NMR Spectroscopy for Chemists and Biologists
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Bloch equations
Lecture No. 03

Welcome to the third class on NMR spectroscopy. In the last class we looked at resonance absorption of energy by a spin system. Absorption of energy depends upon the *RF*, the power that we apply and also the spin lattice relaxation time T_1. There is a factor which we derived called saturation factor.

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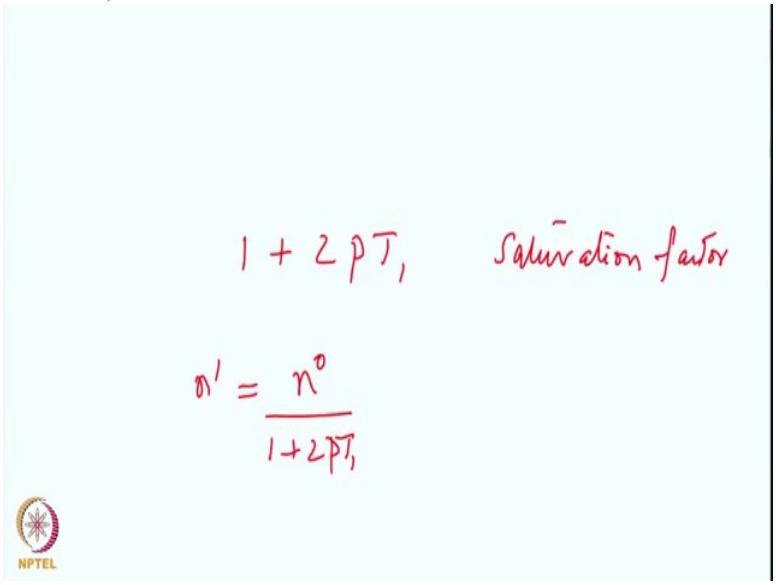

And that is equal to $1+2PT_1$. This is the saturation factor. We showed that in the steady state the population difference between the two levels is

$$n' = \frac{n^0}{(1+2PT_1)}$$

Where, n^0 is the equilibrium population difference between the two states. So if $1+2PT_1$ is extremely large then n' will tend to 0 and then it will lead to saturation and there will be no signal observed.

In fact, I said that was the reason why Gorter missed the Nobel Prize. He chose a sample which has such a large T_1 value that even at very low powers, the signal was getting saturated and he was not able to observe that. So therefore choice of the sample becomes important.

And here *P* is the transition probability which in turn is proportional to the power that we apply in the *RF*.

We now go forward and ask, are there any further restrictions in the absorption of energy? Some principles will have to be understood. In other words, are there any selection rules for absorption of energy?

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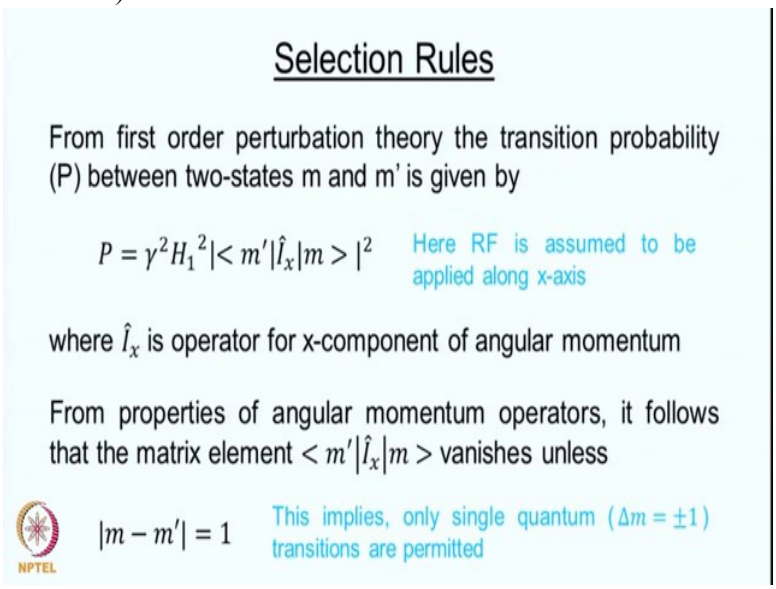

Indeed, there are some selection rules and this comes as a result of quantum mechanical treatment of the interaction between the spin system and the applied *RF*. This is called first order perturbation theory.

And the *P* what we used earlier can actually be calculated using this first order perturbation theory. We will not go into the details of this calculations. We will simply take this formula which says

$P = \gamma^2 H_1^2 \vee ¿ m' \vee \hat{I}_x \vee m > ¿^2$

Where two states m' and m between which we are considering the transition of the spin system. Here $\hat{I}_x$ is angular momentum operator, *x* component of the angular momentum. It comes here as $\hat{I}_x$ because we have assumed that the *RF* is applied along the *X-axis*. If it were applied along the *Y-axis* then $\hat{I}_y$ operator will come. But that does not matter so far as the conclusions with the regard to the *P* are concerned.

And now to calculate this, of course one has to go into the theory of angular momentum operators, we will not go into the details of that one. We will simply take the result which says that this element which is called the matrix element here of the operator $\hat{I}_x$ between the states m' and m, this vanishes unless.

$|m'-m|=1$

What are m' and m? m are the azimuthal quantum numbers of the spin I, we said m takes value from $-I \ldots +I, 2I+1$, values, for a given I. So if $I=\frac{1}{2}$, then we have m is equal to plus half and minus half, these two states possible. So what is the implication of this? If I say $|m'-m|=1$

This implies only single quantum $\Delta m=\pm$, transitions are permitted. Let us look at this in little bit more illustrative manner.

