Experimental Physics - III
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Lecture - 29
Electron Spin Resonance (ESR)

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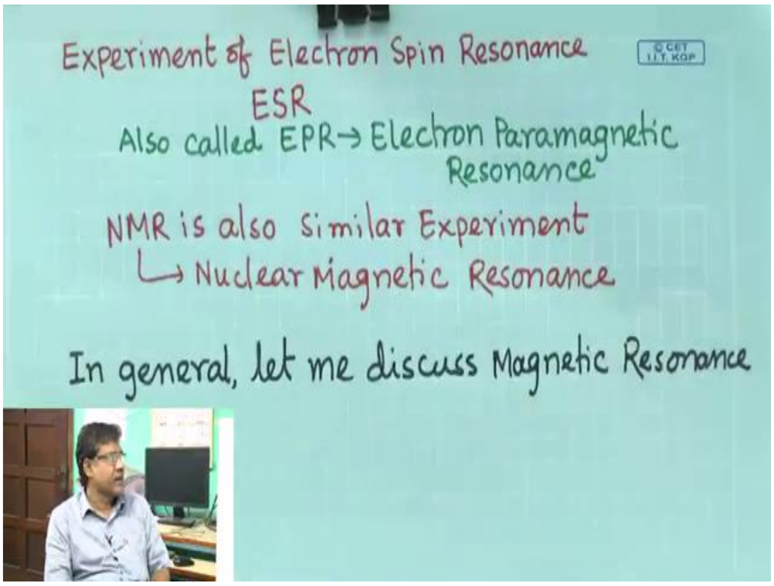

Today I will discuss about Experiment of Spin, Electron Spin Resonance. Electron Spin Resonance it is an ESR. It is also called EPR Electron Paramagnetic Resonance both are same. NMR is also similar experiment; similar type of experiment NMR is Nuclear Magnetic Resonance. It is it is a magnetic resonance. In general, let us discuss, what is magnetic resonance?

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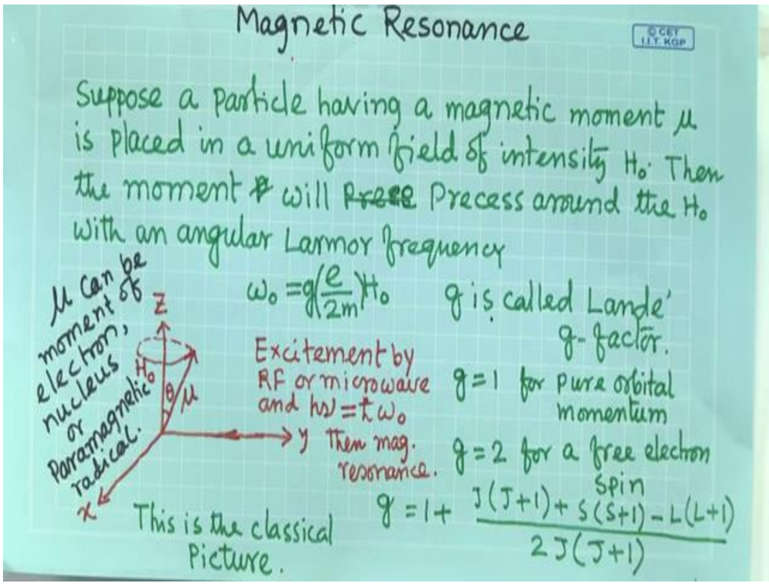

Magnetic resonance suppose a particle having a magnetic moment mu is placed in a uniform magnetic field of intensity H 0. Then the moment will precess around the magnetic field H 0 with an angular Larmor frequency that frequency omega 0 will be g e by 2 m H 0.

g here is called Lande g factor, g equal to 1 for pure orbital momentum. And, g equal to 2 for a free electron. And, for in general the g generally we tell g J that is equal to 1 plus J J plus 1 plus S S plus 1 minus L L plus 1 divided by 2 J J plus 1.

