INDIAN INSTITUTE OF TECHNOLOGY BOMBAY

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**NATIONAL PROGRAMME ON TECHNOLOGY
ENHANCED LEARNING
(NPTEL)**

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**MOLECULAR SPECTROSCOPY:
A PHYSICAL CHEMIST'S PERSPECTIVE**

**PROF. ANINDYA DATTA
DEPARTMENT OF CHEMISTRY,
IIT BOMBAY**

**Lecture No. – 55
Basics of NMR Spectroscopy**

Today's discussion is going to be a recapitulation for almost all of us I think, so now for the rest of this course we are going to discuss NMR spectroscopy, except maybe for the last class.
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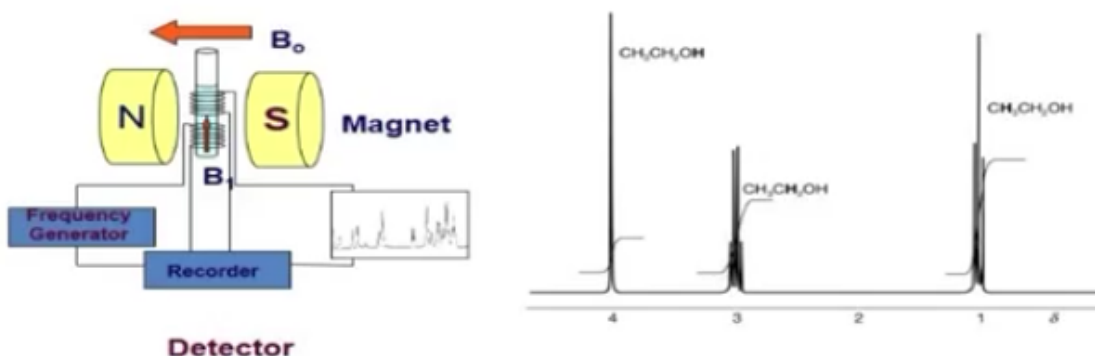
Now everybody knows what NMR stands for, nuclear magnetic resonance and in chemistry courses of course you have come across NMR data and all in different courses, and even beyond chemistry you know that when we have soft tissue injury what we do is we go and get MRI image many times, because it's a very useful technique, several noble prizes have come out of this field of study, and it is a great bone to chemists, because as we have discussed sometime towards the beginning of the course, the problem with being a chemist at one point of time was that you make some new compound after a lot of trail and then you spend one year to find out what it is by wet chemistry, if you have to do it by wet chemistry, so the kind of experiments you have perhaps done in your undergraduate days, you want to find out what the function of database by doing the daiso test, rinne test, right, esterification and so on and so forth.

So if you have to do that first of all you spend this compound that you have made with so much of effort, and secondly it takes a lot of time and everything is indirect anyway, so that was not such a happy situation, things change drastically because of the advent of spectroscopy, and as we have discussed in IR spectroscopy we can actually tell which functional group it is without having to do a reaction, but then even IR is not enough. The one spectroscopic technique that has made the life of chemists much easier is NMR spectroscopy, you do an NMR spectrum, you get a NMR spectrum you understand which compound you have been able to make and that is what everybody does all the time, okay, so very often the chemists are actually accused of practicing palmistry using all this spectroscopic techniques, if you put it in more polite terms then palmistry we can say it is pattern matching, to see whether how many lines are there and where, what is the chemical shift, whether it's a doublet or triplet and so on and so forth, you can figure out which compound it is.

So the other common allegation against chemists is that chemists pretend as if they can see molecules, well actually we can, we can see molecules through the spectrum, but in this course we are not going to learn how to identify molecules using NMR spectroscopy, in fact I am quite bad at interpretative NMR spectroscopy, that is what almost all of you will learn next semester in CH521 formally, you might have done some in other organic inorganic courses.

In the next couple of weeks, if this course we are going to try to understand how NMR spectroscopy works, alright, and we are going to talk about one NMR spectrum by enlarge, and that spectrum is displayed right in front of you, the NMR spectrum of alcohol that is all that we will do in this course, but we'll try to understand why this NMR spectrum looks like what it does, so what we are now doing is if we look back at what we have done in this course,
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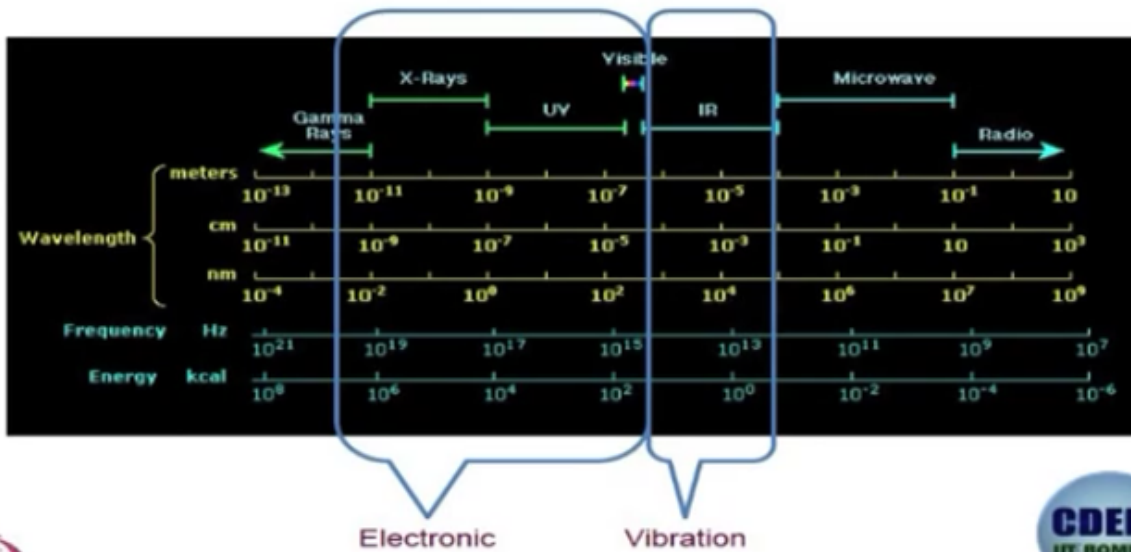
Electromagnetic Spectrum
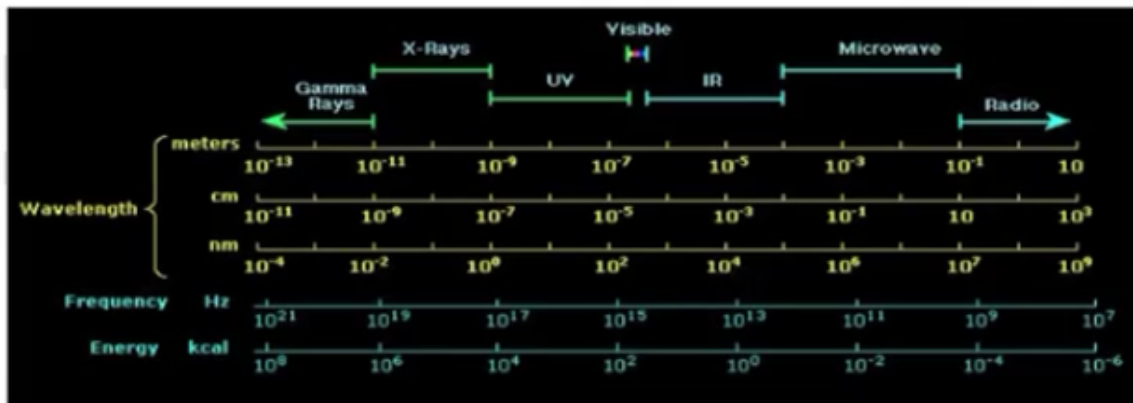
we are trying to understand how light interacts with matter, and when you talk about light interacting with matter you know very well that according to energy light can be classified in many ways and electromagnetic spectrum actually spreads from very high energy to very low energy, you have not really talked about anything to do with gamma rays and all, but we have talked about the kind of spectroscopy that uses ultraviolet, visible and x-rays.

What kind of spectroscopy is that? UV-Vis and x-rays, okay, UV-Vis spectroscopy uses UV-Vis spectrum, what kind of an answer is that? So say something else that is obvious, so using UV-Vis electronic spectroscopy, if we get to learn about electronic levels and that's what we have been doing immediately before, okay.

Then using IR, what is the information that we get about molecules?
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Electromagnetic Spectrum

Vibrations, okay, and using microwave what is the rotation? Now we have almost covered the entire electromagnetic spectrum except for gamma rays and all, right, so what we'll do for the rest of the course is that we'll talk about radiofrequency, and what do radiofrequency tell us about? Radiofrequency are used,
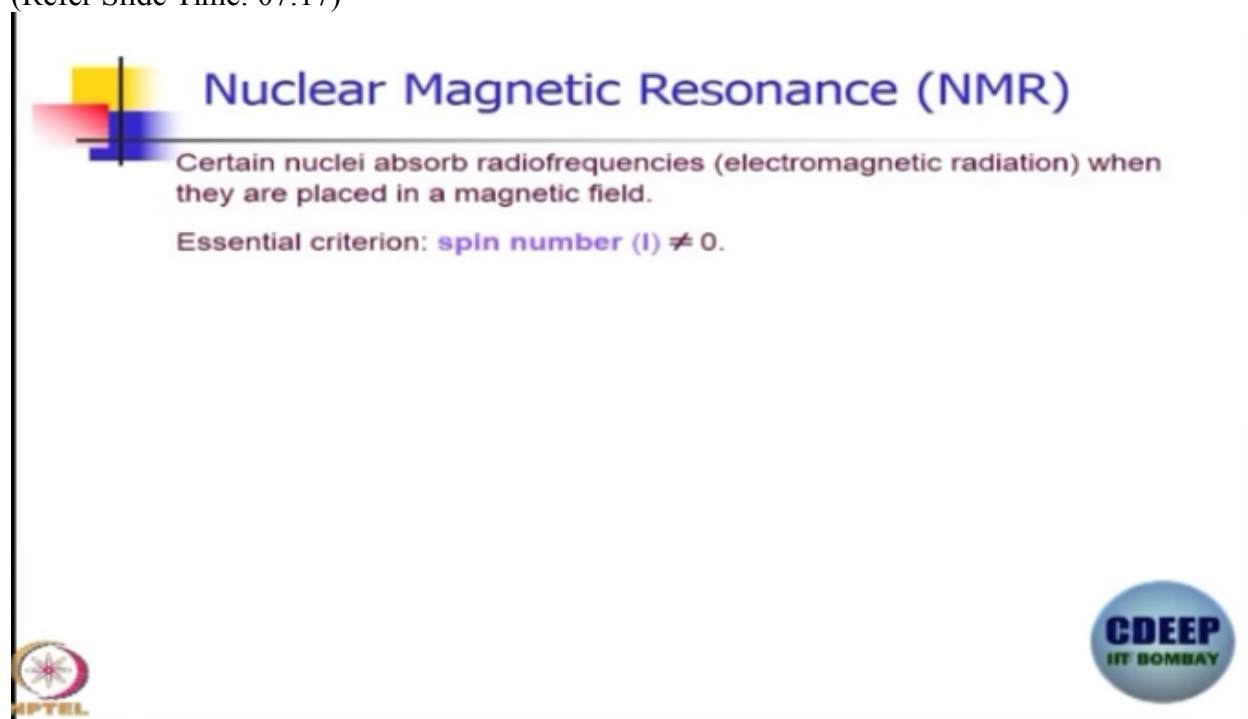
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Electromagnetic Spectrum
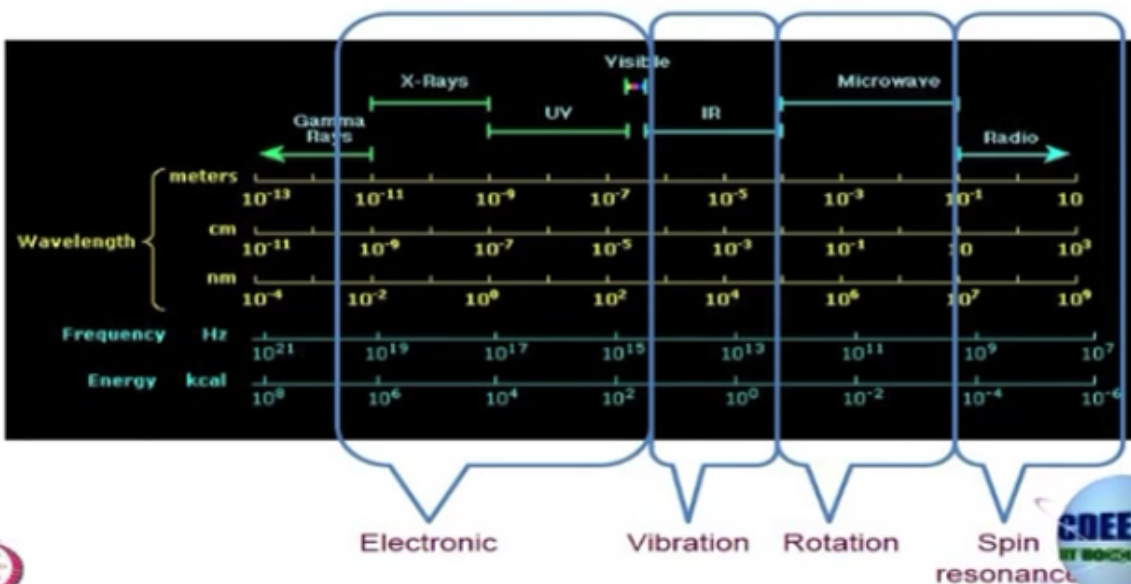
radiofrequency understand they're very, very small energies are there, right, smaller than rotation, so radiofrequency are typically, they have the energy that are associated with what we will call spin resonance, we are familiar with spin in some way or the other, right, so when we

