Principle and Applications of Electron Paramagnetic Resonance Spectroscopy

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Lecture – 02

Introduction to EPR Spectroscopy

Hello there, see in our last lecture we have seen that Uhlenbeck and Goudsmit made a very bold proposition that electron has an intrinsic angular momentum that is called electron spin angular momentum and that explained a host of experimental observation.

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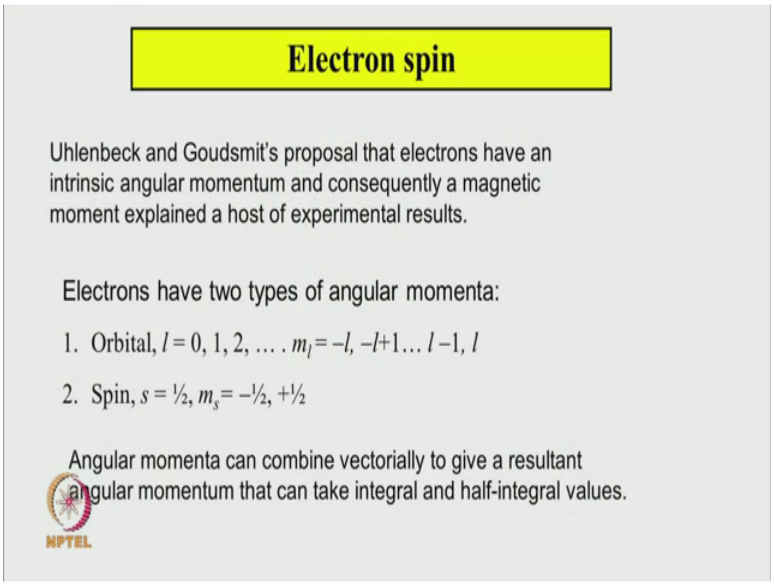

Electron spin

Uhlenbeck and Goudsmit's proposal that electrons have an intrinsic angular momentum and consequently a magnetic moment explained a host of experimental results.

Electrons have two types of angular momenta:

1. Orbital, $l = 0, 1, 2, \ldots$. $m_l = -l, -l+1 \ldots l-1, l$
2. Spin, $s = \frac{1}{2}$, $m_s = -\frac{1}{2}, +\frac{1}{2}$

Angular momenta can combine vectorially to give a resultant angular momentum that can take integral and half-integral values.

So, here we say that now electron can have 2 types of angular momentum that is orbital angular momentum and spin angular momentum and according to Bohrs model orbital angular momentum takes only integral values one and spin angular momentum.

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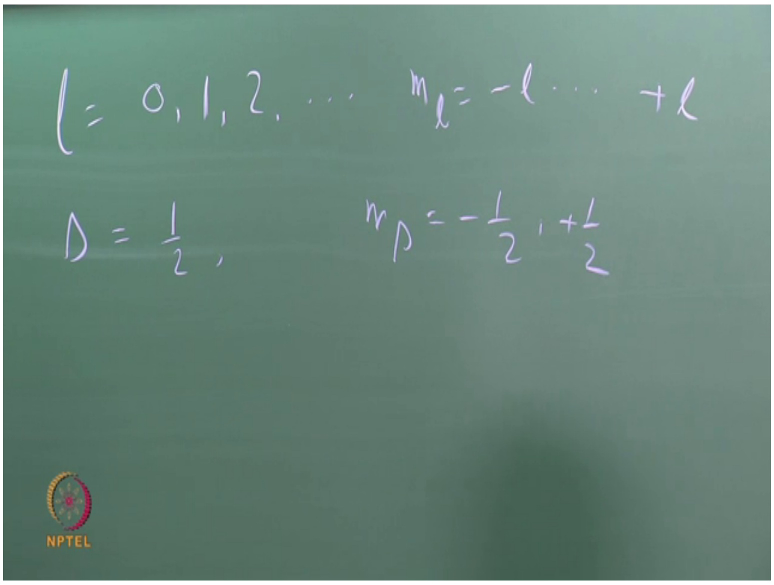

$l = 0, 1, 2, \ldots \quad m_l = -l \ldots +l$

$s = \frac{1}{2}, \quad m_s = -\frac{1}{2}, +\frac{1}{2}$

Now, according to uhlenbeck and goudsmit takes only half see component of this will be m of l minus l to plus l and component of this spin angular momentum we will write s equal to minus half and plus half. So, angular momentum is a vector quantity it has certain direction and this way or that way if the spin component is minus half or plus half orbital angular momentum also is a is a vector quantity. So, this can take various components depending upon the value of this and correspondingly different directions.

So, these 2 angle momentum which are vectors they can now be added to generate a net angular momentum and that kind of various combination it can take integral values or half integer values depending on this And let us see how this explains the various experimental observation.

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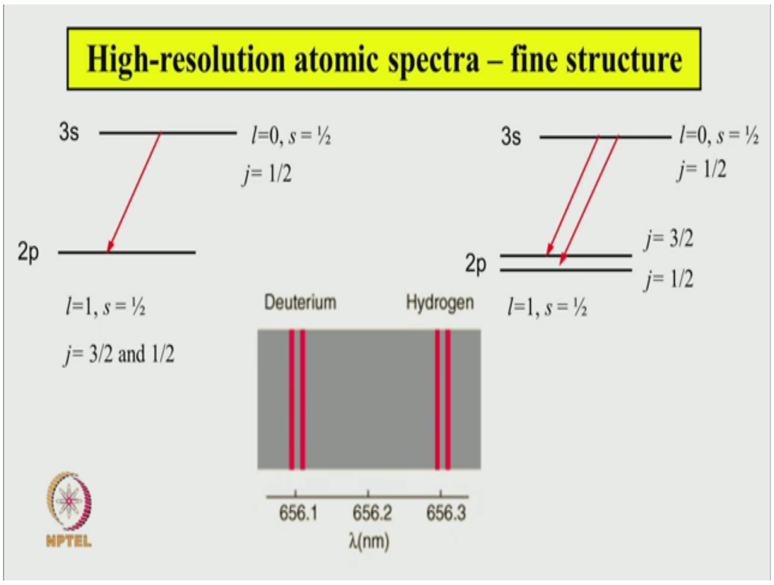

High-resolution atomic spectra – fine structure

Last lecture I showed you the fine structure of spectrum of hydrogen atom and deuterium atom here 3 s and 2 p were connected by only 1 transition.

Now, this one equal to 0 for 3 s and spin s is half together can give rise to total angular momentum of j equal to half. Similarly for 2 p state l equal to one and s equal to half this 2 or angular momentum combined together to give rise to value of j which is 3 by 2 and half. So, these 2 now can have energy level which is shown on the right hand side. So, earlier 3 s and 2 p or connectable one transition because of this 2 p can have 2 types of total angular momentum j equal to 3 by 2 and j equal to half. Now, I have 2 transitions.

So, these 2 transitions are actually the what is seen in the spectrum given by deuterium and hydrogen. So, these are the fine structure and how easily this can be explained with introduction of another angular momentums s, which takes value of half. The Zeeman Effect the splitting of spectral lines in the presence of magnetic field also can be now easily very easily explained by these 2 possible orientations of the magnetic moment in a magnetic field.

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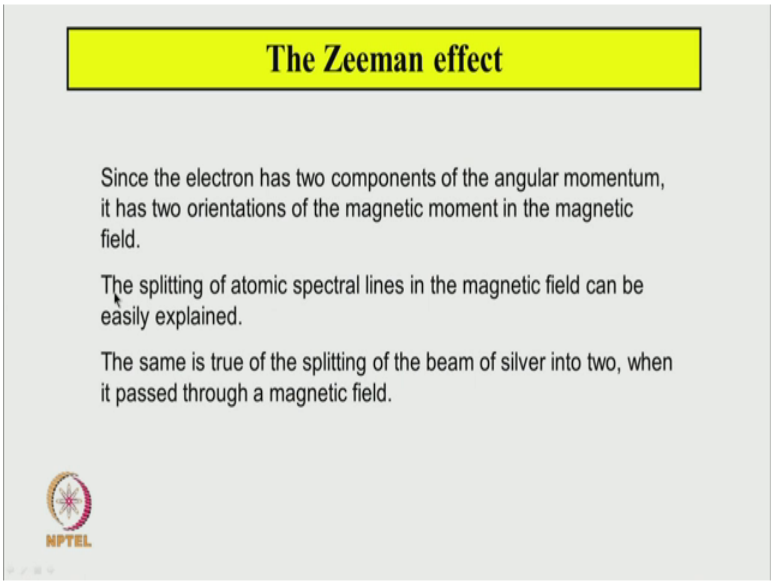

The Zeeman effect

Since the electron has two components of the angular momentum, it has two orientations of the magnetic moment in the magnetic field.

