NMR Spectroscopy for Chemists and Biologists
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Relaxation
Lecture no. 4

Welcome to the fourth lecture on this course on NMR spectroscopy. In the last class we looked at the solutions of the Bloch equations, which represent the motion of the spins in the presence of the *RF* field and also the main magnetic field. We also looked at the modifications of the Bloch equations which had to be done or which Bloch himself did, including relaxation effects. We saw there are two kinds of relaxation times are involved, one is the so called spin lattice relaxation which is also called longitudinal relaxation which brings the populations back to equilibrium. In other words, it brings a z component of the magnetization back to equilibrium and this is represented by the symbol capital T_1.

The other relaxation time is called the transverse relaxation time and that is represented by T_2. It is also sometimes called spin-spin relaxation time. The solution of the Bloch equations were obtained under the steady state conditions, going into the rotating frame of the *RF*. Why do we go into the rotating frame because we actually observe the nuclear spin system's motions. In the presence of the *RF* and we see to the *RF* and looked at it, so steady state solutions can be obtained in the rotating frame and we indicated that as u and v to represent the magnetization, along the axis of the *RF, u* and *v* represents the orthogonal component to it.

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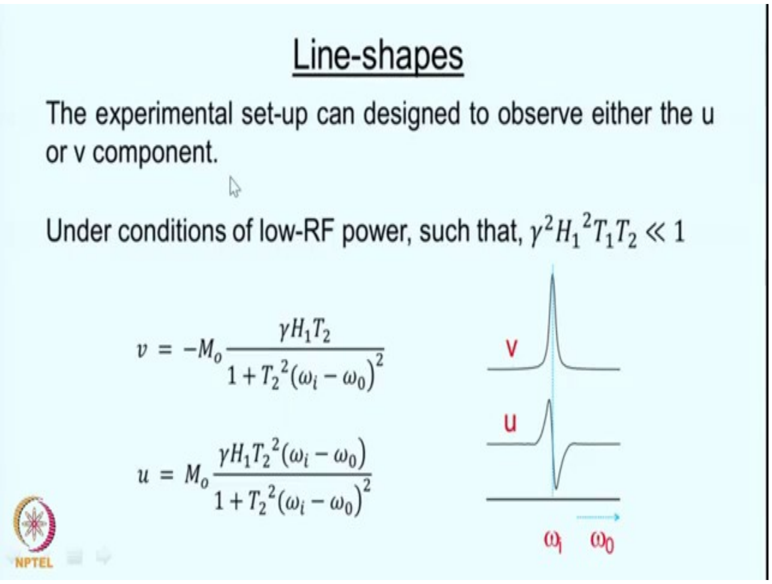

Line-shapes

The experimental set-up can designed to observe either the u or v component.

Under conditions of low-RF power, such that, $\gamma^2 H_1{}^2 T_1 T_2 \ll 1$

$$v = -M_0 \frac{\gamma H_1 T_2}{1 + T_2{}^2(\omega_i - \omega_0)^2}$$

$$u = M_0 \frac{\gamma H_1 T_2{}^2(\omega_i - \omega_0)}{1 + T_2{}^2(\omega_i - \omega_0)^2}$$

So we will continue from there now, the experimental setup can be designed to observe either the *u* component or the *v* component. Under conditions of low-*RF* power, such that, $\gamma^2 H_1^2 T_1 T_2 \ll 1$

This condition is called as no saturation condition, under these conditions, this term can be neglected in the expressions for *u* and *v* and they expressions will

$$v = -M_0 \frac{\gamma H_1 T_2}{1 + T_2^2(\omega_i - \omega_0)^2}$$

u is given by

$$u = M_0 \frac{\gamma H_1 T_2{}^2(\omega_i - \omega_0)}{1 + T_2^2(\omega_i - \omega_0)^2}$$

These actually represent the line shapes that we observe, if you plot this component here as a function of the frequency omega naught because this is what we vary, the precessional frequency is fixed depending upon the nuclear spin and the magnetic field, *RF* frequency is what we can vary. So as we vary the *RF* frequency ω_0 the *v* function looks like this okay. So this is an absorption line and we generally observe this component.

The *u* component goes in this manner it is so called dispersive line shape which has the positive component and a negative component and a long tail. Typically one uses this for drawing the NMR spectra or sometimes this is also used in cases where you want to monitor the field drift and things like that, specially for locking purposes which we talked about earlier for those purposes dispersive line shapes are used because this is easy to see the deviation from resonance condition you see here under the resonance condition this signal has the maximum and this signal has the minimum, this is *0* here.

Any deviation in the magnetic field causes a shift along this line and therefore it produces a certain signal for the spectrometer to correct. So that it brings a field backs to the value it should be, but for the spectra this is a most convenient one and this has a non-zero integral but at the integral of this line shape it is non-zero, whereas the integral of this line shape is *0*.

So having said, so about the line shapes and how the NMR signals are observed, we now return to the question of relaxation to look at it in somewhat more in detail. We go into the mechanistic aspects. What brings about the relaxation?

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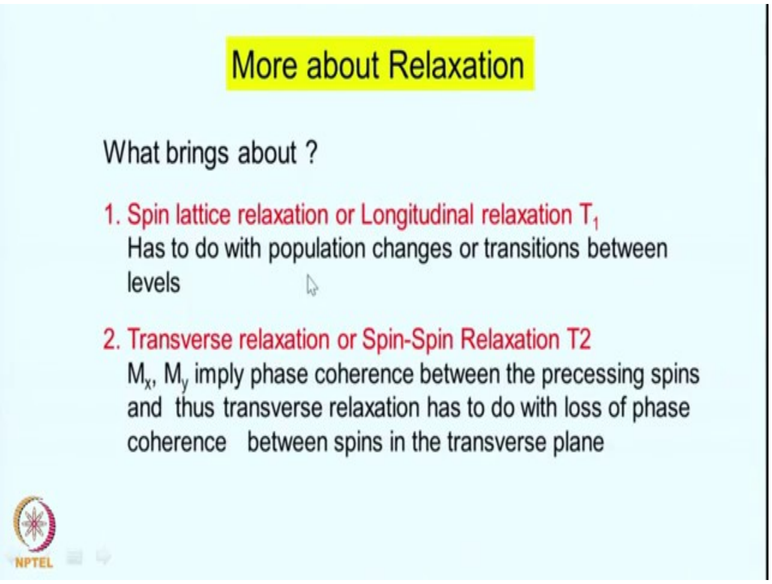

More about Relaxation

What brings about ?

1. Spin lattice relaxation or Longitudinal relaxation T_1
   Has to do with population changes or transitions between levels
2. Transverse relaxation or Spin-Spin Relaxation T2
   M_x, M_y imply phase coherence between the precessing spins and thus transverse relaxation has to do with loss of phase coherence between spins in the transverse plane

We said there are two kinds of the relaxation, spin lattice relaxation or longitudinal relaxation T_1. What it has to do with the population changes? We said it has to do with the magnetization along the *Z-axis* or really it has to do with the population changes between levels. The transitions between levels if there are transitions, the population will change and therefore, the spin system will relax.

The second one is the transverse relaxation which is a spin-spin relaxation this has to do with the transverse components of the magnetization, remember in the Bloch equations we had this T_2 appearing in the equations for M_x and M_y and this was the appearing for the equation for Mz. The transverse relaxation has to do with the loss of phase coherence between the spins in the transverse plane.

We said if there is no phase coherence in the transverse plane there is a distribution of spins all along in the transverse plane therefore the total cancelation of all the components therefore, at equilibrium there is no transverse magnetization. But if, somehow you are able to bring in a certain coherence between the spins which are moving in the transverse plane it results in a certain net M_x or the M_y component that means there is a phase coherence between the spins.

The appearance of the transverse magnetization implies, phase coherence between the spins. Therefore anything that causes loss of this phase coherence, contributes to the transverse relaxation. Now, how does this happen, how do the transitions occur and how does the phase coherence is lost, how is the phase coherence lost?

