Principles and Applications of Electron Paramagnetic Resonance Spectroscopy

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Lecture - 25
Spin Relaxation and Bloch Equations II

Hello. We are going to continue a discussion on Bloch equations.

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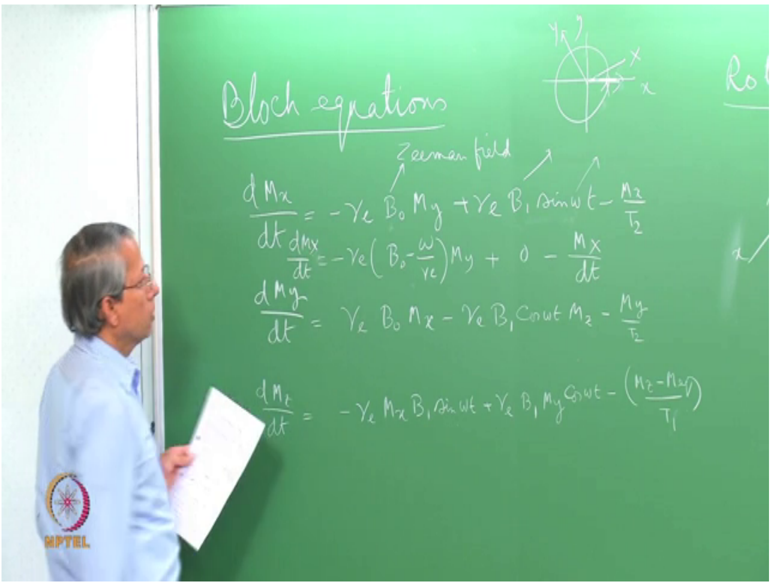

In your previous lecture we saw that the Bloch equations in the presence of a magnetic field and an oscillating magnetic field which rotates in the x y plane the time dependence of the magnetization is given by these 3-differential equations. This for the x component, this is for the y component and this is the z component. Let us briefly recapitulate how we arrived at this 3 differential equations. Here this is the Zeeman magnetic field pointing along the z direction, and B 1 is the amplitude of the oscillating magnetic field, which is rotating in the x y plane with an angular velocity omega here.

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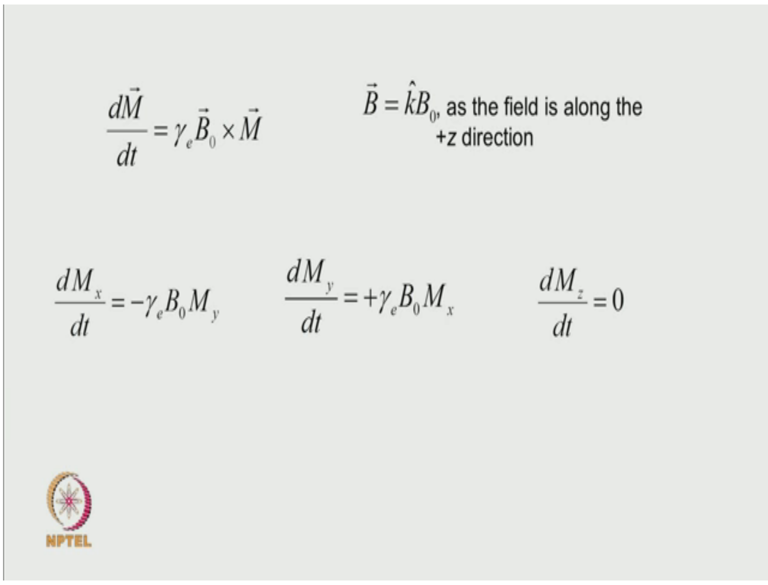

So, how we arrived at this one? We first have this time dependence of the magnetization in the magnetic field given by this equation. Now when only magnetic field is present here the Zeeman field then this give rise to this simple differential equation. And then Bloch introduces the relaxation of this 3 magnetization.

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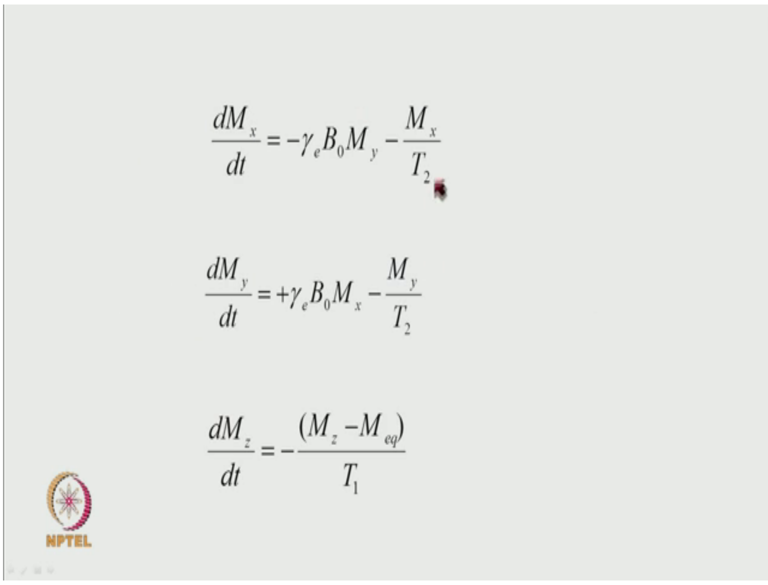

In this fashion; that is, Mx and M y becomes time constant of T 2, and m z increases with T 1 to bring the non-Boltzmann magnetization to the equilibrium magnetization here.

