

Principles and Applications of Electron Paramagnetic Resonance Spectroscopy

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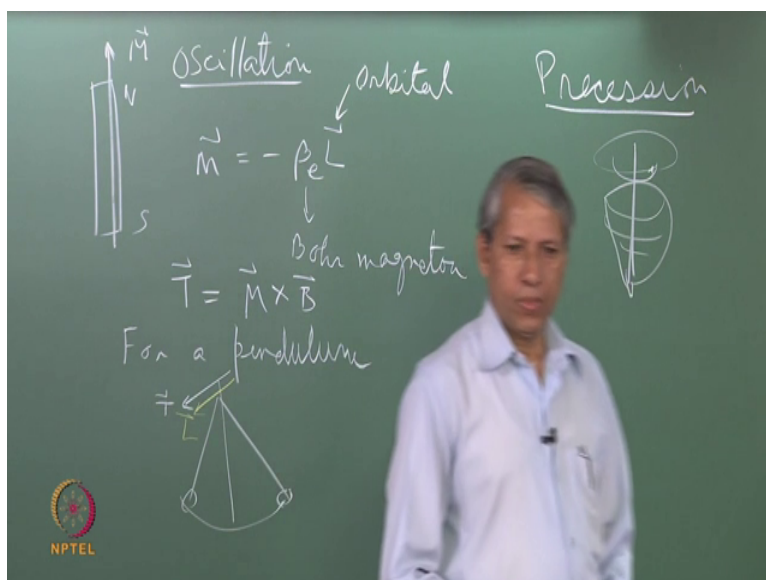
Tata Institute of Fundamental Research, Mumbai

Lecture – 06

Magnetic Moment in Magnetic Field – II

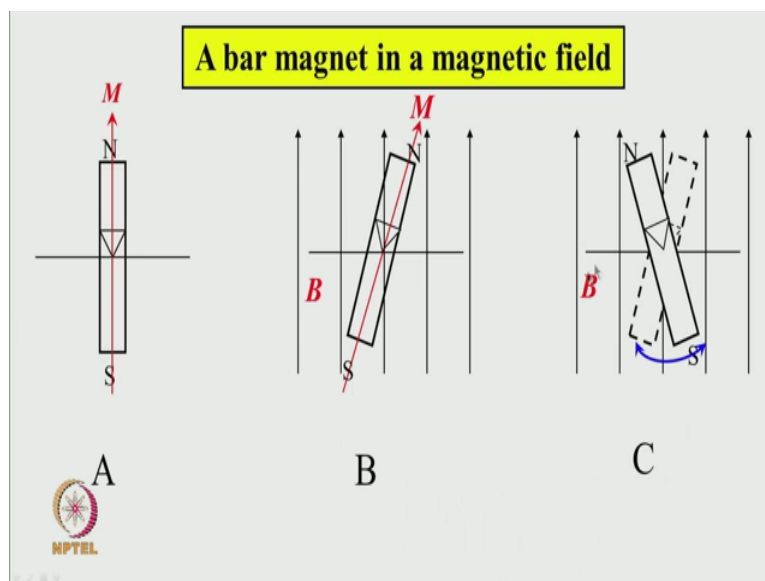
Hello, we started our discussion of the motion of a magnet in a magnetic field and we have seen earlier that if we keep a bar magnet in a magnetic field, it undergoes to and fro motion.

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This is the magnetic moment and if you put a magnetic field there then it undergoes to and fro motion as we saw earlier.

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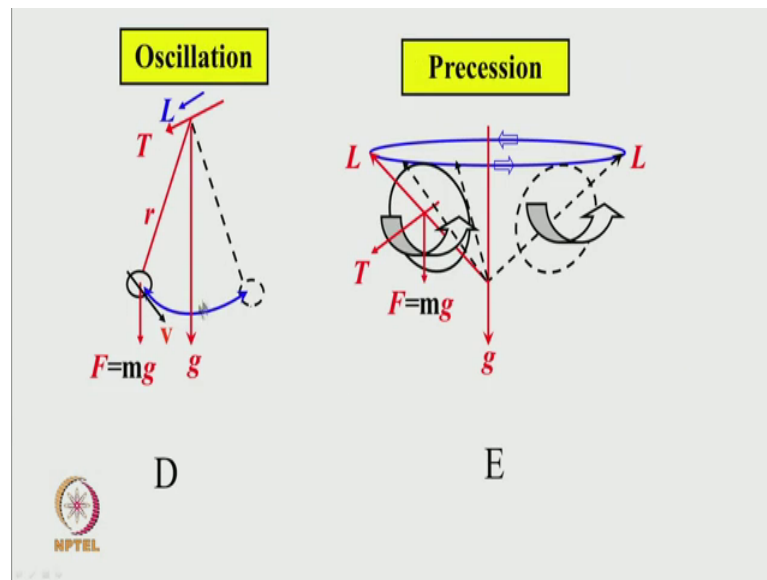