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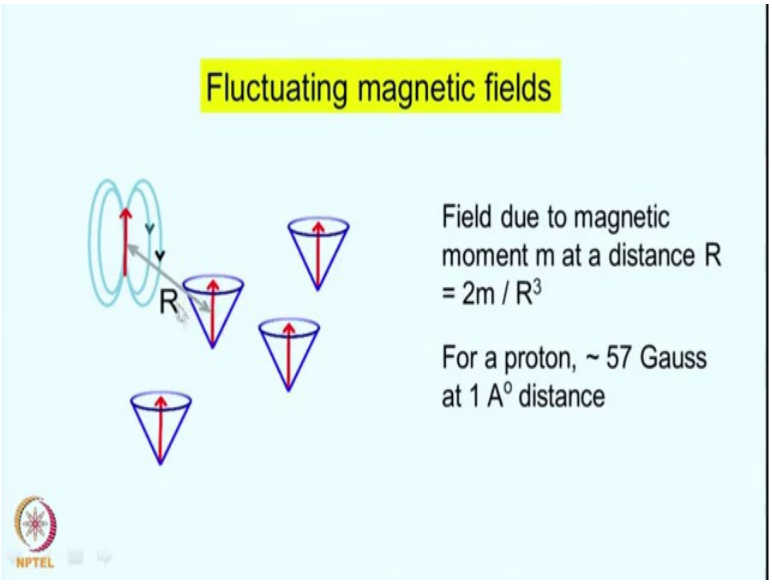

Fluctuating magnetic fields

Field due to magnetic moment m at a distance R $= 2m / R^3$

For a proton, ~ 57 Gauss at 1 A° distance

Let us look at the ensemble of the spins, we have lots of spins we have a particular spin and there are many spins which are in the lattice and all of them are precessing around the magnetic field. If this is the direction of the magnetic field, all of them are precessing in the magnetic field in the form of a cone, like this here indicated they can represent anywhere in the surface of the cone as indicated by hypothesis of random phases we described earlier and since each of them is a magnetic moment it is a magnetic dipole. It produces its own field and this is represented by the flux lines given here.

The flux lines go in this manner and all of these will have such kinds of flux lines, now if the spin precesses around this cone, this flux lines also will move, so they will also move if this is the cone here moving the flux lines are there around it so along with that all the flux lines also will move .Which means and the flux lines meaning one this is a field right, so the field has the therefore a z component and a transverse component and as the as the flux lines move the transverse components also keep moving they keep oscillating.

So therefore, the motion of the spins in the solution causes fluctuations in the flux lines of the individual magnetic dipoles. Now, when there many magnetic dipoles like this there will be an interaction between them, each one of them interacts with the other, suppose this nuclear spin comes close here to this one, then of course this nuclear spin sees the flux lines of this and it will experience a different magnetic field.

Depending upon whether it is here or here or anywhere here, it sees a different magnetic field. So the z component of the magnetic field keeps fluctuating depending upon whether this spin is here or here or somewhere and likewise the transverse component of the magnetic field will also influence their transverse component of the spin here there is a fluctuating magnetic field in the transverse component. So the interaction between these two spins is responsible for what we call as the, is the process of that relaxation.

We will see how that happens, just for sake of magnitudes, if we consider a distance of R here, okay. Notice this one is actually μ this is not m here, so this is a magnetic moment .The field due to magnetic moment at a distance R, typically is in certain range

$$R=\frac{2\mu}{R^3}$$

Where, μ is the magnetic moment and if the R unit dipole if we take as a unit magnetic moment here, the field created by this magnetic moment μ at this particular site is $\frac{2\mu}{R^3}$.

So when there is another magnetic moment here this will interaction between the two is $2\mu_1.\mu_2$ that will be the interaction. So for a proton, suppose this is a proton the field created by it at a distance of 1 A°, is the approximately 57 Gauss. This is not a small number, this is a huge number, okay. So if this spin keeps moving or this one keeps moving, the field created at the site of this, will keep on varying in all the three dimensions all the *X-axis*, *Y-axis* and the *Z-axis*. So, you are, imagine an ensemble which all fluctuating here in the, in the solution so there is a continuous fluctuation in the magnetic fields at the site of this particular nucleus and this magnetic field has components along the *Z-axis* and the *X-axis* and the *Y-axis*.

We call this field is a h_{loc} field, the h local field where is along the *Z-axis*, the *X-axis* and the *Y-axis*.

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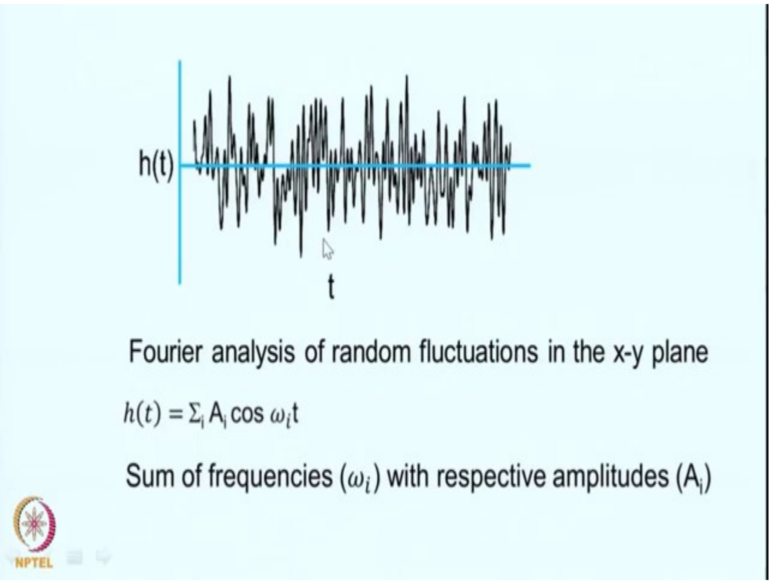

Fourier analysis of random fluctuations in the x-y plane

$h(t) = \Sigma_i A_i \cos \omega_i t$

Sum of frequencies (ω_i) with respective amplitudes (A_i)

So if I were to plot the transverse component of this h_{loc} field the x and the y components you can take any one of those does not matter and you plot it as a function of time and what this time represents? This represents the motions of the spins in the solution, notice that if the tumbling spin, if the molecule has a vector like this if the it orients like this the magnetic moment still remains like this only magnetic moment does not become like that it still remains like that only.

So therefore, the fluctuating magnetic field this cones are always in the same direction for every particular spin, α state or like this β state or like this okay. Now so, if I were to plot the local field, the transverse magnetization created at a particular site by the fluctuating positions of the other spins then the field seen here fluctuates like this in a random manner okay.

So, what is implication of this, does it have any frequency components? In fact, it has the frequency components any fluctuating thing can be described by certain frequencies, if there is a time-dependent fluctuation. It will have a frequency component it may have one frequency component, multiple frequency components, so typically one can write this as fluctuation,

$$h(t) = \sum_i A_i \cos \omega_i t$$

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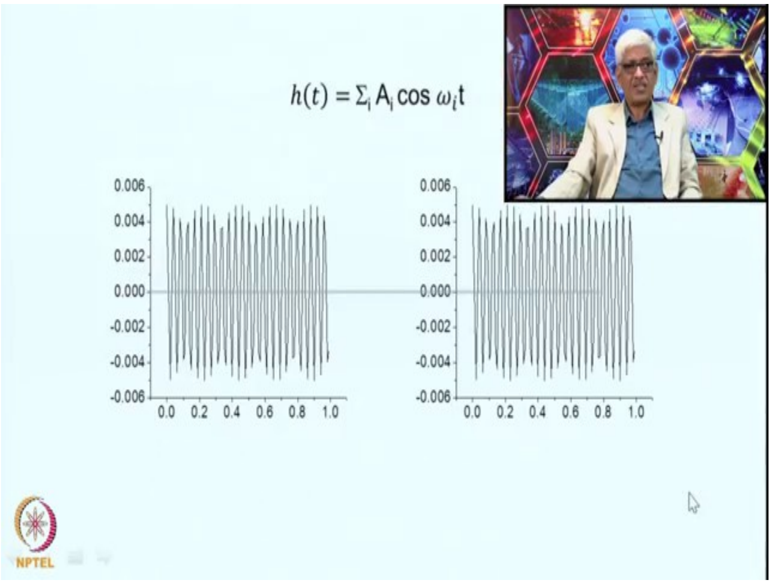
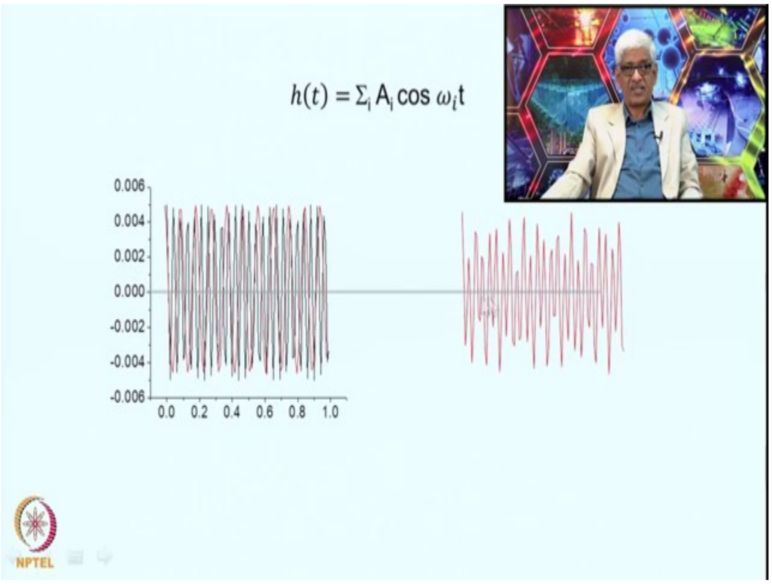