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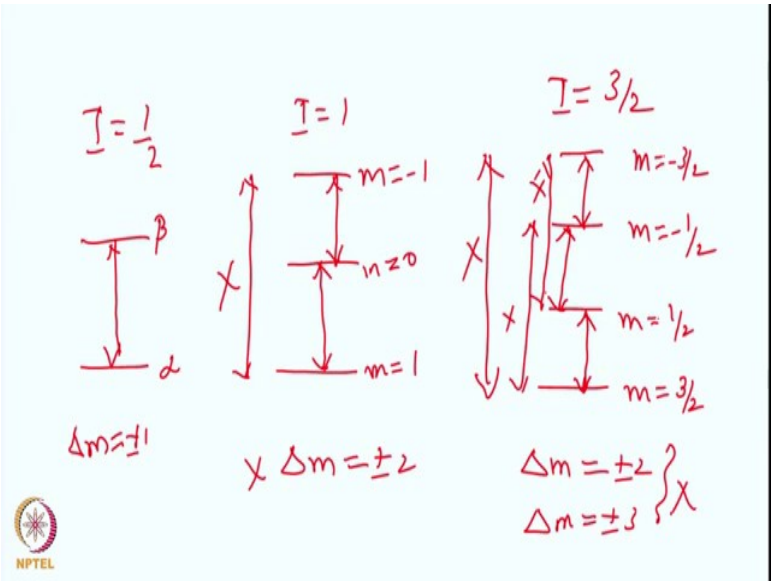

Let me write here ¿$\frac{1}{2}$. I have two states, α and β. This is for $m=\frac{1}{2}$ m and $m=\frac{-1}{2}$. Suppose $I=1$, then I have 3 states. Here $m=-1, m=0 \wedge m=1$. If, $I=\frac{3}{2}$ how many states are there here? $2I+1$is 4, therefore there will be 4 states. Notice all of them are equally spaced. The energy levels are equally spaced. And here $m=\frac{3}{2}, m=\frac{1}{2}, m=\frac{-1}{2} \wedge m=\frac{-3}{2}$

What is the implication of the selection rule what we showed just now? That the transition between this is always allowed because here the $\Delta m = \pm 1$. This transition is allowed. This transition is allowed. $\Delta m = -1$, for this, but this one is not allowed. So $\Delta m = -2$, is also not allowed.

Let us look here. So here there are four energy levels. We can draw many transition possibilities here. This is, $\Delta m = 1$, is allowed. This is also allowed. This is also allowed. All of these correspond to $\Delta m = -1$.

But if you look here, this is not allowed, likewise this one is not allowed. And similarly this one is also not allowed. So $\Delta m = -2, \Delta m = -3$, is not allowed. These are the selection rules. These are the selection rules for *RF* induced transitions. So we say when $\Delta m = \pm 1$, these transitions are called as single quantum transitions.

$\Delta m = \pm 2$ are called as double quantum transitions. $\Delta m = \pm 3$ are called triple quantum transitions. There is also, of course, $\Delta m = 0$which we do not come across here in this kind of spin system. They will come later. Those are called as zero quantum transitions. Those also will not be allowed by *RF*.

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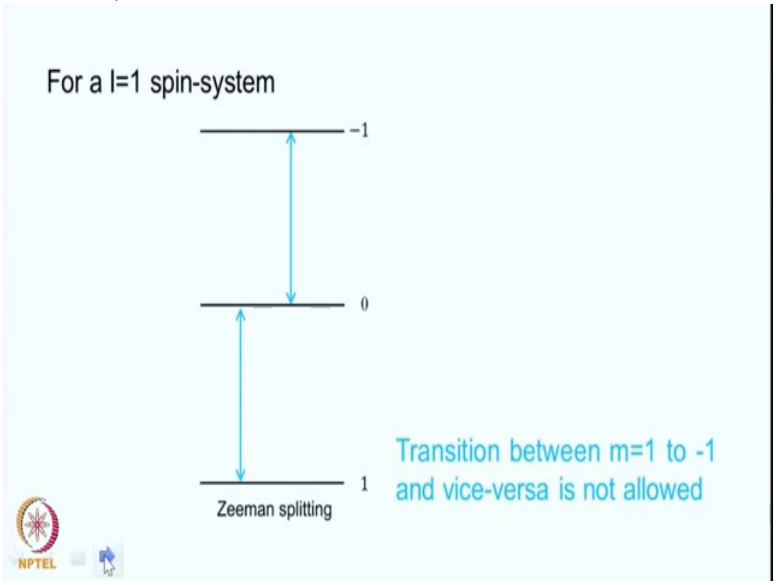

See the same thing is stated here. Transitions between $m = 1 \wedge m = -1$ and vice versa is not allowed, which is what I explained just now.

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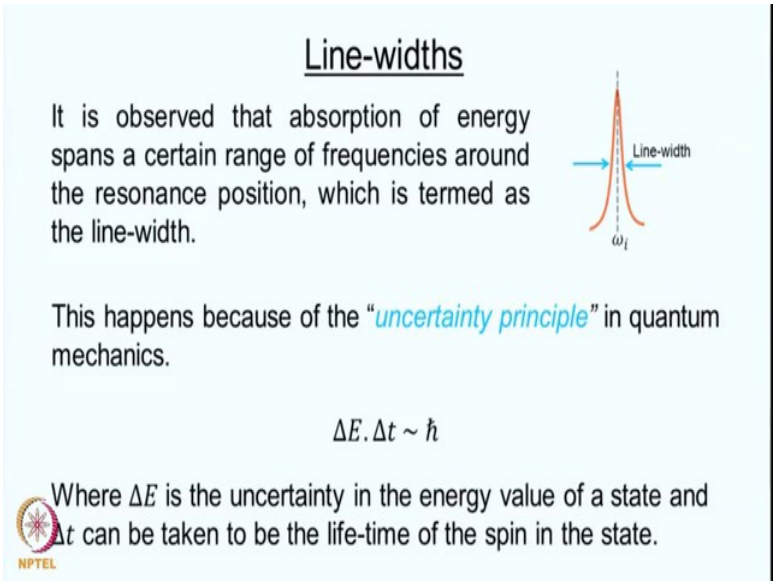

Now if an absorption of energy happens, the energy should correspond to the actual value of the energy difference.