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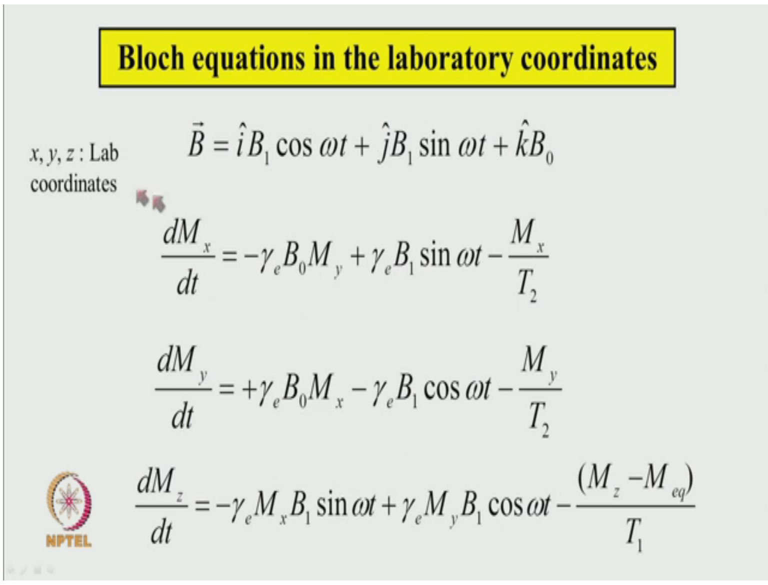

Then the total magnetic field that the magnetization experiences due to the external magnetic field B 0, and the oscillating magnetic field B 1 cos omega T in the x component, B 1 sin omega T is a y component total magnetic field. Then we get these 3 equations. And here this x small x small y, and small z these are the laboratory fixed x y z coordinate any particular the B 0 the Zeeman field is applied along the z direction.

So, to solve this one, one can of course, use the mathematical techniques of first order differential equation and solve them. That is possible, but somehow it is not very illuminating. So, we are going to solve this differential equation in a different way using a special technique called rotating coordinate system. This technique is very much used in magnetic resonance.

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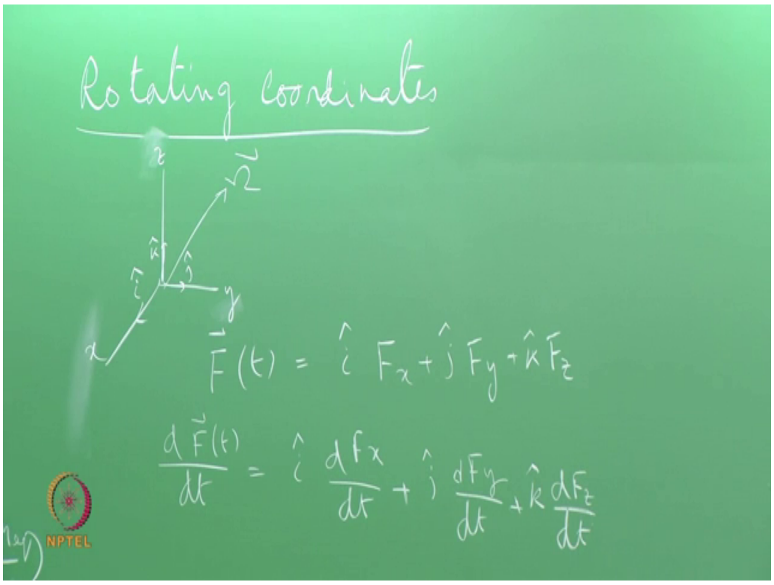

Suppose I have got a coordinate system, let us call it capital x y and z, and this is rotating in a certain direction may be let us I have say I have got this capital x and y and z a coordinate system, which is rotating about an axis at a certain angular velocity omega.

So, in this rotating coordinate system, how is the equation of motion of any vector going to change? First learn that. Suppose I have got a vector, f which is a function of time. So, this could be written as in terms of are usual coordinate system, which is my this laboratory coordinate system, which is x y and z. These are of course, fixed with respect to space, and this is the vector which is got 3 components, in this coordinate system this is i vector j. And this is the unit vector k. So, time dependence of this is given by the time derivative of each of this component here. Nothing new is happening here. See this i j k and see little vectors fixed along this x y and z direction. So, rate of change of this with respect to time is given by the corresponding rate of change of these 3 components of the vector along these 3 reactions. But now we want to be moved generally.

Suppose now this coordinate system is rotating in certain direction at an angular velocity omega, around this axis. How is this time going to look like with respect to these coordinates little x 1 which are rotating?

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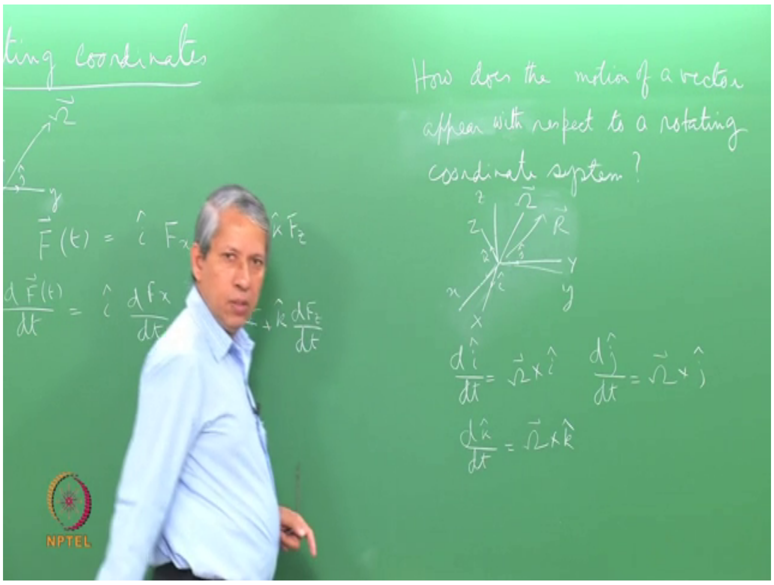

Now, that is the exercise we are going to do now.

