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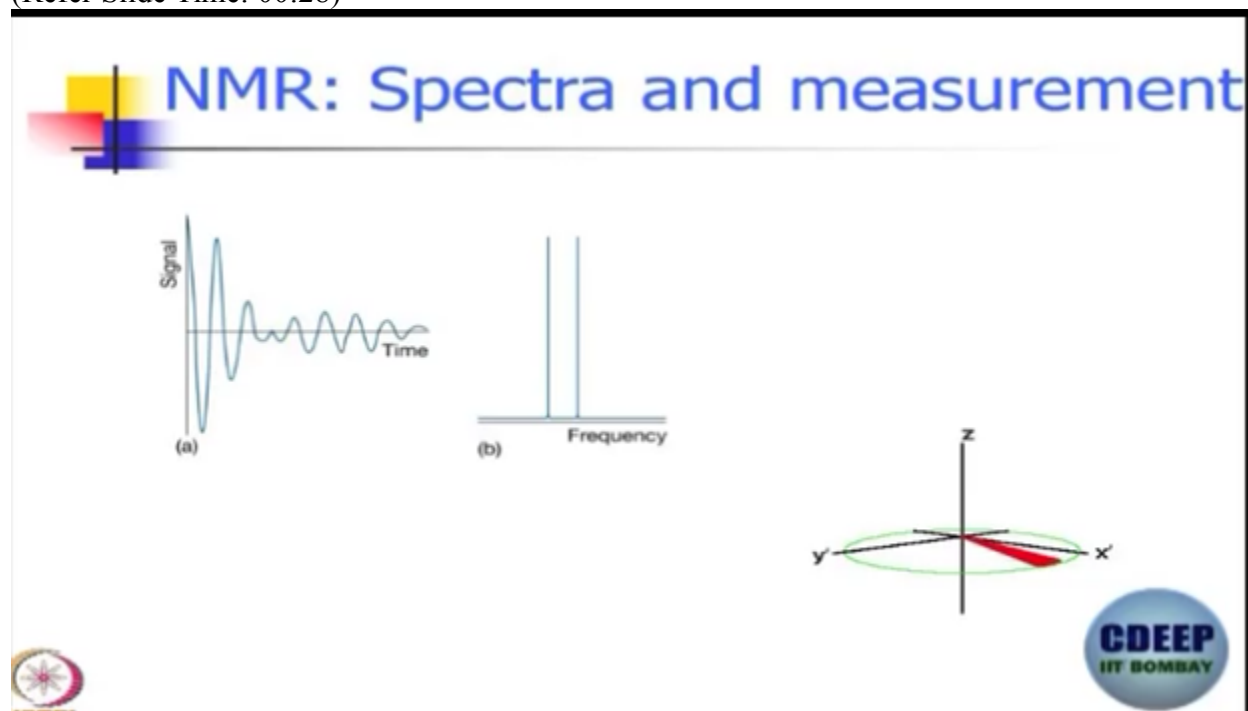
CDEEP
IIT BOMBAY

MOLECULAR SPECTROSCOPY:
A PHYSICAL CHEMIST'S PERSPECTIVE

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Lecture no. – 56
NMR: SPECTRA AND MEASUREMENT

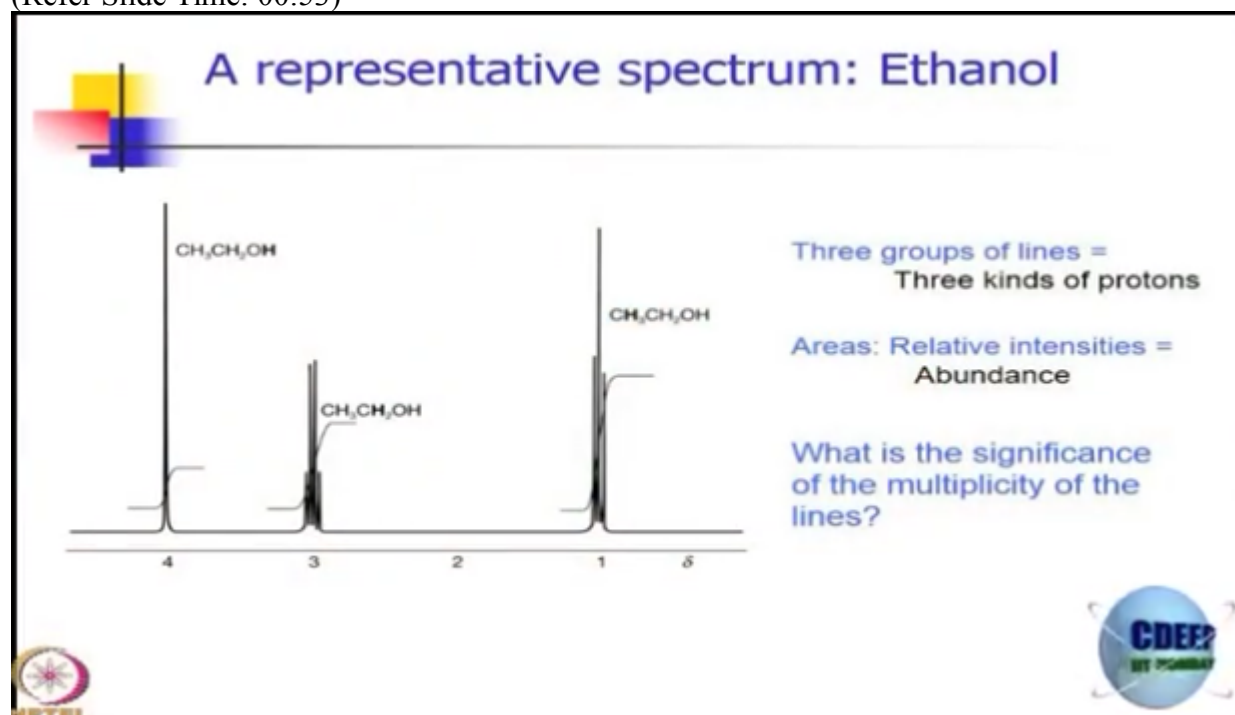
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The slide features a title 'NMR: Spectra and measurement' in blue text at the top left, accompanied by a colorful graphic. Below the title, there are three diagrams: (a) a plot of 'Signal' versus 'Time' showing a decaying oscillation; (b) a plot of two vertical lines versus 'Frequency'; and a 3D coordinate system with x, y, and z axes, where a red and green elliptical shape is centered at the origin. The CDEEP IIT BOMBAY logo is in the bottom right corner, and a small circular logo is in the bottom left corner.