$h(t) = \Sigma_i A_i \cos \omega_i t$



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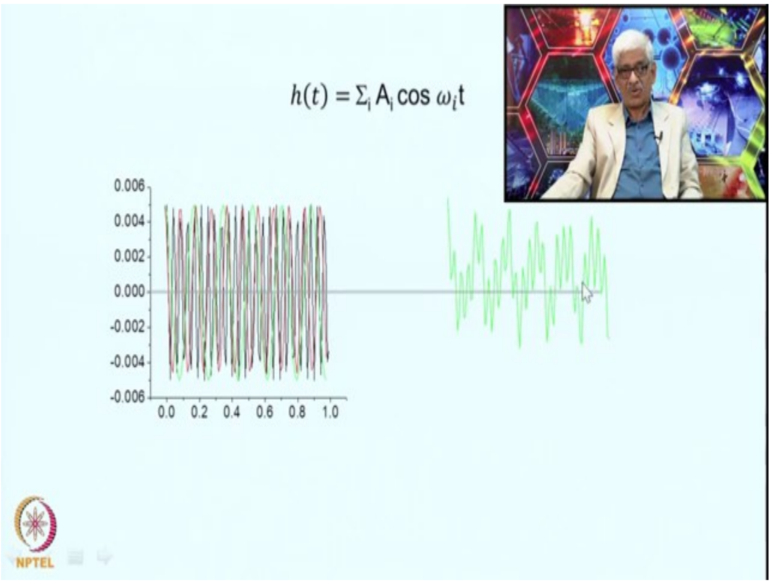

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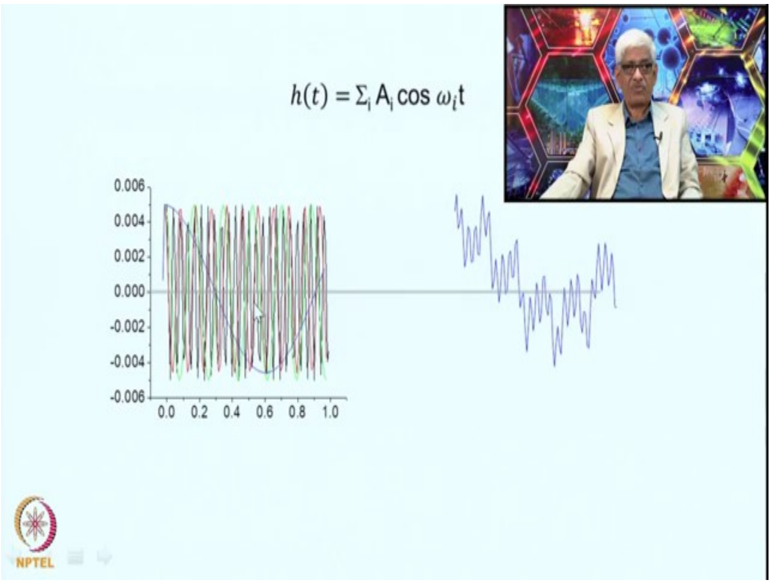
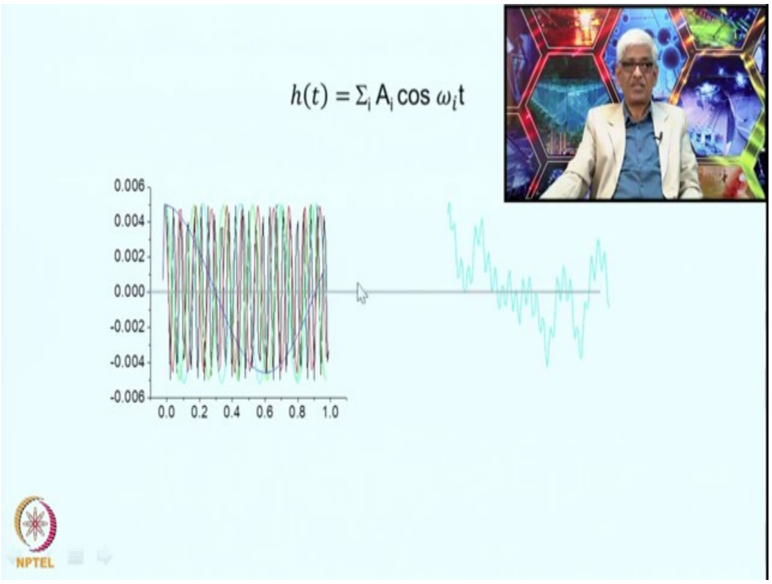
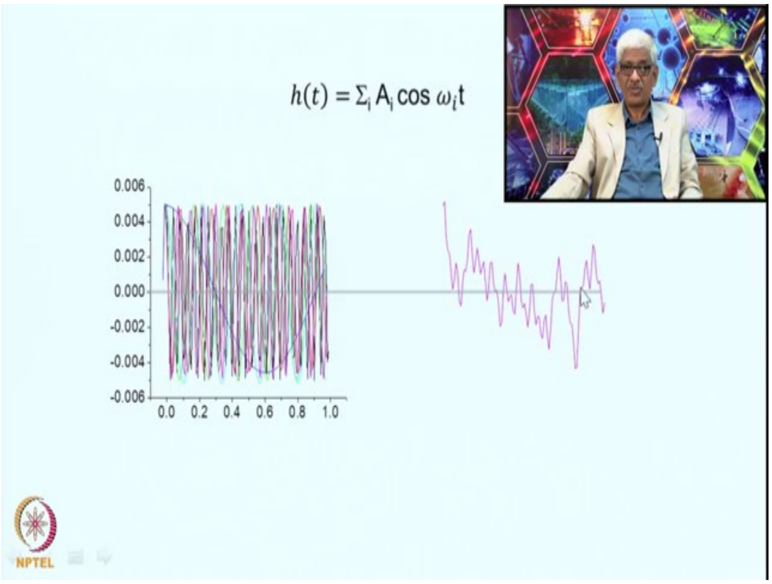


$h(t) = \Sigma_i A_i \cos \omega_i t$



$h(t) = \Sigma_i A_i \cos \omega_i t$



$$h(t) = \Sigma_i A_i \cos \omega_i t$$

Let me just demonstrate this to you here, this is one particular frequency here, now to this I add another frequency and this is the sum of the two frequencies, I add a third frequency this is the sum of the three frequencies, I add a fourth frequency this is sum of four frequencies, fifth frequency sum of five, sixth one sum of six and so on.

See what we have seen here as we are adding regular frequencies with different amplitudes A_i. I am generating a time dependent function which looks quite random. So the noise which I showed earlier at the *h(t)* is the summation of all these cosine frequencies here they all look like this.

Now recall back the *RF* field what we had applied is actually a function like this we wrote

$$RF = H_1 \cos \omega_0 t$$

So that means here there are many *RF* frequencies present, in this random fluctuations of their field components. The h_{loc} fluctuation creates a multiple *RF* fields here, I want to write it in a more formal way in a more general manner to analyze that, we call it as the summation of the cosine terms which we said is basically what we call as the Fourier transform.

