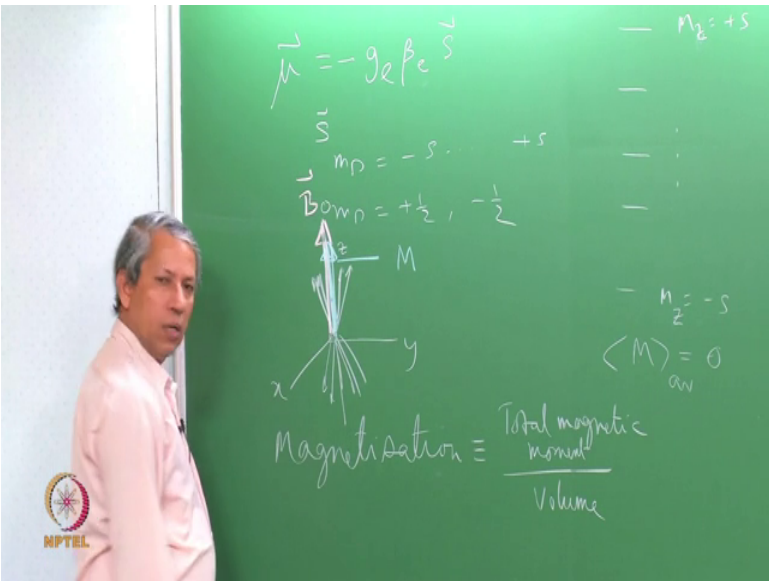
Principles and Applications of Electron Paramagnetic Resonance Spectroscopy
Prof. Ranjan Das
Department of Chemical Sciences
Tata Institute of Fundamental Research, Mumbai

Lecture - 24
Spin Relaxation and Bloch Equations - 1

Hello. I have said many times in these lectures that if a spectrum appears in the form of a lorentzian line shape, but I have never explained why that should be. So, today we are going to learn and see how spin relaxation processes actually decide the line shape. So, before we start let us look at the concept of a magnetization today little more carefully earlier. I have used the term magnetization without defining it very rigorously. So, for that let us consider not a single spin, but a collection of spin something like Avogadro number of spins which are typically used in an experiment.

So, as this many spins are put in a magnetic field they will point along various directions given by their allowed angular momentum and allowed values of the magnetic movements so.

(Refer Slide Time: 01:33)



We know that mu is a magnetic movement for an electron this is given as minus g e beta e S and. So, S can take various components in a magnetic field. So, M S value here given minus 8 to plus S changing in units of 1.

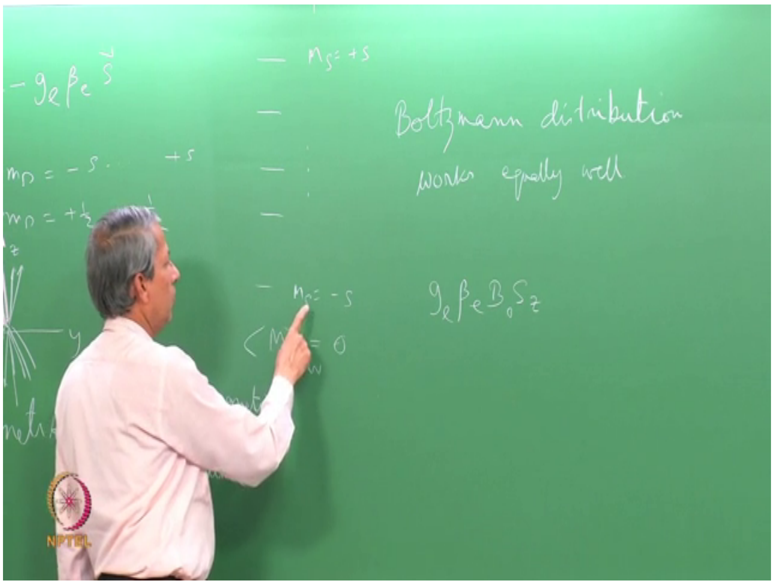
So, for a spin half system for example, electron you have a larger amount of spins then M S takes plus half or minus half and we know by now that in a magnetic field which is pointing along let us say this is the B magnetic field, pointing on a z direction, many of this little spins will point in around the positive z direction and also many of them will point along the negative z directions this with x y and z. So, it is a sum of all these will give rise to term net magnetic movement of all these particles.

So, magnetization is defined as total magnetic movement divide by the volume, now total magnetic movement of course, has to be obtained by adding all these individual magnetic movement of the individual particles.

Now, you see that if these 2 orientations for this one are equally populated, then there will be as many number of spins which are going up and as many number of spin going down will all equal. So, net magnetic moment will be 0 and net magnetization also be 0 and that is true for not just S equal to half I have S of some other value then I can have these set of next energy level staring from M is equal to minus S to M is equal to plus s. So, if all the levels are equally populated by the various spins then if I sum over all the magnetic moments here I will get the magnetized total magnetic moment average will be precisely 0.

But in thermal equilibrium when this spins are distributed among various energy levels the distribution is governed by Boltzmann distribution, now we all know that electrons are spin of particles. So, they are supposed to follow Fermi Dirac statistics they are called fermions that is absolutely correct, but the type of system we have here that these particles which really do not interact very much they behave almost like independent particles for such weakly interacting particles or non-interacting particles.

