowing that. We knew H11 is half into nuA + nuX in the previous example, with J = 0, only this is the additional term coming because of scalar coupling. So they are the terms H11 now, this is H0 term, this is H11 term; both are added. And this is the one of the diagonal elements H11.

Similarly, H22 the other diagonal element which turns out to be like this. H33 is other diagonal element, which turns out to be like this. H44, like this. So, now we have got 4 diagonal elements very clearly. The matrix is now we can divide into 2 1 by 1 matrices and one 2 by 2 matrix here. So, we can write down the matrix because we have off-diagonal element J23 also as 1 over 4 JAX that that I have not ignored. So, only I am writing diagonal elements, what about H 23 = 1 / 2 JAX, I know other is H32 is = 1 / 2 JAX.

So, if you write down the Hamiltonian matrix here, it turns out to be like this, H11, H22, H33 and H44 and then H23, and H32 all other terms are 0. So, this is the matrix. So, now I can resolve this into sub matrices; 2 1 by 1 matrices, and 1 2 by 2 matrix. This is the way I can resolve.

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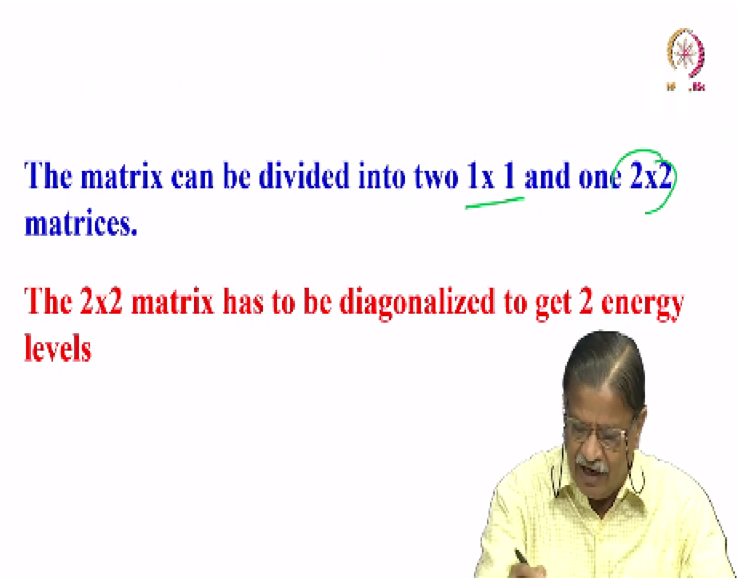

The matrix can be divided into two 1x 1 and one 2x2 matrices.

The 2x2 matrix has to be diagonalized to get 2 energy levels

Now what I am going to do is, if I do that, I can get the Eigen value from these 2 1 by 1 matrices very easily, just straightforward. Now 2 by 2 matrix, I have to diagonalized, again. And I have to diagnose and get 2 diagonal elements for that. And that will give me 2 energy levels. So that is what I have to do. If I take 2 1 by 1 matrices and take one 2 by 2 matrix and diagnose it, I am going to get 4 energy states, 4 diagonal elements, I have to do that.

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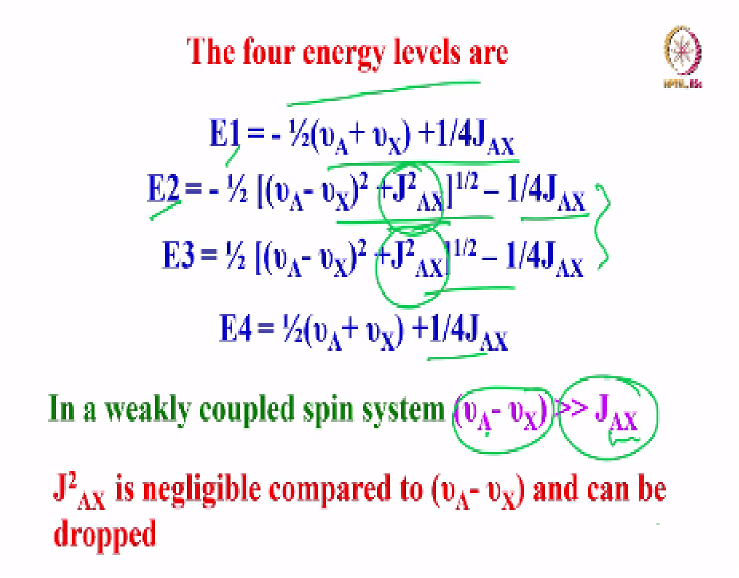

The four energy levels are

$E1 = - ½(\upsilon_A + \upsilon_X) + 1/4J_{AX}$

$E2 = - ½ [(\upsilon_A - \upsilon_X)^2 + J^2_{AX}]^{1/2} – 1/4J_{AX}$

$E3 = ½ [(\upsilon_A - \upsilon_X)^2 + J^2_{AX}]^{1/2} – 1/4J_{AX}$

$E4 = ½(\upsilon_A + \upsilon_X) + 1/4J_{AX}$

In a weakly coupled spin system $(\upsilon_A - \upsilon_X) >> J_{AX}$

J^2_{AX} is negligible compared to $(\upsilon_A - \upsilon_X)$ and can be dropped

So, 2 by 2 matrix is very simple to diagnose, I do not want to work it out very simply you work it out. And these are the 4 energy levels if you do that. So, I am going to get E1 energy state 1 where ¼ JAX was added second was E2, and this is turned out to be like this with the 1/4 JAX one case it is negative. It was a negative sign was there and the other one is positive. Now, you know everything very clearly. So, now work it out very, very clearly, in a weakly coupled system, nu A - nu X is very much larger than JAX.

That is very well known, I have been telling you, if I consider chemical shift difference, it is much, much larger than the JAX that is a weakly coupled spin system, in which case what about this one off-diagonal elements that 23 if I consider, I can simply ignore it. Because in such a situation, this is such a large value, this is a small value, it is so small, negligible compared to this chemical shift separation for calculation purposes, I will drop it, so I am going to just drop this JAX squared.

