Principles and Applications of Electron Paramagnetic Resonance Spectroscopy
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Lecture - 10
EPR Instrumentations - IV

Hello there. We have seen how a direct detection EPR spectrometer works. Let us recapitulate that once again.

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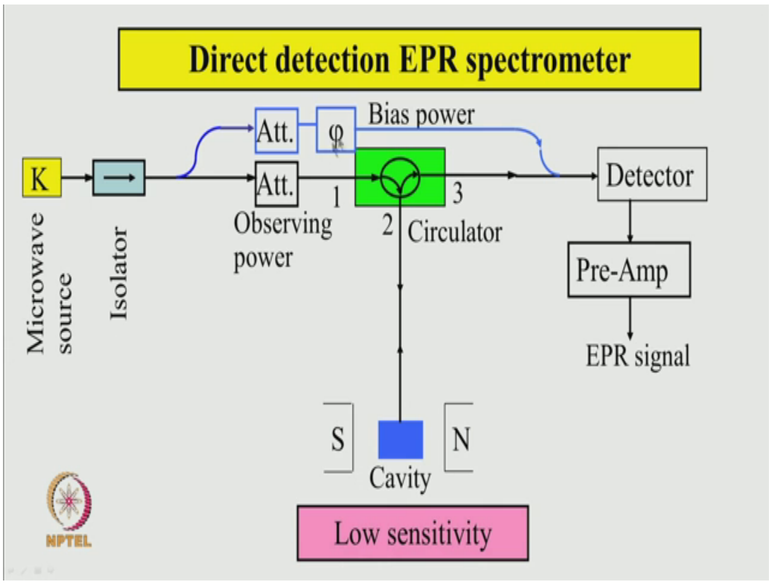

In the slide this shows the direct detection EPR spectrometer. Microwave comes from a source, goes through isolator, then main power comes to this observing path it is a and intensity is adjusted by the attenuator enters the circulator port 1, appears in port 2 and goes to the cavity, gets reflected enters port 2. And appears in port 3 and goes to detector. To bias the detector some amount of micro power is taken through this blue path, again it is amplitude is adjusted phase is adjusted. And then it is allowed to form a detector. To balance the micro bridge such a way that very little reflection takes place from here, and you work a just a little under couple condition.

The reflected micro power is detected by the detector, and amplified by the pre-amplifier. It is output gives the EPR signal.

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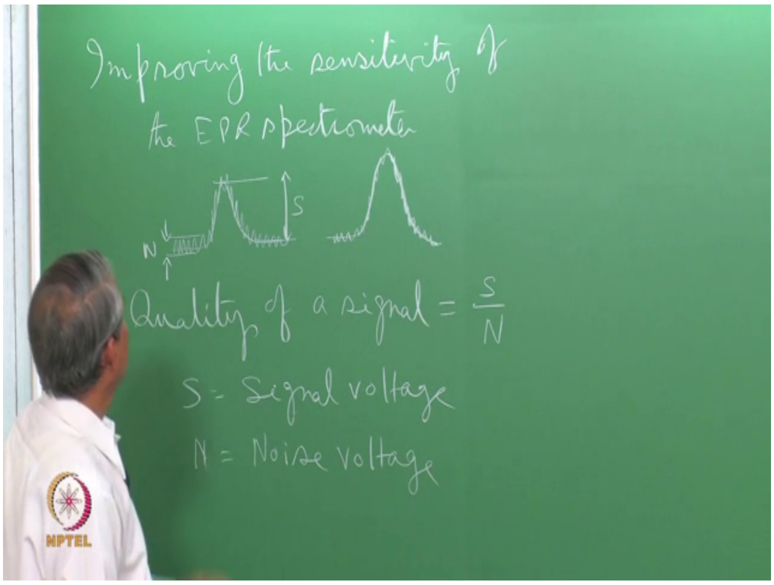

Now, this spectrometer of course, does not have very high sensitivity. So, how to improve the sensitivity? We are going to discuss that in this lecture; improving the sensitivity of the EPR spectrometer. Now sensitivity is a measure of how small signal one can detect, of course, it depends on the amount of sample that is present there. So, this smallest amount of sample that a spectrometer can detect is it is sensitivity.

So, the signal that we see let us say some absorption spectrum these kind. Now it may have electrical noise of this kind, let us say. So, the quality of the spectrum depends on how much this noise present here and how much signal that is present here. So, is defined to be this numerical signal to noise ratio S by N. S is a signal voltage; which visually measure from let us say middle of this path to this here. This is the signal voltage. And N is the noise voltage, which is measured by this width of this patch this by noise voltage.

So, naturally a good signal is the one for which the signal voltage is high, noise voltage is low. So, let us say another one which has got this rock thing here, a little less of noise of this kind. So, for both of these the signal voltage is a about the same, but noise being smaller here, signal to noise ratio for this signals more than this one this is a better-quality spectrum. So, we want to see now how we can improve the sensitivity of the EPR spectrometer, in other words the signal that it collects will have as little noise as possible, without sacrificing the signal voltage.

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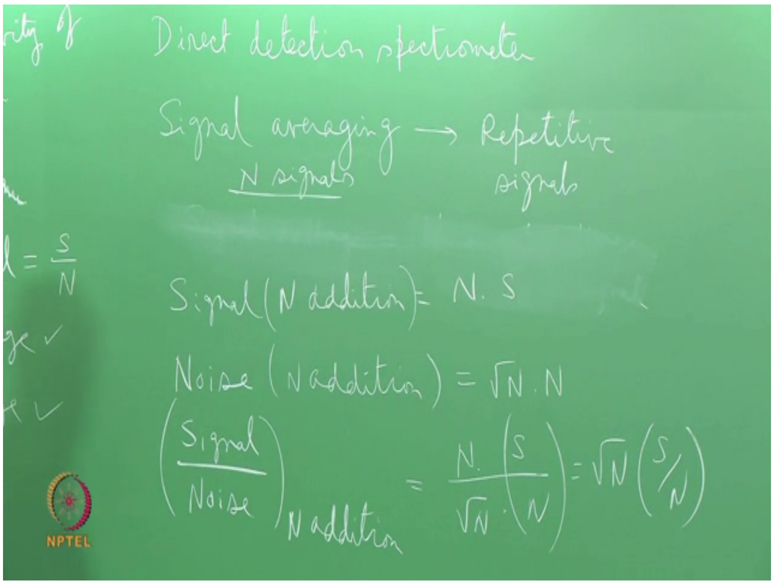

Now, for direct detection spectrometer, which is used for capturing fast events like transient radicals or measuring relaxes and time using pulse techniques; we have to use the way it is. So, here to improve the signal noise ratio, what one does is to do the experiment repetitively again and again and again. And use this simple technical signal averaging. And this is possible for repetitive signal. So, repetitive signal suppose you got a signal of this kind, whatever may be the source of that one if I keep on adding this again and again and again, then what happens? S is my signal voltage and N is a noised voltage for one experiment, which is of this kind.