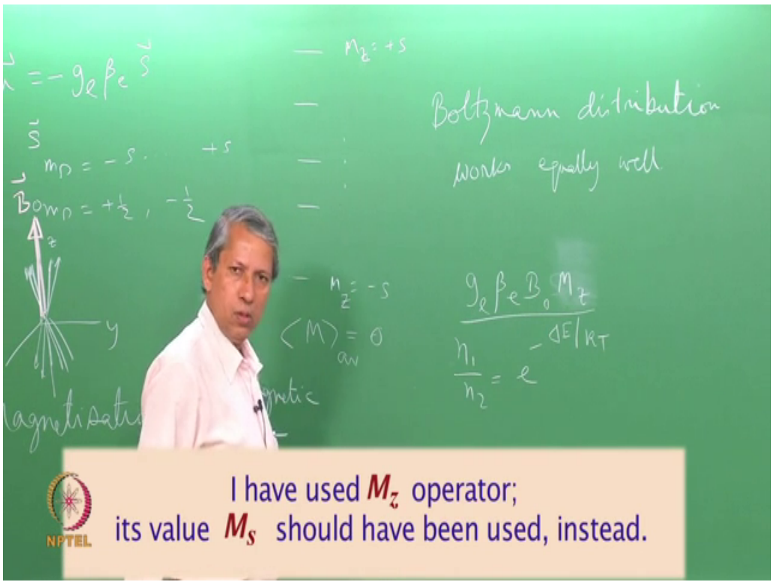
(Refer Slide Time: 05:33)



The Boltzmann distribution works equally well. So, we will use this distribution to find out how this various particles will be distributed among the various M S values is a lower level to be more populated than the higher level this will be little bit less it will be still less this will be still less this will be the least populated 1. So, now, if I add all the magnetic moment then net result is not going to be 0 therefore, the system will have a net magnetization.

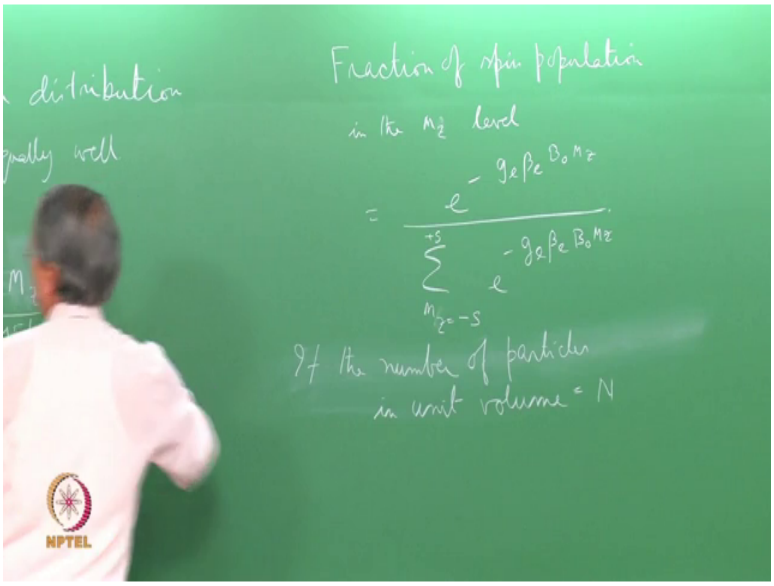
So, each of this M S values will have it is own energy as I said with that that is given by g e beta e if B is 0 is the magnetic field which is pointing along the z direction then g e beta e is 0 S z is the energy corresponding to M z is the energy corresponding to the energy level given by the corresponding M z values. So, this should be M z here and M z there.

(Refer Slide Time: 07:05)



So, we know now that for Boltzmann distribution the number of particles is n 1 by n 2 follow this type of distribution, where delta is the energy difference between the level which is n 1 particle and this is n 2 for, here the various energy levels are given by this set of expression and M z varies from 1 level to the other.

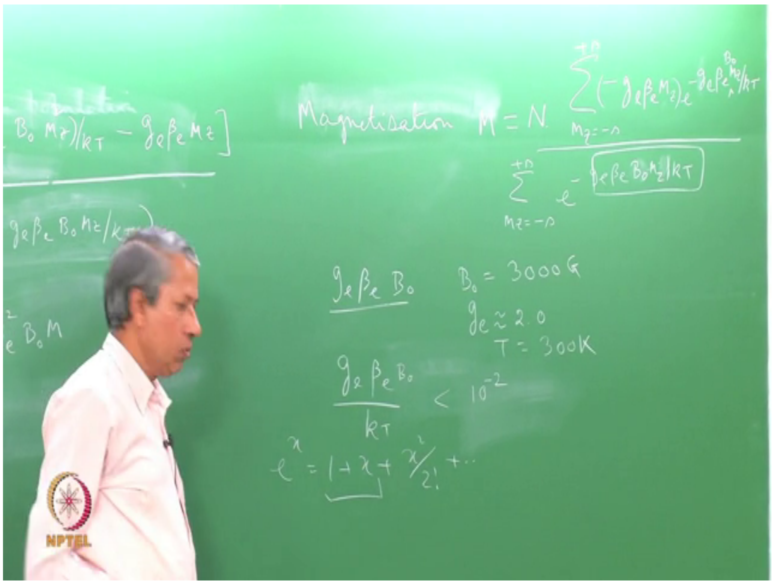
(Refer Slide Time: 08:04)



So, we can calculate the fraction of particle that this various levels will have is given by, Let us call is spin population in the M S or I will call it M z level is given by this is understandable then this is the sum of all the possibilities. So, that is a normalisation factor. So, this ratio gives the fraction of population at a level which is characterized by the value of M z. So, if we take sum of all M z this is the total likelihood.

