Advanced NMR Techniques in Solution and Solid – State

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Module-16
Quantum Mechanical Analysis of AX Spectra
Lecture - 16

Welcome back all of you. In the last class, I introduced you to the spin system nomenclature, I discuss what is a strongly coupled spin system and what is a weakly coupled spin system and how are they represented by using Roman alphabets. I said if they are weakly coupled spins, we represent let us say for 2 spin half nuclei which are coupled between themselves, by 2 letters which are far away in the alphabet. Whereas for the strongly coupled spins we use the letters which are next to each other or close to each other like AB, ABC etc. And for the chemically equivalent spins when they are coupled among themselves, I said we can use prime notation, if we have magnetically equivalent spins, we can use subscripts like A2X2, A2M2X2 like that, or AA prime or XX prime if there are chemical equivalent.

So, these things I just briefly touched upon. And I showed you if I have 2 weakly coupled spin system, there are 4 possible energy states, corresponding to 4 energy states like alphaalpha, alphabeta, betaalpha and betabeta. And I showed there are 4 possible transitions using the selection rule for single quantum transitions, where the change in the magnetic quantum number between any 2 energy levels is either +1 or -1.

And I showed diagrammatically for weakly coupled AX spin system, there are 4 possible transitions, theoeretically. Pictorially we understand everything, but we also wanted to understand quantum mechanically, how to generate these energy levels, how to understand, how the spectrum comes when this spin systems are coupled? whether it is weakly coupled or strongly coupled?

I also said for quantum mechanical treatment, 2 spins we can do comfortably, if you go to 3 spins can be done with some difficulty, but beyond that, it is going to be a very difficult task. So, I wanted to show you, I started how we can use quantum mechanical treatment to get the energy level diagram and also the transition frequencies for 2 coupled spin system. I took an

example of AX spin which are weakly coupled. And I said, first of all for the quantum mechanical treatment, what you have to do?

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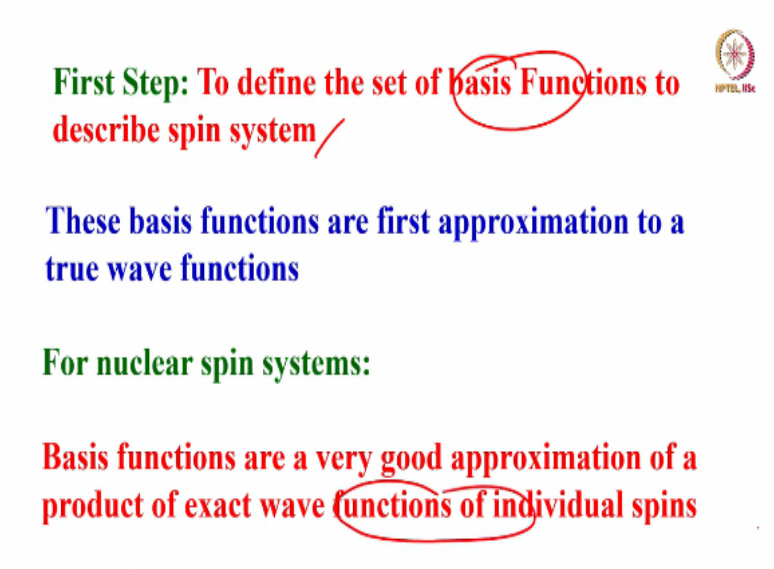

The first step is to define the set of basis functions to describe the spin system. And I said, the basis functions, the first approximation are the true wave functions. Especially, when you are dealing with the nuclear spin systems, the product of basis function, is the exact wave functions of individual spins. That is what I said.

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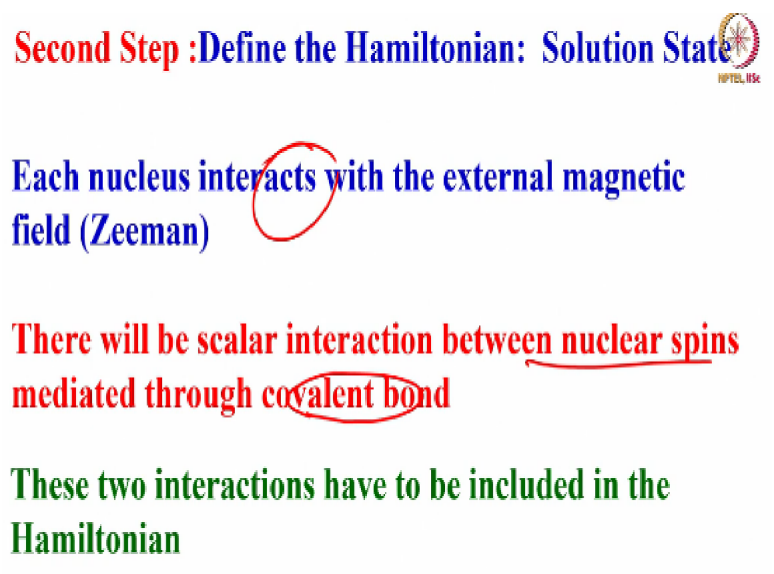

So, what are the wave functions I explained to you, for a spin half nuclei there are 2 possible wave functions alpha and beta corresponding to orientations. Of course, what happens if you have 2 spins, we will work out and I will tell you, the first step is to find out the wave function, to define the wave function. Second step, define the Hamiltonian and we will be

dealing with the solution state NMR, not solid-state NMR because the interactions will be much more, and more interactions will come into picture and we are not going to touch upon at the moment. So, we will deal with the analysis of the spectrum of 2 weakly coupled spin system in the solution state. So, we have to define the Hamiltonian for such a system that is the next step. And each nuclei, each nuclear spin interacts with the external magnetic field, which is what we call as Zeeman interaction.

In addition to that, between the 2 spins which are interacting, there is a scalar coupling which is mediated through covalent bond, this is what we discussed about the scalar coupling. These are the interactions of the 2 nuclear spins mediated through covalent bond through electrons. There is a polarization transfer between 1 spin to other spin through covalent bond. So, these 2 interactions have to be included in the Hamiltonian. This is the second step to define the Hamiltonian.

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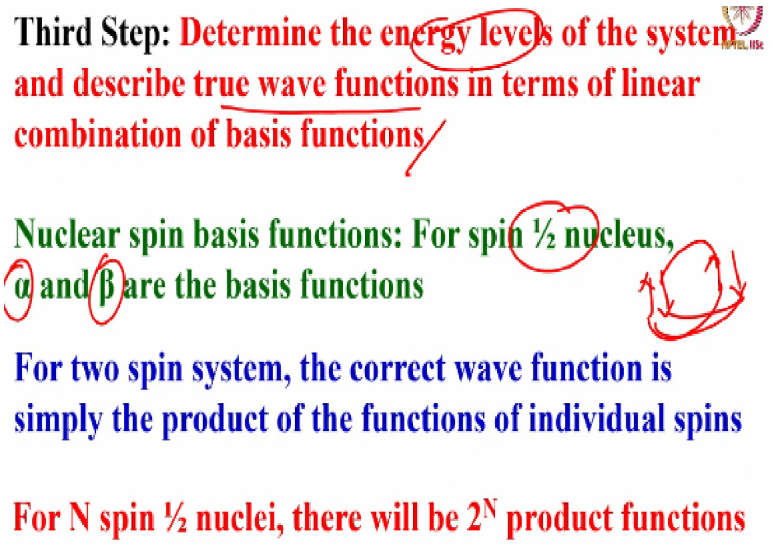