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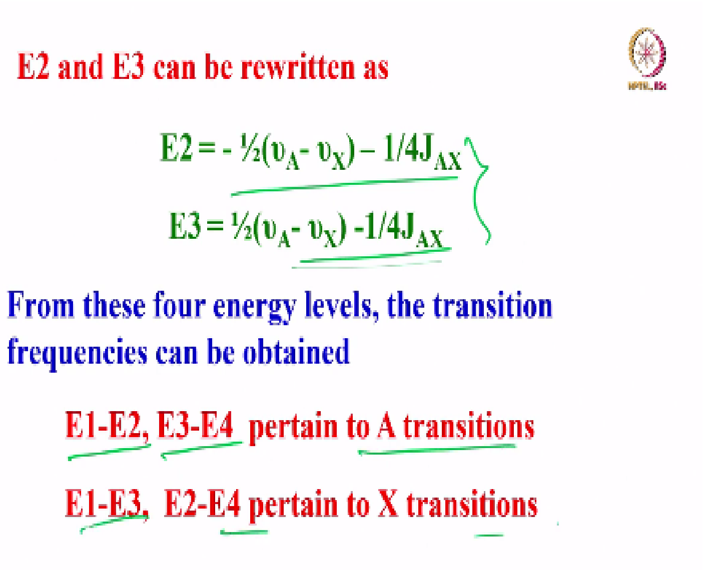

E2 and E3 can be rewritten as

$$E2 = -\tfrac{1}{2}(\nu_A - \nu_X) - 1/4J_{AX}$$

$$E3 = \tfrac{1}{2}(\nu_A - \nu_X) - 1/4J_{AX}$$

From these four energy levels, the transition frequencies can be obtained

E1-E2, E3-E4 pertain to A transitions

E1-E3, E2-E4 pertain to X transitions

Especially in the case of weakly coupled. So, in which case the energy level E2 and E3, which was obtained by diagonalizing 2 by 2 matrix I can write like this very simple. So, from this, now, we have 4 energy levels worked out, E1, E2, E3 and E4. E1 and E4 obtained by single 1 by 1 matrix. Now we diagonalize 2 by 2 matrix and got this thing and we ignore ¼ JAX, assuming that chemical shifts are quite large, so the contribution from JAX was negligible.

So, these are the 4 energy states, again, like in the previous case E1 - E2 and I am sorry this is E3 – E4 this correspond to A transition, this correspond to X transition very easily you can work out from that.

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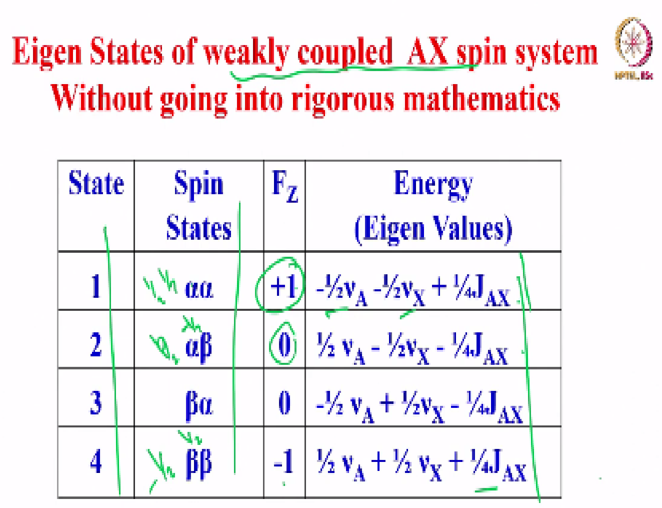

Eigen States of weakly coupled AX spin system
Without going into rigorous mathematics

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	$\frac{1}{2}\nu_A + \frac{1}{2}\nu_X + \frac{1}{4}J_{AX}$

So, do that and I am going to write a table like this, these are Eigen states of the weakly coupled spin system. And now, I have 4 energy states, these are the spin states and the total magnetic quantum number for each of the state is like this alpha alpha = 1, alpha beta is 0, beta alpha 0, beta beta is -1. This is because these minus half minus half will become 1, this plus half plus half have become 1, this is a plus half and minus half these becomes 0. So, for each of the energy state, I know what is the energy level, we have worked out.

In the first case E1 is minus half A minus half nuX, I have written in an expanded form, plus 1/4 JAX. In the second case, this one, third energy E3 and E4; all the 4 energy states you worked out. These are the energy levels, whatever I have worked out previously, I have put it in the form of a table here, that is all.

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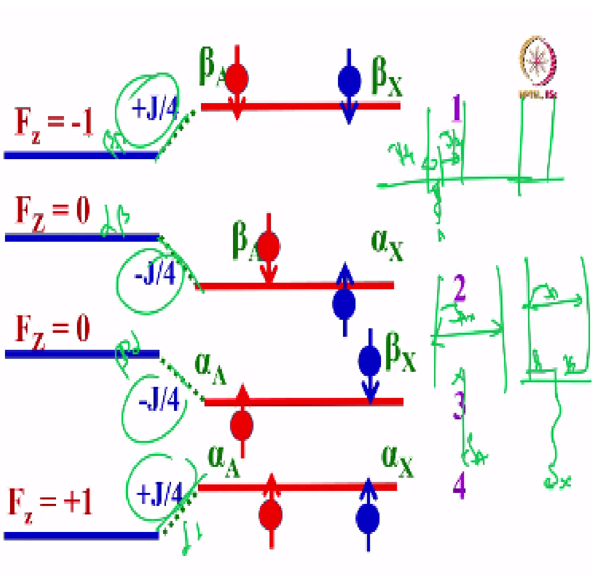

Now, let us see diagrammatically how it works. Very easily, now, if I consider a situation like this, this is the beta beta, this is the alpha alpha state, they are un paired they will have a lower energy, they are unstable states; as a consequence they are shifted up by J/4; both of them, beta beta is shifted up and alpha alpha both of them shifted up by J/4. What about alpha beta and beta alpha? they are all paired states, they are more stable. They are more stable as a consequence, the shifted down by J/4, by – J/4 these 2 are shifted up by +J / 4 and these 2 are shifted down by –J/4. This is exactly what we explained pictorially.

When I explained with the energy level diagram in one of the classes, when 2 get weakly coupled spin system are there, these are 2 transitions for A and 2 transitions for X like this. But since the coupling is present, they are like this; for A there will be 2 transitions. For the X there will be 2 transitions. And this is the chemical shift of A at the centre, this is a chemical shift of A, this is separated by J/4, this is separated by J/4. So, this is what is going to happen. So, that means the total separation of this doublet if you consider this is JAX and the centre of this doublet correspond to chemical shift of A, similarly for the X also tbe centre of this correspond to chemical shift of A, this is JAX and then from centre, this is separated by 1/4 JAX and half JAX, this is separated by JAX this is what is going to happen.