So, now if the number of particles in unit volume equal to N, then I find out how many of this n are distributed in various energy levels here and each of them will have a magnetic moment given by expression of this kind. So, I get the average value of the magnetization coming out for this N particles and say n is the number particles in unit volume that average magnetization will essentially give rise to the magnetic moment.

(Refer Slide Time: 10:30)

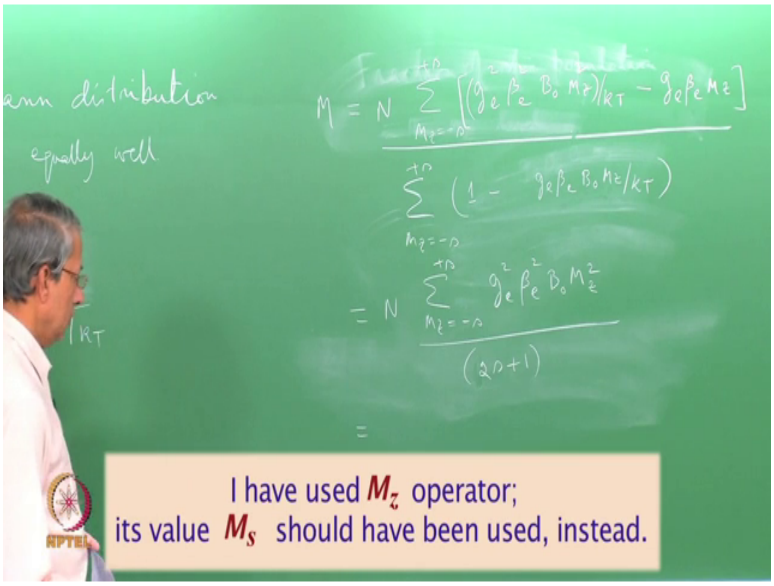


Give rise to the magnetization M is therefore, given by this n times M z equal to minus S to plus S e to the power e 0 is missing here. So, that is it. So, if I can simplify this thing and get some sort of descent looking expression that will be the magnetization, how do I make it decent looking.

Here the energy gap between these various steps are of the order of this g e beta B 0 type of thing and for typical magnetic field of B 0 let us say worth 3000 gauss and g e is typically 2 this factor let this this factor turns out to be less than 10 to the power minus 2. So, of course, an at temperature T is equal to some 300 Kelvin room temperature. So, this is the typically condition we employ in the according to the spectra. So, here this ratio is very small. So, the exponential here can be expanded and we can keep only the first term that is exponential x 1 plus x plus we can keep only this 2 term here.

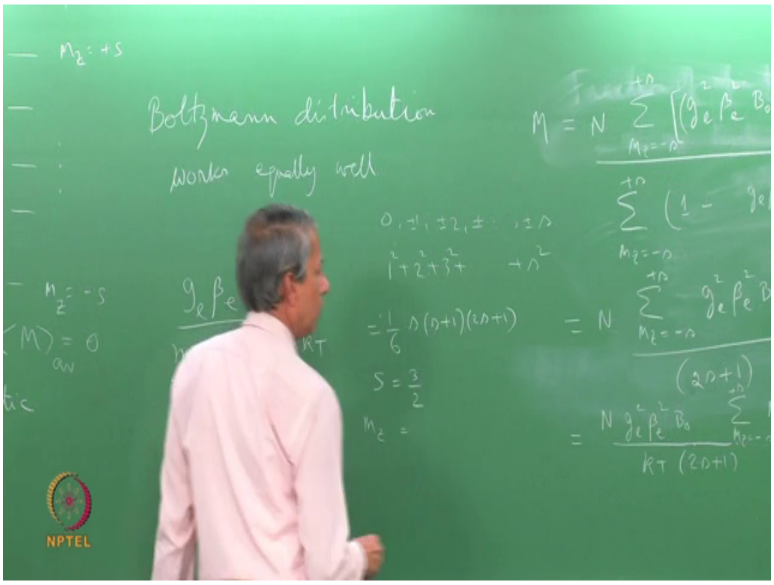
Then let us see how that expression simplifies. So, that the magnetization M.

