Principles and Applications of Electron Paramagnetic Resonance Spectroscopy
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Lecture- 13
Introduction to Spin Relaxation

Hello there, today we are given to discuss, what are the various dynamical processes that go on when the resonance takes place? We will first discuss in general, for any resonance absorption and then in particularly the differences that we need to keep in mind for EPR transition. For simplicity again let us consider only 2 level systems.

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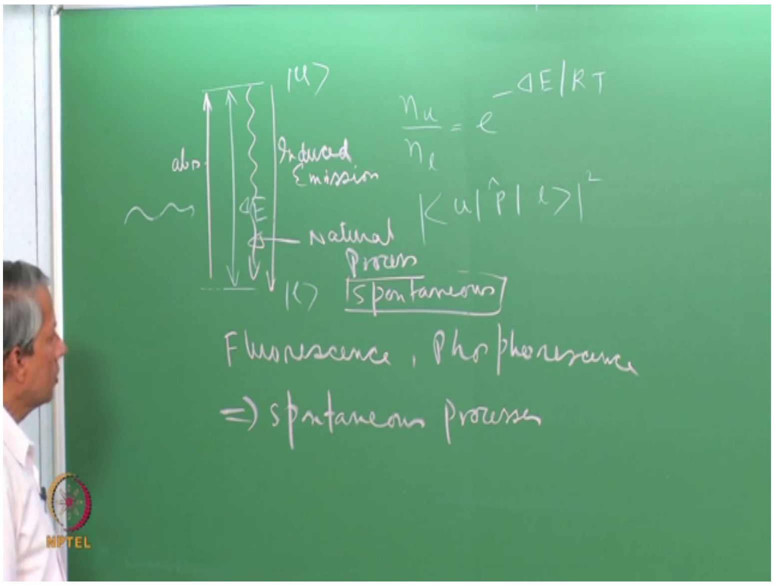

Higher level and lower level; lower level and upper level let us we will call it. And let us say we have got a collection of particles which are distributed in these 2 level according to Boltzmann distribution; number of particle in the upper level by number particle in the lower level is given by where T is the temperature of system and this is delta E.

Now, if; so, radiation falls here which is matching with this energy gap and this selection also satisfied. Then what can happen, because then of course you can absorb radiation and this particle which are lying here can go from here to there. That is the absorption process. This is the absorption let us call it, absorption process. But there are some particles which are here; they can also undergo transition from here to there because of this radiation. Why is that? Because the selection rules we have seen earlier, these one from upper to lower in the presence of some perturbation. This gives the probability of transition from let us say lower to upper or upper to lower. The form is the same. So, probability of transition is actually the same thing whether it starts from here, goes there or it start form here or goes here; that is the perturbation due to the radiation.

So we call that, Induced Emission or stimulated emission. Along with that, the particles which are in the excited state can come to ground state by it is own natural process. Let us call it, some Natural Process. What are the Natural Processes? In optical experiment for example, (Refer Time: 03:30) visible experiment, the Natural Processes are Fluorescence emission, Phosphorus emission. Those are radioactive processes by means of which the particle in the excited state can come to ground state. Now these 3 things can happen in general in all experiment that involves transition in the presence of radiation. Now, this point the these Fluorescence or Phosphorescence.

These are spontaneous processes. This processes can be actually they are nothing but spontaneous process. Why you call spontaneous; because this takes place even in the absences of in such external perturbation. In the pre experiment that involves magnetic resonance like NMR and EPR. In principle this will of course take place. This can in principle take place, but there is a catch. The catch is that, the probability of this spontaneous process that drastically goes down when the wavelength of this experiment or the energy gap between the 2 becomes very small.

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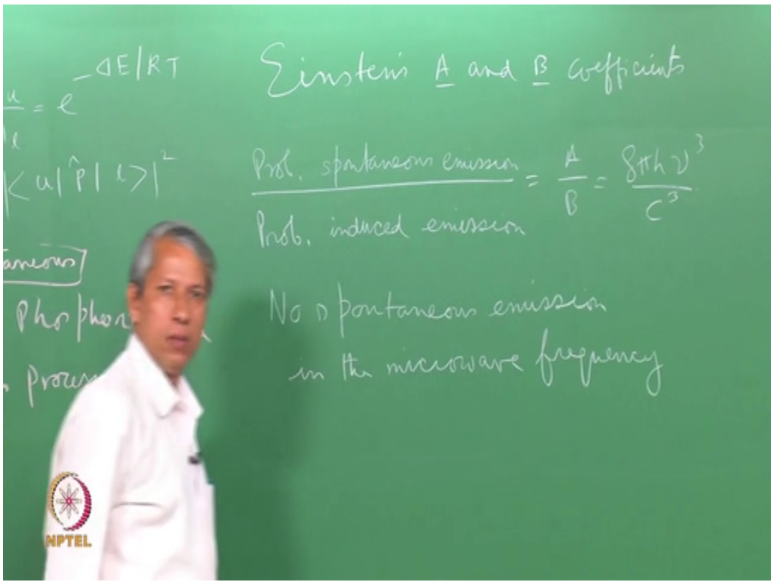