This is the bar magnet in a magnetic field it undergoes the oscillation we call this motion oscillation.

Then we also saw that if the magnetic moment arises from its angular momentum then it correlate the magnetic moment M minus angular momentum vector times the Bohr magneton in case of electron. Specifically we related this orbital angular momentum with the magnetic momentum that should be kept in mind. And why does it undergo this to and fro motion because it experience a torque, torque is equal to vector product of the magnetic moment and the magnetic field.

Now, if a magnetic moment which arises from its angular momentum then what is it going to happen. We will, at that it will not undergoes oscillation it will undergo a special kind of motion what do we call precession motion precession. Now what is precession? All of you must have noticed that one you play a top and it is rotating at high speed you will notice that this axis of its rotation also keeps moving. So, that type of motion is called precession. Let us try to understand little more detail what it is.

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Here this is a simple pendulum, this if you leave it from here it undergoes oscillatory motion. Now, here at this point the gravitational force mg pointing downwards. Now, this is the distance r from where it is hung. So, you see that this r times force produces a torque. So, this torque is trying to rotate this body around it the same time when it comes to the equilibrium precession because of its inertia it continues to move in the other direction then it goes back here. So, this also has an angular momentum which is causing it to move this way around this point here. So, I can therefore, see that a torque is applied here which is changing its angular momentum.

What is the direction of this torque? That is here if you multiply vector ally r cross F this will be the direction that is it will point out of the screen. Now, what is the direction of angular momentum? That will be r cross with the linear momentum the v is in this direction. So, $m v$ will be the momentum pointing direction. So, that also has the same direction L as the direction torque. So, for a pendulum the torque and the L the angular momentum they point in the same direction. This is not the same when top is spinning around its axis, what is the difference. To understand that let us look at this picture.

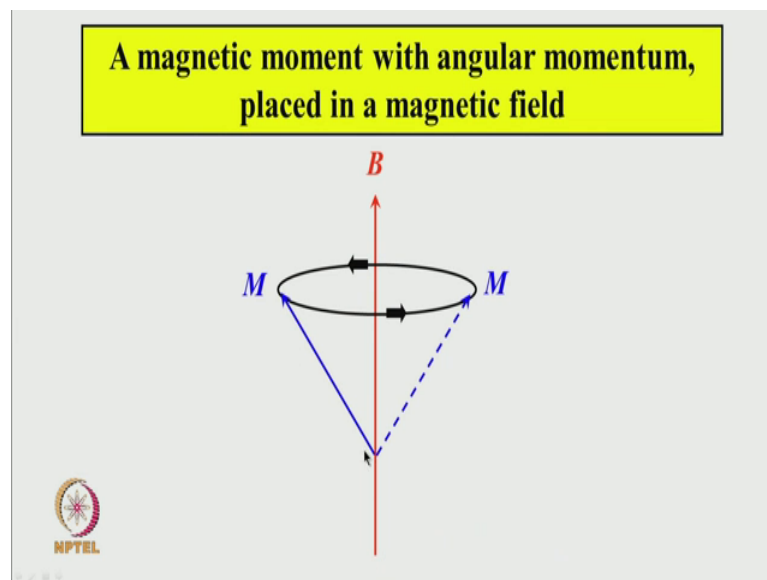
The spherical ball is sort of simplified version of a top and its spinning around its axis given by this vector L which is also the direction of the angular momentum. So, this is the direction of its rotation. Now, the earth's gravitational field acting on it the force mg trying to bring it down. So, the direction of the torque is essentially same as that which is

the direction perpendicular to the plane, but the angular momentum the way it is shown here and the torque now are perpendicular to each other.