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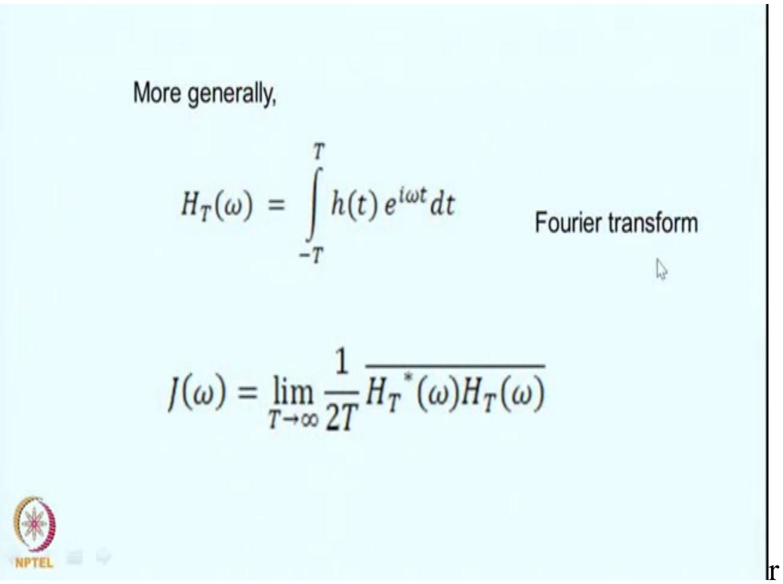

More generally,

$$H_T(\omega) = \int_{-T}^{T} h(t)\, e^{i\omega t}\, dt$$

Fourier transform

$$J(\omega) = \lim_{T\to\infty} \frac{1}{2T} \overline{H_T^{\,*}(\omega) H_T(\omega)}$$

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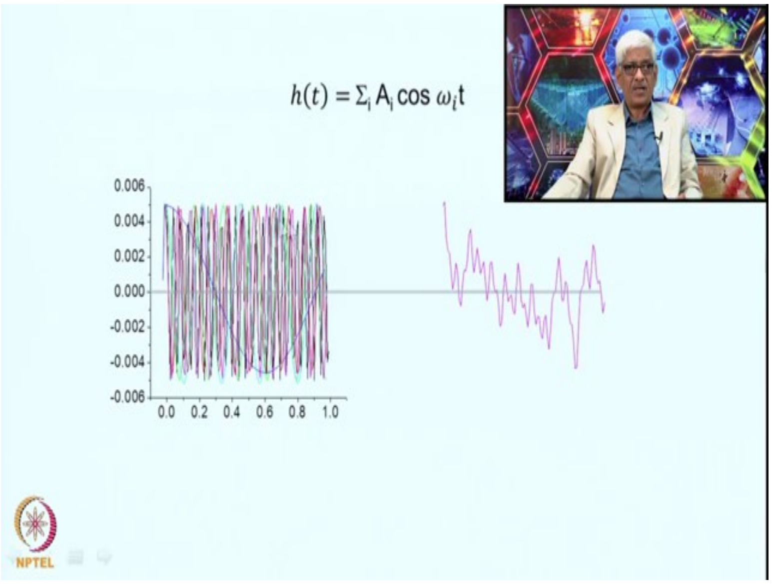

$h(t) = \Sigma_i A_i \cos \omega_i t$

The Fourier transform explicitly is written in this manner, this is the time dependent fluctuation in the *x-y* plane and then you write this Fourier transform equation here and this becomes the frequency dependent part.

$$H_T(\omega) = \int_{-T}^{T} h(t)\, e^{i\omega t}\, dt$$

So this is how you analyze what all frequencies are present in h (t). So there will be multiple frequencies here right, so and these are also be very randomly fluctuating quite frequent positive and negative frequencies both can be present and then, if I define the term which is called $J(\omega$¿ , which is an ensemble average of all these frequency components say we take complex conjugate here.

$$J(\omega)=\lim_{T\to\infty}\frac{1}{2T}\frac{❑}{H_T^{¿}(\omega)H_T(\omega)}$$

Why do I take this? Because this itself the average will be 0, because the average of *h(t)* itself can be 0 and this will be 0. But the square of this will not be 0, so why do we need to take the square? Because, when you look at the *RF*, the $H_1\cos\omega_0 t$. When you look at the *RF* the H_1 was an amplitude of the particular frequency and the square of that represents the *RF* power.

So likewise here, in the summation what we have $A_i\cos\omega_i t$ in the previous equation A_i represents the amplitude and here, the A_i represents the amplitude the square of this represents the power. So what is implication of that, the square of the amplitude of the frequency is present here, it represents the power distribution in the fluctuating magnetic fields. So this is therefore, called as spectral density function.

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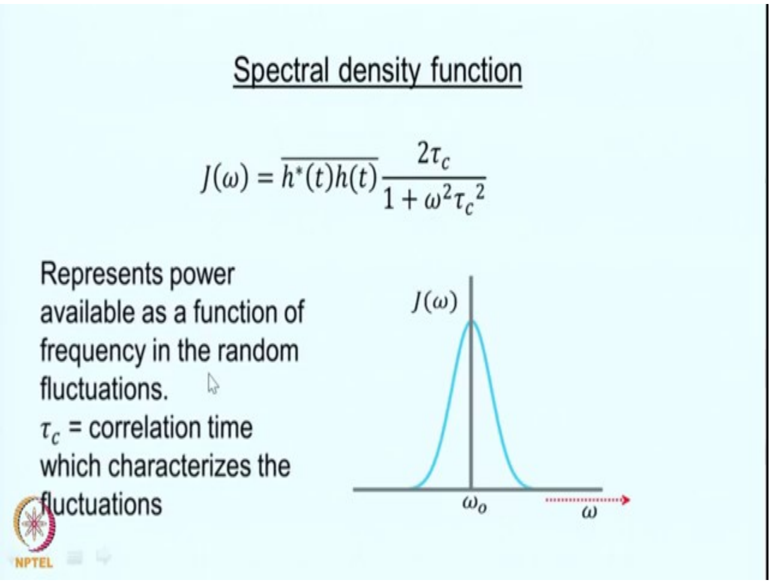

Spectral density function

$$J(\omega) = \overline{h^*(t)h(t)}\,\frac{2\tau_c}{1+\omega^2{\tau_c}^2}$$

Represents power available as a function of frequency in the random fluctuations.

τ_c = correlation time which characterizes the fluctuations

Spectral density means it is a distribution of power at different frequencies in the fluctuating ensemble, without going into the mathematical details of how this actual expression can be derived. We will take this test the result for this course but that will be a quite an involved calculation. We will take that result here and here is an ensemble average of the fluctuating fields in the *x*-*y* plane and we have this function

$$J(\omega)=\frac{\square}{h^{¿}(t)h(t)}\frac{2\tau_c}{1+\omega^2\tau_c^2}$$

$\tau_c$is a time constant called as correlation time. This actually indicates the correlation between the spins when they are moving in the in the ensemble, is there any phase relationship between the spins when they are moving, is there any sort of a relationship or a memory of the faith of the spins when they are moving in the solution in the ensemble?

So this correlation time actually represents the kind of a correlation that maybe present between two spins in the ensemble, okay. In other words this correlation term characterizes the fluctuations how much is the phase coherence between the spins? How much is the time between the two molecules hitting each other colliding with each other every time there is a collision, there can be change in the phase memory of the spin system.

And therefore there can be all these kinds of contributions to the fluctuations in the in the magnetic fields and that is characterized by particular time constant called as τ_c, and this obviously has a units of time and then, if you want to plot this function as a function of frequency it will represent a distribution like this.

Notice, and this is my *RF* frequency here and it can keep changing, you can have various kinds of powers depending upon what sort of a frequency you want to consider, if you have to consider a frequency here it has this much power if you have a frequency here it has this much power, frequency here so and so forth. So, now I consider three particular situations when my spectrometer frequency or the *RF* frequency is represented by ω_0.

