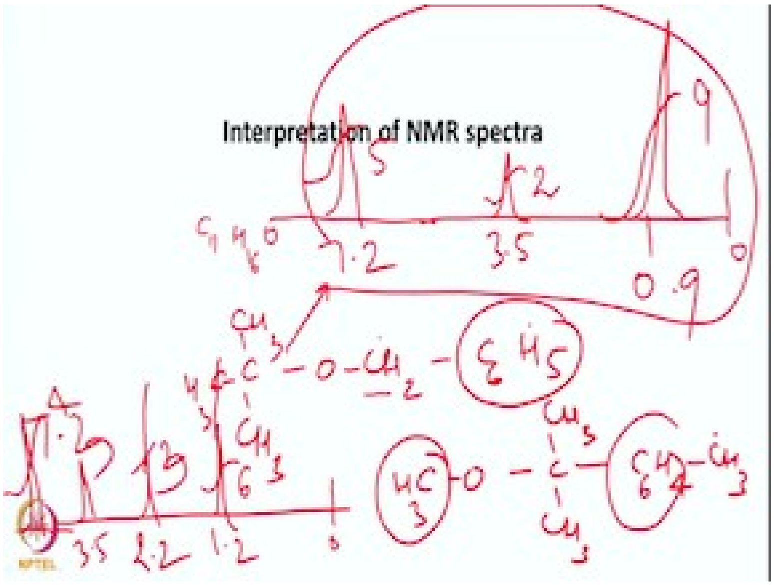
NMR Spectroscopy for Chemists and Biologists
Doctor Ashutosh Kumar
Professor Ramkrishna Hosur
Department of Bioscience and Bioengineering
Indian Institute of Technology, Bombay
Lecture No. 10
Quantum Mechanical Analysis – Part I

Welcome to today's class so we will be continuing with high resolution NMR spectrum of molecules.

(Refer Slide Time: 00:23)


Interpretation of NMR spectra

So let us now using this concept of coupling constant and chemical shift can we start interpreting NMR spectrum of few molecules. And this can be used for distinguishing say isomers. So let us take an example so is I have suppose a molecule which is something like $C_{11}H_{16}O$. This is a molecule which has two isomer. Now isomer suppose is something like this CH3-CH3-CH3 and O-CH2-C6H5 and the other molecule suppose we have CH3-O-CH3-CH3-C6H4-CH3. So if these two are isomer of the same molecule how we can distinguish based on the NMR spectrum that which molecule belongs to what.

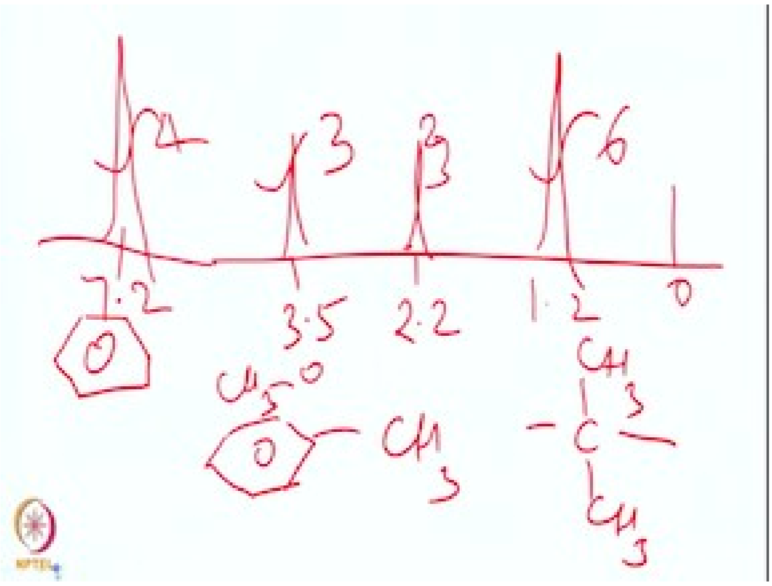
So what will be the NMR spectrum for say first molecule. So let us look at the groups that are present closely here. We have a benzene ring, now as you know benzene ring comes around say 7 ppm, them we have 3 methyl groups and these methyl groups comes quite like a free shifted that that is like a 0 ppm and then we have a methylene group, so three types of carbon mostly we have. 1 here of benzene ring, methylene group and methyl group, so three carbon type.

So essentially we should see three peaks. What are those three peaks? And these three peaks are essentially like this. So here say our 0ppm reference is there. Now we have the equivalent 9 protons that are contributed by these three methyl group. So we have a peak, which will be like this, methyl groups here and that will corresponds to 9 peaks. Then we have another proton, which is methylene group so this is say 0.09 ppm. Then we have another group, which is methylene group and here it is contributed by 2 proton, so that will be around 3.5 ppm.

And then we have far down here around 7 ppm that is one peak, which is given by the 5 protons and that is 7.2. So this is our spectrum for this molecule and what happens to here, this molecule which is there in benzene ring, 1 methyl group here, 2 methyl groups are here and 1 methyl groups are here. If you look at among these methyl group the chemical shift is not same, it is going to be different. Therefore we have a different spectrum for this molecule and this molecule will give spectrum something like this. So the most down field shifted will be these two methyls and that will be certainly downfield than this 0.9.

So here is our TMS so these 6 protons will be around 1.2 ppm, this is 6. Then it comes like a other protons which we have like here and here. So even in these methylene protons we have 3 kind of chemical shift for this, benzene ring it will around 7.2 ppm, them methyl will be around 2.2 ppm this methyl and then we have 1.2 ppm and there is one more methyl which comes around here, that is 3.5 ppm. So we have a 6 protons that will be around 1.2 ppm then 3 protons, 3 protons and this will be 4 protons. So lets go to next page and then I will write it clearly.

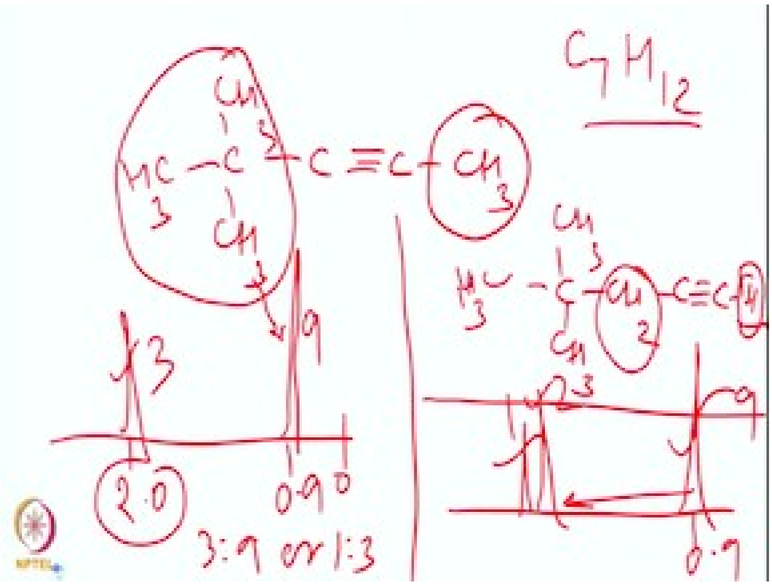
(Refer Slide Time: 04:48)



For molecule like this that we have, here is 0 ppm, we have the most downfield are 6 protons coming from these 2 groups, if you look at CH_3 group and CH_3 group. Now then we have one CH_3 which is attached to benzene ring and that comes around 2 say 2.2 ppm and these corresponds to 3 peaks. Then comes so this is what we are talking about this CH_3, which is attached to benzene ring. Then we have 3.5 ppm CH_3 corresponds to 3 proton and that we are talking about O-CH_3 group.