If a magnetic field H 0 is applied say along the Z direction, then magnetic moment with a particular angle theta, it will precess around the magnetic field. This precession is called Larmor precession. Now, if along the y direction, if you apply a very weak magnetic field, if you apply a very weak magnetic field, then what will happen? In addition, this magnetic field is rotated along the y-axis; rotated taking the axis as Z direction, and then this magnetic field is rotating in an x y plane ok.

Then what will happen? This also it will rotate, it will rotate this, and it will rotate this taking this y direction as an axis. there will be another precession, because this one extra field AC field if I give along the y direction, and that field is rotating in a; rotating in a xy plane around the Z axis.

What will happen? This AC field here. It will change AC field will change and these, here whatever rotation was there, here whatever rotation was there. Now, this magnetic moment also will rotate along the y direction. That and is that angle will not be conserved If, this field is not there so all the time it is rotating with this angle theta.

Now, this theta will change, this theta will change, when it will precess along the along the taking this taking this y-axis as axis. It will rotate so; that means, this theta is will change. This is a classical picture. Here the change of angle, change of angle here classically whatever change of angle, that is equivalent to the; that is equivalent to the change of the splitting of the energy levels. That is equivalent to the change of the splitting of the energy levels. Alternatively, it is equivalent to the splitting of the energy level.

at different angle so splitting of the energy level will be will get different energies, energy level will splitted will get different energy sub levels. That sub levels are at different theta. That is the, that is the analogy with the splitting of the energy level.

Here a particle having a magnetic moment mu this particle it can be electron it can be nucleus or it can be some paramagnetic radical. Depending on this particle different magnetic resonance you will see that is one it is electron spin magnetic resonance, or electron spin resonance simply we tell electron spin resonance, that electron paramagnetic resonance, nuclear magnetic resonance. whatever I told this different name. they works on same principle as I discussed here.

to understand this further so we will consider the quantum picture. It will be more convenient, easier to understand. Let me tell this quantum picture of this magnetic resonance. That spin or nuclear that is the we can find in the atom.

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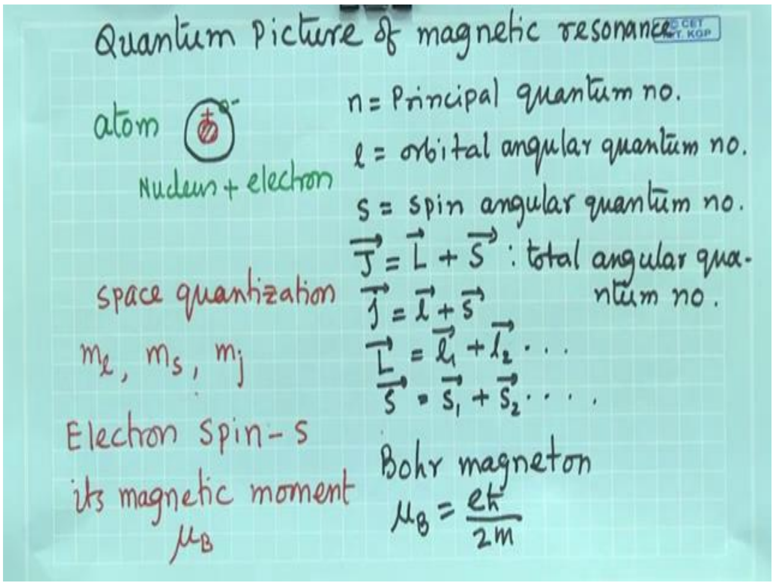

Atom it has a nucleus and electron. Now electrons are in different orbits, similarly nucleus also have protons and neutrons they are in different orbits. for the time being let us not discuss about the nucleus, when we will study the NMR that time I will discuss that, but so let me concentrate here for electron. Electrons are moving in orbit. We specify the electron with some quantum numbers n principal quantum number, l orbital quantum number, and then s spin quantum number.

Then, from L S one can get total J, that total angular momentum J. here I have written capital L and capital S. this L capital L it is the summation of the individual L, l 1, l 2, l 3. Similarly, capital S is for individual s of electron spin up electron S 1, S 2, S 3 etcetera and, for an electron so this total angular momentum small j it will be l plus j. this is the vectorial sum.