We are discussing NMR spectroscopy, we have already discuss the basics, today we will see how far we can get in discussing how NMR spectra are actually recorded, you might be wondering why we have this colored ways going around increasing in size and all, let us see if you can get that today, if not we'll get that tomorrow.

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But so far this is what we have discussed, we have introduced the only NMR spectrum that we are going to show you in this course, of course there is no guarantee that we will not show you or we will not ask you to sketch some other NMR spectrum in end sem that we can do, but what we have said is we have understood that first of all when you have a bare proton in the magnetic field then the energy between alpha spin and beta spin, there is the energy difference that it comes in between alpha spin and beta spin.

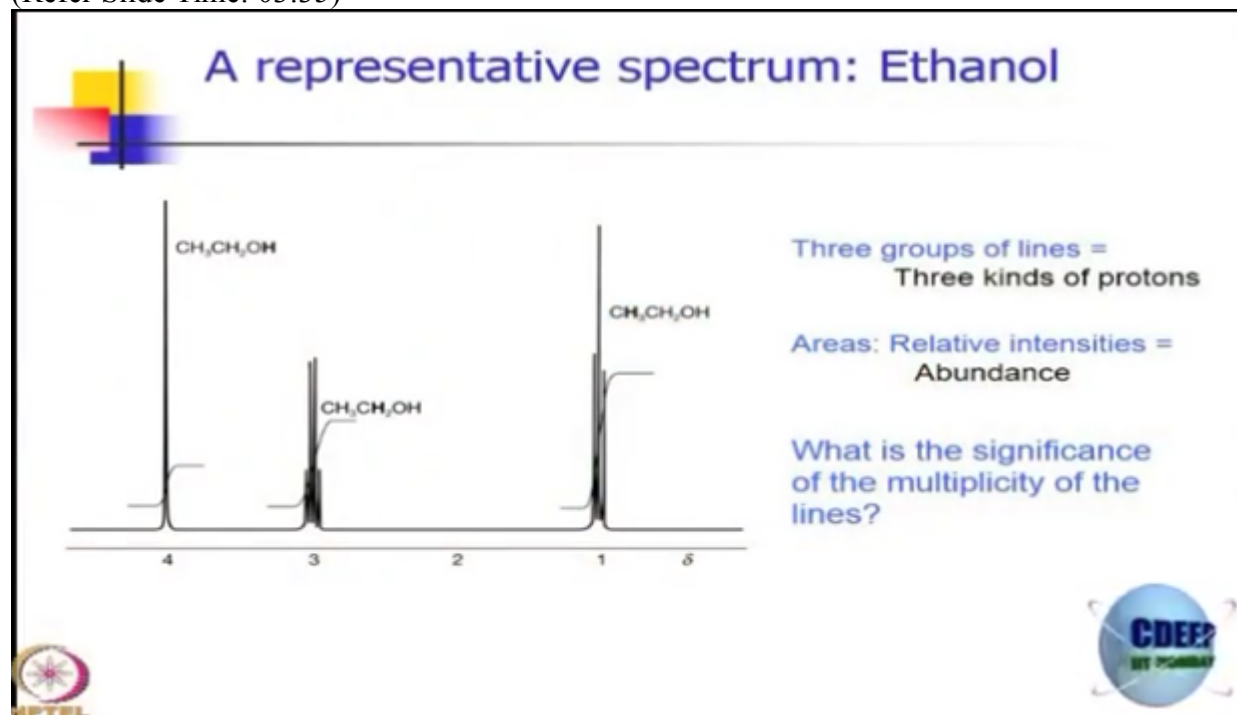
And then we realize that when we talk about molecules we are not really dealing with bare nuclei, bare proton, or bare ^{13}C or whatever, we are dealing with nuclei that are in an electron cloud, a charge cloud and as you have discussed when we subject this molecule to a magnetic field then this electron charge cloud sets up a reaction field even the Sushant also doesn't seem to believe it, and this reaction field depends on what kind of, whether it's CH_2 or whether it's OH , whether it's CH_3 or what, so different protons in a molecule get subjected to a different amount of shielding and consequently different amount of $B_{\text{effective}}$, effective magnetic field.

How much shielding? Depends on what kind of chemical environment it is there, that is why NMR spectroscopy becomes such a useful tool for chemists because now while looking at an NMR spectrum you can understand what is the molecule you are dealing with, NMR spectroscopy is I think the most useful and widely used kind of spectroscopy. Not only in chemistry but also in biology, a lot of biologists actually use NMR because it gives them a lot of information, so after discussing the quantum mechanics let us see if we have time we'll talk about 2D NMR and positive coupling and all that, but I don't know I'm not sure whether we have time for that yet.

But what we have learnt from ethanol is this because of this different kind of shielding that we talked about, there are three groups of lines because there are three kinds of protons: CH_2 , CH_3 , and OH . And then we said that the areas under each of these groups of lines give us the relative abundance.

