NMR spectroscopy for Structural Biology NS
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Lecture: 02
NMR Basic Concepts - II

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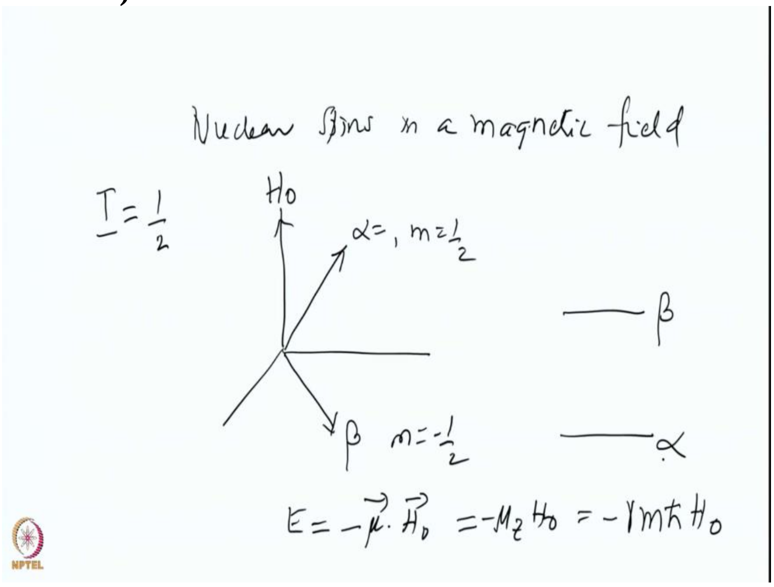

So, we were discussing about the nuclear spins in a magnetic field and let me just briefly recap that what we saw nuclear spins in a magnetic field. Consider a spin with I = ½ we said it has 2 possible orientations in space and if I want to represent them like this. So, one possible orientation like this other one is in like this and this is the orientation with we call it as α state and this is the β state.

And here m = ½ and here m = - ½ the magnetic field is applied along the Z axis and therefore the α state has a lower energy and the β state has a higher energy. So, this the different orientations have different energy values and that energy is given by $E = -\vec{\mu}.\overrightarrow{H_0}$
where μ is the magnetic moment H_0 is applied magnetic field in terms of; so this can be called as $E = -\mu_z H_0 = -\gamma m\hbar H_0$
So, therefore obviously when α = ½, m =½ then the α state has a lower energy compared to the β state and there is a population difference between these 2.

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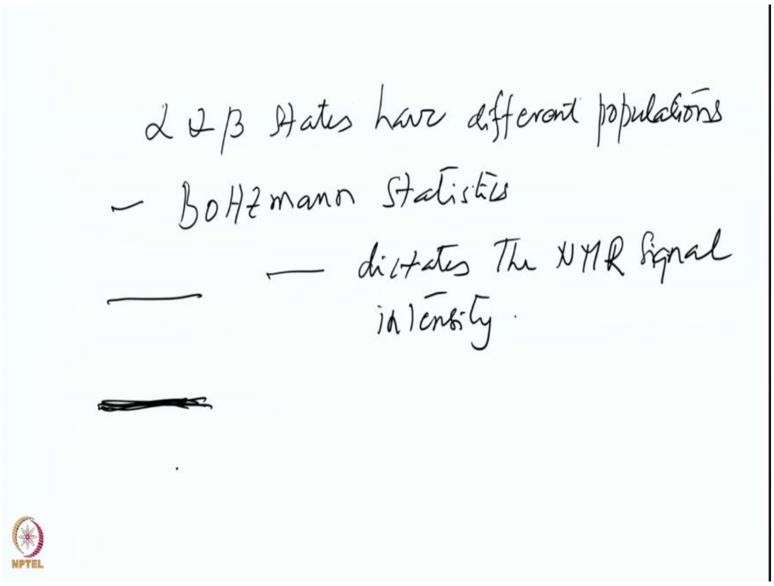

And that is population difference the α and the βstates have different populations which are dictated by Boltzmann statistics. So, you want to represent it like this. So, this is α state there are more spins here and there is this is the β state there are less spins here. So, this population difference is responsible for the NMR signal intensity. So, this dictates the NMR signal intensity how it will? It will see that later.

