Condensed Matter Physics
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Module - 01
Lecture - 24
Magnetic Resonance

In the year 1944, there was a discovery which has had a profound influence on many areas of science and technology, this is the discovery of the phenomenon of magnetic resonance.

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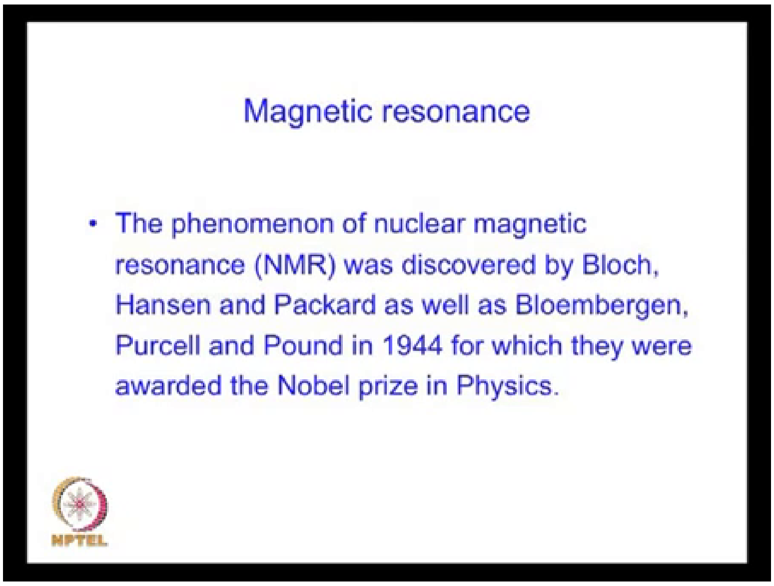

Magnetic resonance

- The phenomenon of nuclear magnetic resonance (NMR) was discovered by Bloch, Hansen and Packard as well as Bloembergen, Purcell and Pound in 1944 for which they were awarded the Nobel prize in Physics.

This will be the topic of our discussion today, the phenomenon of magnetic resonance can take place both in the nuclear spin system as well as in the electron spin system of atoms and molecules. The phenomenon of Nuclear Magnetic Resonance for short it is called NMR was discovered independently by two sets of people in 1944 one was Bloch, Hansen and Packard. The other set of people were Bloembergen, Purcell and Pound both sets were awarded noble prize in physics for this great discovery.

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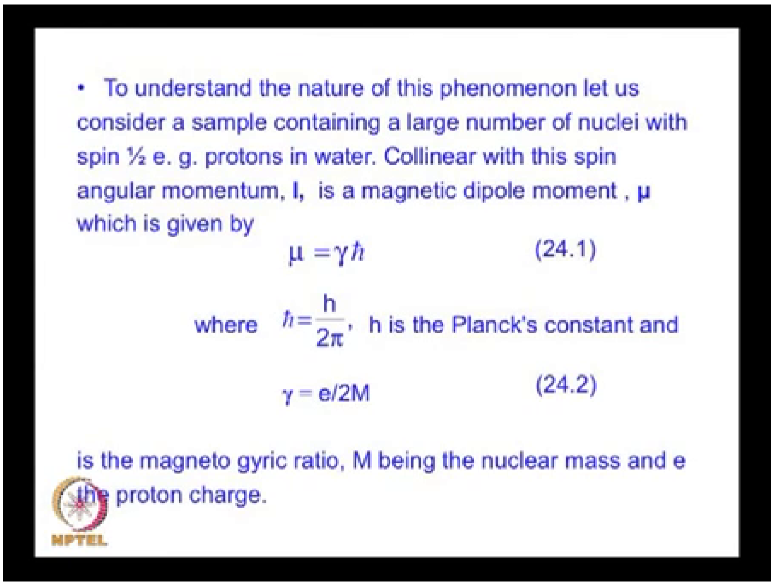

- To understand the nature of this phenomenon let us consider a sample containing a large number of nuclei with spin ½ e. g. protons in water. Collinear with this spin angular momentum, **I**, is a magnetic dipole moment , **μ** which is given by

$$\mu = \gamma \hbar \qquad (24.1)$$

where $\hbar = \frac{h}{2\pi}$, h is the Planck's constant and

$$\gamma = e/2M \qquad (24.2)$$

is the magneto gyric ratio, M being the nuclear mass and e the proton charge.

To understand the nature phenomenon, let us consider a sample containing a large number of nuclei such as protons in water; they have spin half the simplest nuclear spin system. Wherever there is a spin angular momentum there is a magnetic moment which is collinear with this spin angular momentum.

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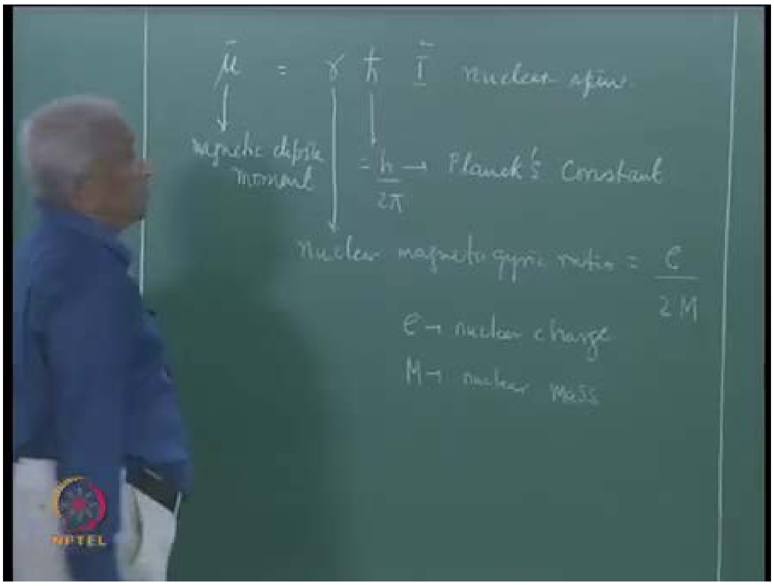

If I is the spin angular momentum, so it is the nuclear spin there is associated with this a magnetic dipolar moment mu, this is the magnetic dipolar moment. And these two are parallel vectors and the relation between them is mu is usually written in this form mu equal to gamma h cross I. Here gamma is the nuclear magneto gyric ratio, previously it used to be called a gyro magnetic ratio, but it is more appropriately called the ratio of the magnetic moment to the gyros scopic angular momentum.

So, it is magneto gyric ratio h cross is h by 2 pi, where h is the Plank’s constant and this nuclear magneto gyric ratio has the value e by 2 M ((Refer Time: 4:00)). Where e is the nuclear charge, which in the case of proton it is just the electronic charge and M is the nuclear mass. So, what we have is the set of protons in water is like an assembly of magnetic dipoles small bar magnets or compass magnets, so you have small dipole magnets which.

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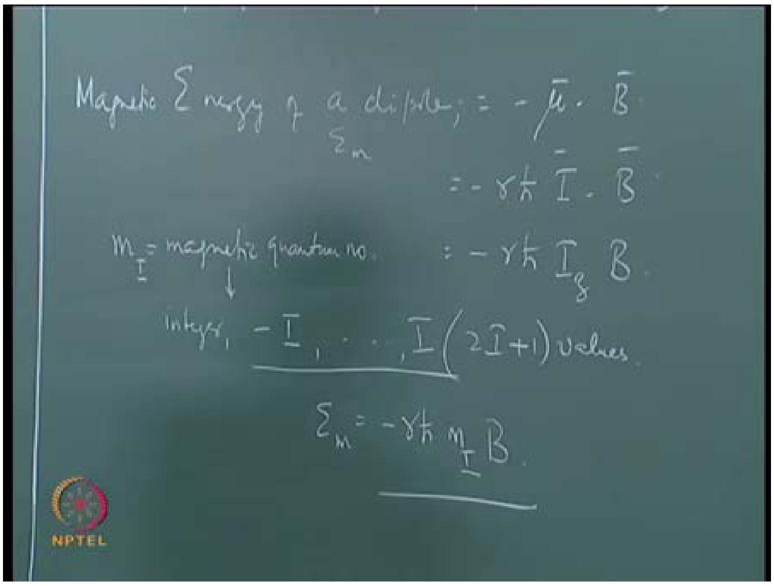

Magnetic Energy of a dipole; E_m $= -\bar{\mu} \cdot \bar{B}$

$= -\gamma\hbar\, \bar{I} \cdot \bar{B}$

$m_{\underline{I}}$ = magnetic quantum no. $: -\gamma\hbar\, I_z B$

$\downarrow$

integer, $\underline{-I, \ldots, I}\,(2I+1)$ values

$\underline{E_m = -\gamma\hbar\, m_{\underline{I}} B}$

To which we apply a uniform static magnetic field of strength B, which is directed along the z axis the effect of this magnetic field is to line up all the magnetic dipoles. As we know for example, if you have a compass needle a mariners compass in the earth’s magnetic field it always tends to line up along the magnetic north south direction this is how mariners used to find direction in sea. So, this is a very well-known matter of common experience, so all the dipoles tend to line up around this z axis and the energy of such a dipole magnetic energy in a static magnetic field is minus mu dot B this is again a well- known result.

So, if we use the value for mu from this, I can write this as minus gamma h cross I dot B and since B is along this z direction. So, this becomes minus gamma h cross I z B where

Iz is the z component of the spin angular momentum and we know that, if m is the m I is the magnetic quantum number. Then we know I z is quantised in units of mI, mI has integral values this in quantum mechanics is a standard well known result that m I is an integer integral half integral values going from minus I to plus I to 2 I plus 1 values. So, because of this, this becomes where m I goes taking this integral values, so corresponding to each value of m I we have a different value of energy and.

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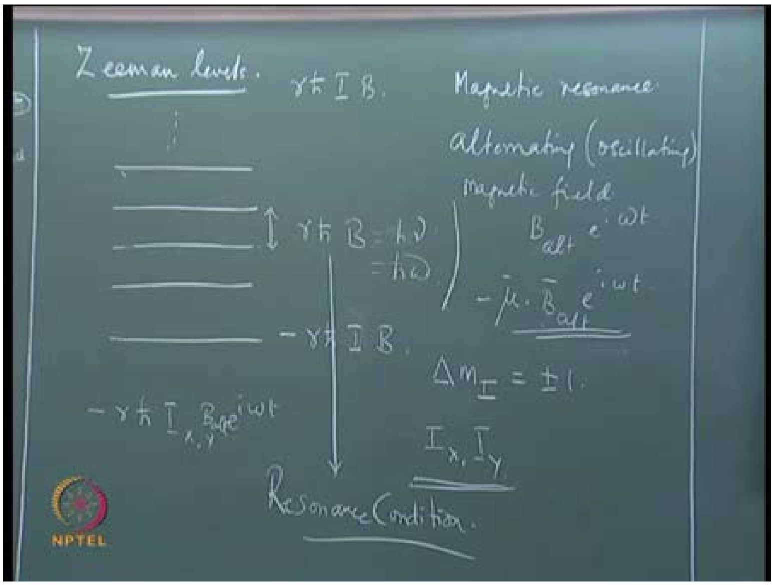

So, these energy level are called the Zeeman levels which are shown in the figure.

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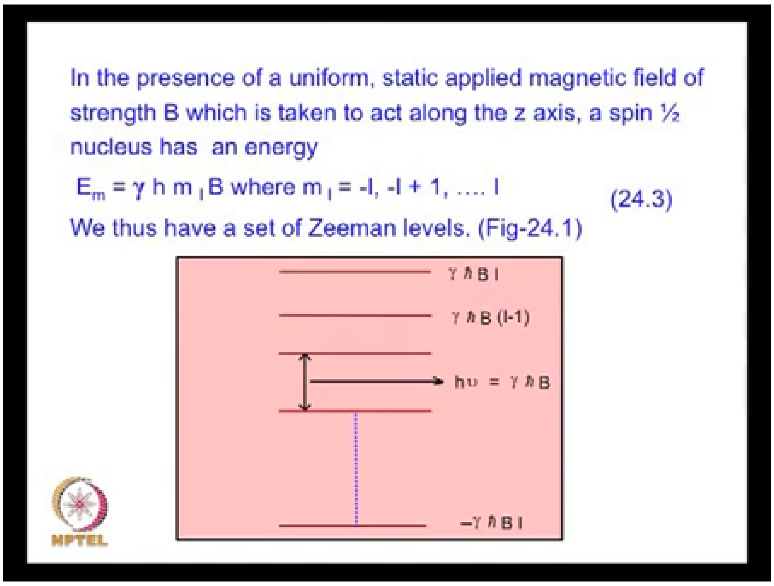
In the presence of a uniform, static applied magnetic field of strength B which is taken to act along the z axis, a spin ½ nucleus has an energy

$E_m = \gamma h m_I B$ where $m_I = -I, -I + 1, \ldots I$ (24.3)

We thus have a set of Zeeman levels. (Fig-24.1)

Now, the zeeman levels are equally spaced, so this is minus gamma h cross I into B and this till gamma h cross I B 2 I plus 1 levels. So, all of them are equally spaced and they adjacent levels have a spacing equal to gamma h cross B, that is the energy difference between adjacent levels these are the energy Eigen values in a static field. And now if i magnetic resonance takes place whenever in quantum systems, whenever you have a system with different sets of stationary Eigen states you couple them by inducing transitions using a perturbing energy Hamiltonian.

So, here this perturbing Hamiltonian has to couple adjacent energy levels. So, this perturbing Hamiltonian and energy term is also magnetic in origin, therefore we call it magnetic resonance and this has to be a time dependent perturbation, so that the levels will be coupled otherwise a stationary perturbation will not couple these adjacent levels. So, in order to induce transitions between these level you have to have a time dependent perturbation.

In general you apply an alternating or oscillating magnetic field and by the same reasoning the oscillating magnetic field if I have B alternating e to power i omega t ((Refer Time: 10:29)). Then this also has a coupling Hamiltonian which is of the form new dot B alternating e i omega t. And therefore, if we want to couple adjacent levels the only way there can be a non-zero transition probability between adjacent levels you have to couple, because they have to induce transition between sum m value here mI value state here and an m I plus 1 state here or vice versa.

