One and Two Dimensional NMR Spectroscopy for Chemists
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Lecture – 62
NMR Instrumentation

Welcome back. In this class, I would like to give you a brief idea about what an NMR Spectrometer is. There are several components; several parts in the NMR spectrometer; each will do its own job. Of course, these are not absolutely essential for this course because this course is devoted mainly for one and two dimensional NMR applications for the chemists, principles, concepts and applications.

However, needless to say you should know something about the spectrometer and also something about data processing, data acquisition etcetera. So, as I thought I will give you bird's eye view or a brief discussion about what an NMR spectrometer is; various parts of it, what it does and some tricks involved.

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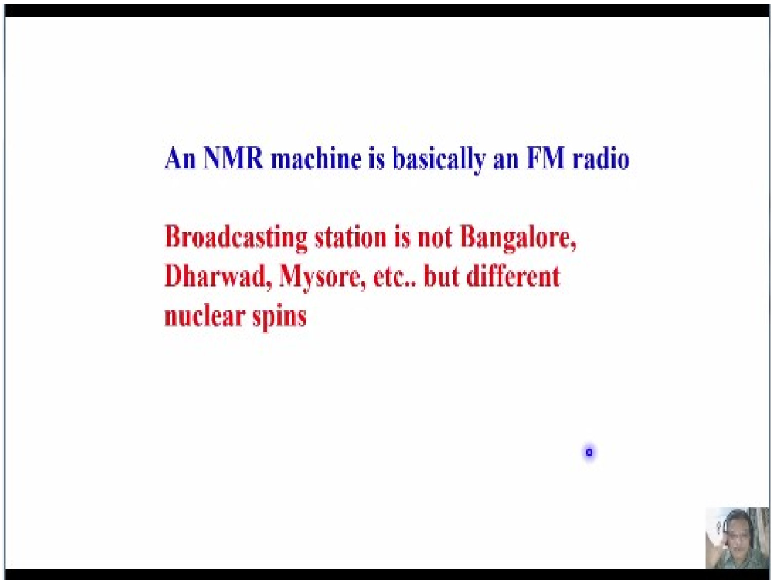

So, this is a overview of an NMR spectrometer. Remember an NMR machine is basically a FM radio; it comes under radio frequency region; it is nothing but a FM radio. What is important thing is to remember that broadcasting stations are not Bangalore, Dharwad, Mysore, etcetera; but broadcasting stations are different nuclear spins. And receivers are individual spectrometers consoles.

So radio frequency signals emitted by the nuclear spins after doing certain tricks in the experiment by sending radio frequency signal, exciting the spins and collecting the signal, we do the Fourier transformation and get the spectrum. This is nothing but a FM radio, okay. So the signals are now emitted, broadcasting station you can assume are different nuclear spins.

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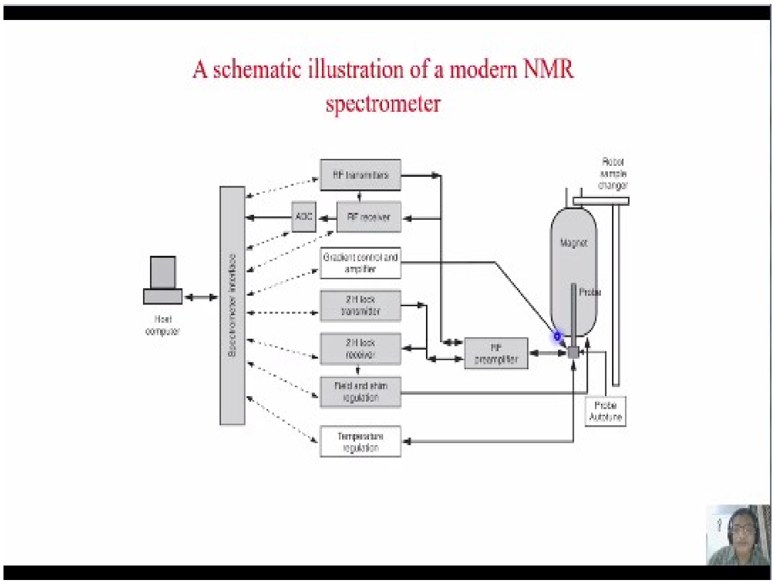

It is a schematic illustration of a modern NMR spectrometer. It consist of a magnet which is superconducting magnet, I will tell you as we go ahead further. And we have a probe which we put from the bottom and you have to insert the sample from the top, nowadays we have robots to do that job. We have preamplifier, the signal detected, you know the EMF induced we collect as small micro volts, very small amount of voltage is collected. It is very low voltage. It has to be amplified by a preamplifier. Then it is taken to the spectrometer to do all sorts of processing.

And of course we have a transmitter to transmit the right radio frequency signal; or the pulse, and in that, we also collect the signal; do the digitization and give it to the spectrometer interface which we call as a console. Here all operations will be done depending upon what is the command the operator gives. You know various functions are carried out and this is the host computer, where your time domain data, frequency domain data, pulse programming, various things can be monitored here.

