One and Two Dimensional NMR Spectroscopy for Chemists

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Lecture – 64
Relaxation Processes

Welcome back. In this class, we will discuss something about relaxation, like spin-lattice and spin-spin relaxation in NMR. Of course, this is a vast topic, one can discuss this for several hours or several days and weeks, we can talk about it. It is a huge topic and a fairly a very difficult topic to understand. But, I will try to make it as simple as it is for you so that you can try to get the concept of what is T1 and what is T2. Okay, that is what is the important thing. And at the end I will give you how to measure T1 and T2 with some experiments, so that you will get a feel for what is T1 and T2, because this is very important. See T1 and T2 values provide information about the dynamics of the molecule. You may have many times come across situations where you want to measure the T1 and T2 to study molecular motions. So better to have some conceptual idea, quickly and probably in this class I will try to tell you what is T1 and T2. Okay.

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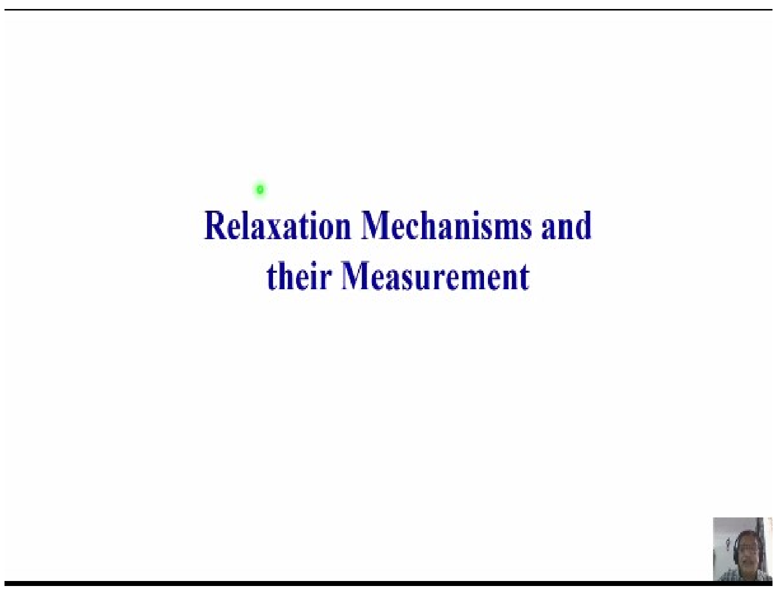

We will look at the relaxation mechanism first and then later their measurements.

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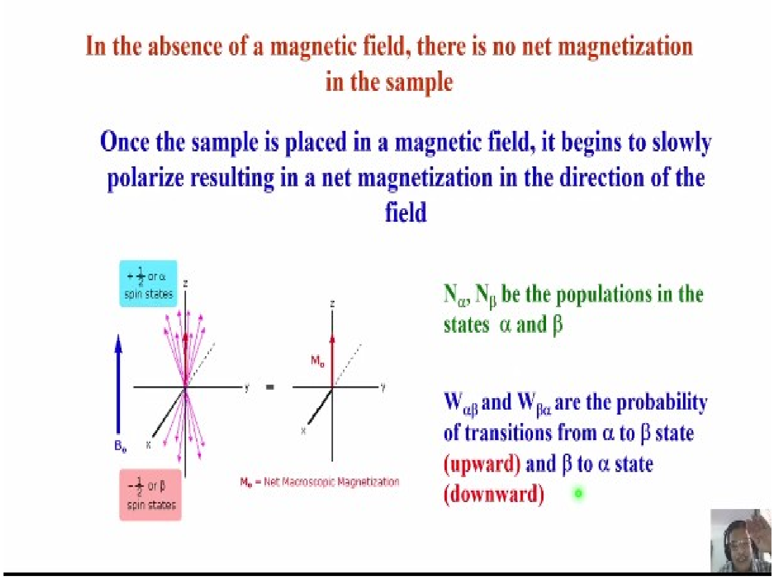

Let us say we have the sample in the absence of a magnetic field. This we have been discussing since the class one. There is no net magnetization. Nuclear magnetic moments are randomly distributed inside the sample of NMR tube, okay. So there is no net magnetization. Now I am going to take the sample, put it in a magnetic field. What is going to happen? As you know, once it is placed in a magnetic field, it starts beginning to align slowly. It has to align in the direction of the magnetic field. Or in other words, we call it polarization in the direction of the magnetic field. And we generate net net magnetization. We discussed about this, which is called bulk magnetization. Okay, this is the situation. These are all net magnetic moments, which are in the two spin states alpha and beta. And we have been discussing many times. We have more spins aligned in the direction of the magnetic field, than in the direction opposite it; the opposite to that of the direction of the magnetic field. It is a statistical average. Not that the spins are always along this axis. On an average if you take, there is a tendency for more spins to be in the direction of the magnetic field, than in the direction opposite to the field. As a consequence, we discussed about the bulk magnetization, where you have the magnetization along Z axis, and because of the random phase approximation, there is no magnetic moment components in the XY plane or in the transverse plane.

You are going to get the magnetization vector in this direction and in this direction. The vector addition of these two results in a sort of net bulk magnetization. This we understood long back. This is a net magnetization. You can treat like a tiny magnet, that is what we said. So, now there are two energy states. Now, because of these two, we have discussed alpha and beta states. Now there is more population in this state, let us say, the ground-state the higher energy state, than in the low energy state, right. So, how this population difference occurred? We should understand that. First conceptually, how did this population; this spin population difference occurred as soon as we put this sample in the magnetic field? To understand, for the two energy states like this alpha and beta, let us say number of population in the alpha state we denote as $N\alpha$. Number of populations, spin population in the beta state, we define as $N\beta$. This we are defining. Number of populations is given by N for alpha and beta. Initially before putting into the magnetic field, there was no preferred alignment, there was no polarization. Now when the polarization has to occur we have to understand that the spins has to redistribute themselves between the two energy states.

Let us define $W\alpha\beta$ and $W\beta\alpha$ are the probability of the transitions from alpha state to beta state, that is upper transition and from beta state to alpha state that is lower transition. The spins, when they have to polarize themselves, some spins are going from lower energy state to higher energy state, and some will come down from higher energy state to lower energy state. As a consequence, there is some difference of population. But what is the probability of this transition? Let us define by these two terms; $W\alpha\beta$ and $W\beta\alpha$ for upward and downward transitions. It is a definition. We are defining that.