Vector model for atomic structure is very successful model. From there this we have considered this quantum number to specify the electrons in an atom. Now, this what about the angular quantum number or angular momentum I showed here. All of them are quantized in space; all of them are quantized in space that is called space quantization.

That it is related with the theta this precession with angle theta for different theta, so it cannot take continuous theta. There is the quantum pictures it can take only some specific theta. That specific theta whatever we are telling. That is because of space quantization of this angular momentum. In addition, that space quantization that we expressed in terms of magnetic quantum number ml for orbital ms for spin and m j for total angular momentum.

for electron spin is S and it is for a one electron it is spin magnetic moment it is magnetic moment is mu B. mu B is called the Bohr magneton and that is equal to mu B equal to e h cross by 2 m. Bohr magneton you know this why from here from this expression you can see, it is a Bohr magneton it depends on the universal constant that e electronic charge, h Planck constant and this m mass of the electron. These are universal constant.

Mu B Bohr magneton also universal constant. that is why we use mu B like electronic charge e. 1 e 2 e 3 e 4 e so we ev use as unit similarly mu be also is used as a unit ok, 1 mu B 2 mu B 3 mu B to express the magnetic moment of an electrons or atoms. the origin of this mu B that is whatever the magnetic moment of an electron of an electron in first Bohr orbit, in first orbit of hydrogen atom.

That is called the Bohr orbit. When an electron in a Bohr orbit in case of hydrogen atom when electron only one electron is there, when it is in this first orbit of hydrogen atom. What is the magnetic moment of that electron orbital magnetic moment of this electron? That value is e h cross by 2 m 1 can derive very easily and that is why it is called Bohr magneton.

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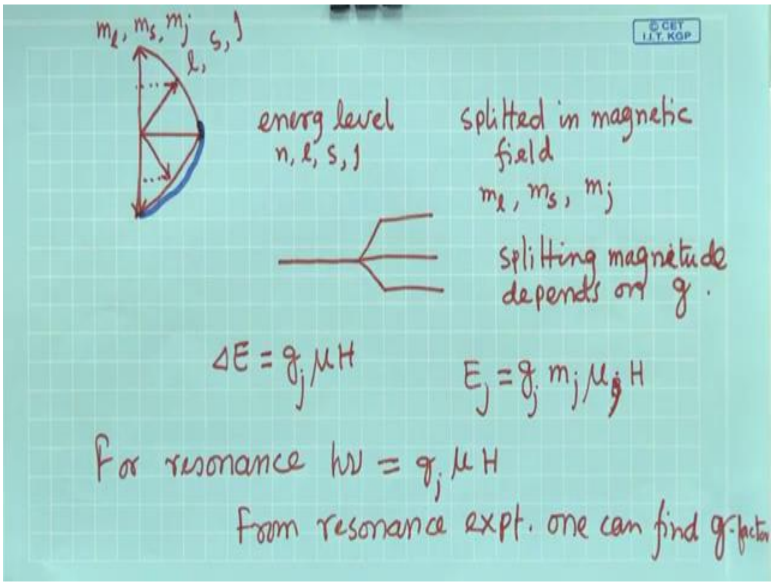

That space quantization as I told this it is showed it is showed with this picture is not properly drawn I think it should be semis semi-circular this angular momentum at different angle theta and so this they so the projection on these on a particular direction space.

That is the magnetic quantum number that gives magnetic quantum number ml ms m j depending on l sj. These due to this space quantization ok, you will get different energy levels. That those energy levels may have same energy, and then we tell it is degenerate states.

Now, this degeneracy is removed when we applies magnetic fields then these energy levels having the degeneracy that degeneracy will be removed means their energy there will be energy will be different so; that means, the energy levels are splitted. it is one energy level will be splitted in a magnetic field say these three it can be, three it can be, 5 it can be 2 depending on the depending on the value of the quantum number.

That splitted that splitted energy that is g j mu H. What a g j this in general I am talking g j? If, you take for one electrons of this will be gs, 1 electron only spin if you take only spin, if you consider then it will be j g s.