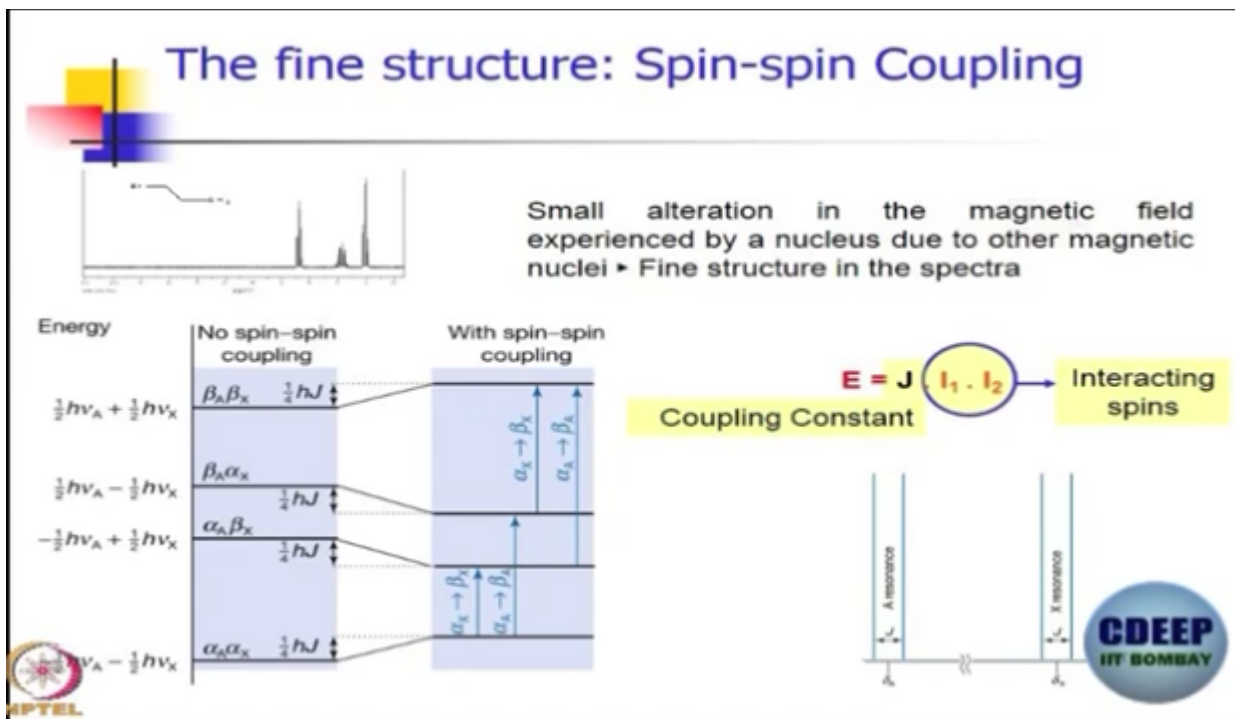
of the different kinds of protons, so just by looking at the areas, since this case is little simple, looking at the areas we can tell that this is for OH, this is for CH₂ protons, this is for CH₃ protons, okay,

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but why do we have a fine structure in the lines? The answer is the fine structure comes due to coupling between the different protons, and that is what becomes, that is what provides an even more different angle, a more insight, little bit of more insight into the structure of the molecules because looking at the patterns of coupling as we are going to see in the next few minutes we can understand what kind of groups of proton it is, whether it's CH₂ or CH₃ or what?

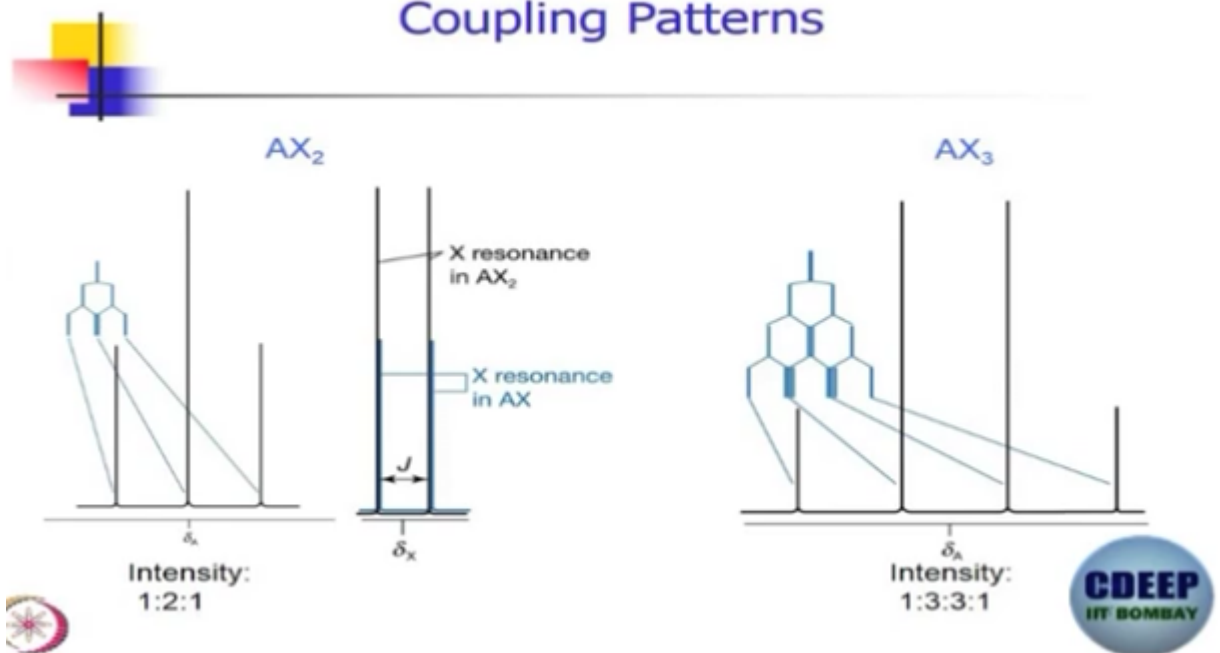
And this is the discussion we have done about coupling, we have understood that alpha-alpha
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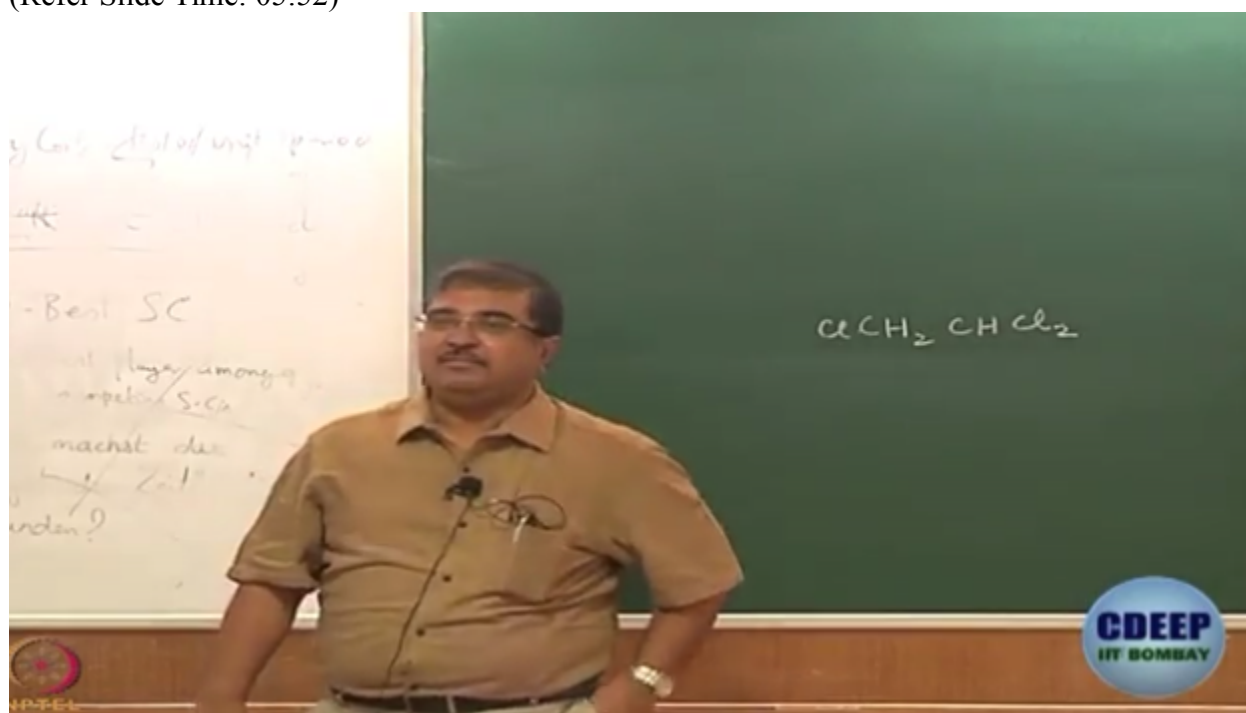
and beta-beta spins their energies get increased as a result of coupling from the uncoupled scenario and for alpha-beta and beta-alpha their energies are lower from the uncouple scenario as a result of coupling. We are going to do a little more detail treatment of this starting tomorrow or Wednesday whenever we can get to it, but for now this is the picture and we said that as a result when we have AX kind of a situation, AX means we have two groups of, not groups we have two protons, we designate one as A and the other as X, and we have two protons of very different chemical shift, okay, so in this situation the spectrum you expect is instead of one line you expect two lines for A and two lines for X.