So, now let us look at this in a different way and this is what actually Felix this was the approach which Purcell had taken this is a quantum mechanical description of the interaction of the spins with the magnetic field Felix Bloch had looked at it in a different way. And he said you take analogy with the magnetic moments in general when you apply a magnetic field to a magnetic moment what happens?

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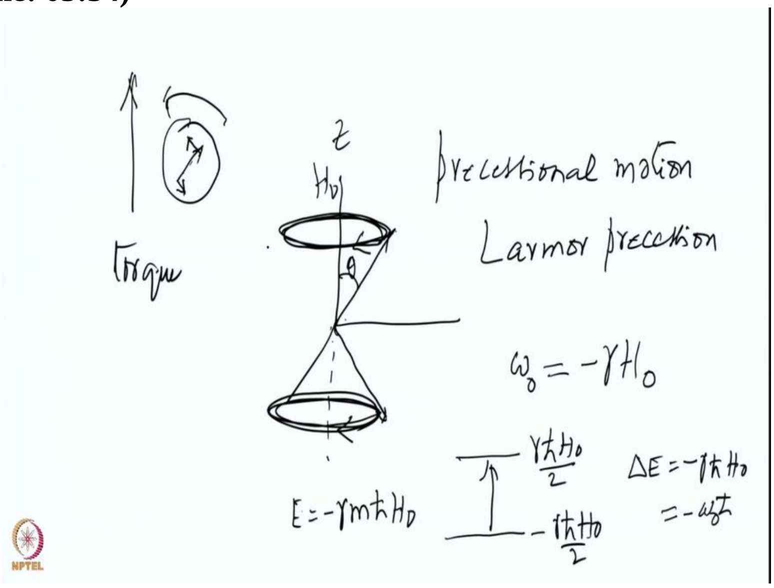

Suppose for example I have a compost needle a compass needle is a tiny magnet. So, suppose I have a compass needle like this which has orientation if you put it in a magnetic field what happens to the compass needle. So, everybody knows about this. So, it will reorient itself move it like that and orient itself with respect to the magnetic field and this is used to determine the directions you know as north south directions because it orients itself with respect to the earth's magnetic field.

So, the similar analogy is possible with this analogy we can describe about the nuclear magnetic moments as well however only to a certain extent and why is that so? Because this is the bar magnet this is the large magnet it can orient itself this is the classical description it can orient itself aligned itself parallel or into the anti-parallel to the earth's magnetic field. In the case of the nuclear spins however that kind of a motion is not possible there is a definite orientation of spins as I mentioned to you.

They are either here or here we cannot change this angle if I call it theta we cannot change this angle. So, now what will happen then why does the composition needle move when you apply magnetic field because it experiences what is called as a torque. The north pole and the south pole of the tiny magnet will experience forces like this and since there is a distance between the 2 north and the south pole it has a certain length this results in the motion of the of the compose needle in a particular direction.

Now here also of course there will be a torque. Torque will be present here but it cannot orient itself with respect to the Z axis like this. It cannot become exactly parallel or anti-parallel to the field what does it do? In such a case the classical description is this spin will start exhibiting a kind of a motion that it will keep going round like this. And similarly here this also will keep going like that.

And of course the origin of this lies in quantum mechanics we will not go into that detail but the classical description is that this kind of motion is called as precessional motion and it goes by the name Larmor precession. Larmor is the name of the scientist who actually described this quite early. And therefore this motion is called as the Larmor motion and this goes in a particular direction it goes in this clockwise direction and the frequency of this motion if I want to write it as ω_0.

This is related to the magnetic field by this equation H naught is the strength of the magnetic field and gamma is your magnetogyric ratio. So, now is there a parallel between this and the energy level diagram what we had. Energy level diagram also showed let me draw that here energy level diagram we had this energy here $E = -\gamma m\hbar H_0$
So, for this one this is $m = \frac{1}{2}, \frac{-\gamma\hbar\, H_0}{2}$

Because m = +½ here and m = - ½ here and what is the energy difference between these 2. So, this is minus energy difference $\Delta E = -\gamma\hbar H_0$ delta E is equal to minus gamma h cross H naught. You see so this is very similar to what we have here ω_0 is the frequency and therefore this is $\Delta E = -\omega_0\, \hbar$. So, therefore the classical description of Larmor precision and the quantum mechanical description of energy level diagrams are identical.