Of course, the major important component of the spectrometer is that you have a gradient control also; most important is the 2H lock. We have a deuterium lock to prevent the field from drifting. You have a lock transmitter, lock receiver and important we have field-shim regulation. We have shim coils where we pass the current and generate a counter acting magnetic field to nullify the inhomogeneity, if any, to make the magnetic field homogenous.

And of course all the experiments, in spite of being a superconducting magnet, nowadays magnets are superconducting, the experiments are carried out at the room temperature. And this sample temperature, if you want to study the dynamics, can also be regulated, can also be monitored. So this is basically a schematic or the block diagram of an NMR spectrometer.

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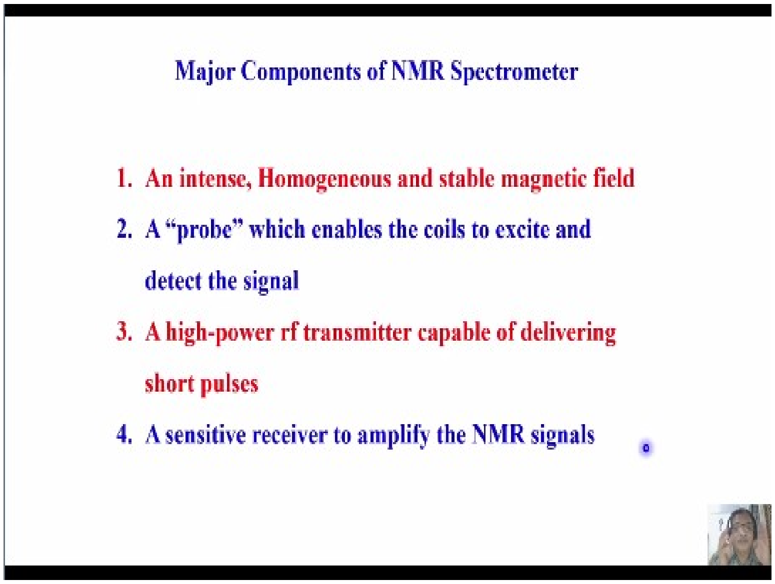

And just to give you a brief description about the components. It requires an intense, homogenous and stable magnetic field. Remember, three words, intense that is very strong magnetic field, very high magnetic field. Homogenous over a sample volume about 1 centimeter or 3 – 4 centimeters in which you have put the sample, the receiver coil will be there, over the entire receiver coil area where you are going to collect the signal, the magnetic field has to be perfectly homogenous. The homogeneity should be one part in 10 to the power of 10. So that in a spectrometer of higher frequency like 600 MHz or1000 MHz, you must be able to differentiate two peaks separated by 0.1 Hertz. That much is the resolution you require. So magnetic field has to be perfectly homogenous. And it has to be stable, field should not drift. The magnetic field invariably keeps changing, drifting, so the position will change and during the magnetic field drift what will happen, you will have multiple resonances, consequently the peaks get distorted. It has to be avoided. So you need an intense, homogenous and a stable magnetic field.

You need a probe; probe has a coil RF coil. It does the job of both excitation and detection of the signal. There is a coil in the probe, which I showed you in the previous diagram, which is inserted from the bottom of the magnet. The radio frequency pulses when you send, it will excite the nuclear spins. It is the same coil which not only acts as the transmitter but also acts as receiver, it receives the signal, detects the signal.

Of course, high-power transmitter is required to generate the frequency and send short RF burst of pulses. We need to have a sensitive receiver to amplify the NMR signals, I showed you the signals what we are going to generate, the EMF is very small and is of the order of micro volts and we need to amplify it; thus we have a preamplifier to amplify the signal. Then we have another amplifier, so finally we should be in a position to detect the signal and digitize it.

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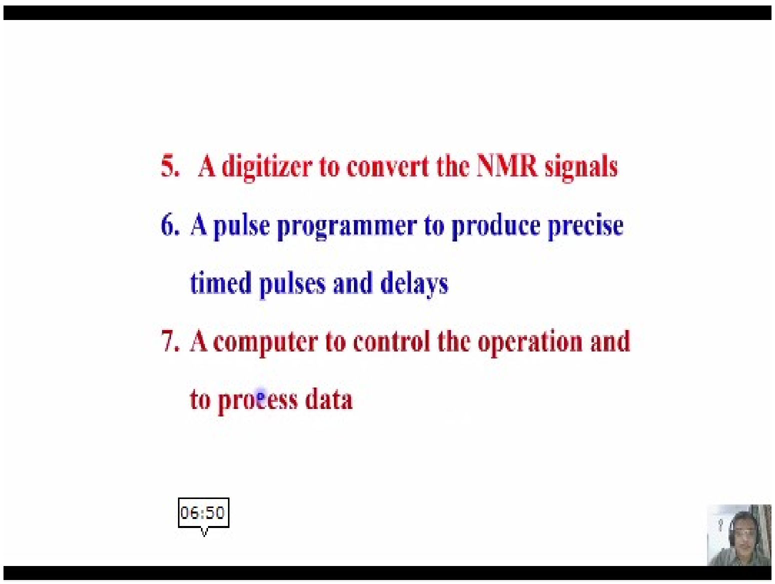