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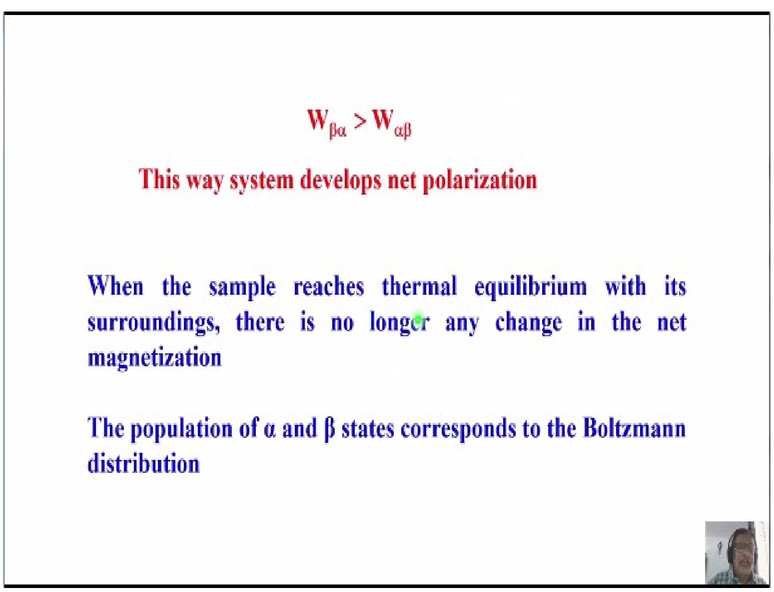

Now Wβα has to be larger than Wαβ. You know, why? That is the only situation you can see. That is the probability of transitions from beta to alpha has to be larger. So, this one Wβα has to be larger, correct. This is probability of transition from upper energy state to lower energy state. This is the transition probability from lower energy state to higher energy state. Wαβ probability it should be lower than Wβα. True right, it has to be. Otherwise system cannot develop net polarization. Because of this condition, Wβα probability of the spins coming from higher energy state to lower energy state is more than this; there is a net polarization developed in the spin system, right.

Now, when the sample reaches thermal equilibrium what is going to happen? It attains thermal equilibrium with the surroundings; then there is no more change in the system. No more change in the net magnetization. It has reached a situation that the population between alpha and beta states has attained what is expected from the Boltzmann distribution, okay. The population of alpha and beta states now corresponds to Boltzmann distribution. And there is no more change in the net magnetization.

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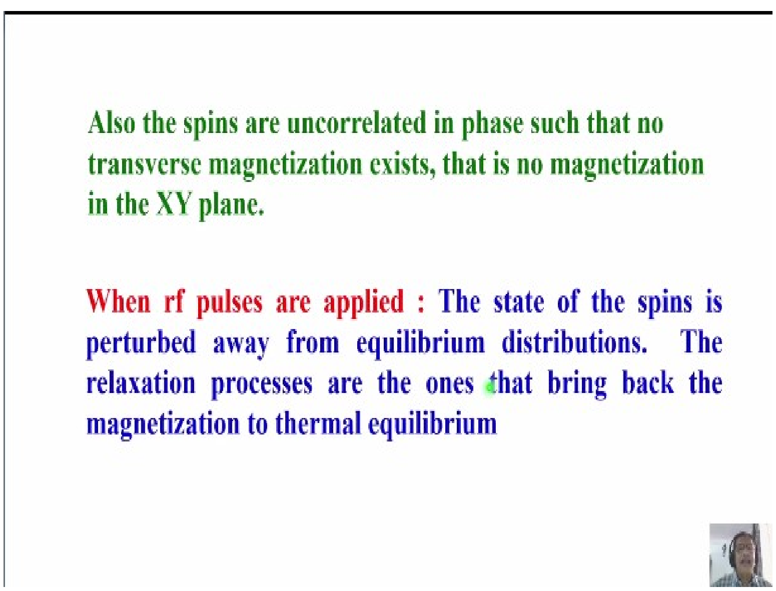

Now, also the spins are uncorrelated in the space, especially in the transverse plane. That is also true. We discussed that, all the spins in the transverse plane gets uncorrelated. That means, we also discussed this long back, there is no net magnetization in the XY plane. That is true. That is conceptually we discussed this long ago. Now, that is one natural situation as soon as you put the sample in a magnetic field spins attain thermal equilibrium. And we discussed what is the transition probability between two energy states, and we understood this should be our assumption, that is Wβα should be larger than Wαβ for developing net magnetization, correct. Now, in the other situation, like when we are collecting the signal, we send a radio frequency pulse in a direction perpendicular to the magnetic field, bring the magnetization to transverse plane, understand. And then you start deophasing in the transverse plane at the same time start growing along Z taxes. That is what we discussed long back. Because the system has to attain thermal equilibrium. The magnetization has to go back to thermal equilibrium. There are certain processes which are responsible for that, okay. Then also, it takes some time to attain thermal equilibrium, okay. You perturbed the spin system from equilibrium. Then after some time, if you leave it like that, it has to go back to equilibrium.

What is the time it requires to go to thermal equilibrium? Exactly, it is similar to what I said. As soon as, we put the sample in a magnetic field it requires some time to attain net polarization, right, in the magnetic field. That is same as the time which is required for spins to attain net polarization in the magnetic field even before applying rf pulse. That is spin-lattice relaxation time. Same thing here also, the time required for the magnetization from a perturbed state to come back to thermal equilibrium along the z axis is what is called a relaxation process, okay. There are two types of relaxation. We will go ahead and understand. This is a one type of relaxation, where magnetization has to come back and grow along Z axis.

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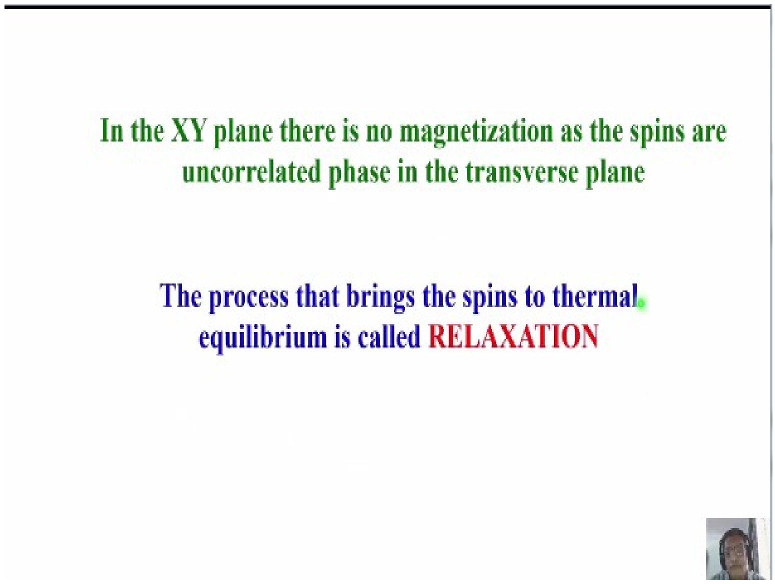

Of course, as I said, there is no magnetization in the XY plane, because they are uncorrelated in the transverse plane. That I already told you. The process that brings these spins to thermal equilibrium is called relaxation. That what just now I said.