The energy separation between the 2 levels is it if in terms of the frequency it corresponds to the Larmor precessional frequency. So, this is a very important concept with regard to the Larmor precessional motion and we are going to use this quite significantly extensively in the subsequent description of resonance absorption of energy and so on. When these arms are executing the motion all the spins go in the same direction.

Whether it is alpha state or the beta state they both go in the clockwise direction and the minus sign indicates that the minus sign means that there is a clockwise description conventionally the anti-clockwise motion is considered positive and the clockwise description is considered as negative. So, now the Boltzmann statistics I already described. Now there is a population distribution as I said.

Now for a way to sit on the; spin and look at the magnetic field. So, what happens the nuclei will not see the field at all and that is what is called as going into the rotating frame of reference.

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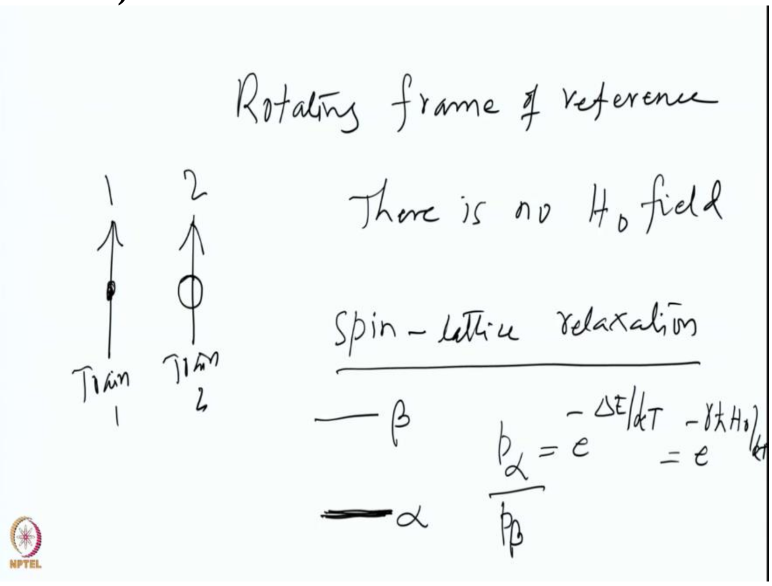

So, if I go into the rotating frame of reference means you sit on the RF and say sit on the spin and look at the magnetic field if you sit on that and then look at the magnetic field it looks as if you are not rotating right. So, it is for the observer the motional frequency is with respect to the observer. So, if the observer is sitting on that thing and look at this then of course it is not moving right. So, that is called as the rotating frame of reference.

A classical analogy for this is that suppose there are 2 persons sitting on 2 different trains there is one train going here train 1 train 2 both are going in the same direction. And if they are going with the same speed if you are going with the same speed then if a person who is sitting on this looks at the person who is sitting on this they feel as if they are not moving . So, that is called as the change in the frame of reference.

So, if they are going with the same speed in the same direction there is as good as stationary if it is stationary which means that they are not moving. In the same manner when you go into the rotating frame of reference there is no H_0 field because it is not moving. In the rotating frame of reference we sit on the spin and look at the magnetic field if the is there any magnetic field perturbation then you do not see the field because it is stationary if the analogy is here.

So, if you are one train the other train if both 2 persons are sitting on the 2 different trains and if the both the trains are going in the same direction. So, this is train 1 and this is train 2 if they are going in the same direction with the same speed then the 2 persons will feel that they are not moving with respect to each other if of course there are different frequencies different speeds then they will see the difference and this becomes an important concept when you are discussing about the absorption of energy and so on.

Let us talk about now an important concept here at this point in time and that is called as the spin lattice relaxation. What is it all about? We said that for the 2 orientations we have the one state here α other state is the β there are certain populations here and this said the population difference will depend upon Boltzmann statistics Boltzmann statistics means that the probability of the spin being in the $\alpha = p_\alpha = -\frac{\Delta E}{kT}$

And similarly $\frac{p_\alpha}{p_\beta}$ this is the ratio of the populations is given by

$$\frac{p_\alpha}{p_\beta} = e^{\frac{-\Delta E}{kT}}$$

ΔE is the energy separation between them and that obviously will depend upon the magnetic field and this is

$$\frac{p_\alpha}{p_\beta} = e^{\frac{-\Delta E}{kT}} = e^{-\gamma\hbar H_0/kT}$$

T is the temperature.