So, if I add N such signal, then the signal due to N let us say addition will be N times s, because all the signals should look the same. They are adding coherently. How would noise? The noise this appears here are random in nature. So, every time I get a signal of this kind, this signal voltage will remain the same to the noise we will look similar, but not quite the same. Actual fluctuations will be quite random. So, this is the noise voltage that you see here, after adding N such thing noise after N addition will add incoherently. And from the statistical nature of the random numbers, this will be square root of N times the noise voltage, which is this one.

So, signal noise ratio after N addition will be N times signal voltage divided by root N times noise voltage. So, this is the signal to noise ratio that initially we had here. Now this becomes square root of N times signal to noise ratio of the single experiment. So, we see here therefore, that if I keep on adding this signal, I can improve the signal to noise ratio by this factor here, square root of n. So, if I do for example, experiment 100 times, then the signal to noise ratio of the added signal will be 10 times bigger than the signal to noise ratio that initially we had for one signal. So, this synchronous addition of repetitive signal therefore, can improve the signal to ratio of direct detection spectrometer. Here you do not sacrifice the speed of the spectrometer. We only have to have repetitive signal. And then we can improve the signal to noise ratio by this signal averaging technique.

Now, this is not very common for most stable radical, where we work on a steady state mode. In other words, radicals stay there forever. Here a technique that is used to improve the signal to noise ratio is called Lock in detection.

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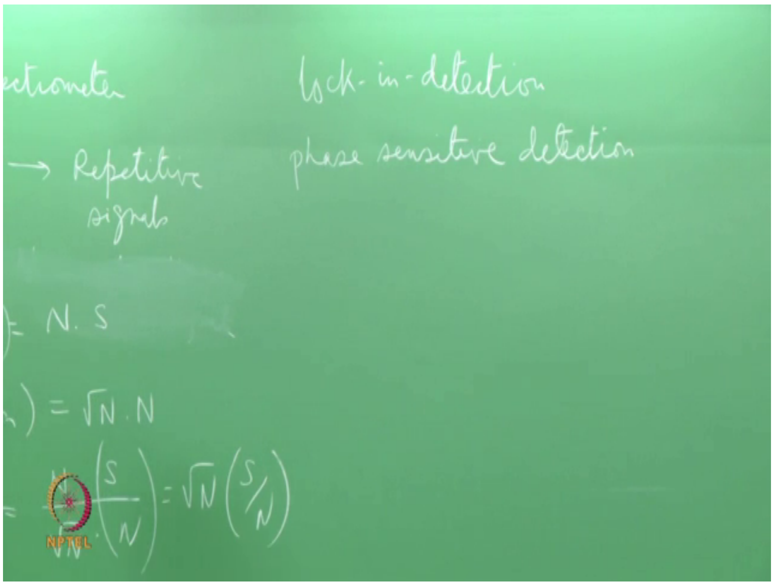

Or also called phase sensitive detection. Let us try to understand what it is the principle of this is explained in this slide.

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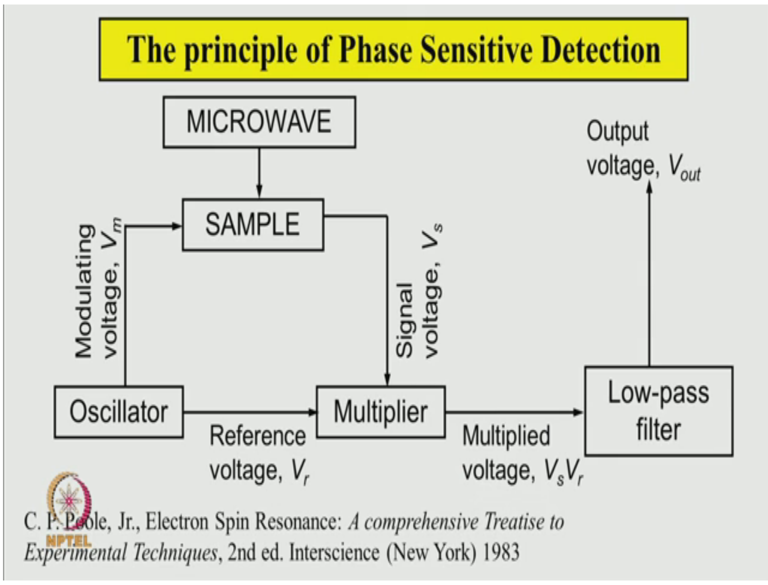

Here, let us say micro comes from this place and falls on the sample and microwave is absorbed by the sample and is producing a signal which comes out here in the form of signal voltage.

Suppose there is an oscillator, which gives certain frequency and it modulates the absorbing property of the sample. What do you mean by that? There whatever signal that is coming here because the absorption microwave this modulating voltage in place suppose the sample is such that this absorption is changed according to this modulating voltage. So, that signal voltage is coming here which is getting modulated at this modulating voltage here. Now there is a some electronic circuit, let us say we call it a multiplier circuit, it takes 2 inputs one is this signal that is coming out from the sample and falling here, the other one is reference voltage which comes from the same oscillator and coming here. And these 2 signals are multiplied. See V m is the modulating voltage, now V s is the signal voltage, and V r is the reference voltage. The output of the multiplier is product of V s and V r, which is this.

Now, this is now passed through a electronic filter which removes the high frequency component, and allows in the low frequency to pass through and that is the output signal. Now this is supposed to be the phase sensitive detection principle. Now in this diagram nothing may make sense. So, to understand what is happening, let us make use of the mathematical part of what is going on here.

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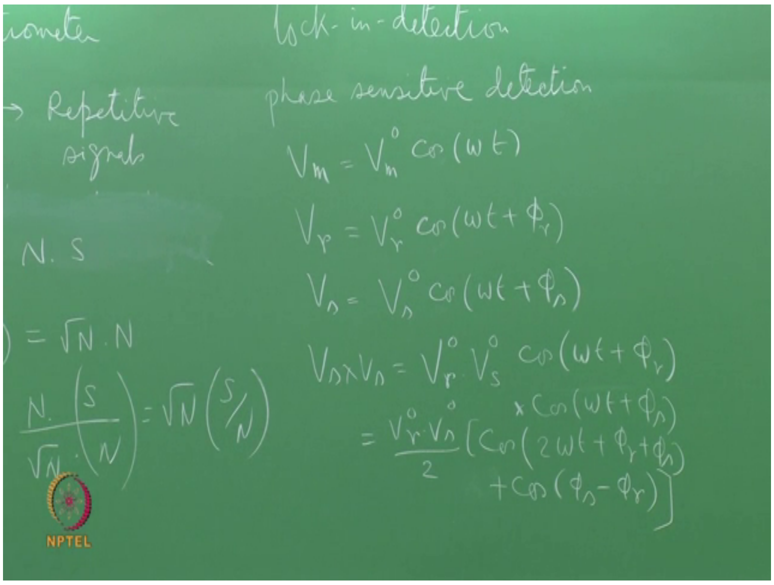

Let us say V m is the modulating voltage, which is let us say V m 0 cos omega t, with the frequency of modulation. V r is the reference voltage that goes to the multiplier, let us call it V r 0 cos omega t plus phi r. And the signal that the sample gives V s similarly, V s 0 is a cos omega t plus phi of signal.