Where does that come from? It comes from the Einstein's. Einstein's, we call A and B coefficient, this gives the probability of spontaneous emission by the probability of induced emission. It is given by A by B which is, this is the expression. So you see, the spontaneous emission and Induced emission, these 2 ratio given by the frequency. This frequency is related to the energy gap here. And not only that, this depends on the cube of frequency. So, as the energy gap become smaller and smaller, this spontaneous emission probability becomes smaller and smaller very quickly. So, whereas in optical experiment, where Fluorescence and Phosphorescence become very common process for excited molecule to come to ground state. When it comes to magnetic resonance experiments NMR or EPR, this is so small that spontaneous emission probability virtually goes to 0. So, no spontaneous emission in the microwave frequency.

So, in these 3 processes that we have here, 1 is out.

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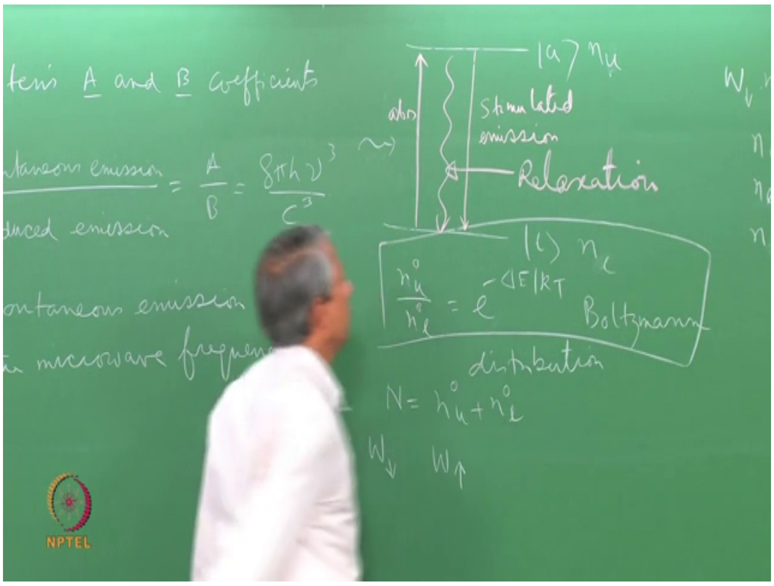

So whatever; we have now, this is the lower level, this is the upper level. So in the presence of radiation, I have absorption process and this is the Induced Emission or stimulated emission if you like to call it. stimulated emission. And this is not present. What can happen now, let us try to imagine. The to start with before the radiation was applied the number of particles in the lower and upper level followed this Boltzmann distribution. So, number particles here, let us call it now n alpha and n sorry n lower and n upper. So, if there was no radiation here present, then n upper by n lower is equal to delta E by k T; and that is the Boltzmann distribution.

Let us put a (Refer Time: 09:02) 0 here to indicate that that is what happens when nothing else is disturbing the system. And thermal equilibrium they are the bubbles in the distribution. And total number of particles N is equal to n 0 alpha plus n 0 upper and n 0 lower. Now, the rate of transition in the presence of radiation will depend on the probability times the number of particles which are present here for going up.

And similarly for these process the rate of stimulated emission will depend on the number of particles which are here and the probability of this. So, I will have the (Refer Time: 09:53) W downward and W upward. These are the transition probability in the absence of this radiation. That is important that these Boltzmann distributions maintain all the time. So, if there are some transitions which are taking place on its own which are not induced by this one and which is maintaining this distribution.