So, angular momentum is in this direction torque is in this direction. So, that way because the torque is acting in the perpendicular direction it cannot change its magnitude all it can do is change its direction. So, this red vector L now tries to move away in a perpendicular direction. So, then it comes somewhere here, but in every instant of time the torque acts always perpendicular to that. So, it will be somewhere here then here then there then here. So, effectively that causes the direction of this angular momentum vector follow this cone and that is the precession motion and that is the type of motion we see when the top is spinning, so this axis starts moving. So, exactly similar thing happens in case of magnetic moment kept in a magnetic field when the magnetic moment is arising from its angular momentum here.

So, I have said that the torque is given by this expression this perpendicular to both M and B .

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So, M is in this direction B is in this direction. So, the torque will be acting perpendicular to the M and B that is essential here and L will be the direction which is vertically up. So, M will therefore, undergo exactly similar precession motion the axis of M will follow this cone. So, in the (Refer Time: 07:38) moment which arises from an orbital motion or

which is associated with the angular momentum will undergo a precession motion in a magnetic field. So, this is the torque which is a vector product of $\vec{M}$ and $\vec{B}$.

Can we calculate the frequency of this precession that is the motion that this $\vec{M}$ is undergoing what is the frequency of this motion and how is it related to the interested in the magnetic $\vec{B}$.

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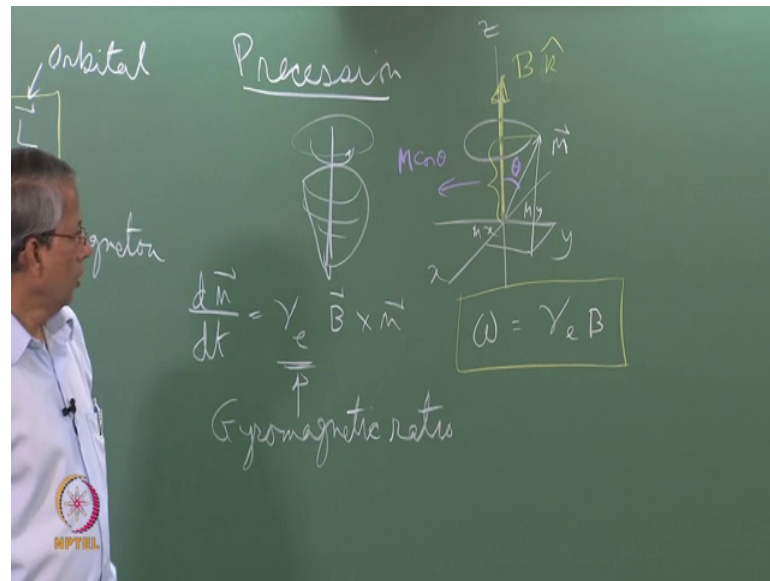
Precession

$$\begin{aligned} \vec{l} &= \hbar \vec{L} & \frac{d\vec{L}}{dt} &= -\left(\frac{\beta_e}{\hbar}\right) \vec{L} \times \vec{B} \\ \frac{d\vec{l}}{dt} &= \vec{T} = \vec{M} \times \vec{B} & \frac{d\vec{M}}{dt} &= -\left(\frac{\beta_e}{\hbar}\right) \vec{M} \times \vec{B} = \left(\frac{\beta_e}{\hbar}\right) \vec{B} \times \vec{M} \\ \hbar \frac{d\vec{L}}{dt} &= \vec{M} \times \vec{B} & \gamma_e &\equiv \frac{\beta_e}{\hbar} \quad (\text{Gyromagnetic ratio}) \\ \vec{M} &= -\beta_e \vec{L} & \frac{d\vec{M}}{dt} &= \gamma_e \vec{B} \times \vec{M} \end{aligned}$$


This is not very difficult to evaluate, we have seen earlier that this angular momentum small $\vec{L}$ vector is measured in units of plus constants of 2π and $\vec{L}$ is the a dimensional quantity. The torque is nothing, but rate of change of angular momentum $d\vec{l}$ by dt is equal to $\vec{M} \times \vec{B}$. Then using this relation small $\vec{l}$ and this capital $\vec{L}$ I can write this, but we also seen in our elevation that magnetic moment and $\vec{L}$ are related in this way, so I can use this and put it here that gives me the rate of change of angular momentum which happens to be now $\vec{L} \times \vec{B}$ this gives the precession of the angular momentum vector in the magnetic field.