So even in the methyl depending upon what is attached here we are getting the different chemical shift and most downfield shifted for 4 protons that is coming because of benzene ring. So benzene ring has 4 protons because 2 groups are attached to position. So that is around 7.2 ppm, that is how we can distinguish. So if you go back, so spectrum of the previous proton here we have different than the current one and that is how you can distinguish between 2 isomers.

(Refer Slide Time: 06:17)

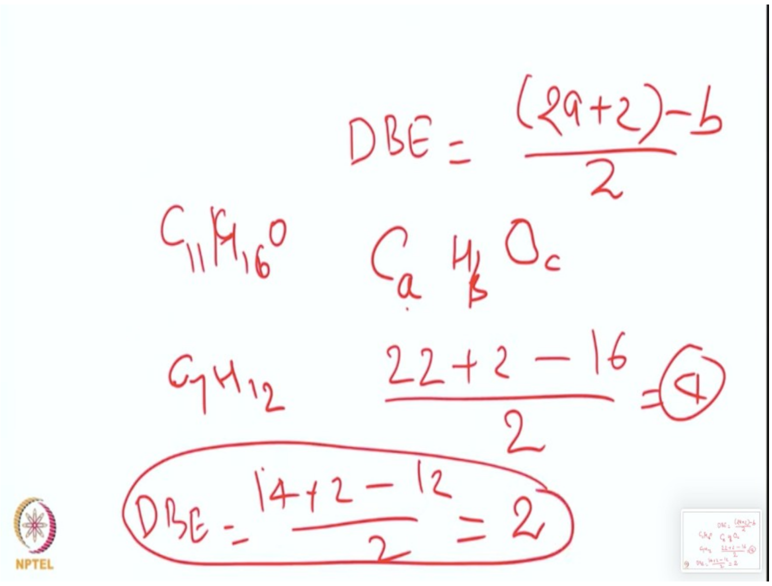


Let us take the another isomer, say its chemical formula is C_7H_{12} and two structures that we have is CH3-CH3-CH3-C triple bond CH3, one is this and suppose we have another CH3-CH3-CH3-CH2-C triple bond C-H. So if we look at here, now what we have is all these are in the same chemical environment. So 9 proton and they will be quite up field shifted near 0 so to have a 9 proton corresponds to these three moiety and we have here 0.9 ppm. Then we have another type of chemical shift, which is coming from proton chemical shift which is coming from here and that is we have one type of proton so that is 3 and this comes around 2.

So if we take ratio 3: 9 or 1:3. So here we have ratio of signal 3:9 or 1:3. For this molecule what we have here, we have a different kind of proton so here are 3 one kind of proton, then CH_2 we have another kind and then CH we have that is third kind of protons. So these CH3 again say all 9 will come at 0.9 ppm then we have another proton, 2 protons which will come around 3 ppm and this 1 proton which will again come very closer to that.

So we have 2 protons and 1 proton that will come very close to each other. This is methylene proton and these are methylene protons so that comes quite downful compared to this methyl protons. So this is how you can distinguish the isomers. So now how like we can do the analysis, just I will go forward and try to explain again. So first thing you need to know if you have a chemical formula, how many kind of protons we can have, so that will be simple given by how many double bonds that we have.

(Refer Slide Time: 08:42)



$$DBE = \frac{(2a+2)-b}{2}$$

$$C_{11}H_{16}O \quad C_aH_bO_c$$

$$C_7H_{12} \quad \frac{22+2-16}{2} = \boxed{4}$$

$$\boxed{DBE = \frac{14+2-12}{2} = 2}$$

So there is a simple calculation which is called double bond equivalence (DBE) that you can find it out by a simple formula called

$$DBE = \frac{(2a+2)-b}{2}$$

2a plus 2 minus b divided by 2. For a compound which is like $C_a H_b O_c$. So here *a* is the number of carbon, *b* is the number of proton. So like whatever we had earlier if you look at $C_{11}H_{16}O$ we have. So how many double bond we are expected to have here? So if you look at here

$$C_{11}H_{16}O \rightarrow a=11, b=16$$

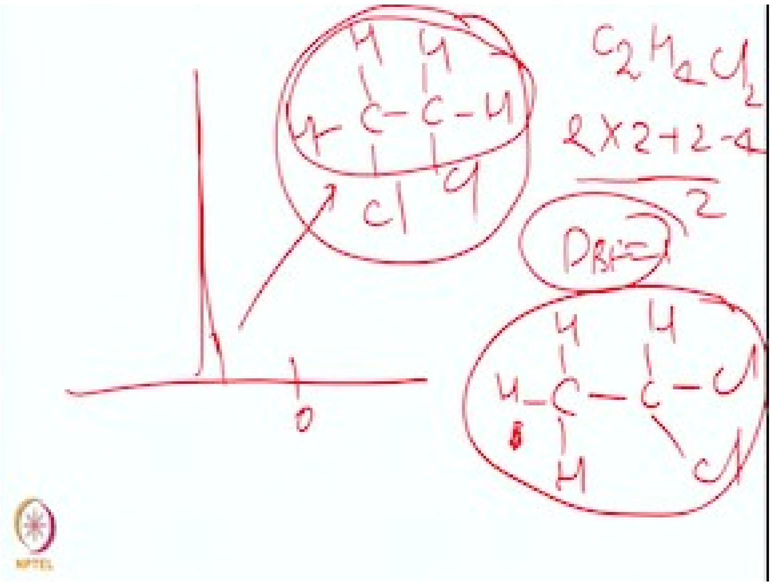
$$DBE = \frac{(22+2)-16}{2} = 4$$

Therefore we had a 1 benzene ring there. Now that is how this can be used, let us take another example that we had in the previous example C_7H_{12}, how many double bond we are going to expect here? So 7 into 2 14, 14 plus 2 minus 12 divided by 2, so that is 16 minus 12, that will be 2 number of double bond, so DBE is 2 and therefore we had one triple bond there, so in the previous example. So that is how we can calculate the number of double bond equivalent.

$C_7 H_{12} \rightarrow a=7, b=12$

$$DBE=\frac{(14+2)-12}{2}=3$$

(Refer Slide Time: 10:23)



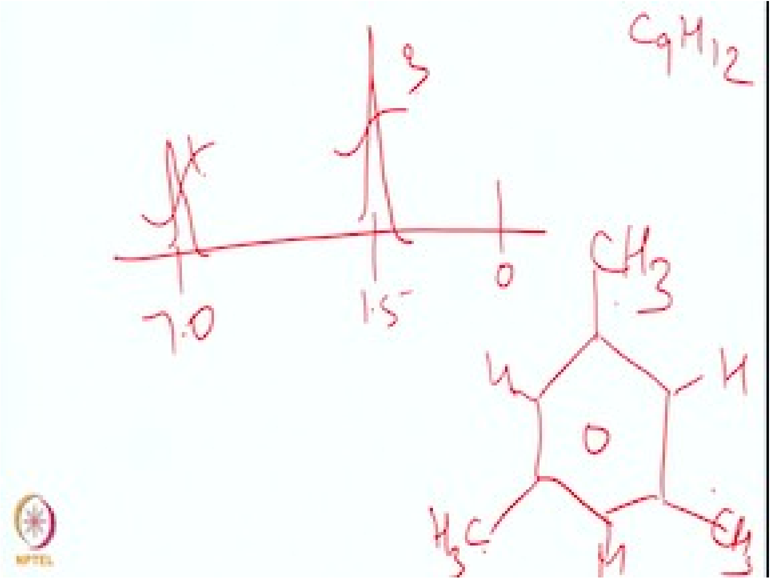
So now let us see if I give you chemical formula and now we have to predict the spectrum for that. So let us see we have a molecule like $C_2H_4Cl_2$. Now if you calculate using that then we do not have a double bond

$$DBE=\frac{(4+2)-4}{2}=1$$

2 so DBE is like 1 so we do not have any double bond here. So that means all carbon are saturated so probably the structure for this can be something like this CH-C-H-Cl -Cl or it even can be like this CH3-CH-CH-Cl-Cl.