So, how does the motion of a vector appear with respect to a rotating coordinate system? So, it is a type of relative velocity or relative motion. So, let us I have got the coordinate system again x y and z and this is the vector pointing in certain direction.

So, it is a question of relative motion. If I sit on this coordinate system, the vector itself will appear to rotate. That is understandable; that with respect to the vector this coordination is rotating means with respect to the coordinate system. The vector is rotating is matter of a rotation of the vector how that appears with respect to static coordination system.

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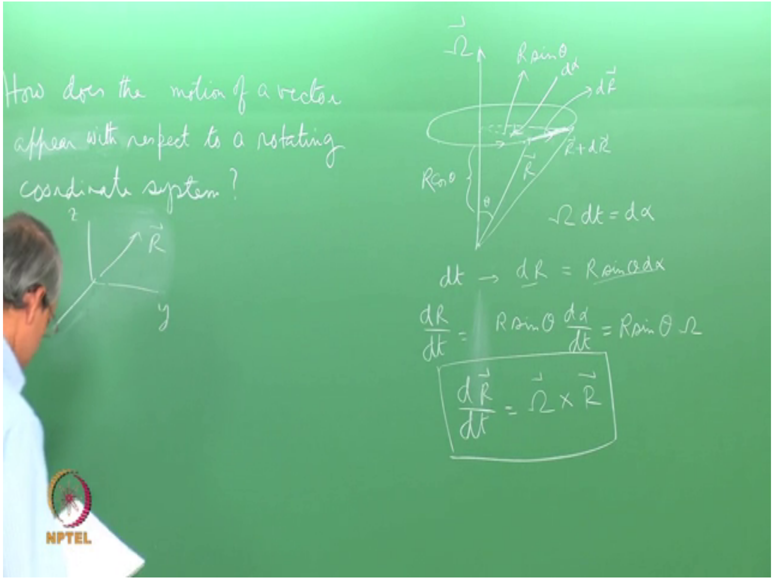

Let us say that this is the direction of the angular velocity omega, and from certain origin this vector R is pointing. So, as I said here earlier the rotation of the coordinate system is as good as imagining that the vector R is rotating around the direction of the angular velocity omega. Suppose at the time T this was here, and then is rotating in this way; so after some time this will appear here, but this vector is different from this vector because the direction has changed, but magnitude has not change is rotating in this way. So, the change here is; I call it dR; this is actually equal to r plus dR; what will be the magnitude of this dR?

So, if this angle is theta, then I draw a normal here this normal there. So, at time dt the change in the amplitude of this is dR. So, for this dR by dt. So, from this angle which will be r cos theta and this magnitude is r sin theta. So, if the angular velocity is omega, then at with time dt this angle hold here, this angle B alpha will be this be this is actually equal to d alpha. This is the angular velocity at time dt this much angle is found here.

So, this will be given by this is the radius and this is the angle. So, will be given by r sin theta d alpha. So, this is therefore, is equal to dR by dt is r sin theta d alpha by dt which is equal to r sin theta omega. That is straight forward. So, this rate of change of this is equal to r sin theta times the angular velocity.

So, these give the magnitude of this. Now we have to or. So, worry about the direction of that. So, this direction dR this incremental vector is in the direction which is normal to r in every instant of time, and also normal to this direction of angular velocity omega. If I write that properly using the vector algebra, this will look like dR by dt is equal to this. This gives the correct magnitude as well as sorry r sin theta omega. So, this gives the correct magnitude as well as the sense of this direction.

Now, coming back to the our rotating coordinate system, when this rotates I have another set of coordinate, let us call it x y and z is they rotating with respect to certain axis with angular velocity vector omega. Then this little each of them will have it is own i j and k. Where these little vectors they keep on changing with time. So, I can therefore, write using this equation di by dt is R vector is replaced by this individual vector i similarly, and k.

So, once again we should not get confused with the respect to the fixed coordinate x y and z i have it is own little i j and k which is fixed with respect to the laboratory phase coordinate, let us say. But the other coordinate capital x and y and z they are rotating in certain direction with angular velocity omega, then the unit vector associated with these rotating coordinate system with these i and j and k and they have a this set of time dependence. So now, coming back here now we can now make it more general by saying that this i j and k also depends on time in this fashion, because with the rotation with respect to this certain direction omega, then I can write in more general way that; f is i times f x j time f y k times f z, but now this time that I have got with respect to the fixed coordinate x y and z.

Now if I and j k they are also changing because with rotation that I have to use another term here, which is the rate of change of this with respect to time.

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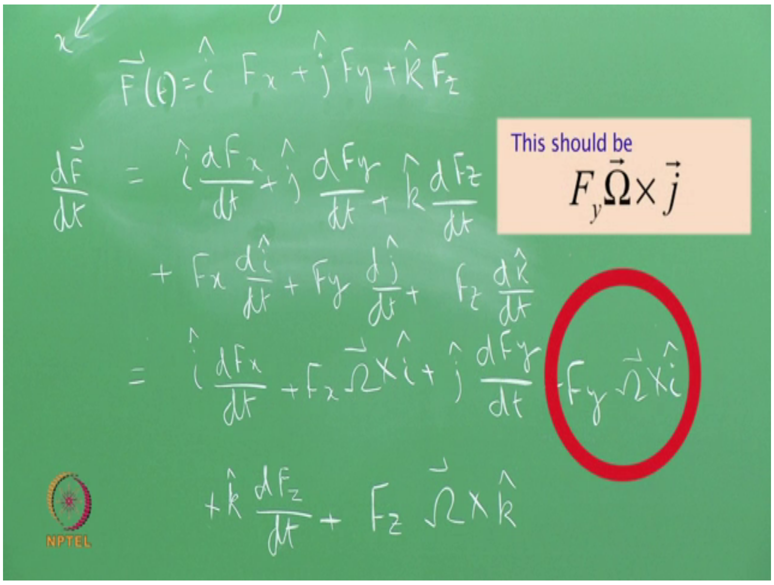

So, this will be f of x di by dt plus f of y d j by dt and plus f of z d k by dt. So, this gives the complete time derivative where coordinate system is also rotating.