Same way now $\vec{L}$ can be replaced by $\vec{M}$ in this fashion using the same a relationship and that gives me the $d\vec{M}$ by dt is equal to some constant here and you see that that the minus $\vec{M}$ can be removed by changing the order of multiplication. So, if we define a constant β_e by $\hbar$ cross is γ_e then this relationship becomes $d\vec{M}$ by dt is equal to $\gamma_e \vec{B} \times \vec{M}$ ok.

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So, this is the equation of motion if you like to call it. This e stands for electron and we call this gyromagnetic ratio. Let us try to solve this equation of motion and then see if we can find out the frequency of the precession.

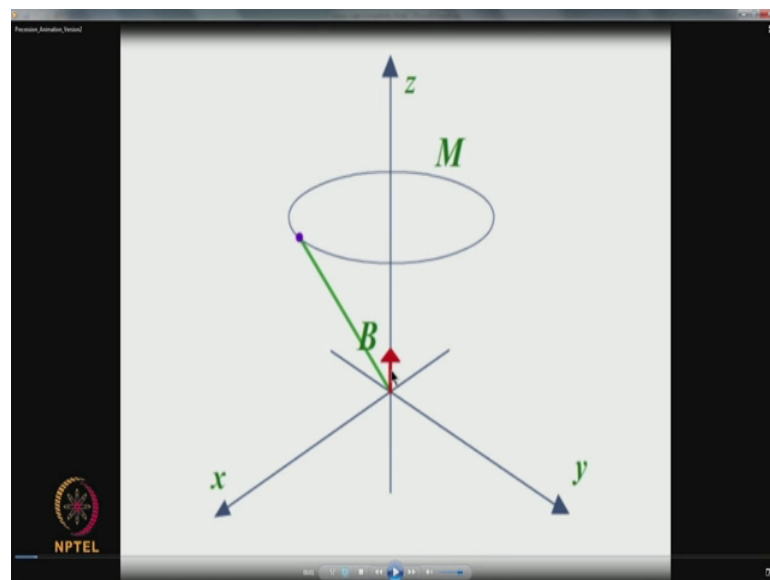
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$$\begin{aligned} \frac{d\vec{M}}{dt} &= \gamma_e \vec{B} \times \vec{M} & M_z &= \text{constant} = M \cos \theta \\ \vec{B} &= \hat{k} B, \text{ as the field is along the } +z \text{ direction} & M_x &= (M \sin \theta) \cos(\gamma_e B t) \\ & & M_y &= -(M \sin \theta) \sin(\gamma_e B t) \\ \frac{dM_x}{dt} &= \gamma_e B M_y & & \\ \frac{dM_y}{dt} &= -\gamma_e B M_x & \text{Angular frequency of precession} &= \gamma_e B \\ \frac{dM_z}{dt} &= 0 & & \end{aligned}$$

We first define the direction of the magnetic field. So, let us say the magnetic field is applied along this z direction this is my B. So, it will be B times the vector if you call it a unit vector k and the magnetic moment is in this direction its precessing in this fashion.