It is easy to understand that why this frequency has to be same, because it is the same oscillator which is giving the reference signal to the multiplier coming from here. And same signal goes to the sample to cause the change in the absorption at this particular frequency. What is possible on the other hand? That phase of this and this need not be the same. This phi r is the phase difference between the modulating voltage and the reference voltage. Similarly phase of this signal need not be same as this one and this is the phase difference between this. What the multiplier does is to multiply these and these. So, V r times V s gives the product of 2 cosine function. See this can be written in terms of the property of cosine, times plus cosine.

Now, here this frequency is quite high, 2 times omega t. So, in this diagram see low pass filter job is to remove the high frequency component out of this product of the voltage that comes from the multiplier. So, what comes out of this low pass filter is nothing but this term.

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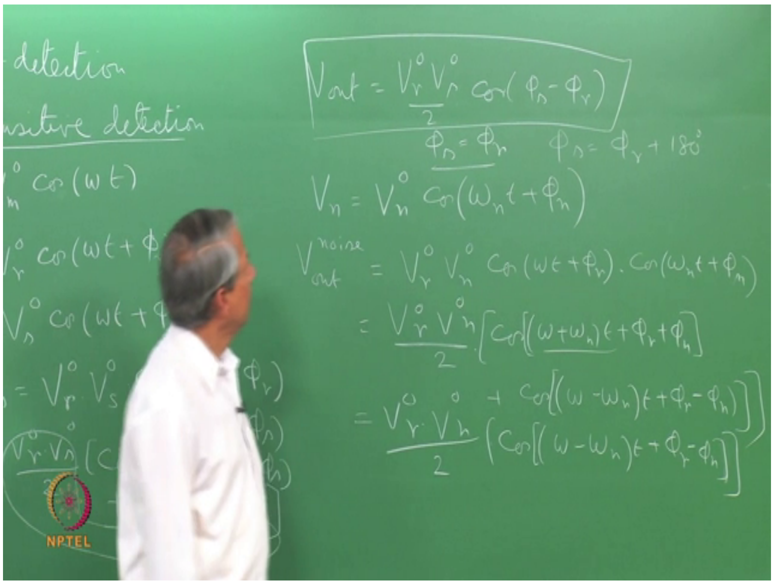

Which is we have this V 0 r, V 0 s times 2 times cosine phi s minus phi r. So, here you see that maximum voltage output will come when this is 0, or in other words phi s equal to phi r when this condition is satisfied, the maximum output will come out of this low pass filter. And that is the EPR signal. How does it help improving the signal to noise ratio? How does this selectively throw away the noise component? For that suppose some noise comes whose voltage let us say V noise could be written as V 0 N cosine omega of N t plus phi of n.

Noise comes in all possible frequencies. It has in general no relation to the frequency of the modulation that is used here. So, let us say one particular noise component has frequency w N, and it is phase is phi N. Now let us go through same type of argument now and see what happens the multiplier will act in the similar fashion. So, output will be let us say output with noise will be V r which will be omega, something like this. Here again the low pass filter will remove this frequency to give rise to this set of output.

Now, see what can happen. In general, these are different. See if this is much higher much different from this one let us say higher or lower then this will oscillate; so rapidly that on the average this will give 0 contribution. So, the output will have contribution only when the noise frequency is very nearly equal to the frequency of the modulation. So, in that time these term, which is appearing here the phase different between the noise and the reference also will decide how much output comes from the noise component, with the phase of the noise is randomly changing, and has no relation to the reference phase then again on the average this cosine term will be giving average value of nearly 0. So, and this will be very small.

So, it is therefore, very important to realize that, only those type of noise components. Which has exactly same frequency of the modulation, and same phase as the reference can presumably give some contribution as a noise. So, every else is getting to be removed by this technique. So, this is a very tremendous improvement that one can expect form this sort of detection technique, and this that we call a phase sensitive detection because detection is done with respect to sudden reference phase. Or the reference phase and reference frequency decides the selective removal of noise also. It is called lock in detection because thus detective signal is sort of lock into certain reference frequency either term is used in this terminology.

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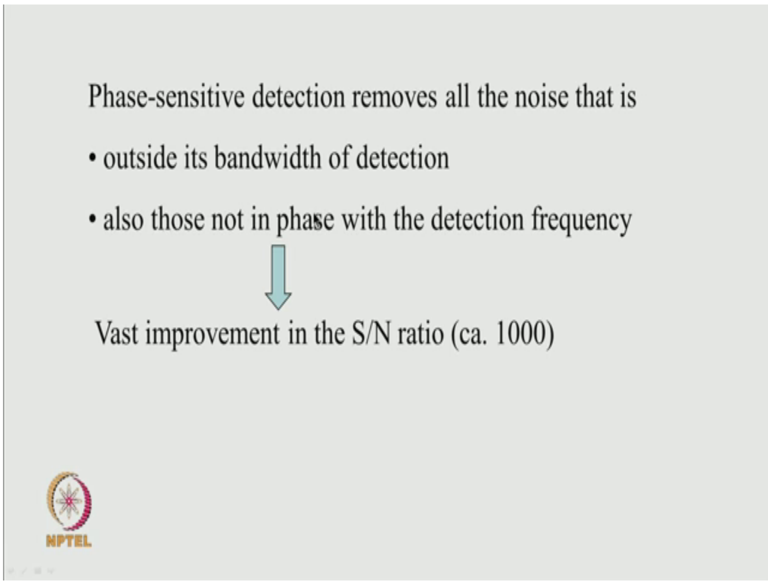

So, phase sensitive detection removes all the noise that is outside it is bandwidth of detection and also, those not in phase with the detection frequency. And one can get a vast improvement in the signal to noise ratio of the order of one thousand. Now what is done in EPR spectrometer which uses this idea?

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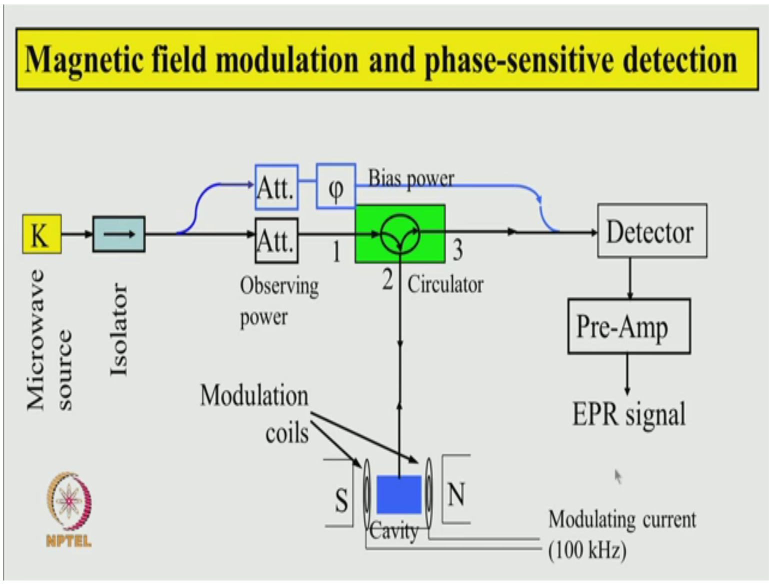

What is done is shown here, that we modulate the magnetic field that Zeeman magnetic field are here by using a pair of Helmholtz coil, which is mounted easily on the cavity. This this modulating current is passed through this coil typically at 100 kilo hertz; so the main magnetic field, which is the Zeeman magnetic field that is modulated at this frequency. What happens then?