Now, I have already got this relationship this in terms of the angular velocity vector omega. So, if I write this here this will look like i d f x by dt plus here f x times, this is omega cross i. Now we can collect all the terms that involve this omega.

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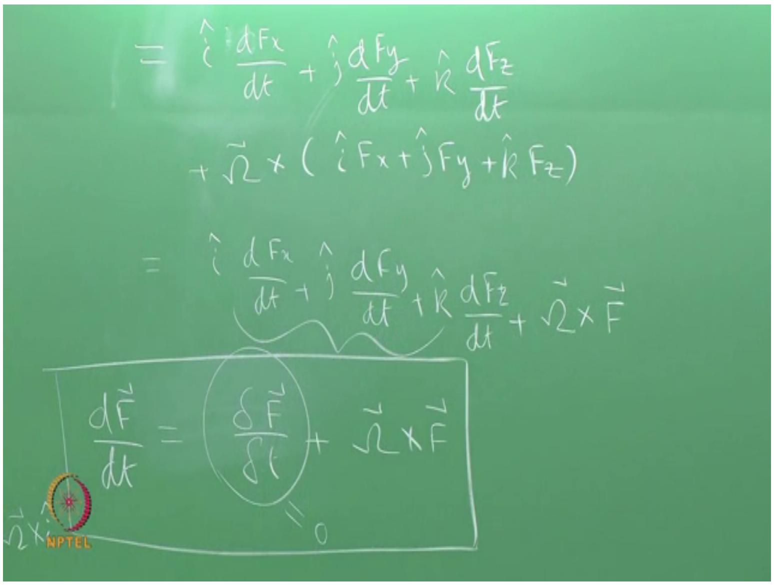

This gives, k d f z by dt plus the omega term i f x j f y k f z. See how all these things have come together, and this is nothing but this vector itself. So, you can write this equal to i d f x by dt j d f y by dt k d f z by dt plus omega cross f. These 3 terms written as dell f by dell T this is omega cross f. So, this the same as d f by dt.

So, this is the equation we are trying to arrive at. What is the significance of this? This says that this part is the time derivative with respect to the rotating coordinates which are rotating around this axis with a angular velocity omega. So, here this i j k the unit vectors are rotating. So, with respect to those rotating unit vectors this is the time derivative. And this is with respect to the space fixed unit vector i j k. So, it also shows that, if this term is 0, then with respect to the rotating coordinate system the 3 component of this vector f do not change. So, this is the equation will find very useful. So, another way to look at it is that; if I want to know the time derivative with respect to a rotating coordinate system, that derivative plus this vector product together gives the time derivative with respect to the space fixed coordinate.

From here now, will try to see how the magnetization can be written in terms of rotating coordinate system, and it is time dependence can be derived in exactly say analogous fashion.

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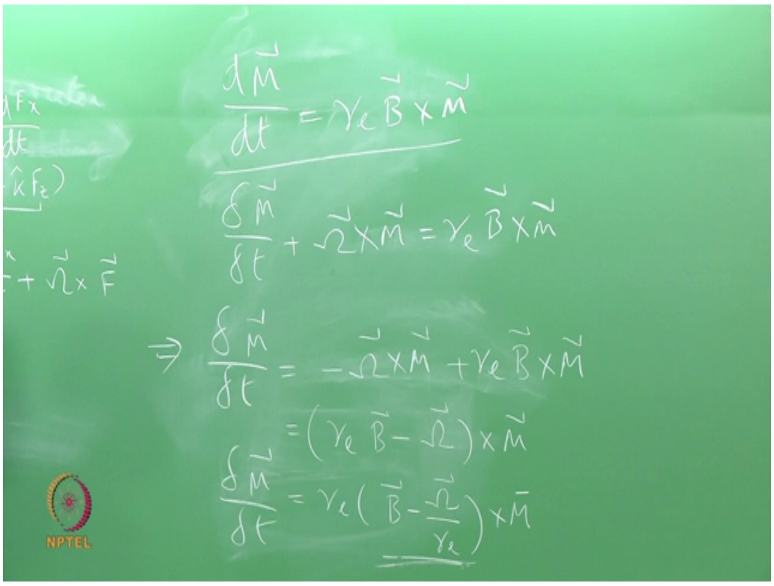

This is the differential equation relating the rate of change of magnetization in the presence of magnetic field here. So, you see from these I can straight away write if the in a coordinate system which is rotating with an angular velocity omega this will look like this there is the extra term that come from here because the rotation of coordinate system. So, this is the time independence of the magnetization in the rotating coordination system, and I get the extra term here and that is the way it is going to be.

So, what does it mean? This means minus omega cross m which is this gives me compare now these equation with this equation. This is written in terms of the laboratory coordinate system and this is in terms of a coordinate system which is rotating in an arbitrary direction with an angular velocity omega. See they look essentially very, very similar. Except that this effective B becomes different in the rotating coordinate system different from the magnetic field B that is present here.