If, you take only orbital motion and magnetic moment for that then it will be gl. Otherwise, in generally g j g j that magnetic moment of this particle this mu a mu and this it is placed in a magnetic field H. g j mu H this will be the splitting. in energy level actually this energy of the energy level sub levels energy sub levels is expressed this way g j m j mu j H For different value of for a particular j it will have different m j value.

How to find out m j value that you know? It m j value will be 2 j plus 1 ok, if j is half. m j will be plus half and minus half 2 j plus 1 j is half. It is a two it will be splitted into 2 energy levels if j is 1. It will be m j will be plus 1 0 minus 1 it will be splitted into 3 levels.

Here you can see the splitting magnitude, splitting magnitude will depend on g, splitting magnitude will depend on g. now, from a picture you can see, if you if energy levels are splitted with this g j mu H. Now, if you give some external energy say microwave or the radio frequency wave of radio frequency radiation of radio frequency. Energy will be H nu is the frequency of this wave.

if you apply these this energy in the system, then now this energy will be absorbed by the particle and it will go up to the higher energy levels. Therefore; that means, whatever energy you are giving that is absorbed and the particle have sufficient energy to go to the upper energy level. This will happen when the H nu that energy of the external radiation ok, when it will be equal to the, when it will be equal to the splitting of the energy level separation ok.

Then we tell this condition, when we achieve this condition we tell this there will be lot of absorption. resonance occurs occurred. under this condition when resonance occur, if you can, if we can visualize this, if we can observe the if we can observe this then, then in this condition these two energy will be same.

h nu will be equal to g j mu H. from this so if you can set the resonance condition and that condition if you can observe this condition experimentally, then this relation will be followed and from this from this type of experiment resonance experiment one can find out the value of g factor.

that value of g factor again g can be g l g can be g a g can be g j g can be g n nuclear moment, for nuclear magnetic moment g n. it can be the electron spin resonance, magnetic resonance, it can be the paramagnetic resonance for radical, it can be the electron, it can be the nuclear resonance magnetic resonance.

Today I will discuss I will demonstrate the electron spin resonance experiments spectroscopy it is the spectroscopy. Electron spin resonance spectroscopy. We will consider only spin for this class. Only spin of an electron.

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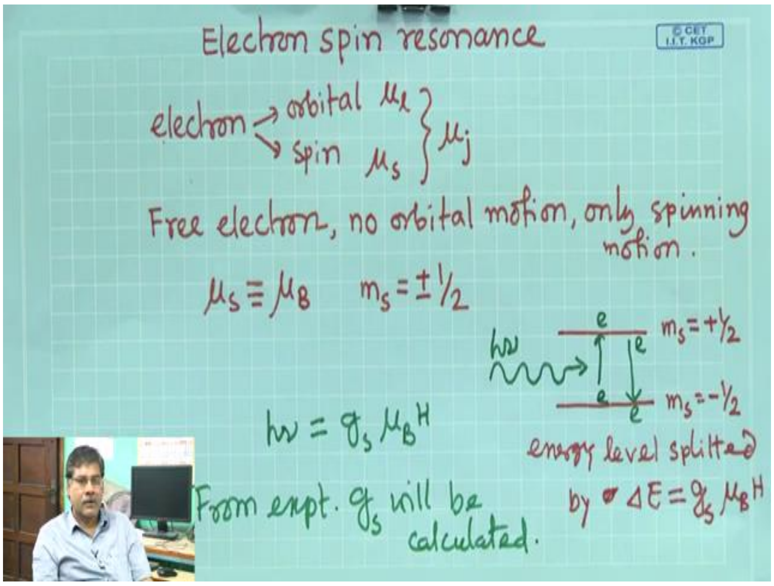

Electron it has orbital motion, as well as it has spinning motion. mu l magnetic moment of corresponding magnetic moment per spin is mu s. In addition, together it will be mu j. for free electron no orbital motion only spinning motion.