As separation between these two lines is J as we have discussed in the last day, so now if you extend it a little more, suppose we have AX₂ kind of situation, okay,
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Coupling Patterns



AX_2 that means I have one proton of one kind, another I have three protons, sorry two protons of another kind. What is the good example? Something like this, let us see, let us not spend too many elements, let us just work with chlorine hydrogen, so here what do we have? (Refer Slide Time: 05:52)



We have one proton of one kind and we have two protons of another kind AX_2 or A_2X depending on what the relative chemical shifts are.

In this case what will happen? Let us think of the A resonance, okay, think of the coupling of A with one of the X first, of course coupling is not as if there is a coupling with 1X first, and with the second X after that, it's not sequential, but it's a little easier for us to understand if you think sequentially that is all, so now first consider coupling of A with one of the X protons, you are going to have a splitting like this, separation will be J.

Now consider the coupling of A with the second X, each of these will split into two lines, right, this separation will be J, this separation will be J, so I hope it's not going to be difficult to understand that the lines in the middle they actually come together, and they'll merge and you are going to have a line that is double the intensity of the other two lines, so when you have AX₂ the line of A is a triplet and relative intensities are 1:2:1, and then for chemistry students it is not any new information, Shubhda are we okay? Alright, this is very simple.

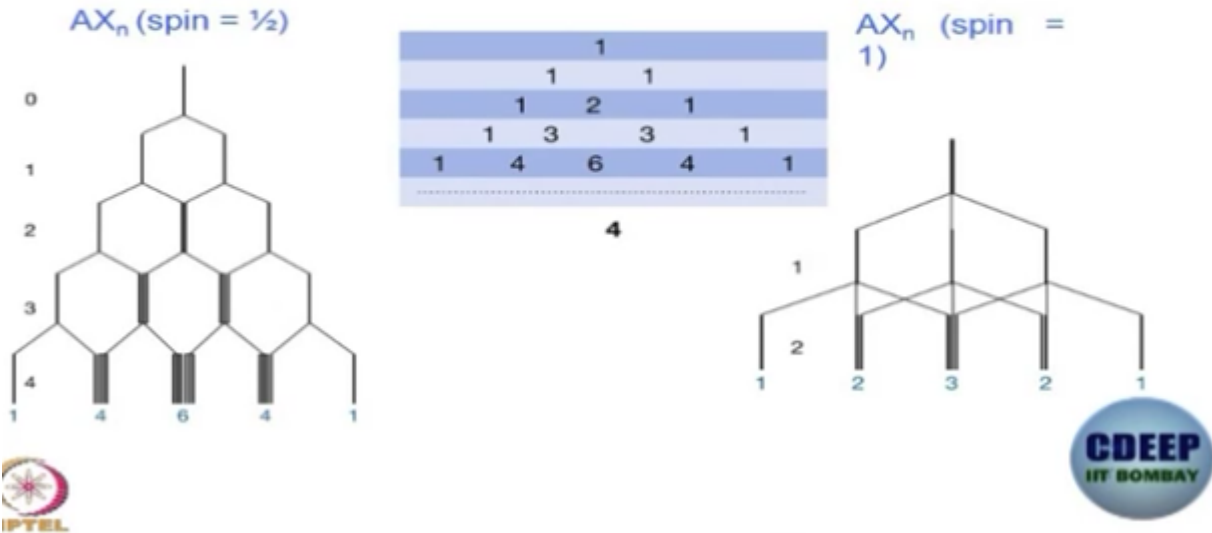
Now in case of X, what will happen? Only 1A is there that is coupling, so it gets split into 2, alright, is that all? Is there a question at this point of time? If you don't ask the question I will.

There is a question that should come to our minds at this point of time, unless you already know a lot of about NMR, the question is this, what happen, we are saying that A couples with X, X couples with A so we are talking about the effect of the A resonance of coupling with X on A resonance coupling with A on X resonance. What about coupling between the 2X? That should also happen and consequently there should be a splitting, but those of us who know that, that does not happen, why not? Why is it that we consider coupling of A with X, X with A, but we don't consider coupling of X with X. Those are regulance, so those are equivalent so they don't couple with each other, why? You are right, but my question is why?