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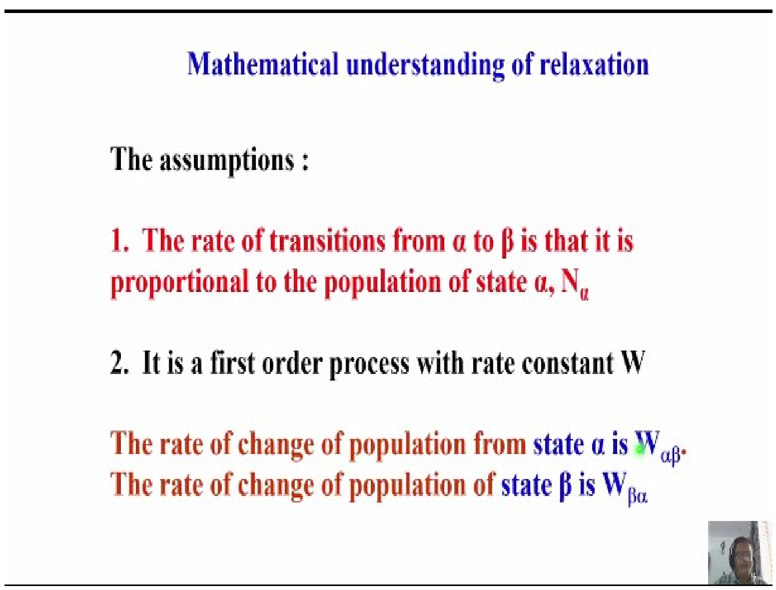

Now, let us try to do simple mathematics. Not a great mathematics, we do not need to worry too much. We will do very simple, what you know. The basic assumption. We will make two assumptions. One, the rate of transition from alpha to beta is proportional to the population of alpha state. The rate of transition W from alpha to beta, Wαβ, we say is proportional to the number of spins in this alpha state. The number of spins is N. So, Wαβ we say is proportional to Nα. That is the first assumption.

Second, we say it is a first order process with the rate constant; it is a simple assumption we do. Now, we understand what is the rate of change of population in the state alpha and in the state beta, okay. So rate of change of population of state alpha is defined by Wαβ, that is what the transition probability. Rate of change of population of state beta is Wβα.

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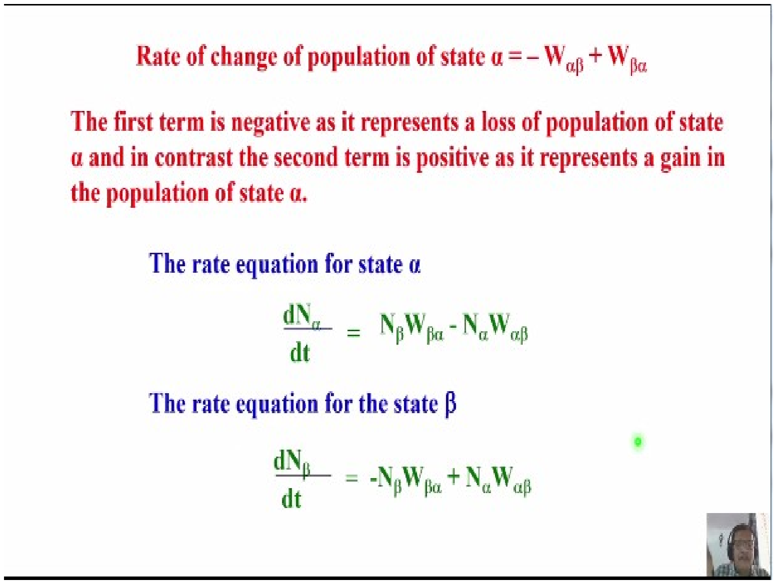

Now, with these assumptions, let us try to work out what is the total rate of change of population of the states alpha and beta. How much is the change of population in alpha state? It is given by the equation; alpha is equal to minus Wαβ plus Wβα. What is the meaning of that? The probability of the spins coming from a higher energy state to lower energy state is more. And this is negative because, at the same time, there is also possibility that spins from the low energy state goes to higher energy state. When it goes from alpha to beta state, there is loss of signal, loss of population in alpha state. When the spins come from beta state alpha state, there is a gain in population for alpha. That is why for first probability it is negative, second probability is written positive. You understand. The spins come from highest state; beta state to alpha state, alpha state population goes up. So, that is plus. But at the same time, spins also go from alpha to beta, there is a loss of magnetization, okay. So, this is why these two terms represent this, taking the probability of the population transitions from alpha to beta, beta to alpha.

Now, we can define a rate equation for the state alpha. What is the rate equation? The rate of change of population, I said rate of transition is proportional to N alpha. Now, the rate equation if

I write as a function of time, the change of population, as a function of time. The rate of change a population is going by simple expression Nβ X Wβα - Nα x Wαβ.

It means number of populations from beta is coming down, using this probability, to alpha. At the same time some spins from alpha goes to beta with this probability. This is what it is. Same thing we wrote as a function of rate equation here. Where the total number of populations in state alpha and beta is taken into account. Now the rate of equation for state β is identical. Only thing is, you have to change the sign that is all. For beta when this goes up, this adds up, when it comes down, it is a loss of population in beta state. Except for these changes, the equation is similar, okay.