(Refer Slide Time: 13:48)



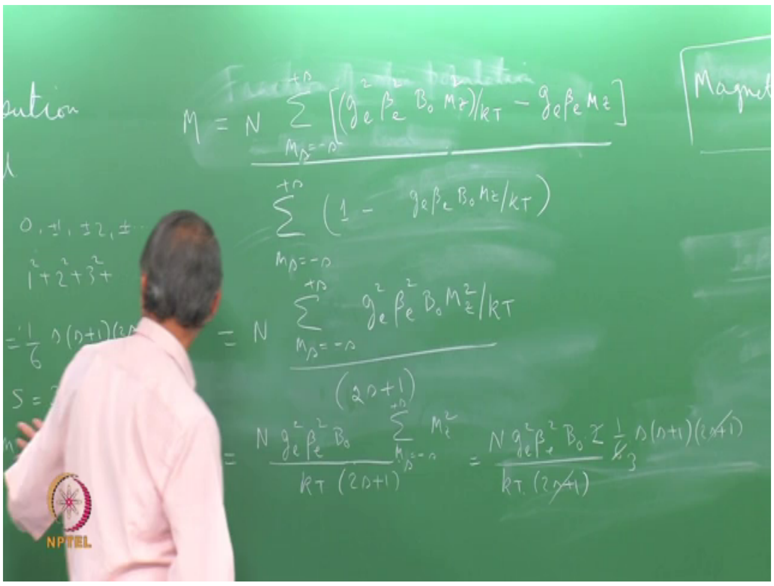
Becomes and the denominator is M z equal to M minus S to plus S 1 minus g e beta e M z by K T, then here where this summation is carried over these term here you see that this will take all the values from minus S to plus S in interval of 1. So, this sum will be 0 in the same way when this is (Refer Time: 15:18) done over this term then again M z takes all the value from minus S to plus S the sum will be exactly 0. So, by this number 1 will be added 2 S plus 1 times. So, this is equal to M z square I forgot this square comes from this region that they already there is one here and then other one comes from the expression here. So, multiply these 2. So, that this will be rise to square of that this will be 2 S plus 1.

(Refer Slide Time: 16:36)



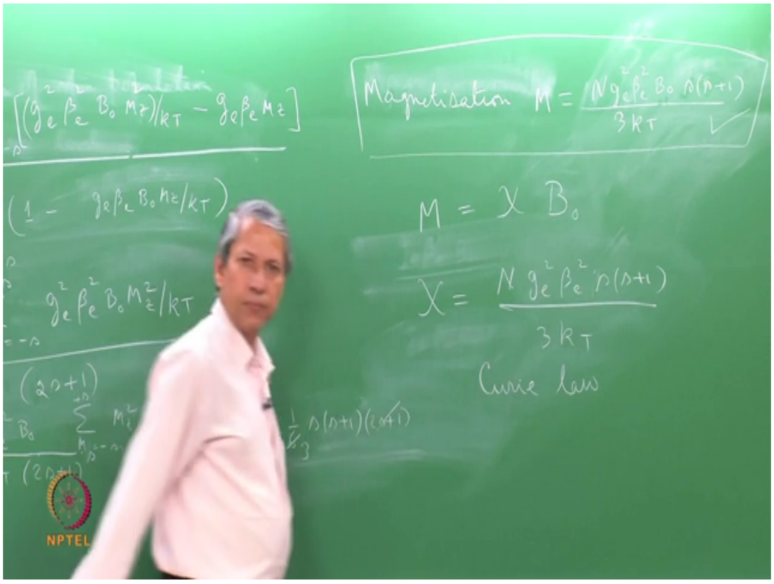
So, this is N g e beta e square B 0 if I have forgot10 K T, here this 1. Now here if now S is a whole number let us say 1 2 3 then M z will take value 0 1 plus minus 1 plus minus 2 up to some number plus minus S these are the possible M S values. So, when I take the square of that for both plus and minus the values are same. So, they will appear in pairs and 0 of course, does not contribute this. So, this is a essentially this summation means that I take the sum of integers of this kind 1 square plus 2 square plus 3 square up to S square and this is known summation is known this is a summation of this, but since this appears in pairs this summation will be 2 times I do not need any more this 1.

(Refer Slide Time: 18:29)



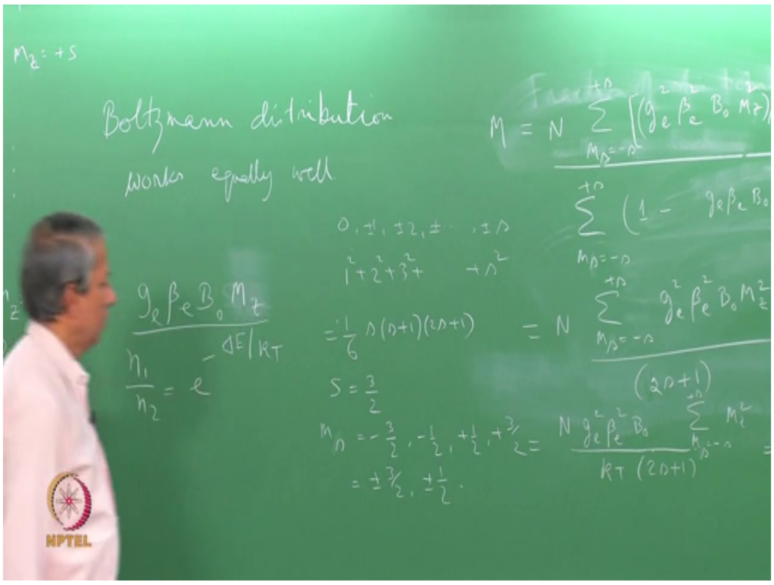
So, what I get from here these 2 cancels well and this gives 3. So, this gives the (Refer Time: 19:19) extension of magnetization is equal to this is S into S plus one by 3 K T. So, this is the expression of magnetisation.