So have a digitizer, because the signal is collected in a digitized manner. And then afterwards we need to have an analog to digital converter for that. A pulse programmer to do the job of all those things. We need to precisely timed with delay of the pulses, angle of the pulses, phase of the pulses everything we need to precisely monitor, manage it up to nanoseconds, up to microseconds. So we require a very good pulse programmer. And of course, for all this operation to control and manipulate and deal with it you need a sophisticated computer, which does the job of operation and processing of the data.

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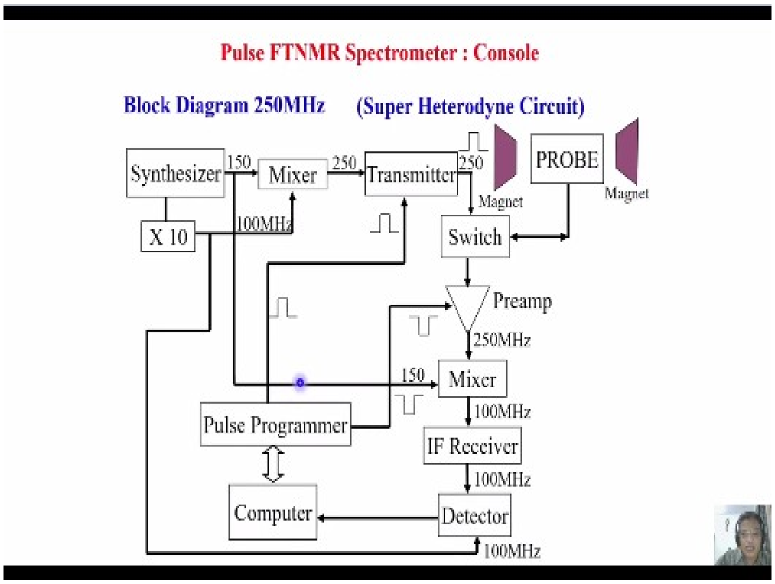

So this is how the FTNMR Spectrometer Console works. Shown is the block diagram of 250 megahertz spectrometer. A super heterodyne circuit is there, as I said. There is a probe and then, of course, synthesizers generate frequency; send to the mixer, transmitter and then we will send this signal, transmit to the PROBE. And we receive the signal give it to the preamplifier and then again mix it, and all this things we do and detect the signal.

The signal is sent back to the computer, and you can also monitor what you can do through the pulse programmer using the computer. And we can also monitor the transmitter frequency everything; and all these preamplifier, everything is controlled by these things. And so this is basically a block diagram of 250 megahertz spectrometer. How it works is a detailed discussion of each and every component. Let us not worry too much. I just wanted to give you the brief overview; a bird's eye view of NMR console.

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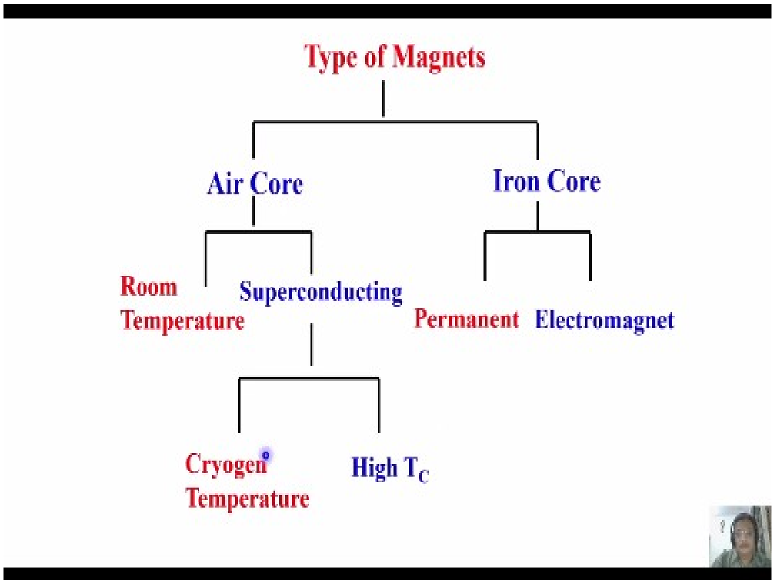

Let us go to the types of magnets. It is very important. Broadly, magnets can be classified into two types; one is Air Core magnet, and other is Iron Core. Two types of magnet are there. Of course, in the iron core magnets, all of you would have understood in your early college days, you have a permanent magnet and the electromagnet so long as we pass the current we have the magnetic field; that is fine.