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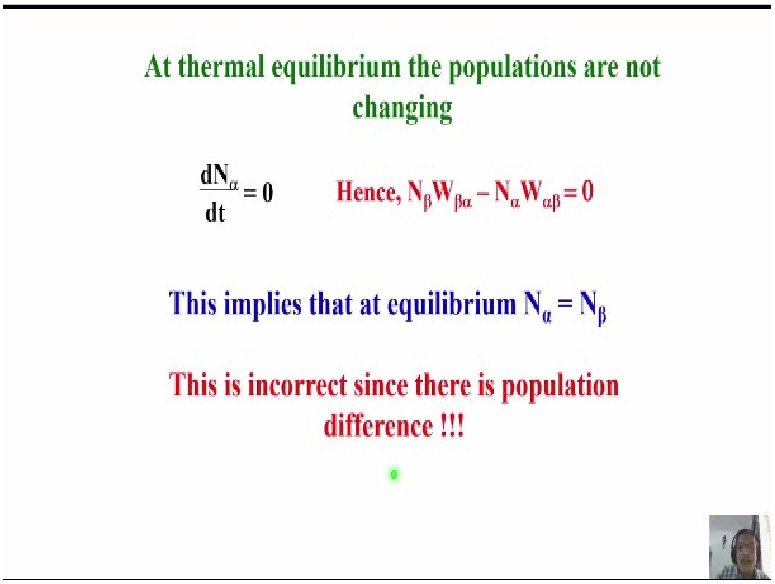

Now another thing, what is the thermal equilibrium situation? At thermal equilibrium, populations are not changing. It has attained Boltzmann distributions, and then no more change of population. That means, at thermal equilibrium, the rate of change of population in state alpha or beta whatever you take should be 0. That is correct, right? There is change of population so we call it 0 at thermal equilibrium.

Now, go back to this equation. Now, put it as 0; equate this term to 0. That is what we do; and calculate. Now, if we equate this thing, what is going to happen? At thermal equilibrium, there is no more change, both are equal. This implies that at equilibrium Nα should be equal to Nβ. It is something strange, okay. Nα has to be equal to Nβ, so that this term goes to 0.

This goes against our assumption, or goes against our conceptual understanding. This is incorrect, because there is a population difference even at thermal equilibrium, okay. There is no rate of change of population, fine. But does that mean there is no difference in population. But it says there is no difference in population here. So, this equation is not correct.

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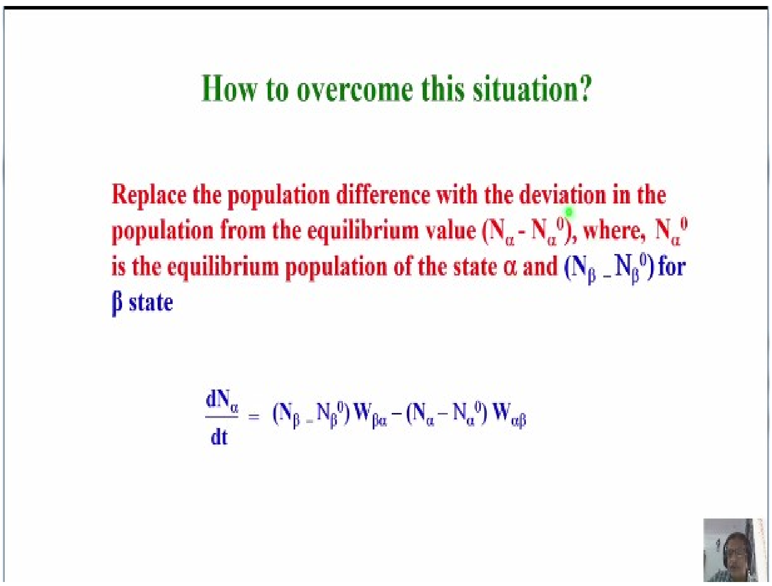

How do you overcome this situation? Now, let us do one trick. You will instead of taking the population difference, we will take the deviation in the population from the equilibrium value. That is something we define. Equilibrium value is at Nα0, we consider. Nα0 is the equilibrium value, the deviation of the population from its equilibrium value is called Nα - Nα0, ie. Nα superscript 0, the equilibrium population of the state alpha, okay. This is equilibrium population, and this is the total deviation from equilibrium. Same way you can define for beta state also. Now put that into this equation, rate equation. So, instead of putting just Nα and Nβ we substituted with these two terms. That is all we did.

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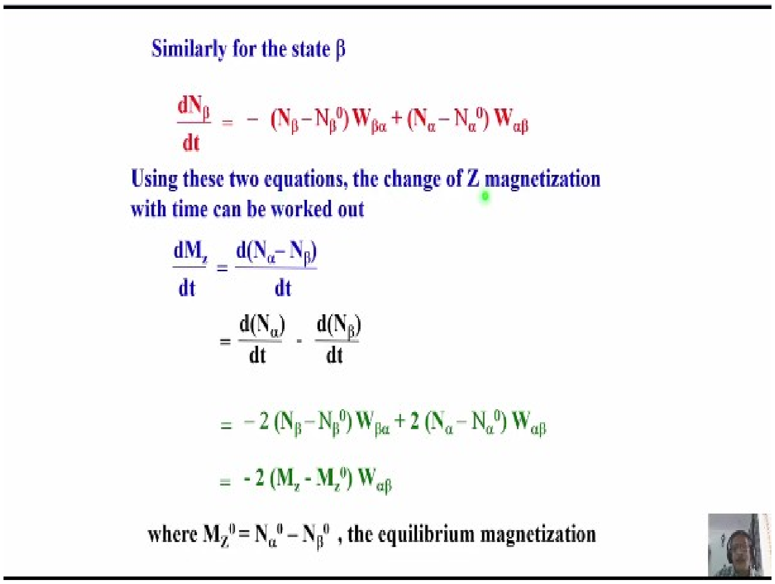

Similarly, will do for the beta state, and do little bit of jugglery, equating these two terms; these two equations. And you can find out what is the rate of change of Z magnetization. That is divided by d/dt(Nα -Nβ), we can work it out with this. And simple mathematic you can do it is not a great mathematic, simple rearrangement of the terms and arithmetic. Then you find out M_Z^0 is equal to N_α^0 minus N_β^0. This is the equilibrium magnetization. Understand M equilibrium magnetization is N_α^0 minus N_β^0. And the rate of change of Mz correspond this one, okay.