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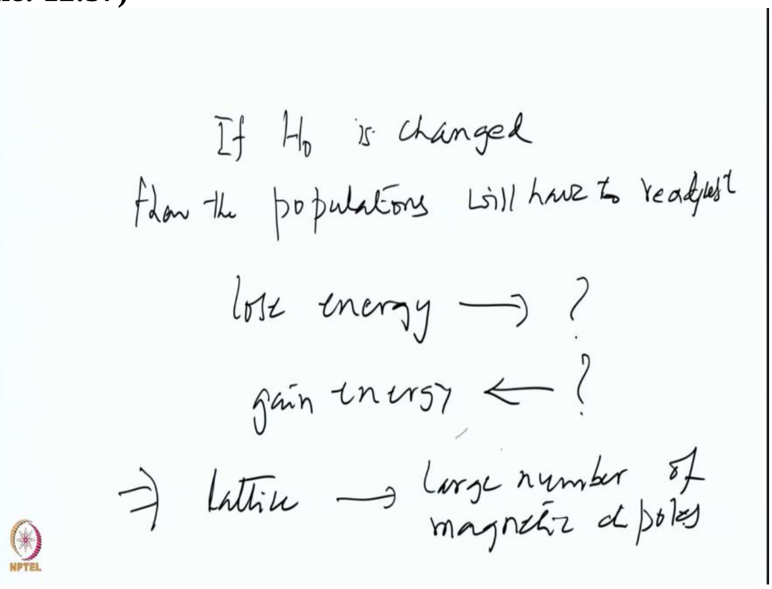

So, if I change the field if H_0 is changed if H_0 is changed then the populations will have to readjust. So, that means that there have to be transitions from one state to the other state forward transition and backward transitions. If both ways it has to happen what brings about these transitions and if a particular spin has to lose energy where does the energy go. So, this means lose energy and where does it go if it has to gain energy if a spin has to gain energy where does it come from.

So, this is the question what is the source therefore here there is a concept which is called as the lattice. So, this brings us to a concept called as lattice which is everything else which other than your actual spin system. So, it is a large number of magnetic dipoles which are present in your system that is this may be solvent molecules or maybe other things. So, they will all have magnetic dipoles and this constitutes what is called as the sink.

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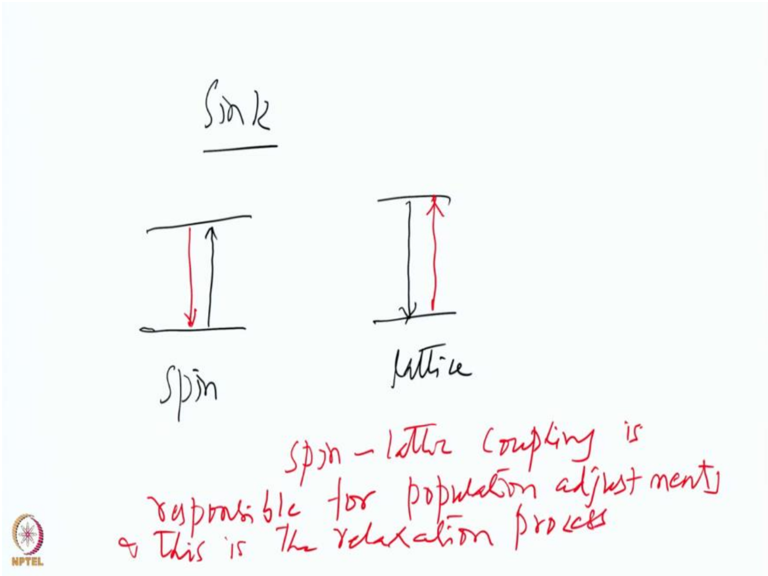

So, I have here the spin system here and here it is the lattice. Lattice is all kinds of energy levels because it has various kinds of magnetic moments and various kinds of interactions possible therefore the lattice is there which is a parallel with respect to the spin system. So, this is your spin system and this is the lattice. So, if absorption has to have to happen transition like this and it has to have a transition like this here.