In the air core magnets, again they can be divided into two types, one you can have magnet at room temperature and you have a magnet at superconducting temperature. It is a superconducting magnet. The superconducting magnets, generally, in the present spectrometers is done at cryogen temperature. That is at the liquid helium temperature, which is at 4.2k. Now of course, we can go further down, so we have very high field magnets working at 2k.

But you can also have a high Tc superconductor. But presently the most popular and routinely employed, which is powerful and available commercially is superconducting magnets, which work at Cryogen temperature, liquid helium temperature.

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So what are the maximum magnetic fields that you can achieve in all these things? Of course, if you have an iron core magnet, the maximum magnetic field that you can achieve is around 2.5 Tesla. Remember it is a unit of magnet field; I discussed earlier also; 1 Tesla is 10,000 Gauss. So whether it is a permanent magnet or electromagnet maximum achievable is 2.5 Tesla. Beyond that it is not possible. Okay. Whereas superconducting magnets has an advantage, you can get magnetic field beyond 21 Tesla, so that you can get even a 900 megahertz spectrometer which is possible. Of course nowadays even more 1 gigahertz; 1.1 gigaertz, 1.2 gigahertz spectrometer will come to the market soon, it will be commercially available. So the spectrometer frequency is going up and up. As a consequence, the magnetic field strength also is very high. And to generate such a magnetic field requires enormous amount of research; we cannot just generate such a magnetic field so easily; just because you know the superconducting nature of a certain material and then make it superconducting by passing the current and generate the magnetic field. It is not true all the time.

There is lot of work involved and the lot of technology is invovled, lot of research has gone; and now people are able to get very stable, strong and homogenous magnetic field for 900 megahertz, 1 gigahertz and 1.1 and 1.2 are also available. The 1.2 GHz instrument will come to the market soon. So present day spectrometers always work in persistent current mode, that is called the superconducting magnet.

What is a persistent current mode? For the persistent mode, take a material make it superconducting by passing the current, generate the magnetic field, then join both ends of the wire that is all. Join both the ends of the wire. Now you do not need external current at all. So as long as you maintain the liquid helium temperature; the coil is immersed in liquid helium at the cryogen temperature, the magnetic field always exists, because the current you have passed once and produced the field, because the current will be always there. It is called a superconducting state. That means there is no opposition for the flow of electrons. The current, once you pass and generate the magnetic field, it persists forever, so long as you maintain the superconducting temperature.

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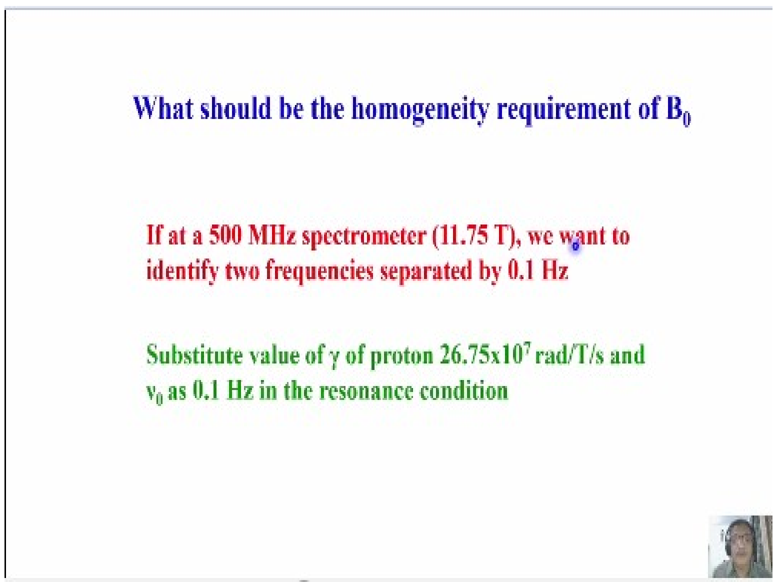

Now as I have been discussing what should be the homogeneity requirement; I said strong and homogeneous magnetic field. What is the homogeneity requirement? In a 500 megahertz spectrometer of 11.75 Tesla, I should be able to separate two frequencies separated by 0.1 hertz. If I know what is gamma of the proton? If I know what is the resolution I require I can calculate, we did that earlier also once, I think.