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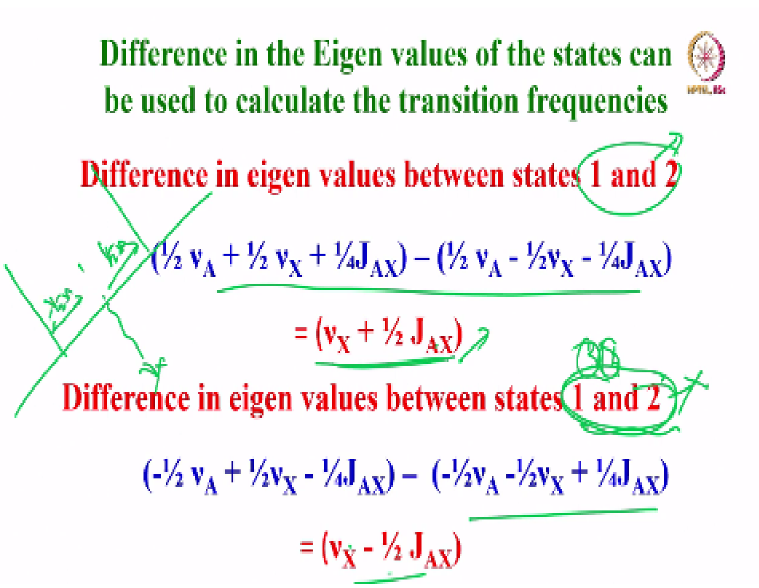

Difference in the Eigen values of the states can be used to calculate the transition frequencies

Difference in eigen values between states 1 and 2

$$(\tfrac{1}{2}\nu_A + \tfrac{1}{2}\nu_X + \tfrac{1}{4}J_{AX}) - (\tfrac{1}{2}\nu_A - \tfrac{1}{2}\nu_X - \tfrac{1}{4}J_{AX})$$

$$= (\nu_X + \tfrac{1}{2}J_{AX})$$

Difference in eigen values between states 1 and 2

$$(-\tfrac{1}{2}\nu_A + \tfrac{1}{2}\nu_X - \tfrac{1}{4}J_{AX}) - (-\tfrac{1}{2}\nu_A - \tfrac{1}{2}\nu_X + \tfrac{1}{4}J_{AX})$$

$$= (\nu_X - \tfrac{1}{2}J_{AX})$$

So, if 2 weakly coupled spin system are there, you are going to get 4 energy levels, you can work it out. Now, this is the energy difference between the states 1 and 2. If you consider this what you are going to get nu X + half J AX. And this is a difference in the eigen states between 1 and 2. Now, you are going to get this one. Sorry this is 1 and 2, this must be different. We are considering, go back from the table and we will find out what is this. So, 1 turns out to be half but this is not 1 / 2; if this is 1 / 2, this would be 3 / 4.

So, this is what you are going to get. In one case nu X, but finally, why find out whether these correspond to X transition, this also should be X transition. Find out what is the X transition and take the energy difference between these 2; maybe there is a typographical mistake, you do not worry; and in one case, you are going to get nuX + half JAX other case nu X - half JAX. Exactly that is what I said. This is a doublet and this is nu X, the chemical shift.

Now, in one case nu X + half J AX and another case nu X - half J AX, so 2 lines from the centre of the chemical shift are separated out by half J AX. And this separation gives rise to J. Identically you are going to get for other one.

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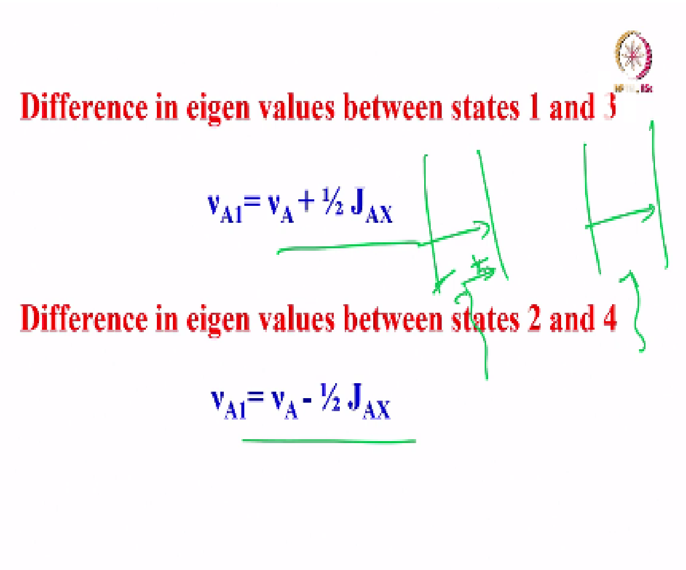

Difference in eigen values between states 1 and 3

$\nu_{A1} = \nu_A + \frac{1}{2} J_{AX}$

Difference in eigen values between states 2 and 4

$\nu_{A1} = \nu_A - \frac{1}{2} J_{AX}$

This for this is for X transition; and identically you are going to get for A transitions; nu A + half JAX and nu A - half JAX. So, JAX you can measure from both the doublets. A will one doublet and X will give one doublet, this will give JAX this will also give JAX. So there is the redundancy of the information, but the chemical shift is centre of this, chemical shift will be the centre of this. And each line of the doublet separated by half JAX from the centre; this is plus half JAX, this is minus of JAX same way here also.

So, these are the 4 transitions; you can work out depending upon the 4 energy levels, depending upon which are the transitions correspond to A, which are the transitions corresponding to X. Take these energy states find out the difference and you can find out the frequencies.