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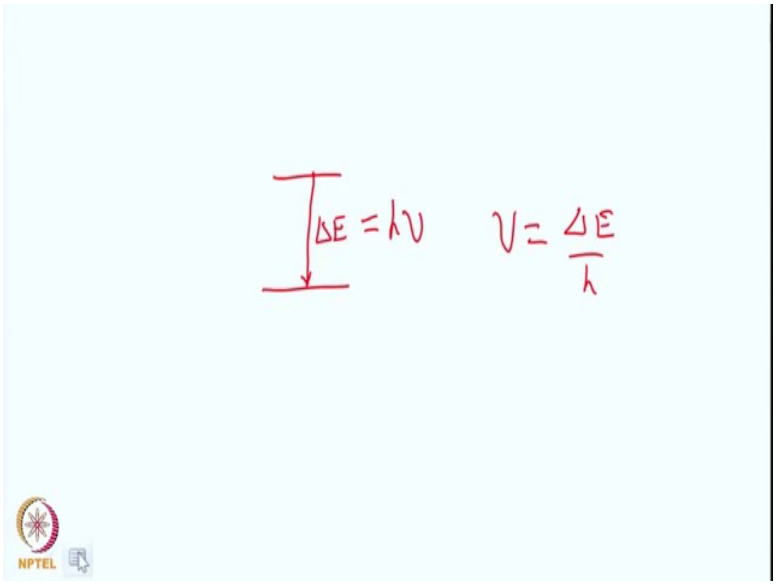

If this energy difference is

$\Delta E = h\nu$

Where, ν is the frequency of absorption then

$\nu = \frac{\Delta E}{h}$

which is a single frequency. However it does not happen this way. It does not happen always that absorption of energy occurs exactly one single frequency.

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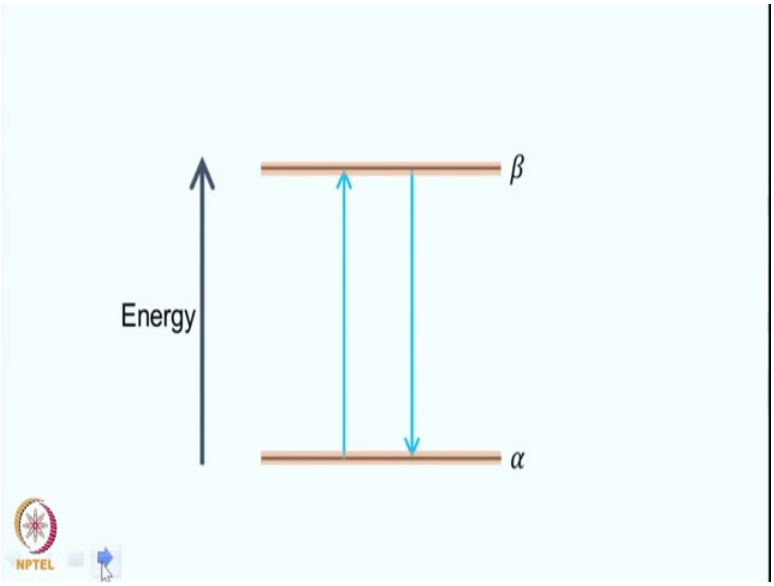

It happens over a range of frequencies

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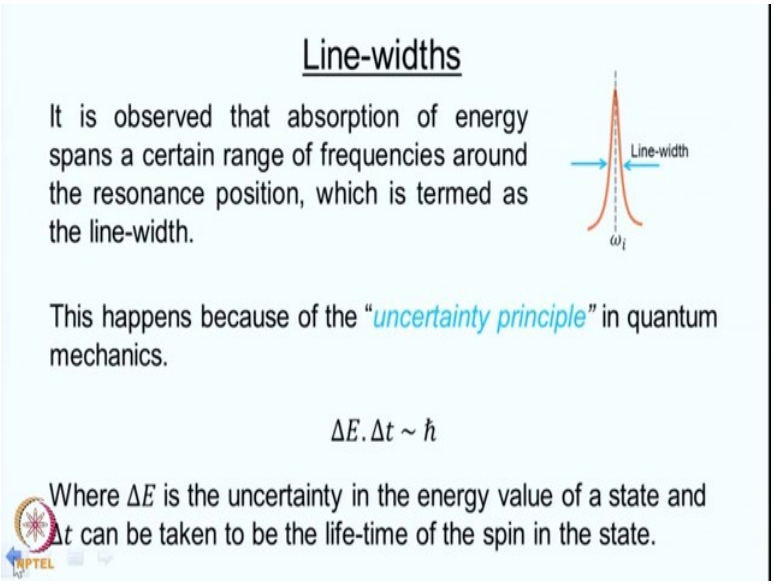

And these contribute to what is called as the line-width. So you see here, the absorption of energy spans a certain range of frequencies. Signal will have a shape like this and see this is the central frequency at which energy should have been absorbed.

But there is of course absorption of energy if the frequency is slightly different, is here or here or here but of course the amount of energy absorbed will be different. So, therefore it generates a line which has a width. And if I take at the half height of this line then this is typically called as the line-width. What is the reason for this line-width?

This again comes from quantum mechanics. There is what is called as uncertainty principle in quantum mechanics which says that

$\Delta E . \Delta t \quad \hbar$

This is the intrinsic principle which quantum mechanics defines. So we will have to follow this. ΔE is the uncertainty energy value of a state and Δt can be taken to be the lifetime of the spin in the state.

A spin when it undergoes a transition from one state to another state, obviously its lifetime in the particular state is changing. It has a well-defined lifetime and therefore it undergoes a transition. So depending upon what is the lifetime of the state then your energy value is not precisely defined. If this is extremely high, then this will be very small. Then the energy value will be very precisely defined. But if this is a small then this energy value is not very precisely defined.