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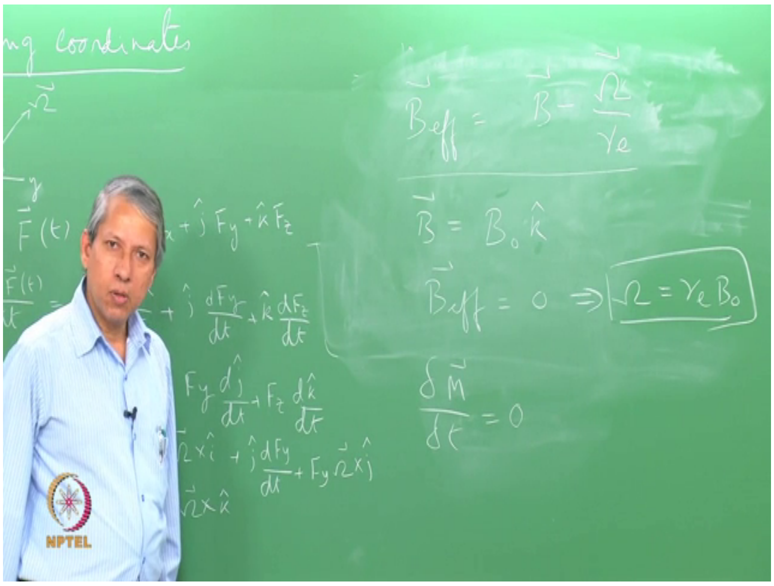

So, when the coordinate system rotates with an angular velocity omega, the effective magnetic field becomes this. So, and then I can use the essentials let the same type of time dependence as in the static coordinate system.

So, with these now is a how easy to visualize the motion of this magnetization in a magnetic field. So, when the (Refer Time: 26:27) B was B 0 k, and even now find out the time dependence of the magnetization. If I choose a coordinate system, which is rotating around the z axis, with an angular velocity this then what happens that, if I choose the frequency such a way that B effective becomes 0, then my dM by dt becomes exactly 0. So, that means, that in that coordinate system which is rotating around the z direction with the frequency omega, such that this is 0. Or in other words my this implies that omega is actually equal to gamma B 0, then in that rotating coordinate system the magnetization does not change. So, it appears static.

So, what is the consequence that? If the magnetization appears static in a coordinate system which is rotating in a frequency omega around the z axis, then in a static coordinate system, the magnetization rotates with a same frequency. See how nicely come to the conclusion which we do earlier is that magnetization increases in the laboratory coordinate system with this frequency and when we look at the rotating coordinate system rotating with this frequency. The magnetization appears static the fixture is the same; s these conserve and comes; so easily by choosing a coordinate system which rotates in this particular fashion. So, this is the advantage of using rotating coordinate system. We can better in sight and expressions also look somewhat simpler.

So, how will the Bloch equation look like in the rotating coordinate system? Now what should we in a coordinate system we should choose here. Here we choose the frequency which is the normal frequency, but for this situation where this B 1 is the micro magnetic feild which is rotating in the x y plane in this fashion. I choose a coordinate system which is rotating in the same angular frequency as this one along the z direction, that is it will may having an angular frequency omega and direction is the z direction. Then what will happen to the B 1 field, in the laboratory coordinate system the magnetic field is rotating in this way, but in the coordinate system now I have got this which is rotating in the same frequency as this one, then this B 1 field will appear static no?

So, at time T is equal to 0, if the B 1 field is applied along this x direction, and the coordination start rotating at time T equal to 0 from the x direction, then in the rotating coordinate system the B 1 will always be along the x direction there will not be any component for that. So, you can therefore, write it very easily from this knowledge. That with when a coordination system rotates, I change the B by this and here in particular the B 1 also has only the one component it is the x and y component.

So, here let us I modify right here so that the difference becomes easy to visualize, this will become B 0 minus omega by gamma e M y. So, this is the change of B 0 by value that is the way we come we got the answer earlier, now this is the y component of the magnetization in the laboratory consistent, but in the rotating coordinate system this is absent. So, this becomes 0 minus now I should call it now dM x by dt this is the capital dM x by dt.

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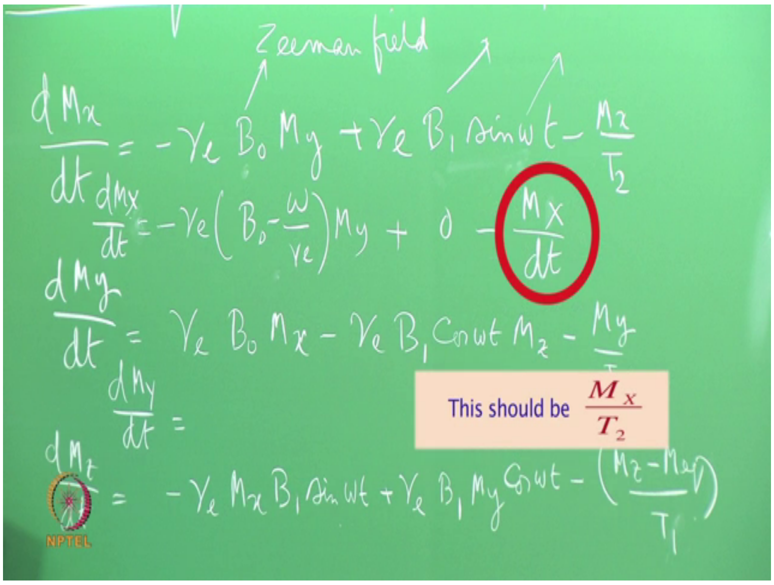

These things indicate that this is the rotating coordinate system. Similarly, for y component dM y by dt will be B 0 will be replaced by this one.