Therefore, you have to have a change in the magnetic quantum number delta m I should be plus or minus 1. So, the kind of hamiltonian that will do this only something which involves the I x or I y, if you have I z it will not induce transitions among them. So, one must have a alternating field, which is directed along the x or y directions

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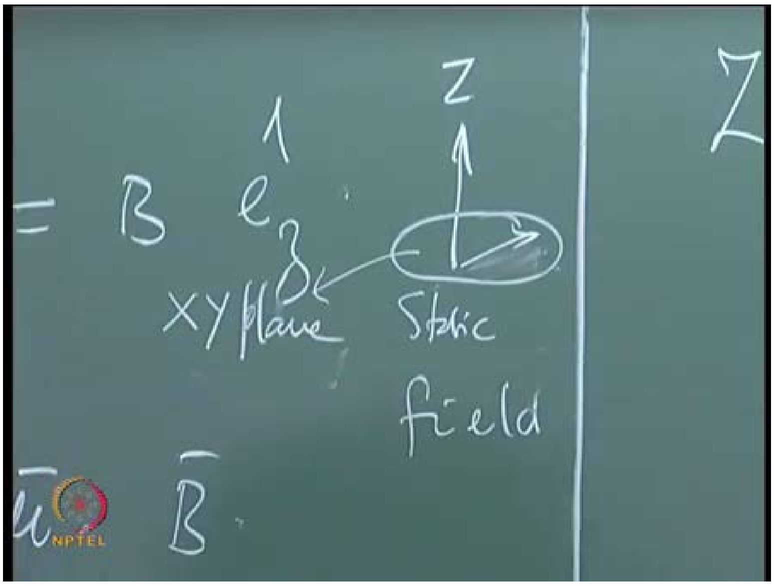

If the applied static field is around the Z direction static field, then the oscillating field has to be in the xy plane, so this is the xy plane. So, the oscillating magnetic field should be directed in the xy plane perpendicular to this axis, so this is how a magnetic resonance transition is induced between the adjacent states. So, the figure shows this situation.

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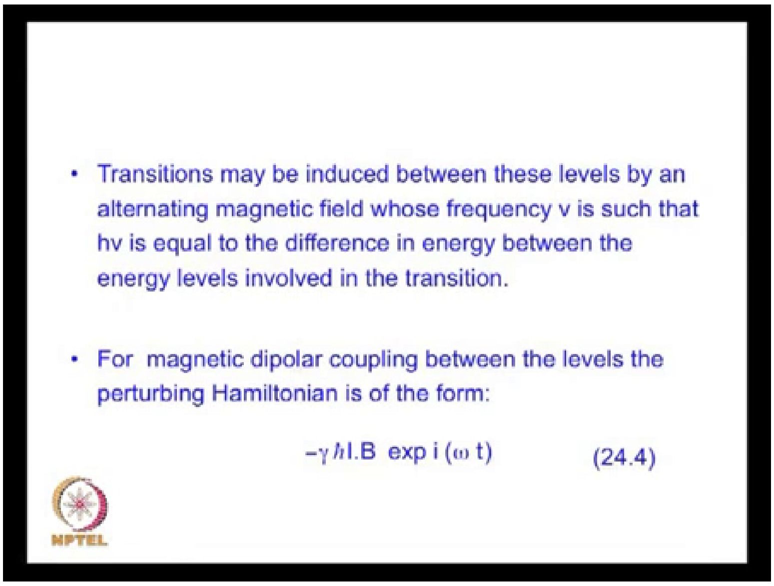

- Transitions may be induced between these levels by an alternating magnetic field whose frequency v is such that hv is equal to the difference in energy between the energy levels involved in the transition.
- For magnetic dipolar coupling between the levels the perturbing Hamiltonian is of the form:

$$-\gamma \hbar I.B \ \exp i\,(\omega t) \qquad (24.4)$$

So, per magnetic dipolar coupling from this we can write this as ((Refer Time: 12:36)) minus gamma h cross I x or y into power i omega t is 0 B alternate.

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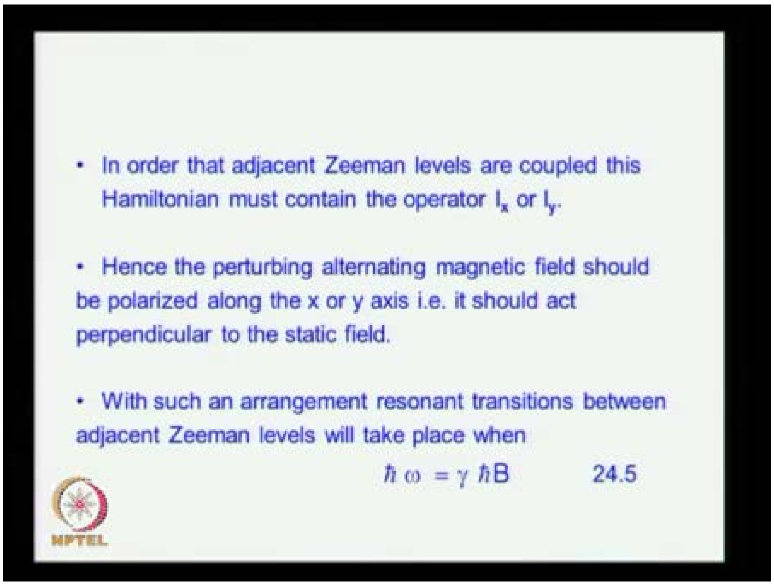

- In order that adjacent Zeeman levels are coupled this Hamiltonian must contain the operator I_x or I_y.
- Hence the perturbing alternating magnetic field should be polarized along the x or y axis i.e. it should act perpendicular to the static field.
- With such an arrangement resonant transitions between adjacent Zeeman levels will take place when

$$\hbar \omega = \gamma \hbar B \qquad 24.5$$

In which case the matching or the energy level should be such that this should h mu or h cross omega ((Refer Time: 12:59)). So, that is known as the resonance condition, so this is the NMR resonance condition written in short.

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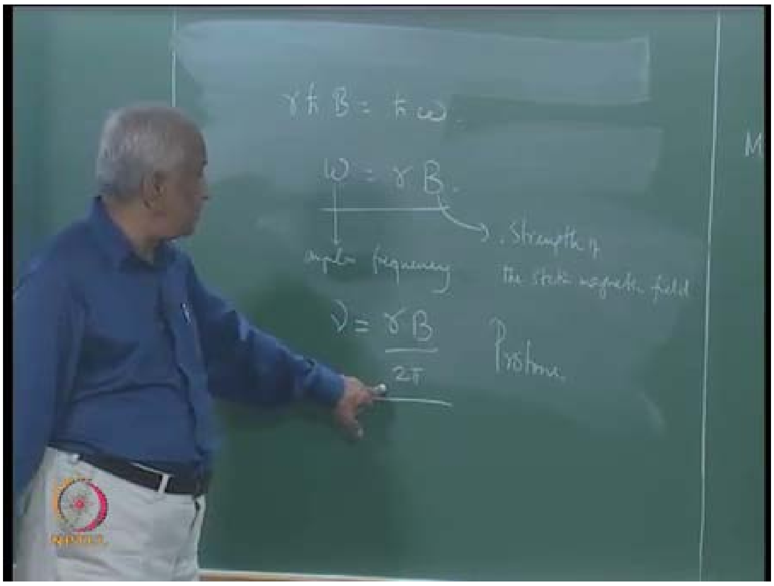

It will be gamma h cross B equals h cross omega or omega into gamma B, where B is the strength of the static magnetic field, omega is the angular frequency of the applied oscillating field, this is the strength of the static field. So, the resonance process involves an establishment of the Zeeman levels using an applied static magnetic field and inducing transition among adjacent Zeeman level by means of an applied alternating magnetic field of angular frequency omega. In other words this can also be written as mu equal to gamma B by 2 pi since omega is 2 pi mu, so that gives the resonance condition.

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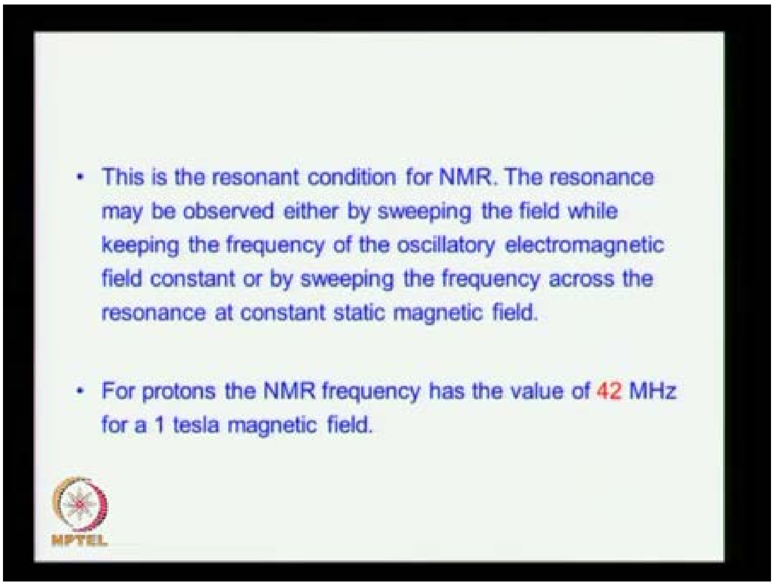

- This is the resonant condition for NMR. The resonance may be observed either by sweeping the field while keeping the frequency of the oscillatory electromagnetic field constant or by sweeping the frequency across the resonance at constant static magnetic field.
- For protons the NMR frequency has the value of 42 MHz for a 1 tesla magnetic field.

This resonance may be observed either by keeping the field constant and sweeping the frequency at the oscillator or you can hold the frequency constant and sweep the field across the resonance; for protons since gamma is a constant e by 2 M and this is 2 pi. So, this can be calculated the value is about 42 mega Hertz for an applied static field of B is 1 tesla. Now, we are talking about time dependent perturbation inducing transitions between adjacent Zeeman levels now what is the transition probability.

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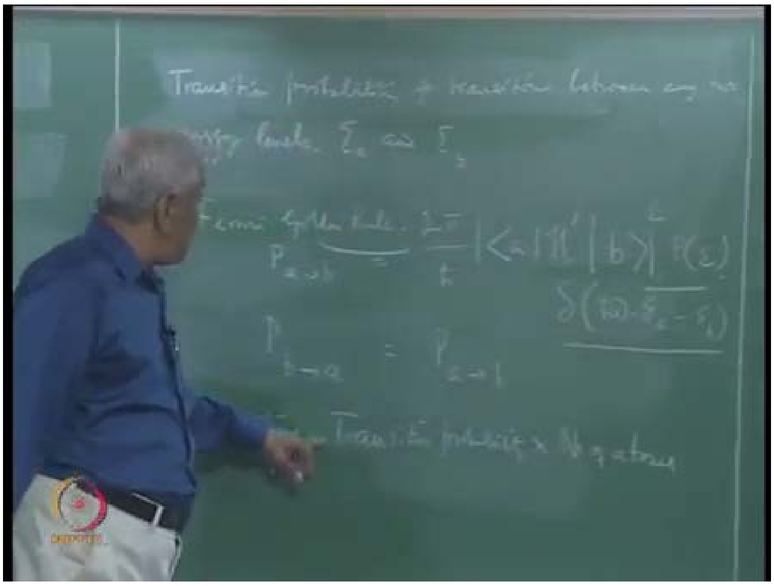

Let us look at this a little closely transition probability, for transition between any two energy levels. Say E a and E b this is given by Fermi golden rule, which has the form 2 pi by h cross a H prime b square delta h cross omega minus E a minus E b into of course, a density of states. So, this is a standard expression for transition probability P a b, now here this means this is the wave function of the state with energy level E a and this is the state E b and H prime is the perturbing Hamiltonian.

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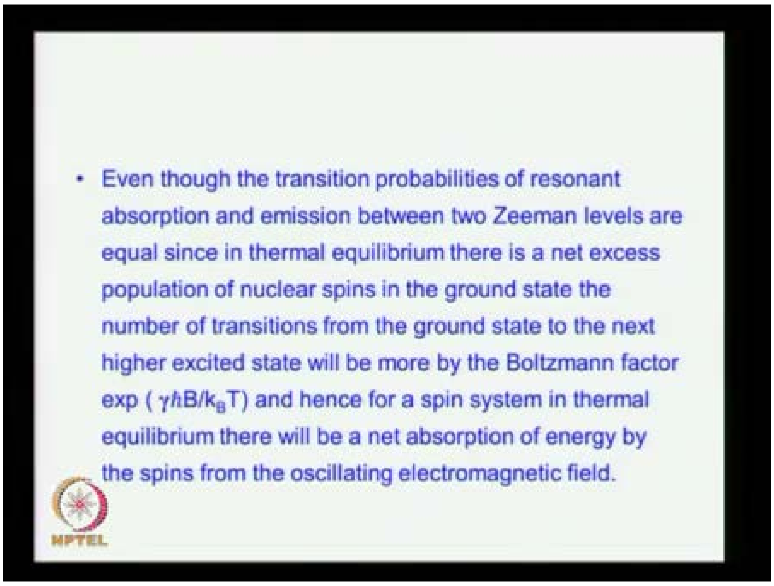

- Even though the transition probabilities of resonant absorption and emission between two Zeeman levels are equal since in thermal equilibrium there is a net excess population of nuclear spins in the ground state the number of transitions from the ground state to the next higher excited state will be more by the Boltzmann factor exp ($\gamma\hbar B/k_B T$) and hence for a spin system in thermal equilibrium there will be a net absorption of energy by the spins from the oscillating electromagnetic field.

So, this is the transition moment matrix element of the perturbing Hamiltonian between the two states it is modular square and this ensures ((Refer Time: 17:21)) that this is a delta function which is one only when E a minus E b is equal to H cross omega that ensures the resonance process. That when the energy difference is exactly matched by H cross omega than there will be a non-zero value. Now, if you argue what is the probability of transition from reverse transition from b to a that is also of the same form because this is completely symmetrical between a and b.

So, the transition probabilities both ways are the same for an upper transition or a downward transition, the transition properties are the same. So, what is the number of transitions? The number of transitions is given by the transaction probability times the number of atoms in a given state. So, if we are interested in the transitions the number of transitions from level a to level b, then this is given by the transaction probability P a to b times the number of atoms in level a.

Similarly the transaction probability downwards from level b to a is given by the same transitions probability P b to a times the number of atoms in the level b. So, the number of transitions will be equally if the number of atoms in the two states are the same. So, they will be non-zero there will be a net preferential transaction in one direction, only if there are unequal populations in the two levels, which are being coupled. Now, in thermal equilibrium it is a standard result that, if there are two energy levels with a level difference of this kind.