Next in the third step, we have to determine the energy level diagrams, energy levels of the system and describe true wave functions in terms of linear combination of basis functions. What does it mean? I said the nuclear spin basis functions for spin half nucleus, I already told you that the alpha and beta are the basis functions. Now, for 2 spin system the correct wave functions are simply the product functions of individual spins; what are the product functions? You can think of all possibilities of combinations of these 2 wave functions for both the spins. If one is in alpha state, other is in beta state. For the other spin also it is alpha and beta, then you can take out the combination of alphaalpha, alphabeta, betaalpha and betabeta; all 4 possible combinations you can think of; These product functions are now the

correct wave functions for the nuclear spin systems. And if I have N interacting spins, there will be 2 to the power of N product functions. Remember there are 2 to the power N product functions, when you have 2 spins, 2 square; there are 4 product functions. If you go to 2 cube, it will be 8. Reasonably big, if you go to 4 spins and above, it will become huge. That is the reason I said the quantum mechanical treatment to analyze beyond 2 or 3 interacting spins is fairly difficult.

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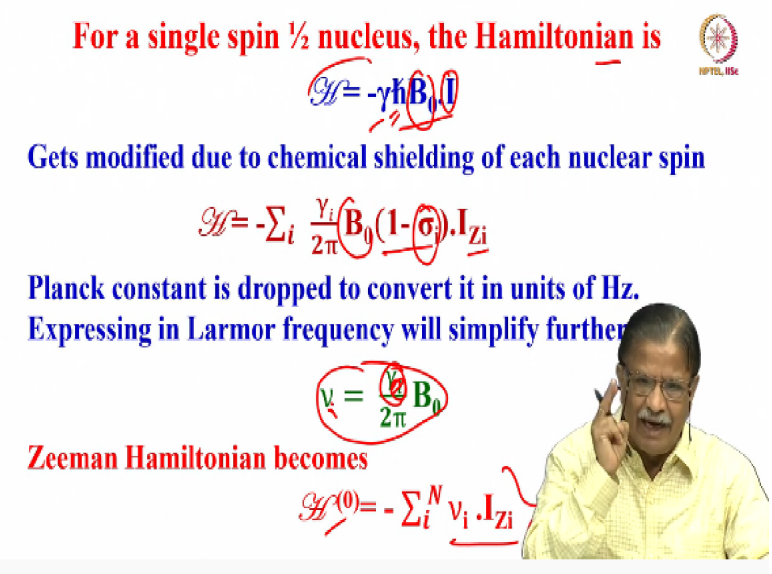

So, we are restricting to spin half nuclei, this Hamiltonian is given as a H = - gamma B naught into I. This is the general Hamiltonian, we know that B naught is the magnetic field, I is the spin of the nuclei and gamma is gyromagnetic ratio; and H cross in the Planck's constant. Now, what will happen to the Hamiltonian? This gets modified; first of all due to chemical shielding, I told you we discussed chemical shielding do the electronic environment surrounding the nucleus; there is shielding effect. So, the nuclear spin do not see the correct external magnetic field; this gets modified because of the shielding of electrons surrounding it. So, as a consequence we include this as the Hamiltonian first. That Hamiltonian is B naught into 1 – sigma i into I Zi. That is what is written. B naught, of course the same thing is modified here, expressed in terms of units of Hertz, in terms of Larmor frequency as it is easy for us to work with this system in a simpler way.

That is why it is taken in the frequency units. So, that we can express in Larmor frequency. And sigma i is the screening constant that is also we discussed earlier. So, in a situation like this, when we express in Larmor frequency, we already worked out what is the basis, what is the resonating frequency? The resonating frequency is given us nu into gamma into B naught

over 2 pi. Here I have put I, because now I have to consider 2 nuclear spins. Each of them may have a different chemical environment. So, the resonating frequency correspond to each of them will be different. And now gamma i, in fact it should have been nu i, gamma should be same because I am considering homonuclear case, it is proton. So, that is why instead of gamma i, I can put nu i = gamma into B naught over 2 pi, i is the resonating frequency it varies for both the nuclei, which I am considering because of the chemical environment.

So, the Zeeman Hamiltonian, I can write like this. Zeeman Hamiltonian H naught into sigma summation i is 1 to N nu i into I_{Zi}. N is the number of interacting spins, in our case it is 2. Presently we are considering 2 interacting spins.

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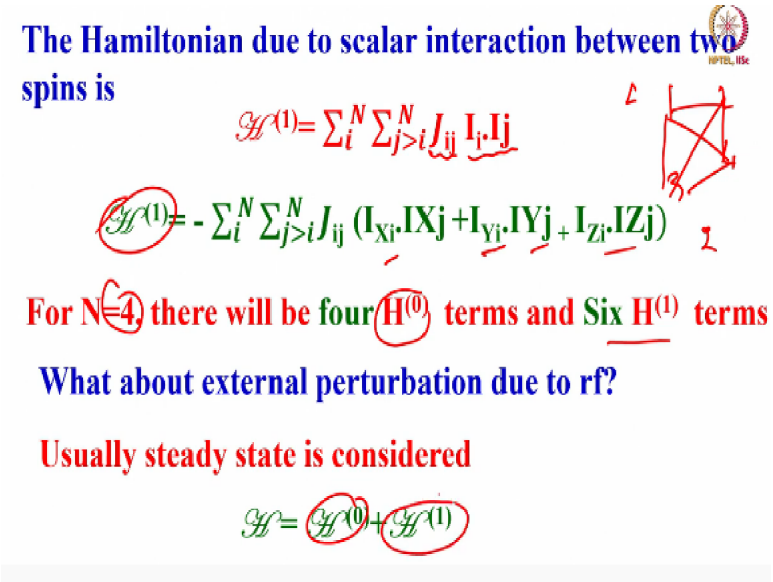

The Hamiltonian due to scalar interaction we will consider now. Again we have this interaction; coupling constant Jij and Ii and Ij are the interaction between 2 nuclear spins. Now, this big vector, I said we can expand it into 3 components IXi IXj, IYi IYj, I ZiIZj. You can write it clearly. Now, for N = 4, how many terms you can think of? Let us think of 4 nuclear spins are interacting, for N = 4, we have 4 H0, because each nuclei will have different Zeeman interaction terms. Now, interaction among themselves there could be many, for example if a consider for nucleai 1, 2, 3 and 4; 1 can interact with 4, 1 can interact with 3 and 4, similarly 2 can interact with 3, 2 can interact with 4, 3 also can interact with 4. So, essentially we have 6 H1 Hamiltonian terms. So, if I consider 4 interacting spins, I have 4 H0 terms and 6 H1 terms.

Right now, we are dealing with 2 spins, we have 2 H0 terms and only 1 H1 term. So now, you may ask me a question we are applying the radio frequency that also interacts with the nuclear spin it will perturb the system. In addition to Zeeman interaction, we discussed as an external interaction, rf also has an interaction. But at the moment we will not consider that, because we are dealing with the steady state of the spin system. So, since we are dealing with the steady state, we do not have to worry, and we consider only H0 and H1; without the interaction with the rf. This is a total Hamiltonian for the 2-coupled spin system.