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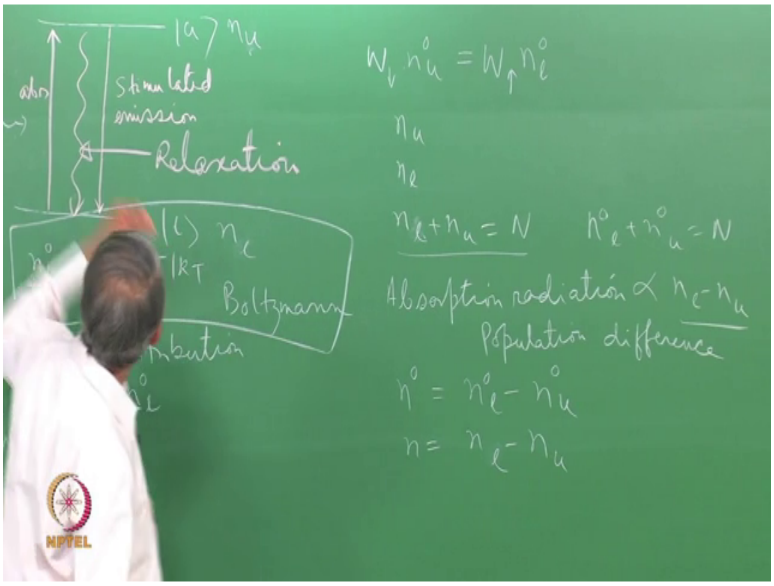

Then what we must conclude from here is that, rate of this downward transition, this is the probability of going down times a number of particles in thermal equilibrium here which is n 0 upper must be equal to rate of upward transition and the number of particles in the lower level. Once again these rates are the not the rate, this is the probability for transition in the absence of any external perturbation. Then naturally, if some transition taking place which is maintaining the thermal equilibrium and maintaining the population distribution according to the Boltzmann law. So in that case, this must be satisfied. This is same as saying that, this is satisfied automatically. Now, if there is some disturbance to the population distribution then, let us say that time n u and n l are the new number particles here which are different from thermal equilibrium values here. Then, n alpha plus sorry n l n u it is also equal to N.

To number of particles remain the same. I may have come to an assertion that these are taking place here all the time even if there is no perturbation, that may sound a little bit farfetched and ad hoc; why do I need that. So, to appreciate that let us once again go back to this situation where nothing else happens that is, this has to removed and these 2 process the taking place there. Then what can happen is that radiation will try to push this molecule from here to there and also push molecule from here to here. Now though in the beginning, there many particles slightly more number of particles here then there; initially, the rate of upper transition will be more than rate of downward transition. If nothing else is happening then what happens, very soon these 2 levels will get equally populated. So that means, we will not see any net absorption of radiation. So, these 2 processes are taking place and then these 2 level become equally populated.

So, no net absorption radiation; so no absorption spectrum that is the problem; if there are no other processes involved here then very soon, the movement the light is shown as resonance cannot be satisfied, the absorption will disappear; 2 levels will get equally populated. That is the key problem that how can we see a net observe to signal if these are the only 2 processes. So, there must be some other process which maintains some set of population difference here which can be sustained even in the presence of radiation. And this population difference is the one which decides the amount of light that is observed and that gives absorption spectrum.

So you see that, that is the requirement we have to fulfill so that we can explain that. Yes, indeed we see the absorption spectrum in the spectrometer. Because we see the absorption spectrometer, we have to incorporate a process other than these 2 and that we call a same Relaxation Process and this Relaxation Process is not same as the spontaneous emission process of the kind that you have normally scene in optical experiment. This is something other than that. So, this is the probability of downward transition and upward transition because of this natural Relaxation Processes and that is present all the time and that maintains the thermal equilibrium.

So, this is the relationship we get. Now, if this population changes, what way the system will try to develop a new steady state condition so that net absorption of radiation can be seen. So, the absorption of radiation of course, proportional to n l minus n this difference, this is the Population difference. See if the Population difference is 0, then there is no absorption of radiation. So, in thermal equilibrium, these are the number of particles in upper and lower level. So, let us say n 0 in thermal equilibrium can be written as n 0 l minus n 0 upper level.

So, as much as here, I have n 0 l plus n 0 u also equal to N, the number of particle also remain the same. Now when the transition takes place, this population difference, I can say n new population difference n alpha minus n sorry n l minus n u, that 1 particle let's say makes transition from here to there, then the population difference changes by 2 units because 1 comes from here to there the difference becomes 2.