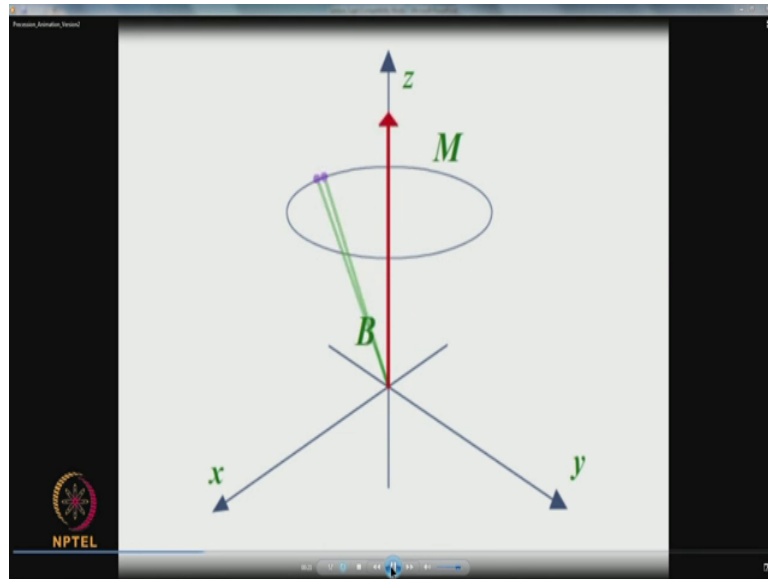
So, in that case if we expand this vector product I get equations of this kind $\frac{dM_x}{dt} = \gamma B M_y$; $\frac{dM_y}{dt} = -\gamma B M_x$ $\frac{dM_z}{dt} = 0$. So, here the last equation is very simple it means that M_z is constant. So, M_z is constant that is this component this component is constant. So, this is the angle that this M makes with respect to z is then this is the component which is $M \cos \theta$ that this magnetic value remains constant on the other hand x and y component it then this is the M_x this is M_y and you see as it moves the component changes its magnitude those are given by these two equations now this is very easy to solve and solution is this M_x is $M \sin \theta \cos \gamma B t$ M_y is $-M \sin \theta \sin \gamma B t$. So, this equation shows that angular frequency of precession is given by γB . So, this shows that frequency of precession is proportional to the magnetic field.

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So, to show that I have made a small animation here B is the magnetic field and this is the magnetic moment vector the green arrow. Now, I will run it is precessing magnetic moment vector is precessing and we are increasing the magnetic field slowly the red vector is increasing and if you notice it is the frequency of precession is increasing gradually.

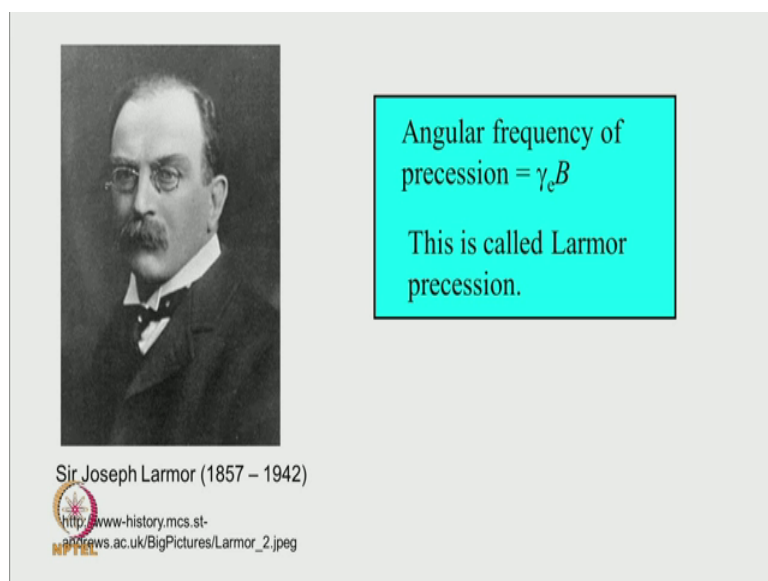
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So, B is very high its precession is very fast and now we are reducing the magnetic field precession is going down again. So, this equation which relates the precessional frequency to the magnetic field. This frequency of precession is called Larmor frequency.

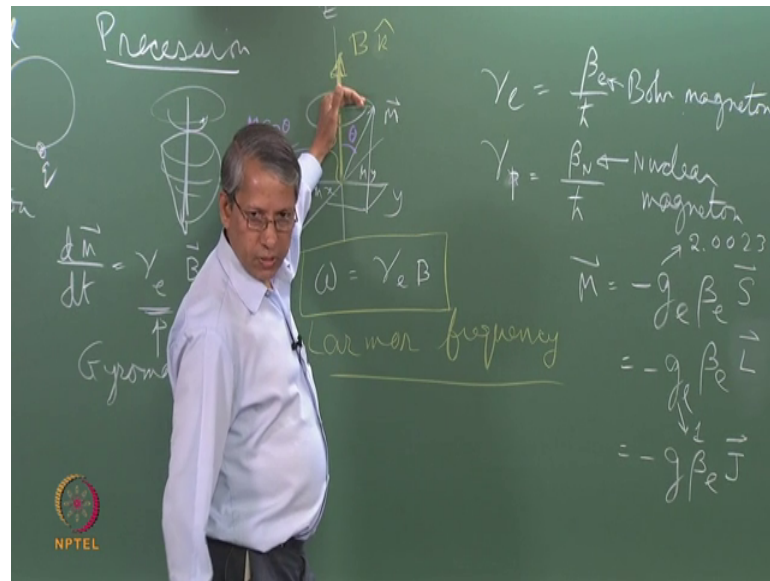
So, whenever the magnetic moment has an angular momentum and only it is kept in the magnetic field it is always going to undergo a precession motion of this kind.