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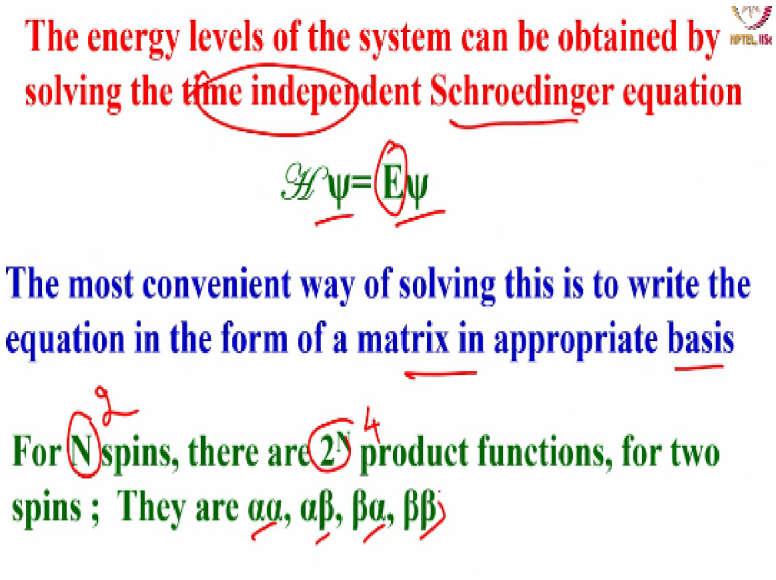

So, once you built this Hamiltonian, what is your next step? You have to solve the time independent Schrodinger equation which is given Hpsi = Epsi. Psi, it is a wave function, you know that. So now, you know the Hamiltonian and we have to calculate the energy levels; that is easy, we have to now work it out. And most convenient way of solving this I told you last time itself. You have to express this in the form of a matrix, this equation can be expressed in terms of a matrix in the appropriate basis set. Now, for N spins especially when I am considering 2 interacting spins, we have 2 to the power of N that is 4 product functions for 2 spins, they are alphaalpha, alphabeta, betaalpha and betabeta. These are the 4 product functions.

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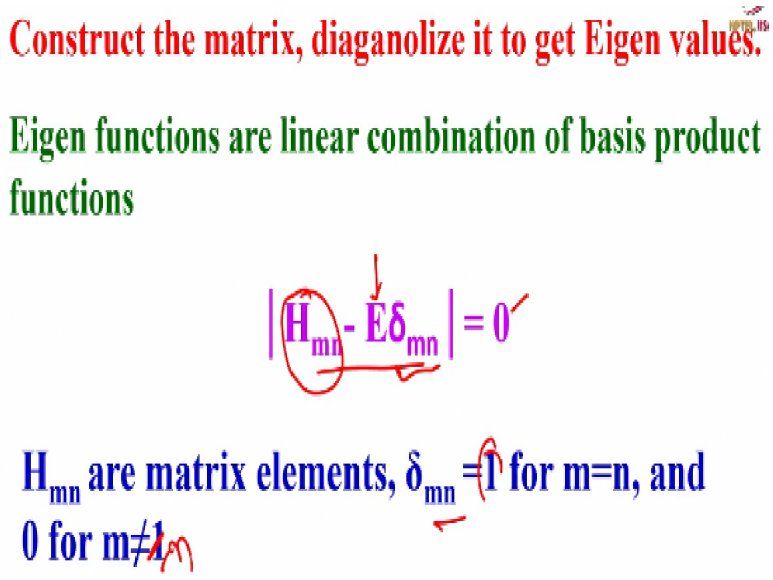

So now, we can construct the matrix, diagonalize it to get the Eigen values and get the Eigen functions which are linear combinations of the basis product function, these things we can do. So, we have to write first the equation for this; we have to now solve this equation and what are these? These are the matrix elements which you have to work it out, that is what we are going to calculate to get the energy level and delta mn is a Kroneker delta, you know that in quantum mechanics basics. When m = n, this is equal to 1, when m is not equal to n and this is equal to 0. This not 1; m is not equal to n, remember there was a typographical error here, it is when m is not equal to n and this is equal to 0.

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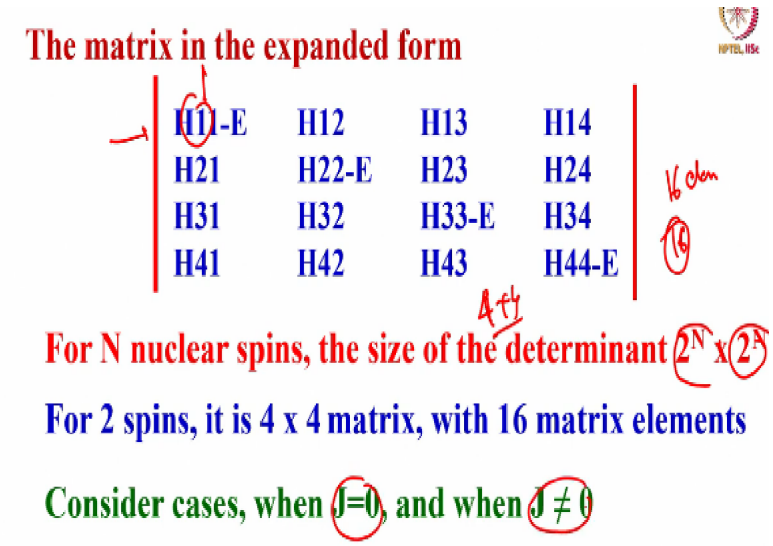

So, the matrix can be written in the expanded form like this, that is H11, I have considered this, 11 is the element, if you take 1 row and 1 column like this and you can write down there is now 4 by 4, we have 4 by 4 matrix; that is 16 elements, we have to calculate all the 16

elements if there are available. If they are existing, we should calculate that. So, for N nuclear spin system the size of the determinant 2 to the power of n, we have got 4 by 4 in the present case. So, 16 matrix elements we are to calculate. That is fine. Now, we said 2 interactive spins. Now there are 2 possibilities you can think of it could be J could be 0, and J could be non 0. There are 2 possibilities. We will consider that now.