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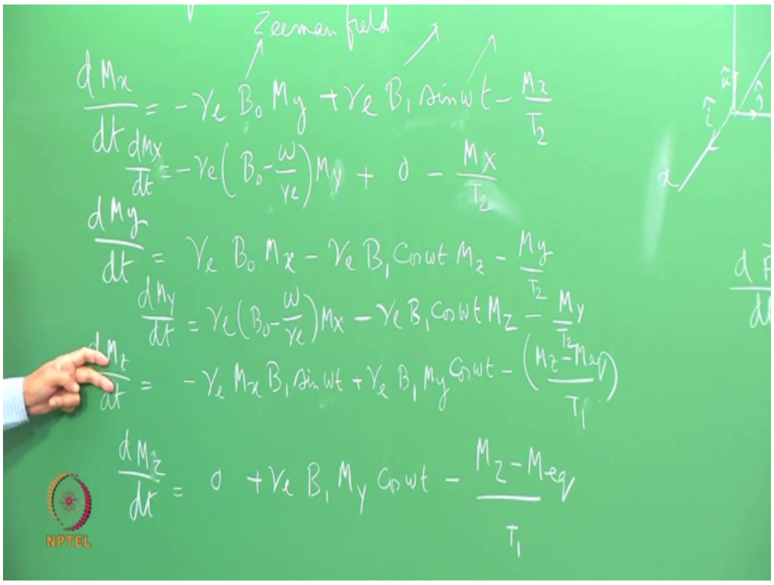

I should have change this also, this will be capital y in a rotating coordinate system. This is the B 1 magnetic field, which is always present in the x direction. This will be present here this a mistake here. Sorry, T 2 and finally, this is capital z. This is again the y component of the rotating magnetic field, which is not present in this coordinate system this is 0. This will be T 1. See how easily we can now transform this laboratory coordinate system that magnetization evolves to a rotating coordinate system. So, I have got a slide here.

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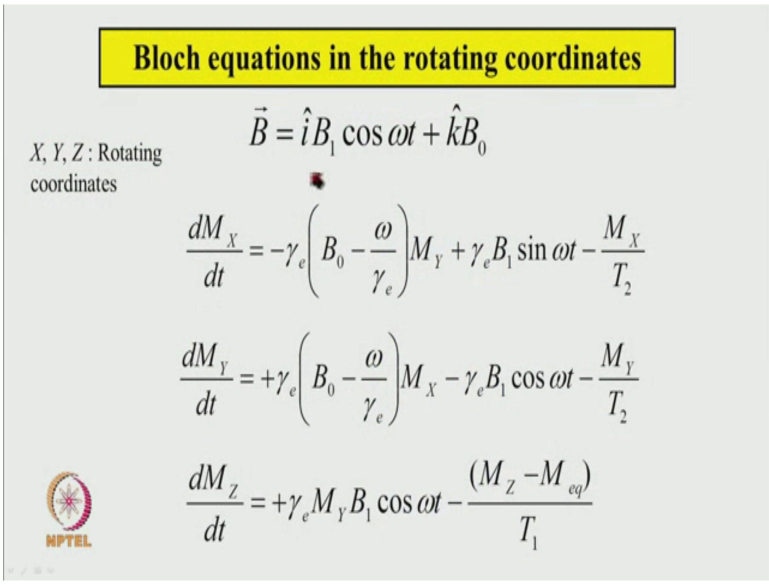

So, that capital x y and z are the rotating coordinate system. Then are the total magnetic field appears only as a x component of the (Refer Time: 33:52) and the Zeeman field is around the y, I am sorry in the z direction, and then this time dependence of the x y and z direction.

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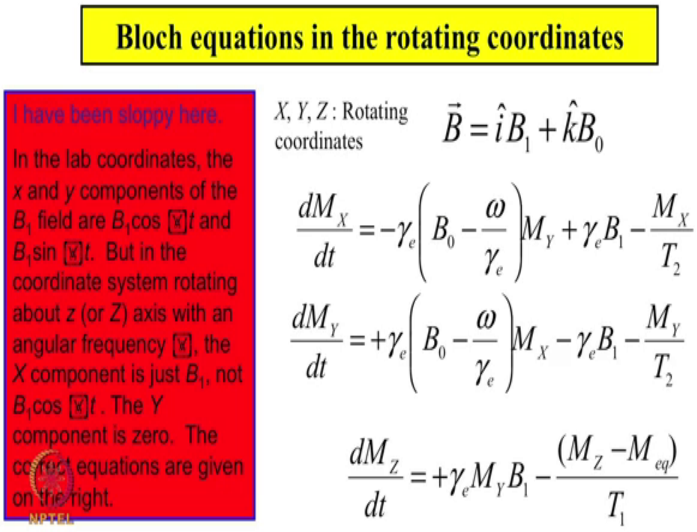

Now, will try to get the steady state solution of the Bloch equation; when the (Refer Time: 34:20) experiment is done all the time dependence have reached a steady state value, and this spectrum is recorded as a function of either frequency or magnetic field, we get the steady state value of the magnetization that detect the spectrometer.

We can solve for the steady state value of the magnetization. From this 3-differential equation by setting this time derivative to be 0 dM x by dt is 0, dM y by dt equal to 0 dM z by dt equal to 0.

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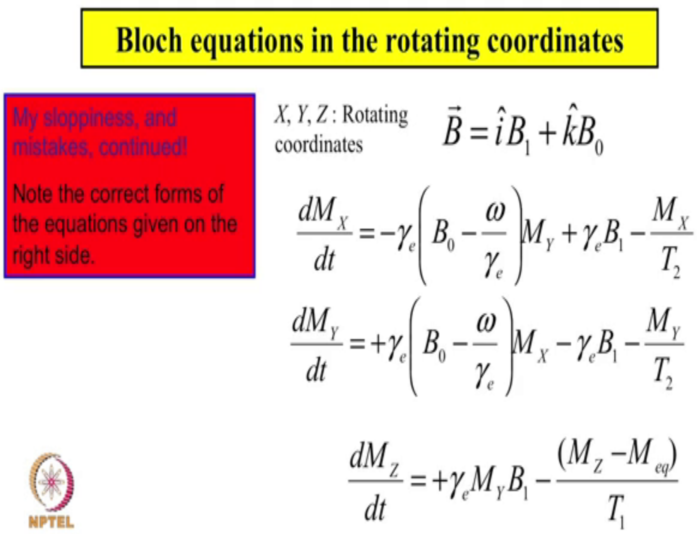

Then we do some algebra and the solution is given in this fashion is called the steady state solution of Bloch equation in the rotating coordinate system.