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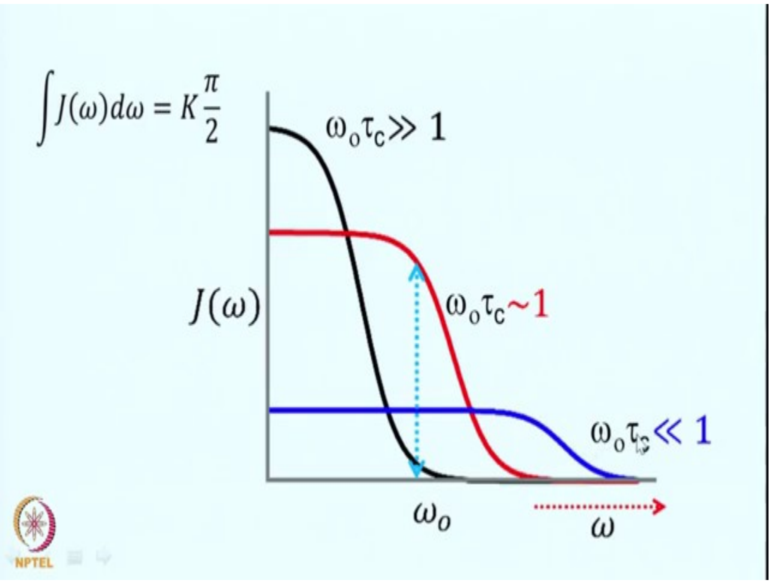
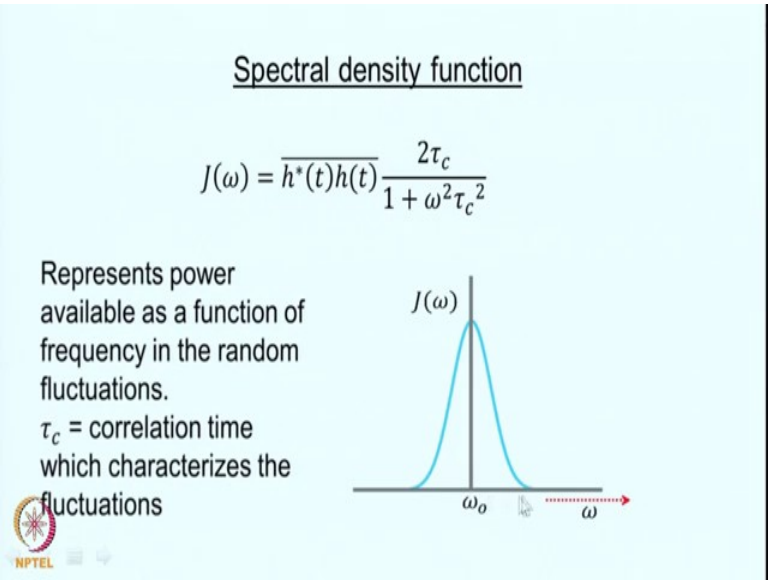


$$\int J(\omega)d\omega = K\frac{\pi}{2}$$



Spectral density function

$$J(\omega) = \overline{h^*(t)h(t)}\frac{2\tau_c}{1+\omega^2\tau_c^2}$$

Represents power available as a function of frequency in the random fluctuations.

τ_c = correlation time which characterizes the fluctuations

$\omega_0\tau_c \gg 1$ that means this tells you , how much is the correlation time there can be a situation, when $\omega_0\tau_c \ll 1$ or $\omega_0\tau_c \cong 1$. In this plot, only one half of this curve is plotted compared to the previous figure, here you had this half and this half on both sides of ω_0 or zero frequency or whatever, and only this half is plotted.

Now, before we actually go into this have a look at this equation, what does this tell you,

$$\int J(\omega)\,d\omega = \frac{K\pi}{2}$$

It turns out that this is a constant, in other words the total area under the curve of the spectral density function is constant because the integral represents the area under the curve, the total area under the curve is a constant which means the total power available in the ensemble from the magnetic dipoles fluctuating is constant.

Now, if you look at this curve $\omega_0 \tau_c \gg 1$ which means compared to the spectrometer frequency τ_c is such that this product is much larger than then the function behaves like this that means, at certain power level this almost approaches zero. All the power is concentrated in this much frequency distribution only, in this much area of frequencies on the other hand, if $\omega_0 \tau_c \ll 1$. That means this τ_c is much much less very rapid motions, very fast motions then this condition will be dissatisfied.

Now, you will see the power is distributed over a whole range of frequencies all, and then eventually much higher frequencies it goes down to zero. For the intermediate case the power lies in between these two. What is the consequence of this so, if I have to consider a transition in my spin system, suppose the transition has a particular frequency here, then of course this much power is available for the transition to occur for the spin system.

If this condition is satisfied, if this condition is satisfied then this much power is available. If this condition is satisfied then at the same frequency this much power is available. So therefore, depending upon the amount of power you apply of course you will have a different signal intensity. On the other hand, if we have a situation something like this here, if you are at this particular frequency, whenever you are looking for ω_i frequency right.

When you are looking at omega i which is at somewhere here, how much power is available at this frequency. That is if you have a condition of this type satisfied then it is this much power available. If this condition is satisfied, this much power is available but if this condition is available, zero power is available.

So therefore, depending upon how much is the correlation time in your in your sample there can be variations in the efficacy of transition at your respective frequencies. So therefore let us consider a switch so, if I have more power then of course I have a transition occurring then the relaxation will happen faster and we have a relaxation time changing. The same thing is now indicated by this particular curve.

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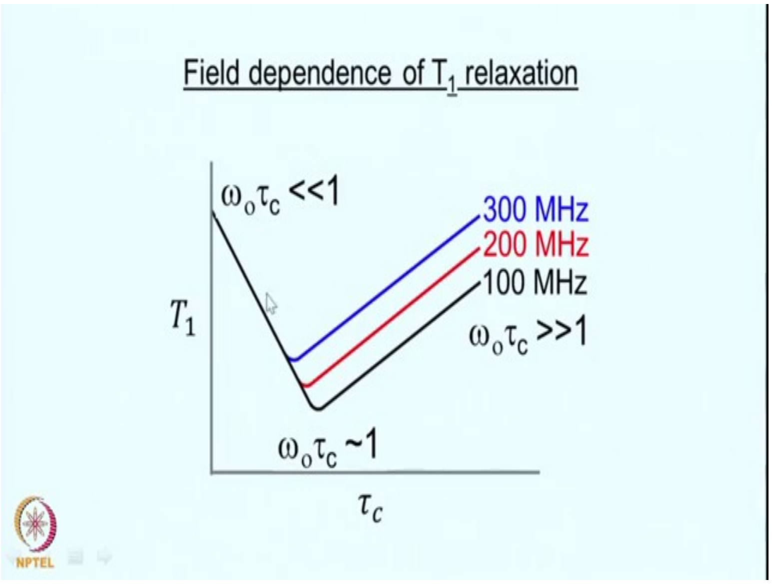
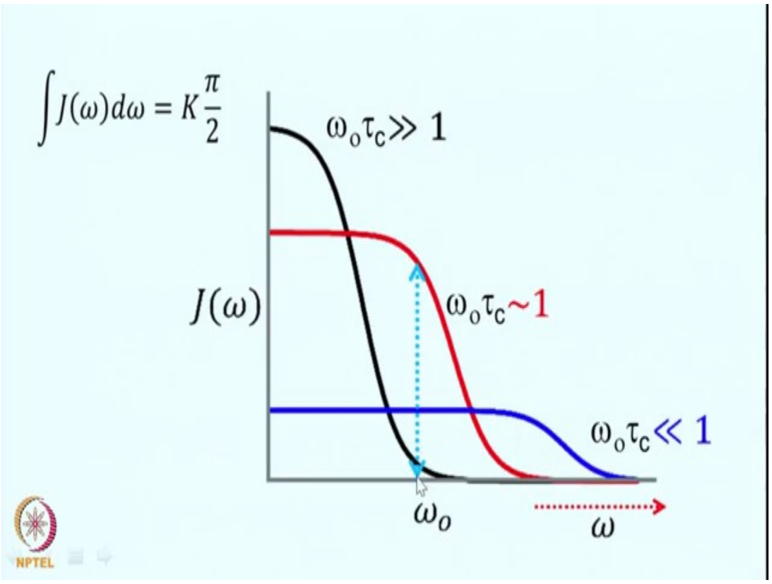

Field dependence of T_1 relaxation



If I were to plot the T_1; T_1 is the relaxation time as I said which causes transitions at the given frequencies. Now if I have $\omega_0\tau_c \gg 1$, then as a function of τ_c, if I plot the T_1 continuously decreases, here as the τ_c increases and then it reaches a minimum value and then it starts increasing from here onwards. For $\omega_0\tau_c \ll 1$ it starts increasing and all this has to do with the power that is available at a particular frequency, where you are looking at.

This can be understood from the previous curve here, suppose I have a frequency $\omega_i$which is here where I am looking for transitions. If this condition is satisfied I have practically no power here, so that is what, it will not cause a transition at all, if it does not cause a transition then the T_1 relaxation time will be very very high because it takes a long time for the system to come back to equilibrium .

If this condition satisfied in my spin system, then this much power is available at that particular frequency, so accordingly, the relaxation time will be determined depending upon how much power is available the it will determine how much time will be required for the system to come back to equilibrium. If we look at this situation, suppose this is the situation, when we have $\omega_0 \tau_c = 1$, then you have the maximum power available at that particular frequency.

That means it will cause the fastest relaxation of the spin system. That means the T_1 time will be the smallest, in other words this indicates how the T_1 time goes through a minimum and this will be the minimum time and this will be the maximum time and this will be somewhere in between right. So that is the indicator here, if you see here you have a time here and then it comes down to a minimum and then it starts increasing again you go on either side of τ_c of this point either side you go the T_1 increases.