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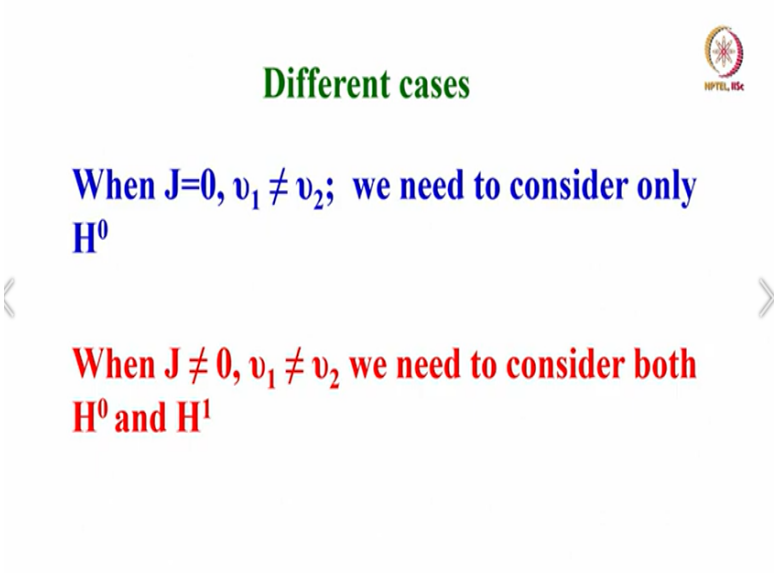

Consider situation J = 0. Since it is AX spin system chemical shifts are different, then nu 1 is not equal to nu 2; that is one situation. So, we need to consider only H0, because H1 we can ignore, there is no coupling. Coupling is 0 and J = 0, nu 1 is not equal to nu 2; then we have to consider both H0 and H1. There are 2 possibilities. Now we will work out the energy levels for both the situations. First, we consider J = 0.

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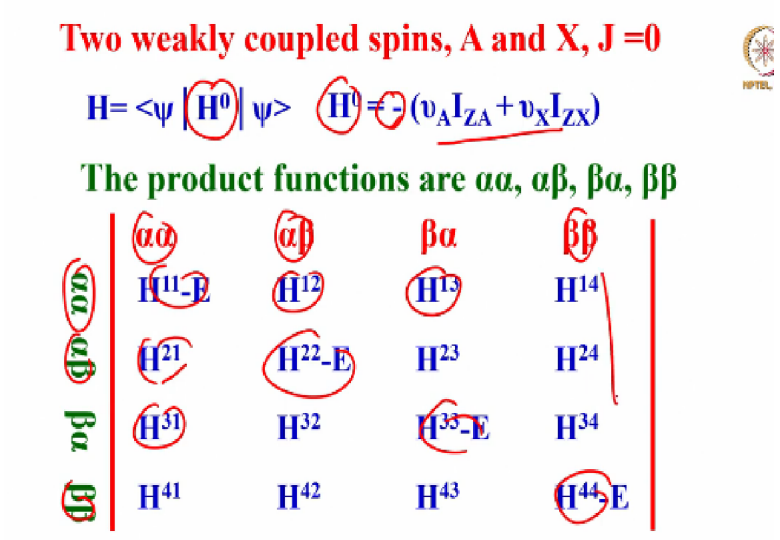

And then see what is the energy level diagram. Now I consider the 2 coupled systems. As I told you, I deal with only H0, I will not consider H1 at all. I am not going to calculate, take H1 as the Hamiltonian, especially for working out energy levels. So, the basic Hamiltonian turns out to be H0, which is only these 2 terms. Because nu A into I ZA + nu X into I ZX. Depending upon how we are going to represent we have a –nu IZA for the resonating condition.

I did not put minus there which I will explain. But in some books you can see it is written as nu is equal to resonating frequency minus gamma into B naught over 2 pi depending upon how you are going to represent it. So, I have taken this as minus, do not have to worry finally, the product functions are; alpha alpha, alpha beta, beta alpha and beta beta. So, now I can construct the Hamiltonian.

So, now for alpha alpha is going to be diagonal element, alpha beta and alpha beta they are going to be diagonal elements. Similarly, beta beta; beta beta here is going to be the diagonal. So, there are 4 diagonal elements and remaining are off-diagonal elements. Remember, matrix is symmetric. So, if I know H12, I know H21. Because the interactions in NMR are mutual, if 1 is interact with 2, 2 also interacts with 1. So, in this case, the matrix is symmetric. So, we have to consider the 4 diagonal elements and 6 remaining off-diagonal elements. How to calculate them? Let us do that.

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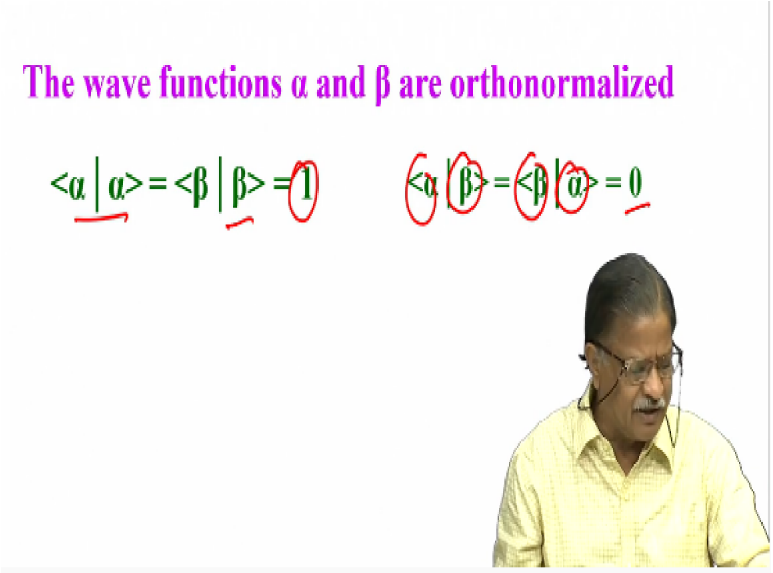

The wave functions alpha and beta, one important thing you should know, they are ortho normalized. What do you mean by orthonormalized? When you say ortho normalized, alpha

operating on alpha or beta operating on beta is always equal to 1. They are orthonormal basis set, if I take alpha operating on beta or beta operating on alpha is equal to 0. That is why these 2 wave functions alpha and beta, I say they are orthonormalized. This you would have understood in the matrix and vector analysis; you would know those things.

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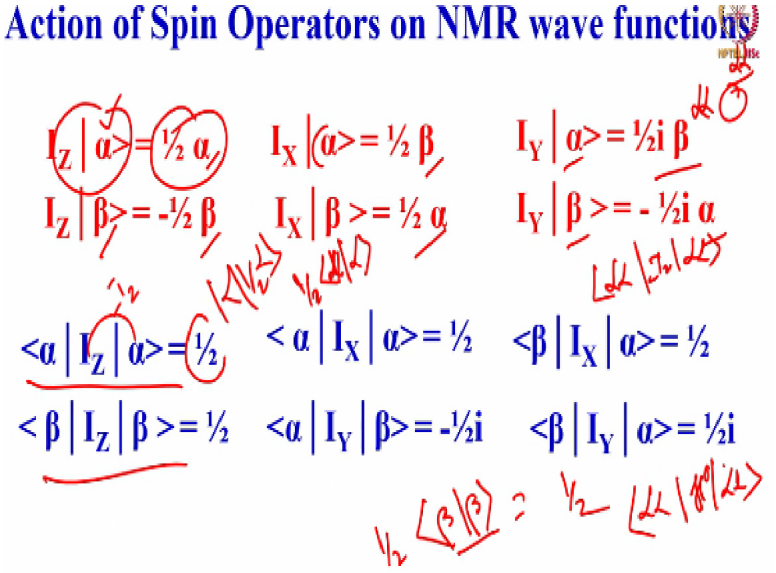

Now, let us find out the action of spin operators and NMR wave functions, this is important thing which you must remember because we can work out, we can use each and every term here. IZ operating an alpha, it becomes a half alpha, very basic quantum mechanics we can work it out, But I am not going into that because it is an enormous time consuming if I work out everything.