have spin flipping alpha to beta, beta to alpha and so on and so forth that is the kind of energy that is involved falls in the radiofrequency region, okay.

Of course it is a different kind of spectroscopy then what we've been doing so far, why because see this rotational levels and all they're already there in the molecule, not so in case of NMR, as we are going to discuss later the way you make the energies of alpha and beta spins different is by applying a magnetic field. In absence of magnetic field alpha and beta spins have the same energy, so the same energy there is no spectroscopy, okay, so first you have to apply a magnetic field, right, you're really being cruel to the molecule, aren't you? The molecule is happy with all spins to the same energy and all, you apply a magnetic field from outside, disturb the molecule, create division between two kinds of spins, it's a really device hive kind of spectroscopy that you do, and then you see how much divided they are, that is essentially how NMR and ASR work. (Refer Slide Time: 07:17)

Nuclear Magnetic Resonance (NMR)

Certain nuclei absorb radiofrequencies (electromagnetic radiation) when they are placed in a magnetic field.
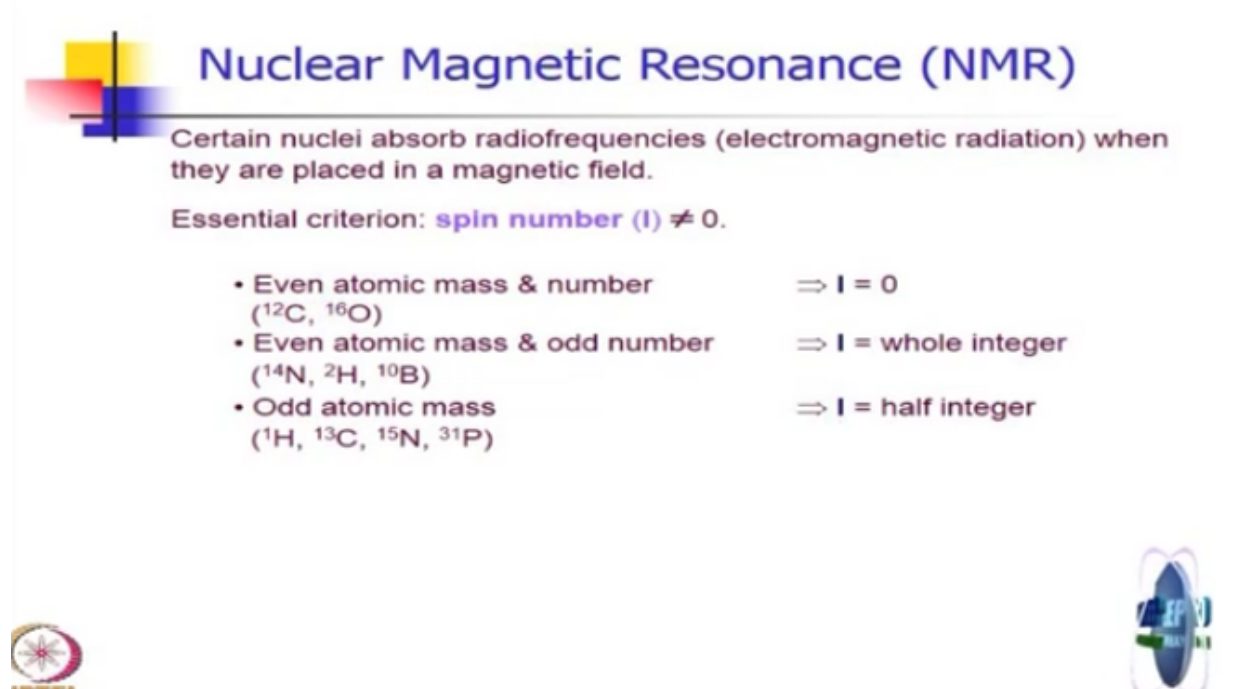
Essential criterion: **spin number (I) ≠ 0.**

So what we are going to use and all this is perhaps are known to you, so it's almost common knowledge now, commonsense right, so the thing is not all, not all nuclei actually absorb radiofrequency even if you place them in magnetic field, so to start the discussion we had to start from the point that is very, very simple right, so right now we are not even talking atoms or molecules or anything, we are talking about nuclei, you can even think we are talking about isolated spins, okay, different kinds of isolated spins.

So it's not necessary that all nuclei will absorb radiofrequency even if you apply magnetic field, what kind of nuclei will absorb? Kajol little louder, what is not equal to 0? That's right, spin not equal to 0, what is spin? When we say spin not equal to 0, spin number not equal to 0 what is that spin number I? What kind of number is it? It's a quantum number you are right, this is a spin quantum number, that's what you said right, so it's a nuclear associated with spin quantum number, so the spin quantum number has to be nonzero.

And how to determine spin quantum number that is little long story to just give you the final result of it this is what it is, if the atomic mass and atomic number are both even, then I is 0, if atomic mass is even and odd atomic number is there,
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Nuclear Magnetic Resonance (NMR)

Certain nuclei absorb radiofrequencies (electromagnetic radiation) when they are placed in a magnetic field.

Essential criterion: spin number (I) ≠ 0.

- Even atomic mass & number   ⇒ I = 0
  (^{12}C, ^{16}O)
- Even atomic mass & odd number   ⇒ I = whole integer
  (^{14}N, ^{2}H, ^{10}B)
- Odd atomic mass   ⇒ I = half integer
  (^{1}H, ^{13}C, ^{15}N, ^{31}P)

then I is the whole integral, whole number, and if you have odd atomic mass then you have 1/2 integral spin quantum numbers, the 1/2 3/2 so on and so forth, some examples are given there, so out of all these most of the time what we do is we work with this proton, then since most of the time you look at organic molecules you do a lot of 13C NMR as well, right.

If you are an inorganic chemist, specially main group inorganic chemist then you might be interested in this phosphorous NMR 31P, 15N is also not very uncommon, so different kinds of nuclei can be interrogated, now the question is how do you know, how do you interrogate proton selectively or 13C selectively, that is what we'll discuss slowly.
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Nuclear Magnetic Resonance (NMR)

Certain nuclei absorb radiofrequencies (electromagnetic radiation) when they are placed in a magnetic field.

Essential criterion: **spin number (I) ≠ 0**.

- Even atomic mass & number $\Rightarrow$ I = 0
  (^{12}C, ^{16}O)
- Even atomic mass & odd number $\Rightarrow$ I = whole integer
  (^{14}N, ^{2}H, ^{10}B)
- Odd atomic mass $\Rightarrow$ I = half integer
  (^{1}H, ^{13}C, ^{15}N, ^{31}P)

Angular momentum = $[I(I+1)]^{1/2}$ h/2π

Z-component of angular momentum = m h/2π

m = I, (I - 1), (I - 2), … , -I

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So but before that just for the record it is a quantum number let us not forget, and what kind of a quantum number is it? We are familiar with the spin quantum number of electron, right, what is it? What is a spin quantum number of electron? 1/2 or + 1/2 and −1/2? No it is 1/2, what is +1/2 and −1/2? Is MS, right spin magnetic quantum number is +1/2 and −1/2, please don't forget this, S is only 1/2, okay.
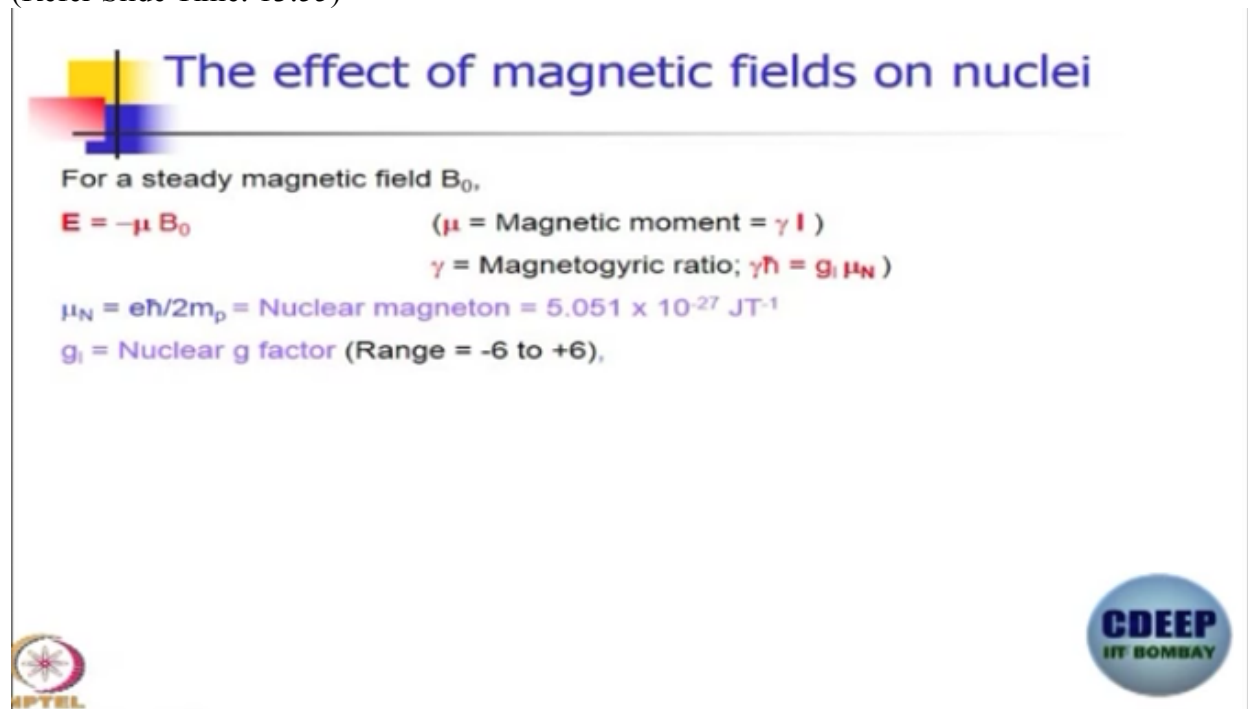
And what does that S give us in case of electron? It gives us the spin angular momentum right, or if you go back even further if you think of L in case of hydrogen atom, right, azimuthal quantum number what does it give us? The total angular momentum, square root of L x L+1 multiplied by H cross, in case of electron spin it is square root of S into S+1 multiplied by H cross, in this case similarly it is square root of I into I+1 multiplied by H cross, right, this is the total spin, so remember total spin means it's the length of the vector, but then even if the length of the vector is defined it can point this way, or this way or this way or this way, so if the direction changes the length doesn't change, what changes actually? I've the same arrow, but I change direction, length will of course not change what will change?