The splitting of atomic spectral lines in the magnetic field can be easily explained.

The same is true of the splitting of the beam of silver into two, when it passed through a magnetic field.

The same is true in the case of the Sterngerlach experiment with silver atom split into 2 is origin again the same that spin angular momentum takes 2 values plus half and minus half gives 2 component of magnetic moment at this cause extra beam to splits into 2.

So, you see how all these experimental results can be explained based on this existence of electron spin.

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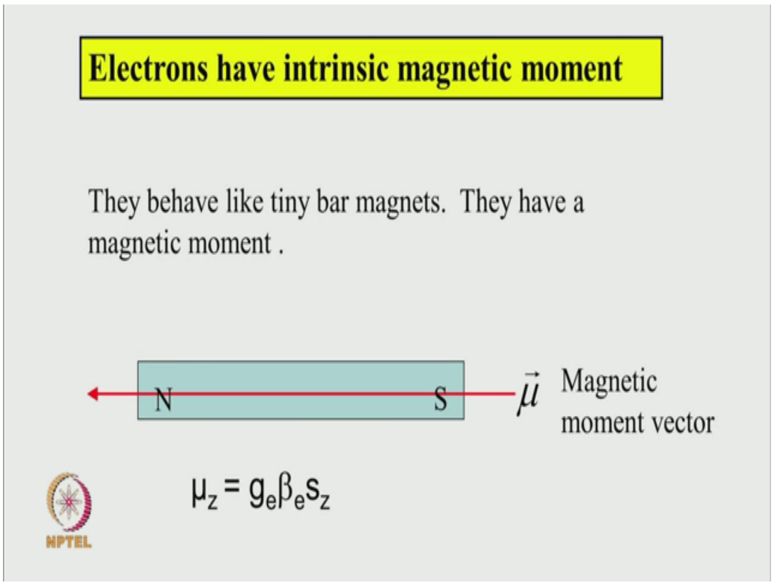

Electrons have intrinsic magnetic moment

They behave like tiny bar magnets. They have a magnetic moment .

Magnetic moment vector

$$\mu_z = g_e\beta_e s_z$$

So, electron has therefore, an intrinsic magnetic moment. So, they behave like a tiny bar magnet. So, the bar magnet has a magnetic moment given by a mu sin mu and it is direction goes from south to north and this is a vector quantity now see the origin of magnetic moment and the angle momentum that we are intimately related the relation is given by this mu z is equal to g e beta e S z where mu z is the component of the magnetic moment vector in a given direction.

g e is a proportionally constant called the g factor beta e is Bohr Magneton and Sz is the component of spin angular momentum.

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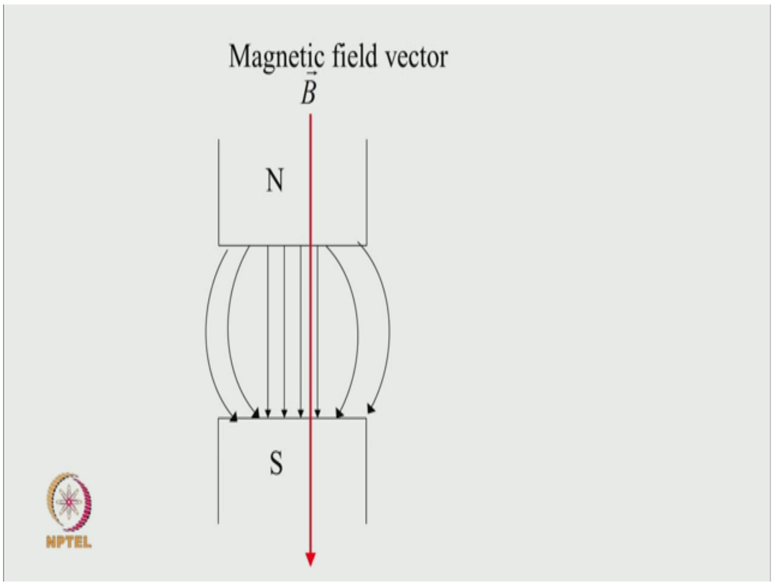

Magnetic field magnetic field also is a vector quantity it shows you the direction of the magnetic field lines that starts from north pole and goes to south pole this the way it is. So, the magnetic field vector direction is given by this red arrow.

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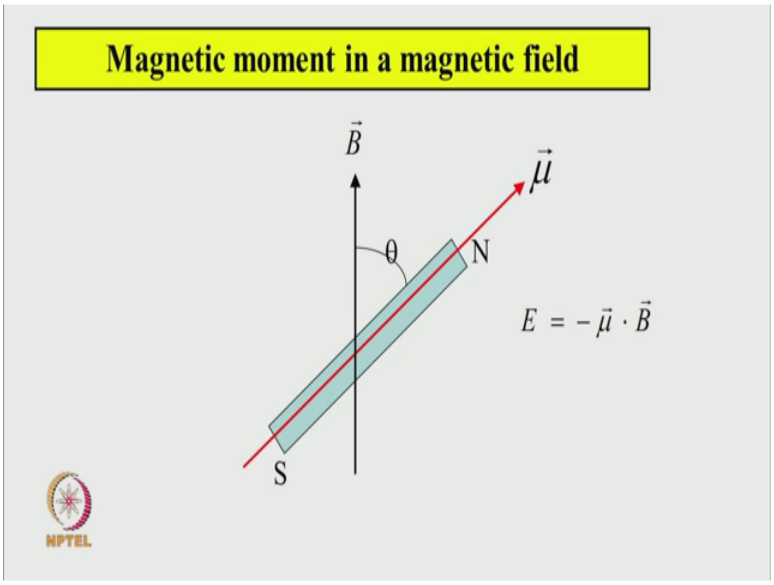

Magnetic moment in a magnetic field

$$E = -\vec{\mu} \cdot \vec{B}$$

So, I have a magnetic moment and a magnetic field if I place them in a magnetic field then what happens they will of course, orient according to the allowed value of the angular momentum.

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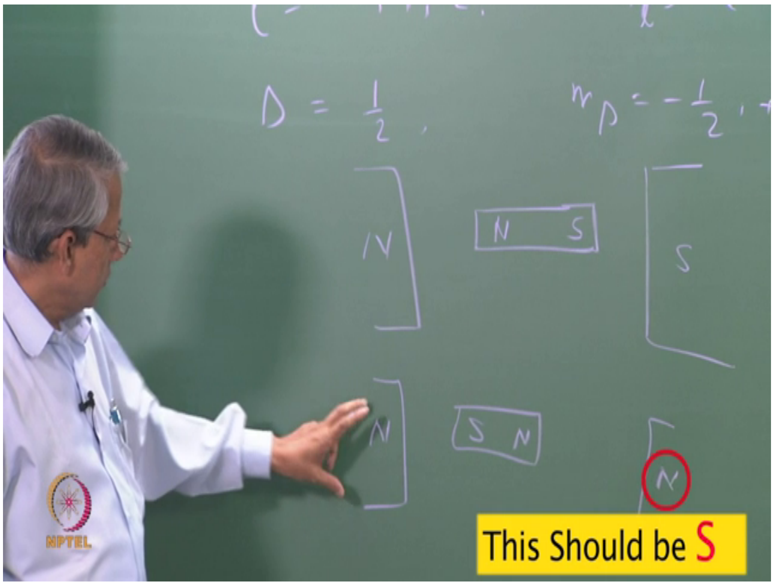

If we take a ordinary magnet see this north pole and south pole if I place in a magnetic field which is this way north and south and you of all of you have experienced that a north facing north, and south facing north, this is not the energetically favorable system what is favorable is that 2 of this bigger magnet.