Therefore there is a certain uncertainty in the energy which means absorption of energy can take place at multiple frequency values. So therefore in an ensemble of spins, some will absorb energy at one particular frequency. Some will absorb at a slightly different frequency and so on. And because of that you get a line-width. What are the factors which influence this line-width?

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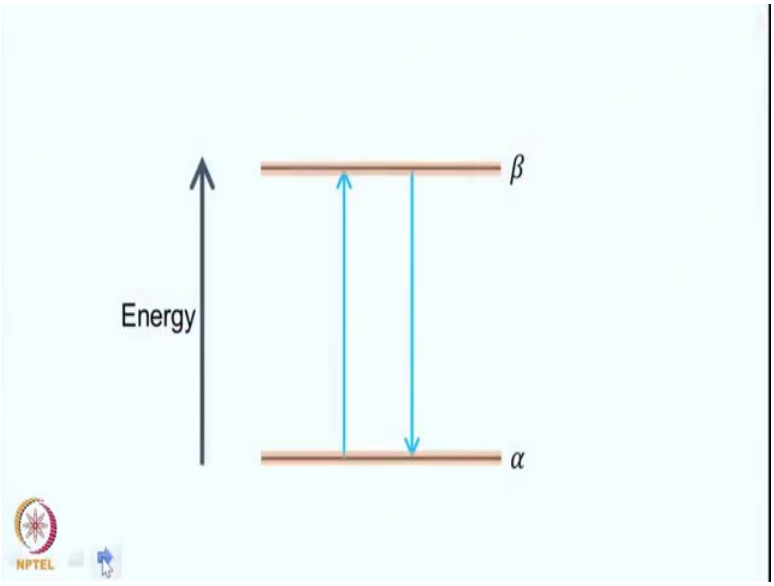

I indicated here, for the 2 spins, for the 2 level system the α and the β states have a certain width in the energy, have a certain width here for each of these states. And because of this there will be a certain width in the frequencies absorbed or emitted. So that is what this leads to what is, we called as the line-width.

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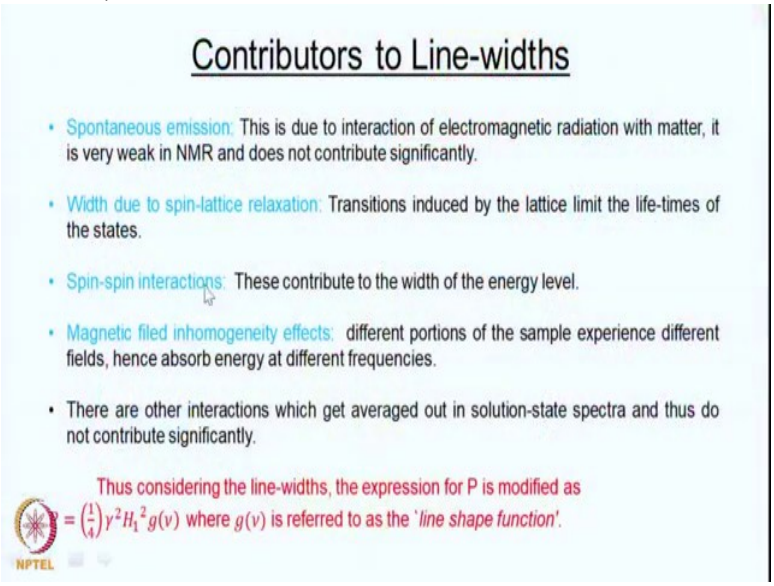

What factors determine the line-width? We will list here some of the important factors. The first thing is spontaneous emission. This is a very common mechanism for line-width in spectroscopy. This arises because of interaction of electromagnetic radiation. RF is electromagnetic radiation with matter. This is a very general quantum mechanical phenomenon.

It depends upon how much is the strength of your *RF*, how many photons are there in a particular volume of the sample? How does it interact with the matter? Depending upon that you have spontaneous emission happening. And that means that it limits the line-width. It limits the lifetime of the state and therefore the uncertainty in the energy and you get a line-width contribution.

However, this is extremely weak in NMR. One could calculate this for the given kind of energies we use and the given kind of powers we use. This will roughly absorbed $10^{-20} \vee 10^{-23}$ something like that and therefore we can simply ignore it. This is not a major contributor to the line-width.

Width due to spin-lattice relaxation, we said earlier that there is a spin lattice relaxation which allows the spins to come back to equilibrium whenever there is a perturbation. So these transitions are always happening. These are lattice induced, there are interactions between the lattice spins and the spin system of your interest. Because of this, the energies are fluctuating. And that limits the lifetime of the state and this contributes to the width of the line.

Similarly the spin-spin interactions, within the given spin system there will be spin-spin interactions which also cause fluctuations in the energy values. It cause transitions between the states and this also results in the line-width. Magnetic field inhomogeneity's effect, different portions of the sample experience different fields hence absorb energy at different frequencies.

We noticed in our spectrometer we have the sample in a tube which is put in the center of the magnet. We assume all the spins in your sample see the same magnetic field. Now this depends upon how homogenous is your field. If your magnetic field is not very homogenous over the sample volume, different spins in the sample experience different kinds of magnetic fields and therefore their precessional frequencies are going to be different. This results in width of the line. This is magnetic field homogeneity effects.

There are other interactions which get averaged out in solution state spectra and we do not wish to consider that here. Overall, considering the line-width the expression for *P* is modified in this manner.

$$P=\left(\frac{1}{4}\right)\gamma^2 H_1^2 g(\nu)$$

This are the factor which we introduced now to take care of the line-widths. So that, which means the transition probability is slightly modified depending upon what the frequency is and that shows up as the line shape function. This is called, g nu is called as the line shape function.