So how do you distinguish whether the spectrum that we are getting belongs to here or not? Now we record the spectrum for this molecule and suppose we are just getting only one peak. Here is our TMS, this is only one peak. So now only one type of proton we have. So only one type of proton can be only this, so like where two protons on each carbon are attach and two chlorines are attach. If we have this case then we have two different kind of protons and this will generate two peaks. So if we are getting only one peak that means this is the correct molecule. That is how we actually interpret the spectrum.

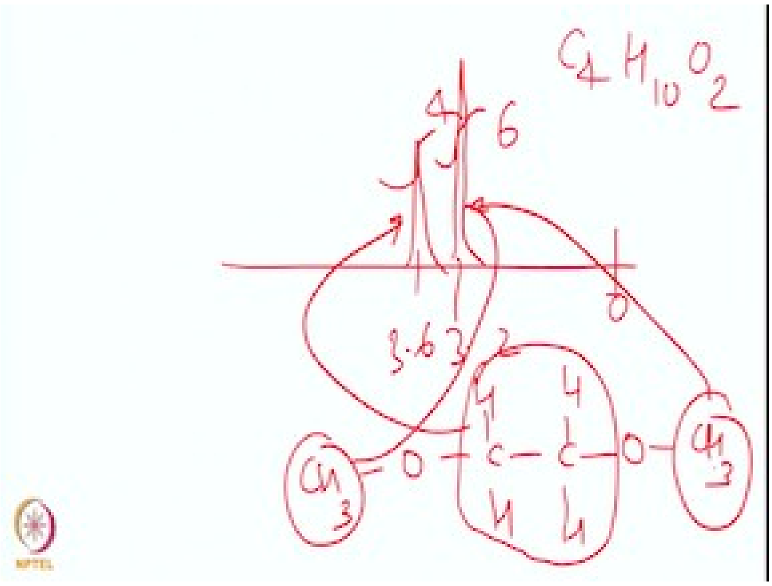
(Refer Slide Time: 11:59)



Now I will give you a spectrum and chemical formula and then we have to find, find what could be the structure of that. So let us see if I have a chemical formula of a molecule which is C_9H_{12} and the spectrum that I am getting is something like here 0 and one peak here, one peak here, ratio is 1: 3, how to find out what could be. So you have similarly calculate the double bond equivalent and then two things are visible if I give you chemical shift. So chemical shit suppose for this is around is less than 2 ppm say 1.5 something like that and here we are giving you around 7 ppm. So it is now clearly evident that we have two kind of proton. One belongs to say methyl group, another belongs to an benzene ring. Now so and ratios are 3:1.

Now we have total of 9 carbon and 12 protons. So 9 carbon and 12 proton if you calculate your double bond equivalent we can find it out that these 3 protons can only come if we have a methyl groups attached to a benzene ring. And those methyl groups seems to be equivalent, chemically equivalent therefore something like this, here one group attached another group attached here and here. So that takes care of our 9 protons, remaining 3 protons are these and therefore we have 2 kinds of proton, one attach to the, directly from the benzene ring and 9 protons attached to these methyl's group, that why we have 1:3.

(Refer Slide Time: 13:47)

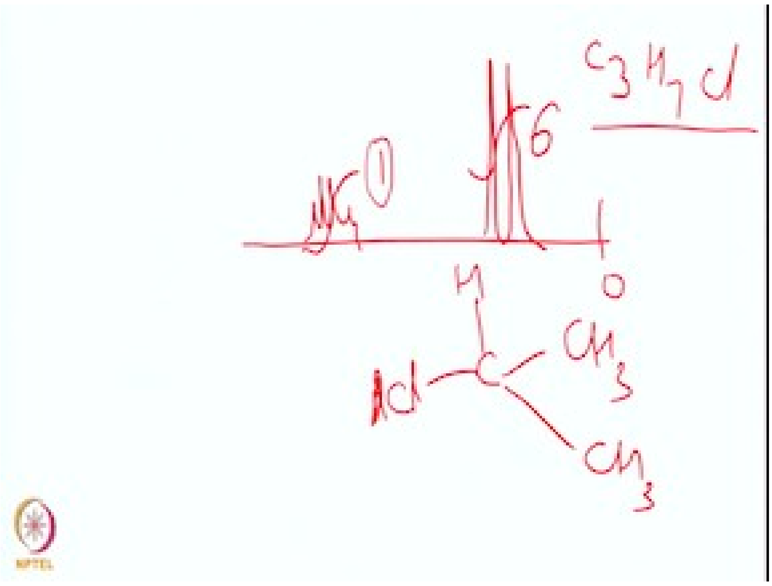


Let us take another example, now here suppose our chemical formula is say $C_4H_{10}O_2$ and our spectrum is say something may be like this, here we have a 6 integration, here we have a 4 integration. And this chemical shift is 3.2 and this chemical shift is say 3.6 something like this, very close. Now can we predict the chemical structure of this compound. So we have a 0 double bonds so one can calculate it. Now one thing is obvious that even there is a methyl group that is quite down field compared to the typical methyl group and that is because 2 oxygen's are attached.

And we have two only two kind of protons, one looks like from methyl group another like from methylene group. Let us put 2 oxygen here and then we have 2 methyl's attached to these. So let us attach those 2 methyl's and then we have remaining 2 carbons and then we can balance the 4 protons. So now these all 4 protons are of equivalent chemical shift and that belongs to these and this and this 2 methyl groups belong to these. So we have 2 kind of proton, one contribute to 6 integration, another belongs to 4 integration.

This is from methyl group, this is from methylene group. That is how we can solve these structures of few of the chemical compound, rest you can practice and then we can discuss in the class if required, if you have any doubt. So let us move back and let us try to do some of the splitting pattern. So what happens when J-coupling is involved here. We have not consider any splitting. So let us consider some of the splitting.

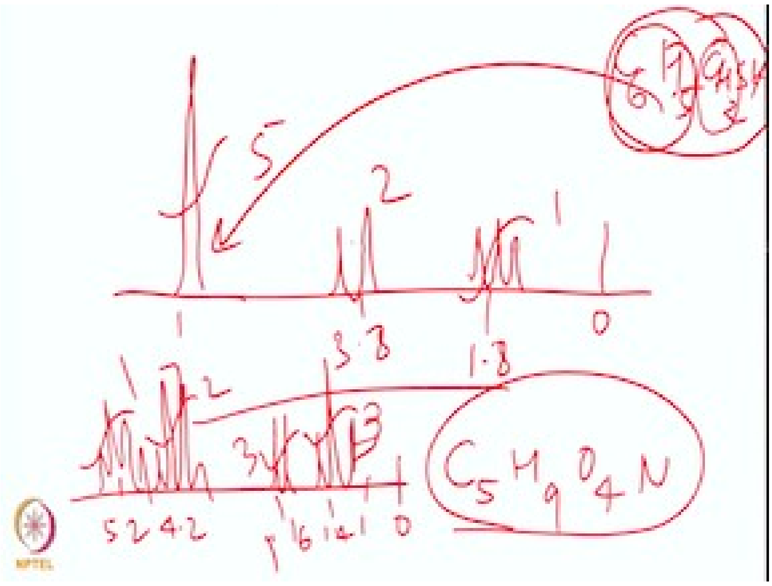
(Refer Slide Time: 15:47)



Now suppose we have a molecule which has a chemical formula like C_3H_7Cl and we have spectrum something like this, here is our 0 ppm, we have 2 close peaks and integration of these together come 6, and here we have a peak which looks like multiplet and here we have integration 1. So C_3H_7Cl, what this could be, so one thing is obvious that we have 2 kind of proton, 6 and 1. So here we have 7, so 6 and 1 very clear. So then probably we have 6 proton so that might be coming from 2 methyl group, so here let us put 2 methyl groups and there is one chlorine.