So, this becomes the lower energy state. So, this is the state this magnet is going to take naturally, but then if I have to turn it this way then I need more energy because this 2 will repel.

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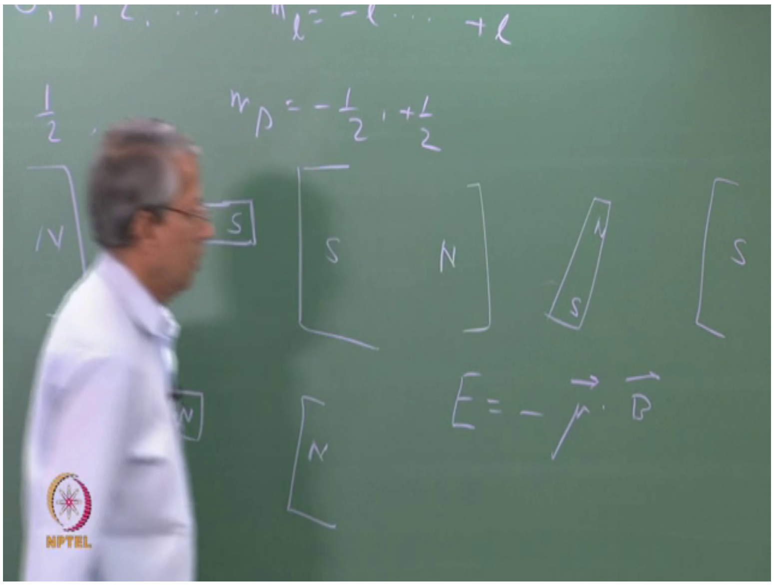

But classical magnetic field classical means the Macroscopy method normally you can see that can take any possible orientation. So, I can. In fact, have this also possible. So, energy of this will be somewhat intermediate between this and that is the least energy the highest energy this is the energy which is intermediate.

The energy E is given as the scalar product of the vector B and the vector mu. So, this is of course, depending on the angle that this magnetic field vector makes with the magnetic moment of the magnet.

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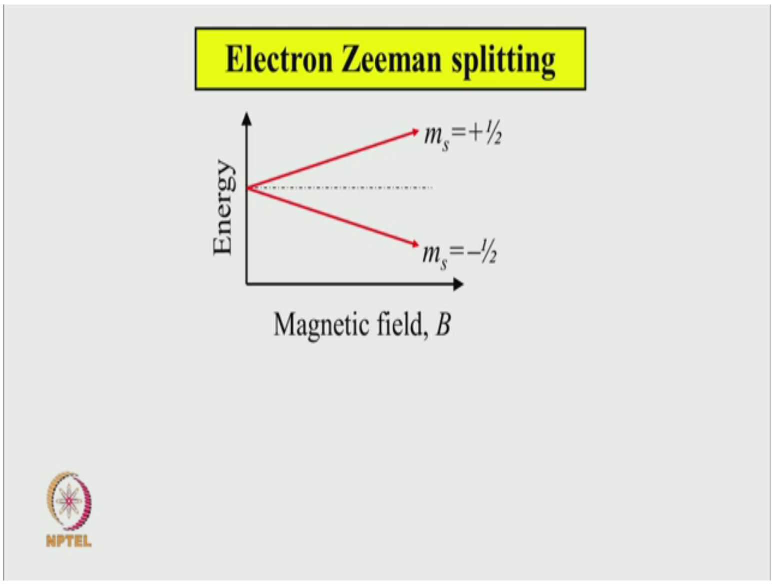

Electron Zeeman splitting

So, classically any such orientation is possible, but for microscopy particle that has been now shown by Uhlenbeck and Goudsmit experiment interpretation and the splitting of silver particles that only 2 orientations possible here. So, because the angular momentum vector takes a 2 while spin angle momentum specifically.

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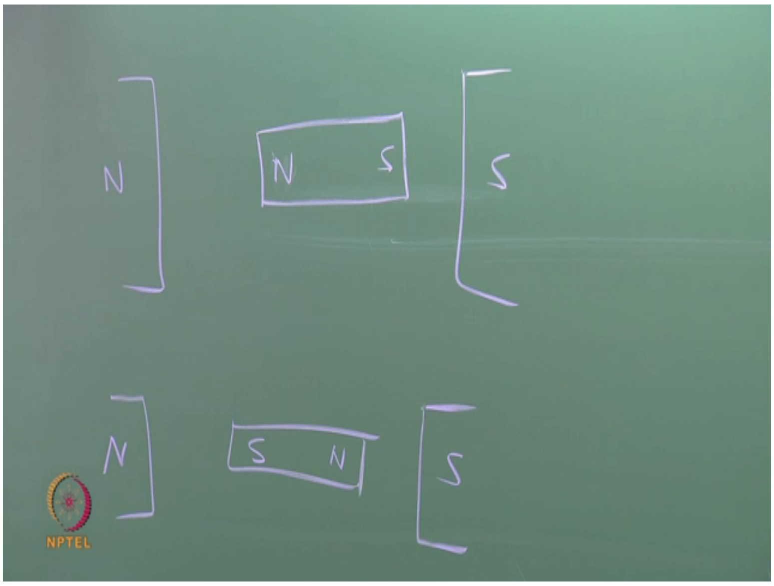

So, even though all these are possible classically for this microscope magnet I only have these possibilities, well higher energy configuration or arrangement other one is lower energy arrangement corresponds to m is equal to minus half or m is equal plus half. So, this is now shown in this diagram here. So, for electron spin in a magnetic field has this type of 2 energy levels which are characterized by the m s equal to minus half or m s equal to plus half this is the electron Zeeman splitting.

Now, I see of course, the splitting the energy difference between these 2 states with m s equal to plus half or a m s equal to minus half is this depend on the strength of the magnetic. It is of course, very obvious if the strength of the field is small the splitting will be small, if the strength is large, splitting will be large the splitting changes linearly with the magnetic field.

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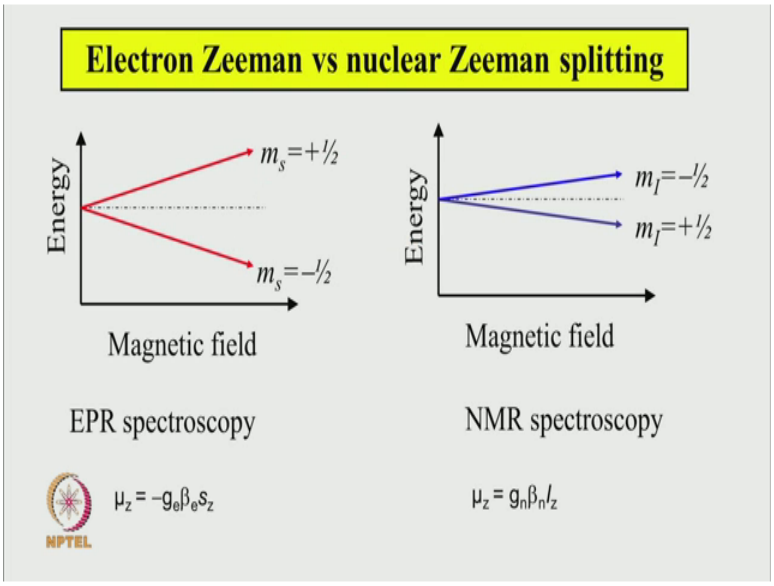

Electron Zeeman vs nuclear Zeeman splitting

EPR spectroscopy

NMR spectroscopy

$\mu_z = -g_e\beta_e s_z$

$\mu_z = g_n\beta_n I_z$

So, I said in the last lecture that n m r and EPR electron parameters resonance and nuclear magnetic resonance are very similar in their characteristic.