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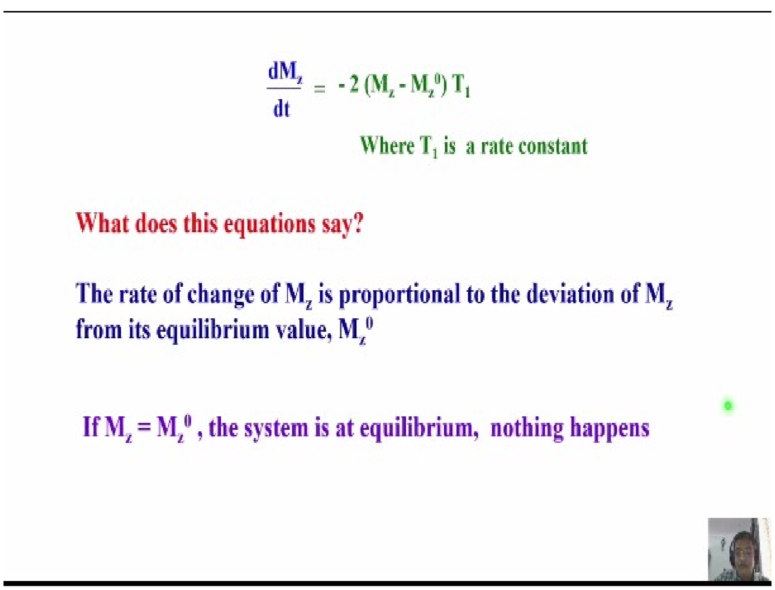

That is simple mathematics, you do not have to worry. Finally, you understand dMz/dt correspond to this term, okay; and whereas this one is already defined as equilibrium magnetization. What is T1 here? T1 is a rate constant. We have defined this as a new term called rate constant. Now, what does this equation say? The rate of change of magnetization is proportional to the deviation from its equilibrium value.

Like individual state, we found out what is the equilibrium magnetization. We have said N_α^0 and N_β^0. But for the entire magnetization when we consider, equilibrium value is Mz^0. And the deviation from equilibrium is $Mz - Mz^0$, okay. That is what this equation says. Now I put Mz equal to Mz^0. What happens? When Mz equal to Mz^0; that is the equilibrium. There is no deviation, okay. This is deviation from the equilibrium value. But when these two are equal, this term becomes 0. There is no deviation from equilibrium. Then Mz equal to Mz^0, the system is at equilibrium, nothing happens, okay. That is what we want; we were thinking, right.

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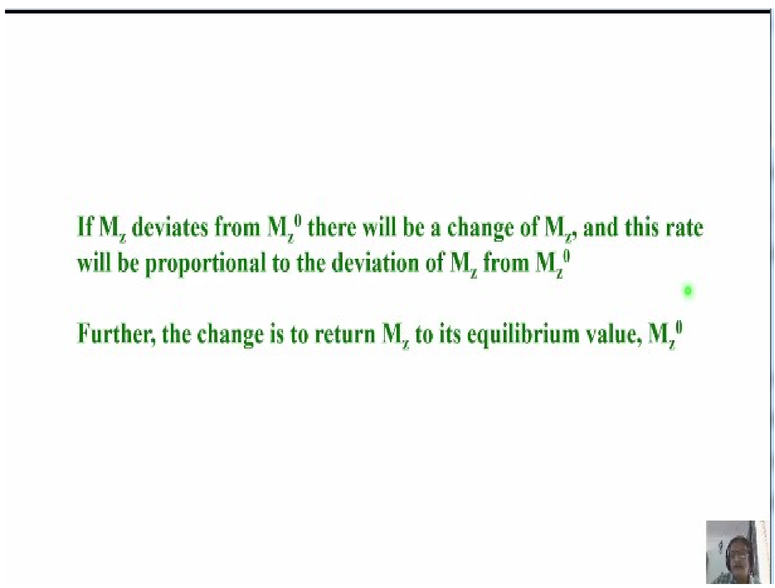

So, Mz deviates from Mz^0, there will be change of Mz, and this rate will be proportional to the deviation from this one. Further, when there is a change of the magnetization, it will return to Mz from its equilibrium value. That is an important term. Remember, okay.

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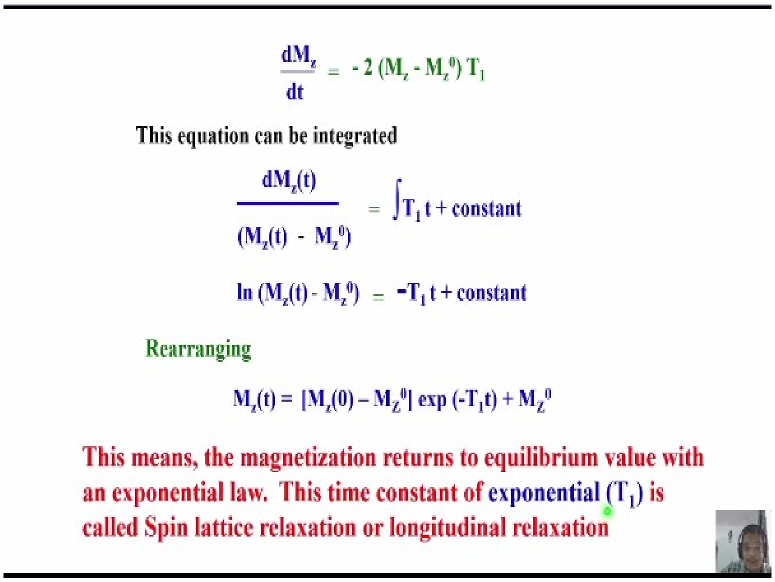

So, now this equation you tried to do some jugglery. You can integrate this equation and everything and find out what it is. Do some rearrangement of the mathematics here? Then you get an exponential term here, okay. The magnetization how it returns to equilibrium, when it is deviating from equilibrium. But after some time, it will come back to equilibrium by an exponential function. The time constant for that exponential is given by T1. This is time constant. This is the time, that is required for the magnetization which is deviating from equilibrium to attain thermal equilibrium; to reach thermal equilibrium, is called spin-lattice relaxation time. Or also called longitudinal relaxation for the magnetization to come along z-axis, this is the time constant, okay.

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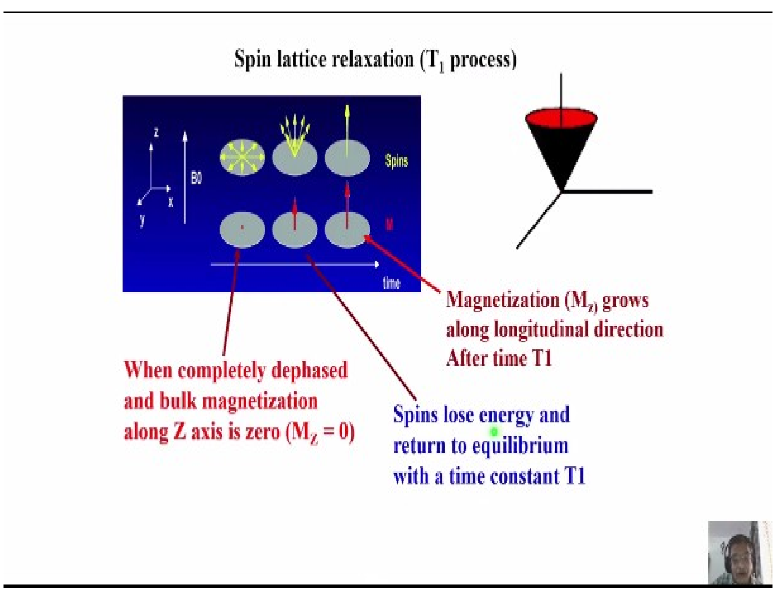

So, this is what it says. Look at this in the diagram article. See that is a simple basic mathematics. Of course if there was whiteboard I could have written every step and worked out for you; but since we cannot do it online and on the computer terminal, I am just giving you the idea. This type of expressions case should be discussed only on the blackboard or whiteboard, so that we can discuss everything.