T_1 therefore, goes through a minimum here whether it is $\omega_0 \tau_c \gg 1, \omega_0 \tau_c \ll 1$ it keeps on increasing. Now omega naught also can change if I change the omega naught, what will be the implication of that? The $\omega_0 \tau_c = 1$ will be reach at a different value of τ_c.

There if I increase my ω_0 the spectrometer frequency I make it from 100 Megahertz to 200 Megahertz then the τ_c will be accordingly, reduced so that this condition will be satisfied at a lower correlation time likewise, if I take it 300 Megahertz it will come down even further, it will be satisfied here. So therefore, what is the slow motion at one frequency can become fast motion at another frequency and vice versa.

For example, if I am considering a situation here then this will be in the fast motion limit for the black curve but in the slow motion limit in the blue curve. Which is the 300 Megahertz therefore, this explains why the T_1 relaxation time depends on the spectrometer frequency. It varies with the spectrometer frequency and one has to measure relaxation times at different frequencies to understand about the system better.

Now we talked about the relaxation time behaviors, how much time it will take and how does it depends upon the spectrometer frequencies. We can go into little bit more details with regard to the mechanisms. Now, we said it is a dipole-dipole interaction which causes the relaxation. Okay, so let us continue and look at how the transitions are brought about. You remember the expression for the transition probability, when we consider the *RF* induced transitions.

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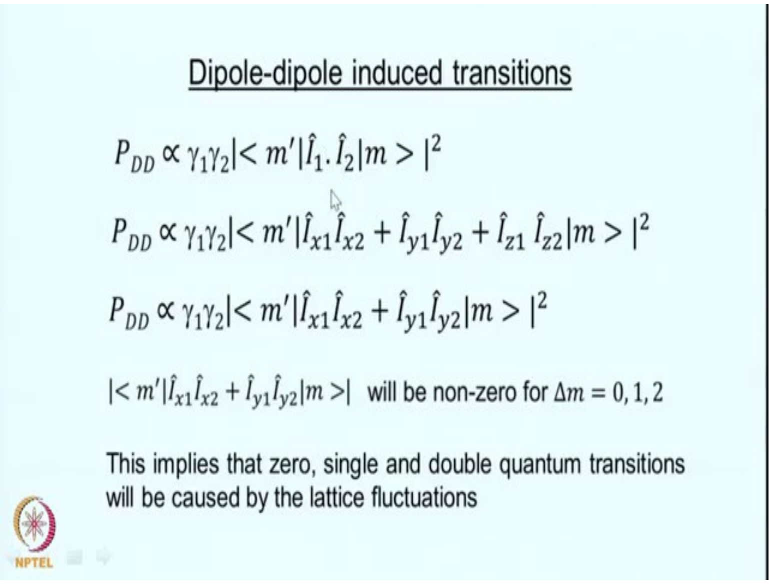

Dipole-dipole induced transitions

$$P_{DD} \propto \gamma_1\gamma_2 |< m'|\hat{I}_1.\hat{I}_2|m > |^2$$

$$P_{DD} \propto \gamma_1\gamma_2 |< m'|\hat{I}_{x1}\hat{I}_{x2} + \hat{I}_{y1}\hat{I}_{y2} + \hat{I}_{z1}\,\hat{I}_{z2}|m > |^2$$

$$P_{DD} \propto \gamma_1\gamma_2 |< m'|\hat{I}_{x1}\hat{I}_{x2} + \hat{I}_{y1}\hat{I}_{y2}|m > |^2$$

$|< m'|\hat{I}_{x1}\hat{I}_{x2} + \hat{I}_{y1}\hat{I}_{y2}|m >|$ will be non-zero for $\Delta m = 0, 1, 2$

This implies that zero, single and double quantum transitions will be caused by the lattice fluctuations

We said here if the *RF* is applied along the *X-axis* the interaction between the *RF* and the magnetic dipole causes this transition probability and we had this term here $\mu . H_1$ or it is simply I_{x1} was there and this thing had come. Here, the perturbation that is causing the transition is the dipole-dipole interaction between two magnetic dipoles.

So therefore here, the perturbation will be represented

$$P_{DD} \propto \gamma_1 \gamma_2 |¿ m^{'}|\hat{I}_1 . \hat{I}_2 \vee m ¿ \vee ¿^2 ¿$$

Where, I_1 and I_2 represent the spins spin operators for the two spins that are interacting. If you want expand this in more explicit form, this will have

$$P_{DD} \propto \gamma_1 \gamma_2 \left| \text{¿} m' \right| \hat{I}_{x1}.\widehat{I_{x2}}+\hat{I}_{y1}.\widehat{I_{y2}}+\hat{I}_{z1}.\widehat{I_{z2}} \vee m \text{¿} \vee \text{¿}^2 \text{¿}$$

In the same manner as we considered earlier we are considering transitions between *m'* and *m*, with some operator algebra of angular momentum theory.

We will realize that, this particular term is the one which is responsive for the transitions. This causes the transition between the states *m'* and *m*, this will not contribute to the transitions between the states *m'* and *m* but it is these two terms which contribute to the transition between the two states. Therefore if we ignore this,

$$P_{DD} \propto \gamma_1 \gamma_2 \left| \text{¿} m' \right| \hat{I}_{x1}.\widehat{I_{x2}}+\hat{I}_{y1}.\widehat{I_{y2}} \vee m \text{¿} \vee \text{¿}^2 \text{¿}$$

we will have only this part and now we do little bit more algebra with the angular momentum operators.

$$m' \vee \hat{I}_{x1}.\widehat{I_{x2}}+\hat{I}_{y1}.\widehat{I_{y2}}+\hat{I}_{z1}.\widehat{I_{z2}} \vee m$$

This will be non-zero for $\Delta m = 0, 1, \wedge 2$ this is in contrast to what we said for *RF* induced transition where we had only one of *RF* and the other one was a static field here both are *RF* kind of things and therefore, here we have transitions possible even when the two states have $\Delta m = 0, 1, \vee 2$. Earlier in the case of *RF* induced transition we had the so called selection rule $\Delta m = \pm 1$.

So here also there are selection rules but different from what is *RF* induced transition, here you can have 0, ±1 and ±2. We will face this situations when we consider multiple spins or spins with the higher I values and so on so forth. So this implies that 0 and double quantum transitions will be caused by lattice fluctuations.

Okay, now going into the Bloch equations a little bit more detail once more. Now, with respect to the h_{loc} field. h_{loc} is the one which is created by the fluctuating magnetic moments or magnetic dipoles.

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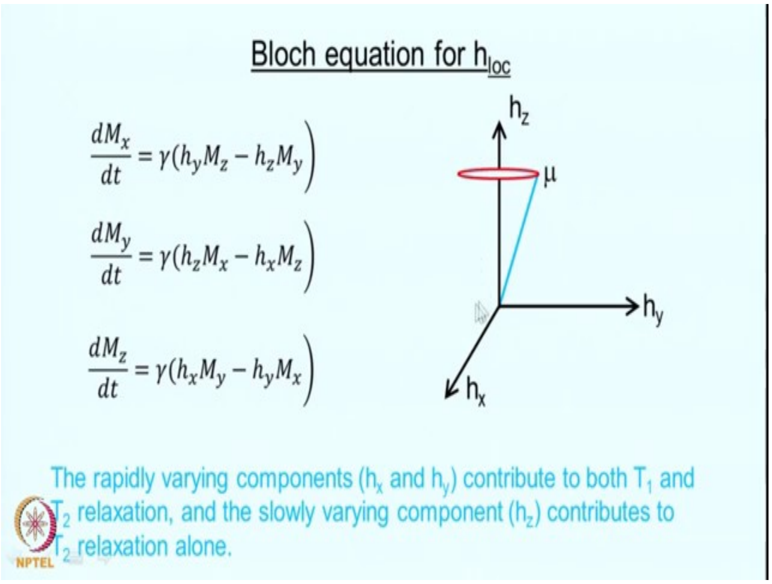

Bloch equation for h_{loc}

$$\frac{dM_x}{dt} = \gamma(h_y M_z - h_z M_y)$$

$$\frac{dM_y}{dt} = \gamma(h_z M_x - h_x M_z)$$

$$\frac{dM_z}{dt} = \gamma(h_x M_y - h_y M_x)$$

The rapidly varying components (h_x and h_y) contribute to both T_1 and T_2 relaxation, and the slowly varying component (h_z) contributes to T_2 relaxation alone.