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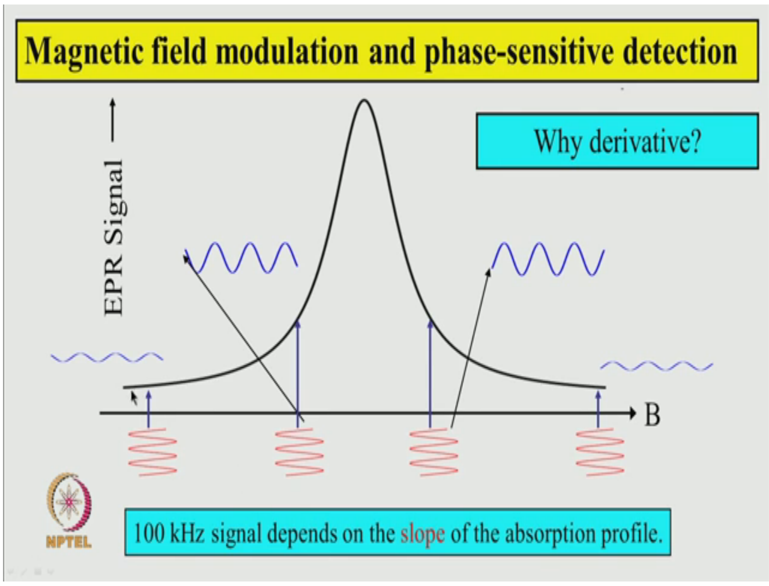

That to understand, now what happens, let us say this is the absorption profile of a EPR signal. And this Zeeman field is slowly scan from left to right this is the Zeeman field here. And every instant of time the Zeeman field is modulated by this red oscillatory magnetic field. So, as the field is being shift very quickly it is going left and right left and right.

So, here let us say at this instant if this is the EPR signal whether magnetic field goes down this voltage signal goes down when this goes up again it goes up. So, I get a EPR signal which will have oscillator component of this kind. When the same amplitude of modulation is at present all the time, but the Zeeman field is now brought somewhere here. Again this is modulating magnetic field and see here when goes from this to this the voltage changes in this direction I get a similarly oscillatory EPR signal, but it is magnitude has now become bigger than what was here.

See if you keep going in the same direction, and somewhere here now in the other side of the absorption graph, magnetic field modulating the same fashion. Now where now here the reference with the modulation of the magnetic field goes down here it goes up. The signal goes up. So, the same oscillatory EPR signal is seen here, but the phase of this is exactly opposite to this side now if you continue to move the magnetically further away from resonance here. Again, I get oscillatory signal, but of smaller amplitude. Now let us animate this one and see what way it looks like.

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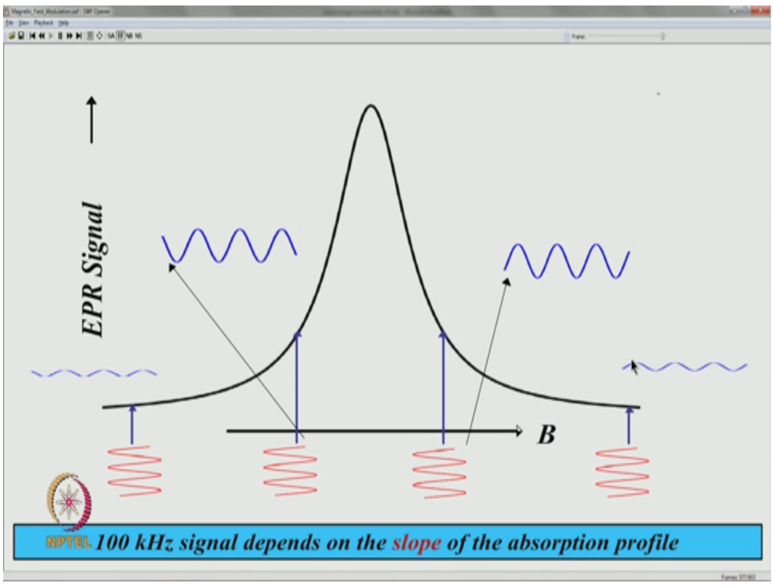

So, a magnetically modulation is shown as red, and the output signal is shown in the blue color at different places of the Zeeman magnetic field. You notice here the phase of this magnetic field modulation is same, where the how the output is changing, it is phase go from left side to right side.

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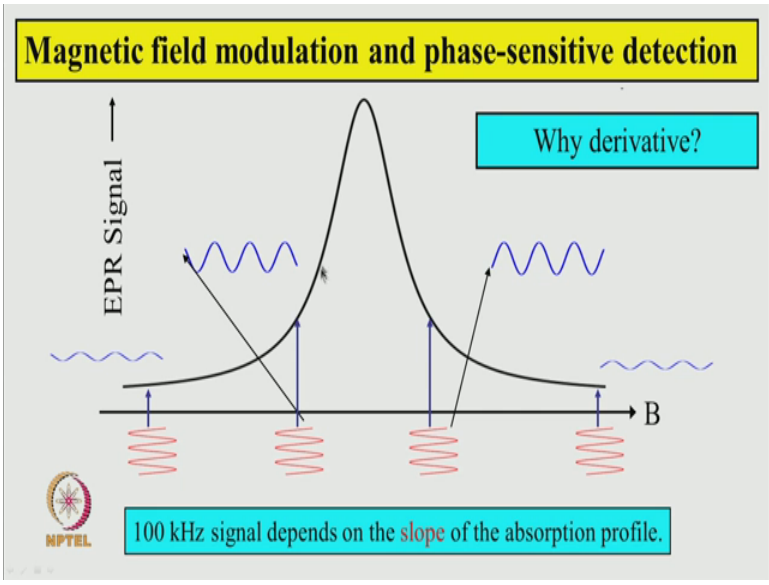

So, the amplitude of this signal depends on the slope of this absorption profile. So, longer this amplitude of modulation are very large. And also, the phase of depends on the whether it is left side or right side.

So, if you do now a phase sensitive detection, now we have described here we will get a signal which will be a measure of this oscillatories voltage and also the sign of this one. Notice the here that if it is exactly this at the peak of the absorption profile, then what happens? Here if we modulate the field in this fashion here.