So as a result of changing angle which property of the angular momentum changes? Z component of angular momentum right, if it is like this then it is large as the angle changes this goes down, and here it is 0, if it goes down then it goes down in this way, okay, Z component of angular momentum you'll remember is determined by the magnetic point of number, in this case also your magnetic quantum number that is, we just write M for now, sometimes you write MI or NS, so Z component of angular momentum is given by M x H cross, and as usual M goes from +I to –I, so it's a 2I +1 values, okay, so the treatment is very similar to this angular momentum that we have done in case of electronic orbits or even for spin.

So for proton the spin, what is the spin for proton? I think you know this, spin for proton, spin quantum number for proton, 1/2 so what are the values of M for proton? +1/2 and −1/2, so you

have something pointing upwards that is one possibility or you can have it pointing downwards that is another possibility, can it be like this? Can it be like this or this? No right, that has to be an angle, why? What is the length? What is the length of the arrow? Spin quantum number is 1/2, so the length of the arrow is square root of 1/2 into 1/2 + 1, 3/2, so what will it be? Root 3/2 H cross, and what is this Z component? Z component is H cross/2 isn't it? Right, so if this side is H cross/2, this side is root 3/2 H cross, you can understand that if the angle can never be 0 right, that has to be some angle and you can work out what the angle is from the sine or cos values, some well-defined angle. So what angle is this theta? Right, angle be Z axis is theta, what is the phi value? Phi value is not defined, this is important to remember very soon we'll start drawing cones, reason why we draw cones all the time is that for the spin theta is well-defined because you have a specific value of M and a specific value of I, phi is not defined, so you can think that this is the localized all over the cone for which a particular theta value is defined, alright.

So now we have the spin, fine, what happens when you apply a magnetic field?
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The effect of magnetic fields on nuclei

For a steady magnetic field B_0,

$E = -\mu B_0$ (μ = Magnetic moment = γI)

γ = Magnetogyric ratio; $\gamma\hbar = g_i \mu_N$)

$\mu_N = e\hbar/2m_p$ = Nuclear magneton = 5.051×10^{-27} JT^{-1}

g_i = Nuclear g factor (Range = -6 to +6),

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Of course we are going to do a proper quantum mechanical treatment of this next week, and when you do a proper quantum mechanical treatment we'll talk about the interaction we have to write the Hamiltonian and so on and so forth, but if we, for today if we take a little easier approach then this is what we can think, for a magnetic field B0, if mu is the magnetic moment that is associated with the nucleus that magnetic moment classically is given by gamma into I, well gamma I think you know is magnetogyric ratio or gyromagnetic ratio, both terms are used, it is given by GI into mu N, mu N is your nuclear magneton, are you familiar with the term Bohr magneton, you learnt it in context of hydrogen atom perhaps, this here is the nuclear equivalent, nuclear magneton which has a sum specific very small value, okay.

So the interaction energy is given by E = -mu x B0, not very difficult to understand you can even intuitively you can perhaps accept this result –mu x B0 and then if you consider the field to be along Z direction,
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The effect of magnetic fields on nuclei

For a steady magnetic field B_0,

$E = -\mu B_0$ (μ = Magnetic moment = γI)

γ = Magnetogyric ratio; $\gamma\hbar = g_I \mu_N$)

$\mu_N = e\hbar/2m_p$ = Nuclear magneton = 5.051×10^{-27} JT^{-1}

g_I = Nuclear g factor (Range = -6 to +6),

Considering the field to be along the z-direction,

$\mu_z = \gamma I_z = \gamma m \hbar$; $E = -\mu_z B_0 = -\gamma m \hbar B_0$

Different spin states have different energies in the presence of a magnetic f

of course field will be along a particular direction and the convention is you define that direction to be Z, so you can write it in terms of Z.

Now what will be important really is the Z component of the nuclear magnetic moment, right mu Z so if the field is along Z direction then you write mu Z is gamma IZ so E will be –mu Z x B0 extrapolating from here that will be –gamma M H cross B0, okay, now you see if I apply a magnetic field, now what happens, what are the possible values of N for a nucleus, for a proton? +1/2 and –1/2, M is + 1/2 and – 1/2 don't forget, right, so if it is +1/2 what is the energy of interaction? This M is 1/2, so 1/2 – 1/2 multiplied by gamma H cross B0, and if M is –1/2 then what will it be? Same but with a plus sign, so minus and plus what is the difference? Energy minus means lower energy or higher energy, lower energy stabilization, energy plus means higher energy so you can think of a situation like this, but before that well this is just a prelude of what will happen next week, so now that you know this term you know very well how we formulate quantum mechanical problems, we think of the classical mechanical interactions as far as possible, and from there we try to construct the contributions to Hamiltonian that is what we'll do next week using this Hamiltonian.

But for now you can think like this, when the field is off,
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Nuclear Magnetic Resonance

Spin ½ nucleus (^{1}H, ^{13}C)

Field off

when the field is off is there any energy of interaction? Of course not, if there is no field what will the nucleus interact with, so both alpha and beta have the same energy, here we are showing some proton, now when the field turns on you've told me that the alpha spin that is stabilized and the beta spin is destabilize, so this is the situation, all this figures that we used today are from Atkins textbook, so you can study this part from Atkins or from Banwell, it doesn't matter it's quite easy.
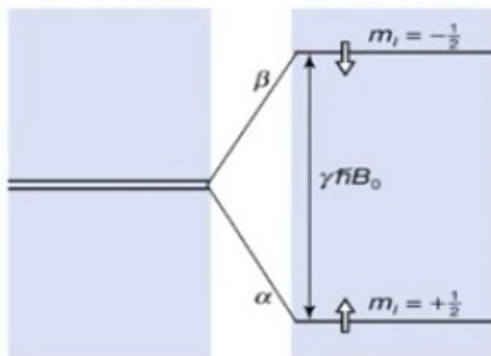
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Nuclear Magnetic Resonance

Spin ½ nucleus (^{1}H, ^{13}C)

Field off   Field on

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

β

$\gamma\hbar B_0$

α

$m_I = +\frac{1}{2}$

$$\Delta E = E_\alpha - E_\beta = \tfrac{1}{2}\,\gamma\hbar B_0 - (-\tfrac{1}{2}\,\gamma\hbar B_0) = \gamma\hbar B_0$$

Next part you can study from Mcquarrie and Simon or I'll tell you another book, okay, so this is what happens, alpha spin is stabilized, beta spin is destabilized and the magnitudes are in both cases 1/2 gamma H cross B0, so the difference of course becomes gamma H cross B0.

Now it is not at all difficult to see that this difference depends on the magnitude of the field you use, if B0 increases then the splitting is also more, right, the separation between energies of alpha and beta spins are also more, okay, so this is where it is different from what we have been studying so far, say vibrational spectroscopy or rotational spectroscopy, the energy gaps are intrinsic properties of the molecules or atoms are disturbed, of course do you say atoms how will it rotate or vibrate, molecules that you study, but in this case the energy gap that you have is very much a function of the field that we use, and that allows us to change the resolution of our experiment, as you have understand more splitting means better resolution, do you agree with me? Is it easier to measure 1 micron or 1 foot? 1 foot, right, so if you can make the separation bigger it is easier to measure, of course there is a limit to it, it is easier to measure 1 foot than the distance between earth and what is the star that has been found very recently earlier this week? Let us see who can answer this question. Icarus, that star has been named Icarus of course I'll leave it to you to study the story of Icarus, why it is called Icarus, that you can study, but of course it's not so easy to measure that distance, so there is always some compromise value somewhere.
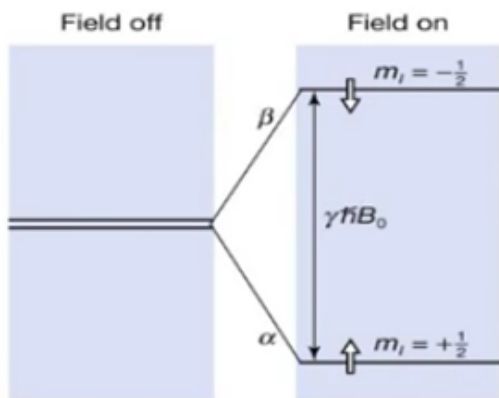
So greater B0 means bigger splitting and therefore better resolution, we'll develop on this point a little later again, but for now you can say that now if I bring in light whose energy is equal to gamma H cross B0, then I have resonance, Bohr resonance condition is satisfy, so this is your Bohr resonance condition equal to gamma and nu L, when nu L is the frequency of light that you are using, and typically this would be in radiofrequency rigid, okay, the kind of magnetic field that are used, if you use too bigger magnetic field then actually some other effects come in, so you don't want to do that, so the splitting that you typically induce is in microwave regime so you can use microwave to Cobbett, so once again this is somewhat like a pump probe experiment is it not, we have discussed pump probe earlier, we use a pump to excite to create an excitation population and then you use a probe to investigate it. In this case also it's a little different, you are absolutely creating the excited state itself by using the magnetic field and then you use the light to probe the differences, alright.
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Nuclear Magnetic Resonance

Field off   **Field on**

Spin ½ nucleus (^1H, ^{13}C)

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

β

$\Delta E = E_\alpha - E_\beta = \frac{1}{2}\gamma\hbar B_0 - (-\frac{1}{2}\gamma\hbar B_0) = \gamma\hbar B_0$

$\gamma\hbar B_0$

$= h\nu_L$ i.e. $\nu_L = \gamma B_0 / 2\pi$

Resonance: The energy of the EM radiation matches the energy gap

α $m_i = +\frac{1}{2}$

$B_0 = 12T$, $\nu_L = 500$ MHz for protons

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Now the reason why we write nu L, okay we'll come to that but we are here, your typical value, if you use a magnetic field of 12 tesla, is 12 tesla large magnetic field or a small magnetic field? So okay, let's put things in perspective, you've seen bar magnets, how many tesla is there? Small bar magnets, yes, maybe even less than that. 12 tesla well you can work with bigger magnetic field as 12 tesla is not very small, see sometimes you read off accidents in MRI machines right, somebody entered with the gas cylinder and immediately got sucked into the machine and somebody died right last month or something, so it is not too smaller magnetic field, 12 tesla is definitely not too smaller magnetic field, that is why if you have specsmaker and all you are asked not to go near, when we enter NMR lab we're asked to discard all metallic object, and if you have say some operation by which some screw or plate has been inserted in your body you better stay away from NMR machine, it is not too smaller thing.