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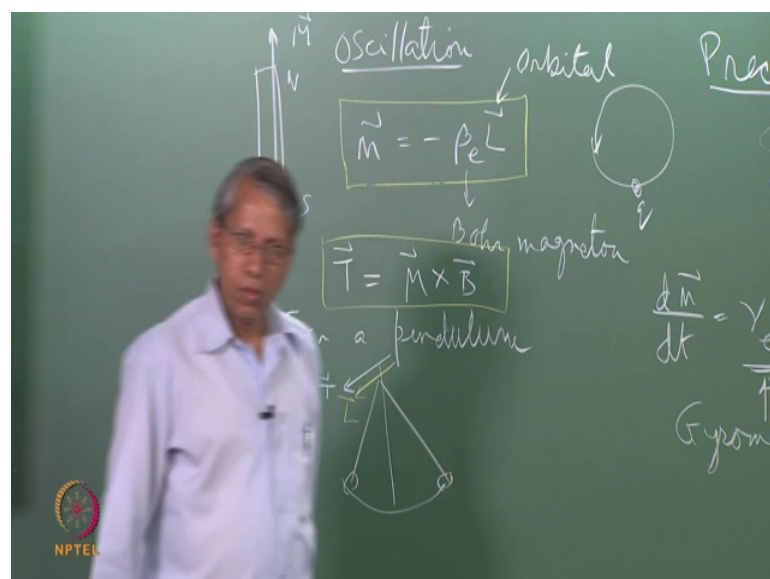
This was given by this person Larmor whose picture is shown here.

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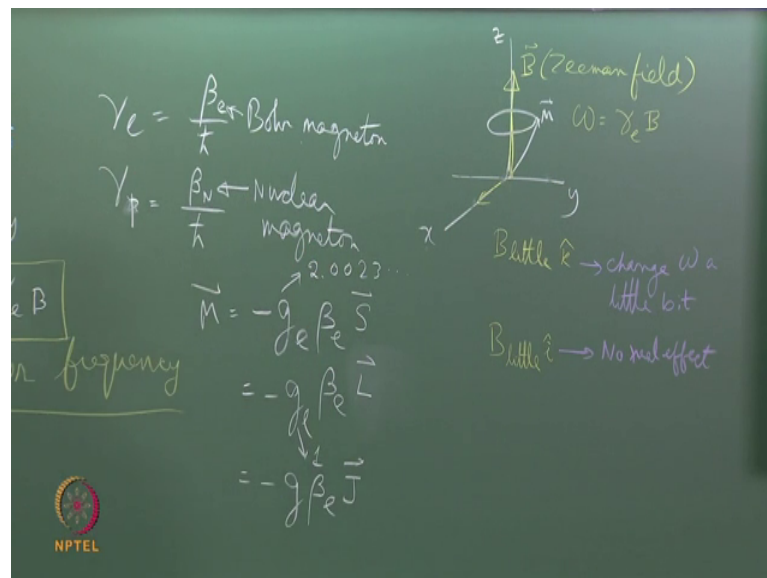
If we go back to our derivation we will notice that we have defined gamma e to B this is the Bohr momentum by h cross. So, exactly similar derivation can show that for nuclear magnetic moment relationship will be its gamma for nucleus, so proton example will be this will be nuclear magnetron by h cross. This is once again nuclear magnetron and this is Bohr magnetron a little more clarification is said here. So, we have arrived at this equation where the moment is related to the orbital motion, we go one step back we actually derived it by using a sort of circular loop of wire where some charges q was moving this is certainly orbital motion and from that we arrived at this one.