So, energy required will be gained by this and if a loss has to happen if it has to lose energy where does the energy go it has to go here the lattice will take this energy. So, therefore it is a kind of a sink or the resource. So, therefore lattice and spin are constantly interaction interacting. Therefore this is spin lattice coupling is responsible for population adjustments and we call this as the relaxation process and this is the.

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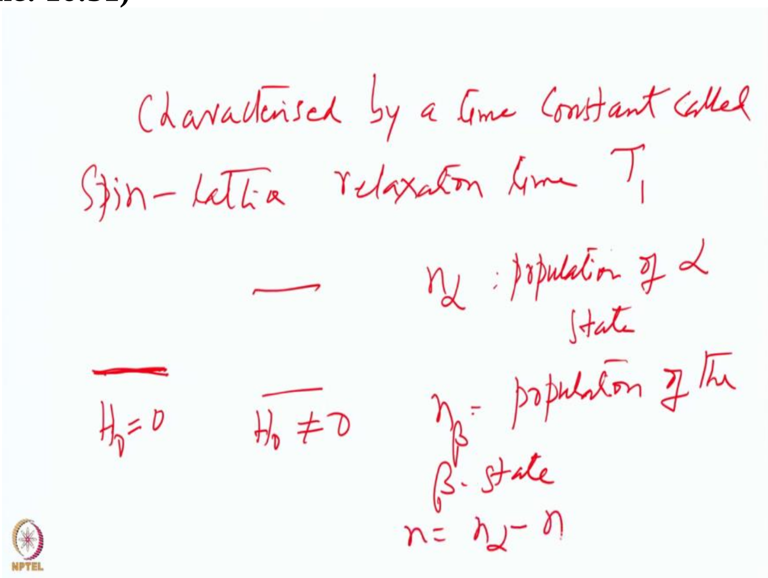

So is characterized by a time constant called spin lattice relaxation time and it is represented as T_1. The same thing is responsible for the adjustments of the populations starting from 0. So, in the absence of the magnetic field all your spins were here in one particular state right. So, here $H_0 = 0$ and when H_0 is non-zero $H_0 \neq 0$ then we generated 2 states and the readjustment of the populations took place.

So, therefore how do I characterize this without going to the theoretical details of this let me just give you the how does the population difference change. Suppose n_α is the population of the α state and n_β beta is the population of the β state. And if I define $n = n_\alpha - n_\beta$

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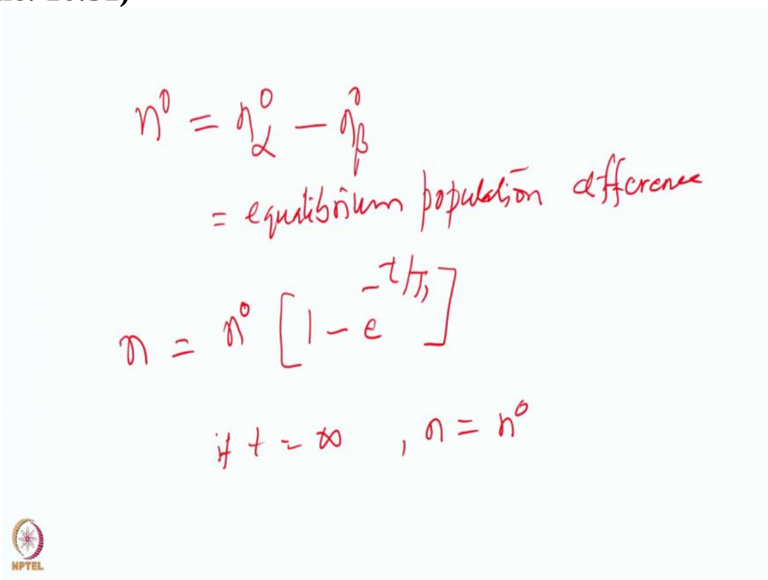

If $n^0 = n = n^0_\alpha - n^0_\beta$ this is the equilibrium population difference. Then we can write an equation for how the system will approach the equilibrium as in this manner

$$n = n^0 \, [1 - e^{-t/T_1}]$$

So, therefore you see T_1 is a time which determines how fast the system will reach. So, n naught is the equilibrium population difference so the rate at which it will approach the equilibrium population difference is given by this equation.

Now obviously if $t = \infty$, $n^0 = n$. So, depending upon the value of T_1 it will approach the equilibrium value slowly or rapidly and this becomes an important factor as we will see later on. So, now we will see how we do an NMR experiment. So, this is so far as the spin systems are concerned what happens to the spin system in the presence of the magnetic field.