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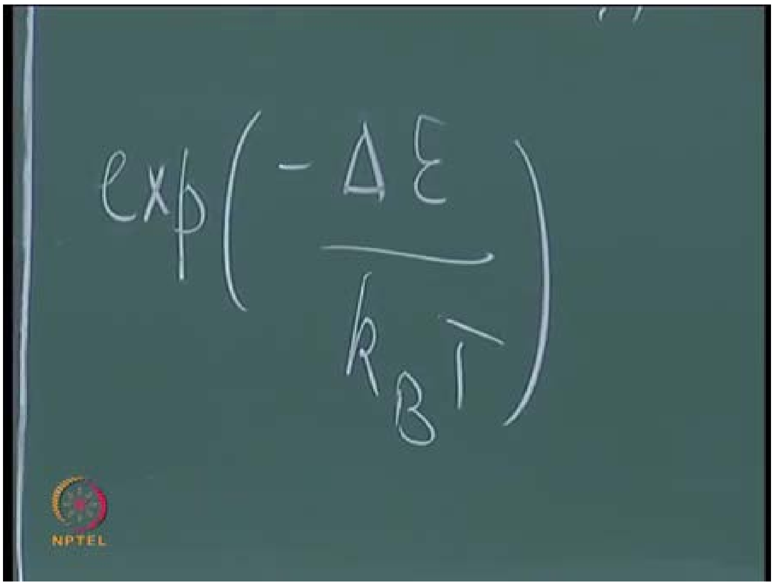

$$\exp\left(-\frac{\Delta E}{k_B T}\right)$$

Then there will always be a population difference given by for any spin system in thermal equilibrium at a temperature T with a a level difference delta e, then the lower level will be will have an excess population, which will be given by this factor with respect to the upper level. So, it is this net population difference in thermal equilibrium which makes it possible to have a more transition from the lower level to the upper level than from the upper level to the lower level, if there is more transition from the lower level to the upper level there will be absorption.

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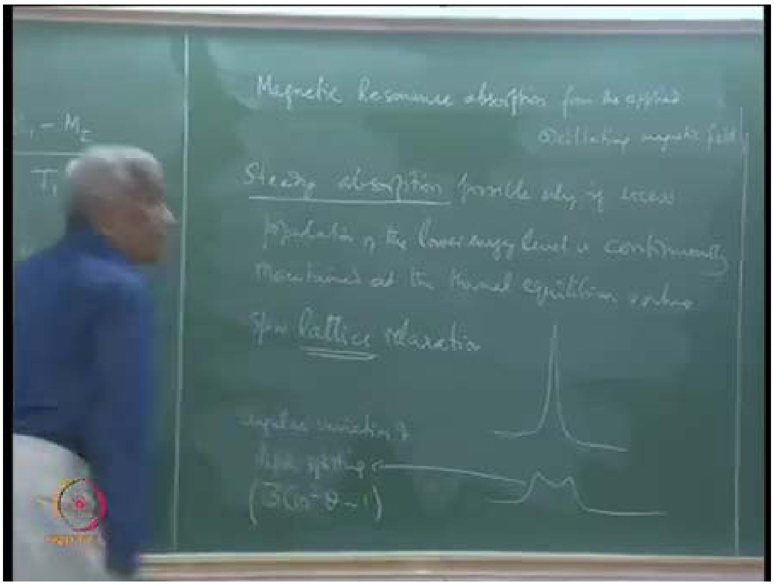

Magnetic Resonance absorption from the applied oscillating magnetic field

Steady absorption possible only if excess population of the lower energy level is continuously maintained at the thermal equilibrium value through spin lattice relaxation

Angular variation of dipolar splitting

$(3\cos^2\theta - 1)$

So, because thermal equilibrium ensures that the lower level is more populated there will be a net magnetic resonance absorption of energy at resonance from the applied oscillating fields in a laser. For example, the upper level the excited state is more preferentially populated in excess by what is known as a population inversion process. And therefore, there will be a laser emission because the number of transition from the upper to the lower level will be excess. So, there will be an emission of light and that is what we call laser emission, so laser emission is just the reverse of magnetic resonance absorption.

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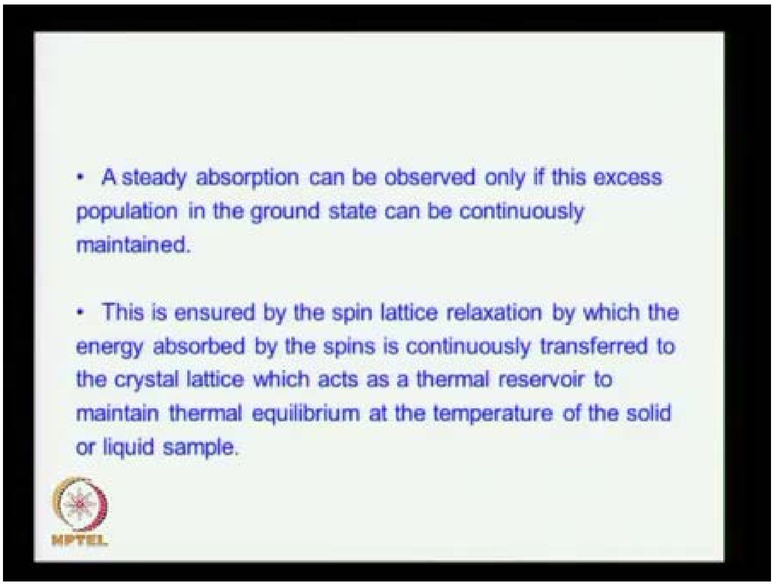

- A steady absorption can be observed only if this excess population in the ground state can be continuously maintained.
- This is ensured by the spin lattice relaxation by which the energy absorbed by the spins is continuously transferred to the crystal lattice which acts as a thermal reservoir to maintain thermal equilibrium at the temperature of the solid or liquid sample.

Now, a steady absorption if we want there be a absorption. So, the the spins will be go from the lower level to the upper level and eventually the two populations will get equalized and then there is no excess population in the ground state and therefore, there will be no absorption anymore. So, if you wait for some time the absorption will die off. So, if you want to observe a steady absorption this is possible only if possible, only if excess population of the lower energy level is continuously maintained at the thermal equilibrium value.

In other words when energy is absorbed by the spin system, which is in thermal equilibrium at a temperature t and if the energy is absorbed from an external magnetic field then this has the effect of heating of the nuclear spins. So, the temperature tends to rise, so unless this heat energy this energy which is absorbed is leaked away, so that it comes back again to the same original temperature and thermal equilibrium is maintained. In order to do this this energy absorbed should be continuously leaking away to the external world, the spins are usually embedded in a crystal lattice.

For example, the protons in water are inside the bulk of the water which serves as a thermal broth. So, the water absorbs this energy absorbed by a process this process of leaking away energy is called a relaxation process known as thin lattice relaxation, the external broth which access a heat reservoir which absorbs all the heat which goes into the spin system that is called collectively as lattice. So, the bulk of the water is the lattice in this case this is because in a crystal solid crystal this is a lattice.

So, because of that that term has stuck, so there is a relaxation of this spins through the coupling between the spins and the lattice and this relaxation means it is as if you are heating up a system a rod is being heated up and this rod is also radiating away this heat to the external rod. So, it is similar to that the spin system is an temperature t and then it is connected thermally to the outside lattice and there is a connection, there is a thermal connection between the spin system and the lattice system and there is a time taken for this heat to be leaked away.

So, it is called a relaxation process, it is the spin lattice relaxation which ensures that the energy absorbed by this spins is continuously transferred on to the heat broth namely the bulk of water or the crystal lattice which acts as a thermal reservoir. So, that thermal equilibrium is maintained at the temperature of the nuclear spins, so this is necessary in order for [vocalised noise] a steady absorption to take place.

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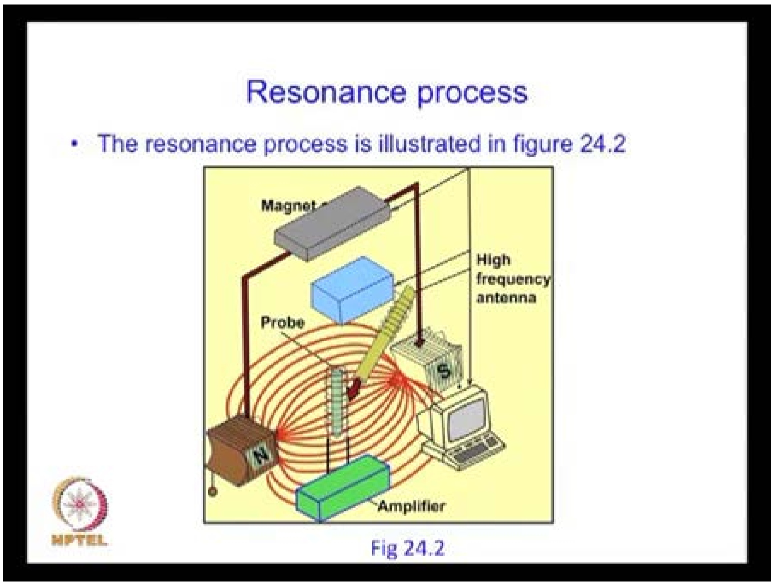

Resonance process

- The resonance process is illustrated in figure 24.2

Fig 24.2

So, the resonance process is illustrated in the next figure, where you have what is shown is a magnetic which produces a static field, the north south direction shows the lines of force. And then you have a sample inside it that is called the probe here and then there is a high frequency antenna which couples the alternating magnetic field to this spin system and you can sweep by either the magnetic field or the frequency of the oscillator. So, that the resonance takes place and the resonance absorption from the oscillator is coupled as a signal into a amplifier and then displayed, so that is the basic schematic of the resonance process.

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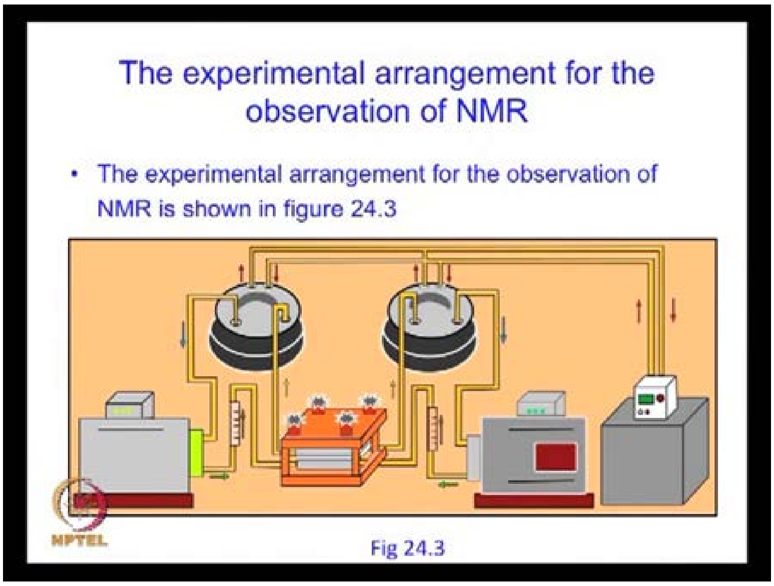

The experimental arrangement for the observation of NMR

- The experimental arrangement for the observation of NMR is shown in figure 24.3

Fig 24.3

The experimental arrangement is shown in the next figure which is of course, a little more detail and that is the way it is seen in any laboratory with an NMR spectrometer.

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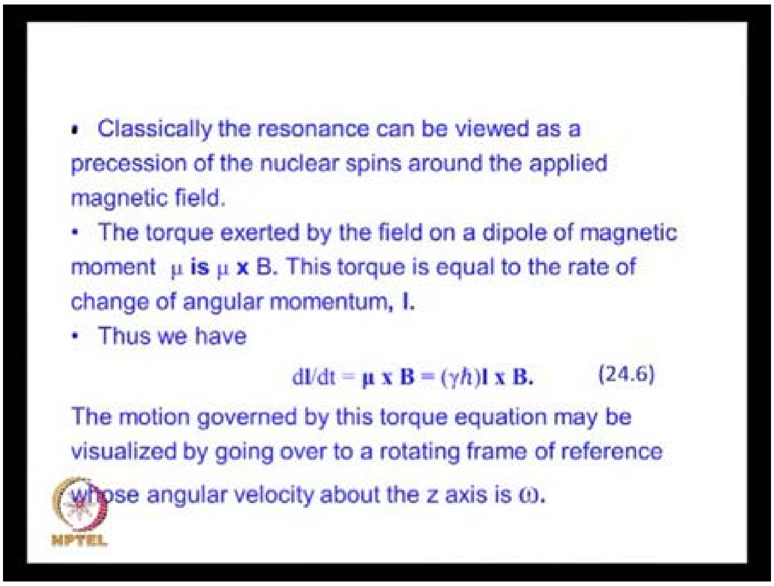

- Classically the resonance can be viewed as a precession of the nuclear spins around the applied magnetic field.
- The torque exerted by the field on a dipole of magnetic moment μ **is** μ **x** B. This torque is equal to the rate of change of angular momentum, **I**.
- Thus we have

$$dI/dt = \boldsymbol{\mu} \times \mathbf{B} = (\gamma\hbar)\mathbf{I} \times \mathbf{B}. \qquad (24.6)$$

The motion governed by this torque equation may be visualized by going over to a rotating frame of reference whose angular velocity about the z axis is ω.

Now, this all quantum mechanics one might ask is there no way of understanding this process resonance is known classically magnetic field electrodynamics magnetic field and it is interaction with nuclear angular momentum all these are classical ideas. So, why should we have a quantum mechanical explanation, the answer is the resonance can be explained classically and the way to explain this is via the tarque accepted by a magnetic field.

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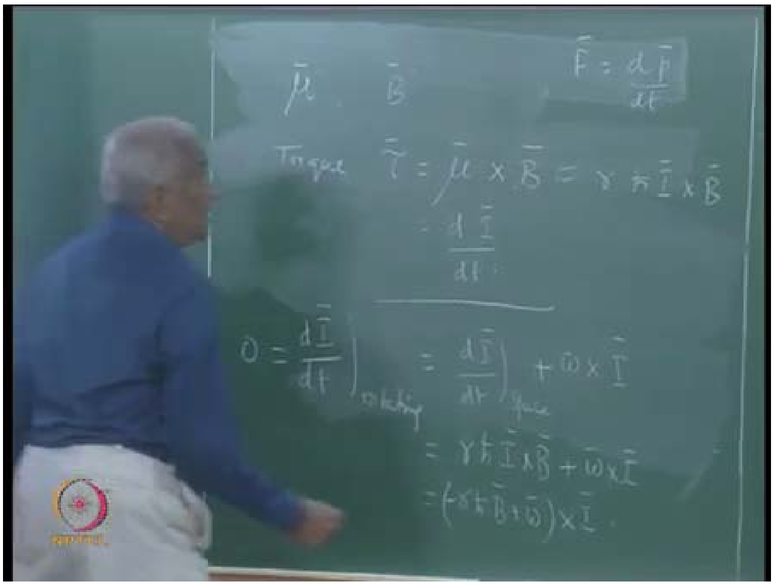

If I have a magnetic moment a dipole moment mu then if i have a field acting on it, then there is a tarque it is a well-known result of classical electro dynamic that the tarque is mu cross B. Now, by tarque equation which is just the analogue of the Newton’s equation for the force and the momentum rate of change of linear momentum, the tarque is connected to the rate of change to the angular momentum. So, it is the I by the t this is just the analogue of the newtons equation F equal to d p by d t. So, instead of F you have the tarque here for a rotational motion and then instead of the linear momentum, we have the spin angular momentum, so this is the tarque equation, so now, substituting for mu I can write this as gamma h cross I cross B .