So if you use 12 tesla then this frequency is 500 megahertz for protons what will it be determine by? It will be determine by not only B0, but also gamma the magnetogyric ratio, so for protons it is 500 megahertz. Now those of you who are little familiar with NMR spectroscopy would know that in our department we have an NMR machine, don't we? How many megahertz machine is that? 600 is there in safe, not in our department, in our department we have a 500 megahertz machine, it's huge right, huge actually what is huge is the diver but then the magnet inside is also huge, so the reason why or machine in the department is called a 500 megahertz machine is this, the magnet inside that machine is at 12 tesla magnet, alright, then of course you can figure out what is the, how big the magnet, what is the magnetic field strength of the machine in your safe? In safe you have a 600 megahertz machine. From these values can you not calculate? What is the magnetic field of that machine? It's directly proportional, isn't it? It's directly proportional to B0, so if 500 megahertz corresponds to 12 tesla, 600 megahertz corresponds to how much? 12 multiplied by 6 divided by 5, okay you can do the math.

So we also have a 750 megahertz machine in, well the same building as safe 7 tiers that you can calculate what is the magnetic field of that magnet there, okay, so basically the bigger, this megahertz value is bigger is the magnet, stronger is the magnet that to say, okay, that is all that is there.

Why do you want to use a stronger magnet? Because you get a greater splitting and even intuitively we have said that a bigger splitting is better, so as we go further in this discussion we'll understand in a little more detail, why it is better to get a greater splitting, we'll come slowly, but for now don't forget we're talking about the isolated proton, the physics, not so interesting so far, not chemistry yet, when it becomes chemistry then it is interesting, right Shubna? Alright.

Now but before we go there one thing, whether I should say is that nu L,
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Nuclear Magnetic Resonance

Spin ½ nucleus (^{1}H, ^{13}C)

Field off   Field on

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

β

$\gamma\hbar B_0$

α $m_I = +\frac{1}{2}$

$\Delta E = E_\alpha - E_\beta = \frac{1}{2}\gamma\hbar B_0 - (-\frac{1}{2}\gamma\hbar B_0) = \gamma\hbar B_0$

$= h\nu_L$ i.e. $\nu_L = \gamma B_0 / 2\pi$

Resonance: The energy of the EM radiation matches the energy gap

$B_0 = 12T$, $\nu_L = 500$ MHz for protons

ν_L : **precessional frequency**
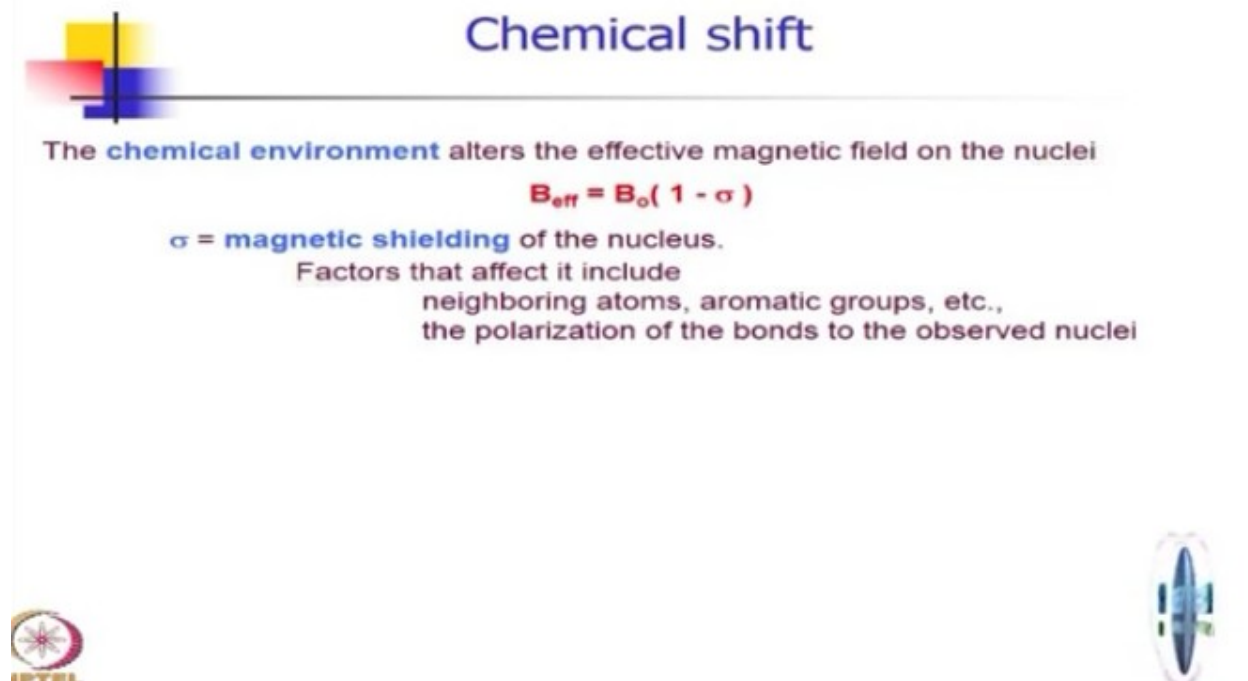
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that L is not for light, L is for Larmor, LARMOR, it is called the Larmor precessional frequency. Now see the thing is this when we discuss NMR, the right thing to do is to use quantum mechanics and proceed accordingly, fortunately for us you can understand what is going on even without using quantum mechanics, the classical model can give you at least qualitatively more or less correct picture, and the classical model is if you have this kind of an angular momentum in a magnetic field, what kind of a motion do you expect? We expect a precessional motion, okay, I'll not work it out here because it's too simple, if you read this portion from Banwell's book you will see the frequency of this precessional motion has been worked out and the expression for this, what is called Larmor precession frequency comes out to be the same, so that is something that is a kind of amusing, the frequency of precession of the angular momentum around the applied field axis is exactly the same as the frequency of light required for a transition from alpha spin to beta spin, okay, it's just like that, what can we do about it? So this is your

homework, please read this portion about precessional frequency either from Atkins book or from Banwell's book, right.

Whatever I have said all that was physics so far, now it becomes interesting when you think of its applications in chemistry, right, what is the hindi for chemistry? Hindi word for chemistry? Rasaayan right? Yeah so, there may be some other version I don't know but then the ras comes only when you enter the saayan, so the reason why it becomes so interesting for chemist is that, if you now move from bare nuclei to nuclei inside molecules, then something interesting happens.

Now see when it's inside molecules you can think that you have this nuclei enveloped by charge cloud provided by electrons, right, so one extreme is no charge cloud, so you have something, if you have a charge cloud then what happens? Then charge cloud itself there some magnetic, some reaction magnetic field will be generated when you apply a magnetic field, right, that is going to, well as the first approximation that is going to sort of shield the nucleus to some extent from the magnetic field that has been applied, right, so this is like survival instinct of the molecule, you apply a magnetic field immediately the electrons that are there set up a magnetic field which is opposite in direction, that is of course physics, right, so but then the thing is in a molecule if you think of different nuclei, they are in different chemical environments which translates as they are surrounded by different amounts of charge density, so this shielding part that is there is different for different nuclei in different chemical environments, as a result what you get is you get something called chemical shift.

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Chemical shift

The **chemical environment** alters the effective magnetic field on the nuclei

$$B_{eff} = B_0(1 - \sigma)$$

σ = **magnetic shielding** of the nucleus.
Factors that affect it include
neighboring atoms, aromatic groups, etc.,
the polarization of the bonds to the observed nuclei

So what are we saying? We are saying that the effective magnetic field failed by the nucleus is something like this B0 multiplied by 1 – sigma, where sigma is the shielding constant, it depends on how much of electron is there around that particular nucleus, and in even in the same molecule different nuclei will have experience different amounts of electron charge cloud around

them and therefore will have different values of sigma, shielding constant, right, so what happens is if you now instead of B0 if you write B effective in the expression of Larmor frequency this is what you get,

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Chemical shift

The **chemical environment** alters the effective magnetic field on the nuclei

$$B_{eff} = B_0(1 - \sigma)$$

σ = **magnetic shielding** of the nucleus.
Factors that affect it include
neighboring atoms, aromatic groups, etc.,
the polarization of the bonds to the observed nuclei

$$\nu_L = \frac{\gamma B_{eff}}{2\pi} = (1-\sigma)\frac{\gamma B_0}{2\pi}$$

Larmor frequency is 1-sigma multiplied by gamma B0 divided by 2 pi.

Now suppose you focus on one kind of molecules, one kind of nucleus sorry, protons, you use a 12 tesla magnetic field, what is the expected Larmor frequency? 500 megahertz, okay, but then if you have 3 kinds of protons, let's say go back to the only example that will be using alcohol CH3, CH2 OH, so OH proton, CH2 proton, CH3 proton they're in different kinds of chemical environments and they'll have different sigma values, and therefore nu L will also be different, right, so that is what it is.
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If you look at a low resolution NMR spectrum of alcohol then you actually expect three different lines or three different Larmor frequencies depending on what kind of chemical environment each kind of proton is, okay, now why CH3 protons are in high field, why OH protons are in low field let us not even worry about that at the moment that is not very difficult to understand, but the point to understand here is that you should have 3 different kinds of Larmor frequencies.

Of course the problem here is that if you want to work with these frequencies or this, then the issue is we just said that the frequencies are dependent on the magnetic field that you use, okay, so instead of 12 tesla magnetic field if I use 16 tesla, what will happen? The Larmor frequencies will all change, right, and in fact at 12 tesla magnet that we have here, and a 12 tesla magnet that we might have in Pune, actually 12 is never 12 right, there is always a tolerance, so even between 12 machines there will be a variation of spectra that's not a happy situation, okay, when I get a spectrum I don't want to say that this is recorded on the booker machine situated in IIT Bombay Chemistry Department, this is the latitude, this is the longitude, this is the time of measurement, but actually even on the same machine if you measure now and 5 years later your frequencies will be different because magnetic field is not something that does not change overtime, so there must be some way in which we can find the way of defining these chemical shifts sigma without being dependent on the magnetic field that we have used, that is why instead of sigma we use this delta scale, okay.

What is delta scale? We've already said this two, delta scale is defined like this,
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The δ scale

- The frequency of resonance is field-dependent

- A relative scale, is a less ambiguous representation of the signal of a particular nucleus.

$$\delta = \frac{\nu - \nu_0}{\nu_0} \times 10^6 \; ppm = \frac{(1-\sigma)B_o - (1-\sigma_0)B_o}{(1-\sigma_0)B_o} \times 10^6 \; ppm$$

so what you do is if you want to eliminate the dependence on the instrument then the best way to go about it is to wake up and to use a reference, okay, so what you do is you do back to back measurements, you use some reference, let us say nu for the reference is nu 0, and let us say nu for your sample is nu, then delta is defined by nu – nu 0/nu 0, we could have actually stopped there but then that comes out to something like 10 to the power -6, okay, because nu- nu 0 compared to nu 0 is small so it is for good measure multiplied by 10 to the power 6 and the unit is given us parts per million PPM, so when that happens you put in the values of these nu and nu 0 you get 1 – sigma multiplied by B0 – 1 – sigma 0 multiplied by B0 divided by 1 – sigma 0 multiplied by B0, okay, even without simplifying this any further you can see that B0 cancels in this expression right, there is one B0 in the numerator and one B0 in the denominator they just cancel off, so you are left with something like I don't know why I did not write the next step, but bear with me, so we are left with something like sigma 0 – sigma divided by 1 – sigma 0, alright, so this is your delta scale. The good thing about delta is that delta on one hand is field independent it does not matter whether you make the measurement here or in kamtschatka you get the same value of delta always.