Simply remember these things, if IZ operates on alpha, you are going to get half alpha. Similarly, IX operating an alpha gives half beta, IY operating an alpha gives half beta, same thing if IZ operates on beta, you get minus half beta, IX operating on beta gives half alpha, IY operating on beta gives minus half Ialpha. These are the things which I keep on using it very often. Now, similarly, we can represent like this, if alpha IZ operates on alpha, then it turns out to be 1. The reason is I can take IZ outside. If I take IZ out then IZ operating an alpha is going to be half alpha, alpha half alpha. So, half I can take it out, it is going to be half alpha, alpha. Half alpha operating an alpha as I told you they are orthonormalized, it is going to be 1. Similarly, if I take beta for example, beta operating on this is 1, so I can say IZ operating this beta is going to half. So, I am going to take half outside beta and then beta I write like this, which is going to be 1.

So, it is going to be half; this value is half. Like that, now, for each of the diagonal elements we can work out, now I took only for single wave function. What happens if I take the product? It could be alpha alpha in which IZ operating an alpha alpha or alpha alpha operating on the let us H0 or H1 etcetera, operating, then what will happen? Like that all 16 elements we have to consider.

The 16 elements I told you in the matrix alpha alpha I consider and I am operating on this alpha alpha and I calculate the diagonal element. Similarly, all off-diagonal elements and diagonal elements I can calculate.

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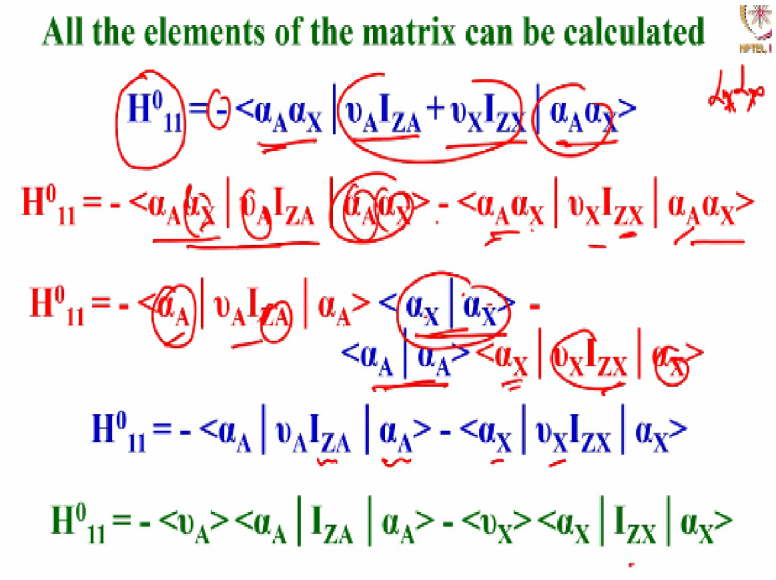

So, very easy. Now, we start calculating the matrix elements. So, what the first thing is, first we calculate the matrix element H11 0. H11 0, now, I write in the explicit form alpha A, alpha X, I wrote alpha alpha as alpha A and alpha X. Because now I am able to distinguish 2 spins A and X here, for calculation purpose. Now, nu A and IZA, is the Zeeman interaction term for A, nu X I ZX is the Zeeman interaction term for X spin.

And I am considering the diagonal elements. So, alpha A, alpha X operating on this H 0 term with alpha A and alpha X here. So, now, we can work it out. If you see, simple terms what I should do is there was a negative sign here, I expanded it completely, if I take individually both the terms I can write alpha A, alpha X, nu A IZA and this one minus, I will say alpha A alpha X nu X IZX and alpha A, alpha X.

I did not do anything, but simply separated out 2 items, the 2 terms are there. I just separated out these interactions. Now, we will apply what just now have found out what are the operating rules when IZ operating an alpha, what happens to the action of the different terms I found out; what are those things when IZ operating an alpha, IZ operating a beta everything, simply remember that and we use those terms to evaluate this.

Now again it is further since you know nu A is operating and dealing with only alpha A. So, alpha X I can take it out because I am not dealing with the X spin here. So, I can write like this; alpha A operating on nuA IZA with alpha A and then alpha X is taken out here, it will become alpha X into alpha X. Similarly, this term I write as minus half. Now, with these X is operating, so, I can take alpha A, alpha A.

So, alpha A operating in alpha A and alpha X becomes nuX IZX into alpha X. I resolved the terms depending upon which spin is operating on which nuclei. So, in this case, I mean which wave function is operating on which nuclei. So, now in this case alpha is operating on A. So, I took A here and the X was not operating as it is separated out. In this case X wave function is operating in X. I took it like this.

Now, I can simply write like this, because you know alpha X, alpha X, I told you orthonormalized, I said it is 1. So, this is going to be 1 and again here also alpha A, alpha X this also is going to be 1, this is 1. So, both are 1. So, this term boils down to this thing simple term, now, minus of alpha A nuA IZA alpha A - alphaX nuX IZX alpha X, so, it became very simple; 2 terms we got.

Now, further we have not completed, we will go further, this can be further resolved, what I am going to do is I will take nuA outside; that is not going to disturb the system only we are worried about IZA operating in alpha A. So, I take out nuA. So, alpha IZA operating an alpha A. Similarly minus I take out nuX here, nuX when I take it out alphaX operating an IZX and alpha X here.

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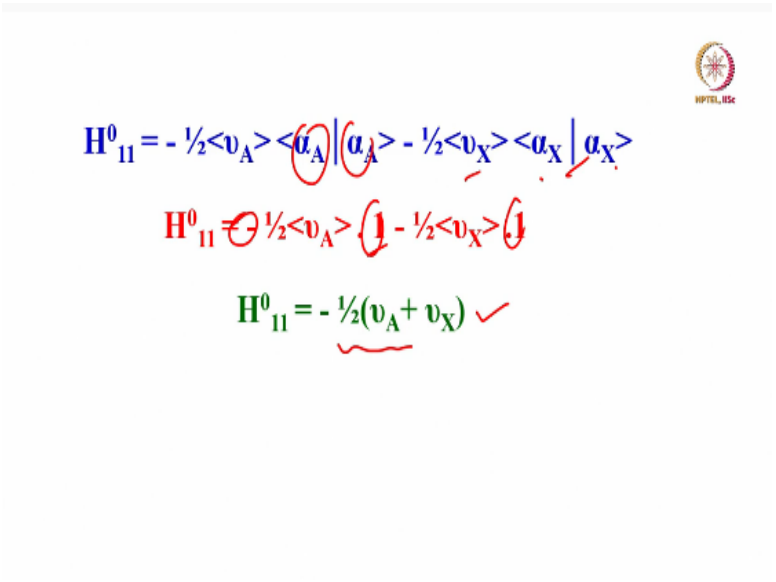

So, the terms can be further simplified. Now, you know what did, I explained earlier; that is why I asked I said we should remember when IZ is operating an alpha, it is going to give half alpha. So, I take this half alpha, the alpha A is there, you go back here and see carefully here alpha A is there, this will become half alpha A. So, you can write it as alpha A into half alpha A; half I will take it out; this is alpha A, alpha A. Then what will happen? Alpha A, alpha A is orthonormalized set, this will become 1. So, now, you are going to get half into nuA and this will become 1. Similarly, here I will take out nuX, then alphaX, alphaX orthonormalized wave functions. Now, what will happen? This will become 1. So, it will become half; in the previous if you see here, IZ is operating on alpha X, it could be again half. So, what we are going to get is H11, only 2 terms, this will become 1, this will become 1.