So let us attach that chlorine here, Cl here, now then there is only one proton which is attached here. Now what is happening here. This proton is splitting this methyl group into 2 and therefore we have two equivalent like height methyl protons and integration total is 6. Now these 6 protons are splitting these single proton into septate and that is why we have multiplet and that comes to be 1, that is how you can find it out that this is the chemical structure given the chemical formula is this.

(Refer Slide Time: 17:09)

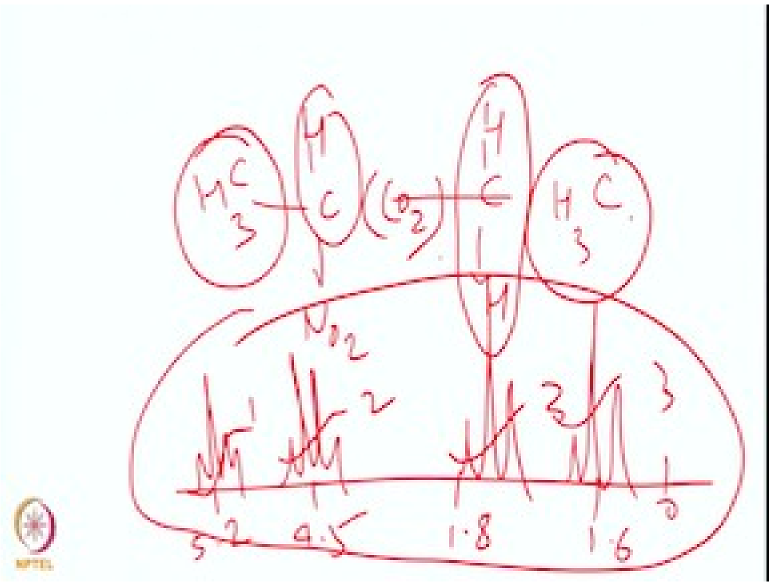


Let us go to next example, suppose we have a chemical formula like $C_6H_5CH_2SH$;. So now this spectrum is something like this, here is 0 ppm, here we have a triplet of 1, here we have again 2 and here around 7 ppm so here is 7 ppm, we have a 5 protons, here 2 protons which is less than 4 so 3.8 ppm and this is say 1.8 ppm something like this. So now we have to find the structure for this. If we have this compound so we can clearly identify that these peaks 5 protons coming from from this one C6H5 and then so these triplet this this is CH_2 so that will split SH proton into triplet.

Therefore, we have one SH triplet at 1 and then this H will split this CH_2 into doublet so we have here doublet structure. So that is how looking at this spectrum and looking at the chemical structure one can identify few of these compounds. Let us take an complicated one, now you can maybe you try to do it by yourself. If we have something like $C_5H_9O_4$ and N and suppose spectrum I am getting something like this. So here we have two kind of protons that shows doublet and here we shows triplet and this is say 1 ppm and this is say 1.4 ppm, this is 1.6 ppm.

Integration of this is 3 or integration of this is 3 and then we have one around 4.2 ppm and here we have a quartet like this and then around say 5.2 ppm we have again a quartet something like this. So integration of this is 1, 2 and here we have a 3 and 3. Now can you identify what this compound can be given the formula is like this. So let us try to solve this as well. So we have two 3 protons, that looks like there will be two methyl groups. So looking at these there is no chemical equivalent.

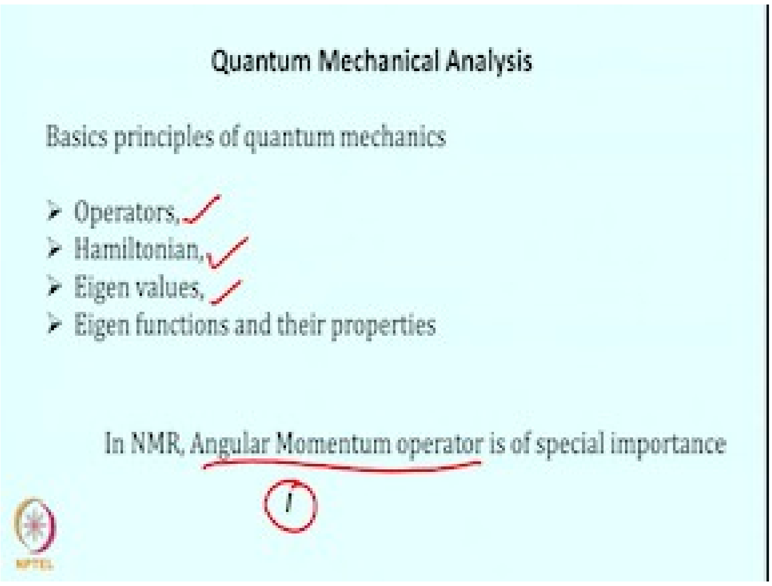
(Refer Slide Time: 19:50)



So there will be two methyl groups. We can write it two methyl groups at two end and then we have two other protons, which are equivalent too so like CH_2 and here CH. Now we have we can have one NO_2 and there will be some CO_2, which will be entrapped here. So CO_2, so our compound something like this we should have a to get down the exact chemical formula I am giving you hint, we have two methyl group, there will be one CH_2 group, one CH group that will corresponds to the spectrum that we just now draw it.

Here we have a triplet corresponding to 3 protons, here we have a another triplet corresponding to 3 protons, here we have a quartet corresponding to 2 proton and here we have again quadrate corresponding to 1 proton. 5.2, 4.5, 1.8 and 1.6, so identify how these molecules corresponds to this kind of spectrum and I will suggest you guys to do practice, take any organic chemistry NMR spectroscopy book. Practice it, take the spectrum and then try to deduce the chemical structure of that or take a compound and try to draw the spectrum for that.