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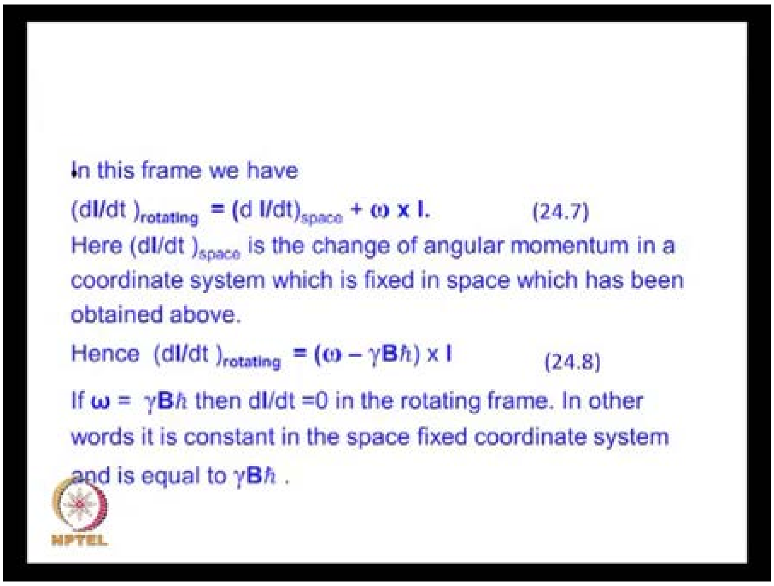

In this frame we have

$(dI/dt)_{rotating} = (d\,I/dt)_{space} + \omega \times I.$ (24.7)

Here $(dI/dt)_{space}$ is the change of angular momentum in a coordinate system which is fixed in space which has been obtained above.

Hence $(dI/dt)_{rotating} = (\omega - \gamma B\hbar) \times I$ (24.8)

If $\omega = \gamma B\hbar$ then $dI/dt = 0$ in the rotating frame. In other words it is constant in the space fixed coordinate system and is equal to $\gamma B\hbar$.

Now, in order to make this understand the physical content of this tarque equation, let us just go from a static reference frame of coordinate system of coordinates to a rotating frame and classical mechanic tells us that the rate of change of any vector. Then viewed from a rotating frame which has an angular frequency omega is related to the rate of change in space fixed coordinate system plus omega cross I this is a standard result in classical mechanics. So, let us apply this, to this situation and get this as gamma h cross I cross B plus omega cross I.

I can bring it together by writing gamma h cross B minus omega cross I minus, so this time rate of change will become 0 if the resonance condition namely.

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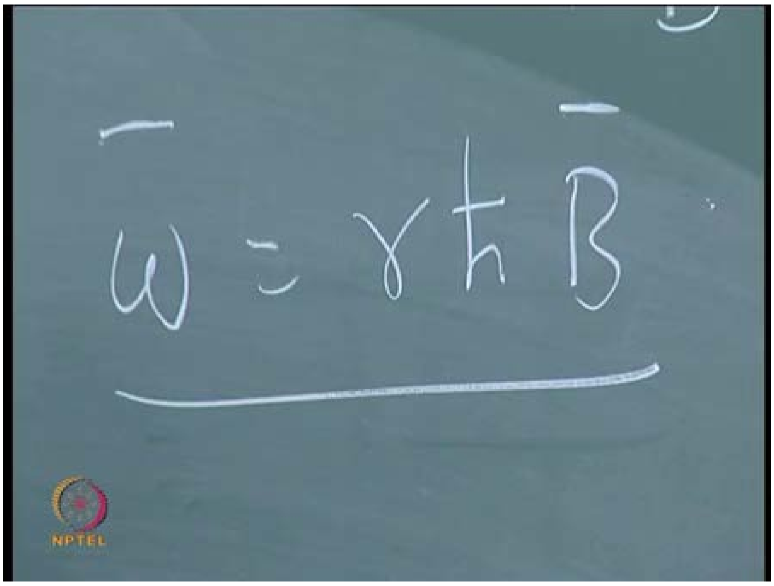

$$\bar{\omega} = \gamma \hbar \bar{B}$$

Omega equal to gamma h cross B is satisfied, so this is again the resonance condition. So, we have classically the result that if you go to a rotating frame, which is rotating with an angular or frequency which is equal to the resonance frequency, then again we will have a resonance process in which energy is absorbed from the oscillating magnetic field by the nuclear spin system. So, this phenomenon because the angular momentum is fixed ((Refer Time: 31:15)) because it is time rate have changed zero, that is a fixed vector in space and that is the phenomenon which is known as precession, we know this from the motion of a top or a gyroscope in classical mechanic.

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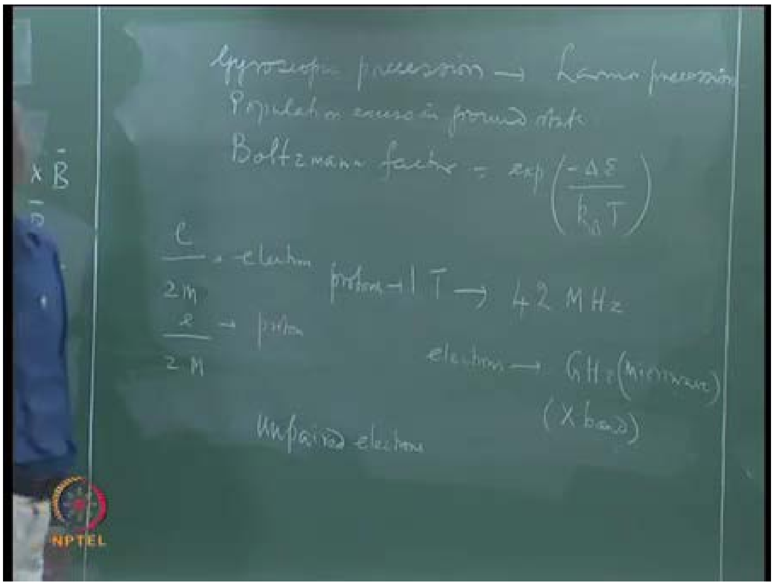

Gyroscopic precession → Larmor precession

Population excess in ground state

Boltzmann factor = $\exp\left(\frac{-\Delta E}{k_B T}\right)$

$\frac{e}{2m}$ - electron

$\frac{e}{2M}$ → proton

proton - 1 T → 42 MHz

electron → GHz (microwave)

(X band)

unpaired electrons

So, this is gyroscopic precession, which was first recognised by a person called Larmor, so this is known as Larmor precession.

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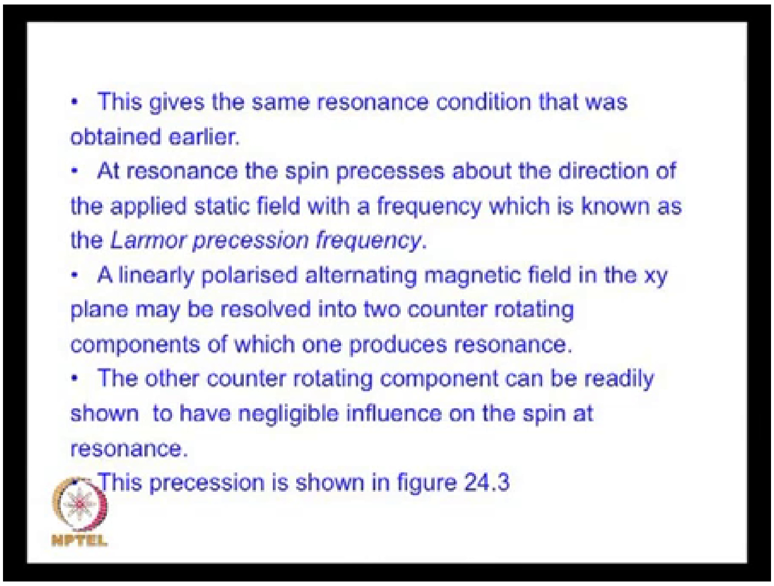

- This gives the same resonance condition that was obtained earlier.
- At resonance the spin precesses about the direction of the applied static field with a frequency which is known as the *Larmor precession frequency*.
- A linearly polarised alternating magnetic field in the xy plane may be resolved into two counter rotating components of which one produces resonance.
- The other counter rotating component can be readily shown to have negligible influence on the spin at resonance.
- This precession is shown in figure 24.3

So, the angular momentum is preserved the spin is precessing about the direction of the applied static field with an angular frequency equal to the resonance frequency. So, the resonance frequency is nothing but, the lamor precession frequency

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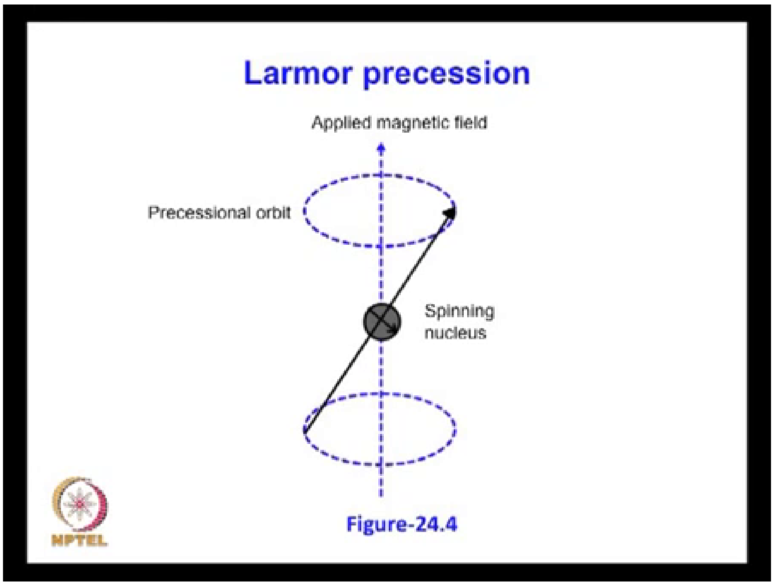

Larmor precession

Figure-24.4

So, this precession is shown in the next figure, so you have the applied magnetic field and then the precession takes place about this field direction.

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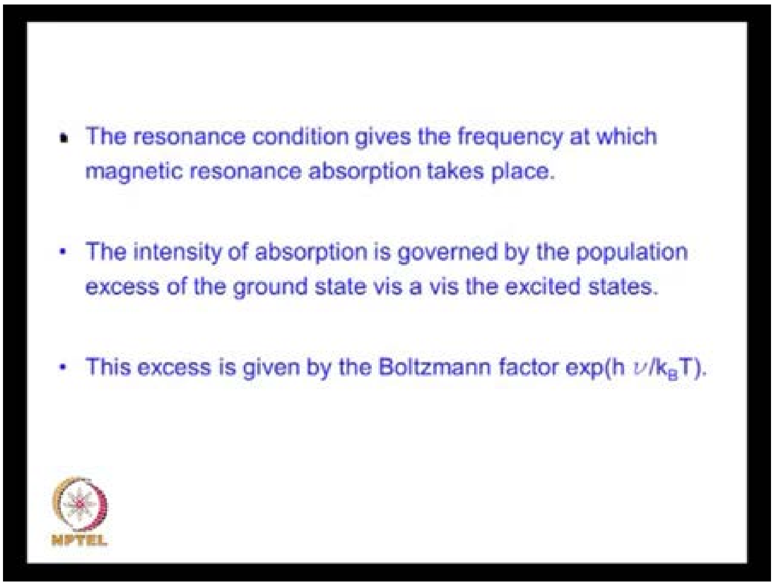

- The resonance condition gives the frequency at which magnetic resonance absorption takes place.
- The intensity of absorption is governed by the population excess of the ground state vis a vis the excited states.
- This excess is given by the Boltzmann factor exp($h\nu/k_BT$).

So, the resonance condition gives the frequency at which magnetic resonance absorption takes place and the intensity absorption is governed by again as I discussed already the population excess of the ground state by vis a vis the excited states. Now, this is this excess of population is given by the Boltzmann factor population excess in ground state ((Refer Time: 33:00)) is given by the Boltzmann factor exponential minus delta e by k B T. This explains why for example, if you take the electrons and the nuclei, we can also have a similar consideration of electron resonance as well.

Now, the magneto gyric ration is e by 2 M in the case of the electron or l for protons it is e by 2 capital M, where M is some 2000 times 2873 times the mass of the electron. And therefore, the proton magnetic moment is that much weaker a factor of thousand weaker and therefore, the energy levels are smaller whereas here the energy levels are much higher. So, 1000 times larger, therefore we already saw for a 1 tesla field the nuclear resonance for protons and water takes place around 42 megahertz. Whereas, the corresponding frequency for electrons per spin resonance will be in the gigahertz range or the microwave region of the electromagnetic spectrum for electrons usually in the expand.

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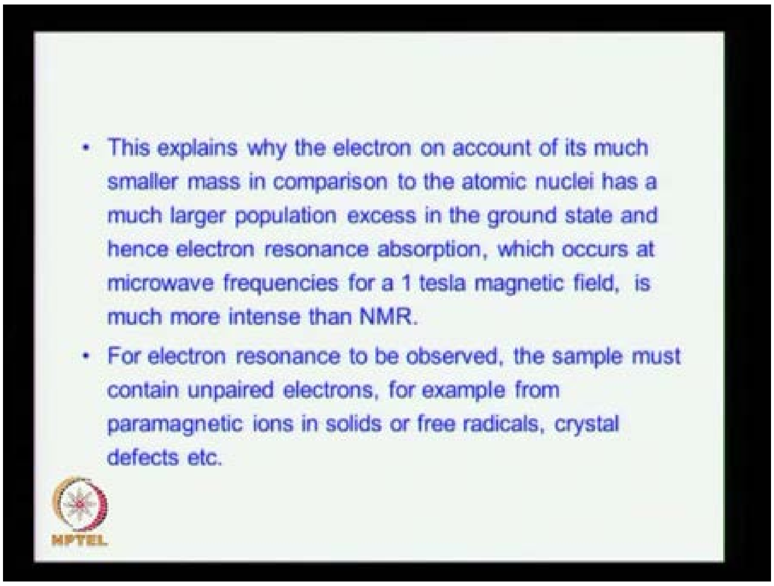

- This explains why the electron on account of its much smaller mass in comparison to the atomic nuclei has a much larger population excess in the ground state and hence electron resonance absorption, which occurs at microwave frequencies for a 1 tesla magnetic field, is much more intense than NMR.
- For electron resonance to be observed, the sample must contain unpaired electrons, for example from paramagnetic ions in solids or free radicals, crystal defects etc.