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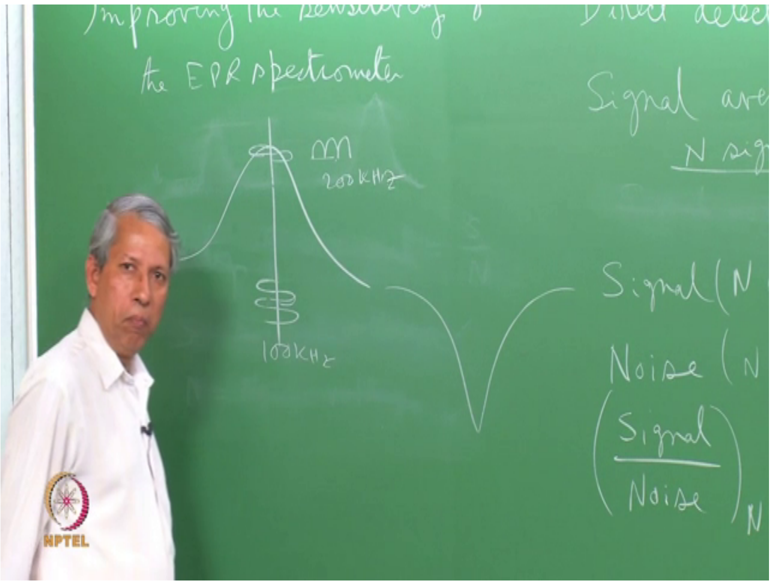

So, it goes down here, but then. So, in in one cycle it actually completes one here. This half cycle is here another half cycle it goes here. So, this will have this set of behavior, where this frequency is actually 2 times the frequency of this one. See if this is 100 kilo hertz this will be 200 kilohertz.

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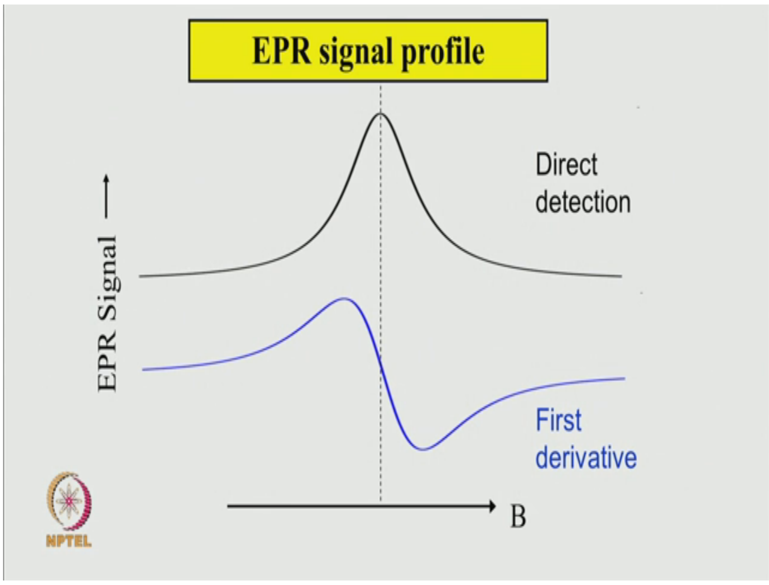

So, there will not be any 100-kilo hertz component here. So, the signal will therefore, look like this. So, this black curve shows the direct detection EPR signal absorption profile, and the first derivative signal will be having this set of profile here, goes up and then goes through 0 and in the opposite direction comes here. Because the sign of the 100-kilo hertz modulated signal that comes from the cavity changes from left to right, then it exactly 0 here. So, this lock in detection or phase sensitive detection gives rise to a very impressive improvement signal to noise ratio.

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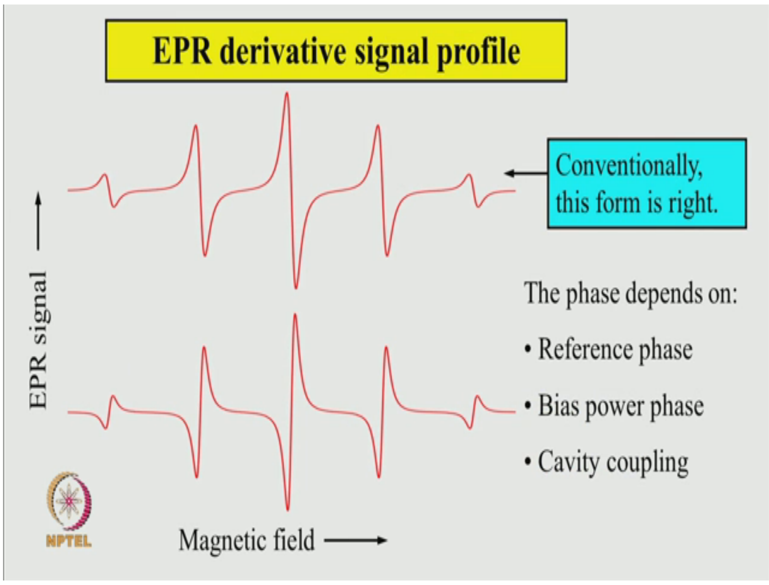

But what will be the ultimate appearance of the EPR spectrum? I said the phase changes through the peak of this thing. So, the absorption profile could be either this way first it goes up comes down, and goes up or comes down. Or it could be first goes down and then comes up or goes down or comes up. What does depend on? Now of course, depends on the reference phase first for here for example.

The output signal depends on the phase difference between the signal and the reference if this is 0. Then you get maximum signal, but also if it is a phase of the signal is actually phase reference plus 180 degree, then this will change sign. So, by changing the phase of the reference power the if your signal can be converted from this to this, but I also seen earlier their absorption profile, this itself can change to this if the bias power phase changes. So, that will also change the derivative signal from this to this. And finally, the cavity coupling whether it is under coupled or over coupled, changes the phase of the micro power by 100 degree. That will also change the appearance of the absorption profile either from here, to there or which in turn can change the derivative signal from this to this.

So, all this thing will decide the final appearance of the derivative signal. So, one has to decide what way a spectrometer is operating and once and for all agree the expectable representation of the derivative signal. So, conventionally this is the form that is taken to be the right profile. Though there is no reason, but that is the way it has been taken to be conventionally right. That is first the signal goes up and then comes down goes up and comes down. This is easy to understand that if you have the absorption profile which looks like this.