How there is we considered with spin is I = ½ but the same things will apply for other spin systems as well I = 1 or whatever spin systems we consider the same principles will be valid. So, now we consider the NMR experiment that is the resonance absorption of energy.

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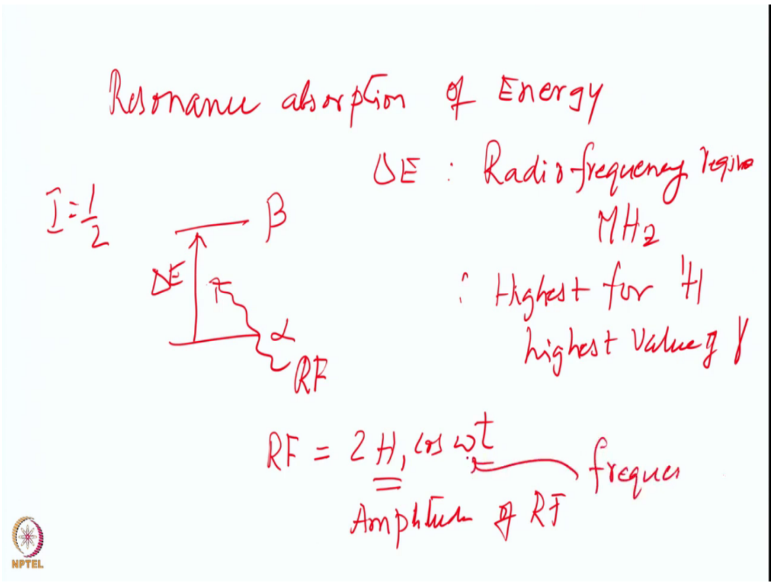

What is resonance absorption of energy we said we have the population difference resonance absorption of energy. We can look at it in 2 different ways will easier one is to look at it in the quantum mechanical picture again we will consider I = ½. First we have the 2 states and this energy difference is equal to ΔE and this we say ΔE is in the in the radio frequency regime that means in the megahertz. So, it may be 100 megahertz 200 megahertz and once you go into the gigahertz it will go into the microwave regime.

So, therefore this energy difference is in the radio frequency regime why is it so? Because it depends upon the γ, the γ and the H_0 , γH_0 is the ω_0 that is the frequency of precision and that will turn out to be for the range of values of gamma what we have it will be in the radio frequency region. And this is the highest for proton for proton because it has the highest value of γ.

So, typically when we always say we have 100 megahertz spectrometer 200 mega spectrometer we always refer to the proton absorption frequency. So, what does that mean? Now if apply a RF here radio frequency which corresponds to this energy difference whose frequency corresponds to this energy difference then absorption of energy will take place by the spins to go from the alpha state to the beta state.

And the RF is what RF = 2 H_1 cos ωt and this is the amplitude of RF radio frequency and this is the frequency. So, if this energy RF energy matches this energy separation ΔE then there will be maximum absorption.

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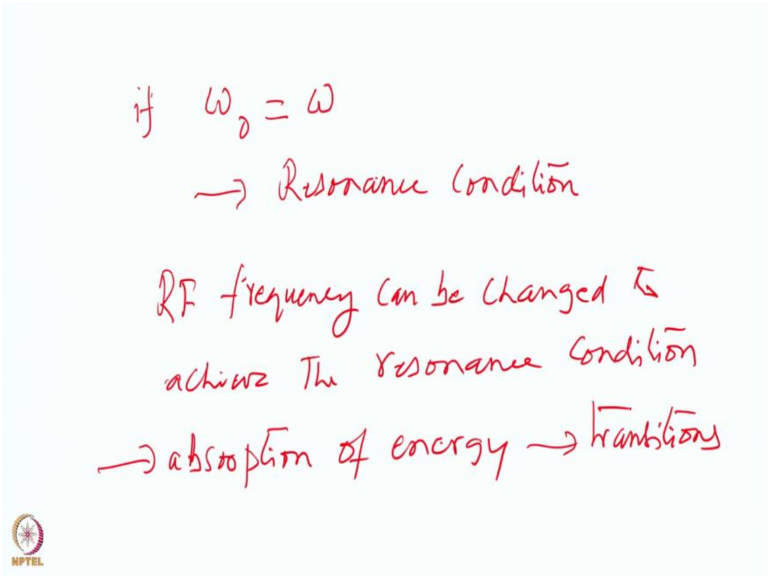

If $\omega = \omega_0$, ω_0 was what that was the energy correspond frequency corresponding to the energy difference between the 2 states and omega is the RF frequency if $\omega = \omega_0$ this is called as the resonance condition. So, this is nuclear magnetic resonance so you have the RF which has a frequency which of course you can change this frequency this is in your electronics control.