So let us see if we can get there as well, when we do our discussion of quantum mechanical discussion of this problem, hopefully we will be able to understand why it is that 2 is don't couple if we can get that, but I'm not sure if you can, we'll see.

So consequently AX₃, what will happen in AX₃? For the first coupling split into two, now consider coupling with the second X, this was split into two, this was split into two, so you get 1:2:1 but that's not all, there is one more X further splitting will be there, so 1 2, here what will be the intensities? This is already 1:2:1, so basically this becomes half, right, when this splits into two, intensity will become 1/2, 1 will come here so this is the kind of intensity you will get, 1:3:3:1 very easy math we can work out by itself,
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Coupling Patterns (contd.)



the cuts of the matter is if you have AX_n kind of situation then the number of lines and the intensity of lines for a spin half system is given nicely by this Pascal's triangle, we have all encounter Pascal's triangle in class 11 or earlier, so this Pascal's triangle is something that shows up in NMR spectrum as well, okay, so that is the beauty of science, right, mathematics arises everywhere and you can actually express everything even biological phenomena mathematically.

There is book I forgot by whom, which kind of discusses why is it that mathematics appears naturally in everything around us, unfortunately I forgotten the name of the book as well as the author, if I remember I can tell you it's an interesting phenomena, alright, so much for coupling.

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Problems

What is the transition frequency (in Hertz) for protons at 11.7T? At 21.1T?

$$\gamma_{\text{proton}} = 26.752 \times 10^7 \text{ rad/T sec}$$



Now and what we have discussed so far we can work out some simple problems, there is something that I had talked about briefly in the previous class I think, if I ask you what is the transition frequency in hertz for protons when the magnetic field use is 11.7 tesla, what is it at 21.1 tesla, can you tell me? What I have to give you of course is gamma proton, what is gamma? Gyro magnetic ratio or magnetic gyro ratio that is an intrinsic property of the nucleus that is given, so how will we find out? What is frequency going to be? We know the expression for lambda frequency, we can work it out and the answer we get are these,
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Problems

What is the transition frequency (in Hertz) for protons at 11.7T? At 21.1T?

$$\gamma_{\text{proton}} = 26.752 \times 10^7 \text{ rad/T sec}$$

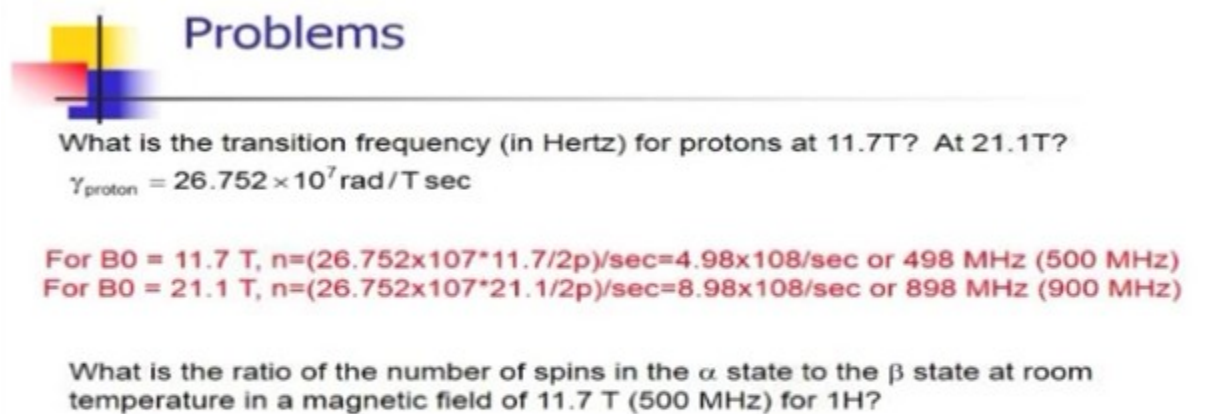
For $B_0 = 11.7 \text{ T}$, $n = (26.752 \times 10^7 \times 11.7 / 2\pi) / \text{sec} = 4.98 \times 10^8 / \text{sec}$ or 498 MHz (500 MHz)

For $B_0 = 21.1 \text{ T}$, $n = (26.752 \times 10^7 \times 21.1 / 2\pi) / \text{sec} = 8.98 \times 10^8 / \text{sec}$ or 898 MHz (900 MHz)



so 11.7 tesla, 11.7 tesla the frequency is 498 megahertz is approximately 500 megahertz for applied magnetic field of 21.1 tesla the frequency is 898 megahertz approximately 900 megahertz, so as we had discussed earlier this is the meaning of this 400 megahertz, 500 megahertz, 900 megahertz NMR machine. It essentially tells you in a little round about fashion how big magnetics, so you can see when you go from 500 megahertz machine which we have in chemistry to 900 megahertz machine which we don't have anywhere in this institute, there is one NMR then the magnetic field has to increase from 11.7 tesla to 21.1 tesla almost double, and the cost does not double, it goes to the power of something, it's a power law, so that's what it is, you use a bigger magnet you get higher resonance frequency, and as we have discussed earlier the higher resonance frequency also means better resolution, okay. We'll come back to this topic later as well.

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Problems

What is the transition frequency (in Hertz) for protons at 11.7T? At 21.1T?

$$\gamma_{\text{proton}} = 26.752 \times 10^7 \text{ rad/T sec}$$

For $B_0 = 11.7 \text{ T}$, $\nu = (26.752 \times 10^7 \times 11.7 / 2\pi) / \text{sec} = 4.98 \times 10^8 / \text{sec}$ or 498 MHz (500 MHz)
 For $B_0 = 21.1 \text{ T}$, $\nu = (26.752 \times 10^7 \times 21.1 / 2\pi) / \text{sec} = 8.98 \times 10^8 / \text{sec}$ or 898 MHz (900 MHz)

What is the ratio of the number of spins in the α state to the β state at room temperature in a magnetic field of 11.7 T (500 MHz) for ^1H ?