So, for electron resonance to be observed sample again should have unpaired electrons carrying a net angular momentum, we already discussed this situation in connection with electron magnetism. So, for example, paramagnetic ions or free radical ((Refer Time: 35:18)) crystal defects.

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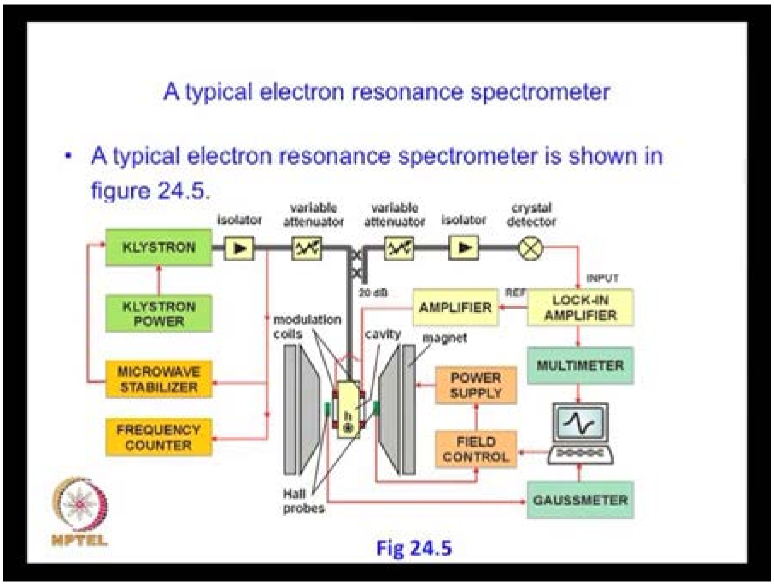

A typical electron resonance spectrometer

- A typical electron resonance spectrometer is shown in figure 24.5.

Fig 24.5

So, that a next figure shows a typical electron spin resonance spectrometer the components are self-explanatory they are standard micro gear and techniques for observing the resonance and so on.

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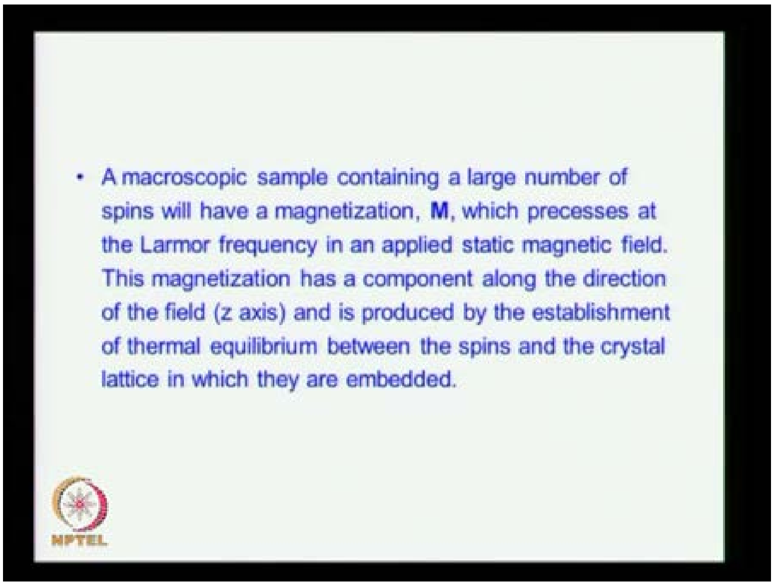

- A macroscopic sample containing a large number of spins will have a magnetization, **M**, which precesses at the Larmor frequency in an applied static magnetic field. This magnetization has a component along the direction of the field (z axis) and is produced by the establishment of thermal equilibrium between the spins and the crystal lattice in which they are embedded.

So, if we have a macroscopic sample we wrote all these equations were written for a single dipole, but if we have a macroscopic sample containing some 24 spins then we have to change the discussion to the magnetization M, the it is the case of the magnetization vector, which is the resultant of all the spins that has to be discussed.

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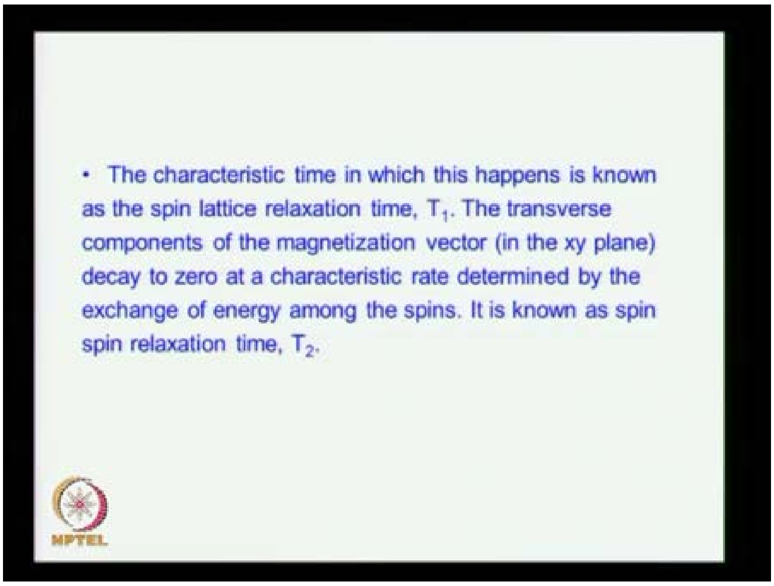

- The characteristic time in which this happens is known as the spin lattice relaxation time, T_1. The transverse components of the magnetization vector (in the xy plane) decay to zero at a characteristic rate determined by the exchange of energy among the spins. It is known as spin spin relaxation time, T_2.

So, it is the precession of the magnetization vector and this pressesses.

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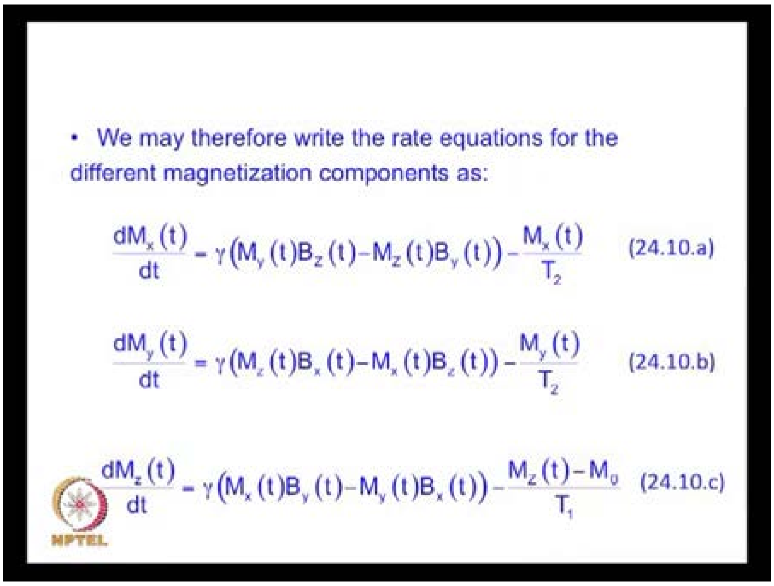

- We may therefore write the rate equations for the different magnetization components as:

$$\frac{dM_x(t)}{dt} = \gamma\left(M_y(t)B_z(t) - M_z(t)B_y(t)\right) - \frac{M_x(t)}{T_2} \qquad (24.10.a)$$

$$\frac{dM_y(t)}{dt} = \gamma\left(M_z(t)B_x(t) - M_x(t)B_z(t)\right) - \frac{M_y(t)}{T_2} \qquad (24.10.b)$$

$$\frac{dM_z(t)}{dt} = \gamma\left(M_x(t)B_y(t) - M_y(t)B_x(t)\right) - \frac{M_z(t) - M_0}{T_1} \qquad (24.10.c)$$

At a rate which is determined by the spin lattice relaxation time etcetera, therefore we can write the time rate of change of the magnetization vector as follows.

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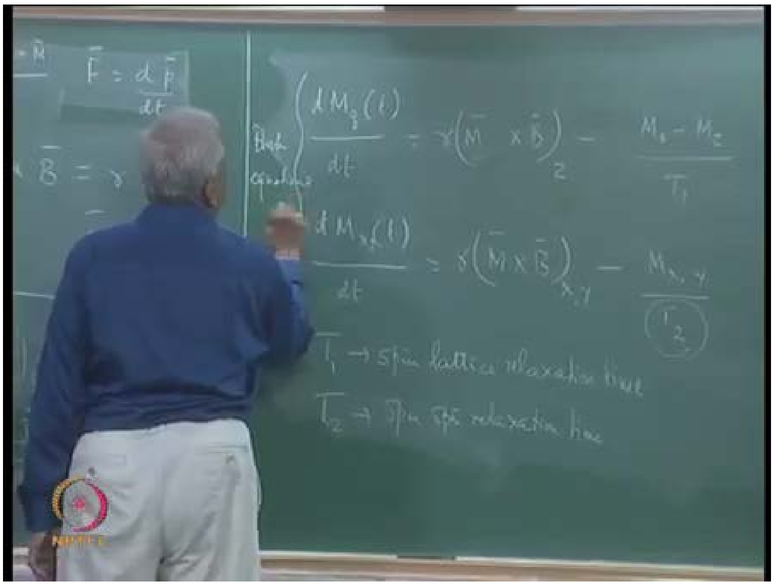

So, we will write the time rate of change for the different components of the magnetization this will be by the tarque equation ((Refer Time: 36:48)) the z component of the M of the cross product and then minus. So, this is the time rate of change according to the spin lattice relaxation time. And similar equation for the M x the transfers magnetization opponent M x or y. Now, the transfers magnetization the decay of the transfer magnetization is governed by a different spin time constant.

So, T 1 is known as the spin lattice relaxation time as explained already it gives the decay of the z component of the magnetization and it is evolution to go into the steady state value of the magnetization. The steady state equilibrium magnetization is established in a time of the order of the spin lattice relaxation, while the transfers magnetization is decays at the rate which is governed by the energy exchange among the spins. So, it is called the spin spin relaxation in this form these equations are known as the blocked equations, which describe the resonance process.

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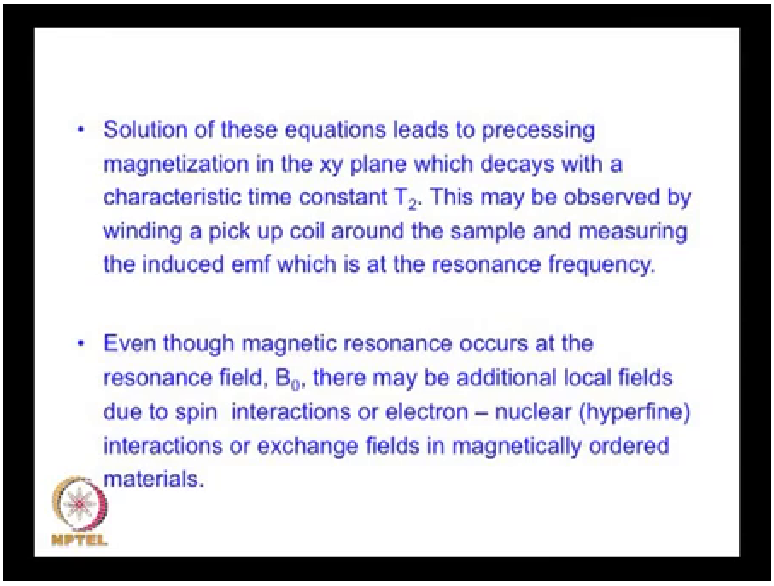

- Solution of these equations leads to precessing magnetization in the xy plane which decays with a characteristic time constant T_2. This may be observed by winding a pick up coil around the sample and measuring the induced emf which is at the resonance frequency.
- Even though magnetic resonance occurs at the resonance field, B_0, there may be additional local fields due to spin interactions or electron – nuclear (hyperfine) interactions or exchange fields in magnetically ordered materials.

Solution of these equation in any given situation leads to a precessing magnetization the x y plane which decays with a characteristic time constant T 2 and if there is a precessing transfers magnetization component if you bind a pick up coil around this sample, one can measure the induce EMF by a Faraday law which is at the resonance frequency. So, this is the phenomenon known as nuclear induction ((Refer Time: 39:04)) even though magnetic resonance occurs usually at the resonance field value, which is given by the resonance frequency as discussed already.

We may be thinking that we are applying a resonance field, but there may be additional internal local fields due to interactions among spins and these fields can be of different origins. Now, if such a field exist a local field an internal field then the resonance is shifted by an amount equal to the local field for example, in a liquid sample this shift is known as chemical shift.

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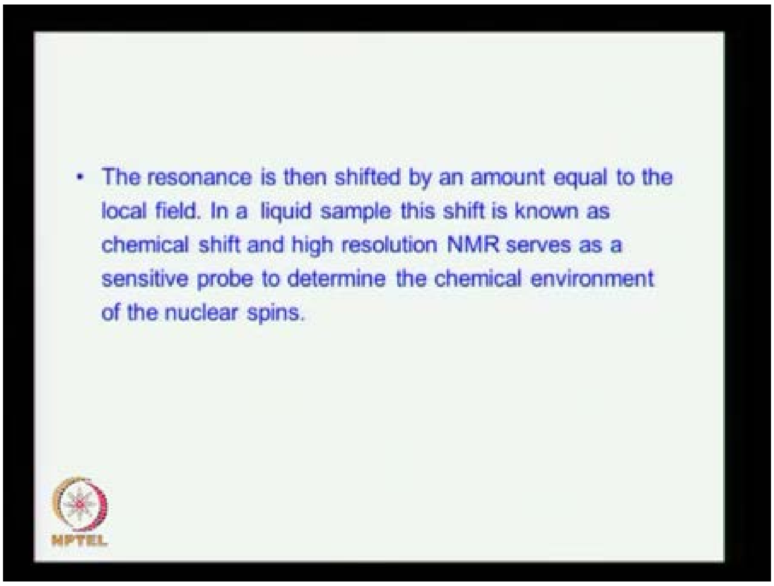

- The resonance is then shifted by an amount equal to the local field. In a liquid sample this shift is known as chemical shift and high resolution NMR serves as a sensitive probe to determine the chemical environment of the nuclear spins.

And one can look at high resolution it is called high resolution NMR which can serve as a sensitive probe to determine the chemical environment of the nuclear spins.