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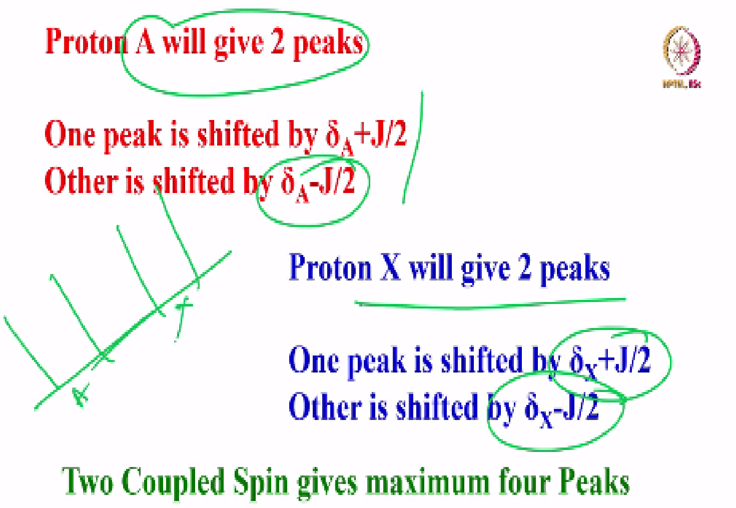

Proton A will give 2 peaks

One peak is shifted by $\delta_A + J/2$
Other is shifted by $\delta_A - J/2$

Proton X will give 2 peaks

One peak is shifted by $\delta_X + J/2$
Other is shifted by $\delta_X - J/2$

Two Coupled Spin gives maximum four Peaks

So, from this what you understand proton A will give 2 peaks, one peak is shifted by delta A + J / 2 other is shifted by delta A – J / 2. Similarly, proton X, we will give 2 peaks one shifted by delta X + J / 2 other is shifted by delta X – J / 2. This is what is important which I wanted to tell you. So, 2 coupled spin system can give maximum of 4 lines, it cannot give anything beyond that, 2 for A and 2 for X; these are the transitions you are going to get. So, quantum mechanically we can work out and find out the frequencies and everything.

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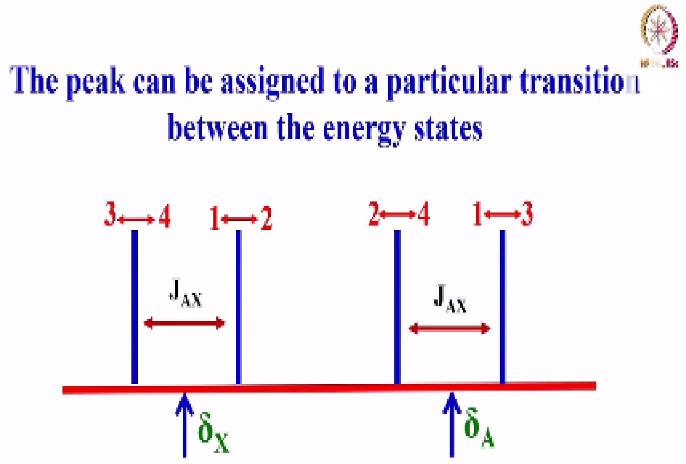

The peak can be assigned to a particular transition between the energy states

And you can assign for each peak correspond to the particular spin, because we know what is the selection rule, take the difference in the energy states, you find out which frequency servives whether nu A servive or nu X servive and that is the corresponding to the spin A or spin X, easily you can identify transitions corresponding to each of these, we can assign to a particular spin.

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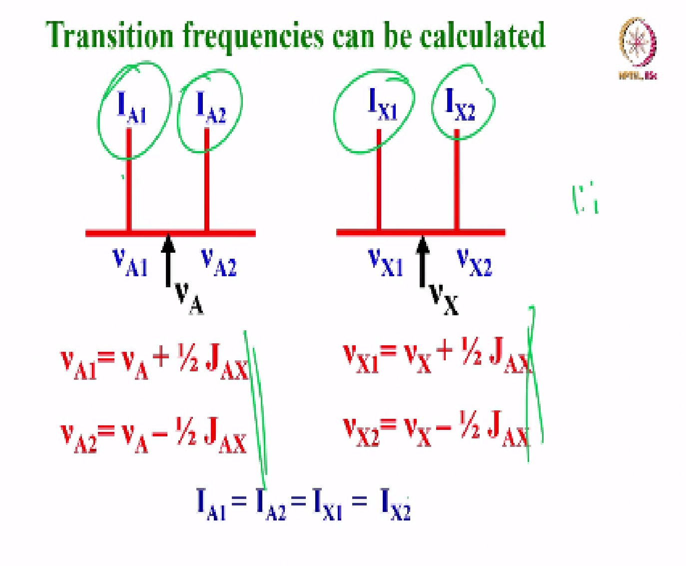

Transition frequencies can be calculated

$\nu_{A1} = \nu_A + \frac{1}{2} J_{AX}$

$\nu_{A2} = \nu_A - \frac{1}{2} J_{AX}$

$\nu_{X1} = \nu_X + \frac{1}{2} J_{AX}$

$\nu_{X2} = \nu_X - \frac{1}{2} J_{AX}$

$I_{A1} = I_{A2} = I_{X1} = I_{X2}$

So, the transition frequencies have been calculated like this, for each of them and intensity also, we can work it out very in detailed way. But remember, in this weakly coupled case, already I showed you they are all of equal intensities, 1 is to 1 is to 1 is to 1. All the 4 peaks are of equal intensity. And these are the 4 frequencies you obtain, the intensities are same and 4 frequencies are obtained.

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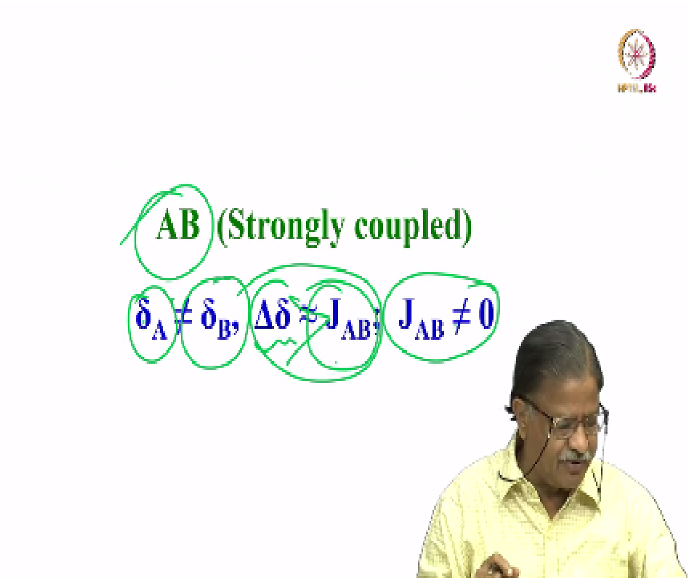

AB (Strongly coupled)

$\delta_A \neq \delta_B$, $\Delta\delta \approx J_{AB}$; $J_{AB} \neq 0$

So, this is a simple example, for a weakly coupled we worked out quantum mechanically, the energy states, ofcourse we can also work out the stationary state wave functions and everything in detail, but I am not going into that because that is not much of interest. As of now, our interest is to get the frequency of the transitions.