(Refer Slide Time: 21:19)



Quantum Mechanical Analysis

Basics principles of quantum mechanics

- Operators, ✓
- Hamiltonian, ✓
- Eigen values, ✓
- Eigen functions and their properties

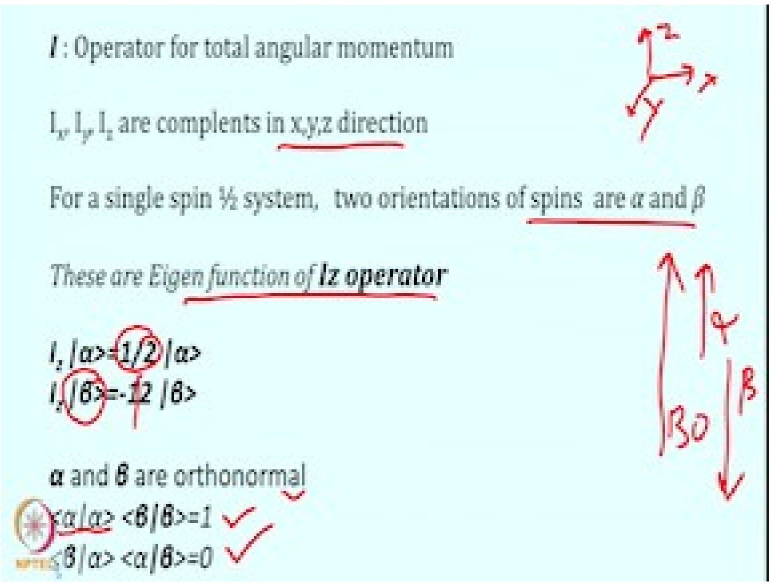
In NMR, Angular Momentum operator is of special importance

I

But to understand how these lines comes we have to go into little rigorous details of explanation for their intensity, for their resonance frequency, all those comes if we understand little bit of quantum mechanical analysis. So what I will do today for this explanation I briefly venture into quantum mechanical description of these spins so I will just like you to go through the basics of quantum mechanics but we will be wherever required we will introduce it some of the phenomena.

So let us take with a basic principal of quantum mechanics. So as you have studied in your undergraduate also for basic principal of quantum mechanics we have a operator, which operates on a Eigen function. So we have a operator and we need to define a Hamiltonian function and operator operates on Eigen function and gives its Eigen value. So these are basic terms like operator, Hamiltonian, Eigen values and Eigen function. In NMR we particularly are interested in something called angular momentum operator and this is defined as I.

(Refer Slide Time: 22:45)



I : Operator for total angular momentum

I_x, I_y, I_z are complents in x,y,z direction

For a single spin ½ system, two orientations of spins are α and β

These are Eigen function of ***Iz operator***

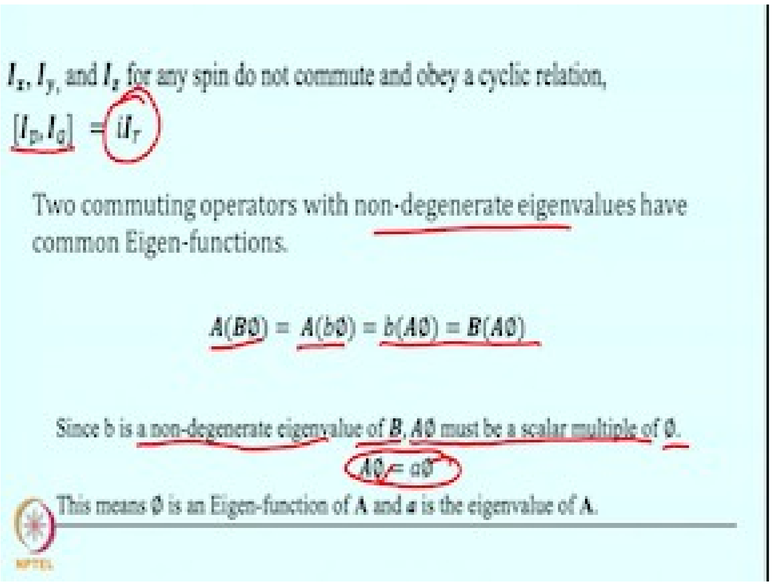
$I_z|\alpha\rangle = 1/2|\alpha\rangle$
$I_z|\beta\rangle = -1/2|\beta\rangle$

α and β are orthonormal
$\langle\alpha|\alpha\rangle \langle\beta|\beta\rangle = 1$
$\langle\beta|\alpha\rangle \langle\alpha|\beta\rangle = 0$

So angular momentum is of our particular interest and we define that and *I, I* is a operator of total angular momentum, *I* has three direction *x, y, z* and so here I_z direction or *x* direction and say *y* direction or vice versa. So it has 3 component, 1 in *z* direction, *x* direction, and *y* direction in all three direction. So for a single spin half system two orientation of spin are possible, one is like along the magnetic field, here suppose we have a magnetic field B_0, one is along the magnetic field, another is against the magnetic field. You can define one is a *α* another is a *β* or vice versa of whatever way you want to define.

So these are the two orientation of spins along the magnetic field or against the magnetic field. So now these are Eigen function of I_z operator, as I said there is a operator and in an NMR is a angular momentum operator. So now I_z is an operator and it is operating on the Eigen function like alpha and beta so if I_z operating on alpha state it gives the value of plus half or if it operates on beta state it gives the value of minus half. So that is what we have. So now if these functions *α* and *β* are orthogonal that means if you take the $<\alpha/\alpha>$ or $<\beta/\beta>=1$ or if you take $<\beta/\alpha><\alpha/\beta>=0$. So that is what we mean by orthogonal function.

(Refer Slide Time: 24:41)



I_x, I_y, and I_z for any spin do not commute and obey a cyclic relation,

$[I_p, I_q] = iI_r$

Two commuting operators with non-degenerate eigenvalues have common Eigen-functions.

$$A(B\emptyset) = A(b\emptyset) = b(A\emptyset) = B(A\emptyset)$$

Since b is a non-degenerate eigenvalue of **B**, $A\emptyset$ must be a scalar multiple of $\emptyset$.

$$A\emptyset = a\emptyset$$

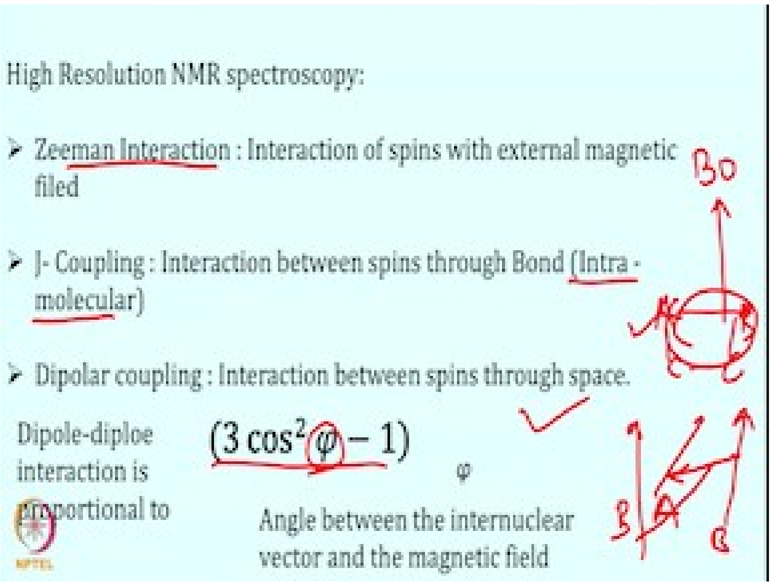
This means $\emptyset$ is an Eigen-function of **A** and *a* is the eigenvalue of **A**.

Now, so as we said that these are operators, I_x, I_y, I_z and these spins, they do not commute but obey cyclic relation. So what we mean by cyclic relation in quantum mechanics that if you take this I_p or I_q they will give you I_r. That means if you take $I_x I_y$ in our angular momentum term they will give I_z. So now two commuting operator with non-degenerate Eigen value have a common Eigen function what I mean by that if your ,

$$A(B\varphi) = A(b\varphi) = b(A\varphi) = B(A\varphi)$$

So here b is non-degenerate Eigen values of function B. so that means $A\ \varphi$ must be an scalar multiplication of φ what we mean φ is an Eigen function of A and a is an Eigen value. So here $A\ \varphi$ is an Eigen function a is Eigen value.