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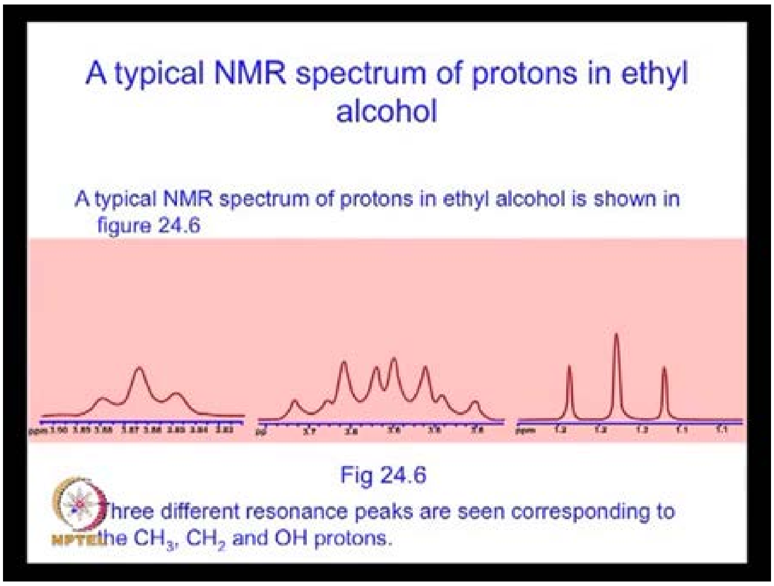

A typical NMR spectrum of protons in ethyl alcohol

A typical NMR spectrum of protons in ethyl alcohol is shown in figure 24.6

Fig 24.6

Three different resonance peaks are seen corresponding to the CH_3, CH_2 and OH protons.

For example a typical NMR spectrum of protons in ethyl alcohol is shown here in ethyl alcohol you have CH 3 and CH 2 and OH all these contain protons. And so, there are three different resonance peaks because each of these have a slightly different chemical environment. So, there is a shift due to these internal field and so, you get three sets of NMR resonance peaks I do not want to go into the details of the additional structure which you see there, so on.

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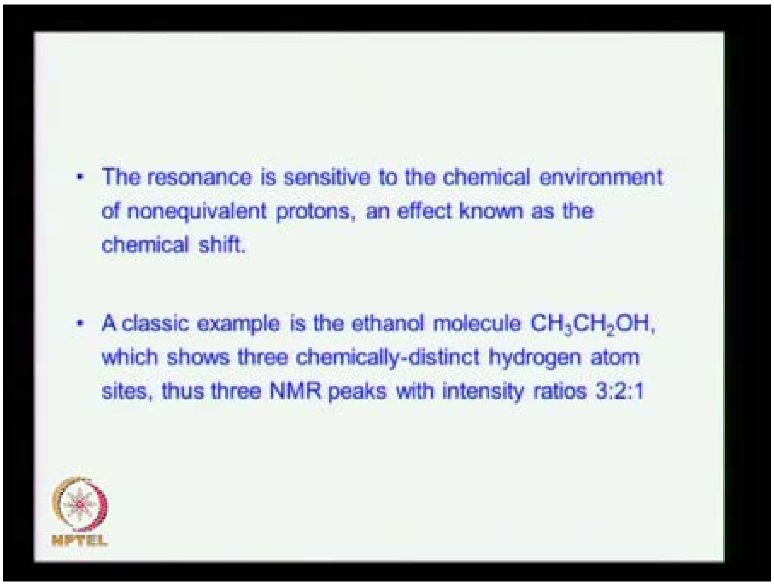

- The resonance is sensitive to the chemical environment of nonequivalent protons, an effect known as the chemical shift.
- A classic example is the ethanol molecule CH_3CH_2OH, which shows three chemically-distinct hydrogen atom sites, thus three NMR peaks with intensity ratios 3:2:1

So, you can get a lot of information about the chemical environment.

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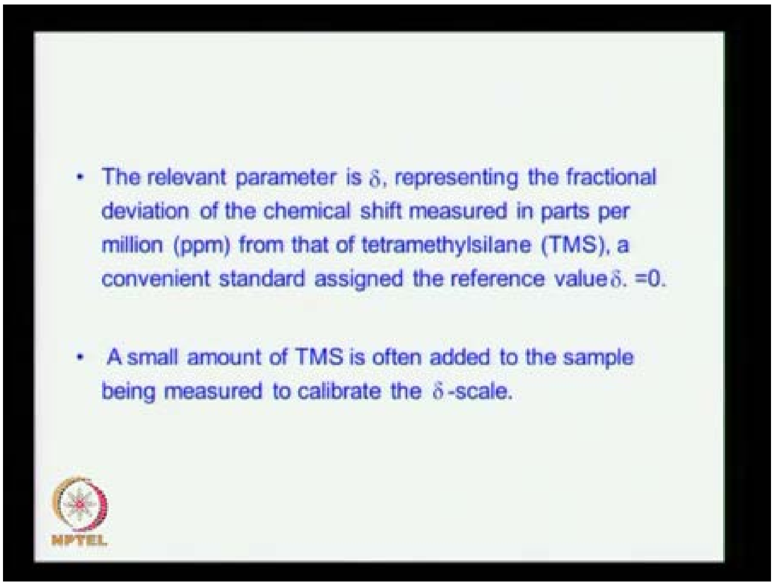

- The relevant parameter is δ, representing the fractional deviation of the chemical shift measured in parts per million (ppm) from that of tetramethylsilane (TMS), a convenient standard assigned the reference value δ. =0.
- A small amount of TMS is often added to the sample being measured to calibrate the δ-scale.

And then you have the intensity ratios can tell you about how many protons are there ((Refer Time: 40:56)) for example, you have CH 3, so you have a much larger intensity and so on depending on the number of protons three protons in CH 3, 2 in CH 2 and 1 in

OH. So, correspondingly there will be intensity differences, so the ratio will be 3 is to 2 is to 1. So, by measuring the relative intensity one can get also information about the relative concentration in a given molecule.

So, the relevant parameter in chemical shift is called delta representing the fractional deviation measured in parts per million as I told you it is a high resolution NMR. So, the changes are in parts per million from that of a standard sample known as usually this is a compound known as a tetramethylsilane it is known as short short as TMS. So, it is is a convenient standard which has a reference value the chemical shift is zero, so the small amount of TMS is always added to the sample. So, that it calibrates the chemical shift measured.

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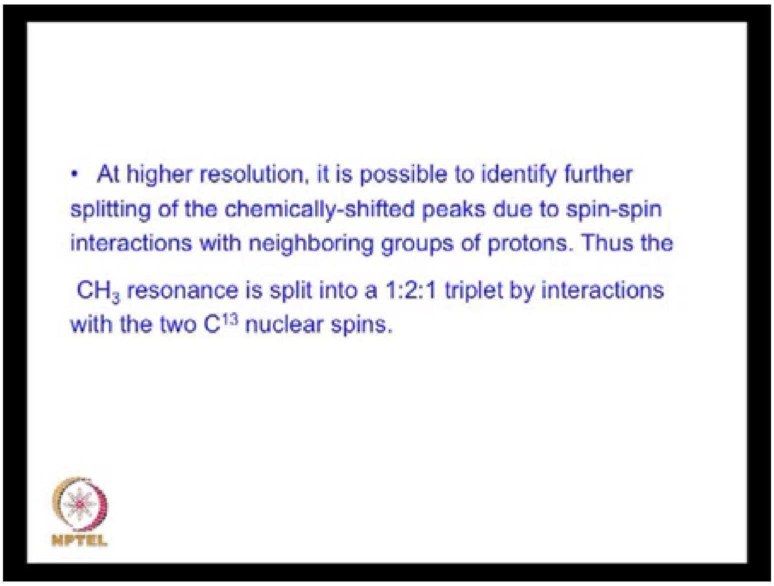

- At higher resolution, it is possible to identify further splitting of the chemically-shifted peaks due to spin-spin interactions with neighboring groups of protons. Thus the CH_3 resonance is split into a 1:2:1 triplet by interactions with the two C^{13} nuclear spins.

And as I already told you with higher resolution it is possible to identify further splitting of the chemically shifted peaks due to spin spin interaction well, I do not want to go into all these details.

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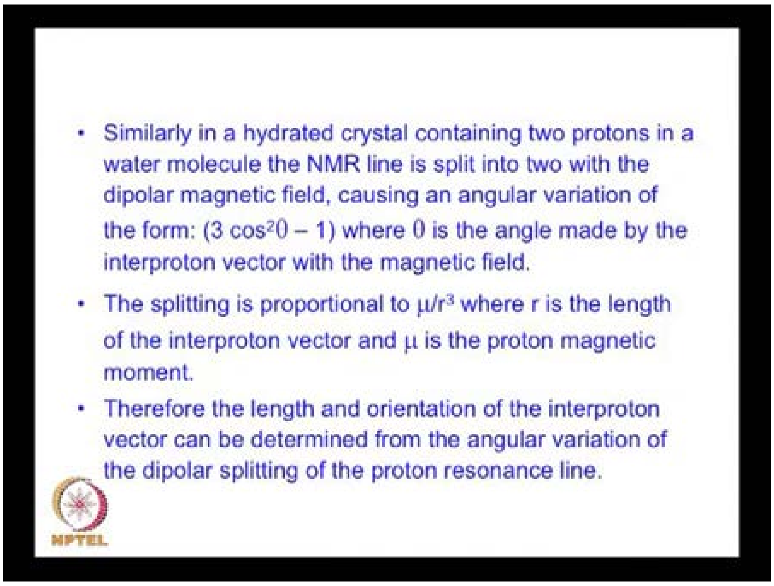

- Similarly in a hydrated crystal containing two protons in a water molecule the NMR line is split into two with the dipolar magnetic field, causing an angular variation of the form: $(3\cos^2\theta - 1)$ where θ is the angle made by the interproton vector with the magnetic field.
- The splitting is proportional to μ/r^3 where r is the length of the interproton vector and μ is the proton magnetic moment.
- Therefore the length and orientation of the interproton vector can be determined from the angular variation of the dipolar splitting of the proton resonance line.

Now, similarly another similar situation occurs in the case of a hydrated crystal, now in a hydrated crystal you have water molecules. So, you have two protons in a water molecule, so because there is an interaction between these two protons there is a dipole dipole interaction which causes the NMR line to split into two.

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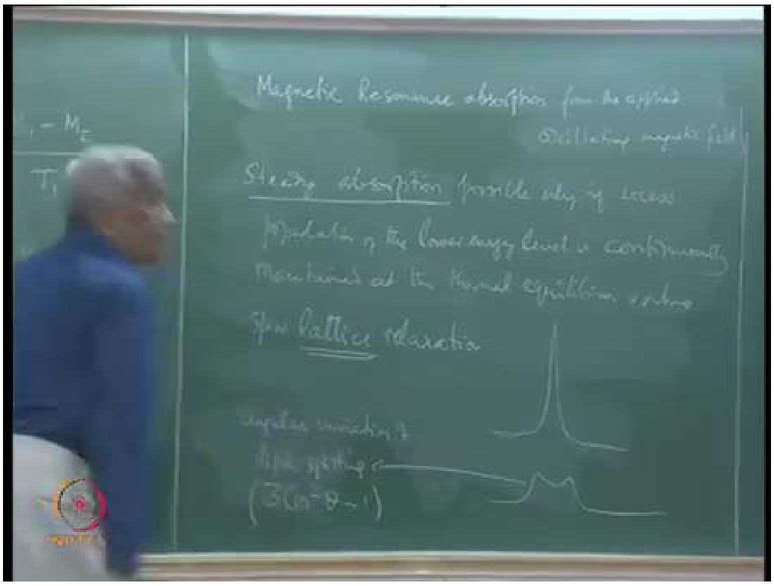

Whereas normally you expect a single resonance peak like this, this splits into two. So, that would be the nature of the absorption, which you observe and this as you change the direction of the magnetic field the direction of the inter proton vector is changed and so, you have an angular variation of this splitting of dipolar splitting. Since it is dipolar splitting this angular variation can be shown to have the form three cos square theta minus 1.

So, by measuring this angular variation one can measure the orientation the inter proton vector inside the crystal and this splitting is proportional to mu by r cube this is the dipolar field, where r is the distance between the two protons. So, one can measure the length and orientation of the inter proton vector from this angular variation.

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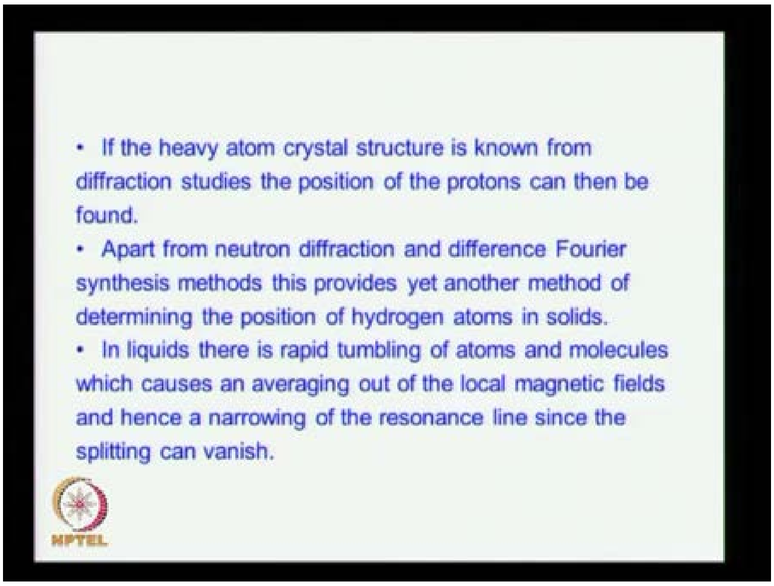

- If the heavy atom crystal structure is known from diffraction studies the position of the protons can then be found.
- Apart from neutron diffraction and difference Fourier synthesis methods this provides yet another method of determining the position of hydrogen atoms in solids.
- In liquids there is rapid tumbling of atoms and molecules which causes an averaging out of the local magnetic fields and hence a narrowing of the resonance line since the splitting can vanish.

And this when coupled with additional crystallographic information from structural data one can even locate the positions of the protons this is as we already discussed this is a rather difficult problem the location of light atoms positions such as proton is normally difficult in x-ray diffraction. Studies usually neutron diffraction is necessary in order to this and neutron defecation is not an experiment which is easily available to everyone. So, NMR provides a an alternative way of determining the position of hydrogen atoms in solids.

Now, this dipolar splitting is determined under the assumption that this spins the two protons are staying fixed, but at any finite temperature in a liquid for example, there is a rapid movement of atoms and molecules, which causes an averaging out of this local fields. And therefore, the resonance field will be narrowed, so it is known as the narrowing due to motional narrowing, so this motional processes also can be studied using such a variations.