Now another small little calculation that is going to be extremely helpful in our subsequent discussion is I have alpha spin, I have beta spin, okay, I have applied magnetic field, so there are two levels and there is a energy difference that comes in as a result of the applied magnetic field, so I should be able to calculate what is the ratio of population, right, will we have more nuclei in the higher state or will we have more in the lower state? We should have more in the lower state, but what will be the ratio? So what I am telling you is what is the ratio of number of spins in the alpha state to that in beta split rate at room temperature when I use a 500 megahertz machine 11.7 tesla magnet for proton, okay, I'll give you the answer, the answer is this N alpha,

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Problems

What is the transition frequency (in Hertz) for protons at 11.7T? At 21.1T?

$$\gamma_{\text{proton}} = 26.752 \times 10^7 \text{ rad/T sec}$$

For $B_0 = 11.7 \text{ T}$, $n = (26.752 \times 10^7 \times 11.7 / 2\pi) / \text{sec} = 4.98 \times 10^8 / \text{sec}$ or 498 MHz (500 MHz)

For $B_0 = 21.1 \text{ T}$, $n = (26.752 \times 10^7 \times 21.1 / 2\pi) / \text{sec} = 8.98 \times 10^8 / \text{sec}$ or 898 MHz (900 MHz)

What is the ratio of the number of spins in the α state to the β state at room temperature in a magnetic field of 11.7 T (500 MHz) for ^1H ?

$$\frac{N_A}{N_B} = e^{\frac{\Delta E}{k_B T}} = e^{\frac{3.313 \times 10^{-23} \text{ J}}{1.38 \times 10^{-23} \text{ J/K} \times 298 \text{ K}}} = e^{8.056 \times 10^{-5}} \approx 1.00008056$$



I don't know why I have written N_A/N_B , it turns out to be 1.00008056, it's actually very close to 1, and it's not surprising because if you remember what we said yesterday is we are accustomed to you working with bigger energy gaps right, we've talked about UV ways, then we talked about vibrational levels those are fairly large energy gaps.

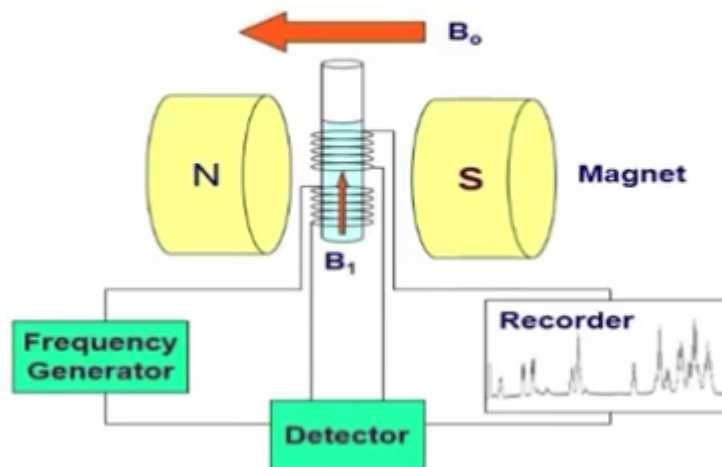
Now we are working in the lowest energy side of the spectrum, right we are talking about radio waves, radio frequency, so energy gaps are really small, since energy gaps are really small what will happen is, at room temperature itself significant number of nuclei will actually be there in the excited state, but excited state can never have more population in the ground state, that much will be ensured, okay, so this is the number 1.00008056, so this is the answer for 11.7 tesla magnet.

What happens if I use a 21.1 tesla magnet? Should this ratio be more or less? Less, thank you for falling in the trap. More, I'm talking about N_A/N_B , it's already more than 1, so if you increase the energy gap more and more nuclei will actually be in the lower energy level, alright, so be careful even if it's a multiple choice question, it's very easy to go wrong especially when you have issues it's A:B or B:A, very easy to get confused, but that kind of changes the answer or mislead. So this is something that we are going to use shortly.

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NMR spectrometer



Now let us go on to what we promise to do at the beginning of this lecture, let us just think what is there inside an NMR spectrometer that has been, the way we have been handling this throughout the course, not only have we talked about the mathematics of it or physics of it, we have also tried to understand how an measurement is done, what is there inside the machine, this will not be any exception, so inside a NMR spectrometer of course the one big difference between NMR spectroscopy and say UV vis spectroscopy or IR spectroscopy is that the energy gap is not there in the system you have to create it, you have to create it by using this 11.7 tesla or 21.1 tesla magnet, okay, so of course you need a magnet.

How many of us have seen an NMR tube? Almost everybody, so NMR tube is it as thick as this or thicker or thinner? Thinner, very thin, it looks like a, it looks like a test tube on diet, thin, thin right, that's what I said test tube on diet, (unknown language 16:01) so it's really very narrow, okay, so that is what the test tube goes in, this is what we've drawn here, it's a fairly accurate scaled up representation of the NMR tube, so when it goes in that is subjected to the strong magnetic field, and then what do you need? You need light and you need a detector.