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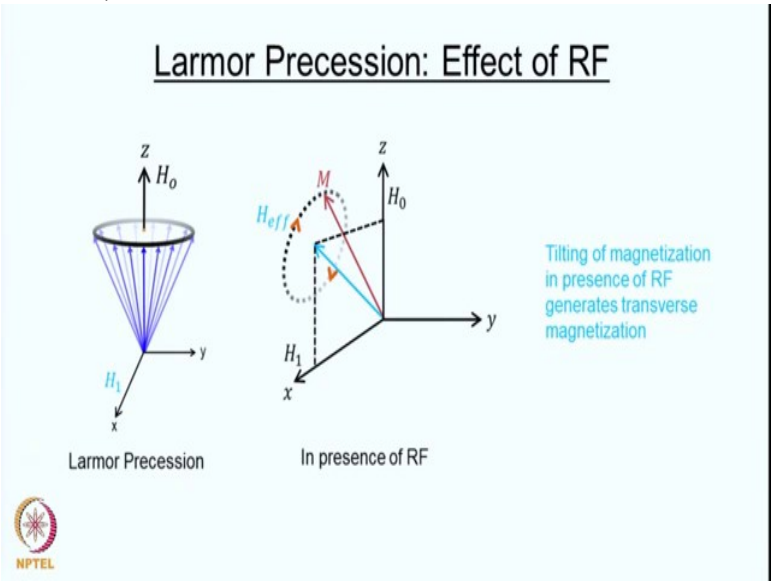

Ok, now let us return to Larmor Precession. This we have already seen, Larmor Precession happens in the presence of the main magnetic field; the nuclear spins precess around the magnetic field direction H_0 with a frequency which is dependent on the magnetic moment and the field. Now what happens when the *RF* is applied? How does it influence the Larmor Precession?

You notice here, if we are on resonance, consider that we are on resonance or we are slightly away from the resonance, what because of the line-width also, line-width we already considered, we have this H_0up right along the *Z-axis* and we applied the *RF*, applied along the *X-axis*. You could have applied along the y-axis also, it does not matter. But we consider here the *RF* applied along the *X-axis* and it has a magnetic field which is H_1. Remember we called our RF as

$$RF=2H_1\cos(\omega_0 t)$$

And the rotating component is $H_1\exp -i\omega t$

So when we are considering this along the H_1, along the *X-axis*, H_1 field, we have a H_0 field here. There will be an effective field which is a vector addition of this and this. And the effective field will be here. Now the spin system sees this effective field. Spin system does not see only the H_0 field but sees the H_1 field as well. Therefore there is an effective field which is in this direction. Therefore the spins will have to precess around this effective field.

This is the cone. The cone which was here earlier now gets tilted to go like this. All the spins are now on the surface of the cone described by this circle. So what is the implication of this? The magnetization now gets tilted. Because effective field is tilted, remember the magnetization is along the magnetic field axis over a long period of time. Now this will be tilted along this axis which means in this laboratory frame there will be certain component of magnetization on the x or the y axis.

Of course, there will be *Z-axis* component but there will be *x* and the *y* components. We call this *x* and the *y* components as transverse magnetization. And what is the implication of transverse magnetization? We said earlier, when the system is at equilibrium, there is no transverse magnetization because all the transverse components cancel out because of the hypothesis of random phases.

Now by implication if there is a non-zero transverse magnetization, it will imply that some of the spins here have acquired a sort of a phase coherence. The ones which were all going randomly like this. Now they have come together in a particular fashion, they come closer, they can move together, this we call it as the phase coherence. The spins move together, then it would mean there is phase coherence. And to that extent the cancellation will not happen. There will be a transverse component of the magnetization.

So therefore generation of the transverse magnetization implies generation of a phase coherence among the spins in the ensemble. This has important implications as we will see later. Therefore now we have *x* and the *y* component of the magnetization in the presence of the *RF*. We also have *z* component of the magnetization in presence of the *RF*.

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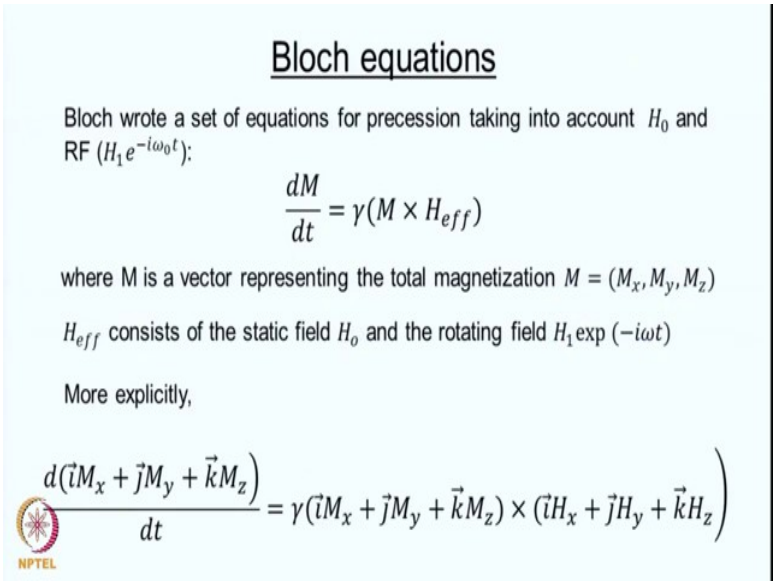

So to describe this motion, Bloch wrote a set of equations. He wrote a set of equations in a phenomenological manner for the precession of the spins considering the effective magnetic field that is given by this. We have the H_0 which is the field along the *Z-axis*. Then you have the *RF* which is

$RF = H_1 \exp -i\omega t$

Putting it together we have the H_{eff} (H effective).

Then he wrote this equation

$\frac{dM}{dt} = \gamma\left(M \times H_{eff}\right)$

This basically represents a force which is experienced by the magnetization in the presence of the field. This is a torque. Basically it represents a torque when the magnetization interacts with the field. So he wrote this equation in a phenomenological manner. It tells you that rate of change of magnetization is proportional to the cross product of magnetization and the H effective, both are vectors here.

Now *M* is a vector representing the total magnetization which has components

$M = M_x, M_y, M_z$

Where, M_x, M_y, M_z are *M* component along the *x, y, z* directions. And H_{eff} consists of a static field H_0 which is along the *Z-axis* and the rotating field $H_1 \exp -i\omega t$, since it is rotating, it continuously generates *x* and *y* components, oscillating *x* and *y* components.