So, many nuclei have magnetic moment and particular proton for example, who is also a spin half system it nuclear spin is half on the right hand side the energy of a proton for example, when placed in a magnetic field the splitting is shown here plus equal to plus half and when m I equal to minus half the left hand side the same splitting as shown earlier is also shown that the electron spin in a magnetic field splits into minus half and plus half, but the difference is in the strength of the interaction. Expressions are also very similar for the electron spin it is mu z equal to minus z e beta e s z.

For nucleus it is plus g n beta n I z, the difference is in the strength of their magnetic moments that is of electron and the proton at 1 nucleus.

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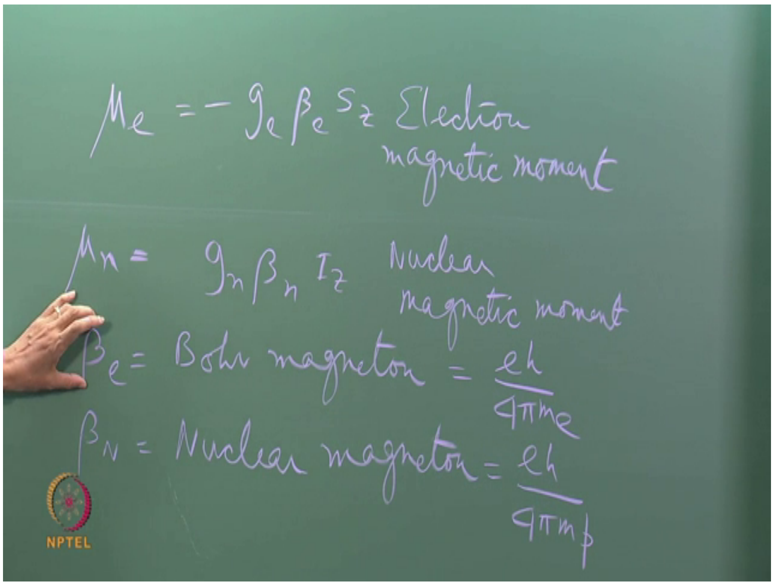

$\mu_e = -g_e \beta_e S_z$ Electron magnetic moment

$\mu_n = g_n \beta_n I_z$ Nuclear magnetic moment

β_e = Bohr magneton = $\frac{eh}{4\pi m_e}$

β_N = Nuclear magneton = $\frac{eh}{4\pi m_p}$

So, we can write this is for electron magnetic moment for nuclear magnetic moment it becomes. So, here the difference is actually in this and this. So, B e is Bohr Magneton and beta n is called these are the units in terms of which the magnetic moment is measured. So, difference is in the magnitude where does the magnitude come in to how does it appear.

Here. So, if I write here this is actually e h by 4 pi mass of electron and this one; similarly will be equal to mass of proton so you all know that mass of proton is about 2000 times heavier than mass of electron and that appears in the denominator here so; obviously, the Bohr Magneton is about 2000 times bigger than Nuclear Magneton. So, that is reflected here typical electron magnetic moment will be 2000 times bigger than nuclear magnetic moment also note this, sign difference here this says that the direction of the electron spin angular momentum vector is opposite to the direction of the magnetic moment of electron.

Here they are the same direction that is of course, related to the charge of these 2 protons have positive charge electron have negative charge. So, we have this difference in this side now when you keep in the magnetic field the interest in energy which is given here, can be now written as in terms of the corresponding spin angular momentum and the energy level is shown here shows that they look very similar the difference is only in terms of what spin state that low energy level correspond to for EPR it is the minus half state for a NMR it is the plus half state here. Now other difference is because of this difference of about 2000 in their values the splitting of the energy level for the same magnetic field will be about 2 thousand times smaller than the splitting that the electron will see.

So, the similarity is here, but difference also here that principle is very similar, but the magnitude of interaction is very very different. So, for typical magnetic field that is using spectrometer NMR usually appears in let us say megahertz region which, but EPR in the similar magnetic field will appear in thousand megahertz region which is called gigahertz we can write here, Megahertz is 6 hertz and other Megahertz is from this is typical NMR this is typical of.

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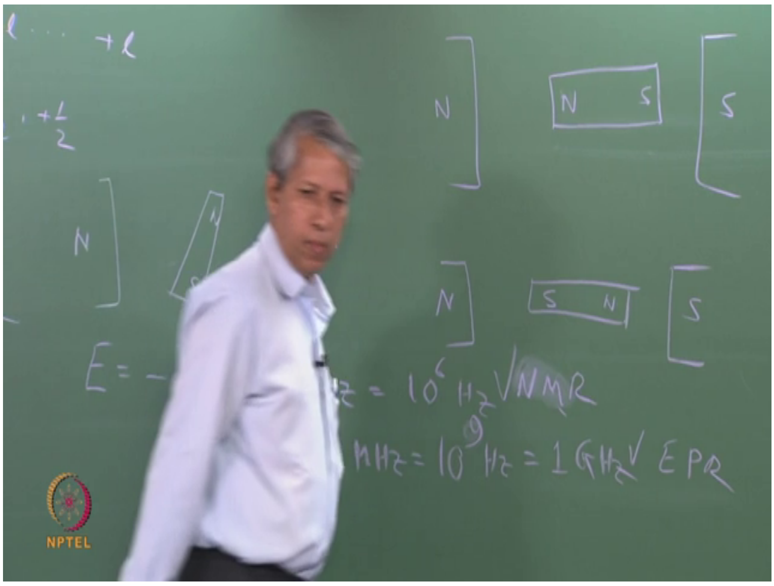

So, having obtained the splitting of energy levels.

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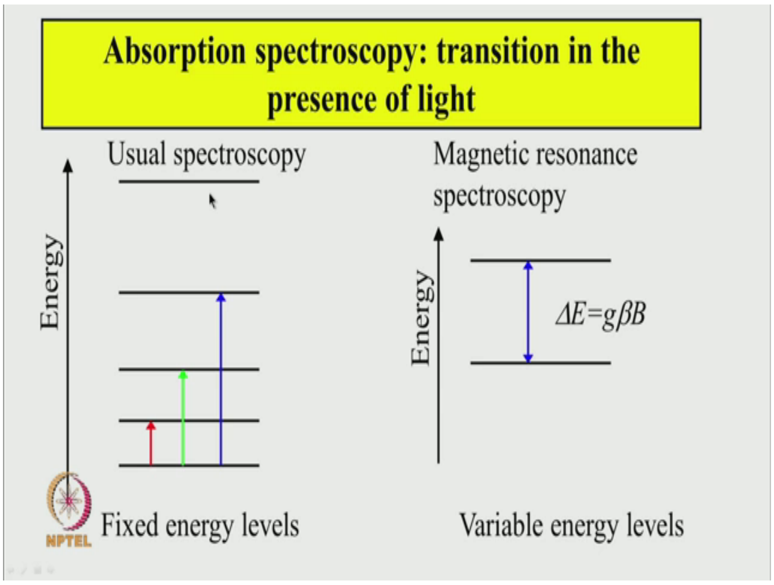

Absorption spectroscopy: transition in the presence of light

Usual spectroscopy

Energy

Fixed energy levels

Magnetic resonance spectroscopy

Energy

$\Delta E = g\beta B$

Variable energy levels

Now, I can look at their spectroscopy how is it done now. So, typical absorption spectroscopy involves shining light and seeing where exactly the light is absorbed and the spectra. So, it could be let us say electronic transition, horizon, transition, rotational transitions almost all of this you must have come across here this energy levels that is shown on the left hand side are actually property of the atoms and molecules they are fixed there all there is are fixed. So, you can not do very much about it all you can do is the shine light of appropriate energy. So, the energy gap of the 2 levels match with the energy that goes inside.