Here alpha A, alpha A, alpha X, alpha X. The term finally points down to only 2 things, H 11 0 will turn out to be, I took the minus as a common factor outside, minus of half A half of nu A + nu X. This is the first matrix element we worked out. Now, remember you have to work out 16 such elements. Well, fortunately, we do not need to worry. Many of them will be 0. And then in this case, only we need to work out only 4 diagonal elements; most of the all the off-diagonal elements are 0.

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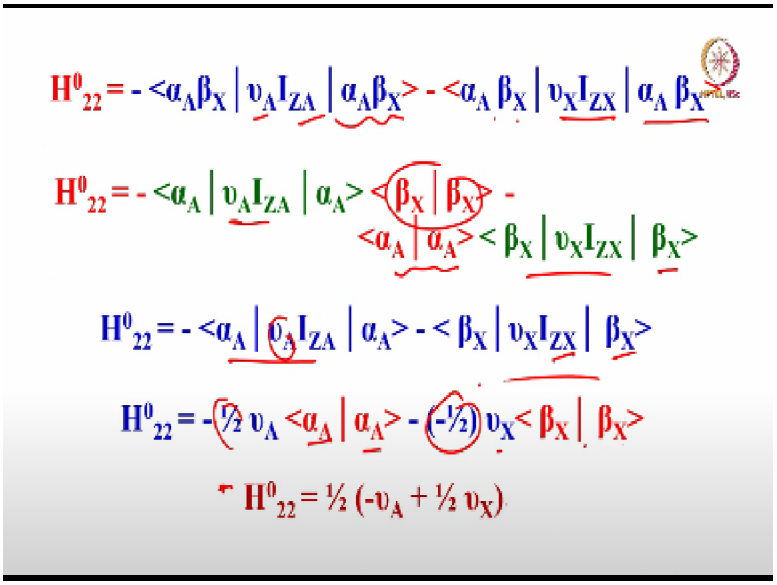

So, now work out H22. H22, in this case, remember alpha beta operating an alpha beta here again. Now, nuA IZA again I separate out the 2 terms alphaA betaX again, diagonal term alpha A beta X, nuX IZX alphaA betaX. Now, I again separate out these 2 terms, what will happen? since I am dealing with only spin A here. I am going to write alphaA nuA IZA alpha A and beta X operating on beta X. This, you know is 1. Similarly I do this similar operation here, alpha A I will take it out, this is becoming 1, then I will take beta X operating on nuX IZX on beta X. So, this will become 1, then again this is a simplified form I write this equation here and this equation here; and now we have only 2 terms; like what we did for H 11 0? same thing you can do. Now, what you can do? Take out nuA outside now IZ operating on alpha gives it half alpha, so half I took out. So, it will become alpha A, alpha A. Similarly, IZ operating on beta becomes half beta. So, minus half beta I will take out. This will become minus half nuX; this will be 1. So, what is going to happen? This is going to be minus H22. This is minus into minus plus. So, I can write it like minus of nu A plus half of nu X. Or in other words, you can write it as half of nu X minus, take out half, it is going to be in nu X - nu A here.

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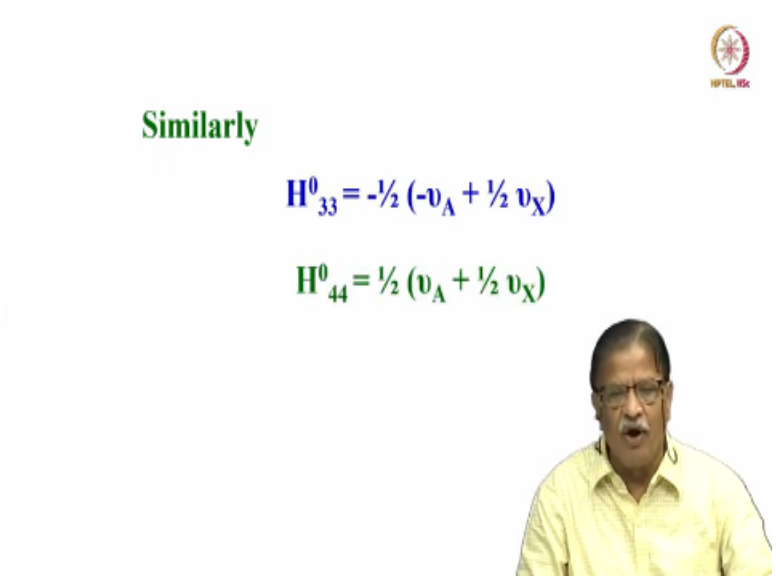

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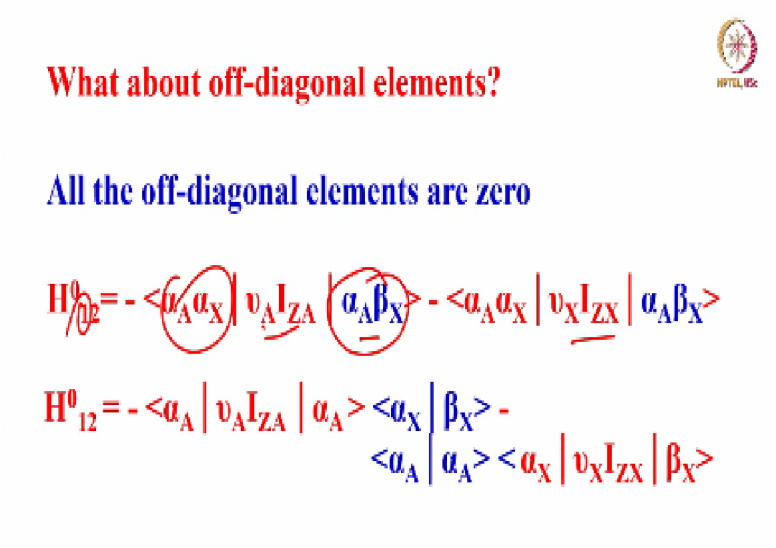

So, you can work out similarly, H33 0 and H44 0. All are diagonal elements, all the 4 elements you can work out. Now the question is what about the off-diagonal elements? Luckily, all the off-diagonal elements are 0 here. I will show you by working out only one of them. Remaining I do not need to work out. If you want, you can work it out yourself, make a simple exercise, you will see that alpha alpha and here I take alpha beta, they are off-diagonal elements. I am now working out for alpha H12 0. H1 is alpha alpha here. I mean 1 is alpha alpha, 2 is alpha beta. So now, I am going to write down again, simply I have already expanded the term, nuA IZA, nuX IZX resolved into different components here. Alpha A nuA IZA alpha, alpha beta and again alpha A I take it out of nuX IZX beta X.