Put this in the more formal way, putting into consider the various components here, the same equation is recast in this manner

$$\frac{d\left(\vec{i}\,M_x+\vec{j}\,M_y+\vec{k}\,M_z\right)}{dt}=\gamma\left(\vec{i}\,M_x+\vec{j}\,M_y+\vec{k}\,M_z\right)\times\left(\vec{i}\,H_x+\vec{j}\,H_y+\vec{k}\,H_z\right)$$

i, j, k are the unit vectors along the *X, Y* and *Z*-axis respectively. So typically you write a vector in this manner taking into account the various components.

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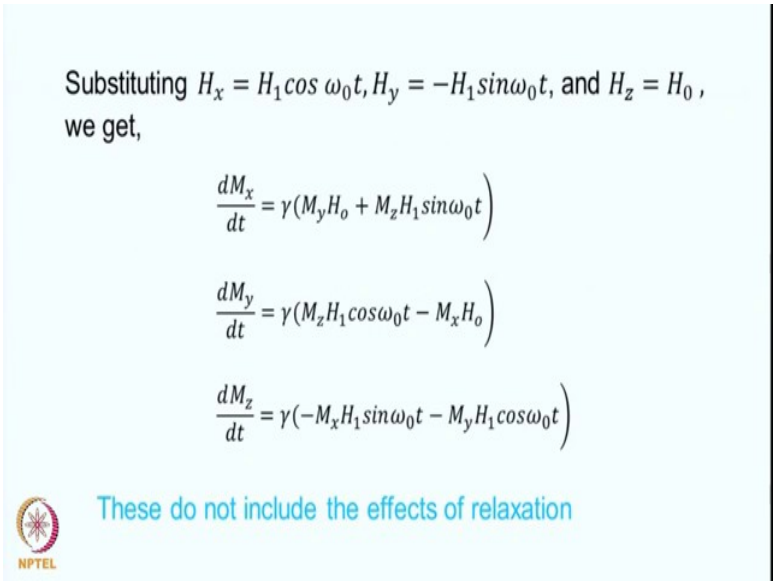

Now we take cross product of this without going into the explicit mathematics details there, we will just write the end result. What is H x?

$$H_x=H_1\cos\omega_0 t\,,H_y=-H_1\sin\omega_0 t\,,H_z=H_0$$

because this is the precessing field, $H_1\exp-i\omega t$ means it is a field which is going around in the *x y* plane. So it generates *x* and the *y* components which are oscillating in time.

So therefore the *x* component varies as $\cos\omega_0 t$ and the *y* component varies as $\sin\omega_0 t$, and taking in the consideration the sense of the rotation, we have put here the minus sign. So

$$H_x=H_1\cos\omega_0 t\,,H_y=-H_1\sin\omega_0 t\,,H_z=H_0$$

So expanding that previous equation, you get explicit expression for the M components of the magnetization.

$$\frac{d\,M_x}{dt}=\gamma\left(M_y H_0+M_z H_1\sin\omega_0 t\right)$$

$$\frac{dM_y}{dt} = \gamma\left(M_z H_1 \cos\omega_0 t - M_x H_0\right)$$

$$\frac{dM_z}{dt} = \gamma\left(-M_x H_1 \sin\omega_0 t - M_y H_1 \cos\omega_0 t\right)$$

It is interesting to see that where the *x* and the *y* components have the dependence of the H_0 here, because it leads to the precession, these are precession-related, Ok and then the M_z component appears here, whereas the M_z here depends on the *x* and the *y* components only on this side and the $M_x H_1 \sin\omega_0 t \wedge M_y H_1 \cos\omega_0 t$, these are the two components of the *RF* field along the *x* and the *y* axis respectively. Notice here the relaxation effects are not included.

This is simply the *RF* is applied and the H_0 is the field and there is no relaxation effect because relaxation is happening. The relaxation happens to change the *z* component of the magnetization and relaxation must also happen for the *x* and the *y* components because if the spins are having a certain phase coherence at a particular point in time, this phase coherence will not last forever.

It will slowly change as the system evolves and therefore there will be decay of this phase coherence. Therefore there has to be some kind of a time constant to characterize this.

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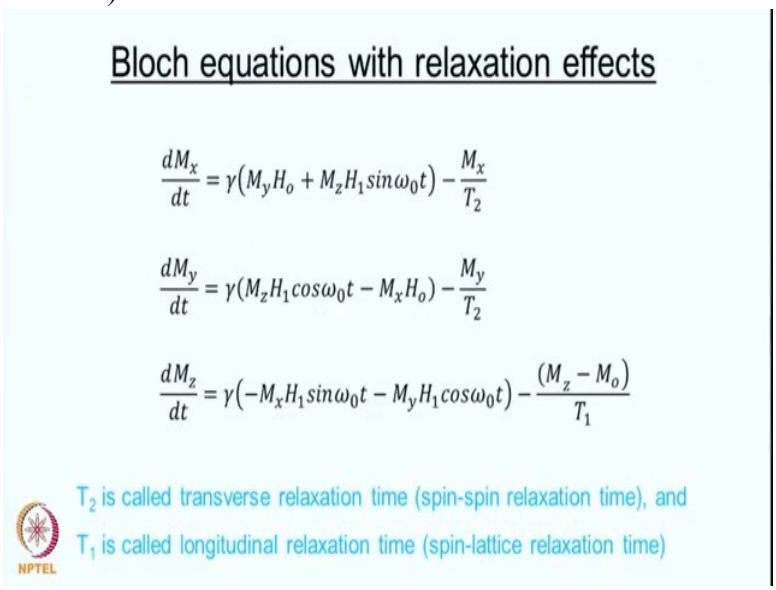

So therefore once again, Bloch modified this equations to include the relaxation effects. He wrote

$$\frac{dM_x}{dt} = \gamma\left(M_y H_0 + M_z H_1 \sin\omega_0 t\right) - \frac{M_x}{T_2}$$

$$\frac{dM_y}{dt} = \gamma\left(M_z H_1 \cos\omega_0 t - M_x H_0\right) - \frac{M_y}{T_2}$$

$$\frac{dM_z}{dt} = \gamma\left(-M_x H_1 \sin\omega_0 t - M_y H_1 \cos\omega_0 t\right) - \frac{\left(M ¿¿ z - M_0\right)}{T_1} ¿$$

This represents the deviation from the equilibrium value which is M_0. This represents the transverse component of the magnetization created by the application of *RF*.