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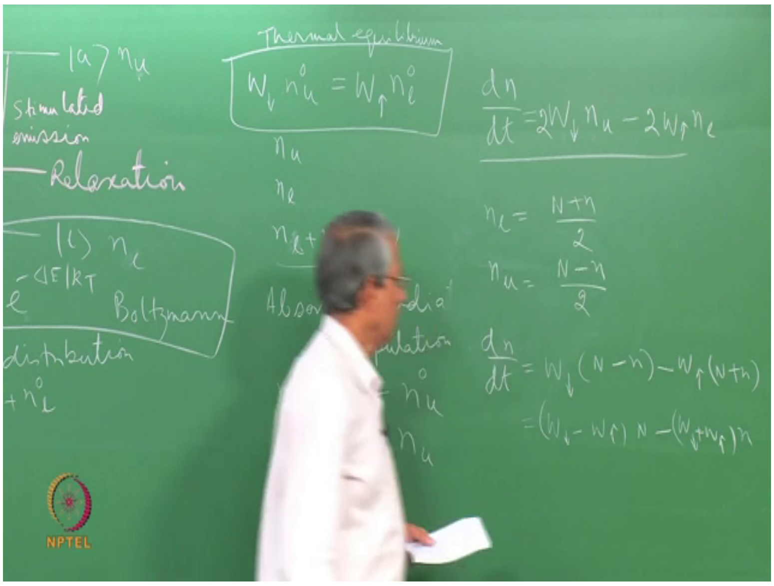

So, d n by d t can be written as probability of this going downward transition times the number particles in upper level, lower level. So, we still consider the situation that how this Relaxation process maintains this population difference. We have not yet applied the radiation yet. So, only the difference is that if the population difference has become different from the thermal equilibrium value that is n l n u, how this Relaxation Process try to bring back the population difference to the thermal equilibrium value. So, this is the probability for downward transition from here to here. So, the number particles which are here similar the upper transition a factor of 2 is because each transition changes the population difference by 2 units.

Using these equations one can write that, this is by the way Thermal equilibrium condition. From this relation this you can write this is in terms of the population difference n and the total number of particle. If we substitute this here, we get this value. Now this could be simplified as, this is the total number of particles; this is a population difference at a given instant.

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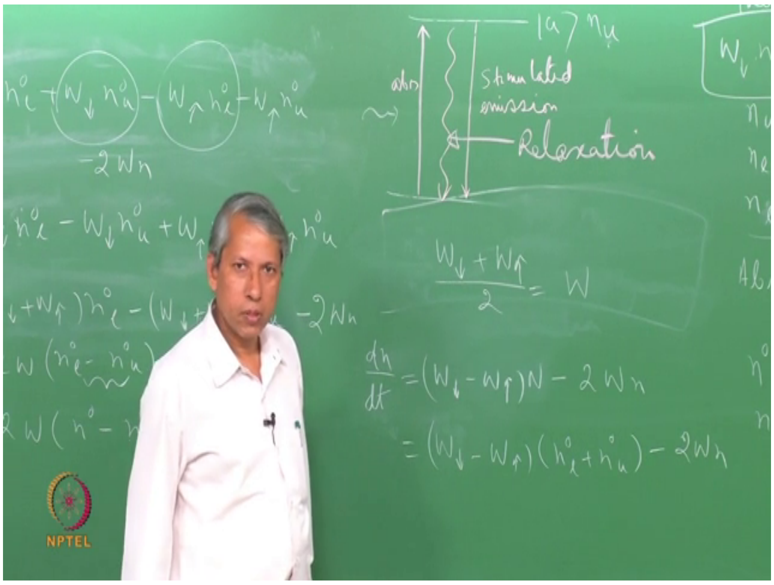

If we define that average of the upward probability and downward probability is W, then I get d n by b t is minus N alright.

Now, let us see here, we use this condition which relates the upward rate in terms of n 0 l and n 0 u and download rate in the process, we can change this equation to look like this.