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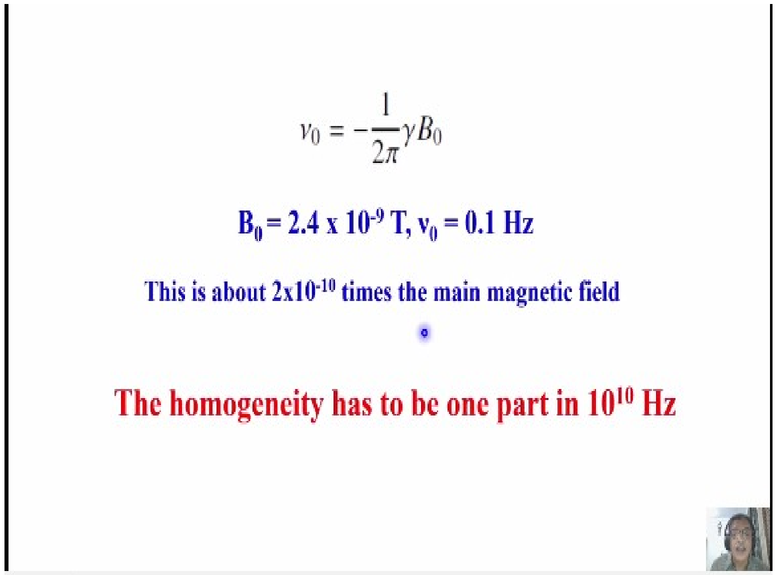

And this is about 2.4 into 10^{-10}. Thus our resolution should be of the order of, one part in 10 to the power of 10. In a 1000 megahertz spectrometer you must be able to separate 0.1 hertz. Imagine the homogeneity, that is the resolution you require. So there is heavy demand on the homogeneity of the magnetic field, okay.

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So, for the requirement of a superconducting magnet, the first thing is high stability with minimal drifts; and of course this I already discussed.

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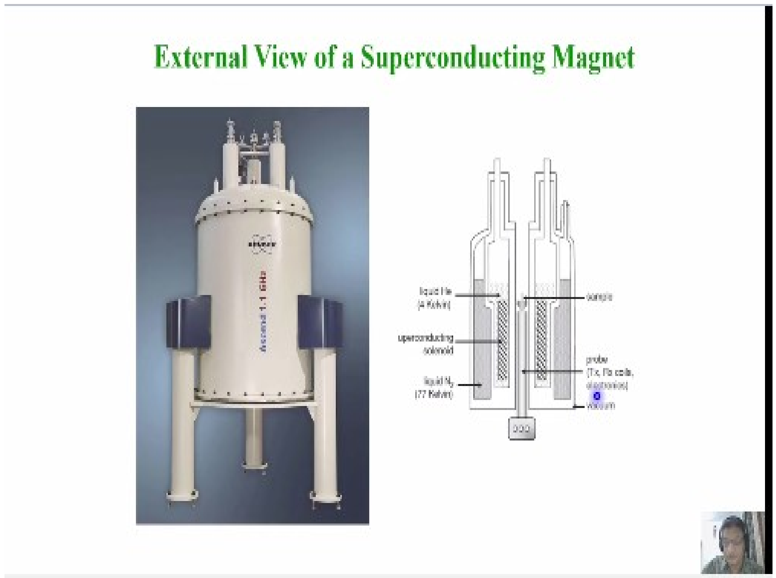

And if I look at the external view of a superconducting magnet, this is how it looks, okay. This is how you see. But inside if you see from the top, let us say, we have; this is the room temperature bore, this is where the probe is put; you put your sample here; all your experiments are carried out at room temperature. Surrounding that, we have a liquid helium chamber, the superconducting coil is dipped in the liquid helium here; which is at 4k. And surrounding that we have a have liquid nitrogen chamber. This is to minimize the evaporation liquid helium; and in between we have lots of things, vacuum and also mylar films, etcetera, to minimize evaporation of helium and nitrogen; so that it can last for a longer duration.

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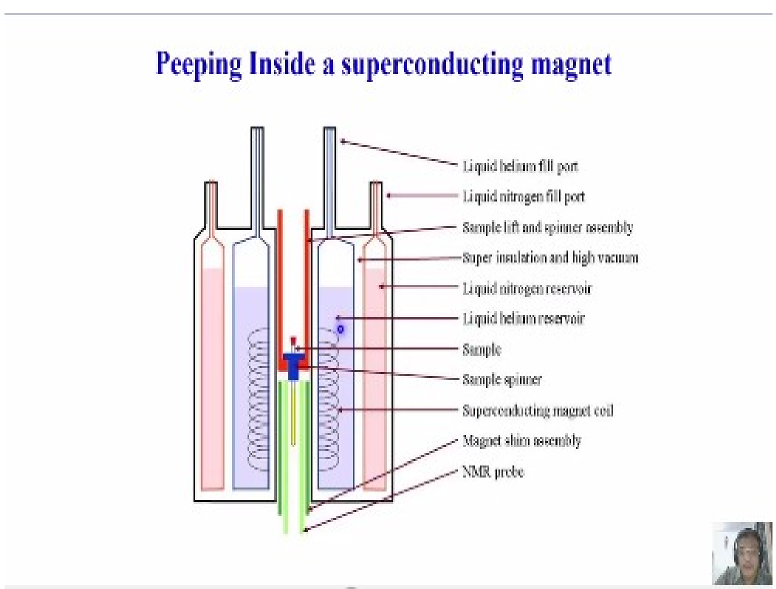

And look at this; if I peep inside more and more; this is a liquid helium filling port, you will see in the magnet. Go to any NMR lab, you see a huge cylinder like material will be standing there, that is a superconducting magnet. It will have several ports like this, this is for liquid helium filling, this one for liquid nitrogen filling. We have a RF coil here, this is a sample holder and then sample is put inside this; this is a probe; Okay. And this is a coil, the superconducting coil is here, it is dipped in the liquid helium chamber and this is a liquid nitrogen chamber.