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The δ scale

- The frequency of resonance is field-dependent
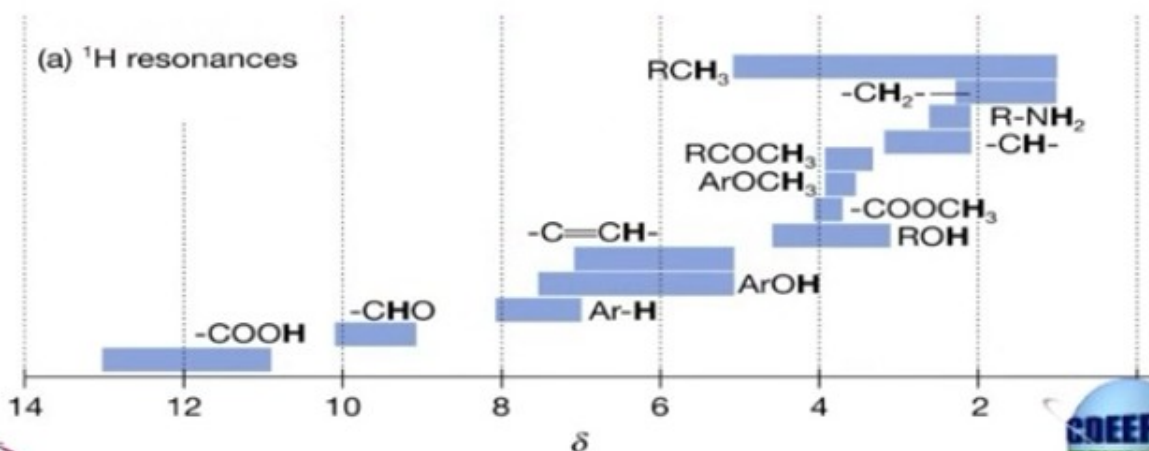- A relative scale, is a less ambiguous representation of the signal of a particular nucleus.

$$\delta = \frac{\nu - \nu_0}{\nu_0} \times 10^6 \ ppm = \frac{(1-\sigma)B_o - (1-\sigma_0)B_o}{(1-\sigma_0)B_o} \times 10^6 \ ppm$$

δ is field-independent
$$\delta \ \alpha \ (-\sigma)$$

And on the other hand delta is proportional to sigma, so it gives you the same information. And as most of us would know the most commonly used reference that is your tetramethylsilane and there are reasons why you use tetramethylsilane, great, so these are the characteristic ratios, and as I said this figures are yes,
(Refer Slide Time: 34:20)

Characteristic Chemical shifts: ^{1}H Resonances

(a) ^{1}H resonances

RCH$_3$
-CH$_2$-
R-NH$_2$
-CH-
RCOCH$_3$
ArOCH$_3$
-COOCH$_3$
ROH
-C=CH-
ArOH
-CHO
Ar-H
-COOH

14   12   10   8   6   4   2

δ

you said something? Once the magnetic field has been applied, so if you remember when you have this kind of a charge cloud you apply the magnetic field, right, then what happens is this reaction field is set up right, you can think classically of this charge cloud in motion, right, the

resultant magnetic field that you get from there is always opposing to the magnetic field that you employ, isn't it? This is something that you must have studied in this electricity and magnetism in 11th and 12th?

Yes so, so you think of it as charge particle in motion, magnetic field is constant electron is not, electron is moving right, so classical picture is moving an orbit, okay fine, but what I'm trying to say is that even if the B0 is same, now what I'm saying is that you fix the magnetic field, so if you think of the big magnetic field, thinks of the lines of force they're all the same, that's what you're trying to say isn't it? No, I mean I thought the moment you apply a magnetic field, the opposing field is set up right, I don't see a problem with that, no, no, no let's just discuss that later, no, when you have a constant magnetic field then also you do get the opposing field, we'll discuss it offline, alright, so these are the characteristic chemical shift and these are the characteristic chemicals well that one was for proton, this is for 13C NMR.
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Ring currents

Ring current

Magnetic field
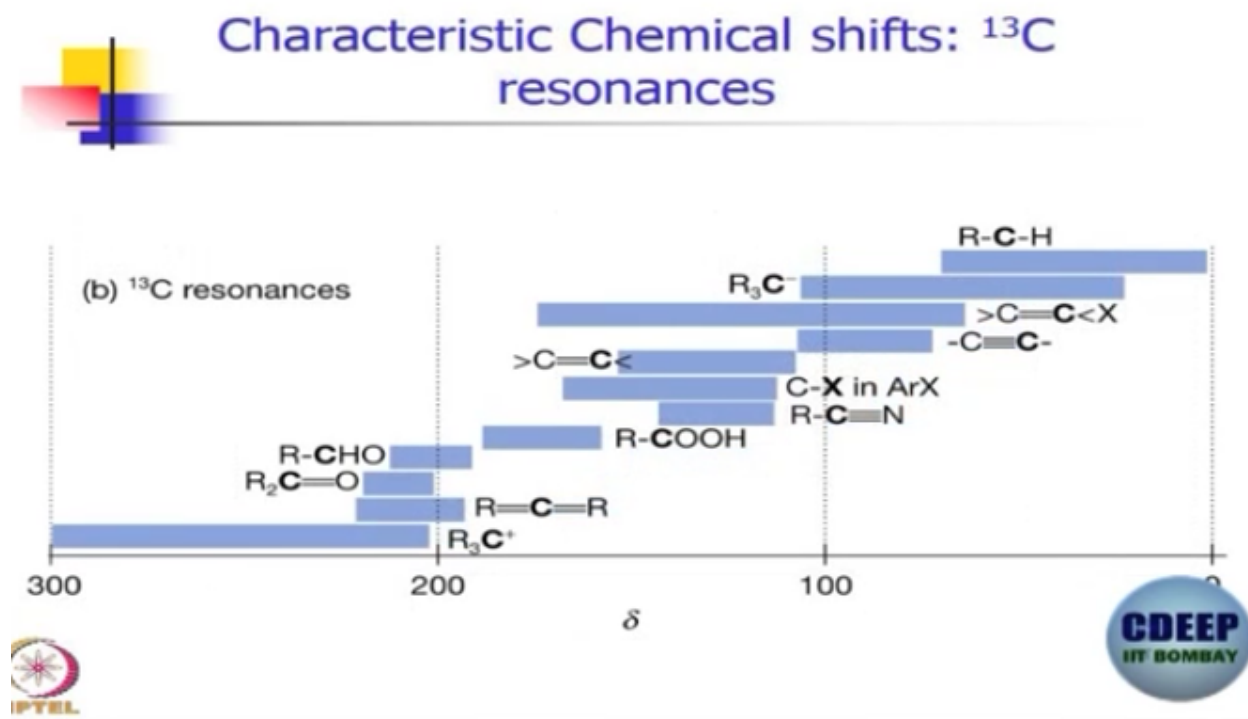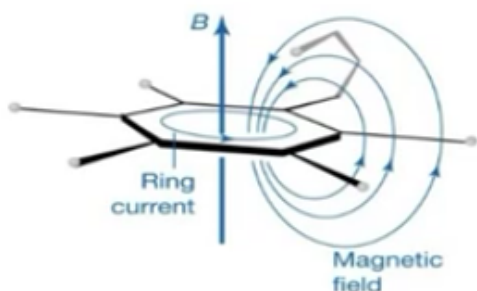
Now so one kind of this opposing field that becomes very important is when you have aromatic systems, because this 5 electron cloud is more loosely held, so ring currents can actually give you a greater shielding and this is an example that perhaps many of us who would know already, here in the same molecule you have protons that are shielded and you have protons that are de-shielded but because of the same field, so what we've shown here is this is the direction of the applied magnetic field, and these are the lines of force of the reaction field, okay.

Now see, you think of this proton, what is the situation in this proton? And what is the situation in this proton? You think of this proton you see the applied field is upward and the lines of force of the reaction field are downwards,

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Ring currents
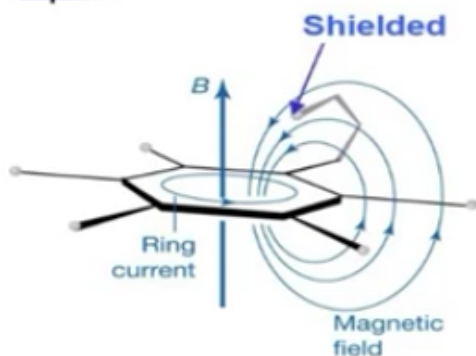
so this proton is actually shielded, the effective field at this proton is less than the applied magnetic field, but if you think of this one here we have something funny, we have an applied magnetic field, lines of force of the reaction field are also pointing upwards, so here in this case actually the reaction field reinforces the applied field for this proton, so this proton here is going to get de-shielded, okay,

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Ring currents
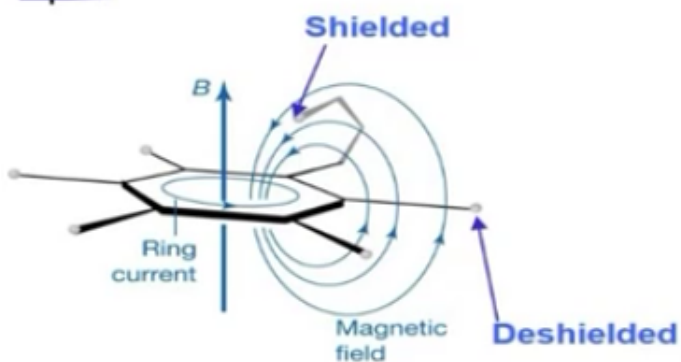
this is what same is true for this one, doesn't matter.