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Steady-state solution of Bloch equations in the rotating coordinates

$$M_X = -\frac{\gamma_e B_1 M_{eq} \Delta\omega T_2^2}{1+\Delta\omega^2 T_2^2 + \gamma_e^2 B_1^2 T_1 T_2} \qquad \gamma_e B_0 \equiv \omega_0 \qquad \Delta\omega \equiv \omega_0 - \omega$$

$$M_Y = \frac{\gamma_e B_1 M_{eq} T_2}{1+\Delta\omega^2 T_2^2 + \gamma_e^2 B_1^2 T_1 T_2}$$

$$M_Z = \frac{M_{eq}(1+\Delta\omega^2 T_2^2)}{1+\Delta\omega^2 T_2^2 + \gamma_e^2 B_1^2 T_1 T_2}$$

Here we made a small substitution gamma e B 0 is defined to be omega 0 and delta omega omega 0 minus omega. This omega is the angular frequency of the micro magnetic field, and this is the frequency correspondent to the Zeeman field or larmor frequency. That is why looks like.

So now EPR spectrometer can be set to detect the Mx component of the magnetization or M y component of the magnetization. Usually we look at the M y component. Which is called the outer phase component because outer phase with respect to this rotating magnetic field which is present there which applied in the x direction. So, we are looking at the y one which is 90 degree out of phase, but one can detect the x component also which is the in-phase component. Now how they will differ the appearance is given by this magnetization, as a function of now the frequency of the micro magnetic field, that is this omega.

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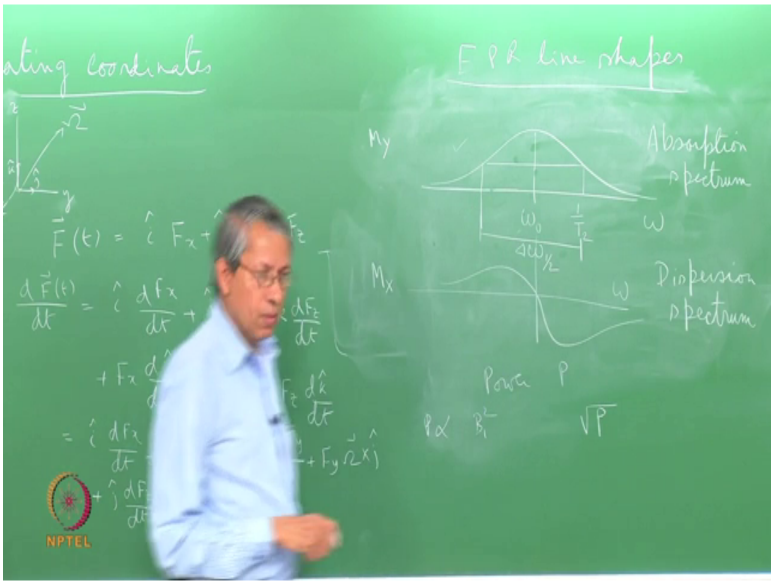

So, if I plot this, that will give the EPR line shape as I said that usually the M y component is rejected. So, EPR line shape will be given by the shape of this.

So, we plot now M y as a function of omega. What we are plotting is this function in a that is the M y in the rotating coordinate system. This will look like this where this peak corresponds to omega 0. So, this is called the absorption profile or absorption spectrum. Similarly, if we plot the Mx component; this will look like this. This is called the dispersion spectrum. Usually this detected in the EPR spectrum.

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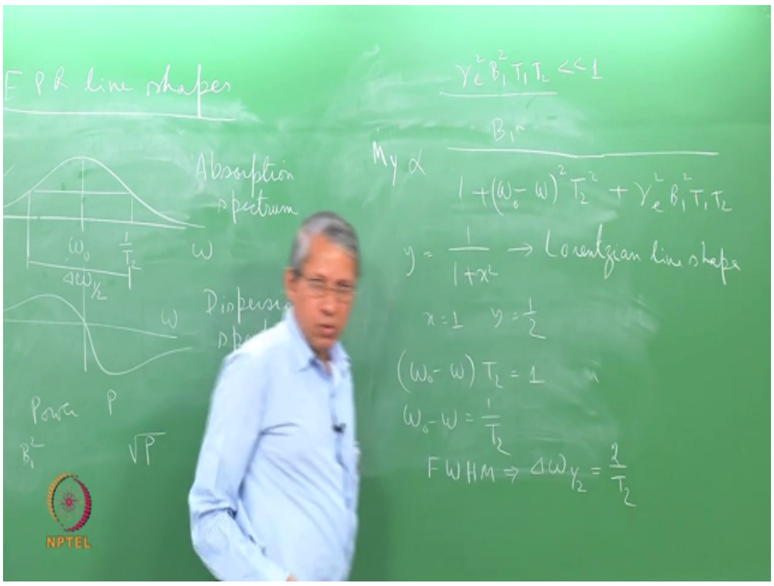

M y is proportional to If here if we neglect this term gamma e square B 1 square T 1 T 2 that is neglected that is very, very smaller than one then it looks like this. Now this is exactly similar to the form y equal to 1 by 1 plus x square, which is the Lorentzian line shape. So, the EPR of those spectrums will therefore, appear Lorentzian when this term is neglected.

Here say x is equal to 1, the value of y becomes half. The same way here when omega 0 minus omega T 2 is equal to 1, then the signal height becomes half of that. So, here this will be half of that when these value is 1 by T 2. Similarly, here also 1 by T 2 or in other words this total this one (Refer Time: 39:45) delta omega half corresponds to the half, intensity of this one or full with and half maxima full with at half maxima corresponds to delta omega half this gives 2 by T 2.