Then we can take this magnetic moment mu as a mu s and mu s is it is value in terms of magnetic moment Bohr magnitude is a 1 mu B basically, for 1 electron the spin magnetic moment the value is 1 mu B. we write just mu B. In addition, the in magnetic field energy levels are splitted because of this m s value plus half and minus half.

That energy level will be splitted into 2 for m s equal to plus half and m s equal to minus half. this energy levels that splitting that different this will be del e equal to g s, as I told here if we consider only free electron, then we will consider g s no orbital. no total magnetic moment g s then mu is mu B and this applied magnetic field H.

Now as I told this if you apply radiation from outside either microwave radiation or the or the radiofrequency radiation see it is frequency is nu it is the energy will be H nu. When this energy will match with this difference then these electrons from the lower state, it will go up and after some time it will again come down. It is going to the excited state or from excited state; it will come back to the downstate normal state.

In case of electro, spin resonance. Then from this relation at resonance, if we can set the experiment to achieve this condition, then from that experiment one can calculate g s value. G s value is what is g s value g s value is for pure electron free electron that is two. Now, this value will be varied under different environment. If you consider the electron spin resonance is solid not a free electron say not a free electron.

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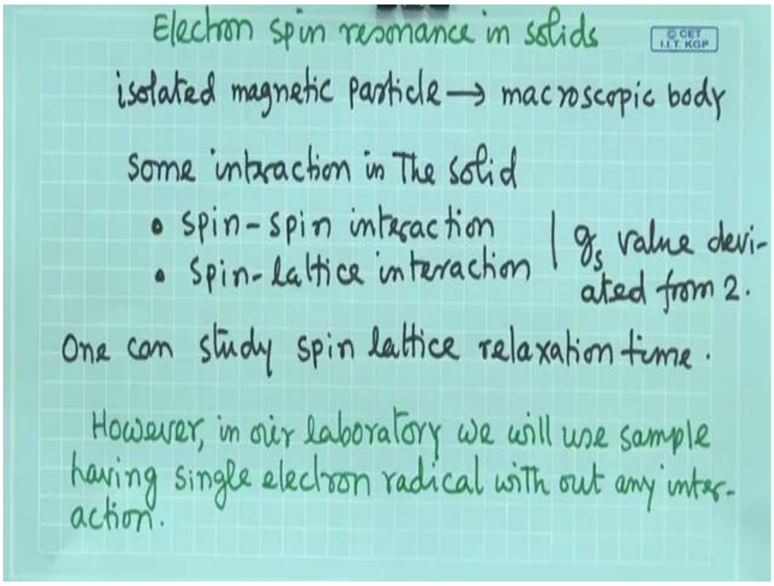

In case of solid isolated magnetic particle is now in a macroscopic body. It has surrounding it has different environment. That spin now it is not alone it has some it will interact with the other spins of the neighbors and there may be spin and lattice interaction.

Due to this interaction the g s value affected and it will deviate from 2 from these type of experiment people can measure g value and deviation of the g value for the ideal condition from isolated condition. one can study the interaction with the environment. That is spin lattice in terms of spin lattice relaxation time we express this interaction.

So; however, in our laboratory we will use sample having single electron, having single electron radical without any interaction. It is a as if it is a just like free electron that type of sample we will use. Generally we use the; we use the DPPH sample.

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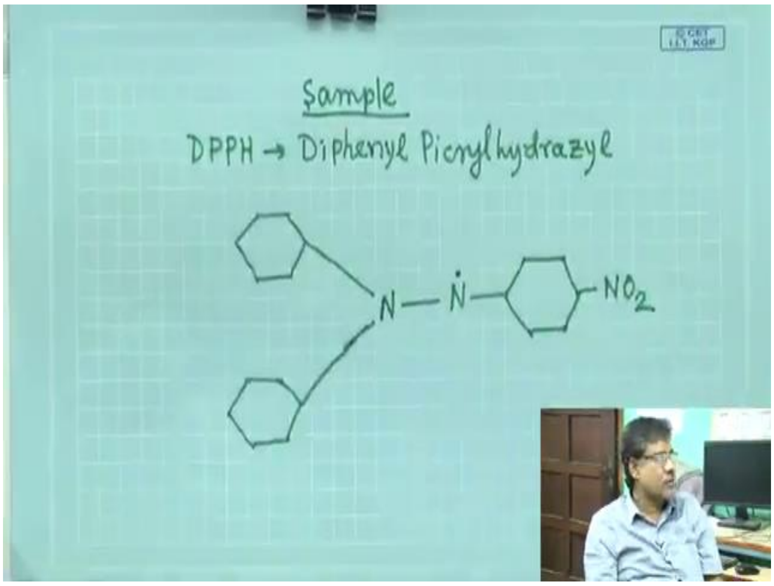