We write that explicitly for the spin systems here, consider this magnetic moment here

$$\frac{dM_x}{dt} = \gamma\left(h_y M_z - h_z M_y\right)$$

$$\frac{dM_y}{dt} = \gamma\left(h_z M_x - h_x M_z\right)$$

$$\frac{dM_z}{dt} = \gamma\left(h_x M_y - h_y M_x\right)$$

and it is rotating under *Z-axis* this will all record in the *Z-axis* presses around the *Z-axis*. The h_x, h_y and h_z are the components of the h_{loc}. Notice therefore there is a precession here and any fluctuation here will cause a precessional frequency change. Any fluctuation will here cause a change in the frequency again and that leads to the loss of phase coherence of the components of this mu in the transverse plane. Therefore, if you look at here the M_x and the M_y can be μ_x.

This $\sum \mu' s$and now you see here you have the hy component appearing here h_z component appearing here, for this also h_z is appearing here h_x is appearing here for M_z you have only h_x and h_y. Among all the three hz is the one which is a slowly varying component because there is no frequency here.

It changes randomly as the system as the spin systems move closer or further and things like that, but a change in the frequency shows up in the h_x and the h_y components. Therefore h_x and h_y are rapidly varying functions, where h_z is the slowly varying function. So therefore, the rapidly varying components h_x and *hy* contribute to both T_1 and T_2 this represents the T_2 relaxation, this represents the T_1 relaxation. M_x, M_y appear in both all the three components. Therefore they contribute both the T_1 and T_2 whereas, the T_1 relaxation is contributed by the h_x and the h_y components only.

Okay, now without going into the much greater details of this calculations. I will give you here the final equations with regard to the relaxation rates.

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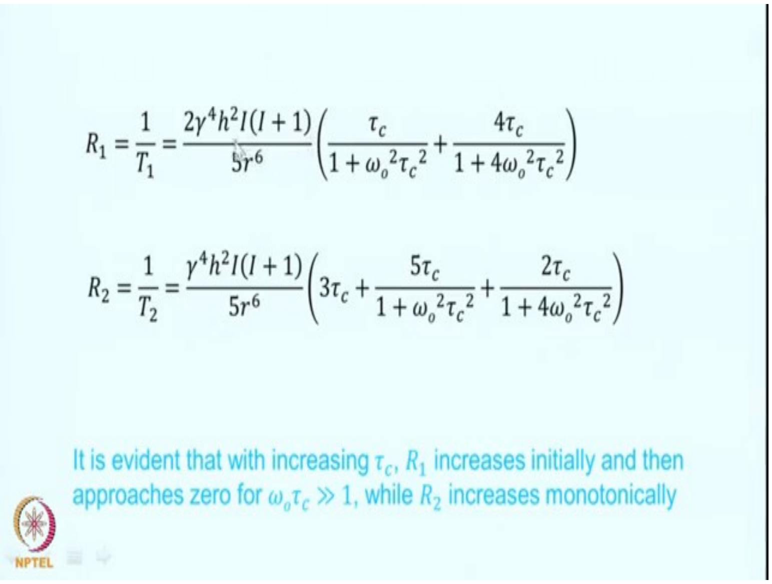

$$R_1=\frac{1}{T_1}=\frac{2\gamma^4h^2I(I+1)}{5r^6}\left(\frac{\tau_c}{1+\omega_o{}^2\tau_c{}^2}+\frac{4\tau_c}{1+4\omega_o{}^2\tau_c{}^2}\right)$$

$$R_2=\frac{1}{T_2}=\frac{\gamma^4h^2I(I+1)}{5r^6}\left(3\tau_c+\frac{5\tau_c}{1+\omega_o{}^2\tau_c{}^2}+\frac{2\tau_c}{1+4\omega_o{}^2\tau_c{}^2}\right)$$

It is evident that with increasing τ_c, R_1 increases initially and then approaches zero for $\omega_o\tau_c \gg 1$, while R_2 increases monotonically

$$R_2=\frac{1}{T_2}=\frac{\gamma^4h^2I(1+I)}{5r^6}\left(3\tau_c\frac{5\tau_c}{1+\omega_0^2\tau_c^2}+\frac{2\tau_c}{1+4\,\omega_0^2\tau_c^2}\right)$$

Now the relaxation rates are represented by R_1 and R_2. R_1 is the inverse of T_1 and R_2 is the inverse of T_2. This is proportional for the spin systems I value their nuclear spin. This is the inter proton distance or inter-nuclear distance R and this represent the spectral density distribution here.

Notice here,

$$R_1=\frac{1}{T_1}=\frac{2\gamma^4h^2I(1+I)}{5r^6}\left(\frac{\tau_c}{1+\omega_0^2\tau_c^2}+\frac{4\tau_c}{1+4\,\omega_0^2\tau_c^2}\right)$$

ω_0^2actually represents the double quantum transition. $\omega_0$represents a single quantum transition ω_0^2 represents the double quantum transition.

Therefore for the R_1 the double quantum transition probabilities also appear we are not going to the details of this theory but we will just take it for granted, this will be discussed later on when we talk about advanced topics later.

$$R_2=\frac{1}{T_2}=\frac{\gamma^4h^2I(1+I)}{5r^6}\left(3\tau_c\frac{5\tau_c}{1+\omega_0^2\tau_c^2}+\frac{2\tau_c}{1+4\,\omega_0^2\tau_c^2}\right)$$

And here it is a single quantum transition and for the T_2 we have here a frequency dependent term $\omega_0\tau_c^2$ and a frequency independent term in other words this is like a zero frequency.

So a slow motions like zero frequency if you treat they contribute to the T_2. Rapid motions contribute to the T_1, slow motions contribute to the T_2. Slow motions of course will also contribute to the T_2. I mean the rapid motions also will contribute to the T_2. In addition, the slow motions and the rapid motions contribute to the T_2 or the R_2 value. So if we were to plot this R_1 and R_2. R_1 is a function of τ_c, we can just simply show it in this manner.

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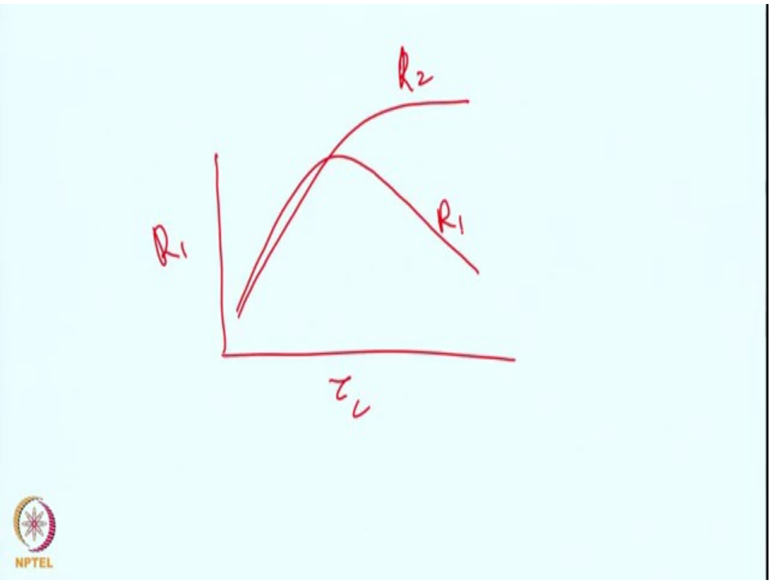

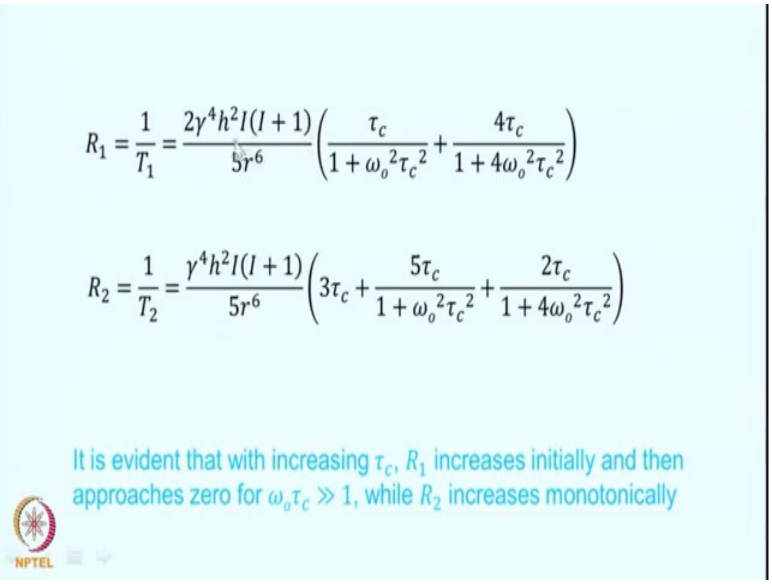

$$R_1 = \frac{1}{T_1} = \frac{2\gamma^4 h^2 I(I+1)}{5r^6}\left(\frac{\tau_c}{1+\omega_0{}^2\tau_c{}^2} + \frac{4\tau_c}{1+4\omega_0{}^2\tau_c{}^2}\right)$$

$$R_2 = \frac{1}{T_2} = \frac{\gamma^4 h^2 I(I+1)}{5r^6}\left(3\tau_c + \frac{5\tau_c}{1+\omega_0{}^2\tau_c{}^2} + \frac{2\tau_c}{1+4\omega_0{}^2\tau_c{}^2}\right)$$