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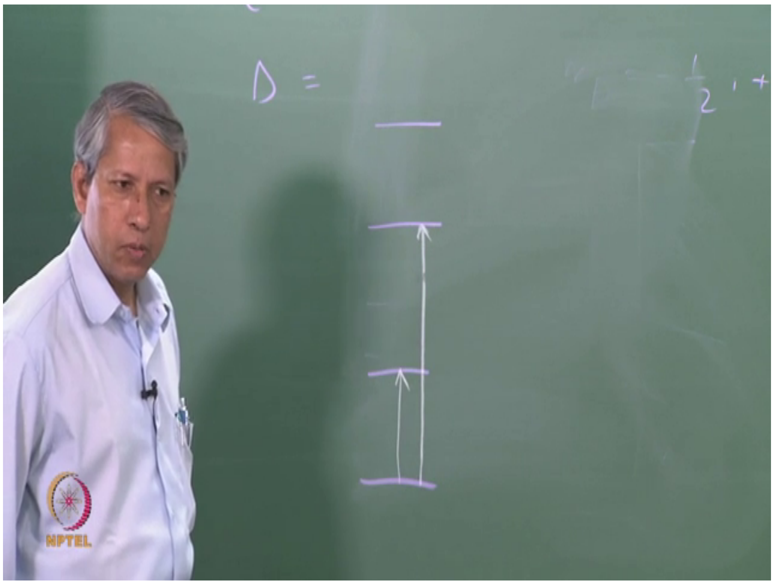

Say these are fixed energy levels and I shine light if the wavelength of the light matches with let us say this much then it can presumably absorb the light and I can get the absorption spectrum, now if the energy of the light is matching with this one then it can also cause absorption and I can get another absorption here. So, these energy levels are fixed in a conventional spectroscopy, but here you have seen that energy level and that gap depends on the external magnetic field. So, they keep changing. So, you change the magnetic field the energy levels change.

So, I have to have a fixed energy gap and the shine light on that, how do I fix the energy gap the delta E that is given here is now really become g beta and B B is the external magnetic field B changes the gap also changes. So, I can fix the energy gap by fixing the magnetic field and the delta I could be equal to the external radiation.

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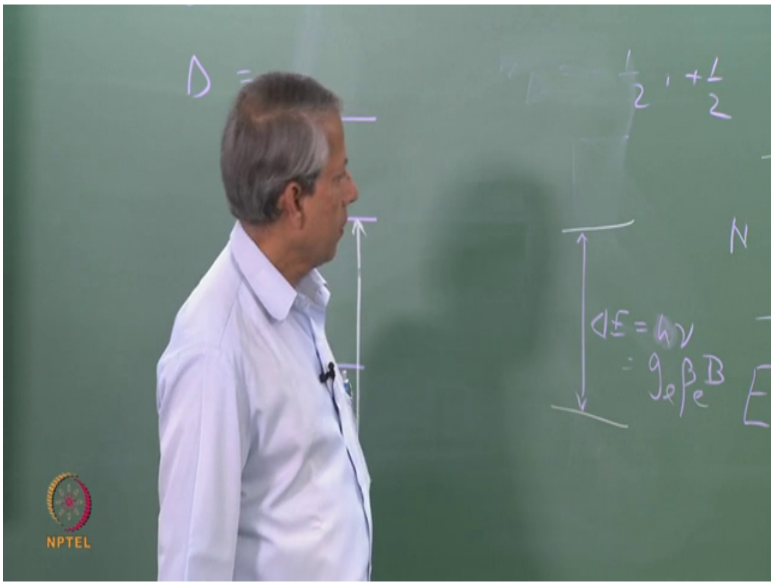

And then which can be now this condition becomes the condition for matching the energy gap with the radiation energy. So, this fundamental relation we call the resonance condition that is satisfied for absorption to take place.

So, I will write it once more here because this is going to be very fundamental to the spectroscopy.

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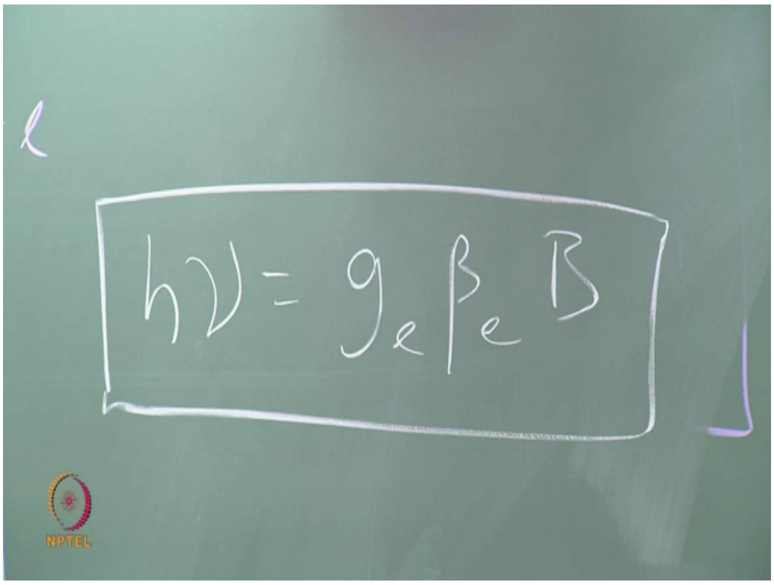

$$\boxed{h\nu = g_e \beta_e B}$$

This is the incident radiation frequency and this is the magnetic field you see they are proportional. So, this again can be contrasted the conventional spectroscopy where this energy gap is fixed. And so we vary the frequency of the radiation to match the energy gap here now I have a variable energy gap which is caused by the magnetic field B. So, I can to make this equation satisfied I can vary this or vary this. So, this we will see later how actual ex the experiment is done to look at the observed spectrum anyhow, but what do you expect the about the spectrum nature of the EPR spectrum when I do the experiment.

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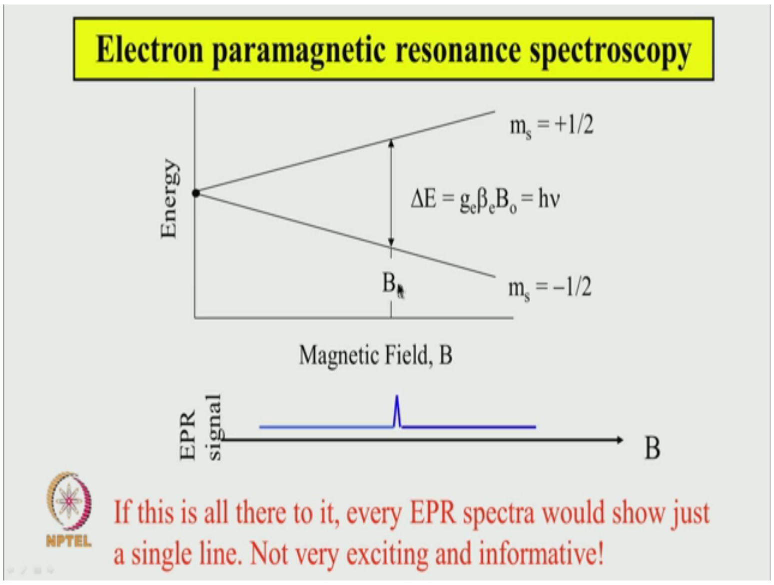

Electron paramagnetic resonance spectroscopy

If this is all there to it, every EPR spectra would show just a single line. Not very exciting and informative!

So, this is the energy gap. So, if the delta e is fixed at a magnetic field B 0 then I need to satisfy h nu to equal to this.

So, the spectrum as A function of magnetic field will have this sort of behavior that I suppose I keep the frequency constant h nu is constant. So, the energy gap is now varied by changing the magnetic field from lower to higher side. So, at this position the energy gap delta E have exactly equal to become h nu then the absorption radiation takes place there, nothing happens if the magnetic field is lower than B 0 or higher than B 0 exactly at this condition this equation is satisfied.

So, the spectrum should look like this one up down and then goes up. So, there one line here. So, this is the electron paramagnetic resonance spectrum of our isolated electron kept in the magnetic field. So, in a sense it is very simple spectrum just only one line, but then the simplicity source that if there is all there to it that if every like one electron put a magnetic field gives one line, then this is not going to be very exciting because all the substances which gives EPR spectrum will give one line spectrum and what information can you get from there very little. So, it is not going to very exciting or informative.