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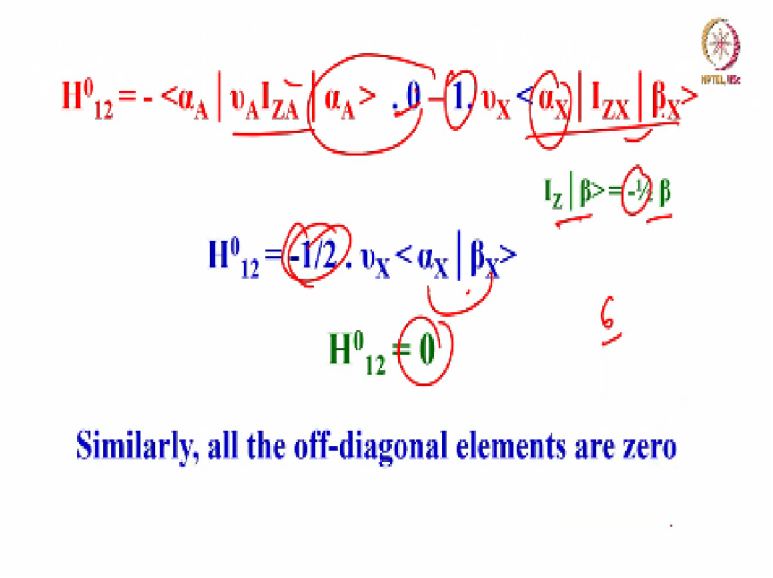

But you know that this is remaining same, but here what is happening? alpha operating on beta, I told you they are orthonormalized, so it is 0. Similarly, here alpha, so this is 0 and this is going to be 1 here. So, this is going to be like this and IZ alpha operating on this becomes minus half of beta. Here beta operating IZ beta will become minus half of beta. So, you are going to write it like that, alpha X is there. Now, beta again come here, alpha X beta X, again they are 0. So, this will be 0, this term is shown to 0, multiplied by 0. Now, if you expand this term in detail, you take IZ beta, which is equal to minus half of beta; half into nuX; this is very nicely written half into nu X into alpha X beta X, because this half is coming here I have taken it out. But nevertheless, positive or negative does not matter, because anyway this term is 0.

Alpha operating on beta here is becoming 0. So, H 12 is 0. Off-diagonal element one of the terms I showed to be 0. You work out for remaining terms, no problem, you will find all the 6 off-diagonal elements are 0 here. So, what do you get? You are going to get only 4 diagonal elements with for this matrix.

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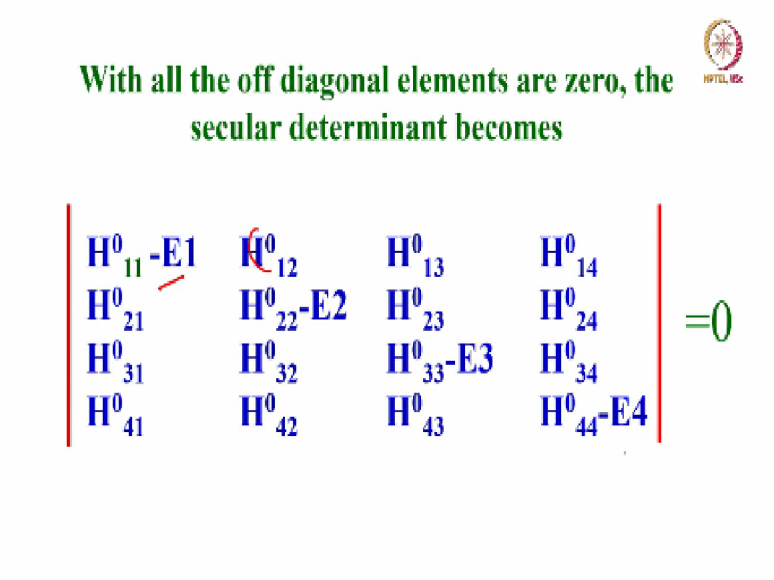

This is a matrix with secular determinant now; this is what we started with. And we say H11 0 is E1, now all other terms are 0. So, we have only secular determinant like this, since all the off-diagonal elements are 0, you have only 4 equations and 4 energy levels.

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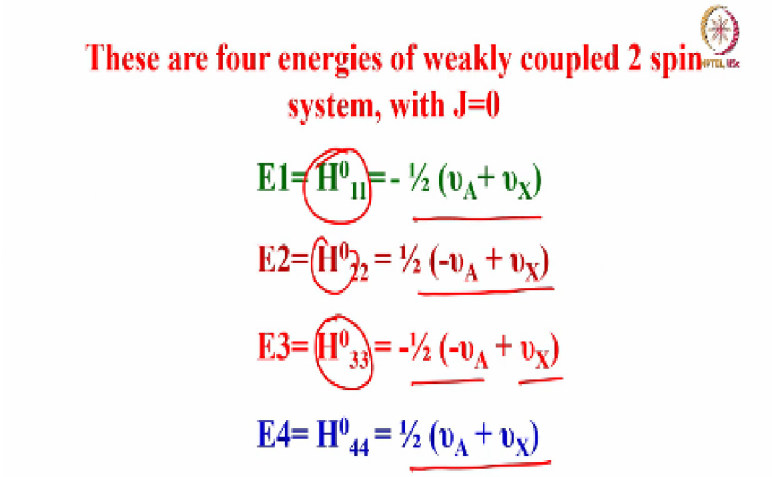

Very easily from this marix you can work out. Now, E1 is equal to this of course, simple matrix algebra, I do not have to tell you, E1 is equal to now, you can write it as this is the first term diagonal term, then E1 becomes equal to H11, you go back here, you do not get confused here, H11 – E1. So, E1 = H11 0. So, H11 0 which is nothing but, we already worked out minus half nu A + nu X.

Now, E 2 we already worked out H22 0 that minus half into minus nuA + nu X. Similarly, E 3 is a diagonal element, this 1 and this is a minus half nu A + nu X and E 4 is half of nu A +

nu X. So, we got all the 4 diagonal elements. With that we get all the Eigen values. Once you get the Eigen values, what next?

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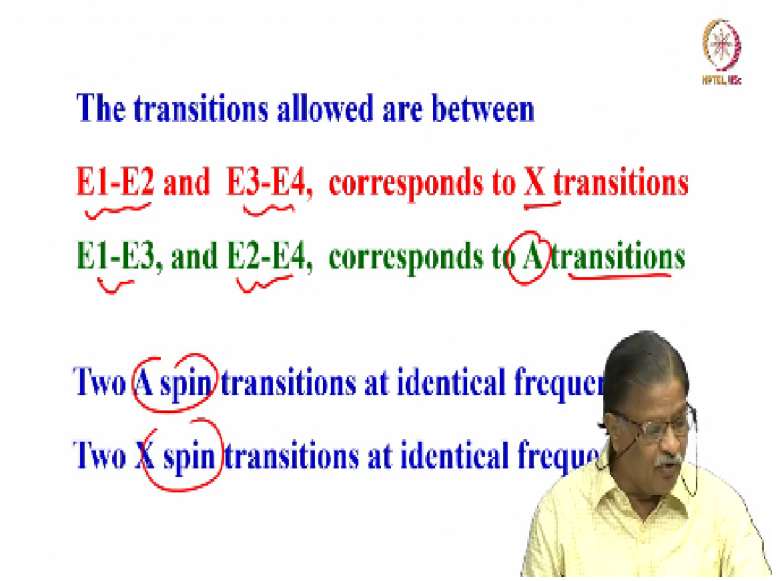

Now, we can find out the frequency of the transitions. We use the selection rule, this we knew that this transition rule if you look at it, changing the quantum number, magnetic quantum number should be either +1 or –1. Using that I can tell you E1 – E2 and E3 - E4 corresponds to X transitions. From the energy level diagram which I wrote in the last class you can see, that correspond to the X transition. Similarly, E1- E3 and E2 – E4 corresponding to A transitions.