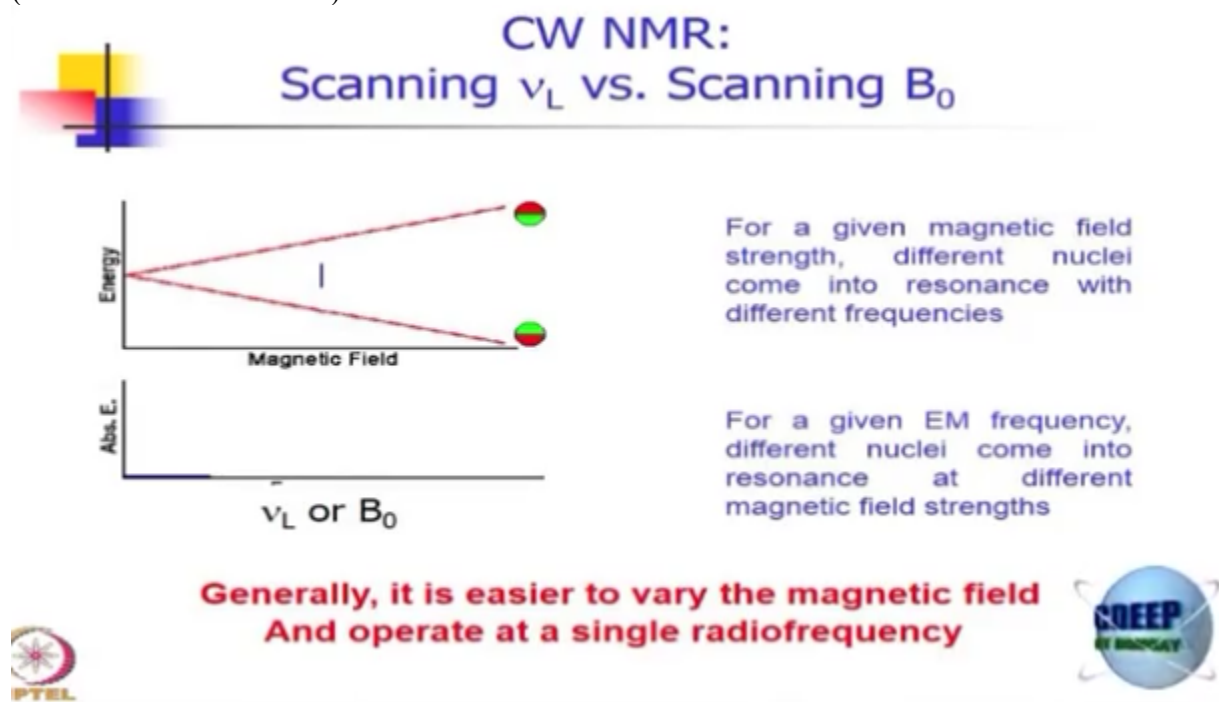
Now once again don't forget when we say light we mean radio frequency, okay. What is a very easily available device in which radio frequency is used? Radio, radio frequency is used in radio, how difficult is that too give that answer, radio, how many of us have opened a radio set? So if you open a radio set, you've opened a radio set you said what have you seen inside? There is a big magnet, okay, okay, but did you see there is this rod and some wire coiled on it, what is that? Can anybody tell me? What is this coil that we see inside radio set? Accha we are not talking about pre-historic radios, so discharge tube does not arise here, transit test side, I'm talking about the, so that's the antenna, if you open the radio you'll see that there is a coil that is essentially the antenna so that is how you receive radio waves and that is how you transmit radio waves also by using antenna, an antenna essentially is a coil of wire perhaps around the core, okay, so you do not have this light falling on it as such, so what you have is this, whether tube goes in there are

two coils, one coil is the light source, RF source, radio frequency source, the other coil is the detector, okay, antenna, one is source, one is antenna, so things are little different when you talk about radio frequency here, alright.

And then of course you have frequency generator which tells you at which frequency the RF, what frequency RF will be generated, that is also pretty much what you have inside a radio transmitter and then you have the recorder detector all those things, detector is already shown here then you have the recorder.

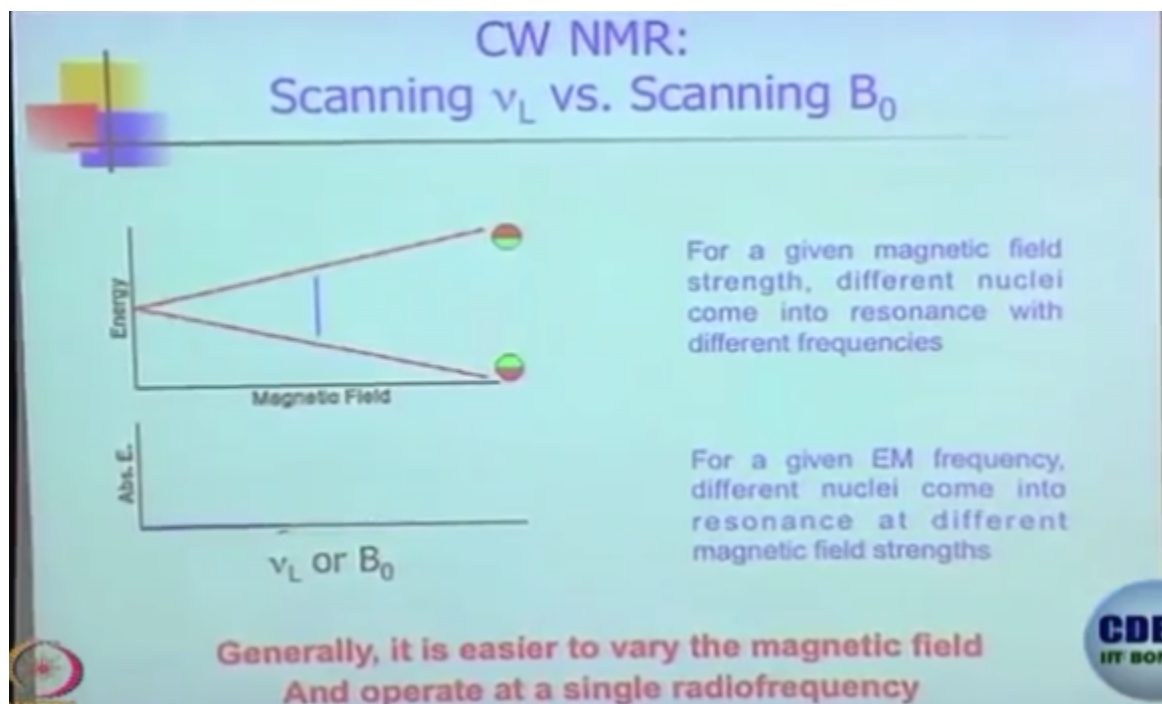
Now this is a very rudimentary picture of a classical NMR spectrometer, okay, what is called a CW or continuous wave NMR spectrometer, now the term CW is nothing new for us in this course I hope, we have talked about femtosecond spectroscopy so we know very well what is CW, what is past.