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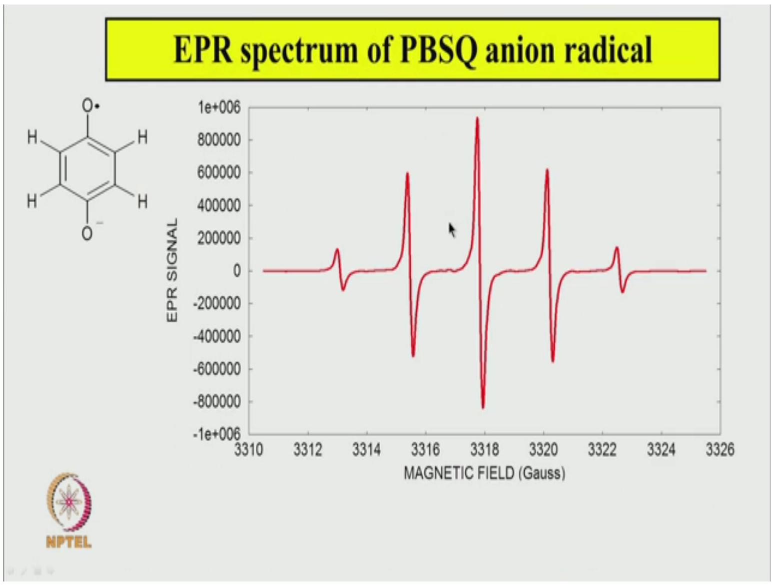

EPR spectrum of PBSQ anion radical

So, now let us see some real experiment early spectrum and how they show their EPR spectrum this is the radical, which is called Para Benzo Semiquinone radical I will write the structure and formula again here.

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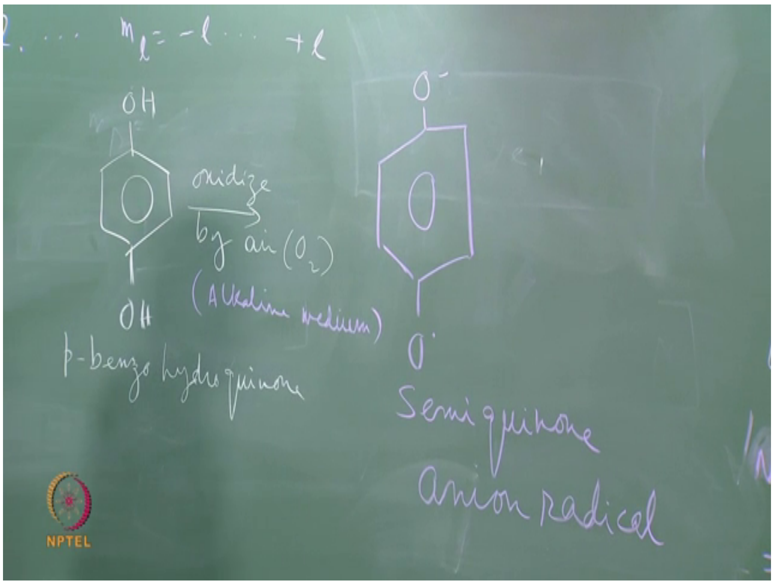

If we start with this hydroquinone, this is hydroquinone and it just oxidized it in oxidized by air actually the oxygen of air.

It is a very simple experiment dissolve it in alcohol and make it alkaline then in alkaline medium this will convert to I just would say this is in alkaline. So, here this O H and O H in alkaline becomes O minus and it half of that gets oxidized. So, O dot. So, we call them Semiquinone and this been anion. So, we call a Semiquinone anion radical if you the EPR spectrum is found here and you see that gives 5 lines and lines are equal gap among them, but intensity is not same this follow a certain pattern, we will see this thing pattern and try to figure out later why they are so, but it shows that this single unpaired electron which is present here they are not giving single line EPR spectrum, but 5 lines are coming.

So, something more is happening something more than what was sort of discussed and we expected to happen.

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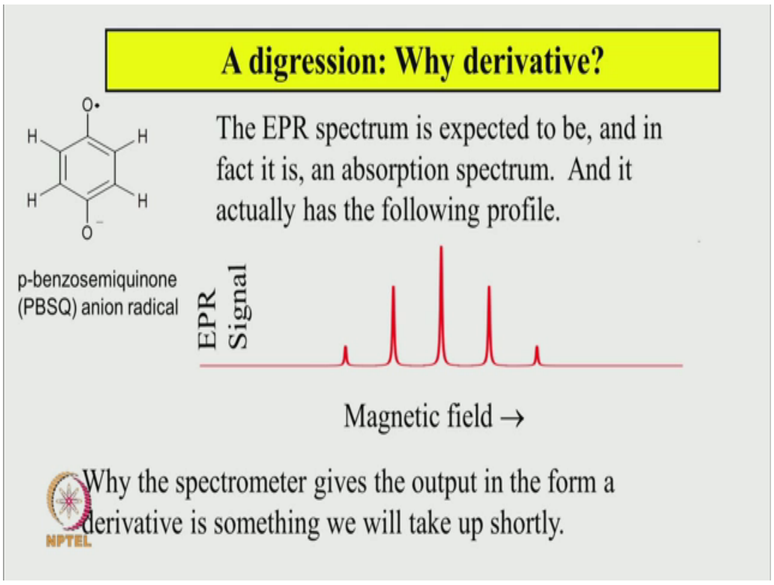

A digression: Why derivative?

p-benzosemiquinone (PBSQ) anion radical

The EPR spectrum is expected to be, and in fact it is, an absorption spectrum. And it actually has the following profile.

Why the spectrometer gives the output in the form a derivative is something we will take up shortly.

Before you go to another example here is a little digression the EPR spectrum that we saw there is the form of a derivative in your previous experience of various types of spectroscopy that you have seen the absorption spectrum you will always look like this type of thing.

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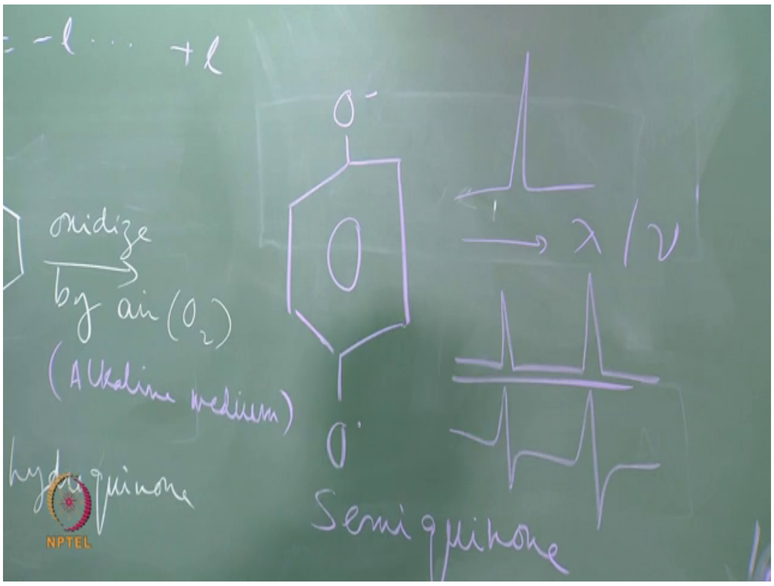

So, intensity of light is absorbed in this fashion as a function of course, a function of wavelength or equivalency here we are plotting the spectrum as a function of magnetic field, but is equivalently that we are doing the experiment that we are looking at that supposed to get absorption spectrum of this kind instead it shows derivative spectrum.

So, why it is so is something again we will see later. So, we just right now take it from me that actually this absorption spectrum of this is of this kind that 5 line absorption line come and they are exactly equivalent to this one. So, what the spectrometer records is the derivative line, but internally the absorption spectrum is this. So, why the spectrometer gives the output in the form of a derivative is something we will take up shortly.