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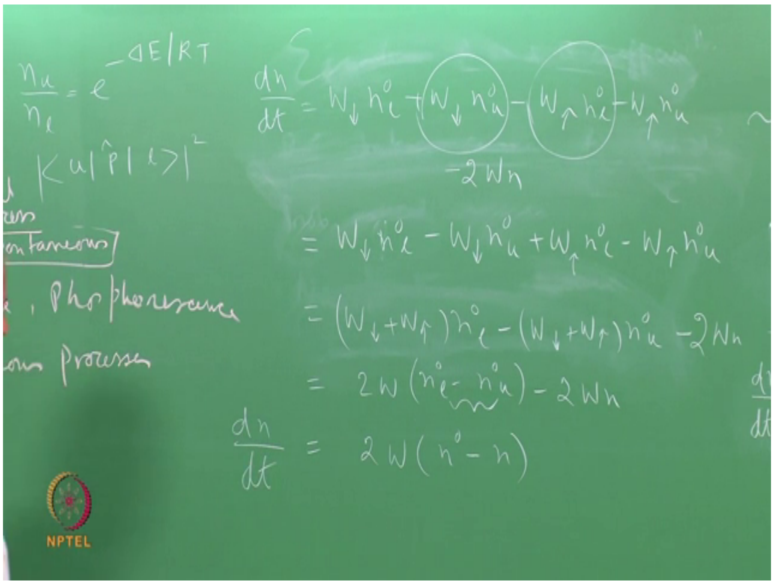

And from here, we write d n by d t we have, expand this and this will give 2 W n. Now here, now see that this is actually equal to this. This is equal to this; here. This is the Thermal equilibrium condition. So, might as well can sell that (Refer Time: 22.29) let us do a little bit of mathematical trick. So, you could as well write this equal to. So this gives me W down plus W up n 0 l minus n 0 u. So here, using the same average value of the probability I can write this is 2 W n 0 l minus n 0 u. Of course, this term is there 2 W n so minus 2 W n. So, this is therefore equal to; now this is nothing but the population difference in Thermal equilibrium. So, we call it n 0.

So, this is 2 W n 0 minus n. So, this is the expression for the rate of change of Population difference in terms of the average transition probability due to the internal Relaxation Processes written in this fashion. So, this shows that any deviation of the Population difference from the equilibrium value can give rise to non-zero value of this one. Or in other words explaining, this is same as equilibrium value this is 0 which is understandable. (Refer Time: 25:08) system is already reached thermal equilibrium, there is no more change in the Population difference.

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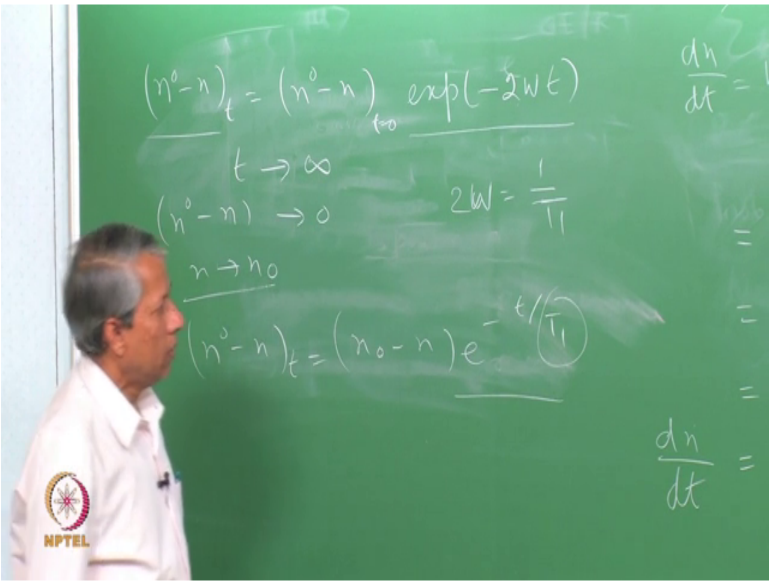

But anyhow, let us see how looks like if n is different form n 0. Then this integration can be carried out very easily. n 0 minus n at time t equal to t is equal to given as n 0 minus n at time t equal to 0 into exponential 2 W t. So, what is the significance of the equation? At t to 0, this is the population difference that radiation of the population difference from the thermal equilibrium value. As t goes to very large value infinity then this goes to 0. So, n 0 minus n goes to 0 or n tends to n 0.

So, that is what the Relaxation Process is trying to do. Any non-Boltzmann distribution that give rise to this n which different from the equilibrium value of n 0 will be brought in to this value if we allow sufficient time to pass. And these are brought about by whatever the internal Relaxation process which are working all the time. So, now we can understand that why it is important that these present there. So there we can see the absorption spectrum. As I said earlier, if these were absent then these 2 processes will make these 2 level equally populated and we cannot see any net absorption signal. So, these are the most important requirement for observing the steady state spectrum which are, we are saying in the EPR experiment or in NMR experiment. Relaxation process are very important.