It is evident that with increasing τ_c, R_1 increases initially and then approaches zero for $\omega_0\tau_c \gg 1$, while R_2 increases monotonically

This is τ_c. If I plot here R_1 the R_1 goes like this and then it decreases and the R_2 goes like this and it keeps going this is R_2 and this is R_1. Why does this R_1 go down further and that follows from the previous equation. If we look at this equation here it $\omega_0\tau_c \gg 1$ >>1 here if you look at this one here is far far less than 1, then we can ignore this condition and then it will be proportional to the τ_c. So as τ_c increases it will go on R_1 goes on increasing but if this condition is such that $\omega_0\tau_c \ll 1$ then it almost approaches zero.

So this is consistent with our previous equation it goes through a minimum. T_1 goes through a minimum, then goes up which means R_1 goes through a maximum and then goes down. Whereas here, this implies that R_2 continues to increase, regardless of the omega naught tau c condition because it is a term which is independent of omega naught tau c and that is indicated here with increasing tau c, R_1. increases initially and then approaches 0, then of course it is, in between there is a maximum there is maximum which will come as indicated to you in the curve and then approaches 0 for $\omega_0\tau_c \ll 1$ and while R_2 increases monotonically this typically happens, when the motions are extremely slow.

When the motions are very slow there will be three contributions to it, one is the fluctuating the magnetic power that is available will be different and if the extremely slow then it is different frequencies superimpose different lines superimpose resulting in the line broadening and that is called inhomogeneous line broadening that contributes the large line widths and this typically is observed in case of solid state NMR and also in systems of very large molecular weights.

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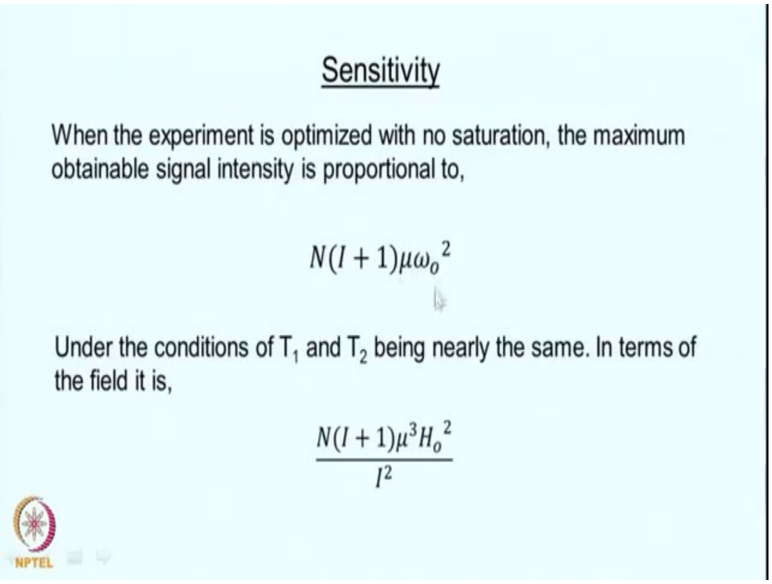

Sensitivity

When the experiment is optimized with no saturation, the maximum obtainable signal intensity is proportional to,

$$N(I+1)\mu\omega_o{}^2$$

Under the conditions of T_1 and T_2 being nearly the same. In terms of the field it is,

$$\frac{N(I+1)\mu^3 H_o{}^2}{I^2}$$

Okay, so the final topic though when the experiment is optimized with no saturation the maximum obtainable signal intensity is proportional to

$$N(I+1)\mu\omega_0^2$$

Notice it is not just proportional to the ω_0 the field it is proportional to the square of the magnetic field or the square of the frequency. Under the conditions of T_1 and T_2 being nearly the same. This is seen from the curve which I indicated there for low $\tau_c's$. For very low $\tau_c's$ T_1 and T_2 curves are actually overlapping and in terms of the field it is given by

$$\frac{N(I+1)\mu^3 H_0^2}{I^2}$$

However this does not include the noise which is contributing typically one does not see the square dependence one sees a $\frac{3}{2}$ dependence because the noise goes as the square root and therefore you typically see a $\frac{3}{2}$ dependence on the magnetic field.

And here is, are some calculations to show what are the relate to sensitivities of the different nuclei.

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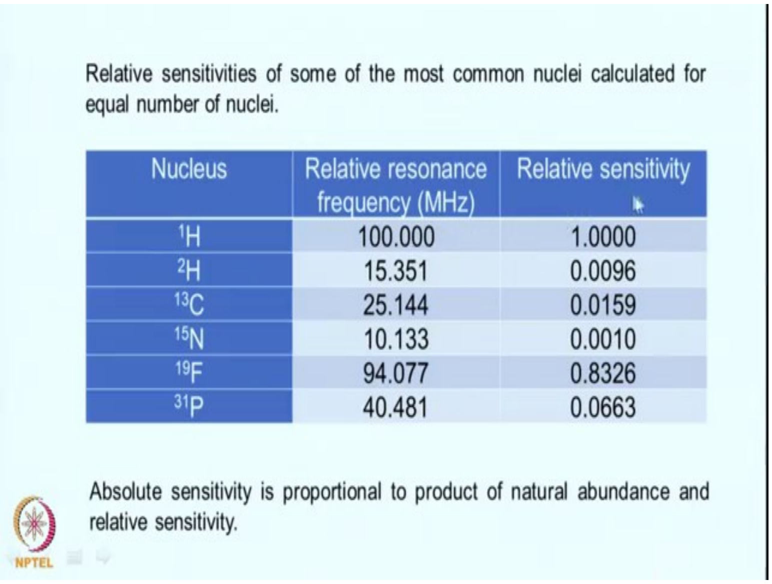

Relative sensitivities of some of the most common nuclei calculated for equal number of nuclei.

Nucleus	Relative resonance frequency (MHz)	Relative sensitivity
^{1}H	100.000	1.0000
^{2}H	15.351	0.0096
^{13}C	25.144	0.0159
^{15}N	10.133	0.0010
^{19}F	94.077	0.8326
^{31}P	40.481	0.0663

Absolute sensitivity is proportional to product of natural abundance and relative sensitivity.

See, the proton has the maximum sensitivity it is 100 percent. If relative resonance frequency is 100 then the relative sensitivity of this one is taken as one with respect to this we put down here the relative sensitivities of different nuclei. Deuterium is just 0096, carbon 13 is 0159 and this is Nitrogen 15 is 0.001, Fluorine 19 is 0.326, Phosphorus 31 is 0.0663. So after proton the one which is most sensitive is fluorine 19 and after that you have the other nuclei typically, we come across protons the carbons and the nitrogen 15.

Notice here the number of spins is treated to be is considered to be the same. Natural abundance is not included in this, this is the relate to sense it is simply, based on the μ, μ^3 you remembered and this is one the gyromagnetic ratio of proton and carbon 13 is 1 by 4. So the 4 to the power cube is 64, therefore this is nearly 1 by 64 of this. Now if we want to include the natural abundance of this, then you got what is called absolute sensitivity. Absolute sensitivity is proportional to the product of natural abundance and relative sensitivity.

Therefore this goes down quite substantially and that is why often one says, the NMR technique while it is so elegant, it is also a very insensitive technique and you require large amounts of samples for recording quality NMR spectra. So with that we come to a close and this chapter we close here. This concludes the first chapter of NMR spectroscopy which has to do with the basic concepts and then we go all on analyzing the details of the NMR spectra in the other lectures. Thank you.