We can work out the mathematics. But I went through the mathematics, do not worry, it is not a big mathematics. Simply you have to understand the deviation from the equilibrium magnetization was given a term; and we know what happens how it attains thermal equilibrium. It needs a term called T1, which an exponential term, that was introduced. And the constant of that is T1, the time constant. That is called spin-lattice relaxation time. That is what the concept.

Now look at it, when the magnetization is completely dephased here, before that. So, what is happening? The magnetization is brought here to the XY plane. And slowly they start dephasing, while dephasing, they also start growing along Z axis slowly. These are spins, which are dephasing. And now you can work out the total magnetization. Initially, it will be 0 as you know, magnetization dephased and the bulk magnetization along Z axis is 0. This is a magnetization along Z axis. As soon as you bring into XY plane, there is no magnetization in the Z axis, please understand. And slowly it is dephasing. At the same time, it is growing along Z axis. It goes on and on and on. When it is completely dephased in the XY plane, then the magnetization would have completely grown along Z axis. Exactly like the animation shown here. They start dephasing slowly; goes along this term.

And here the spins will start losing the energy and give the energy to the system. Because you have already disturbed by giving a radio frequency signal, it has gained energy. And the system has to attain to equilibrium means, it has to give energy to surroundings or somebody; and it loses energy and attains thermal equilibrium with this time constant, okay.

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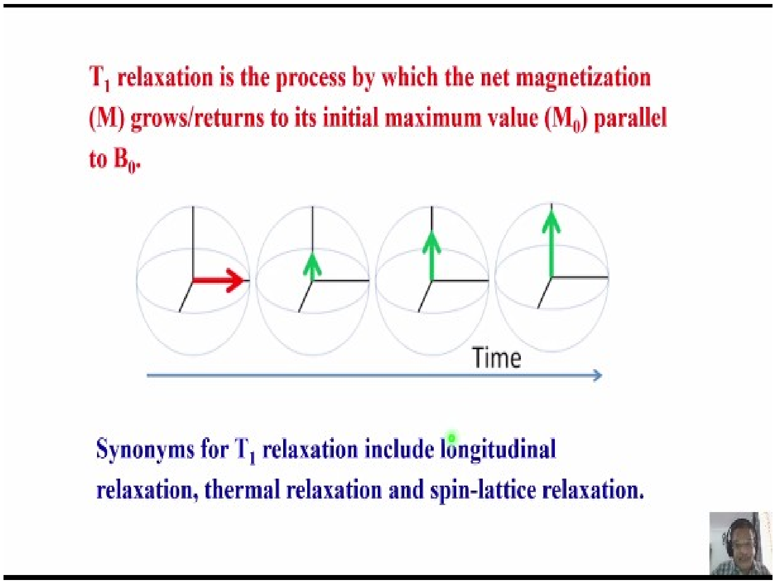

Now, this is the process, what happens. Slowly if you understand, T1 relaxation process is like this, bring the magnetization to transverse plane and they start dephasing here, slowly it goes here, goes here, goes here and after a time constant, it completely recovers along Z axis, okay. And there are certain terms defined for this, some synonyms are there for this. That is it is called spin-lattice relaxation or called T1, also called longitudinal relaxation, also called thermal relaxation, because it attains thermal equilibrium.

So, there are certain synonyms for this. In the books they use various terms like this T1 relaxation, longitudinal relaxation, growth along Z axis, spin-lattice relaxation; all those things, but everything is conceptual same.

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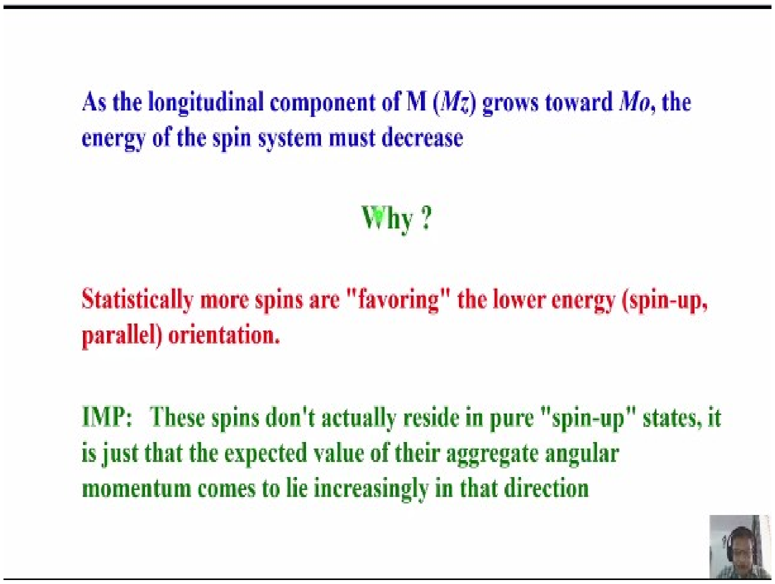

Now, as the longitudinal magnetization, grows to M0 it has to lose energy, I said. Then, why should it lose the energy? Because statistically more spins are favoring the lower energy that is spin-up orientation then other orientation. So, as a consequence, it has to lose some energy, okay. And important point to remember, spins do not actually reside only the spin-up states. There are there are spins in both alpha and beta states. But, only thing is, the average expected value of this, all the spin angular momentum taking together, there is a probability that more spins are in this direction, that is all. Not that, you cannot say that there are no spins in the beta states. It is there. Probability is more along this axis. That we have been discussing many times, okay. So, spin system starts losing energy because the more favored orientation is the excess spin in one of the states.