This shows that Relaxation process also, this rate of change of, this restoration of the population deviation from Thermal Equilibrium is an exponential process. So, we can give a time constant to it. So, if you write it as I say 2 W is equal to 1 by T 1, then this can be written as n 0 minus n t exponential minus t by T 1. So, this is the characteristics time constant which decides or which brings back the thermal equilibrium, if the thermal equilibrium disturbed by whatever means. Now how do you visualize this Relaxation process. We can think of, now in particular an EPR experiment that we have got is a collection of spins may be I allotted number of spins which are put in magnetic field and we have restored a this thermal equilibrium is satisfied Boltzmann distribution. In case of alpha by n beta this is the Boltzmann distribution.

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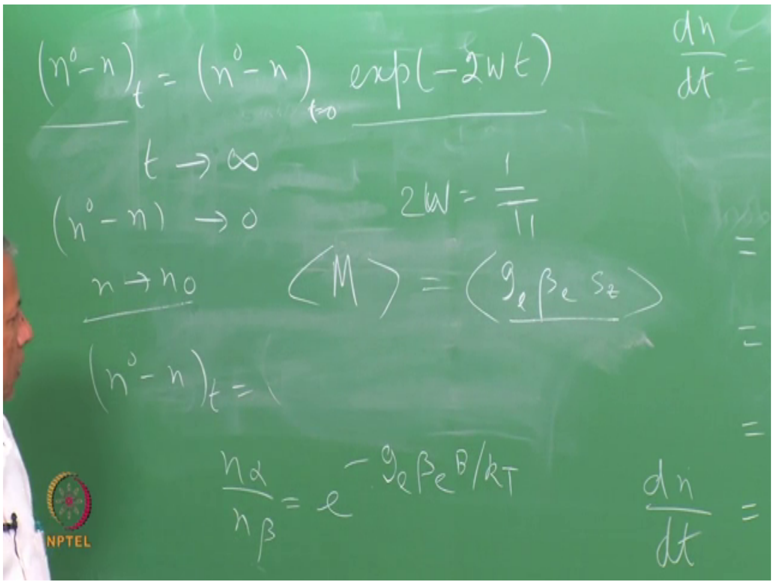

So, all the spins are not pointing in the same direction; some of there will be parallel to the magnetic field, some will opposite direction.

So, effectively therefore, the total sample acquires certain magnetization. I call M which is the average of all this if we take all the particles there, then this magnetization has a certain value because this 2 levels are not equally populated. Now, suppose I suddenly switch off the magnetic field, then this magnetization has to disappear. All spins will get randomly oriented and that take certain time. So, that time is the time that you say here, that system is trying to go from certain orientation to random distribution. So, we can call this is a Relaxation time for this magnetization to get destroyed. And this will follow exponential time difference of this kind. We can do the reveres experiment.

So, the spins are present Avogadro number of spins are present and there is no magnetic field. So, there is no particular direction of quantization. So, numbers of alpha spins are equal to number beta spins. There is no need magnetization. Now certainly suppose I switch on the magnetic field, then they are going to reach this distribution and magnetization going to develop. How much time it takes to bring up that magnetization that process also is going to happen in this fashion in exponential manner and the time taken or characters time for such process is called the Relaxation time for this (Refer Time: 30:38) of the magnetization.

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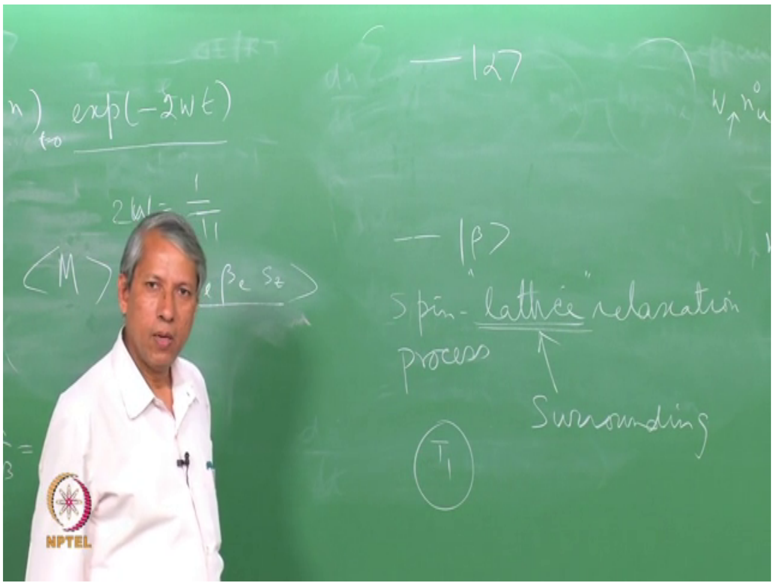