So very simple, basically it is a highest or the most sophisticated quality of a thermos flask, that is all. I mean, I cannot make so cheap statement; it is not that. This is a superconducting magnet, its technology is highly different, okay. So; but the concept you can imagine like a thermos flask.

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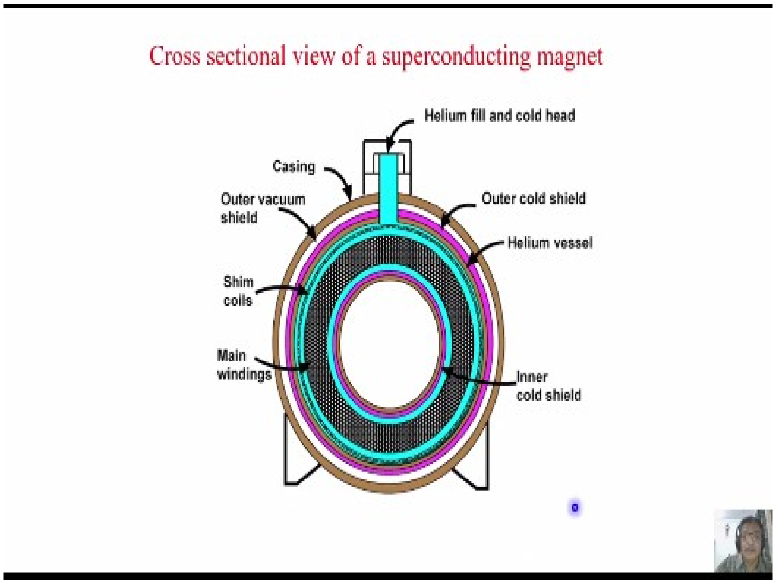

The cross sectional view of a superconducting magnet, if you look at it, if you take a cross sectional view, you see this is a Inner bore where it is at room temperature, probe is put. All your samples are here, in the probe, you do the experiment at room temperature. You saw concentric circles like this, helium filling chamber, we have a casing, a outer vacuum, shim coils, main superconducting windings are there. And then we have a shield inside, between the liquid nitrogen and liquid helium chamber, there are enormous shieldings to prevent the evaporation. And you have to make sure that helium do not evaporate faster, nitrogen do not evaporate faster, everything must be in a high vacuum. All those things are taken care. And to get a homogenous magnetic field of such a very high magnetic field, is a challenging task.

Remember, that is the reason why almost 50% of the cost of this spectrometer goes for the magnet itself, because lot of research work is there and lot of technological development is going on to get a very sophisticated magnet for our requirement; it involves lot of efforts. So as a consequence, when you buy a spectrometer, major portion of your money goes to the magnet part.

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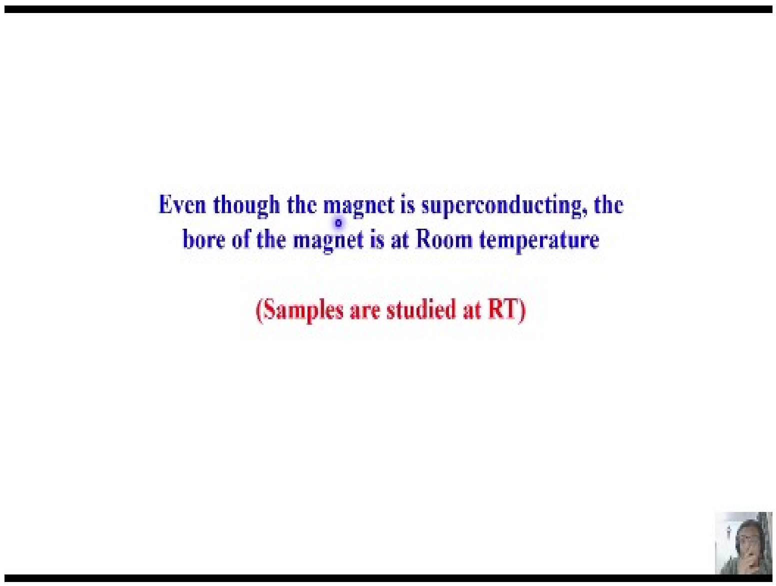

So now as I said even though magnet is superconducting, the bore is at the room temperature, all samples are investigated only at room temperature. Okay.