Now, we will go to another case AB; again 2 spin coupled but what is the condition here, chemical shift A is not equal to chemical shift B and delta delta chemical shift separation is approximately equal to J coupling.

Delta delta is approximately JAB and JAB is nonzero; it is not 0. It is present. And it is a strongly coupled system example I am taking. You understood earlier case that delta A was very much larger than delta X and delta delta was very much larger; delta A and delta X or not same and JAX was not 0. The same condition only thing is delta delta is approximately equal to JAB here, compared to the previous case where delta delta is sufficiently larger compared to coupling constant.

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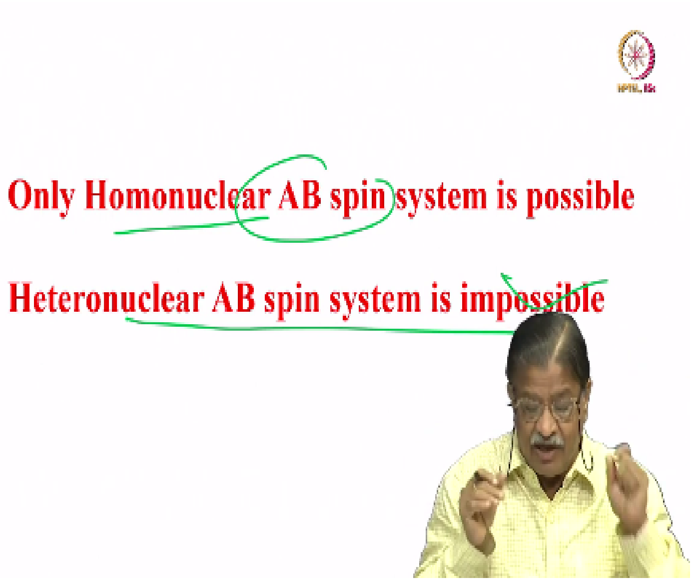

Only Homonuclear AB spin system is possible

Heteronuclear AB spin system is impossible

This is the situation for AB coupled spin system. Now, the question is when do you expect this type of strongly coupled spins? this is called strongly coupled spin system, as I told you I am represented by 2 letters which are next to each other in the alphabet Roman alphabet, because it chemical shift separation is smaller. So, when do you expect this type of strongly coupled case, you can expect only in the homonuclear case, heteronuclear AB spin system is impossible.

The reason is heteronuclear the chemical shift is megahertz away chemical shift in the heteronuclear case you consider the resonating frequency the resonating frequency if consider that is a proton and fluorine. Proton in 500 megahertz will come at let us say 500 megahertz, fluorine comes at 470 megahertz; the 30 megahertz away. Huge chemical shift separation. you can never have the very strongly coupled case, AB in the heteronuclear case , it is always possible only in the homonuclear case.

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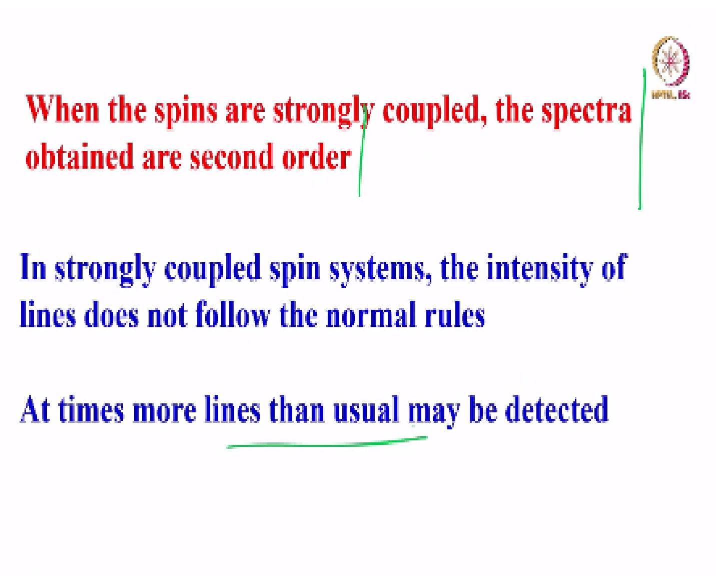

When the spins are strongly coupled, the spectra obtained are second order

In strongly coupled spin systems, the intensity of lines does not follow the normal rules

At times more lines than usual may be detected

So, we can consider that and the important condition which I told you in the earlier case, the spectra of strongly coupled spins are not amenable to analysis using first order like in the case of AX, I know AX doublet A doublet X doublet, I go to the centre of the doublet of A, get the chemical shift of A, I go to the centre the doublet of X get the chemical shift of X, I measure the separation I get J, I can measure the separation and get J very easy, straightforward analysis.

Whereas in the strongly coupled case the straight forward analysis is not possible. And another interesting thing will happen. In the strongly coupled case you get more lines than what is expected generally. Of course not in the case of 2 spin, but if you go to more than 2 spins, I will show you when required for that.