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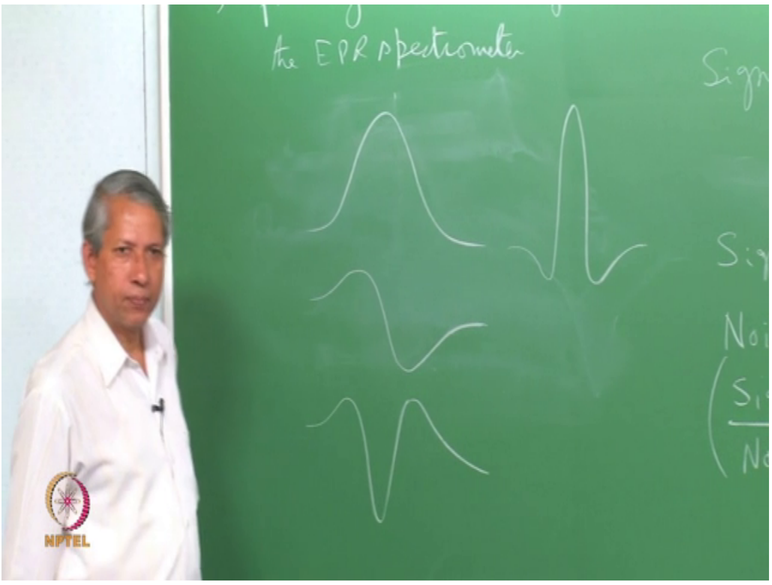

That if you agree to that or direct detection spectrum, it gives absorption in this fashion then naturally the derivative signal should look like this way first positive and negative.

Some EPR spectrometer is said to detect the second derivative mode, instead of detecting at the same frequency as the modulation frequency, it detects the signal at twice the modulation frequency. The second derivative of this will look like if you do this mentally try to see the every point is dependent on slope of this one. Then this is going to appearing in this fashion, but here again conventionally the second derivative representation is given as this type of behavior this type of signal.

So, one simply changes the sign of this 2 appear make it appear in this fashion. The reason we mean that these are some set of resemblance to the absorption profile here. So, second derivative representation is taken be in the correct form, when it is displayed in this fashion, though not mathematically.

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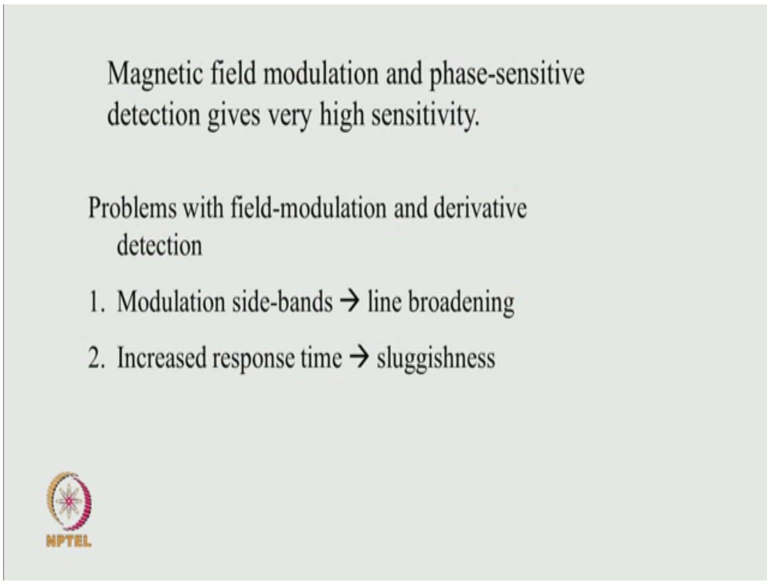

So, we have seen that magnetic field modulation and phase sensitive detection gives very high sensitivity. There are few problems associated with this technique. One is called modulation side band. And this causes the lines to be somewhat broad. What is that?

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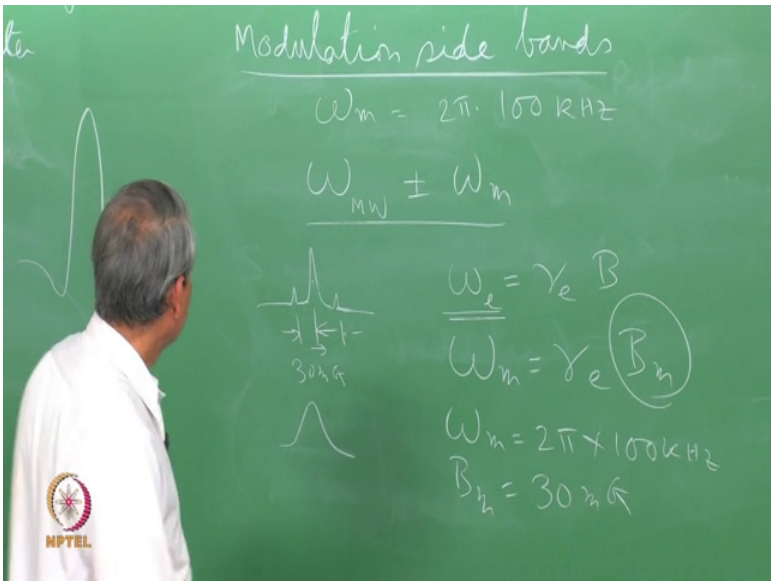

So, here we are using some ac modulation of the order of less typically 100 kilohertz. So, omega of modulation is a 2 pi times 100 kilohertz. So, this frequency is causing the magnetic field to be modulated. So, a here the diode sees a signal that comes out of cavity which is getting modulated with this frequency. So, this will be generating as some frequency and difference frequency of the microwave. At the frequency at it is 9.5 gigahertz. So, diode being a non-linear device, it is somehow that modulating voltage could be generating an addition of this and subtraction of this one.

So, effectively it will generate let us say omega of microwave plus minus omega of modulation. This is the frequency that is going to see there. So, this in turn will be seen as a line which is let us this is the absorption line here, this will because of this 2 type sum and difference frequency present there this will appear as some transition, which is this and this here omega microwave plus omega m or omega microwave or minus omega m. Now how far this is going to be this comes from even from the larmor frequency omega is equal to gamma electron times B.

So, here this is the modulation frequency omega m. So, this becomes a if you call this is the effective magnetic field that is it is going to be seen in the in the spectrum, given by the frequency of modulation. So, here if omega m is 2 pi times 100 kilohertz, then one can calculate corresponding B m appears about 30 milligauss. So, here this is the main peak of the EPR signal. So, this will be appearing at 30 milligauss away from this one similarly another one will be 30 milligauss away, from the main peak here this 30 milligauss is very small amplitude of this separation from the main peak. And one easily does not see this in the experiment. What one sees is that if the line is very, very narrow one tends to become slightly broader line there.

So, the original line width may not be seen if this original line is comparable to 30 milligauss. Broader line will have no effect on this one. So, this is one problem of this modulation broadening due to the side band. So, if someone is interested in getting a true line width of a very, very narrow line then one of course, has to lower the frequency of modulation instead of 100 kilohertz.