In our laboratory or most of the laboratory, it is used. It has. This is the; this is the it is Diphenyl Picryl hydrazyl, so DPPH. it is chemical structure is like this. Here you can see a nitrogen. It has a single electron; it has an unpaired electron, single electron ok.

In this sample as if this it is a at this electron is free electron almost free electron. It is a in this sample DPPH sample one can treat that whatever electron are there. There their free electron so g value we expect that it will be around 2. We will do experiment on this sample and we will measure the g value. This, if we go for measurement, if we go for measurement, whatever theoretical discussion I have done.

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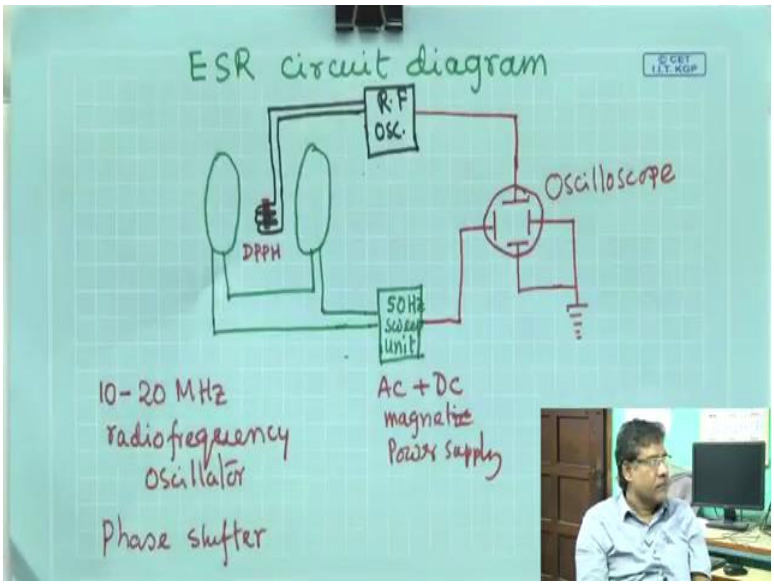

From there that environment that type of experimental setup we have to; we have to; we have to install. We need magnetic field; we need magnetic fields. One can use electromagnet.

For teaching laboratory we here we will use a Helmholtz coil. Two coils so their separation is will be equal to the radius of the coil then one can get the uniform magnetic field between these two coils. For small field one can use the Helmholtz coil and at the center of this on the center axis we passing through the centers of these two coils. Now, middle at the middle point of this axis we will put the sample DPPH ok.

Now our sample is at the sample is in the magnetic field. Now, here you can see this there is an induction coil around the sample, around the sample. In addition, this is R.F oscillators. From this RF oscillator we will excite the sample with RF radiation ok.

Our sample now getting magnetic field as well as it is getting the radio frequency of right. Radio frequency of it is the energy is H nu and the magnetic field, if magnetic field H is applied, and then the energy splitting will be energy splitting will be as I showed that g s mu B H ok.

We have to vary one of them; we have to vary one of them to get the resonance means the H nu has to be equal to the energy splitting of the energy levels. To get that condition one has to be variable, one of them has to be variable and then when they will be equal then that resonance condition will be occurred. In addition, that resonance condition will be observed with an oscilloscope, it will be observed in oscilloscope.

Here in Helmholtz coil we will apply a DC voltage, we will apply a DC current. Corresponding DC magnetic field we will get, now we will sweep this magnetic field with 50-Hertz frequency. DC now AC component will be superimposed on that. It is DC and AC magnetic field we will get the sample will get this magnetic field.