And this kind of shielding and de-shielding in case of aromatic rings is not restricted to protons that are covalently attached to the ring, even if you use a solvent like benzene then you can see this strong shielding and de-shielding effects of solid molecules,
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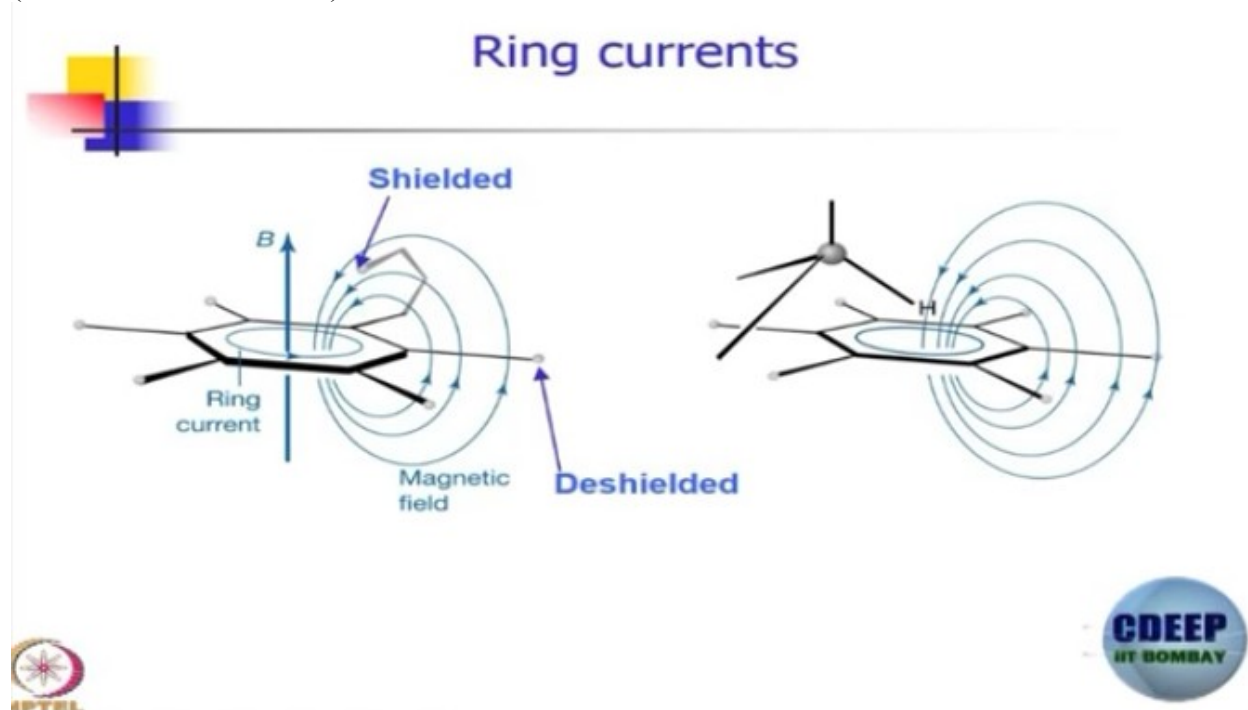
of course this is a transient effects, so interpreting the data is the little more involved than what I might have given the impression of right now, okay.

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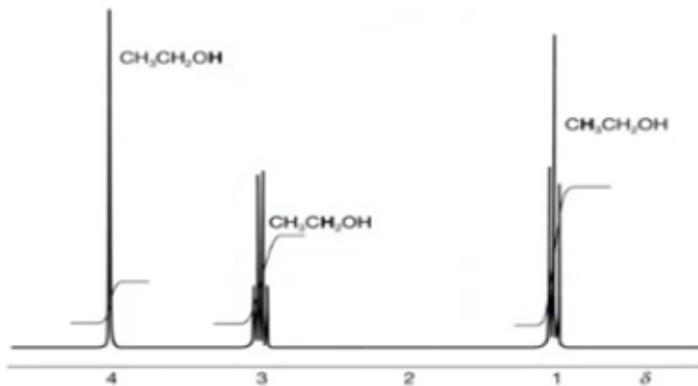
Three groups of lines =
Three kinds of protons

So this here is an actual spectrum, NMR spectrum of ethanol, so what I will see? What do we expect? We expect 3 groups of lines, we have 3 groups of lines, and then we expect the intensities to be proportional to abundance, so the way that is done in NMR spectroscopy is that as you see none of this lines and as we have learnt earlier also,

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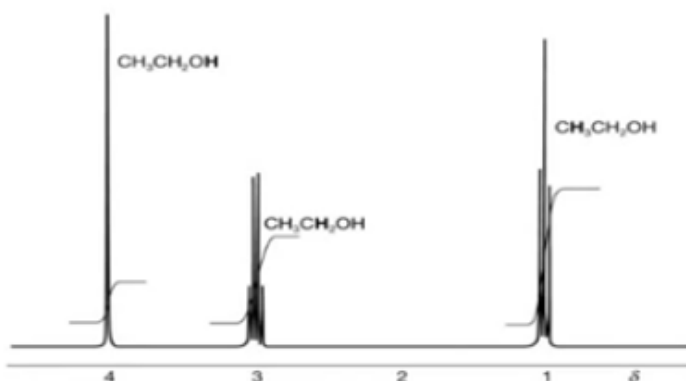
Three groups of lines =
Three kinds of protons

Areas: Relative intensities =
Abundance

a spectral line is never like a delta function, right, there is always a width, so if you want to talk about abundance what you need to do is, you need to work out the area under the curve,

integrate, so when you integrate this is how the data is typically shown, this here you go from here to here, this is 0, this is the length of this sigmoid kind of curve is proportional to the area under the curve, and you can see that this is to this is to this is about 1:2:3, that gives you the number of protons contributing to each of these groups of lines.

So see the area under the curve gives you relative abundance, so since the area under this curve is such large compare to this one, from here we can see that these lines must be for CH3 protons, this one is more than this, double than this, so these must be for CH2 protons, this must be for the OH proton, okay,
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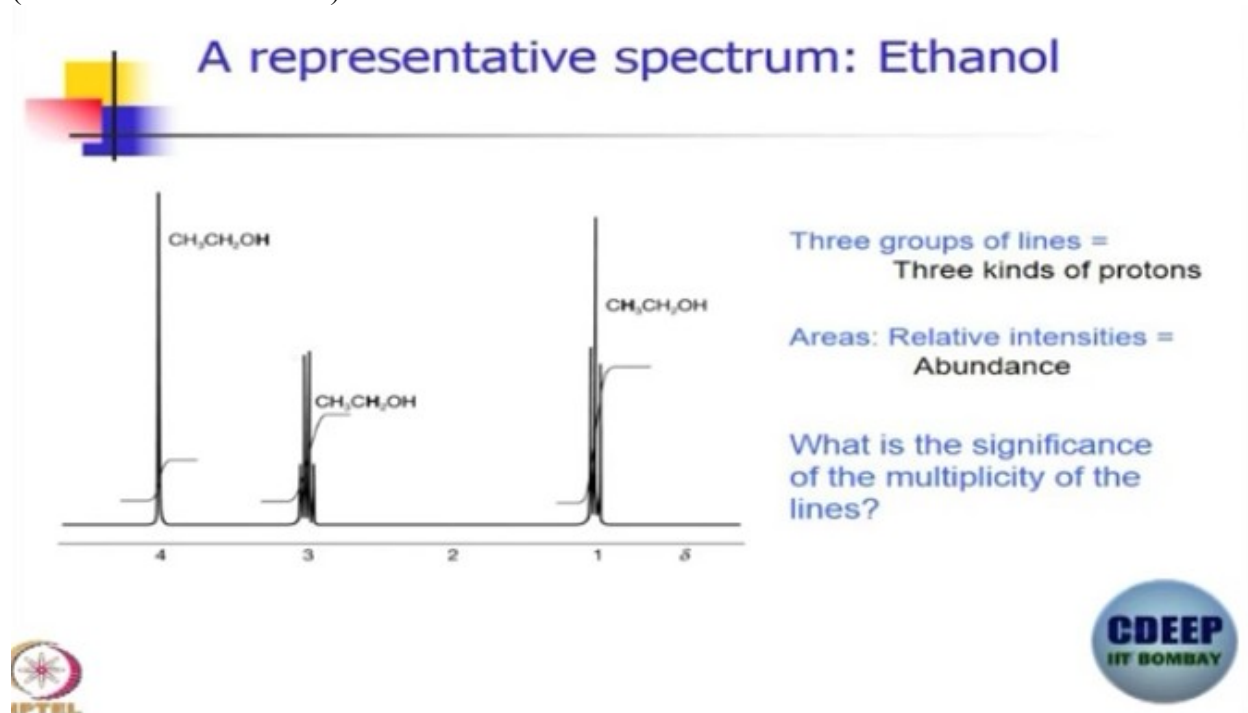
now the question that arises is why is it that we don't have nice single lines, why do we have so much of line structure? And the answer to that is that there is coupling between different kinds of protons, what is the meaning of coupling?
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The fine structure: Spin-spin Coupling
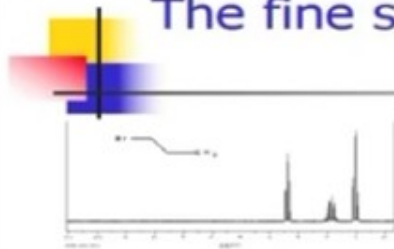
Small alteration in the magnetic field experienced by a nucleus due to other magnetic nuclei ▸ Fine structure in the spectra

 Okay, think of magnet that is suspended, one of the classical experiments that you might have even done yourself when you are in school take a bar magnet, and suspend it using a strength what happens? It orients itself in the North-South direction, okay, that is because that is the direction of earth's magnetic field and that is what causes the preferential orientation.

Now if you bring another magnet near it, doesn't orientation change? Why does it change? Because of the magnetic field of the second magnet you have brought near it, so the analogy with NMR is that you can think the earth's magnetic field is analogous to that 12 tesla, 15 tesla magnetic field that you are using in the NMR machine and the nuclei are like the small bar magnets, since they are closed to each other they will also orient each other's annetts, they will also determine each other's energy to some extent which will be secondary effect, this is called coupling in a very qualitative manner.
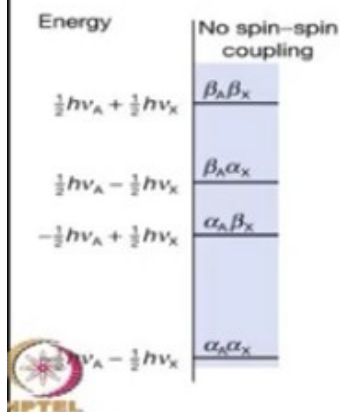
We'll do a little more detailed quantum mechanical treatment of this spin-spin coupling next week.

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The fine structure: Spin-spin Coupling
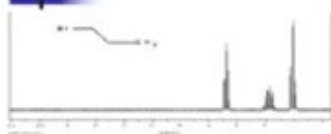
Small alteration in the magnetic field experienced by a nucleus due to other magnetic nuclei ▸ Fine structure in the spectra