Now, here you see that, for this 2 level system, whenever the transition has take place from here to there it involves absorption of radiation. But this Relaxation process tries to maintain equilibrium see they always try to adjust it is population such way that Thermal equilibrium is restored. So, in particular if there are more particles here than here then when this has to reach thermal distribution, some amount of energy has to be given out from this spin system to the surrounding.

So, this process therefore which restores the equilibrium distribution between the 2 levels. We call that spine-lattice relaxation process. Now here, lattice is a very generic term. It implies that for radiation of particles, there is any 2 energy exchange with spin system and the surrounding and the process which does that we call the spin-lattice relaxation process. And because it involves exchange of energy the surrounding, and the surrounding is given a very generic term as a lattice, surrounding is called a lattice. Not necessarily crystal lattice. In fact surrounding need not necessary be the solvent. Is could be different degrees of freedom of the molecule itself. So, this is given a characteristics time that T 1, I have given here and you see that this w is the average of the probability of upward transition and the downward transition each of them involves exchange of energy. Average value of that is called 2 times average of this 1 by T 1. So, there more efficient the Relaxation process, so term will be the T 1. There is another kind of relaxation process involved in magnetic resonance. To understand that, again we go back to this idea of net magnetization in Thermal equilibrium, the spins point either along the direction of magnetic field or the opposite direction to generate a net magnetization along the direction of the magnetic field. The direction of magnetic field is z direction then, at Thermal equilibrium.

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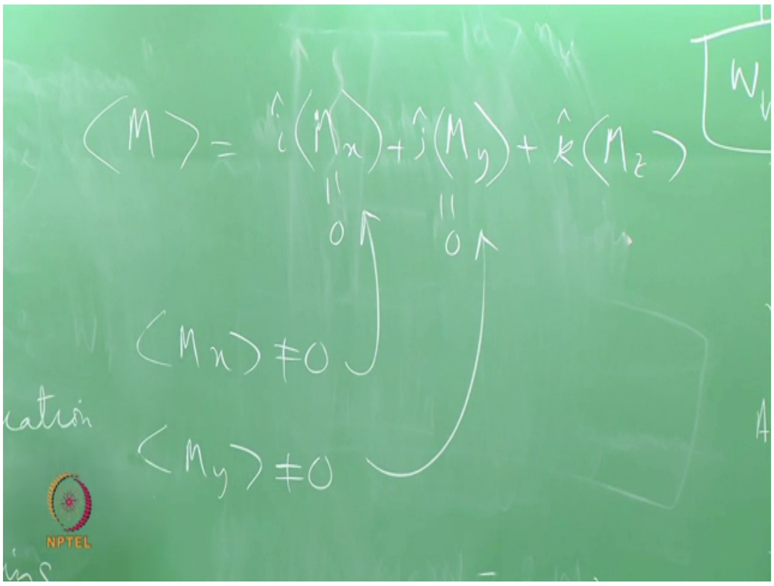

This magnetization has lets say M x M y M z this sort of; These 3 components. For a Thermal equilibrium, there is no x component and no y company; only z component is present there. Suppose there is some disturbance to the spin system and net M x and M y component are created, then what happens; again the their will relaxation process which will try to restore this M x not equal to 0 to this state. Similarly M y is not equal to 0; you try to bring it to this state where these are again non Boltzmann distribution, non-thermal equilibrium.

To restore Thermal equilibrium, this M x M y component of the net magnetization must go to 0. That also involves not the energy exchange with the surrounding, but the spin system must rearrange themselves in such a way that all the M x and M y component goes to 0.