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See in general the angular momentum can come from orbital motion spin motion or combination of the two. So, in general this relationship is modified to write g of electron Bohr magneton times let us say S for spin angular momentum, this will be equal to similarly g of or this is for orbital angular momentum g value for orbital motion, g value for spin motion and it. So, happened that this is actually equal to 1, this is equal to 2.0023 something for free electron, but if it is combination of electron spin angular momentum and electron orbital angular momentum then this becomes some general g value of something like J let us say, J is the total angular momentum this will cause for g value. So, we have seen that the magnetic moment arising from an angular momentum will undergo precession motion.

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What happens now? If we apply another magnetic field starts from here is x , y and z and the let us say the magnetic field pointing in this direction which is B let me call this now a very huge magnetic field let us call which is Zeeman field and this magnetic field is pointing its direction is undergoing precession of this kind.

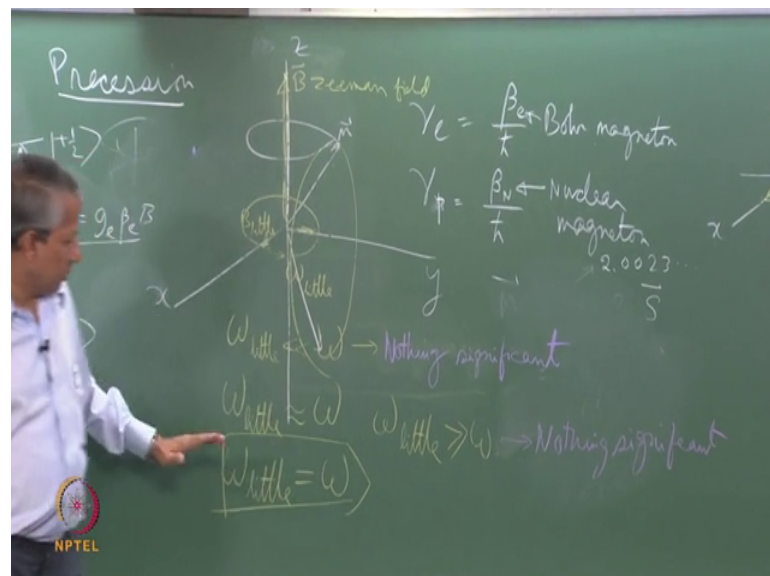
Suppose I bring a small magnetic field and try to see what happens to this precession motion, if I apply that small field let us call it may be I will call it B_{little} small little field and apply along the z direction. So, we will apply along direction k what will happen? This huge magnetic field we already have and I am applying just small amount of field there, what will this magnetic moments see it will find that the field has changed just

little bit. So, what about the precession or frequency that is had given by the relationship that is let us call it that omega into gamma e B this small thing applied here will just added to this one. So, this will undergo just in little bit of change in frequency. So, nothing excide is going to happen therefore. Change omega a little bit.

Now I apply its B little in the x direction here let us I will call it i, then what happens? You know keep in mind that this is really very very small compared to this one this could be our one tesla magnetic field ten thousand guans this could be hardly few milli guans or mega guans little bit here though I drawn it in this scale, but this is tiny compared to this one. So, then what happens or what we expect to happen? This magnetic own is really just see at a very high frequency this fellow is sitting here. So, it will only see that presence of these only for very time because it is precessing very fast. So, effectively therefore, this is not going to disturb this at all, means no real effect because it is going on and on very very fast this will be little bit is there not going to do anything.

Now, let us change our track little more, suppose now this time instead of allowing it to stay static in the x direction I now allow it to move in this direction in the x y plane. So, make it little bit understandable let us clean up the figure and draw it better.

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Now, by this small field B little now starts here now T also moves in this x y plane that is sort of angular frequency let us called it omega little that are imagines scenario this is going on this way very fast rate now this fellow is slowly rotating in this direction then

what will happen. Again pretty much very little because as it is rotating so fast it finds once while this is near it that time it is not per tap anything again it goes ahead it and keeps precessing. So, this is so when ω_{small} is very very small compared to ω_{large} nothing I think you see nothing is going to happen.

Now, let us gradually increase the frequency of its rotation around xy plane then imagine the as if this frequency of the small field comes closer and closer to this precession frequency here it is ω_{small} is becoming comparable to ω_{large} here, then what happens now this will find that even though it is precessing very fast this fellow is also following it almost at the same rate.