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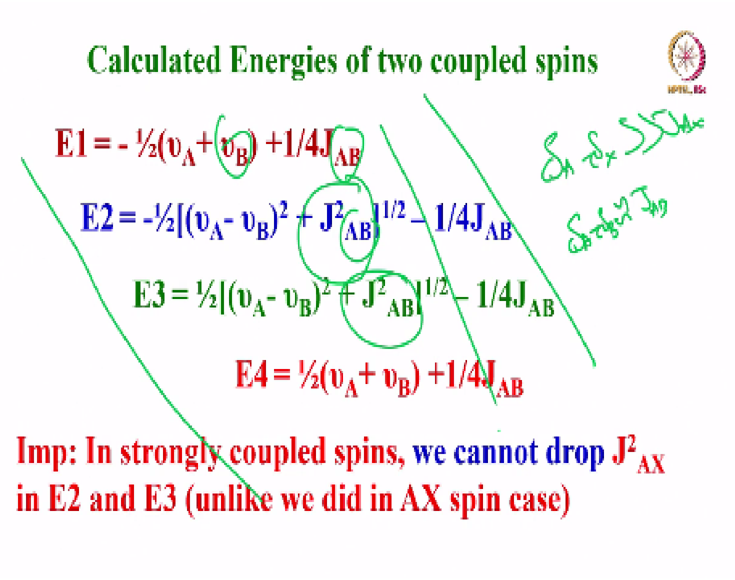

Calculated Energies of two coupled spins

$E1 = -\frac{1}{2}(\upsilon_A + \upsilon_B) + 1/4J_{AB}$

$E2 = -\frac{1}{2}[(\upsilon_A - \upsilon_B)^2 + J^2_{AB}]^{1/2} - 1/4J_{AB}$

$E3 = \frac{1}{2}[(\upsilon_A - \upsilon_B)^2 + J^2_{AB}]^{1/2} - 1/4J_{AB}$

$E4 = \frac{1}{2}(\upsilon_A + \upsilon_B) + 1/4J_{AB}$

$\delta_A - \delta_X >>> J_{AX}$

$\delta_A - \delta_B \approx J_{AB}$

Imp: In strongly coupled spins, we cannot drop J^2_{AX} in E2 and E3 (unlike we did in AX spin case)

And so analysis is not pretty straightforward. Now only thing is we already worked out E1, E2, E3 and E4 very simple, same. Only thing is AX I have written as AB here; that is all. Then what is the idea now, remember earlier when I consider J squared into J AX squared. What did I say, in that case both E2 and E3 energy states J squared AX, we can ignore I said, because delta A - delta X was very much larger than JAX. So, I said those 2 terms I can ignore, but not now, because delta A - delta B is now approximately equal to J.

So, I cannot ignore this term, I have to consider this term for working out in detail. So, that is why the strongly coupled case is difficult. So, we cannot drop this like we did in the AX case.

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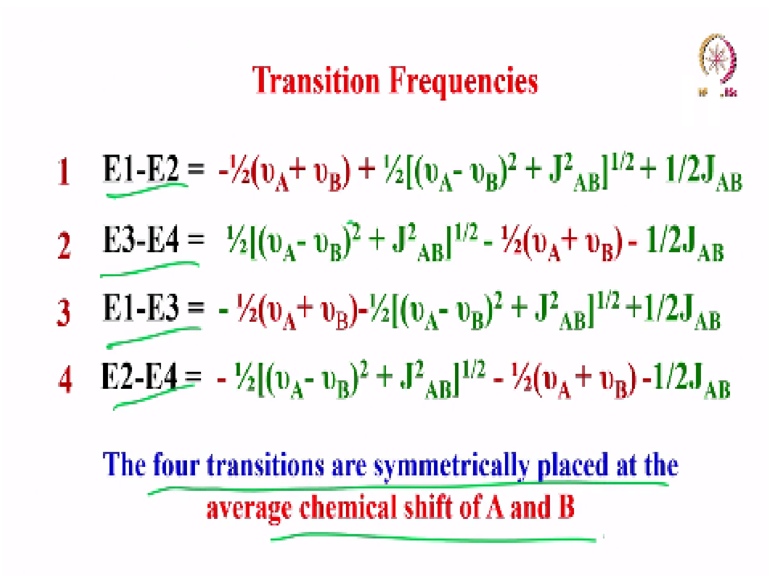

Transition Frequencies

1 E1-E2 = $-\frac{1}{2}(\nu_A + \nu_B) + \frac{1}{2}[(\nu_A - \nu_B)^2 + J^2_{AB}]^{1/2} + 1/2J_{AB}$

2 E3-E4 = $\frac{1}{2}[(\nu_A - \nu_B)^2 + J^2_{AB}]^{1/2} - \frac{1}{2}(\nu_A + \nu_B) - 1/2J_{AB}$

3 E1-E3 = $-\frac{1}{2}(\nu_A + \nu_B) - \frac{1}{2}[(\nu_A - \nu_B)^2 + J^2_{AB}]^{1/2} + 1/2J_{AB}$

4 E2-E4 = $-\frac{1}{2}[(\nu_A - \nu_B)^2 + J^2_{AB}]^{1/2} - \frac{1}{2}(\nu_A + \nu_B) - 1/2J_{AB}$

The four transitions are symmetrically placed at the average chemical shift of A and B

Now work out the transition frequencies, same, everything we know, E1 - E2, E3 – E4 all those things we worked out corresponded to 2 transitions. Same, whatever given here, I use these things and wrote down these differences here; that is all, no extra magic. Simple, I am substituting, very simple arithmetic you do that. Now, you find out there are 4 transitions here, which is symmetrically placed at the average chemical shift of A and B, you always consider the chemical shift of average A and B. You can find out, work out the difference here.

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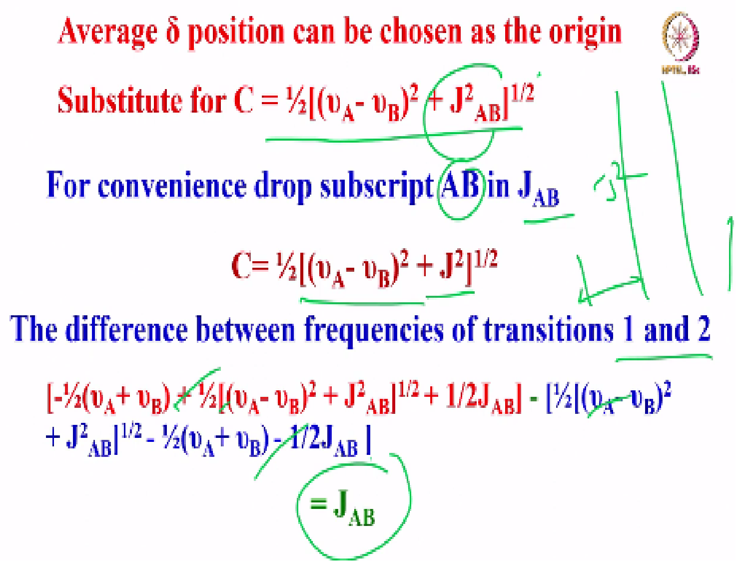