But we can do it actually qualitatively because it can be done qualitatively without much hassle, so if you think of a 2 spin system, okay, I have 2 protons, okay, and we are considering 2 protons with different chemical shifts, this is called an AX system, are you familiar with this terminology? When do I say a 2 spin system is an AB system, when do I say that the 2 spin system is an AX system? Actually it's very easy to understand, think of the English alphabet, B is right next to it, and X is very far away from A that's what it means, if the two groups of protons, if the two protons right now not groups, if the two protons have chemical shifts that are different but not very different close to each other, then that is an AB system, and if the chemical shifts are significantly different then it is an AX system, that's all.
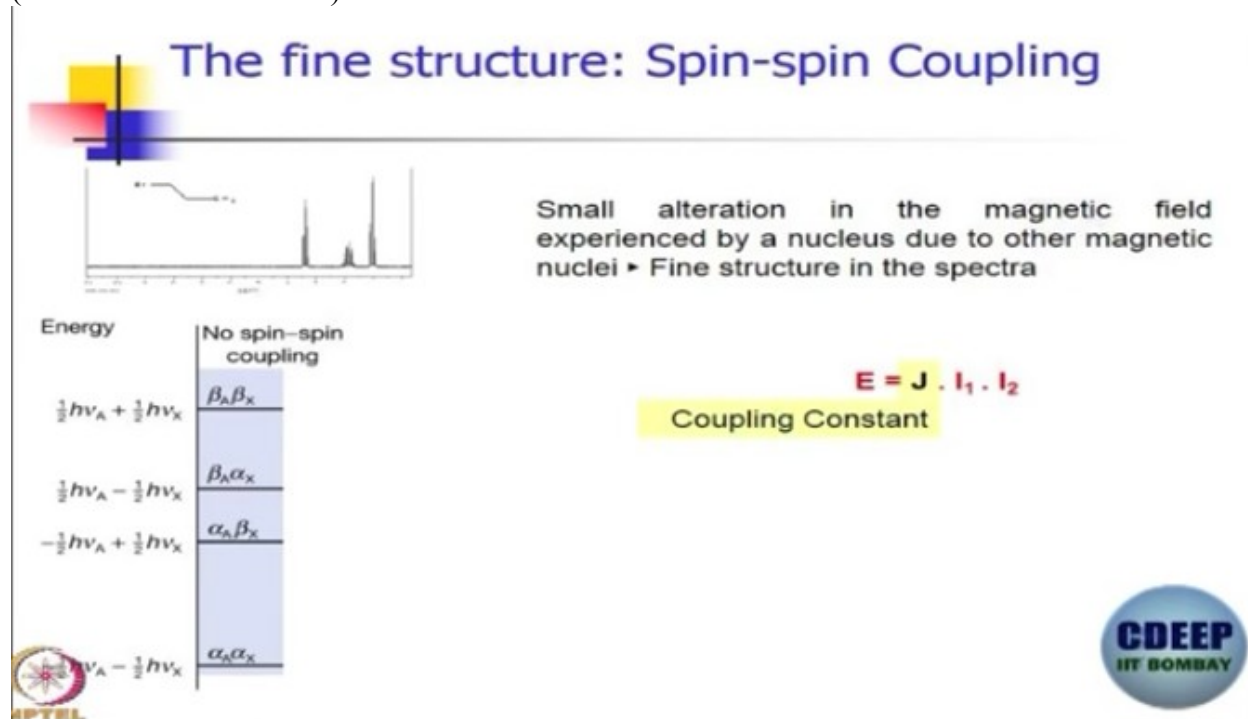
Here we are talking about AX system but the chemical shifts are different, as we are going to discuss at least B3 later on, there is a reason why we want to work with AX systems. If the chemical shifts are very different then the magnitude of coupling is small compare to the chemical shifts, that is what gives us what we call first order spectra, you understand what I'm saying, you have this bar magnet suspended and then it's pointing North South right, so and you bring it another bar magnet, if the strength of the second bar magnet is more or less same as the earth's magnetic field, then you have a more complicated problem, but if this second bar magnet has a small magnetic field then you can treat it as a small perturbation over and above the existing system that is there, okay, so if you have a large chemical shift will coupling change, will coupling depend upon the magnetic field that you use? No right, because coupling is, coupling between nucleus spins they are intrinsic properties.

Now you use a bigger magnetic field and cause a bigger chemical shift, but when I say shift I don't mean delta I mean sigma or nu L if that helps, so then what happens is this effect of coupling does not get convoluted with the effect of chemical shift. We'll elaborate upon this a little later.

For now we have two systems alpha, this A and X, right, what is the happier situation? If you remember the expression for the energy of interaction of the magnetic field with spin, what is that expression? Magnetogyric ratio gamma multiplied by M, multiplied by H cross, is there a minus before that? There is a minus right, so we said that alpha spin with M + 1/2 is stabilized beta spin with –1/2 gets de-stabilized, so now we have a two spin system, if both have up spin, both are alpha, then both will be stabilized thus the least energy situation, so the lowest energy situation is this, this will be the energy –1/2 the way it is written here H nu A –1/2 H nu X, this is the alpha A, alpha X situation, both are up spin.

What is the diametrically opposite situation when both are beta? Both will be de-stabilized, and what is the energy then? Now it is +1/2 H nu A, +1/2 H nu X, beta A beta X, what are the two intermediate ones? One is up one is down, okay one is up one is down, so then these are two alpha A beta X, and beta A alpha X, and this is the situation that we have in absence of any coupling, okay, only external magnetic field is there.
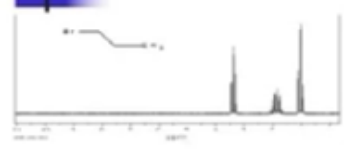
Now let us bring in coupling as a perturbation. So even intuitively we can say that the energy of coupling is going to depend on the, on both the spin quantum numbers right, on both the spins, do you agree with that? The coupling energy is given as $E = J \times I_1 \times I_2$, right, because if I_1 is 0 or $I_2 = 0$ then there is no coupling anyway, so this J is called the coupling constant, (Refer Slide Time: 46:25)

The fine structure: Spin-spin Coupling

Small alteration in the magnetic field experienced by a nucleus due to other magnetic nuclei ▸ Fine structure in the spectra

$$E = J \cdot I_1 \cdot I_2$$
Coupling Constant

Energy | No spin–spin coupling

$\frac{1}{2}h\nu_A + \frac{1}{2}h\nu_X$ $\beta_A\beta_X$

$\frac{1}{2}h\nu_A - \frac{1}{2}h\nu_X$ $\beta_A\alpha_X$

$-\frac{1}{2}h\nu_A + \frac{1}{2}h\nu_X$ $\alpha_A\beta_X$

$\nu_A - \frac{1}{2}h\nu_X$ $\alpha_A\alpha_X$

coupling constant is something that as we will see we can determine experimentally, but you can also find out the value of coupling constant theoretically that is what people like Professor Rajaraman do many times. Theoretically you can actually arrive at the expected coupling constant values.

So if this is the case, now see in, what will happen now? When I say I1, I2, I have to consider the M values when both the M values are +1/2 then what will happen? Stabilization or de-stabilization, de-stabilization 1/2 x 1/2,
(Refer Slide Time: 47:05)

The fine structure: Spin-spin Coupling

Small alteration in the magnetic field experienced by a nucleus due to other magnetic nuclei ▸ Fine structure in the spectra

Energy | No spin–spin coupling

$\frac{1}{2}h\nu_A + \frac{1}{2}h\nu_X$ $\beta_A\beta_X$

$\frac{1}{2}h\nu_A - \frac{1}{2}h\nu_X$ $\beta_A\alpha_X$

$-\frac{1}{2}h\nu_A + \frac{1}{2}h\nu_X$ $\alpha_A\beta_X$

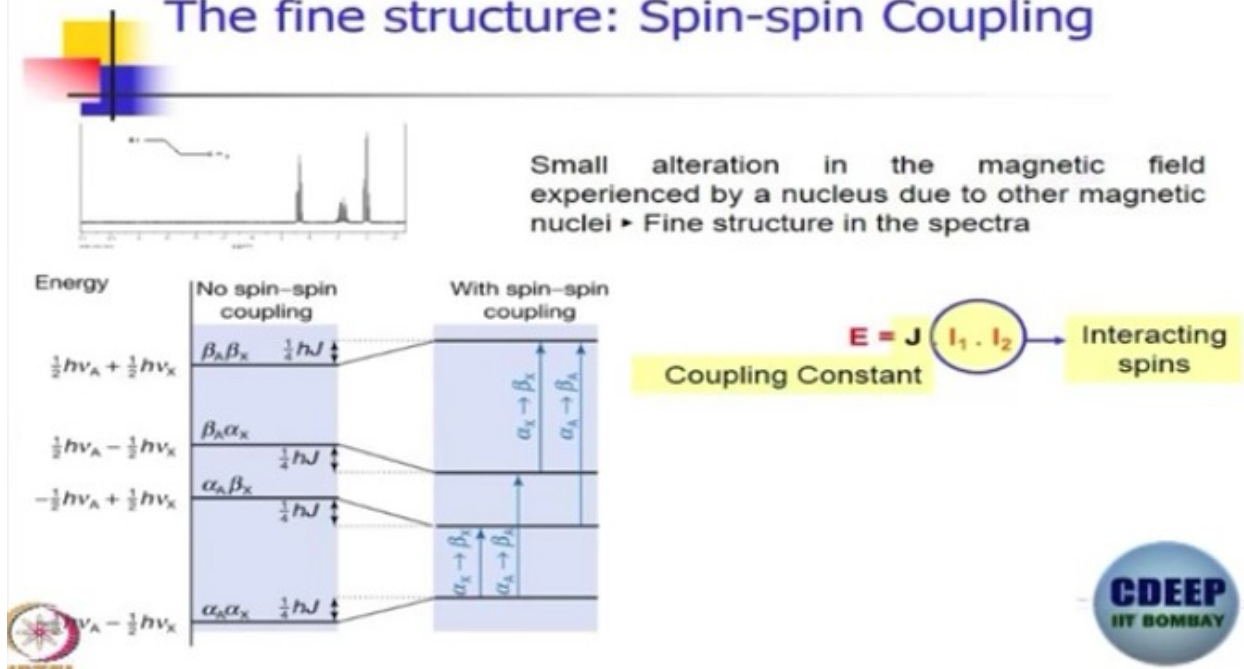$\nu_A - \frac{1}{2}h\nu_X$ $\alpha_A\alpha_X$

$E = J\,(\,I_1 \cdot I_2\,)$ → Interacting spins

Coupling Constant

one fourth so it will be 1/4ᵗʰ multiplied by J de-stabilization by that amount, what happens when both are minus? Again de-stabilization by 1/4ᵗʰ of J, what happens when one is plus, one is minus? You have stabilization by 1/4ᵗʰ of J that is how you get this one.

When you have alpha-alpha or beta-beta you get de-stabilization, when you have alpha-beta kind of situation you get stabilization. Of course one thing we have completely neglected here is, but this is AX, this is okay,
(Refer Slide Time: 47:40)

The fine structure: Spin-spin Coupling

Small alteration in the magnetic field experienced by a nucleus due to other magnetic nuclei ► Fine structure in the spectra

$$E = J(I_1 \cdot I_2)$$

Coupling Constant → Interacting spins

so now what will happen? Let us see what each transition stands for? Suppose you go from here to here alpha A alpha X, alpha A alpha X to alpha A beta X what has happened? Alpha A has remained alpha A, for the nucleus X there has been a spin flip from alpha to beta, right, so what is this transition? Is this transition for A or X or both? Alpha A alpha X to alpha A beta X is the spin flip in transition for A or X or both, X because alpha A is still alpha A, alpha X has become beta X, so going from the first level to second level is really a spin flipping only for X, not for A, and that is evident in the energies as well.

What is the energy of transition? You subtract this from this -1/2 H nu A - -1/2 H nu A that cancels, H nu X - -1/2 nu X that is how much? Yes, so this energy gap is H nu X, so in absence of coupling this transition gives you a line at nu X, the characteristic Larmor frequency of nucleus X, alright.

What happens if you go from alpha A alpha X to beta A alpha X? Alpha A alpha X to beta A alpha X, is it the spin flip for A or X or both, A and not X, clear? And you can again work out that the energy in that case is nu A, frequency is nu A, okay, so in the unperturbed situation when there is no coupling this is what you should get, you get a line at nu A, you get another line at nu X, alright.

What happens when you go from, okay can you go from alpha A alpha X to beta A beta X? If you could, what kind of a transition would it be? Alpha A alpha X to beta A beta X, that means A has undergone spin flip from alpha to beta, X has also undergone a spin flip from alpha to beta, right, can that happen? Can I do it in one transition? We cannot, because that would violate what we call one photon rule.