(Refer Slide Time: 25:37)



High Resolution NMR spectroscopy:

- Zeeman Interaction : Interaction of spins with external magnetic filed
- J- Coupling : Interaction between spins through Bond (Intra - molecular)
- Dipolar coupling : Interaction between spins through space.

Dipole-diploe interaction is proportional to $(3\cos^2\varphi - 1)$

φ Angle between the internuclear vector and the magnetic field

So this is basics of quantum mechanics and as we said that we will come back to quantum mechanics, we reintroduce wherever it is required. So now let us move ahead and then look at the high resolution NMR spectrum so what all the functions and Hamiltonian we have. So main one is a Zeeman Interaction, what we mean by Zeeman Interaction is interaction of spins with external magnetic field. So as we see that external magnetic field is defined as a B_0 and it is in z direction and this is of like if you look at the magnitude its quite a bit because magnetic field is of tesla order or is in terms of frequency it is a megahertz, like 600 megahertz, 700 megahertz and all those.

The next one is J coupling that is another Hamiltonian. So J coupling is interaction between the spins through bond so like there are say here this is interaction between spin A and spin B and through bond how they are interacting, that is what we call it J coupling. So it is a intra molecular interaction and this is of relatively very small magnitude. The third one is called dipolar coupling so two spins in solution, so these are two spins and there is a bond vector between them. So spin A and spin B and this is bond vector connecting them. So the angle between the main magnetic field and this bond vector is given as a φ.

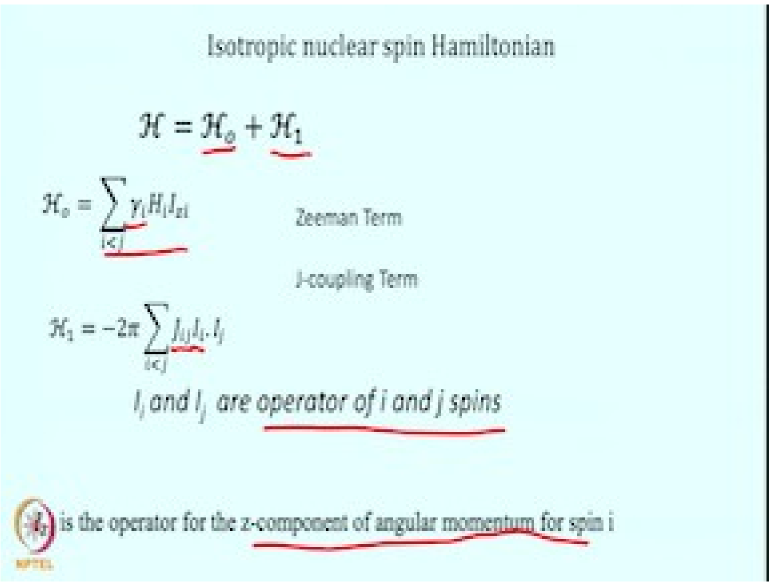
Now the dipolar coupling interaction happens through a space so this was through bond interaction scalar coupling, the dipolar coupling is through a space interaction and that if you remember little bit of this dipolar kind of interaction this is proportional to

$$(3\cos^2\varphi - 1)$$

So φ is the angle between this intermolecular vector of these two spins with the magnetic field. Now what happens in solution the two spins all the time tumbles. So because of this tumbling these term goes to 0 and therefore we do not see any dipolar coupling in solution.

So what we have mostly in Zeeman Interaction and *J* coupling interaction. Dipolar coupling is averaged out in solution, but that is not case in the solids. Solid means these not tumble so if you want to make this term 0 we have to spin faster and faster and that is that we will discuss later whenever it comes. But in liquid state so these is the are the two interaction term that we have mostly coming from the magnetic field, external magnetic field this is order of megahertz then we have *J* coupling which is in order of hertz and dipolar coupling is typically order of kilohertz. So this is the main main field and then we have a *J* coupling.

(Refer Slide Time: 28:31)



Isotropic nuclear spin Hamiltonian

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_1$$

$$\mathcal{H}_0 = \sum_{i<j} \gamma_i H_i I_{zi}$$

Zeeman Term

J-coupling Term

$$\mathcal{H}_1 = -2\pi \sum_{i<j} J_{ij} I_i \cdot I_j$$

I_i and I_j are operator of i and j spins

is the operator for the z-component of angular momentum for spin i

So now let us move ahead if we have these interaction that means these can form the Hamiltonian, which operates on the angular momentum operator. So the isotropic nuclear spin Hamiltonian, isotropic means spins that tumbles in solution. So as you say isotropic that means spinning is happening all the time, it is randomly moving so dipolar coupling is not there we have a Zeeman interaction and scalar coupling interaction which is coming because of J. So total Hamiltonian is

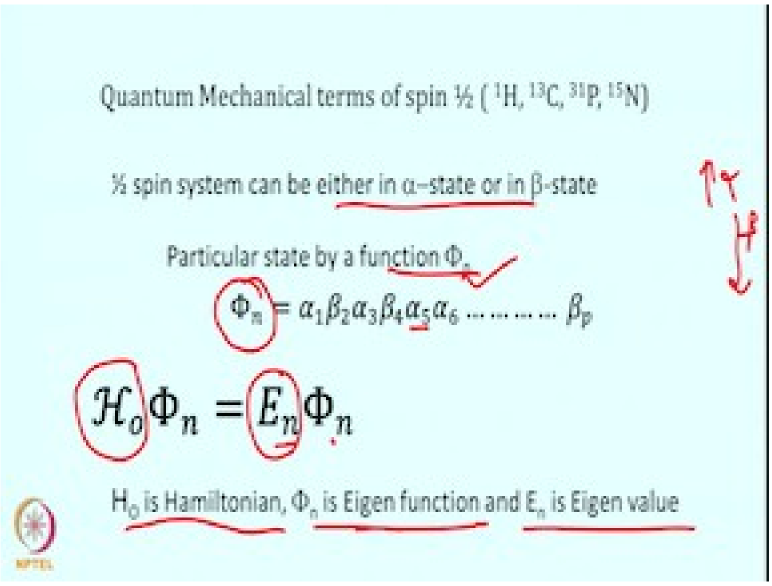
$$H = H_0 + H_1$$

now H_0 is our Zeeman term and H_1 is essentially J coupling term. So H_0 one can define that how different spins I_z, I_i is different spins and J as we said z component of angular momentum, Υ is the gyromagnetic ratio of the each nuclei. So we have to sum over all the nuclei how these term comes. So H_0 the Zeeman interaction term can be given by

$$H_0 = \sum_{i<j} \gamma_i H_i I_{zi}$$

Now H_1 is a J coupling Hamiltonian this cause s the mixing of two spins because two spins now talking to each other through bond so that is how it is J_i, this is a this is coming because of the coupling and here are two spins I_i and I_j. So I_i and I_j are operator of I and J spin and because of this we have a coupling constant, J is a coupling constant. I_z is operator for the z component of the angular momentum from I spin. So these are the two Hamiltonian terms in liquid state.