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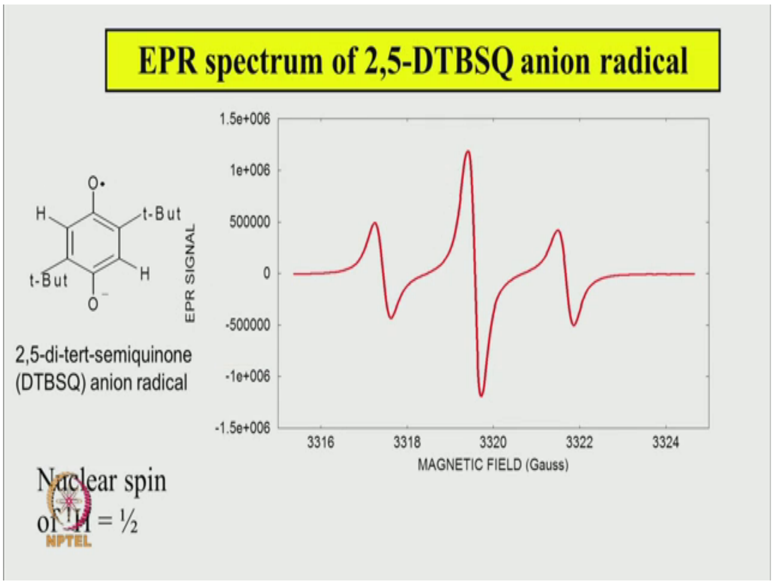

EPR spectrum of 2,5-DTBSQ anion radical

2,5-di-tert-semiquinone (DTBSQ) anion radical

Nuclear spin of ^1H = ½

Another example the same Semiquinone here if we start with now instead of this if we start with this starts a tertiary butyl group here.

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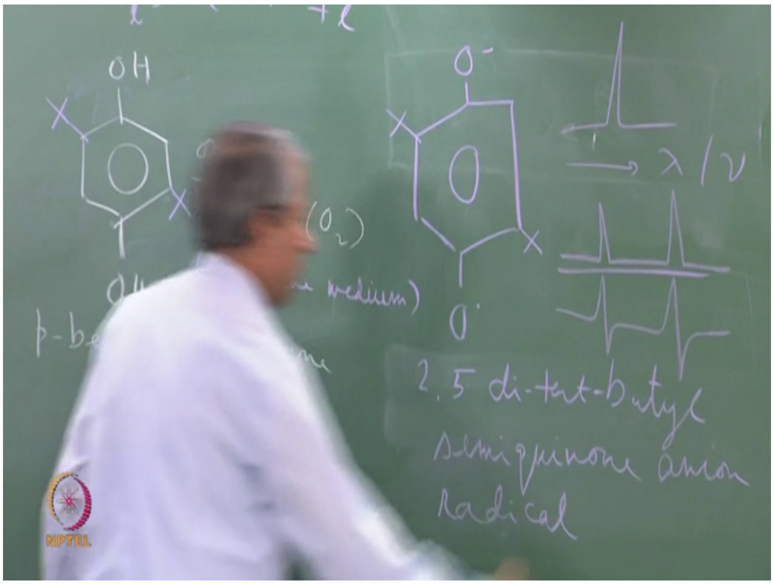

Then this becomes tertiary butyl group there. So, we call it this is the 2 5 these are the 2 groups.

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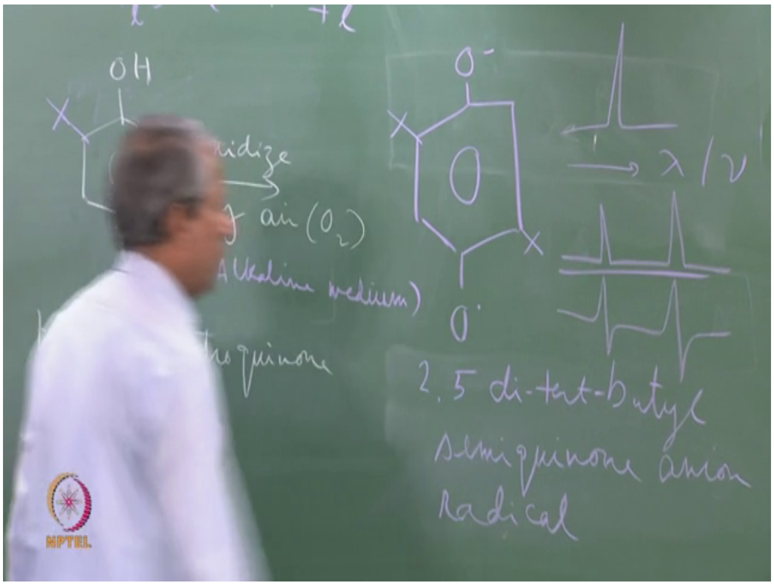

So, we call it 2 5 is a di tertiary butyl anion radical the EPR spectrum this is shown here and it gives only 3 lines it is the same type of radical earlier give 5 lines. Now it is giving 3 lines. So, you see how now the EPR spectrum is becoming interesting that it is something it is now giving information about the structure of the radical.

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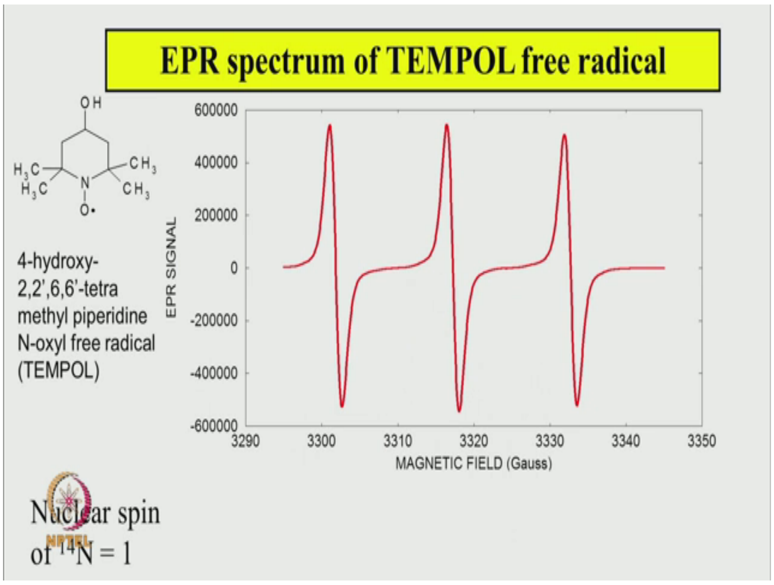

EPR spectrum of TEMPOL free radical

4-hydroxy-2,2',6,6'-tetra methyl piperidine N-oxyl free radical (TEMPOL)

Nuclear spin of ^{14}N = 1

So, it is useful we take some more example now here this is another radical; radical is called TEMPOL is short form, but the structure is shown here it is a Piperidine group with 4 methyl groups attached to that and this N O here the O has 1 or 2 electron that unpaired electron give rise to the EPR spectrum. And the spectrum is shown here gives 3 lines of equal intensity now and the gap is same mind you that here the nitrogen nuclear spin is 1 nitrogen 14 nucleus, we will see that that has something to do with these 3 lines which are appearing there. I said in the introduction that EPR spectra is very useful for characterizing transition metal complexes. So, here is an example of copper complex this is called Copper diethyl dithio-carbamate and this is the chemical formula of this.