(Refer Slide Time: 19:25)



Here in the derivation I have taken the value of S to be a whole integer that is how we could use this expression here and then it simplifies to this, now it is possible that S can be half integer also. So, S equal to for example, 3 by 2 then M z where I should call M S I suppose to M S here the component of the magnetic moment vector here also. So, M S will be Minus 3 by 2 minus half plus half plus 3 by 2 where it appears in pairs of these values plus 3 by 2 plus minus half.

(Refer Slide Time: 20:50)

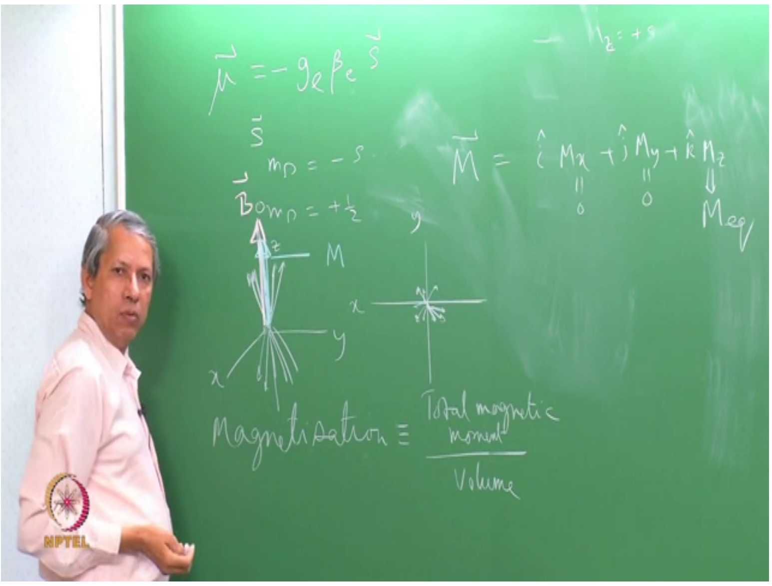


So, here this expression cannot be used exactly as it is. So, one has to change it to this half integral values then do the summation. So, I leave it to you as an exercise and see that you indeed can do that just cleverly manipulate this summation here and then everything will be very similar, because these M z square appear there. So, all the values will appear pair and same. So, you leave it to exercise and see how you can do the summation here, now it turns out that even if the S is half integer this is still valid same expression is valid there. So, this is true for all possible values of the spin angular momentum quantum number.

So, we see now that the moment the numbers of spins are kept in magnetic field it develops a magnetization when kept in a magnetic field B 0 there and of course, now we know this because all the levels are not equally populated. So, there is a term called susceptibility or magnetic susceptibility which is related to magnetization in this fashion called static susceptibility when we kept a magnetic field B 0 and let us say I (Refer Time: 22:52) magnetization this kind then if you compare these with these static susceptibility is nothing, but this N this you should be able to recognize this is nothing, but the curie law the magnetic susceptibility and it is temperature dependence.

So, if the external magnetic field is follow the z direction the net this magnetization that we have calculated this will also therefore, point along this z direction. So, if I have another colour this is the magnetization. So, at equilibrium therefore, this magnetization points along the direction of the magnetic field now if it. So, happens that something is done to the system and we disturb the orientation of the spins such way that this magnetization does not point. Towards the direction and points some other direction in other words what I am trying to say is that see at thermal equilibrium these magnetization which is a considered a vector quantity because it is a direction and also magnitude ahs only the z component it has no x or y component. So, at equilibrium there is no x or y component, but is possible that we can disturb the spin system such a way that this magnetization can have x and y component also this M.

(Refer Slide Time: 24:57)

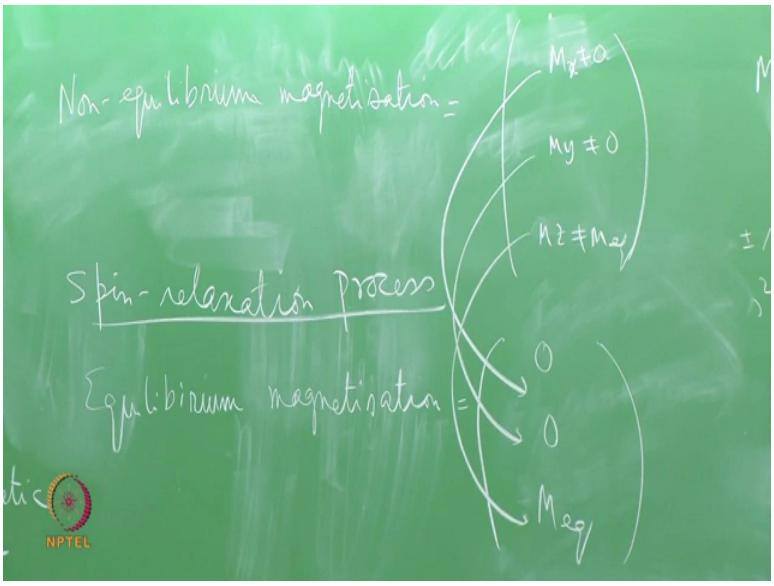


Now, magnetization vector has this component.