(Refer Slide Time: 30:19)



Quantum Mechanical terms of spin ½ (^{1}H, ^{13}C, ^{31}P, ^{15}N)

½ spin system can be either in α–state or in β-state

Particular state by a function Φ.

$$\Phi_n = \alpha_1\beta_2\alpha_3\beta_4\alpha_5\alpha_6 \ldots\ldots\ldots \beta_p$$

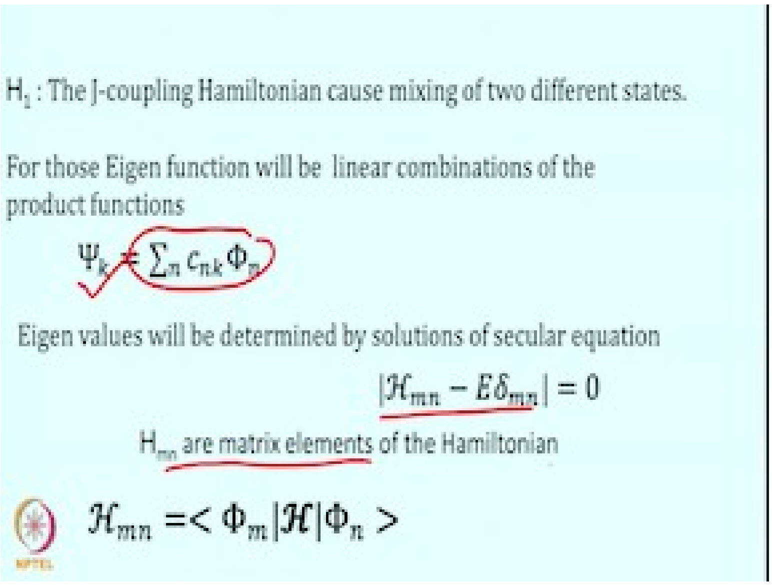
$$\mathcal{H}_0\Phi_n = E_n\Phi_n$$

H_0 is Hamiltonian, Φ_n is Eigen function and E_n is Eigen value

So now quantum mechanical term for spin half spin half that mostly we are looking at, at the moment, so I= ½ nuclei like proton or carbon 13 or ^{31}P or nitrogen 15. Now in these states the half spin system can be either in alpha state or beta state, alpha state or beta state and then we can take the summation of our all states so for a particular states, say we have a n spins. So we can write a particular state by α_1 that means that the spin 1 is in α state, spin 2 is in β state, spin 3 again is in α state, spin 4 is in β sate.

And again spin 5 in α state, so multiplication of all those will be given by a particular function which is φ_n. so φ_n is our Eigen function and Hamiltonian H_0 that is Zeeman Hamiltonian operated on φ_n which gives the Eigen value E_n. So that is what H Hamiltonian gives φ as a Eigen function and E_n is Eigen value.

(Refer Slide Time: 31:36)



H_1 : The J-coupling Hamiltonian cause mixing of two different states.

For those Eigen function will be linear combinations of the product functions

$$\Psi_k = \sum_n c_{nk} \Phi_n$$

Eigen values will be determined by solutions of secular equation

$$|\mathcal{H}_{mn} - E\delta_{mn}| = 0$$

H_{mn} are matrix elements of the Hamiltonian

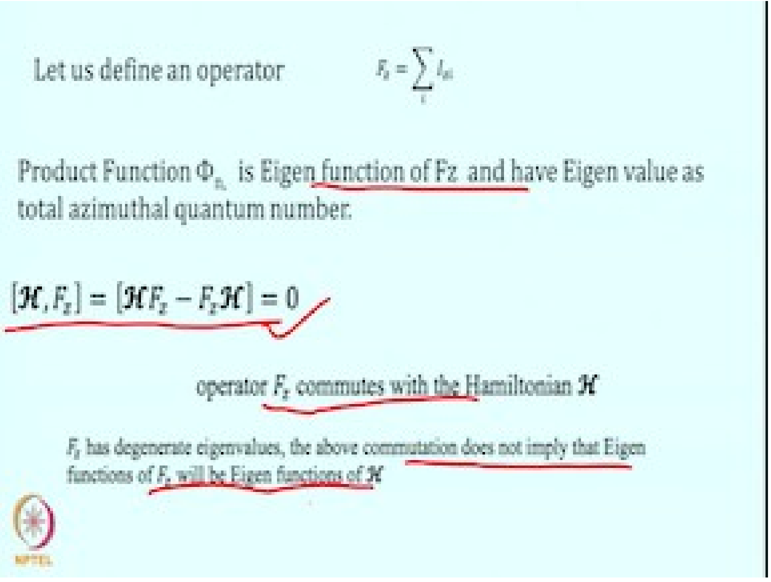
$$\mathcal{H}_{mn} = < \Phi_m|\mathcal{H}|\Phi_n >$$

So now the another Hamiltonian which is H_1 and that is J coupling Hamiltonian these as we discussed cause the mixing of two different states. Now for these two Eigen function there will be linear combination of the product. So what will we mean by that, so if we have a spins like that n spins so we can have a product of these spins and you have to sum over that and that gives you resultant Eigen function. So Eigen function will be determined by the solution of the secular equation you might have studied. So we can solve this equation where

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

The H_{mn} is the matrix element of this Hamiltonian.

(Refer Slide Time: 32:26)



Let us define an operator $F_z = \sum_i I_{zi}$

Product Function Φ_n is Eigen function of Fz and have Eigen value as total azimuthal quantum number.

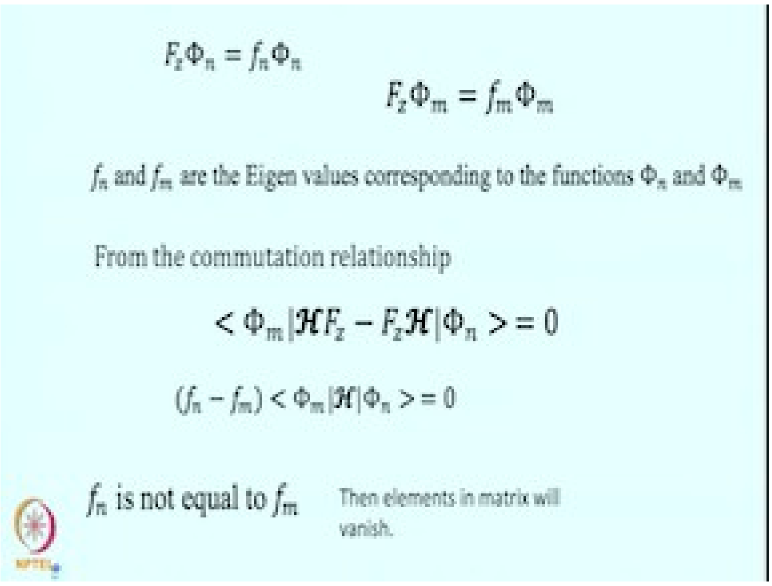
$[\mathcal{H}, F_z] = [\mathcal{H}F_z - F_z\mathcal{H}] = 0$

operator F_z commutes with the Hamiltonian $\mathcal{H}$

F_z has degenerate eigenvalues, the above commutation does not imply that Eigen functions of F_z will be Eigen functions of $\mathcal{H}$

For solving this we have to define our operator which is F_z and the product function which comes from the this J coupling Hamiltonian you can solve this by defining the F_z and if you take this, if we take this product so F_z is Eigen function and have Eigen values like total azimuthal quantum number so one can solve it by doing simple quantum mechanical algebraic operation and F_z commutes with Hamiltonian H. So F_z has a degenerate Eigen value and that have that the above communication does not imply that Eigen function F_z will have a Eigen function of H.

(Refer Slide Time: 33:11)



$$F_z\Phi_n = f_n\Phi_n$$

$$F_z\Phi_m = f_m\Phi_m$$

f_n and f_m are the Eigen values corresponding to the functions Φ_n and Φ_m

From the commutation relationship

$$<\Phi_m|\mathcal{H}F_z - F_z\mathcal{H}|\Phi_n> = 0$$

$$(f_n - f_m) <\Phi_m|\mathcal{H}|\Phi_n> = 0$$

f_n is not equal to f_m Then elements in matrix will vanish.