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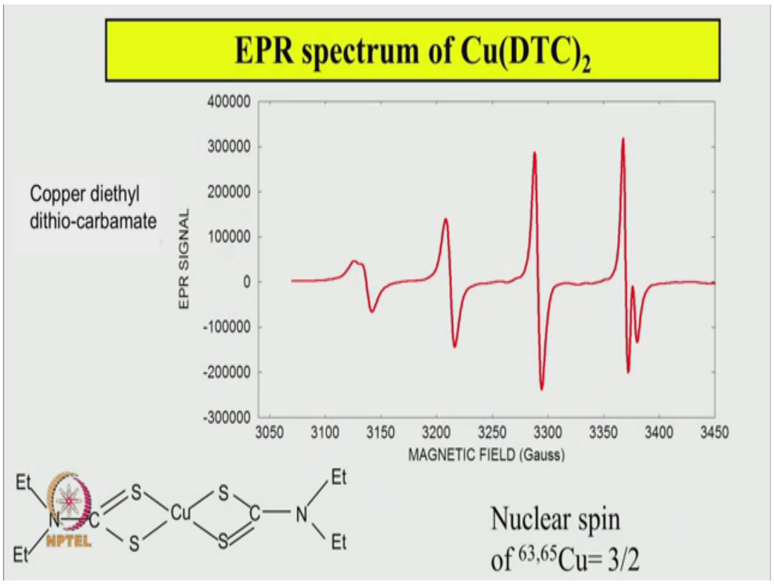

EPR spectrum of Cu(DTC)$_2$

Copper diethyl dithio-carbamate

Nuclear spin of ^{63,65}Cu= 3/2

So, this gives 4 and not quite 4 line, but you see that one group here one here another there third one is there they were funny looking structure, this line is split here and that this line sort of split here, but intensity seems to be quite different for different lines. So, again it shows that EPR is able to give a lot more information than what we sort of anticipate at the beginning. So, it is going to be very useful technique to get the information or electronic structure.

Now, this molecule or copper complexes may be naturally occurring copper and you know that naturally occurring copper has 2 isotopes nucleus will 3 by 2 for both of them, but mass number is 63 or 65. So, if one chemically purifies this isotope and have just pure 63 isotope then this the spectrum looks like this.

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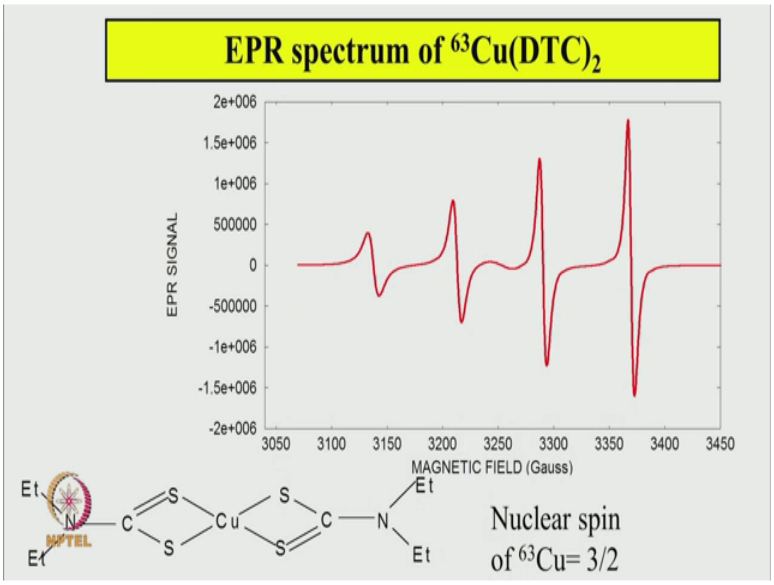

EPR spectrum of ^{63}Cu(DTC)$_2$

Nuclear spin of ^{63}Cu= 3/2

So, here see the simplicity now earlier we had funny looking spectrum of this structure there some structure there that has disappeared, now instead of that we got 4 lines though 4 lines do not seem to have same intensity nevertheless there are 4 lines of this kind and intensity strongest on the right hand side and becomes smaller and smaller, but notice that width also becomes bigger and bigger as you go from right to left.

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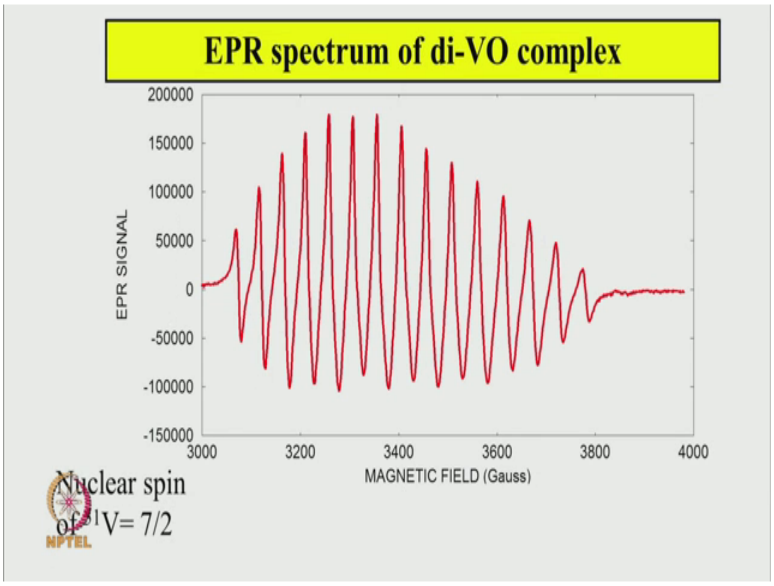

EPR spectrum of di-VO complex

Nuclear spin of ^{51}V= 7/2

But here the way our enriched copper 63 nucleus, the another complex of vanadile this complex has 2 vanadile nucleus and some complicated fashion. So, vanadile nucleus happens to be 7 by 2 and here you see the whole lot of lines there 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 lines are there. And intensities you can see quite unusual and it starts from the left hand side some sort of low intensity they have got bigger and bigger intensity increases again it goes down and down if you look at the width carefully the width becomes narrower and narrower in the middle and then again because broader gives the shape in this fashion.

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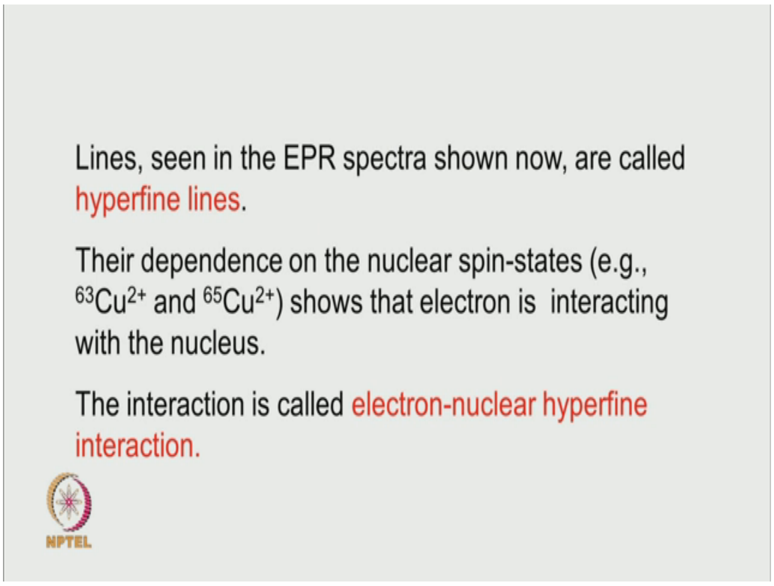

Lines, seen in the EPR spectra shown now, are called hyperfine lines.

Their dependence on the nuclear spin-states (e.g., $^{63}Cu^{2+}$ and $^{65}Cu^{2+}$) shows that electron is interacting with the nucleus.

The interaction is called electron-nuclear hyperfine interaction.

So, these lines that we see lots of lines these lines in EPR spectrum that have shown these are called hyperfine lines one important characteristic of the line is that they depend on the nuclear spin state. So, that is a clue to something that origin of this thing that clue is that is the copper 63 and 65 has given rise to quite different spectrum. So, this must have something to do with the interaction of the unpaired electron with the nucleus so this interaction is called the electron nuclear hyperfine interaction.

So, at this point let us just summarize what we have seen now that EPR spectroscopy gives lots of lines in general and their characteristic of the nucleus that is present there they are also characteristic of the type of radical which is giving rise to the EPR spectrum and from there therefore, we can learn a lot about the structure of the radical or structure of electronic structure of the transitional complexes. And so what not for most importantly now that it is the hyperfine line and the interaction of the electron with the nucleus that gives us to the hyperfine line is the key to this part summary of what you have learnt today.