So, once again at thermal equilibrium M z is this is equal to 0 this also equal to 0 and this takes a maximum value which I have derived here, now I will call it as equilibrium magnetization, I call it M equilibrium, how does one visualise this here again see this individual spins are pointing in all possible directions along the scone here. So, if I take the projections on the x y plane they will have all sorts of orientation here there will not be any preferred orientation of this.

So, naturally sum of this is going to be 0 for both x and y component. So, any spin distribution which changes this magnetization from the equilibrium value to some other value can in general produce. Now therefore, this and this and a value which is different from the equilibrium value so here the spin relaxation process is going to restore this population to the thermal distribution here.

(Refer Slide Time: 26:44)



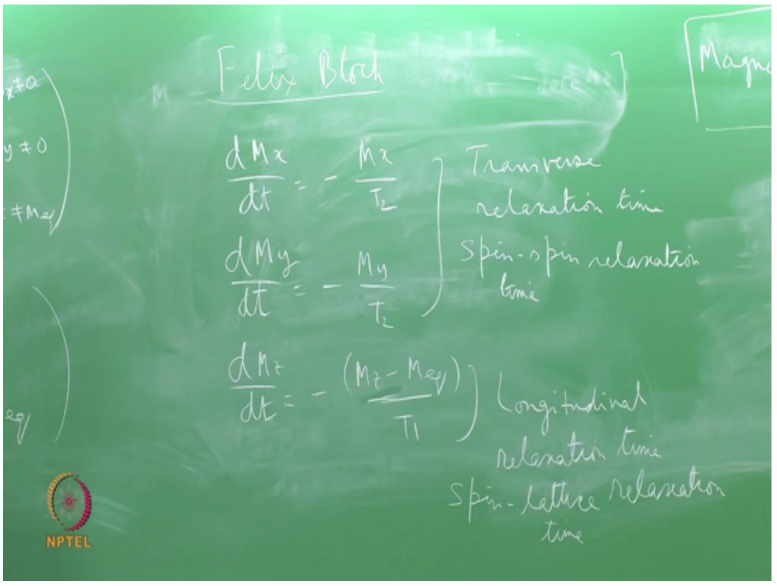
This going to restore the thermal distribution or the Boltzmann distribution that we saw earlier and that Boltzmann distribution gave rise to this equilibrium magnetization for the z component no magnetization for this and this. So, the magnetization which is if we write a this way the 3 component 0 0 M equilibrium and if I what non equilibrium magnetization let us say M x not equal to 0. So, this relaxation process which are there they will try to bring this to this this is the job of the spin relaxation processes.

Now, here the difference between these changes of magnetization from this change of magnetization here is quite significant see the change of M z magnetization involves skipping of spin from one direction to other direction and that needs energy that causes it is some transition to take place.

So, either from here to there or there to here so that energy has to be exchanged with the surrounding and the surrounding must give when spin flips to express in this direction or energy must take away the energy when it goes in the other direction should that involves exchange of energy that is for the change of M z component of the magnetization, but for M x and M y is to bring back these set of random distribution of the spins in the x y plane all is necessary is that this various orientation arranged among themselves. So, that does not need any exchange of energy in the surrounding. So, these

2 processes do that just rearranging the all the spin orientation such a way that net M x and M y common0. So, we therefore, characterize them by 2 different terminology and give different time constant for their processes.

(Refer Slide Time: 30:11)



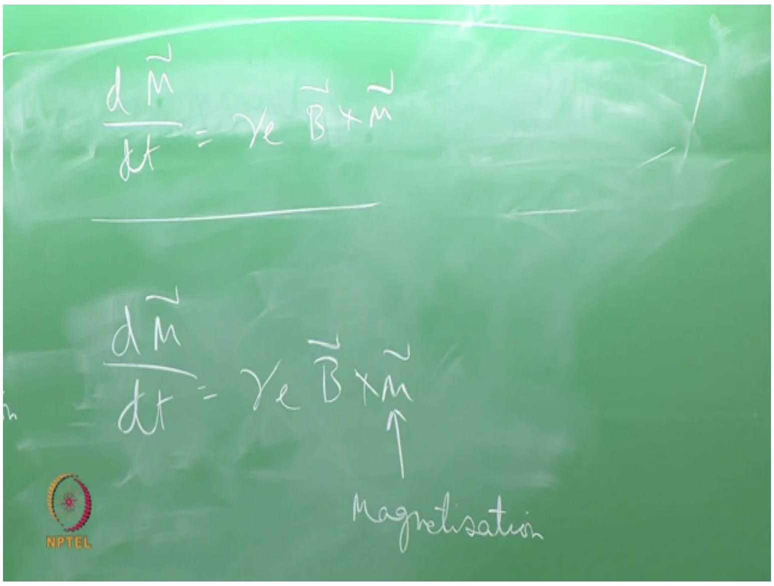
The time constant for this processes are given by certain time constant I call them define them in a moment, but importantly till it is blocked you propose that these restoration of this magnetization from the non-equilibrium value to equilibrium value this process is a first order process.