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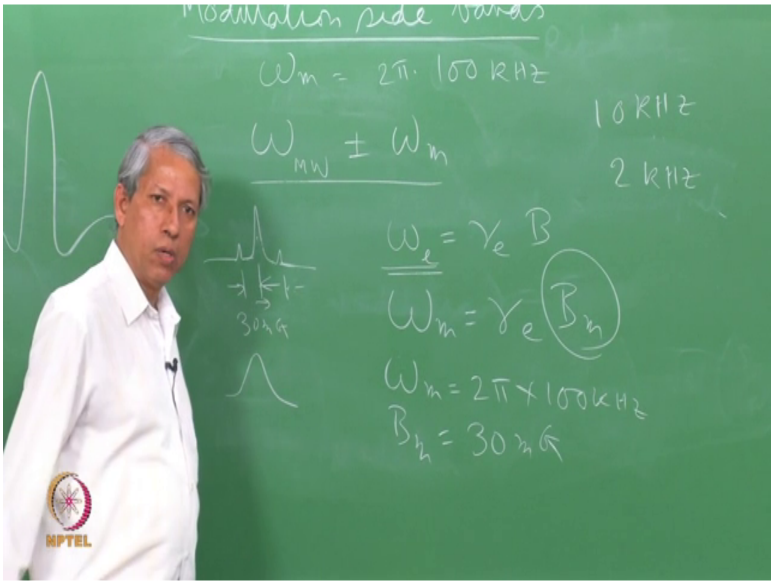

One can go to, let us say 10 kilo hertz or even 2 kilohertz for the magnetic field modulation. And then this will be correspondingly very smaller, but then at the same time one sacrifices the sensitive of the spectrometer in this fashion. I said in or the earlier lectures the diode detection has it is own characteristic noise spectrum. Noise that the diode gives out is not constant in all frequencies. It has this type of spectrum.

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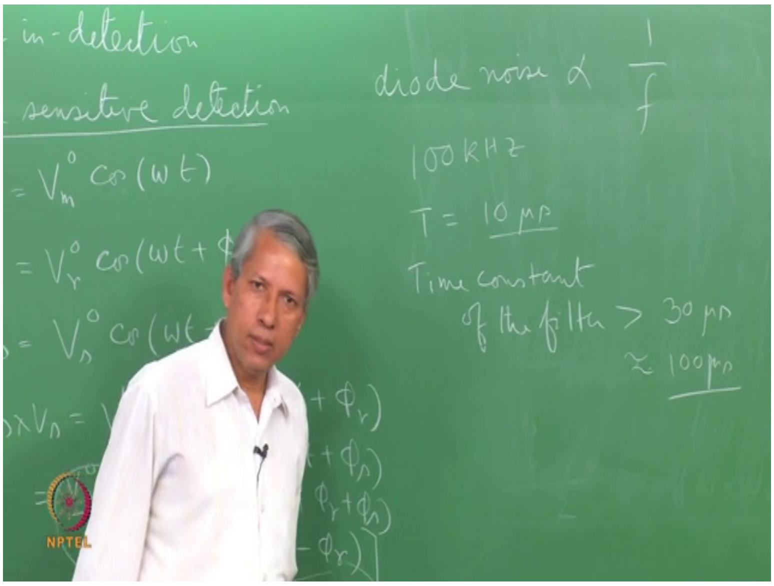

That is, diode noise is inversely proportional to the frequency.

So, if you work at a high frequency detection for example, 100 kilo hertz whatever noise I see here, it will be 1 by 100 if you 100 kilohertz. If you worked a lower frequency, this will be 1 by let say 10 kilohertz. So, corresponding that noise from the diode will be on more. So, if you detect the signal at higher frequency diode, contributes less noise to that. So, that way we have to compromise on the sensitivity if we are interested in recording very narrow line by working at lower frequency of modulation.

And second problem is that the increased response time of the spectrometer. That is, spectrometer becomes very sluggish. I said that direct detection spectrometer is fastest one, where one can get the first time of the order of 100 nano second, but that is not possible here. The reason is very simple that the low pass filter is supposed to remove this, high frequency component that is generated because of the multiplication here.

So, typically let us say 100 kilo hertz is the modulation frequency. And that has to be removed by the filter r. So, 100 kilo hertz gives the time period t is equal to 10 micro second. So, this has to be removed by the electronic filter. So, typically one uses a time constant of the filter, which is at least 3 times higher than this frequency that I am going to remove. So, typically therefore, the time constant of the filter will be greater than less at least 30 microsecond, presumably 100 microsecond something like this. This at least so, be 30 microsecond 3 times that one or may be more than that.

So, the signal which is changing with these time vision cannot be seen by this technique. So, this is the problem of this magnetic field modulation of phase sensitive detection. It makes this spectrometer slow. So, anything slower than that can possibly be recorded by this technique. So, first signal which changes in micro second time range cannot be seen by this spectrometer. Never the less this universally used because almost always this spectrometer is used to detect steady state, EPR sample for which time is not an issue.

So, with this we complete the discussion of the EPR spectrometer. And it is various functions, but one important part we have still not addressed that is how to maintain the matching of the cavity that you have seen earlier that the cavity micro per goes in and comes out it maintains a good matching condition. So, the deflected power always remains very, very small, that we have not yet discussed. It is very important because even if you manually match it is possible that the frequency of the microwave can change slowly either the power supply is changing it is voltage, or the cavity itself is changing it is property it is being may be it is becoming slightly warm because sample is kept there microwave is falling on that. So, this matching can change.

So, unless there is an automatic electronic control then micro frequency always remains matched to the cavity. This experiment cannot be done.

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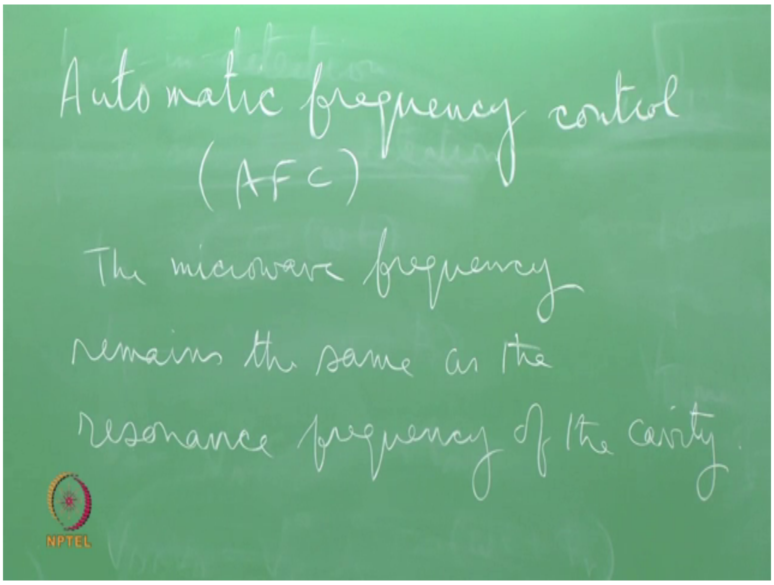

So, that technique is called the automatic frequency control. First of all, AFC, it is job is to ensure that the microwave frequency remains the same as the resonance frequency of the cavity. And this has to be done one extended period of time. How is it done? To understand that it is again recall how the cavity responds to change in the frequency of microwave.