Average δ position can be chosen as the origin

Substitute for C = $\frac{1}{2}[(\nu_A - \nu_B)^2 + J^2_{AB}]^{1/2}$

For convenience drop subscript AB in J_{AB}

$C = \frac{1}{2}[(\nu_A - \nu_B)^2 + J^2]^{1/2}$

The difference between frequencies of transitions 1 and 2

$[-\frac{1}{2}(\nu_A + \nu_B) \cancel{+} \frac{1}{2}[(\nu_A - \nu_B)^2 + J^2_{AB}]^{1/2} + 1/2J_{AB}] - [\frac{1}{2}[(\cancel{\nu_A} - \nu_B)^2 + J^2_{AB}]^{1/2} - \frac{1}{2}(\nu_A + \nu_B) \cancel{-1/2J_{AB}}]$

$\boxed{= J_{AB}}$

See, in which case I am going to get like this, what I am going to do is I will simplify this equations by putting a condition C, I substituting C which is equal to half into nu A – nu B whole squared + J AB squared to the root of half. This is what I am going to substitute for C in the above equations, I consider this nu A - nu B squared + half into J AB squared to the power of half here. You know here this one, I consider this as C just for making my analysis simpler.

So, for convenience, I will drop the subscript AB, so, the instead of every time writing JAB squared, I can write J squared, very easy. So, this is for easy analysis, but you cannot drop it. Just to show that analysis becomes simpler I am writing that otherwise, every time I have to write JAB square etcetera. So, C will be like this nu A – nu B whole squared plus J squared to the power of half. Now, the difference between the frequency of the transitions 1 and 2 you can consider write down these things.

And then this turns out to be JAB. I have simply substituted these things and you can find out what is going to happen; these chemical shift terms, these things will go. The transition if I consider 1 and 2. There are four transitions here, transition 1 and 2, if I consider the chemical shift gets cancelled out and you get only JAB.

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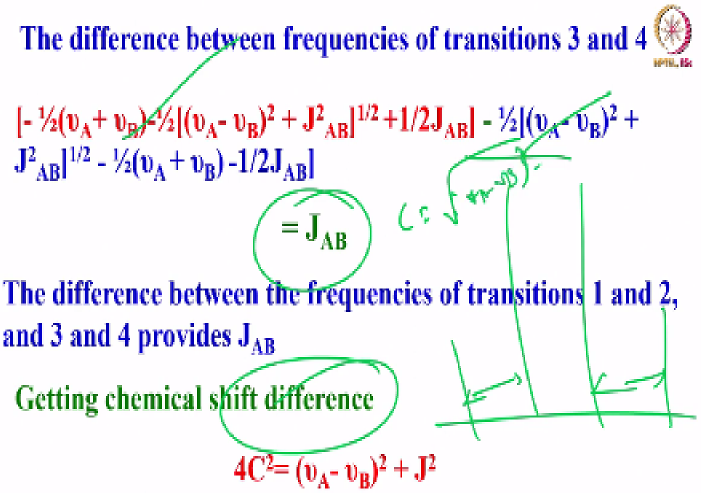

The difference between frequencies of transitions 3 and 4

$[-\frac{1}{2}(\upsilon_A+\upsilon_B)-\frac{1}{2}[(\upsilon_A-\upsilon_B)^2+J^2_{AB}]^{1/2}+1/2J_{AB}]-\frac{1}{2}[(\upsilon_A-\upsilon_B)^2+J^2_{AB}]^{1/2}-\frac{1}{2}(\upsilon_A+\upsilon_B)-1/2J_{AB}]$

$= J_{AB}$

The difference between the frequencies of transitions 1 and 2, and 3 and 4 provides J_{AB}

Getting chemical shift difference

$4C^2 = (\upsilon_A-\upsilon_B)^2 + J^2$

Similarly, difference between 3 and 4 we calculate; again chemical shift term gets cancelled out and you get only JAB. So, difference between 1 and 2; and 3 and 4 provides me J coupling. So, the separation between two outer lines of the 4 lines always gives me J coupling. Irrespective of the coupling strength ,outer lines gives me only J coupling. But how do you get the chemical shift? you do not get chemical shift A and B individually here unlike in the weakly coupled case, I know what chemical shift of A and what is the chemical shift of X.

Here you do not know, you get only difference of the chemical shift here. And that you can obtain from this equation which I wrote, C is equal to root of nu A – nu B whole squared + J square, square root of that. So, I now do the simple arithmetic, then it will turn out to be, if I take this, since there was a square, multiply this.

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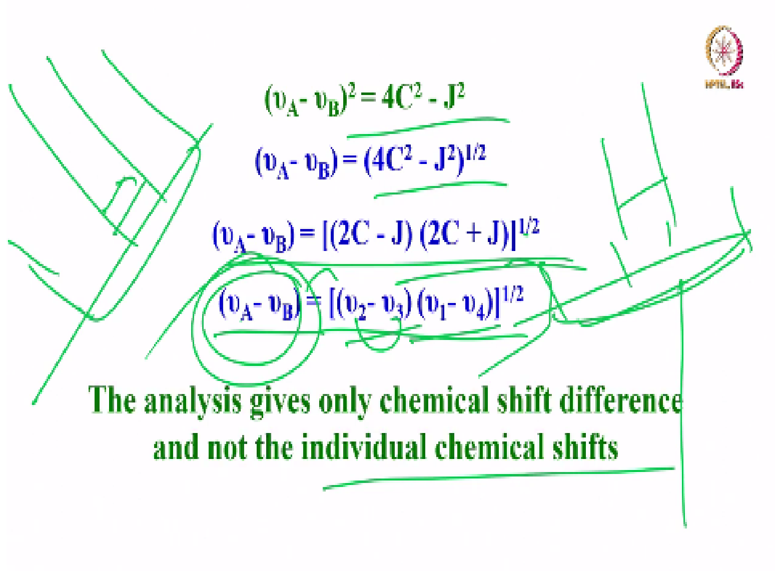

$$(\upsilon_A - \upsilon_B)^2 = 4C^2 - J^2$$

$$(\upsilon_A - \upsilon_B) = (4C^2 - J^2)^{1/2}$$

$$(\upsilon_A - \upsilon_B) = [(2C - J)\,(2C + J)]^{1/2}$$

$$(\upsilon_A - \upsilon_B) = [(\upsilon_2 - \upsilon_3)\,(\upsilon_1 - \upsilon_4)]^{1/2}$$

The analysis gives only chemical shift difference and not the individual chemical shifts

And do the simple arithmetic, nu A – nu B whole squared, I will solve this equation rearrange them. And then it turns out up nu A – nu B equal to this one. And which is nothing but nu 2 - nu 3 into nu 1 - nu 4 to the power of half. So, analysis of this will give me only chemical shift difference and not the individual chemical shifts, you understand? What I did is, you go back to this equation, this is simple equation, you rearrange them that is all I have done, nothing as simple arithmetic.