And notice here we have a different relaxation time here. This is called T_2. T_2 is called as the transverse relaxation time and T_1 is called as the longitudinal relaxation time because this has to do with the *z* component of the magnetization. These have to do with the *x, y* components of the magnetization. And therefore these are called as transverse relaxation time. Sometimes they are also called as spin-spin relaxation time here $T_2$and this we will discuss later.

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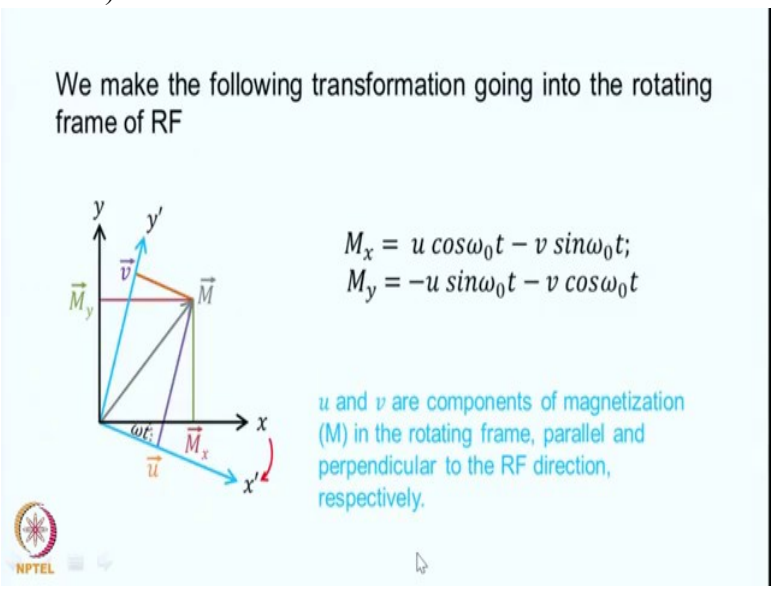

Ok, now to solve these equations it is a long effort. However we make some simplifications in this expressions by going into what is called as the rotating frame. Because we observe sitting on the *RF*, we make a measurement sitting on *RF*, with respect to the *RF* therefore if we go into the rotating frame and look at the magnetization components how they behave and that will give us the greater insight into the behavior of the spin system as, as time passes.

If we make this transformation here, we define a new axis *x'*, *y'*, *Z-axis* remains the same. We make a transformation here.

$M_x = u\cos\omega_0 t - ¿\, v \sin\omega_0 t\, ¿$

$M_y = u\sin\omega_0 t - ¿\, v\cos\omega_0 t\, ¿$

This is basically a coordinate transformation. *u* and *v* are the components of magnetization in the rotating frame parallel and perpendicular to the *RF* direction.

If the *RF* is applied along the *X-axis*, we are sitting on the *RF* and what is a component of the magnetization on the direction of the *RF*? And that we call it as *u* and the one which is orthogonal to that, we call it as *v*. So *y'* component is v, the *x'* component is u' and there is angle between them is $\omega_0 t$ because it is with this frequency the *RF* is moving.

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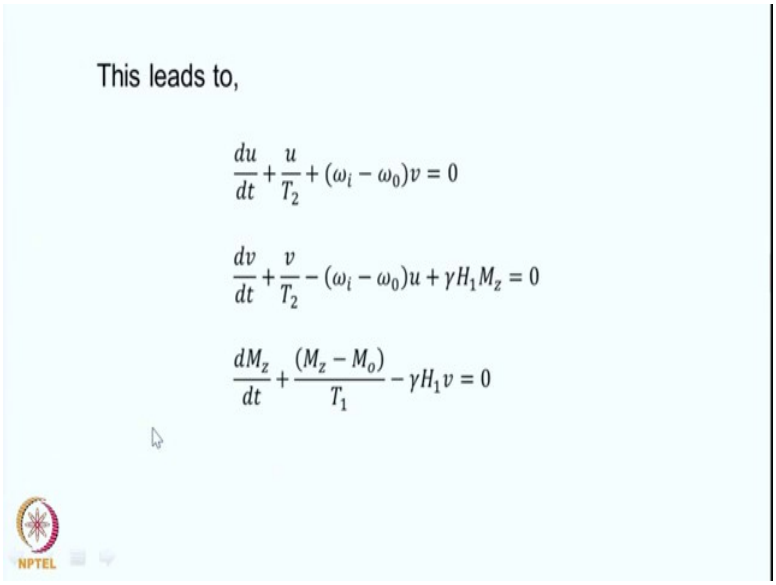

The consequence of this is, the expressions become very simple. You get three expressions for *u, v* and *z*. Ok this is algebra; of course we will skip this algebra here. Those one can work it out.