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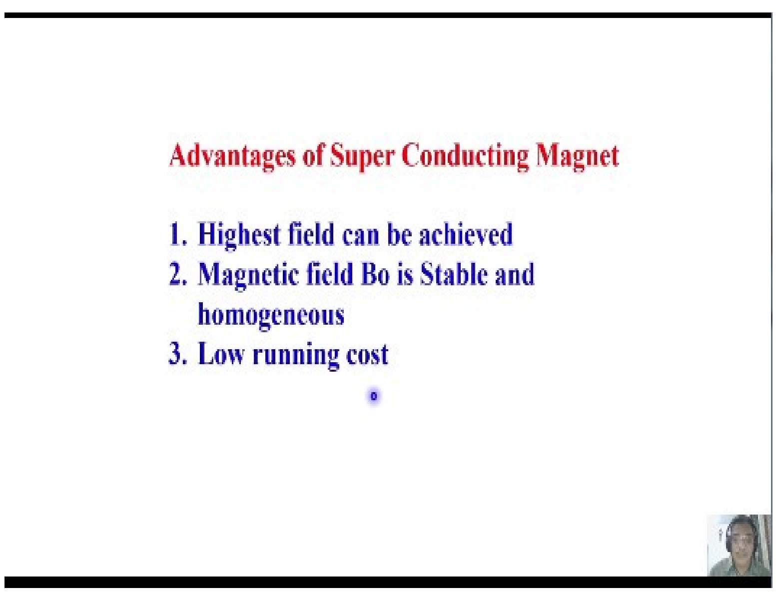

Now next, what are the advantages of a superconducting magnet? First thing, we can achieve highest field which is not possible to achieve in iron core magnets, permanent or electromagnet. There is a limitation of 2.5 Tesla. Here maximum possible; now it is 24 to 27 Tesla, which we can easily achieve. Magnetic field is stable and homogenous. And the running cost is low. Of course, we will have to take into account the liquid helium and liquid nitrogen which we have to constantly keep on replenishing, when they evaporate. That itself is a lot of cost for the maintenance. This statement we have to take with a little pinch of salt. This is said because we do not need electric power regularly, etc. Once you pass the current you are in a superconducting state, and the magnet is always maintained, that is the reason. But of course, helium requirement is there, nitrogen requirement is there, liquid helium and liquid nitrogen are very expensive, constant requirement; you have to continuously keep replenishing, keep filling when they evaporate. So that is a very, very huge running cost.

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And of course, basically if you have high field spectrometers, NMR spectrometers have lot of advantages. We have high chemical shift dispersion, improved selectivity in the spectral editing scheme. Sensitivity goes up by $B0^{3/2}$. Remember, higher the magnetic field, higher the sensitivity, spectral simplification is possible, we can do first order analysis. Like I said second if the spins are strongly coupled, they can become weakly coupled, and first order analysis is feasible at very high magnetic field. You can see TROSY effects, which I did not discussed, do not worry about it. T1 increases at a high field, a small disadvantage which does not matter. We can study T1 also.

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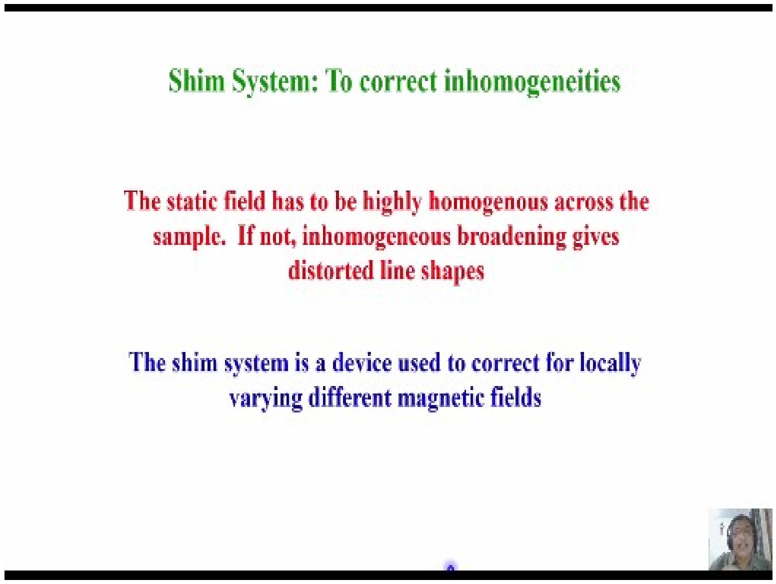

So now to get a homogenous magnetic field; In general all the magnetic fields; when you make magnetic fields, it is not that they are perfectly homogenous over a sample volume of 3 or 4 centimeters at the rate of one part in 10 to the power 10 homogeneity. It is not always true, cannot happen. There will be inherently in homogeneity, we need to correct it.

The static field has to be highly homogenous across the sample. Otherwise we will get distorted line shapes or broadened peaks. What you will do for that? We have what is called shim system. Inside the magnet, at the outer chamber we have, what is called a shim system, which is a device used to correct locally varying fields. Locally there will be inhomogeneity in the magnetic field and we can correct that.