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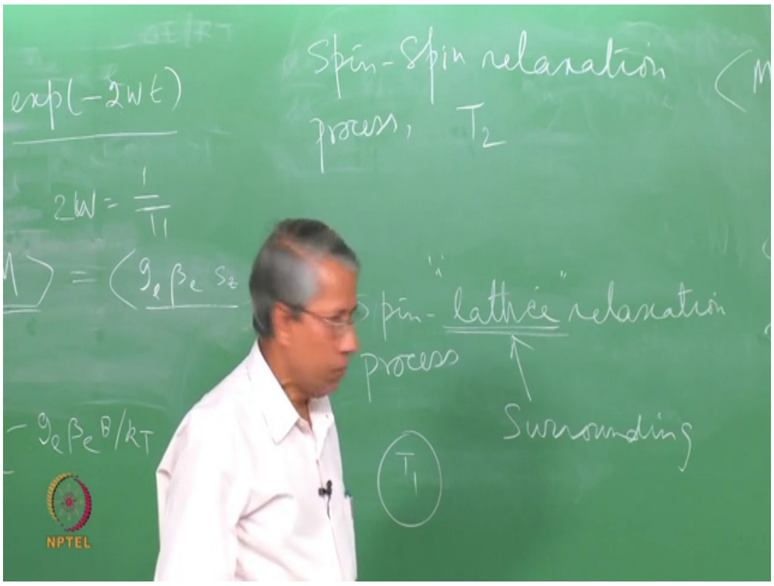

That is also a Relaxation process; we call that spin-spin relaxation. And it is usually it is written by give a time constant written in terms of designated as T 2. Now finally, we just examine what role it plays in deciding the signal of an absorption spectrum.

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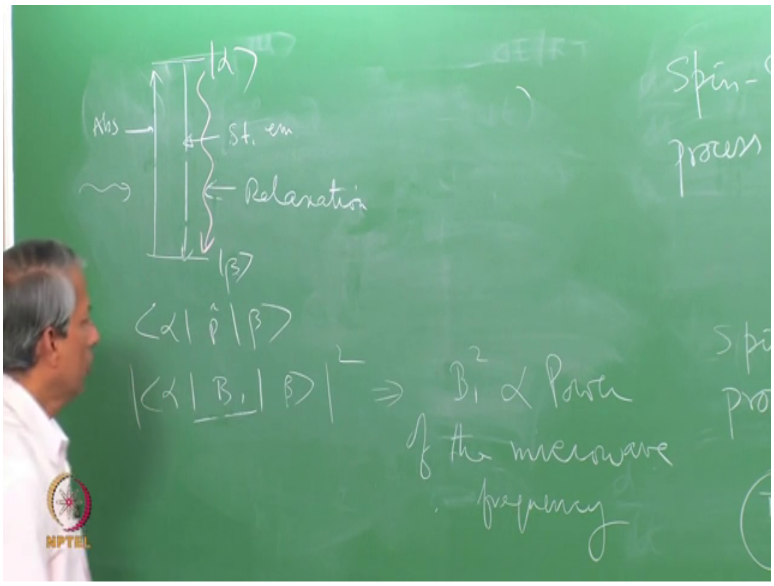

Qualitatively, what we are observing here are the result of 3 process (Refer Time: 35:31) this 1 alp beta this alpha and radiation comes in, so this causes this Absorption, Stimulated emission and the Relaxation which is trying to maintain the population difference.

So, this the Relaxation process. So, this is Stimulated emission, this is the Absorption. So, if now if this rate becomes very strong or very efficient compared to this one then, this 2 population difference becomes smaller and smaller that this process is not efficient enough to bring rest out of the thermal distribution. So, the population difference will go down and effectively signal will also go down. So, magnetic resonance this efficiency of this 2 process can be decided by the this transition alpha, perturbation, beta. This we have seen earlier lecture that this is nothing but B on field that is present there with x y plan. And square of that gives rise to the probability of this set of transition there.

So, here this is related to the microwave magnetic field that is used to observe the EPR signal. And square of that, B 1 square is proportional to power of the microwave frequency. So, if the power becomes high, these becomes more and more efficient and this may not be able to cope up with the stimulate absorption emission process. So, signal will become smaller and smaller, because this 2 level becomes more and more equally populated.

So, one has to be careful in deciding how much micro power to use to observe the EPR signal. For those systems the Relaxation is very efficient, this will not be of much serious concern. But for some systems when it is Relaxation is not very efficient, this could be a potential problem. So, you see here; therefore, the Relaxation process which are always present their place a fundamental important role in allowing us to see the EPR signal and without that we may not be able to see the spectrum at all if the Relaxation is very inefficient.

With this we come to the end of this lecture.