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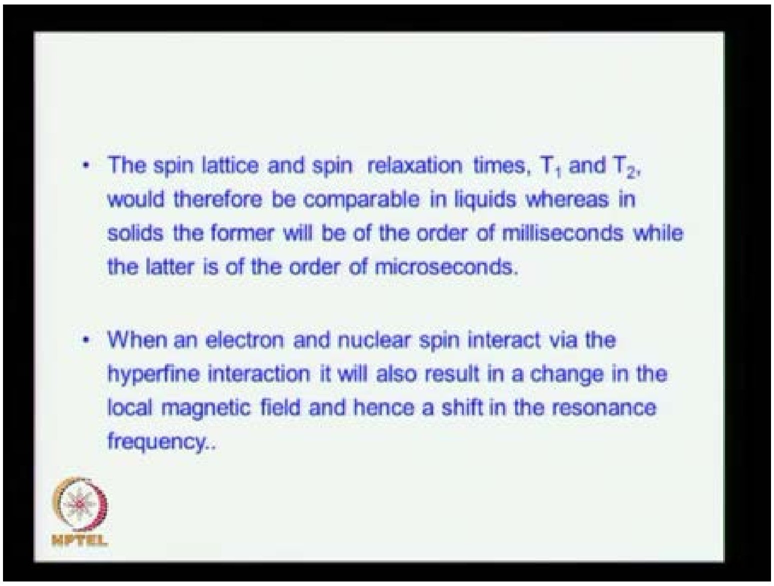

- The spin lattice and spin relaxation times, T_1 and T_2, would therefore be comparable in liquids whereas in solids the former will be of the order of milliseconds while the latter is of the order of microseconds.
- When an electron and nuclear spin interact via the hyperfine interaction it will also result in a change in the local magnetic field and hence a shift in the resonance frequency..

Now, let us a spend a little time looking at electron resonance, in the case of electrons we can have very similar considerations for a observation of an electron resonance, because the electrons in an unpaired electron spin system are have an net angular momentum. So, the resonance process is very similar except that it is shifted out to microwave frequencies for the same fields, but again just like the dipolar splitting due to internal fields. Similarly the electrons interact with nuclei the electrons are nuclear spins interact via what is known as the hyperfine interaction.

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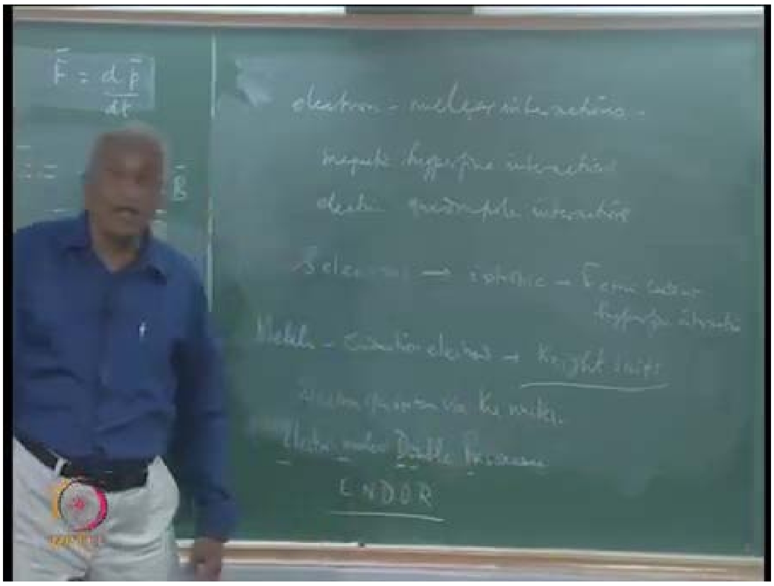

So, electron nuclear interactions they are of two kinds hyper fine interaction magnetic hyper fine interaction and electric quadpole interactions, we will not go into all these, but when an electron and nuclear spin interact via the hyperfine interaction it will again change the local magnetic field and so, the resonance frequency will be shifted.

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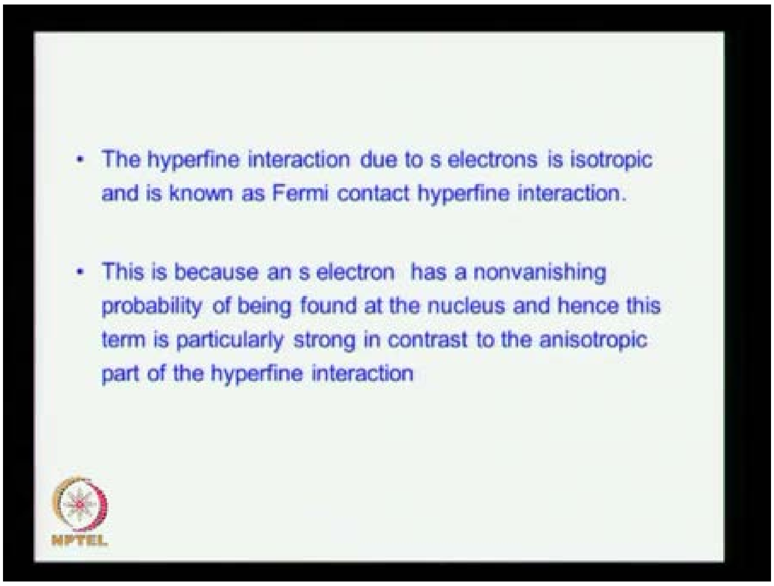

- The hyperfine interaction due to s electrons is isotropic and is known as Fermi contact hyperfine interaction.
- This is because an s electron has a nonvanishing probability of being found at the nucleus and hence this term is particularly strong in contrast to the anisotropic part of the hyperfine interaction

Now, the hyperfine interaction due to s electrons ((Refer Time: 47:14)) which has an isotropic angular distribution is isotropic it does not have an angular variation, this part is known as Fermi contact interaction hyperfine interaction, then you have p electrons and d electrons which have an isotropic hyperfine interaction.

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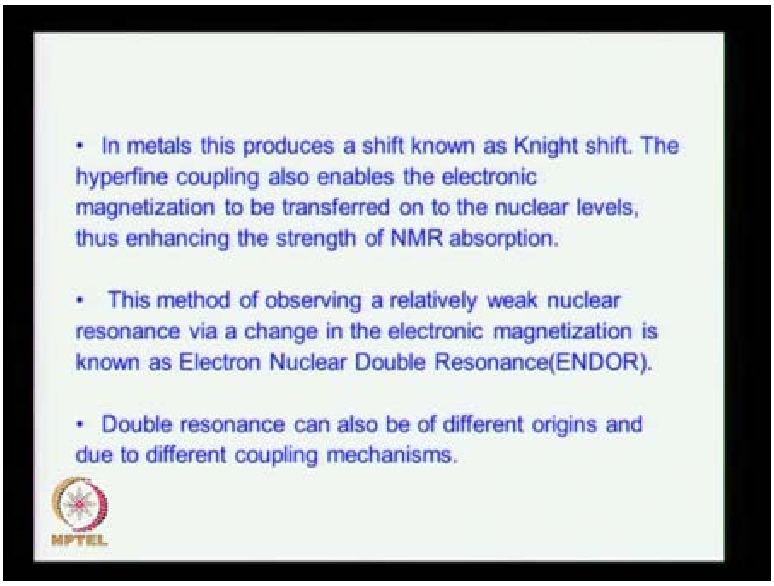

- In metals this produces a shift known as Knight shift. The hyperfine coupling also enables the electronic magnetization to be transferred on to the nuclear levels, thus enhancing the strength of NMR absorption.
- This method of observing a relatively weak nuclear resonance via a change in the electronic magnetization is known as Electron Nuclear Double Resonance(ENDOR).
- Double resonance can also be of different origins and due to different coupling mechanisms.

Both these can be investigated using electrons resonance as well as nuclear resonance in addition in metals we have conduction electrons. So, the conduction electrons again interact giving rise to a local field and this produces a shift in the NMR which is known by the term knight shift. So, by measuring the knight shift this can again tell you about the conduction electrons spin densities now you can also have because of the electron coupling you can polarise the electron spin system or magnetise if you like; why are the nuclei, because there is a coupling between the two system they are interacting.

So, and as we already saw it is much easier to observe electron resonance than nuclear resonance because the energy level differences are much higher. So, the intensities are much stronger here. So, if you can transfer the nuclear polarisation to the electronic system, then you can observe the nuclear transitions via the electron resonance that is known as the doubled resonance technique. In this case it is known as Electron Nuclear Doubled Resonance ENDOR. So, the doubled resonance technique is of great interest because you can use the sensitivity of the electron spin system and the measure a relatively weak spin signal which occurs in the nuclear system via the electronic coupling.

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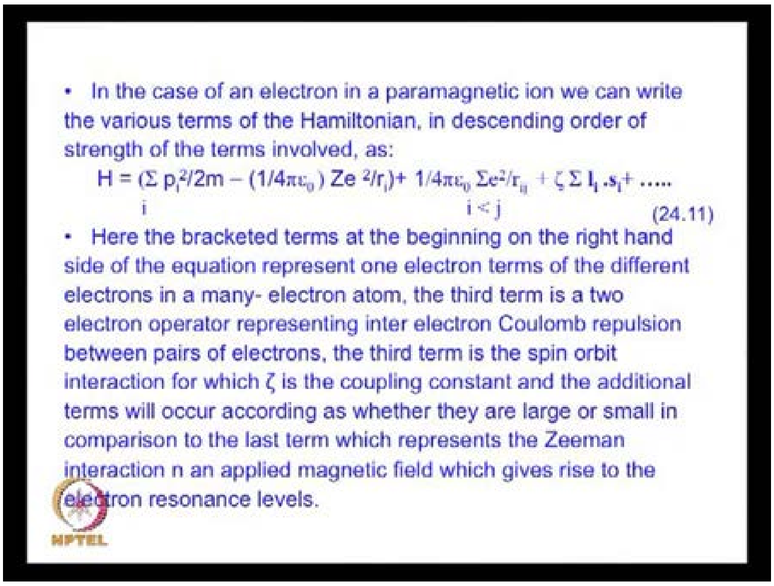

- In the case of an electron in a paramagnetic ion we can write the various terms of the Hamiltonian, in descending order of strength of the terms involved, as:

$$H = (\sum_i p_i^2/2m - (1/4\pi\varepsilon_0)\, Ze^2/r_i) + 1/4\pi\varepsilon_0 \sum_{i<j} e^2/r_{ij} + \zeta \sum l_i . s_i + \ldots.. \quad (24.11)$$

- Here the bracketed terms at the beginning on the right hand side of the equation represent one electron terms of the different electrons in a many- electron atom, the third term is a two electron operator representing inter electron Coulomb repulsion between pairs of electrons, the third term is the spin orbit interaction for which ζ is the coupling constant and the additional terms will occur according as whether they are large or small in comparison to the last term which represents the Zeeman interaction n an applied magnetic field which gives rise to the electron resonance levels.

Now, looking at the electron spin resonance process a little bit closer detail in order to do this.

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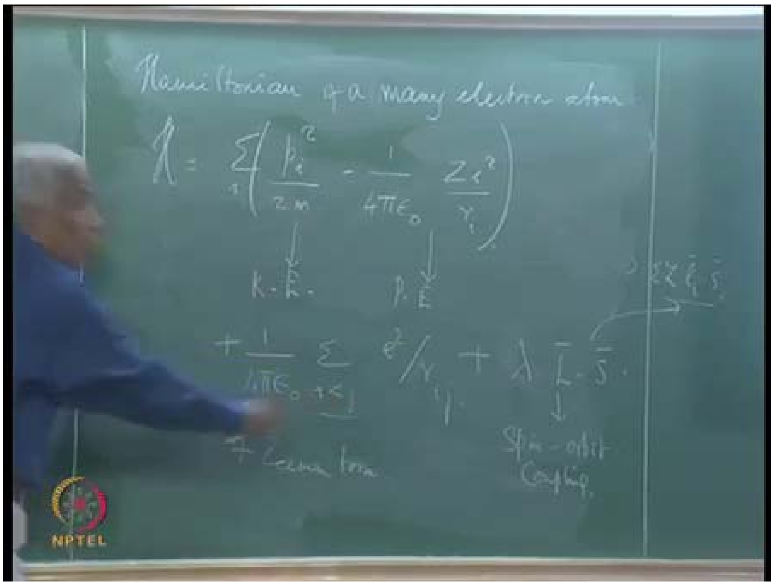

We should start with the Hamiltonian of an electron of a many electron atoms the hamiltonian is sigma pi square by 2 M this is the kinetic energy of the electrons summed over the all the electrons labelled with the index I then we have the coulomb attraction between nucleus and the electron. So, both are the kinetic energy this is the coulomb potential energy of the electron in the presence of the nucleus then you have many electrons. So, you have inter electron repulsion I write i less than j because we do not want to count twice this way we write r 1 2, but we do not write r 2 1.

So, r 1 2 and r 2 1 are the same interactions. So, we do not want to count them twice. So, this is a summation over all such pairs of interactions. So, this is the inter electron repulsion then we have the spin orbit coupling this is the coupling between the electronic spin and orbital angular momentum. Then, we have this is actually a resultant of, then we has the Zeeman field depending on how strong or weak the magnetic field is relative to the other interaction here.

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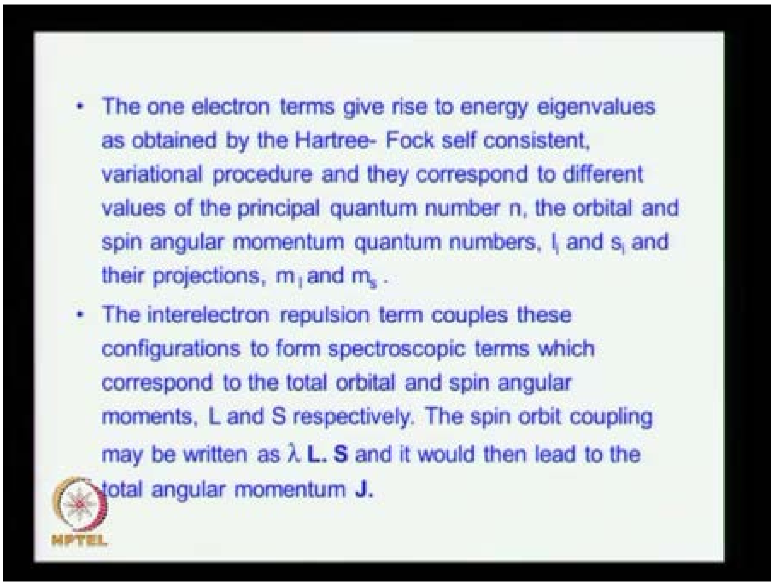

- The one electron terms give rise to energy eigenvalues as obtained by the Hartree- Fock self consistent, variational procedure and they correspond to different values of the principal quantum number n, the orbital and spin angular momentum quantum numbers, l_i and s_i and their projections, m_l and m_s .
- The interelectron repulsion term couples these configurations to form spectroscopic terms which correspond to the total orbital and spin angular moments, L and S respectively. The spin orbit coupling may be written as λ **L. S** and it would then lead to the total angular momentum **J.**

So, this will give you the different terms, which are involved in the Hamiltonian in descending order of energy and then sometimes the spin orbit coupling will be weak in comparison to the Zeeman coupling. In other cases the spin orbit coupling will be strong in comparison to the zeeman term. So, depending on that we have to consider the zeeman term and it is effect on the nuclear electron spin system appropriately.