We will work out what is E1 – E2? That essentially you have 2 A spin transition and 2 X spin transitions. You go back and calculate here and you will see that and find out the E1 – E2 difference E3 – E4, E1 - E3 and E2 – E4 simple equation, linear equations are there. And you will find out 4 frequencies, 2 of them overlap. For example, in this case I tell you 2 A spin transitions are at identical frequency. Similar to X spin transitions are at identical frequency.

That means, there are 4 transitions, but 2 of each transition, for each spin are overlapped. A a consequence, for A spin, we get a single frequency a single peak, for X spin we get a single frequency.

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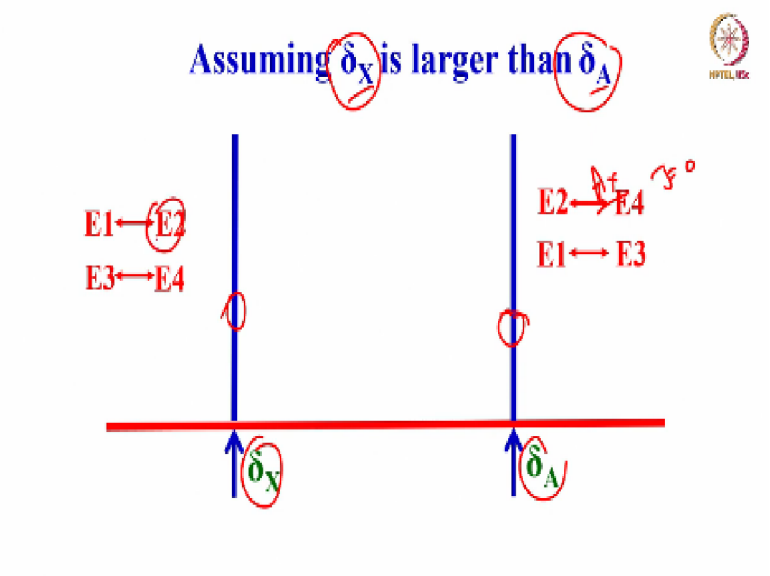

But it appears single, but 2 are overlapped, you should remember that, when you make the quantum mechanical calculations, you know that. Now I assume 1 condition, chemical shift of X is larger than delta A. This is just an assumption; it can be anything you can make this as delta A, this as delta X, it is your nomenclature, does not matter. So, just to show the spectrum, I have assumed that delta X is larger than delta A. And this is a type of spectrum. In an AX spin system, when they are coupled, weakly coupled A and X. And J coupling is 0. Chemical shifts are far away separated, they are weakly coupled and we get only 2 transitions, one for X and one for A. Well separated singlets that is what you are going to get. And you can see by quantum mechanical analysis for 2 coupled spin system. When J is = 0, you are going to get 2 peaks of identical intensities well separated and each of them have 2 frequencies overlapped. This is E1 E2 and this is E2 E4 and E 1 E 3. So, this corresponds to X transition and this correspond to A transition.

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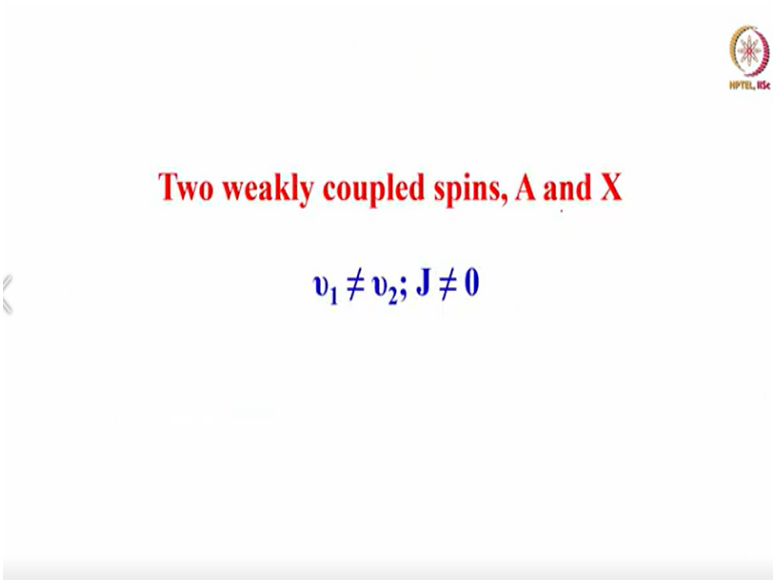

Now, we will consider a situation of 2 weakly coupled spins; A and X. In a situation where nu 1 is not equal to nu 2, of course that has to be because of A, X. In this situation now J is not equal to 0, we will bring in J interaction now, what do you have to do when you bring in J interaction? you have to bring in H1 Hamiltonian also. In the previous case, we ignored H1 we took only H0. Now, we have to consider both H0 and H1; and then same procedure.

Of course, now we already know the wave functions; only to construct the matrix and get the Eigen values and solve this secular equation to get the Eigen values and Eigen function, and then get the frequency of transitions. That is what we have to do in this situation. Now it is time up so what I am going to do is I will stop here. In the next class, we can analyze this weakly coupled 2 spin system with J not equal to 0.

So, in this class, what we tried to do; quantum mechanically we try to understand taking 2 weakly coupled spin systems, we first constructed the wave function, then we defined what is the Hamiltonian. We constructed the Hamiltonian also, then after what we did? We have to calculate the eigenvalues for that. So, we expressed it in the form of a matrix which is a secular equation, we already know that H mn - delta mn; we wrote that equation.

That secular equation when it is equal to 0, you express in terms of matrix. We have 2 spins, we have 2 to the power of N, into 2 to the power of N; there are 16 matrix elements for 2 coupled spin system. But we also assumed the J coupling is not there, all the off-diagonal elements are 0. We calculated and showed that only 4 diagonal elements are present. And using these diagonal elements we calculated the transition frequencies.

They are nothing but Eigen values used to get the transition frequencies. There is a selection rule, there are 4 transitions allowed. 2 for A and 2 for X. 2 A transitions are of identical frequencies. 2 X transitions are also of identical frequency. So, that means instead of 4 peaks, we get only 2 peaks for each of them; 2, 2 transitions are overlapped. If I assume one of the chemical shift is quite large compared to the other, may be X or A, when I assume that the X is quite large and it is coming at the downfield, A is at the high field, I showed in a simple stick plot, only 2 peaks you can get for 2 weakly coupled spin system, with J = 0. So, in the next class we will analyze a situation quantum mechanically when J not equal to 0. Thank you.