So, in this spectrum are recruited as function of frequency we can straight away get the spin spin relaxation time. From this relationship the second consequence of this Bloch equation here see the intensity of M y is proportional to B 1, which is the measure of the micro magnetic field. When B 1 increases the signal height will also increase is proportional to B 1, where micro power is p then p is proportional to B 1 square. So, when the EPR signal is recorded at various setting of micro power, the intensity will change as square root of power. All these are true when we have neglected this factor, this one. But as you keep on increase in the micro power this becomes more and more significant and is possible that this may not be neglected. Then the line shape will starts showing distortion. So, we call this signal when this we can appreciable then this appears here as gamma square T 1 T 2. So, the signal will now try to become smaller and smaller, where this is becoming appreciable. We have got B 1 here, for then as this because larger than this, similarly start.

Therefore initially keep going up and then because of this will be start going down. So, we say that system is undergoing partial saturation. That is relaxation process is not able to maintain the population difference while. So, signal height does down, but this itself could be used as a tool to measure. The spin lattice relaxation time, how? So, let us call this factor.

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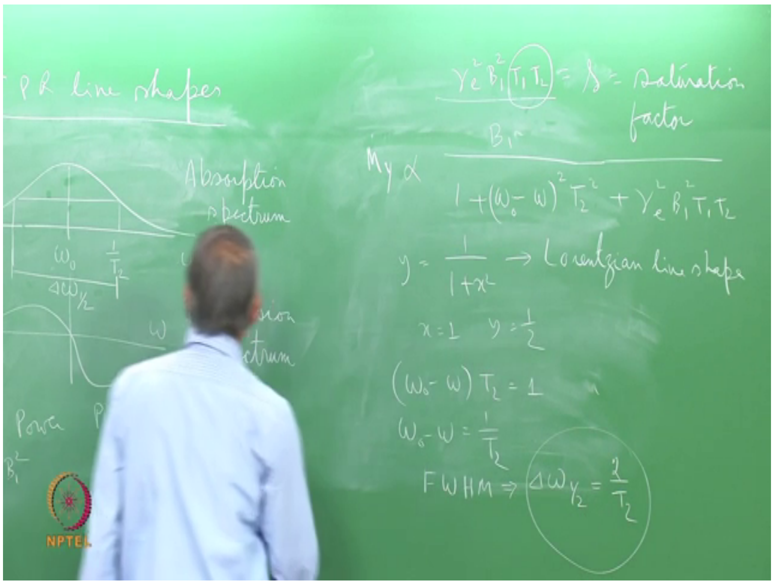

So, if I plot this signal height now as a function of various settings of B 1, as I said initially will go up and then it will start coming down because of this one. So, by plotting in (Refer Time: 42:42) function of micro power, I can get an idea of this value saturation factor. So, this is proportional to B 1 square. So, from that experiment I get idea of this product now. And then I can get T 1 by knowing that from the unsaturated condition, when the line shape is strictly Lorentzian and (Refer Time: 43:08) as small I can get T 2, and partial saturation is achieved again a T 1 and T 2 from this I can find out T 1 also.

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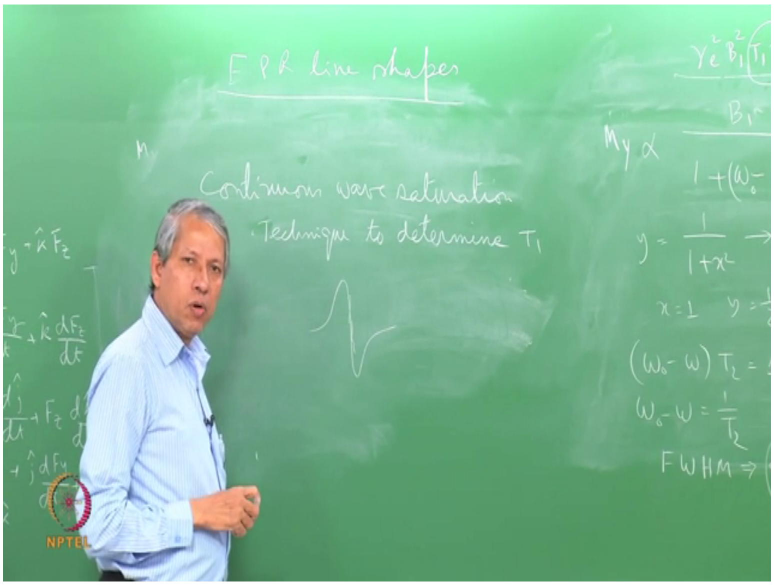

This technique can measure in that spin as relaxation time is called continuous wave saturation technique. Now to measure the T 1 and T 2 from this line shape analysis, one needs to keep in mind that the line shape should follow Lorentzian there; mean there should not be any unnecessary high-power line. There each high-power line must strictly cross from one transition there is no residual line which are hitting here. In that case one will get a wrong value of T 2, and if you get wrong value of T 2 you will get of course, wrong value of T 1 because this is obtained from the product of T 1 and T 2.

And also, one has to have very accurate measurement of the micro magnetic field B 1, and that is not very easy to know analyse one (Refer Time: 44:34) careful estimate of B 1. We can measure the micro power very accurately, but how is that micro power (Refer Time: 44:40) standing of inside the cavity? And how the B 1 field is experienced by the sample? That needs very, very careful measurement. That is not a very easy task. Never the least this way of measuring T 1 and T 2 are possible, if one takes care of this things now.

Before concluding a little small note of a importance; that we do not do the experiment in terms of micro frequency. We do the experiment at least micro frequency, but vary the magnetic field. So, we modify this Bloch equation, which are here in terms of least micro frequency of vary the magnetic field. So, that is shown here. So, steady state solution of Bloch equation in the rotating coordinate system in terms of variable magnetic field here looks they are quite equivalent of course.

Now to conclude that we have seen how the introduction of relaxation by Bloch in the time dependent magnetization gives rise to the line shape. And explains a host of things like saturation B i B r, how that T 1 and 2 are (Refer Time: 46:04) built into the line shape. And one can learn from and one can measure those from the line shape analysis.

With this we come to an end to this lecture.