So, which looks like this similar and d M z by D T is equal to. So, these are all first order chemical kinematic types of expression here that the time constant for this process is given by this T 2 for this and this and T 1 for this. So, reason for these 2 being different from this is I already mentioned that this involves energy exchange between the surroundings. So, the processes or the mechanisms which makes this process to take place suppose to be quite they have different from the mechanisms which makes these process to occur naturally they are time constant in order to be same.

We call this process transverse relaxation time and this is called longitudinal relaxation time also this is called spin spin relaxation time and this is similarly called spin lattice relaxation time the meaning is cleared that energy exchange between the spin system and the surrounding is involved lattice is a general term to designate the surrounding or anything that is other than the spin system.

We have seen earlier that the time evolution of a magnetic moment in a magnetic field follows this set of relation.

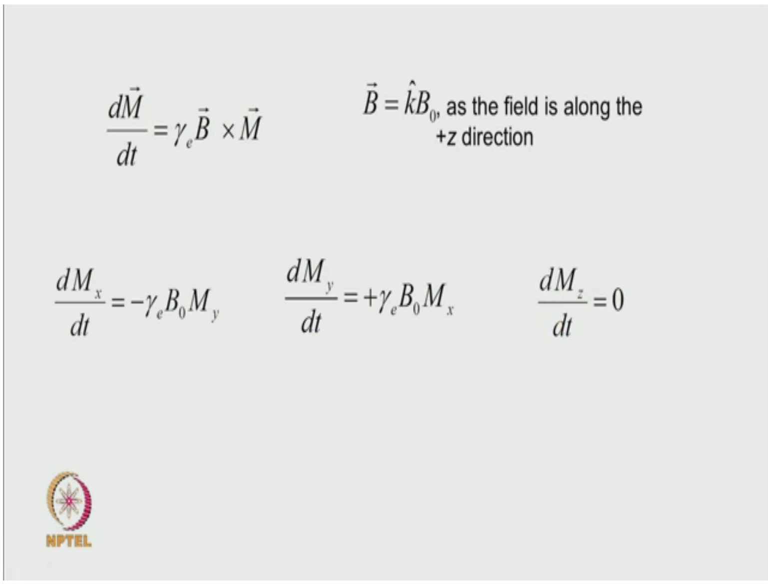
(Refer Slide Time: 33:24)



Where we have this M was the magnetic moment of a particle or subsystem and here we are using the same letter M to designate the magnetization because we are dealing with the collection of particles, now since each of this little spin contributes to the total magnetization this exactly a similar relation holds good for the magnetization also.

So, where this is the magnetization I expect that they should not have any confusion in going to here to there we are reaching earlier this equation to describe the time evolution of a magnetic moment in a magnetic field, now same exactly similar equation is used to describe the time evolution of a magnetization kept in a magnetic field. So, here look at this slide here.

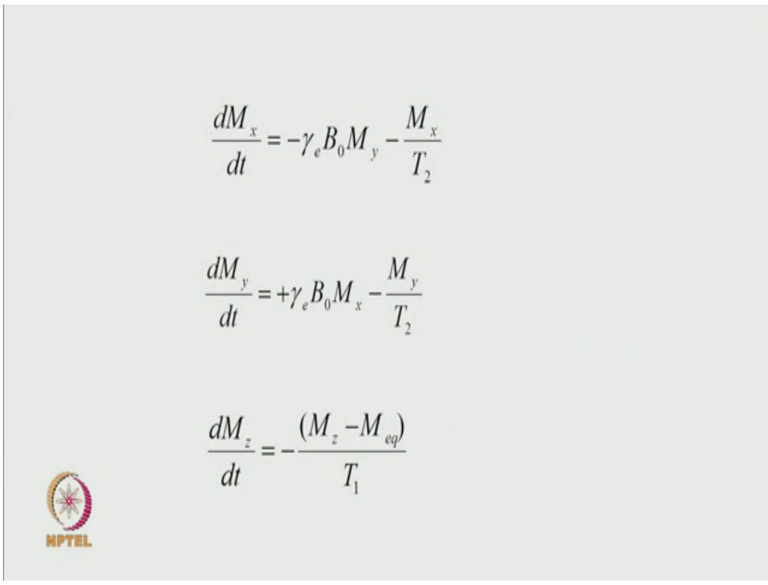
(Refer Slide Time: 34:41)



This given here so when the magnetic field B is along the z direction you know one can expand this term and we get 3 equations of this kind d M x by d T is minus gamma e B 0 M y d M y by d T is plus gamma e we to have b 0 M x and d M z by d T is 0 that is M z component does not change.