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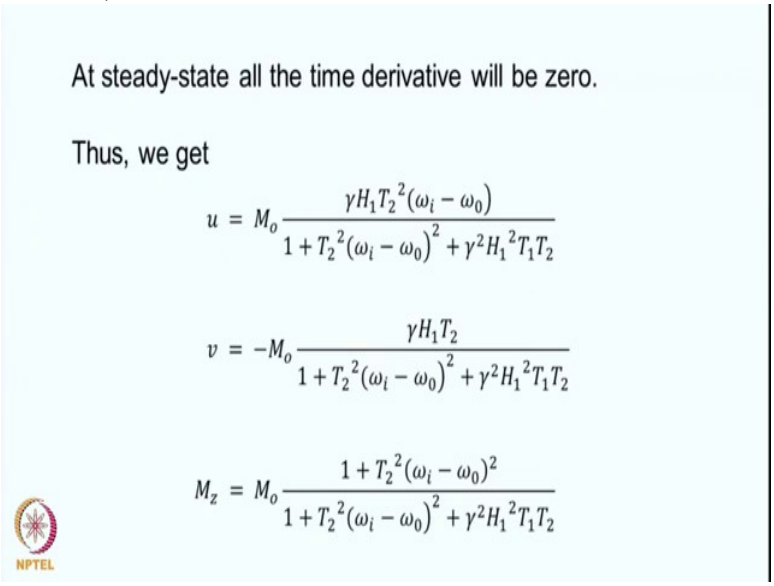

So at steady state, most important thing for us to look at is the steady state solutions of this.

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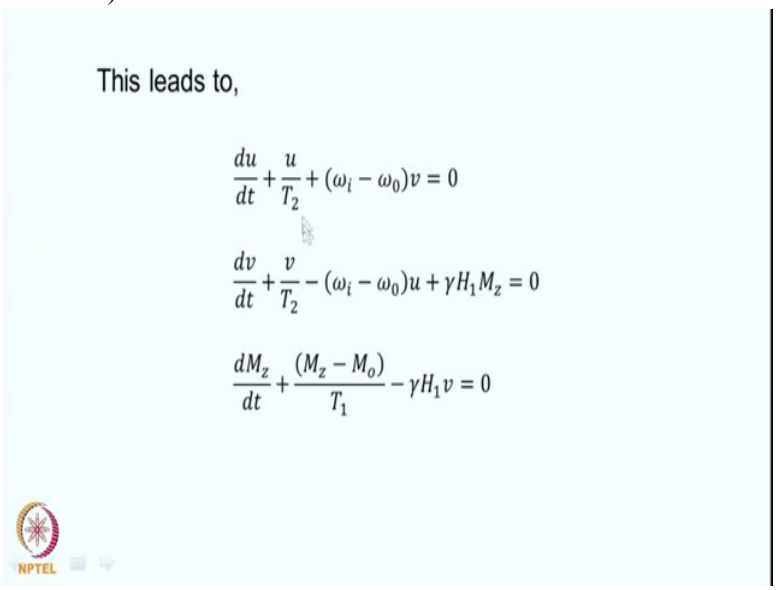

At the steady state all derivatives will have to vanish.

$$\frac{du}{dt}+\frac{u}{T_2}+(\omega_i-\omega_0)v=0$$

$$\frac{dv}{dt}+\frac{v}{T_2}-(\omega_i-\omega_0)u+\gamma H_1 M_z=0$$

$$\frac{dM_z}{dt}+\frac{(M_z-M_0)}{T_1}-\gamma H_1 v=0$$

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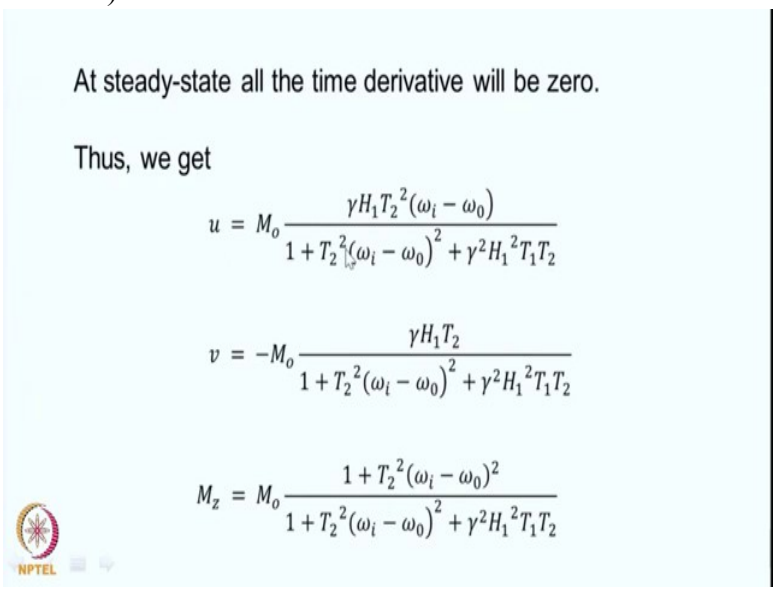

Once you put in that, you get expressions for

$$u = M_0 \frac{\gamma H_1 T_2^2 (\omega_i - \omega_0)}{1 + T_2^2 (\omega_i - \omega_0)^2 + \gamma^2 H_1^2 T_1 T_2}$$

$$v = -M_0 \frac{\gamma H_1 T_2}{1 + T_2^2 (\omega_i - \omega_0)^2 + \gamma^2 H_1^2 T_1 T_2}$$

$$M_z = M_0 \frac{1 + T_2^2 (\omega_i - \omega_0)^2}{1 + T_2^2 (\omega_i - \omega_0)^2 + \gamma^2 H_1^2 T_1 T_2}$$

These are all proportional to the frequencies here. ω_i is the frequency of precession and ω_0 is the frequency of your *RF*, the *u* is now proportional to this expression, as indicated proportional to the power amplitude of the *RF* and proportional to the T_2 value and there is a factor here, $\gamma^2 H_1^2 T_1 T_2$We will see what it means. And this factor is common in all of these. And M_z represents the *z* magnetization.

How does it recover to equilibrium as a function of time? And in this case, of course, we are talking about their magnetization in the rotating frame. Ok, so therefore we have now got the solutions of the equations of Bloch in the rotating frame. These result in the description of resonance phenomenon.

We will go into the details of the line shapes, how they allow us to measure the line shape in the next class. And we take forward from there with regard to the relaxation phenomenon. So we will stop here. Thank you very much. If you have any questions, keep it and we will try and answer those.