So if we solve this equation

$F_z\varphi_m = f_m\varphi_m$

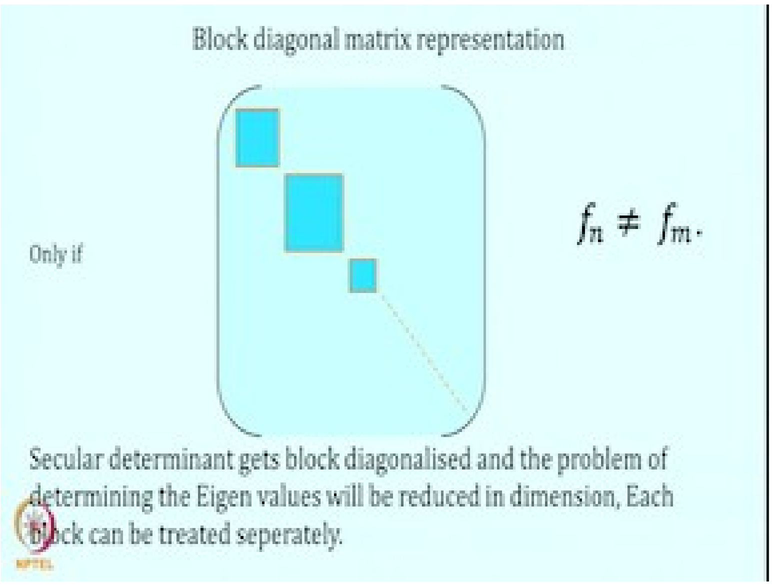
so f_n and f_m are Eigen value corresponding to two function φ_n and φ_m and you solve this commutation relation

¿$\varphi_m \left| H F_z - F_z H \right| \varphi_n >$¿$0$

$\left(f_n - f_m\right) < \varphi_m \left| H \right| \varphi_n >$¿$0$

and one can find it out so like this operation so $f_n \neq f_m$ and then the matrix elements will vanish and then that helps us actually solving these equations.

(Refer Slide Time: 33:44)



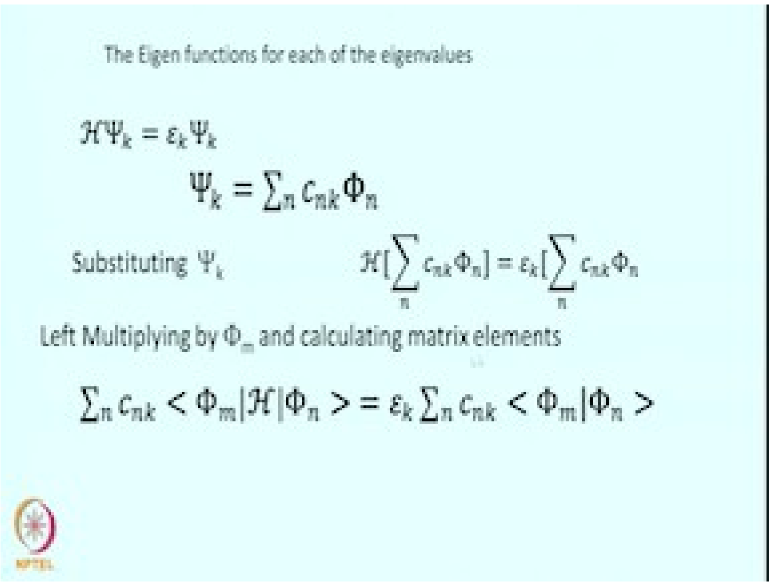
Block diagonal matrix representation

Only if $f_n \neq f_m$.

Secular determinant gets block diagonalised and the problem of determining the Eigen values will be reduced in dimension, Each block can be treated seperately.

So you can block diagonalised this matrix representation taking the case of $f_n \neq f_m$. So if you do that then secular determinants gets the block diagonalised and the problem of determining the Eigen value will be reduced to dimension, and then each block can be treated separately for solving these these functions, so that is how we can solve it.

(Refer Slide Time: 34:10)



The Eigen functions for each of the eigenvalues

$$\mathcal{H}\Psi_k = \varepsilon_k \Psi_k$$

$$\Psi_k = \sum_n c_{nk} \Phi_n$$

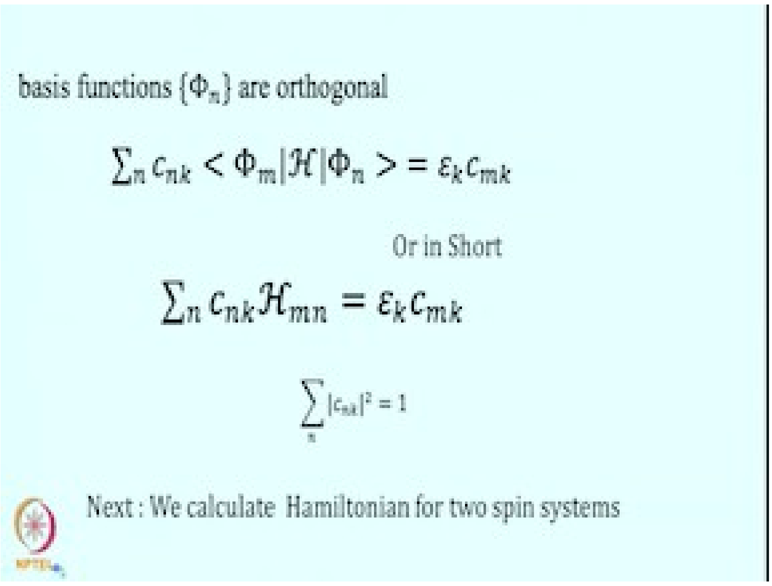
Substituting Ψ_k $\mathcal{H}[\sum_n c_{nk}\Phi_n] = \varepsilon_k[\sum_n c_{nk}\Phi_n$

Left Multiplying by Φ_m and calculating matrix elements

$$\sum_n c_{nk} < \Phi_m|\mathcal{H}|\Phi_n > = \varepsilon_k \sum_n c_{nk} < \Phi_m|\Phi_n >$$

The Eigen function for each of these value can be solved and if you can substitute then one can find the (multi) by multiplying phi m and calculating the matrix element and one can do that.

(Refer Slide Time: 34:22)



basis functions $\{\Phi_n\}$ are orthogonal

$$\sum_n c_{nk} < \Phi_m|\mathcal{H}|\Phi_n > = \varepsilon_k c_{mk}$$

Or in Short

$$\sum_n c_{nk}\mathcal{H}_{mn} = \varepsilon_k c_{mk}$$

$$\sum_n |c_{nk}|^2 = 1$$

Next : We calculate Hamiltonian for two spin systems

Then what we found the basic functions and finally we come to by solving this we come to such kind of coefficient so now doing that we can calculate the Hamiltonian for two spins. So now the complex problem will be now simplified two spin system and now next we move ahead and try to solve and look at how we can calculate the Hamiltonian for two spin system and from there we build up the concepts and we try to we will try to get it to the solution for these spins.

So today I would like to end up here, just I will summarize that we looked at how the splitting happens and what is the basic rule for splitting and where is the resultant chemical shift average comes, what is what will be the rules for intensity of these terms. So for a detailed analysis of these splitting patterns one has to go to quantum mechanical formalism and we looked at basics of quantum mechanic, how to solve these. So we will continue from there to calculate the Hamiltonian for two spin system and then we build up from there. Thank you very much and looking forward to see you in the next class.