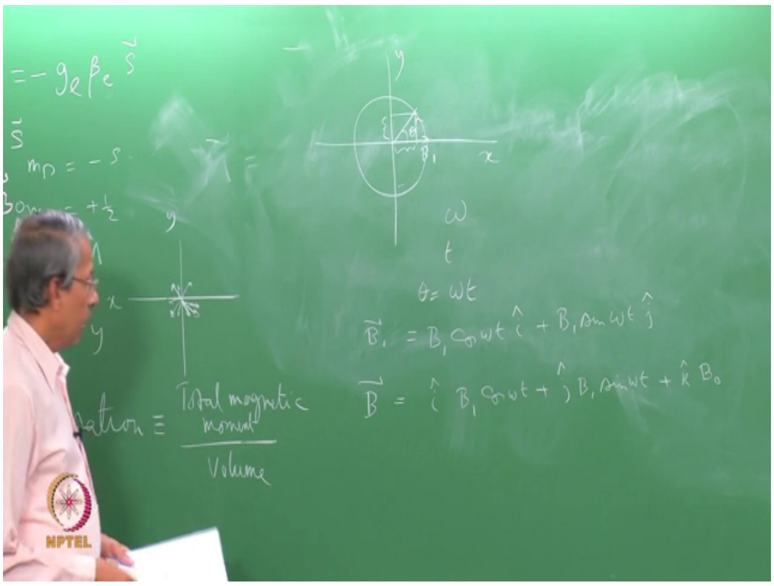
So, here of course, it shows the simply the evolution of the magnetization in a magnetic field and we know that this is nothing, but the precision on motion of the magnetization, now to this we add this relaxation processes then the equation will look different of course, here.

(Refer Slide Time: 35:27)



All I have done is add these 3 terms here to the corresponding 3 terms that this equation gives. So, that is it. So, here this shows the evolution of the magnetization vector M x M y M z component of them in this fashion relaxation terms are included here, but in the pair experiment along with this B 0 we also apply a an oscillating magnetic field in the x y plane to cause the transition. So, this oscillating magnetic field rotates in the x y plane with a frequency omega. So, how do I show that?

(Refer Slide Time: 36:35)

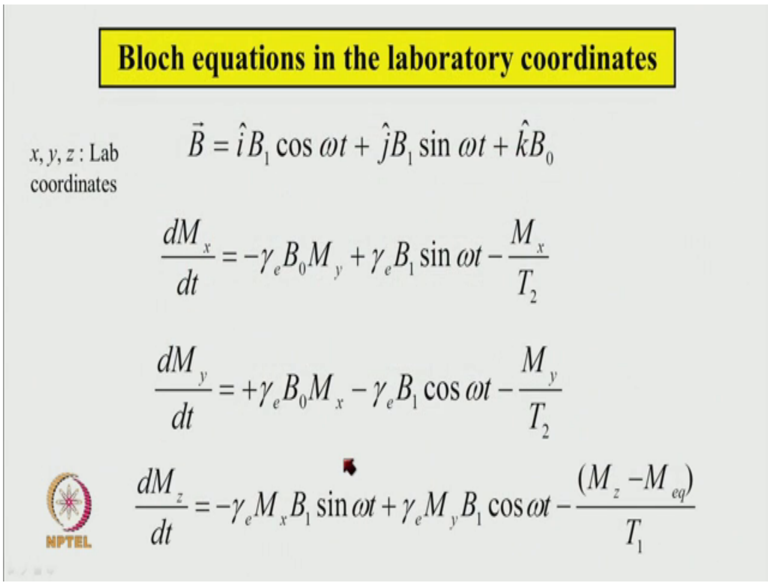


So, this is my x y. So, this is b one is the oscillating magnetic field it starts at time T equal to 0 and on the x direction and starts rotating in the x y plane along the z direction at an angular frequency omega. So, after time T the angle that would form here we let us call theta. So, theta will be equal to omega T. So, at this time x component of this is given by this and y component is given by this. So, here therefore, that B 1 cos omega T I B 1 sin omega T j can be thought of as the B 1 vector, this is the one which is applied along the x y plane and it is moving around the z axis with an angle w T omega this is precisely the type of vector expression this will have.

So, in this case the magnetization sees 2 fields one is due to this other is due to this one which is appearing along the z direction. So, that total field B seen by the magnetization is given by therefore, I cos omega T this is x component B 1 sin omega T is a y component k B 0 this is the z component. So, this is the total magnetic field that is experienced by the magnetization.

So, again I can include that in the equation here and then find out the time dependence of this in the presence of the oscillating magnetic field and that is done in this slide.

(Refer Slide Time: 39:01)



So, the x y z are the laboratory coordinate and this total magnetic field in the laboratory coordinates is given by this and that given when this expression is inserted here to get the time dependence of the M x M y M z component of the magnetization. So, will try to solve it using some special technique at this stage let us summarise what we have done we have taken a collection of spins and then when the it is thermal equilibrium the different energy levels have different number of spins. So, using that information we collected the static magnetization or equilibrium magnetization which appears here then we introduced this Bloch's idea of the first order chemical kinematics type of term which can restore the non-equilibrium magnetization to equilibrium magnetization and introduce this 2 different time constant for that and finally, we got this time dependence of the magnetization in the presence of all the magnetic fields that the magnetization sees.

So, these equations are called the Bloch equation or the time dependence of magnetization this is a very famous in magnetic resonance studies. With these we stop this lecture and will continue our discuss in the next one.