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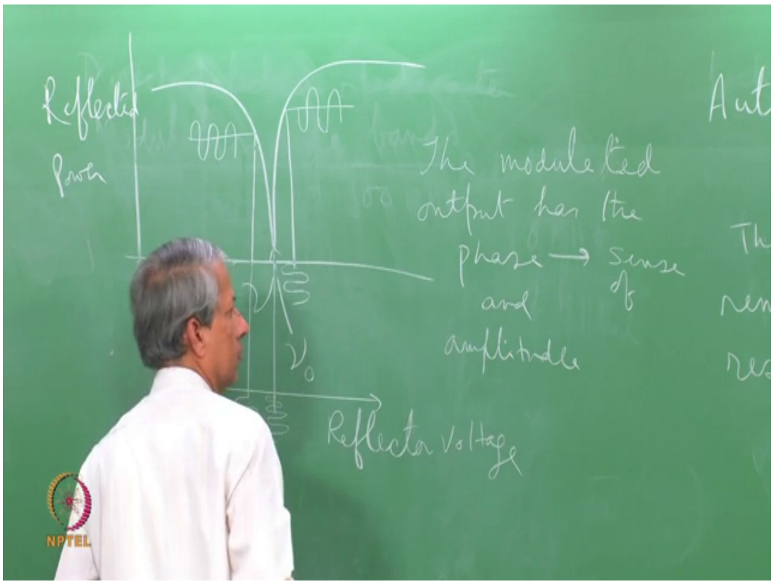

That is again given by this curve graph, that is the frequency of microwave and this is the reflected power.

So, this is the let us call it the resonance frequency the cavity. What is necessary is that microwave power that is going to the cavity must always remain same. As this one it is possible that user itself may shift because I as said the sample can become warm, in course of time because it is observing micro wave property of the cavity changes that changes this one. Or the frequency itself can change because of the instability of the source of the radiation. How is it done? Now for a (Refer Time: 38:4) this frequency can be changed by modulating the reflected voltage. So, this could as well written in terms of the reflector voltage.

So, what is done here? Now suppose at this reflected voltage I apply a small amplitude ac modulation. This fashion; see it is a similarity between these at the magnetic field modulation and phase sensitive detection to generate the derivative signal of the EPR signal very similar ideas used here. So, we modulate the reflector voltage in this fashion. What happens now? As it is going this way or that way the power will be reflected from the cavity we will examine 2 region now. Suppose we were here. And the modulation is this y. So, as we go down and up here the reflected power will have, this set of behavior up down up down here you goes down; means it goes up it goes down means it goes up here.

Now, here similarly suppose another here. Again, we go down up down up here. So, here it goes down it goes down, then goes up goes down, goes up again you see that the phase of this exactly opposite when it we are in this side or that side with respect to the modulating voltage here. So, the phase tells me that whether the actual frequency is lower than the cavity resonance frequency or higher than the resonance frequency, and also it depends on the how far you are away, you are very close or faraway.

So, the amplitude of this decides the extent of deviation. If the deviation is very small, these amplitude will be very small, if deviation is large this deviation is also very large this amplitude is also very large. So, the modulated output has the phase and amplitude. So, this gives me the sense of deviation.

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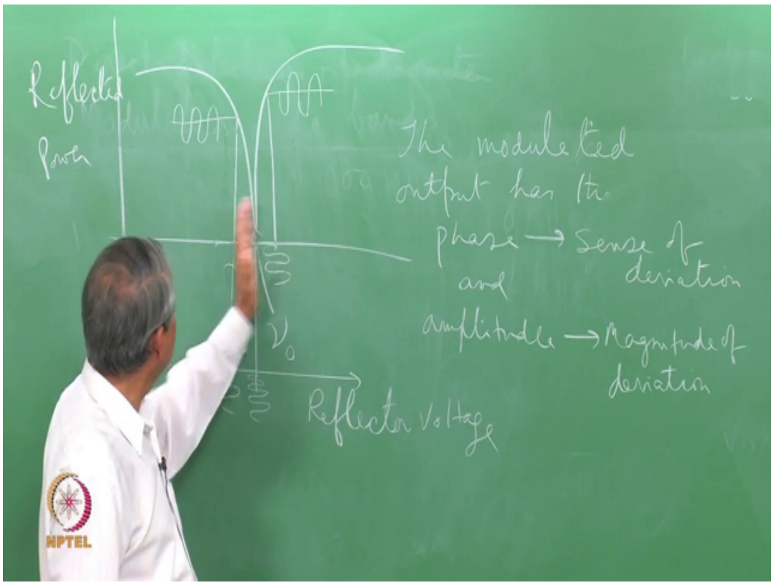

And this gives me the magnitude of deviation. So, again if we do the lock in detection at the same frequency, I can get the voltage which will be the measure of the deviation from the cavities resonance frequency. And that is exactly now the correct information that I need to bring back, the micro frequency to the desired value. If that voltage used to change the voltage of the reflected that is produced in the microwave.

So, similar technique is used also in gunn oscillator, whose frequency is modulated and exactly same technique is used to control the frequency that comes out of the oscillator. So, we have now seen the application of this phase sensitive detection into instances, and how cleverly the noise can be rejected, and signal can be amplified and how it is used to generate the derivative EPR signal also generate the automatic frequency control of the micro frequency. Also, you see how cleverly it can distinguish various types of signal, the detector sees the microwave modulated by 2 modulation frequencies.

One is the magnetic field modulate by the EPR signal, the other is the frequency modulation of the frequency at typical frequency of the AFC. 2 phase sensitive detectors said to 2 different frequencies. Pick up the correct signal based on their reference frequency. And that way it can separate the signal.

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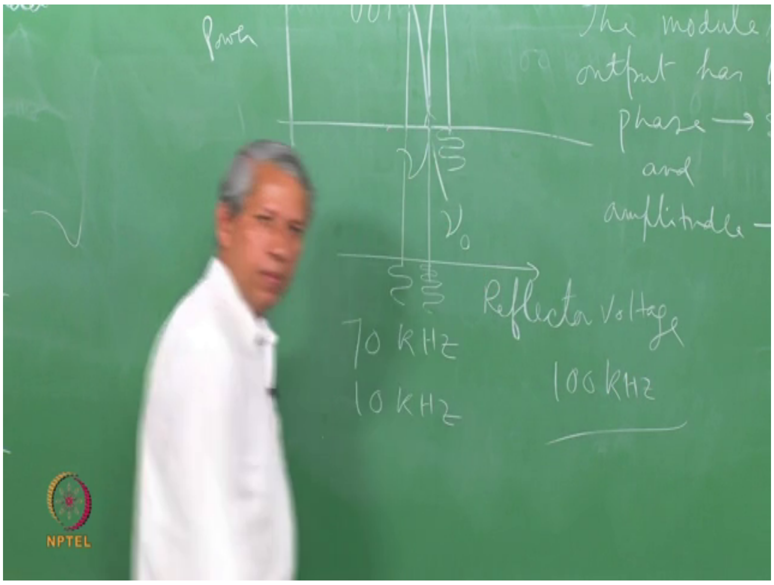

So, typical frequency of modulation is sometimes used as 70 kilohertz, or sometimes 10 kilo hertz. And this is kept sufficiently away from the magnetic field modulation, which works at typically 100 kilohertz.

With this discussion now brings us to the complete idea of an EPR spectrometer.