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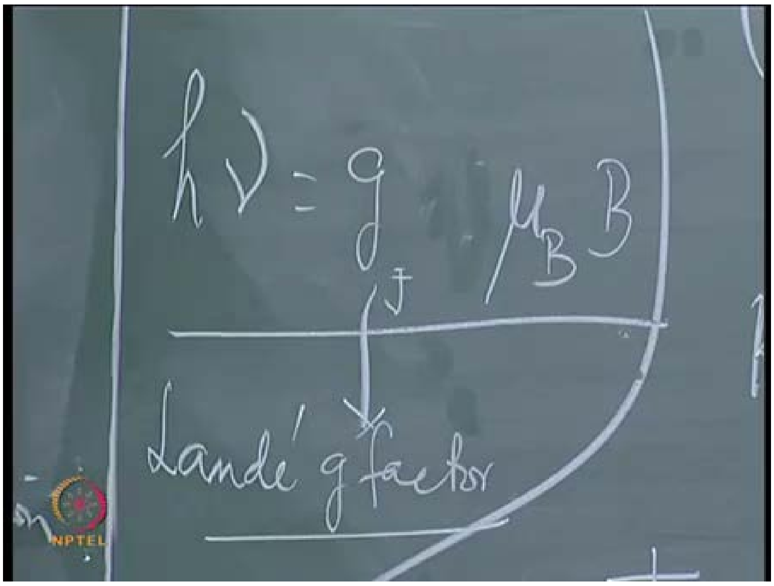

$$h\nu = g_J \mu_B B$$

Landé g factor

So, this will again give you the resonance condition in the form this is the resonance condition where g j is the lande g factor you considered these already magnetic. So, that will be the electron spin resonance condition.

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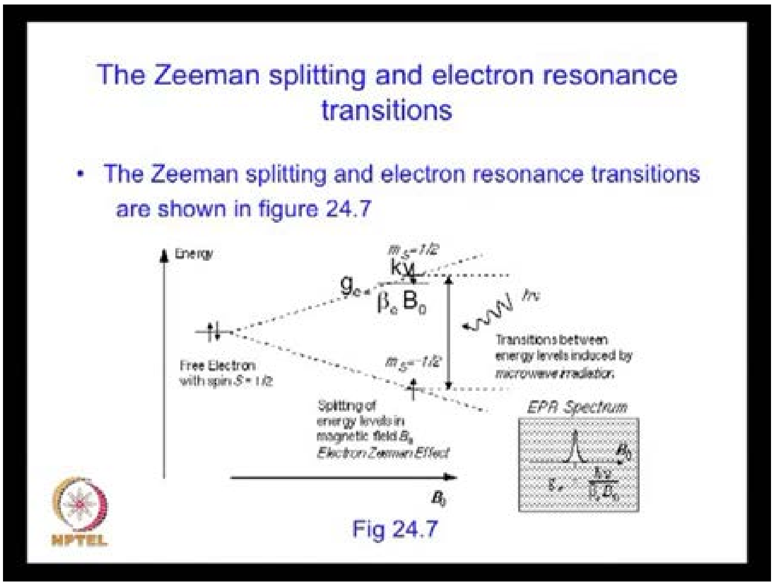

The Zeeman splitting and electron resonance transitions

- The Zeeman splitting and electron resonance transitions are shown in figure 24.7

Fig 24.7

And the electron spin resonance transitions are shown in schematically in the figure where you have a field and the zeeman splitting which is linear splits this as the field is increased and then transitions are induced between the two Zeeman levels adjacent zeeman levels where an oscillating field.

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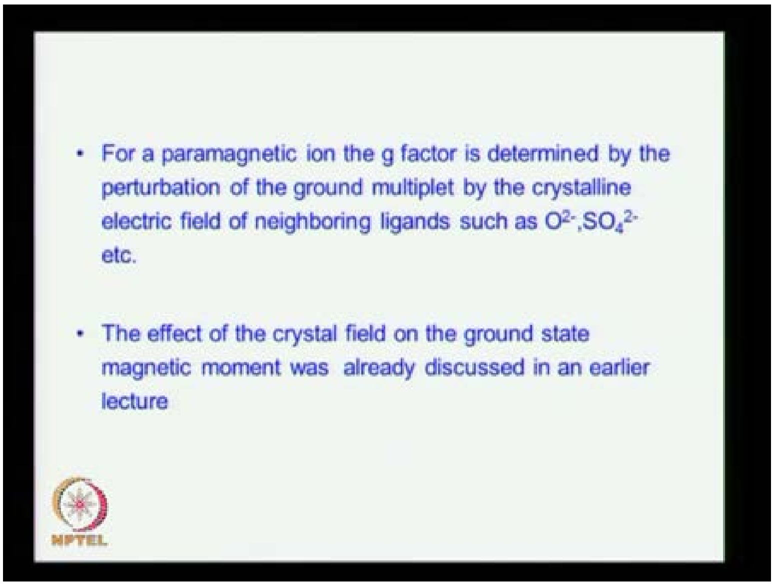

- For a paramagnetic ion the g factor is determined by the perturbation of the ground multiplet by the crystalline electric field of neighboring ligands such as O^{2-},SO_4^{2-} etc.
- The effect of the crystal field on the ground state magnetic moment was already discussed in an earlier lecture

So, the g factor is determined by a perturbation of the, so called ground multiplet by the crystalline electric field of neighbouring ligands as we discussed already such as O 2 minus sulphate and so on. So, the effect of the crystal field is something which we have already discussed.

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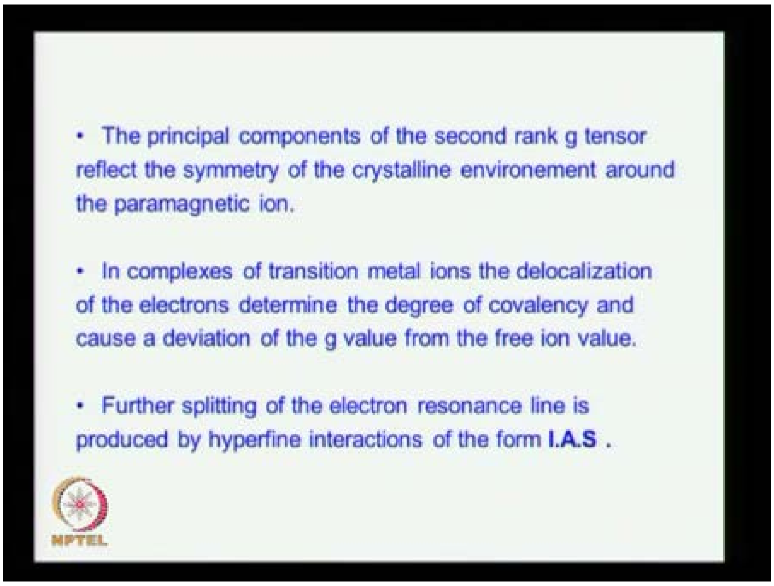

- The principal components of the second rank g tensor reflect the symmetry of the crystalline environement around the paramagnetic ion.
- In complexes of transition metal ions the delocalization of the electrons determine the degree of covalency and cause a deviation of the g value from the free ion value.
- Further splitting of the electron resonance line is produced by hyperfine interactions of the form **I.A.S** .

And therefore, the g tensor is a second rank g tensor a second rank tensor which reflects the symmetry of the crystalline environment around the paramagnet ion. So, you as if you have a microscope to look at the internal crystalline invalent in complexes of transition metal ions, the delocalisation of the electrons we already discussed covalency. This delocalisation determines the degree of covalency and causes a g deviation of the g value from the free ion value and further splitting of the electron resonance line as we already discussed is produced by hyperfine interaction.

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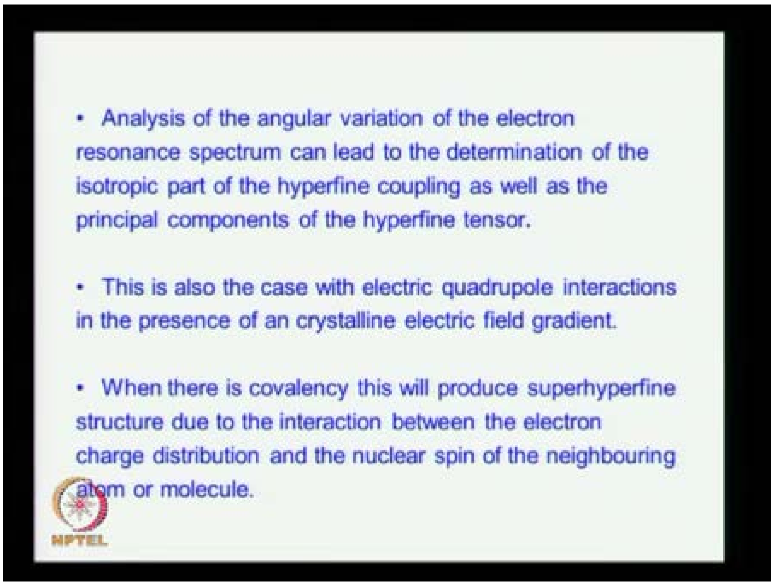

- Analysis of the angular variation of the electron resonance spectrum can lead to the determination of the isotropic part of the hyperfine coupling as well as the principal components of the hyperfine tensor.
- This is also the case with electric quadrupole interactions in the presence of an crystalline electric field gradient.
- When there is covalency this will produce superhyperfine structure due to the interaction between the electron charge distribution and the nuclear spin of the neighbouring atom or molecule.

So, the general analyses of the angular variation or the electron resonance spectrum can lead to the determination of the isotropic part of the hyperfine coupling as well as the principal components of the hyperfine tensor, is also the case with electric quodropolent actions of the presence of the crystalline electric field gradient and when there is covelency this can also produce. So, called super hyper fine structure due to the interaction between the electronic charge distribution and the nuclear spin of an neighbouring atom or molecule, so that is called super hyperfine interaction.

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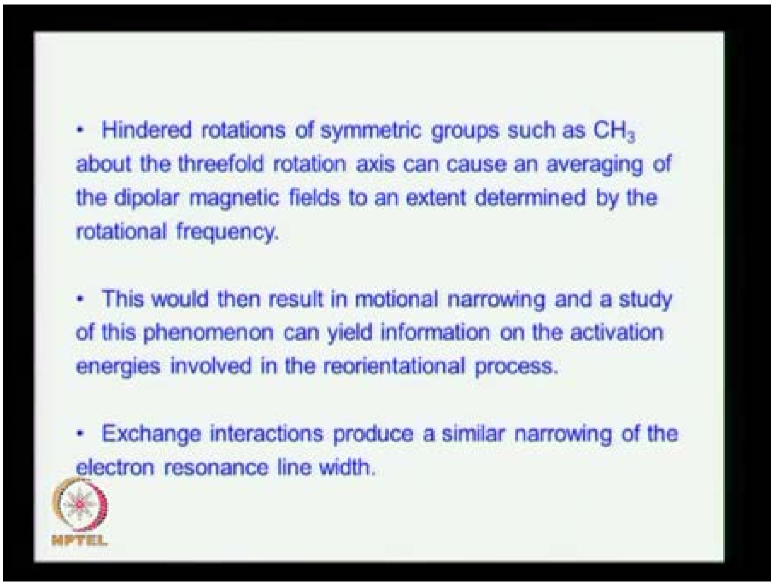

- Hindered rotations of symmetric groups such as CH_3 about the threefold rotation axis can cause an averaging of the dipolar magnetic fields to an extent determined by the rotational frequency.
- This would then result in motional narrowing and a study of this phenomenon can yield information on the activation energies involved in the reorientational process.
- Exchange interactions produce a similar narrowing of the electron resonance line width.

We already discussed how motional narrowing can affect the NMR profile, now we discussed exchange interactions between electron spins and that can produce a similar narrowing of the electron resonance line width, so this is known as exchange narrowing.

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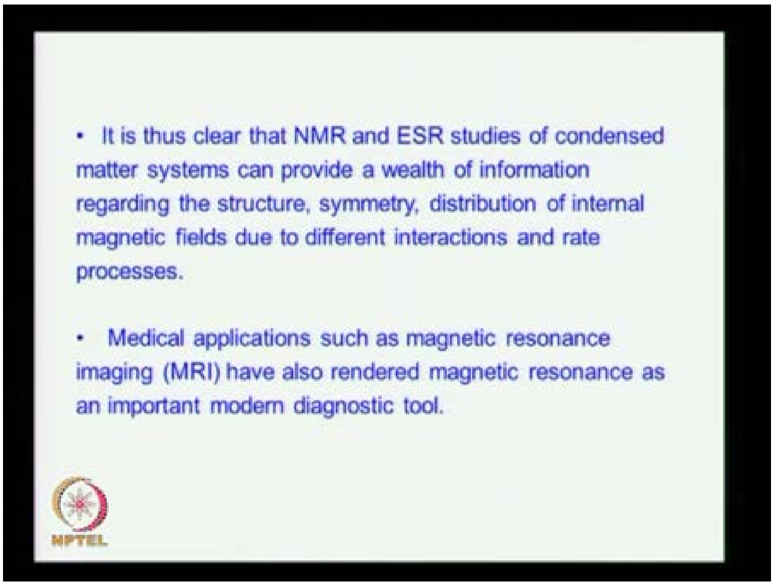

- It is thus clear that NMR and ESR studies of condensed matter systems can provide a wealth of information regarding the structure, symmetry, distribution of internal magnetic fields due to different interactions and rate processes.
- Medical applications such as magnetic resonance imaging (MRI) have also rendered magnetic resonance as an important modern diagnostic tool.

So, thus we clear that NMR and ESR studies of condense matters system can provide a wealth of information regarding the structure, the symmetry, the distribution of internal magnetic fields due to different types of interactions and the various rate processes. Now, I should mention medical applications for example, the Magnetic Resonance Imaging

MRI also entered magnetic resonance is an important modern diagnostic tool; well that is magnetic resonance can provide a very high resolution probe into condense matter.