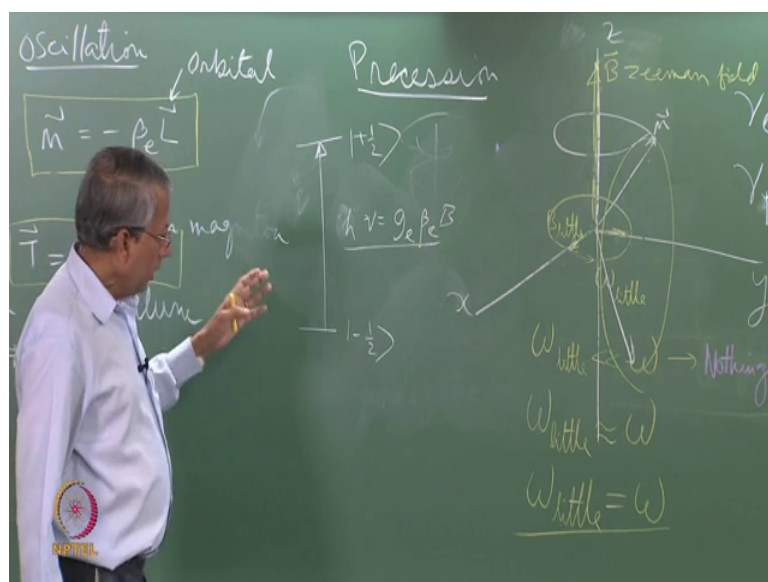
So, this is sticking around telling it all the time almost of the time because they are not exactly same the effect may not very seen very much, but this finds that another one just following me almost all the time. So, again this the torsion of torque will be applicable. So, it finds another magnetic field is little manipulates here, it will also try to precise around it. So, it will try to therefore, bend from this vector S going to come out of that, not the extreme case when exactly equal to ω_{large} then whatever it is this is just near that exactly the same face there may be as it is rotating this is also rotate the same frequency therefore, there always a constant phase relationship between the two that is in the change.

So, it find that is in the vicinity there is a small vet fixed magnetic field is present there. So, this will also try to precise around this small magnetic field. Now what happens in the process thereby once it starts precise let us say here this has to precise in this fashion. So, mission is complicated, but not very difficult to visualize this complicated motion consists of a very very high frequency precession on this, but a low frequency around this one if that happens now this has to come out of this then you go to the next, that is this vector now point in this direction now. You see the magnetic moment is changed this plus z exist to minus z from the low energy to high energy state it is observe the energy and goes to higher energy state which is now if you relate it to the magnetic relevant transition. So, just change its spin from plus half to minus half if it is for proton or electron change from minus half to plus half this spin has flit.

So, this is going to happen moment this convention satisfied it does not matter how small this magnetic field is compared to this one this could be very high, but when this two

have the exactly same frequency relationship even a very very small magnetic field you can completely change the orientation of the magnetic moment and it can cause the it to change from one direction to the other direction which is nothing, but the change of spin flip of transitions in magnetic resonance.

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In the previous slide it is for the earlier that the minus half spin trace given by this plus half spin high energy. So, here the low energy is here and high energy is here. So, moment the small oscillating magnetic field is applied in the xy plane this can cause transition from here to here it is an important requirement is this now, therefore, that this oscillating magnetic field has to be applied in a direction which is perpendicular to the external magnetic field.

We saw that when it is parallel nothing really happens also the frequency has to be exactly equal to the frequency of its Larmor frequency precessional frequency. So, that is the resonance condition that need to be satisfied not just the energy gap here, that is $\hbar \omega$ this is the relationship we said earlier, but we find a little more inside to what were the experiment has to be done that not only matching of this energy gap, but the direction of application of the external magnetic field has to be perpendicular to the direction of the external magnetic field.

If we keep increasing the frequency of this ω a little more than this ω then what happens? Then again this magnetic moment vector will go out of sync with this ω

which is little moving in the xy plane see if you keep on increasing this frequency of this omega little higher and higher this will go even further out of sync. So, this will rotate in the xy plane at a very very rapid rate compared to this one. So, this will find therefore that most of the time they nothing near it. So, there will be again no precession of this around this omega little therefore, there is going to be no effect again. So, you see that therefore that this condition that when this two frequencies are exactly same then even in a small magnetic field can completely turned out magnetization from this direction to this direction and that is precisely the resilience condition.

So, with this we come to an end of this discussion.