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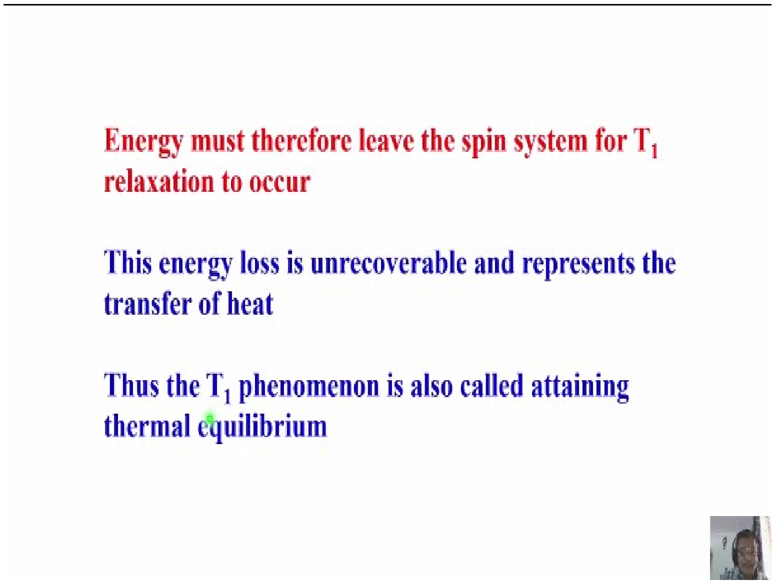

For this relaxation to occur, I said energy must leave the spin system. This energy when it leaves the spin system, I said here; the energy of the spin system must decrease; not only decrease it has to leave the spin system, okay. It leaves. Where does it go? It has to go somewhere. And when you give the energy like that somebody has to take that energy. And something should happen to that whoever takes energy and this energy loss is not recoverable, it is a one-time loss, keeps going. It is unidirectional.

How does it loses the energy? It takes energy and give to somebody in the form of heat. It is sort of a transfer of heat. And this one generates heat to surroundings, which gives the energy. It is so small, it does not get noticed at all, because it leaves out heat and comes back to equilibrium; that is the reason why T1 phenomenon is also called attaining thermal equilibrium, understand. It is energy loss which is unrecoverable and which represents transfer of heat. So, this phenomenon is called attaining thermal equilibrium because of this reason. It gives out energy in the form of heat.

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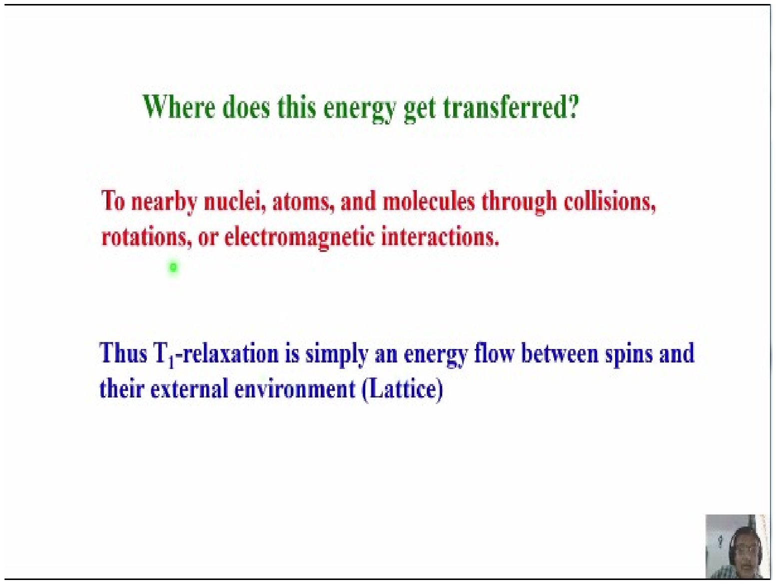

Now, the question I still have to answer, where does this energy get transferred? It always gives energy to nearby nuclei, atoms, molecules some other spins; it need not be J coupling or anything; any surroundings**.** Everything which is surrounding that spin. It can give. transfer the energy to neighboring nuclei, neighboring spins, neighbor atom, molecules, etc.

How? Through collisions, rotations and various types of electromagnetic interactions, they all can happen, any of them. It can collide with other atom and give energy. It can undergo molecular rotation and give; it can undergo electromagnetic interaction. So, all these things are there. These are the process through which it will give energy to the surrounding, which will be absorbing energy.

And what do you call that? the system which absorbs energy, which is given by spins, is called Lattice. Lattice is not what you think like Crystal-Lattice. Any external environment for this nuclei of interest, which absorbs energy given by the spin is colloquially termed as Lattice, okay. T1 relaxation, simply an energy flow between spins and lattice, Lattice is nothing but, anything surrounding that spin. It is called a Lattice.

It is simply an external environment. So, what do you mean by that? Relaxation is nothing but a energy flow, especially T1, energy flow between spins and Lattice, that is all. You please understand, relaxation is the energy flow between spins and Lattice; that is T1.

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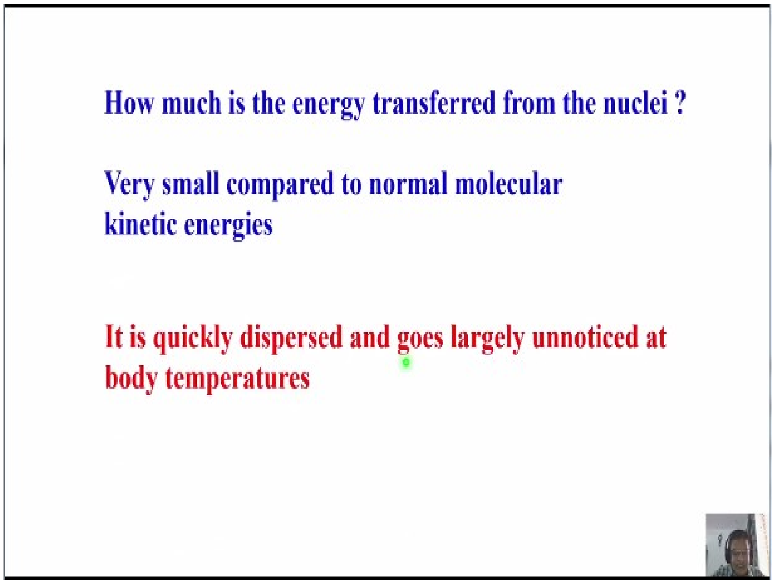

But how much is the energy transferred from these nuclei? I already said, it is much, much, much smaller than the kinetic energy. Normal molecular kinetic energy, there is a kinetic motions going on; the thermal motion will always be there, compared to that is much, much smaller. So it largely goes unnoticed at all. At room temperatures, it largely goes unnoticed. And this quickly gets dispersed into the system.