Once you have a magnetic field H_0 magnetic field the precessional frequency is determined by the magnetogyric ratio and the H_0 that we cannot change and the obviously you do not know where this one is. So, therefore you have the RF which you can keep changing RF frequency can be changed can be changed to achieve the resonance condition. When that happens this leads to absorption of energy in the quantum mechanical picture because it will cause transitions. Let us also look at this in a classical picture.

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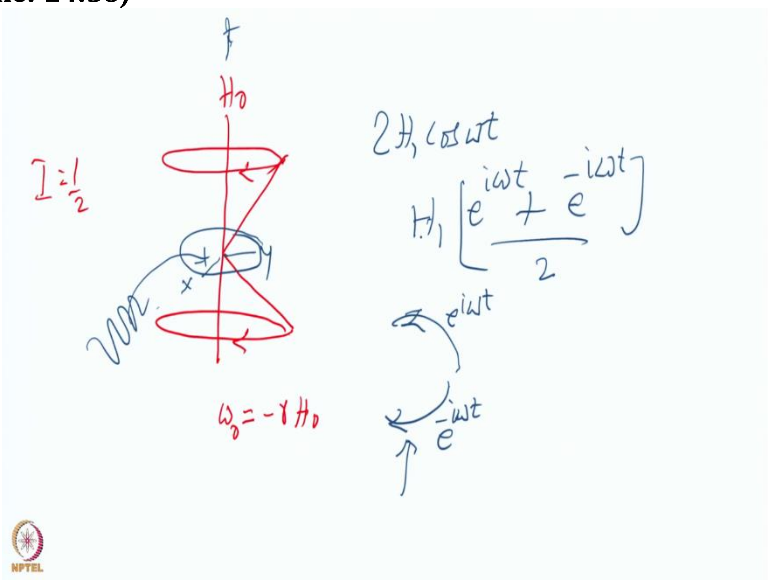

The classical picture again we go back to the singles spin half system I is equal to half. We said in the classical picture these ones are precessing like this these are also precessing like this and this frequency of precision was given by

$$\omega = -\gamma H_0$$

omega is equal to minus gamma H naught and this is H naught. Now this is the transverse plane. I have here the transverse plane this is the Z axis here remember this is the Z axis.

And here I have the x and the y components X and the Y axis here the RF has to be applied in the transverse plane. So, I have up apply here it RF is the radio frequency RF is the radio frequency this is applied is the electromagnetic spectrum right. So, you have applied this. So, I have here 2 H_1 cos ωt. So, I can break this up into 2 components $H_1 \left[\frac{e^{i\omega t} + e^{-i\omega t}}{2}\right]$ this is the expansion of the cosine function.

So, what does this is $e^{i\omega t}$ meaning $e^{i\omega t}$means a rotation along the this axis in the this direction this is $e^{i\omega t}$ and the other one is the rotation in this axis $e^{-i\omega t}$ is the rotation in this direction. Now out of this which one do we consider we consider the e to the -i omega t because it goes in the same sense as your nuclear spins are precessing.

So, this is the one which we can say that because if you consider the $e^{i\omega t}$ it goes in the opposite direction therefore there is no time for the spins to interact with the RF. So, this is remember this H_1 amplitude is the magnetic field. So, this is the magnetic field the magnetic component of the RF which you are looking at the electromagnetic spectrum has both electro electrical component and a magnetic component.

We are talking about the magnetic component because we are talking about nuclear magnetic resonance magnetic interactions therefore we are here the magnetic component of it and interaction will happen with the magnetic component which is the H_1. And therefore if the spins have to interact with H_1 we have to consider the frame in which we are sitting and then how we look at the RF. So, all right so let me let me stop here and we will continue for the next class from here.