Now in conventional CW NMR, there are two ways in which you can achieve this immense, remember there are two things right,
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on left hand side you have the frequency ν_L , on right hand side you have something multiplied by the magnetic,

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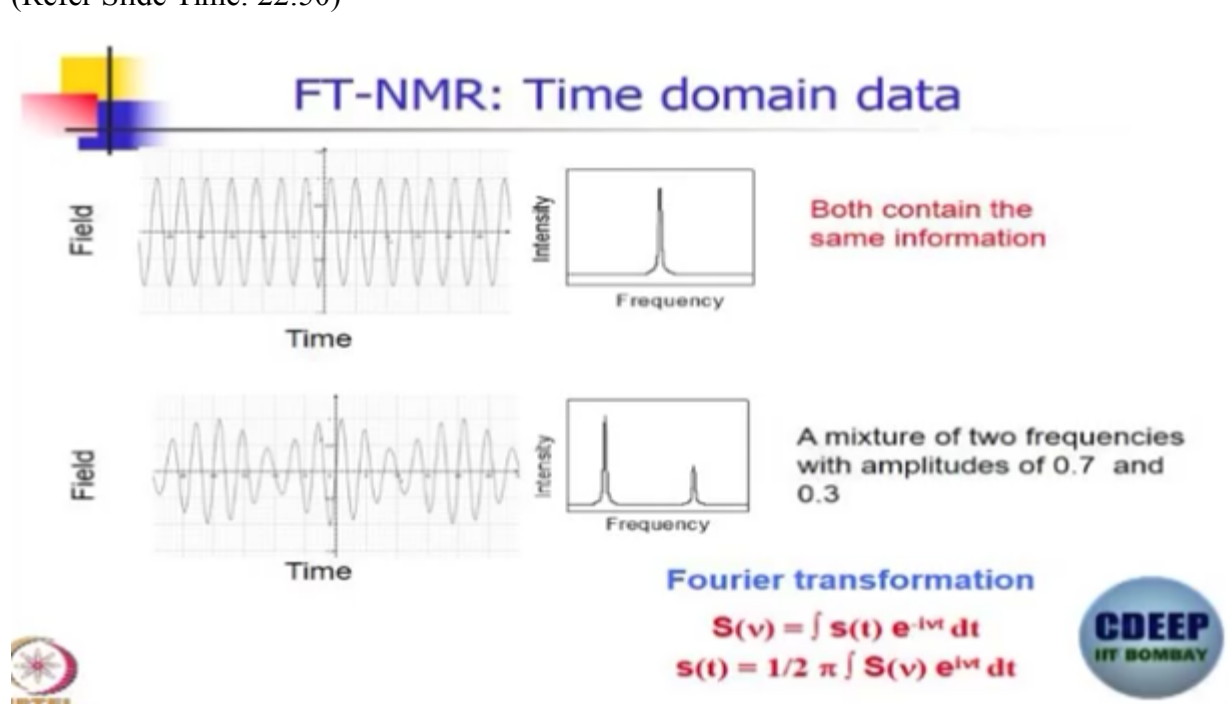
magnetic field B_0 or $B_{\text{effective}}$ whatever you want to say.

Now one way of achieving resonance is by changing the frequency, you work with the fix magnetic field and keep on changing the frequency, at one particular frequency if you go back to our example of ethanol CH_3 protons will come into resonance at another frequency, CH_2 will come into the resonance at another frequency, OH proton will come into this, so simpler is that, that is one way, can you tell me what is the other way of doing it? If I suppose I don't want to change the frequency, I want to work with one radio frequency 500 megahertz of whatever it is 400 megahertz, 900 megahertz, then how can I achieve resonance, I don't have many radio frequency, yes Kajol? By changing the magnetic field, is it easy to change the magnetic field? Is it difficult to change the magnetic field? It's actually easy, it's not difficult, because all you need is, you need that big fat magnet 11.7 tesla, but don't forget this σ is not very large right, so effective magnetic field is not very different from B_0 you have to just change B_0 by small amount, so what you can have is you can have the big magnet and you can have an electromagnet along with it, electromagnet as you know, as you increase the current magnetic field will go up, right, is it easy to increase the current or is it difficult? Say not increase, is it easy to change the current or is it difficult to change the current, so very easy, right, you change the regulator, everybody has use the fan at home, change the regulator and old fashion regulator all it has is it has a resistance, and the regulators we have now is the inductance, so just change the resistance in the circuit you can change the current if voltage is constant ohm's law, right, so it is very easy to change the magnetic field.

If you want to change now 11.7 tesla to 21 tesla that is not so easy, but if you want to change now 11.7 tesla to say 13 tesla at, and if you want to keep changing at resolution of 0.01 tesla it is very easy, okay, so this second method is what is usually done, you keep changing the magnetic field as, here it is the first method, as a magnetic field changes what happens is the energy gap between alpha and beta changes, and at different magnetic field values different protons coming

to resonance with this monochromatic radio frequency that is there in the machine, okay, so this is what is typically done rather than sweeping the frequency. Are we clear? Are we clear? Is there any question? Can we go ahead? Okay.

Then let's go ahead and say that nobody does this anymore, this is a classical way of recording NMR by using what is called CW method, what is used now is everybody records what is called FT NMR Fourier transform NMR, of course in this course Fourier transformation is also something that is not new to us, isn't it, we are familiar with recording the data in time domain, not only in frequency domain and we have discussed already towards the beginning of the course that time domain and frequency domain spectra actually have the same information, okay, you can either have frequency on the X axis or have time on the X axis, so this here is the depiction of a monochromatic ways in time domain, (Refer Slide Time: 22:50)

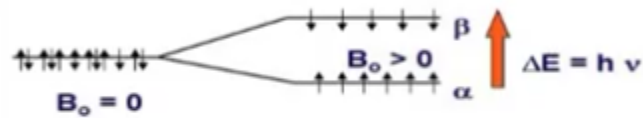


same way in frequency domain, here we have a mixture of two colors, two wavelengths in frequency domain, the same thing in time domain, we have discussed interferograms and all that, so we don't have to reopen that discussion, one thing that I did not write explicitly is how do you go from time domain to frequency domain, you go by doing Fourier transformation, these are the two relationships that allow you to go from time domain data to frequency domain data or the other way around very very easy, so what is done nowadays, and when I say nowadays I mean quite a few decades is you don't use continuously radio frequency we use pulses, and you try to get time domain data, frequency transform it and get almost noise free, good looking NMR data very quickly, okay,

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Population Excess and Bulk Magnetic Moment



$$N_{\alpha} / N_{\beta} = \exp(-\Delta E / kT)$$

$$\Delta E \text{ for } ^1\text{H at 400 MHz (} B_0 = 9.5 \text{ T)} \\ = 3.8 \times 10^{-5} \text{ Kcal / mol}$$

$$N_{\alpha} / N_{\beta} = 1.000064$$

The small excess of up spins give rise to a **Bulk Magnetization M_0**



so that is what we'll discuss in the next part.

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