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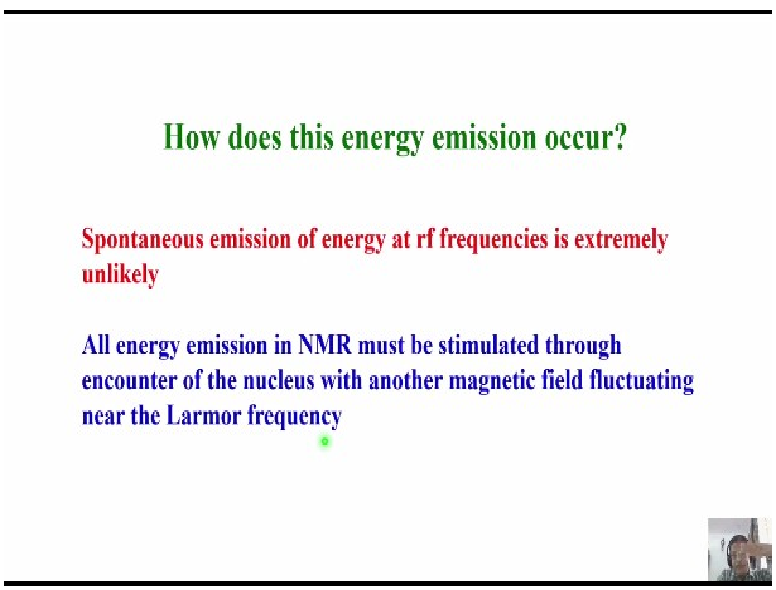

Now the question is; fine it also happened. But, how does this emission occur? How does the energy emission occur? You cannot simply give the energy to somebody just like that. There must be a medium for it, right. So, how does this energy emission occurs? Of course, one of the thing is, you can consider the Lattice energy state and spin energy state. When spin has to give the energy; and if let us say it has gained energy and gone to excited-state. If it has to come down, it will give energy to the Lattice. The Lattice will go up here. The spins of the Lattice will go to the excited state. But then how does it come down? Can it come down from excited-state to ground-state; from beta to alpha state spontaneously? No, remember earlier also we discussed, the spontaneous emission in the radio frequency region is almost negligible, because it goes by the cube of frequency, I already told you long back.

So, all energy emission in NMR must be stimulated. There must be a stimulated emission, so that this nucleus can give energy to other surroundings. And what is the stimulation? Where do you get the stimulation from? The nucleus, if it has to give energy by stimulated emission, there must be some stimulation, where do you get this? This is the simulation that comes because of the encounter of the nucleus with another fluctuating magnetic field.

Where do you get that fluctuating magnetic field? It comes because of molecular motions, see molcules keeps oscillating, keeps rotating. It is getting changed its state. And it is undergoing fluctuation. So, this fluctuation frequency is at the Larmor frequency, because it has to match the energy separation of the spins; then only they can undergo the transitions. The spin energy is given to the lattice, so the lattice will go up, okay. So it must match with the Larmor frequency. The fluctuating magnetic fields have to match with the Larmor frequency, okay.

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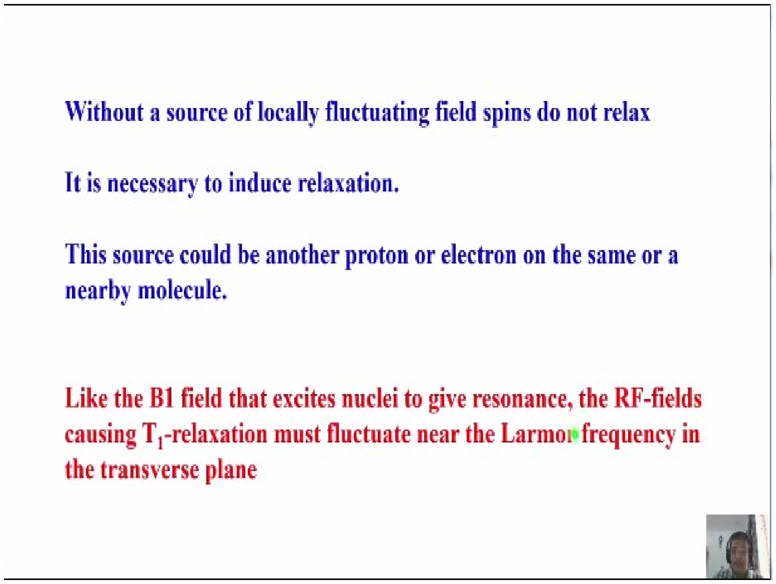

And without that fluctuating magnetic field, and without that source spins do not relax at all. And it is necessary to induce relaxation. And this or this source could be another proton another electron or any nearby molecule, okay. So, if you apply a radio frequency pulse and excite the spins to give resonance, same radio frequency fields causing relaxation must also fluctuate near the Larmor frequency.

Remember I said when we apply radio frequency field, it must be an oscillating field, I said, static will not work. That is what I said. I very well remember. So similarly, this also will be oscillating; the fluctuating field must be at the Larmor frequency in the transverse plane.

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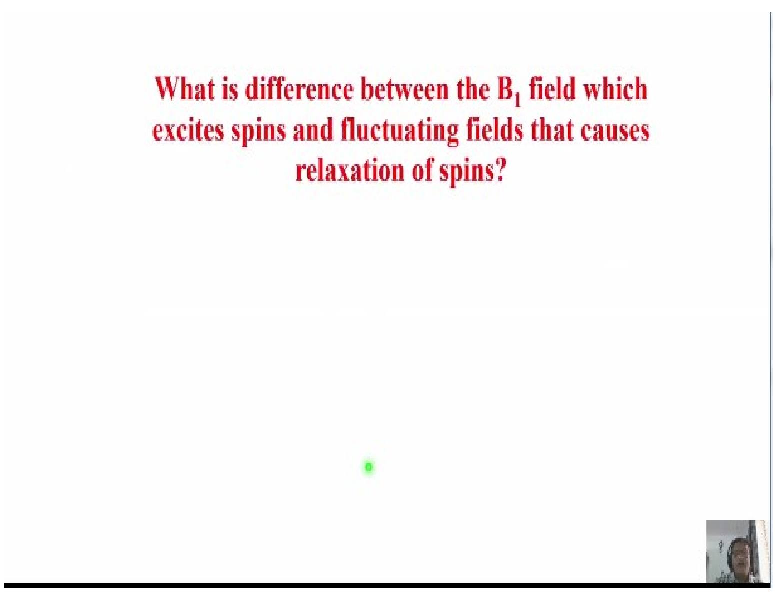

Now, the question is; what is the difference between this B1 field which excites spins; and fluctuating field that causes spin relaxation? Okay.