And you will find out nu A – nu B = nu 2 – nu 3 into nu 1 – nu 4 to the power of half, nu 2 - nu 3 the chemical shift difference between the 2 central peaks, and nu 1 - nu 4 the chemical shift difference between outer peaks. So, this frequency difference and this frequency difference you take, multiply these 2 and take the square root of that you are going to get chemical shift difference. So, in AB coupled case, very easy, take the difference of this and this and this and this, this difference and this difference multiply and take a square root to get delta AB. So, analysis gives you only difference in the chemical shift.

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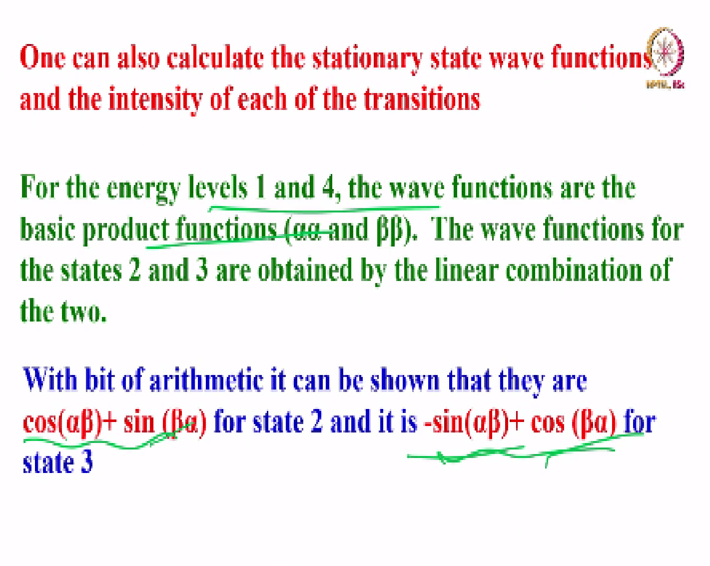

One can also calculate the stationary state wave functions and the intensity of each of the transitions

For the energy levels 1 and 4, the wave functions are the basic product functions (αα and ββ). The wave functions for the states 2 and 3 are obtained by the linear combination of the two.

With bit of arithmetic it can be shown that they are cos(αβ)+ sin (βα) for state 2 and it is -sin(αβ)+ cos (βα) for state 3

Of course, we can also calculate the stationary state wave functions, and intensities of peaks, but I will not worry about it. So, I will say that for the energy levels 1 and 4 the wave functions are the product functions, only for 2 and 3, we have to bring in the mixture of the energy states in one case sin alpha beta + sin beta alpha, I am sorry cos alpha beta + sine beta alpha. In the other case - sin alpha beta + cos beta alpha, for the state 3. And these are the stationary state wave functions which are different compared to weakly coupled case. We can work it out, let us not worry because we are interested only in knowing how we get the spectrum and energy levels.

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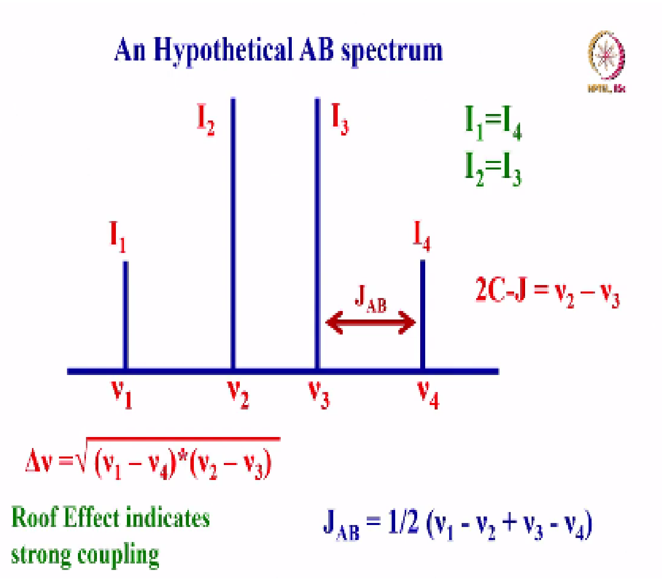

An Hypothetical AB spectrum

$I_1 = I_4$
$I_2 = I_3$

$2C - J = v_2 - v_3$

$\Delta v = \sqrt{(v_1 - v_4)*(v_2 - v_3)}$

Roof Effect indicates strong coupling

$J_{AB} = 1/2\ (v_1 - v_2 + v_3 - v_4)$

And this is the type of spectrum.

The the time is up. We will discuss about the spectrum later. Right now I am going to stop here. What I wanted to tell you is for the AB coupled case, in the previous we worked out AX, and in the AB coupled case, we wrote down the Hamiltonian; well worked out and showed that off-diagonal element you have to consider because unlike in the AX case, we cannot ignore JAB squared we cannot ignore, we cannot neglect that because chemical shift separation is comparable to J.

And then the energy levels we wrote down explicitly for all the 4 energy states and took the difference between the different energy states that correspond to different transitions. And we found outer 2 lines of the 4 line pattern in the AB case we use it to determine J coupling. For the chemical shift take the frequency separation of the outer 2 lines and the frequency separation between the 2 central lines, take multiply them, and take the square root of that you are going to get chemical shift difference. I said in the strongly coupled case, you cannot find out chemical shift individually A and B; you get only chemical shift difference. And we did not work out the stationary wave functions, I said stationary wave function for the energy state 2 and 3 are very easy for energy state 2 is cos alpha beta + sine beta alpha in the other case, cos beta alpha - sin alpha beta. This what I discussed we will discuss about the intensity pattern everything and then go to A2 in the next class. So thank you very much, I will stop here.