Now you can imagine there for DC field. The splitting is this now, due to AC component, now the splitting, now it is it will varied it will varied. Splitting of the energy levels it will vary like this now, if I apply these radiofrequency radiation on the sample it is energy is fixed for a particular mu.

Now, that mu H nu that energy will match with some energy separation as it is varying. magnetic field is varying means energy levels daily are varying we are varying the splitting of the energy levels keeping the keeping the radiation radio frequency radiation of constant energy.

Due to the variation of the magnetic field when the energy of this H nu will be equal to this splitting of the energy level. At that point there will be absorption, there will be absorption and that absorption here the circuit is there.

There is a detector and this amplifier, I have not shown here. Whenever the energy will be absorbed by the sample. Corresponding signal will get and that signal is given to the y plate of the oscilloscope. In addition, the variation of the magnetic field that signal will be given to the x plate of the oscilloscope ok.

In oscilloscope, this resonance condition the resonance phenomena we will observe. That is the simple ESR circuit diagram and this diagram we will use in our experiment.

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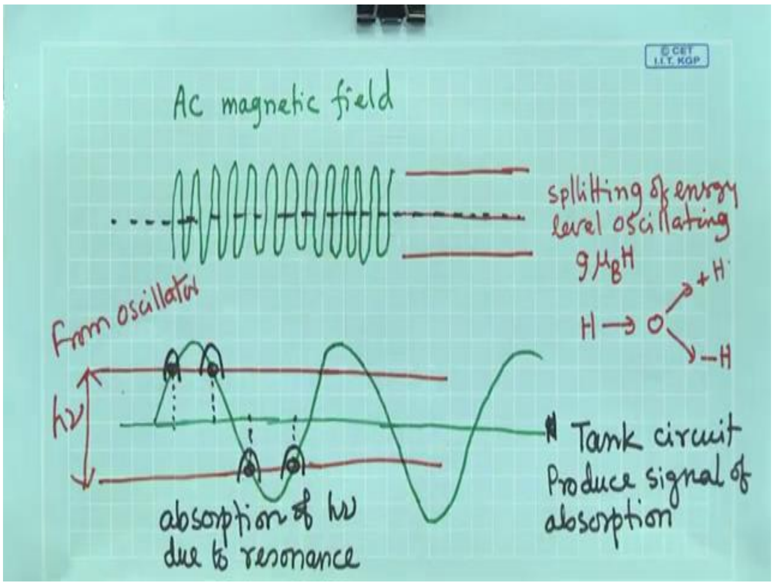

As I described AC magnetic field with respect to a DC. AC magnetic field it is a varying with this particular frequency, it is a generally in our laboratory we will use 50 mega Hertz 50 Hertz, simply 50 Hertz.

Now, due to this variation of the magnetic field the splitting of the energy level will vary splitting of the energy level will vary. The from oscillator H nu that radiation it has if this is the energy level this is the energy. If I express by this level and this level. If this is the magnetic field. The splitting of the energy levels will vary in similar way this H nu will be equal is for a one cycle of the magnetic field. This energy H nu will be equal to the splitting of the energy level at the 4 point, this point, this point, this point and this point.

At this 4 point for a one cycle 4 times energy will be absorbed and corresponding signal corresponding signal will go to the cro y plate. There we will see a peak kind of things we will see a peak kind of things like. 4 peaks we will see. Now, phase shifter is there changing the phase shift we can make this 4 peaks into 2 peaks, 4 peaks into 2 peaks. From these 2 peaks.

In CRO along the y-axis, we have applied the magnetic field and along the x axis we have applied the radiation and then corresponding signal is coming to the CRO y-axis.

There whatever these peaks 4 peaks using the phase shifter we will make them coincidence coincide these two with the other two. Ultimately, we are getting 2 peaks.

peaks peak we will see here we can see peak we will see that whatever field, other peak we will see other peak we will see at a or x axis that are away from this first peak.