Did we talk about one photon rule earlier in this course? Okay, so what did we say at that time? That our photons are not like Rajnikanth's bullet, right, one photon is one packet of energy, it

cannot suddenly split and then cause one transition here and one transition there, okay, since photons are not Rajnikanth's bullets we cannot have alpha A alpha X to beta A beta X transition, are we clear? But what about these? Can I go from alpha A beta X to beta A beta X? Yes, so what is it? Alpha A beta X to beta A beta X? Which nucleus undergoes a flipping? A, and not X, and beta A alpha X to beta A beta X? X, what are the energy differences? Alpha A beta X to beta A beta X, what is the energy difference? Yes, H nu A or X? There are only two options, H nu A right.

Alpha A beta X to beta A beta X, 1/2 H nu A - -1/2 H nu A that is H nu A, and you have 1/2 H nu X – 1/2 H nu X that cancels, see it is A that is undergoing spin flipping, so energy has to be corresponding to the Larmor frequency of A and not X, okay. So even for this transition you expect the line at nu A nowhere else, and for this one you expect a line at nu X nowhere else, are we clear? So if there were no coupling then you expect 2 lines precisely at nu A and nu X, but now coupling has taken place, now what happens? So as we agreed energy of alpha A alpha X has been increased by HJ divided by 4, energy of this alpha betas have been decreased by 1/4th HJ, energy of beta-beta has been increased by 1/4th HJ, okay.

Now try to do it once again, now when we go from here to here what kind of transition is it? Alpha A alpha X to alpha A beta X, which nucleus undergoes a spin flip A or X? X, so this is your energy of one of the spin flips of X of course this diagram is very, very highly exaggerated, the stabilization, de-stabilization are not this much, but then if you draw it to scale you won't even sit perhaps, so now this energy you agree is the energy for transition of X, right, what is this energy? This whole thing was H nu X that has now gone down by 2 x 1/4th HJ, that is 1/2 HJ, is that right? This energy gap, what is it? H nu X, what is this energy gap? H nu X – 1/2 HJ, so now for that transition we will not get a line at nu X, where will we get the line? Somewhere here, and what will be the separation? 1/2 J/2 isn't it? H is gone because I'm plotting new and not energy, alright, so you don't get the line here for that transition, you get a line at a little lower energy, lower by J/2.

Now what is the other X transition from here to here? This one is beta A alpha X, this is beta A beta X, so when you go from here to here once again there is a spin flip of X that takes place. Once again this energy gap is H nu X, what is this energy gap? This time it is larger isn't it, it is larger by the same amount, so once again for that transition also you are not going to get a line here anymore,
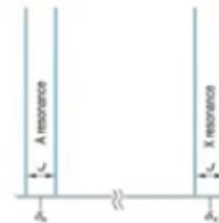
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The fine structure: Spin-spin Coupling
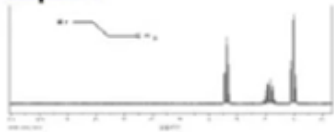
Small alteration in the magnetic field experienced by a nucleus due to other magnetic nuclei ► Fine structure in the spectra
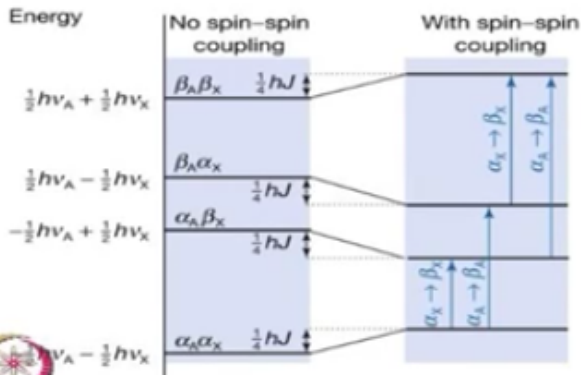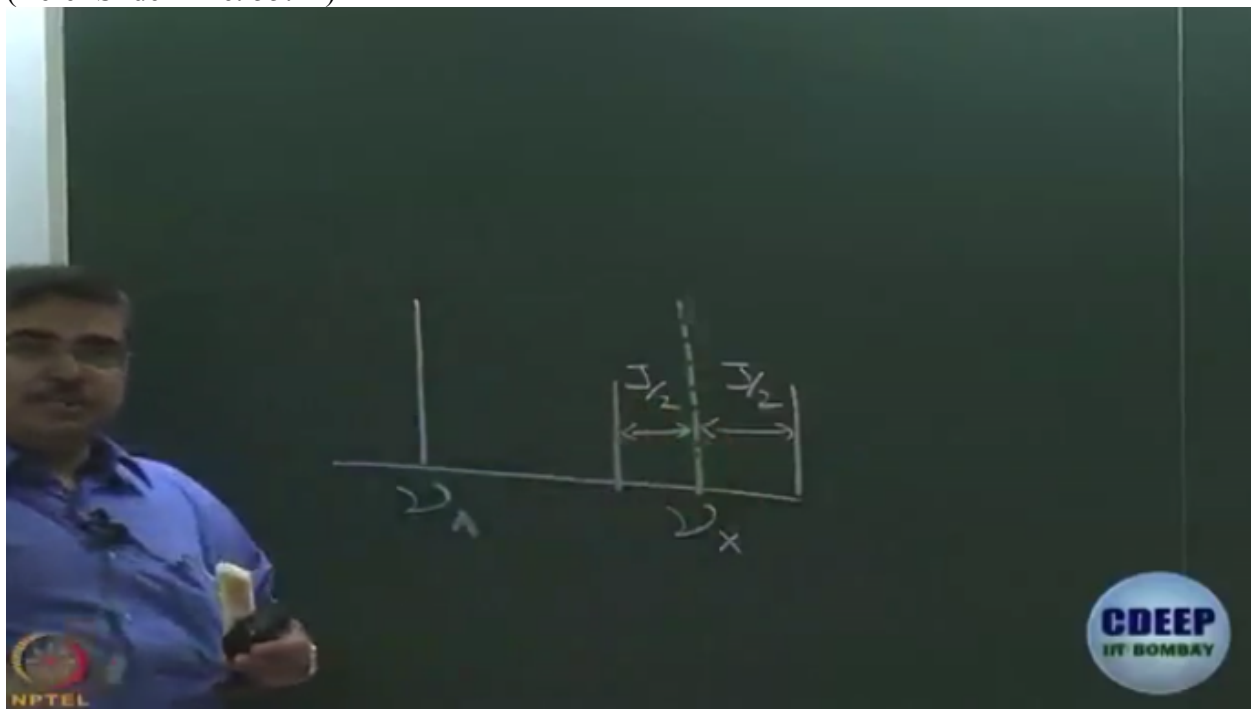
$$E = J (I_1 \cdot I_2) \rightarrow \text{Interacting spins}$$

Coupling Constant

you are still make it dash rather you are going to get a line which is higher in energy and there difference in frequency is J/2, so instead of a single line at nu X you get 2 lines at nu –J/2 and nu +J/2,
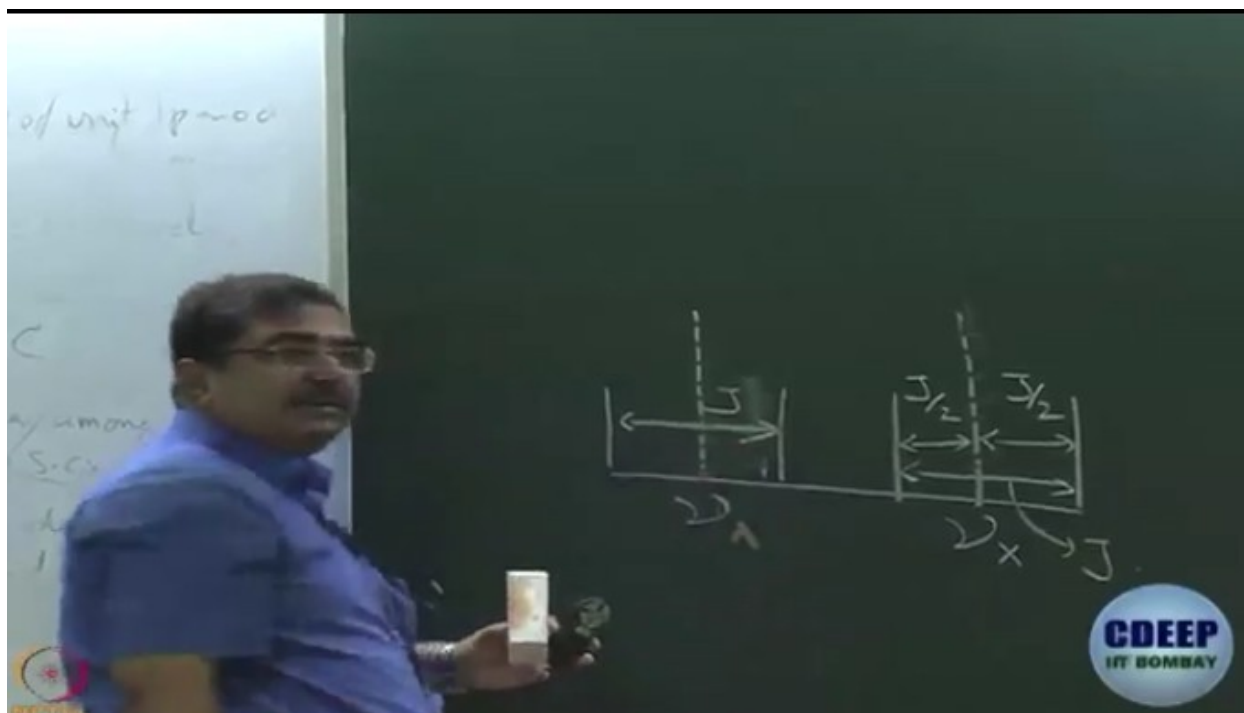
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what is the separation between these two lines? J, and you can work out yourself that instead of one line at nu A you will get a similar thing, you will once again get a doublet that is separated by J,

(Refer Slide Time: 55:47)

I don't do that cut cut cutters, then I'll teach for 15 minutes longer. I'm done, give me one or two minutes, alright.

So now see that is what gives us, what was the question I hope you have not forgotten the question and all this. The question was why is it that in case of ethanol we don't get single lines at three different frequencies, each line seems to comprise of more than one line except for OH, why is that so? This is the reason, because of coupling you get this multiplet structure and in fact if you look at the spectrum if you see by how much this lines are separated you get a, you can estimate the value of J, alright.

And now you can understand I hope why I want a high field, why is it that chemistry department through away this 60 megahertz machine and bought first 400 megahertz machine then a 500 megahertz machine, why is it that in safe and 7 tiers we have 600 and 750 megahertz machine, why is it that in TI FR they have a 900 megahertz machine? Because this separation between nu and nu X depends on the magnetic field, this separation J does not, so if you use a small magnetic field nu and nu X will be very close to each other right, then what will happen? If they come so close that this line crosses this, and this line crosses this, then actually you get a complicated spectrum, and it is not also as simple as just lines crossing each other, they'll be interaction, so the situation is such that you cannot handle it using first order perturbation theory, you get what is called second order spectra, which are extremely difficult to interpret, that is why use, want to spend more money and beta magnets, so that your spectra are first order as far as possible.

And of course you know who uses that 750 megahertz machine we have in side in 7 tiers, no chemistry uses it, biologist, people who work on protein NMR, there of course you understand they were 100s and 1000s of protons, chemical shifts are very close to each other, so if you use a very large magnetic field then only you can hope to get something that is possible to interpret,

alright, so we stop here today, next day we'll come back and talk about AX2, AX3 systems and then take it from there.

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