Initially what we have to do initially we have to; we have to adjust the x gain of the CRO to make them make this make the peak, make the peak, with some at larger distance. That distance we can express in terms of divisions ok.

If say these are number of divisions are P. this P is total number of this we need to calibrate the magnetic field. this corresponds to the magnetic field Now, for resonance condition whatever peak we will get; we will get that peak separation it will depend on the it will depends of this on this energy you know.

If this energy see this it is lower. You will see the separation or higher, if this H nu is higher. They will be closure that again peak to peak that separation, if this number of division, if it is Q during the resonance, if it is Q. that total separation p it was for an initial magnetic field H and that field is known to us and for that field that magnetic field. Total division was P.

Now, for q division what will the field? Q by P if you multiply this factor with the magnetic field then you will get field for resonance that if it is H 0. Your H 0 will be this separation of these 2 peaks along the x-axis. That value from CRO itself we can find out ok.

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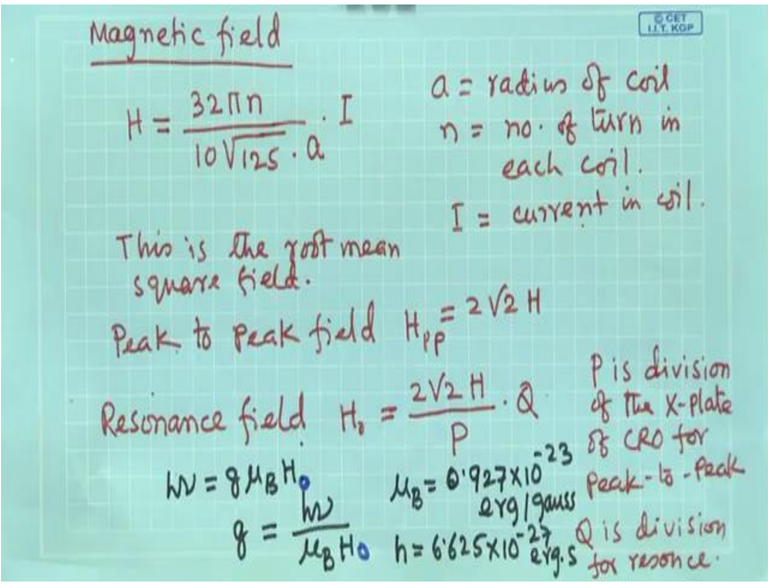

is this circuit diagram I showed you magnetic field H that is from Helmholtz coil it is formula is 32 pi n divided by 10 square root of 125 this into a is the radius of the coil into I. a is in denominator I is in numerator. In addition, this n is the total number of turns in each coil I is the current coil ok.

One can calculate the magnetic field using this formula for a particular current. For this field, what is the; what is the total number of division between 2 peaks. That that we have to note down that field is calibrated with the number of division of the of the y-axis of CRO ok, if it is P, then for our resonance condition. What will be the field counting that is that is number of division if it is Q that one can find out one can find out.

here these values is the root mean square value in case of AC field but peak to peak field peak to peak to peak that from CRO that will measure that one basically. Relation between the peak-to-peak fields with the RMS root mean square field. These 2 square root of this RMS value of field H. you are measuring this from there, you can find out H.

Now, that H for that H, for that H during resonance if this peak separation are Q division. Then the P division was for these value peak to peak, because we are measuring peak to peak. This value, this value for this magnetic field that was a P division. Part division what is the field for Q division then you can find out at resonance condition. That will be H 0.

We have to experimentally, we have to find out these P and Q P and Q measuring the just from the peak-to-peak value of the magnetic field. Before resonance condition what is the magnetic field applied from their P division and for a particular H nu this radiation RF radiation what is the peak to peak value for the for this resonance condition, that division. If, it is Q then we will be able to find out the magnetic field at a resonance condition and then from this equation it should be H 0 it should be H 0 not H.

One can find out one can find out the g value. In addition, mu B value I have written here H value these are standard value. This is the experiment electron spin resonance experiment will perform in the in our experiment based on our discussion in next class.

Thank you.