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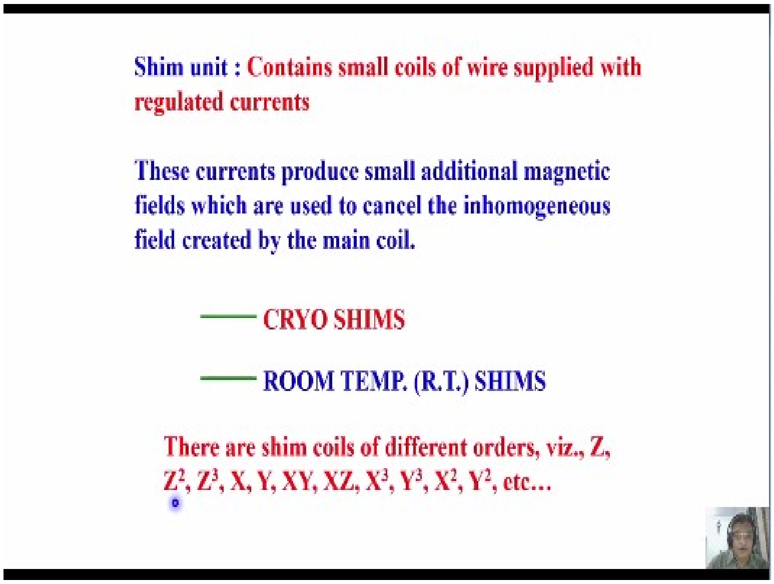

And for that we use shim unit. what is the shim unit, it is nothing but small coils of wire, which are supplied with regulated currents. I can regular the current flow inside the coil and they are all in different shapes. It is kept in different shapes at different places within the unit, such that if there is inhomogeneity at z-axis or x-axis or y-axis, I can put a counteracting current and generate a counteracting magnetic field to nullify the inhomogeneity. I can cancel out inhomogeneity created by the main superconducting coil.

So, these are the advantages we have in shim unit. We can correct the magnetic field. But this, the shim to correct the magnetic field inhomogeneity can be both Cryo shims and room temperature shims. When you have inserted the superconducting material in the liquid helium chamber, when you are passing the current, at that time also you have to homogenize. That is called Cryo shimming. And afterwards we have to homogenize it at the room temperature, when we are routinely doing the samples. This you do not touch regularly.

Once it is done at the time of charging the magnet, nobody is going to touch it, you are not allowed to touch, you cannot do it. Whereas these things, the room temperature shims are in our hands. As I always say, you have to get good homogeneity, you have to utilize this room temperature shim coils, there are about 24 to 36 different field coils will be there like Z, Z1, Z2, Z3 up to Z6 gradient; X, Y, XY in different directions. The counter acting magnetic field can be produced to cancel out the inhomogeneity. There are several like this.

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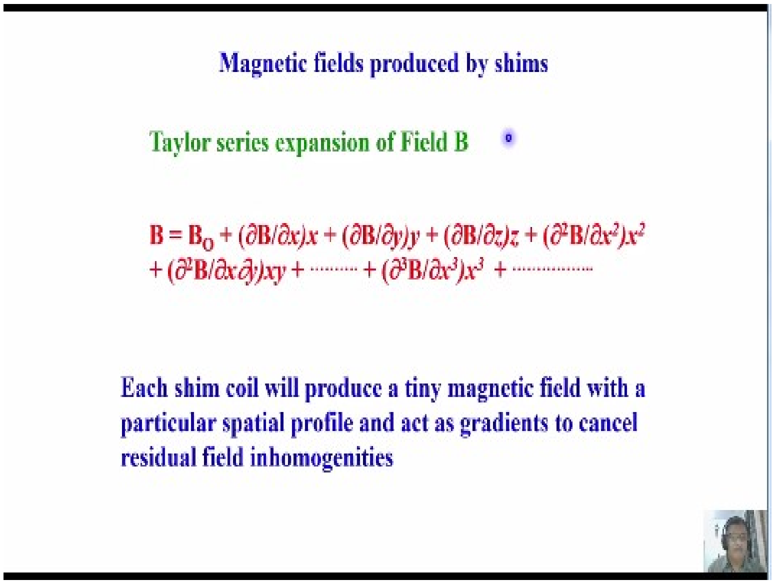

And magnetic fields produced by the shim currents can be given by a mathematical expression like this. You can expand like a Taylor series. B = B naught main field plus additional field, x variation you know, the deviation in the x-axis, y-axis, z-axis, x squared, xy. All these components of the Taylor expression you can consider; and each shim coil will produce a tiny magnetic field with a particular spatial profile and act as gradients to cancel out the residual inhomogenities that is produced by the main field.

So that is why you can have expansion of this for n number of terms. That is why we have different shim coils, so you can vary the magnetic field in the x direction, y direction, z direction, x squared that is a parabolic path, xy, x cube; these are all shim coils where you can change, produce the counter acting magnetic fields in different spatial profiles.

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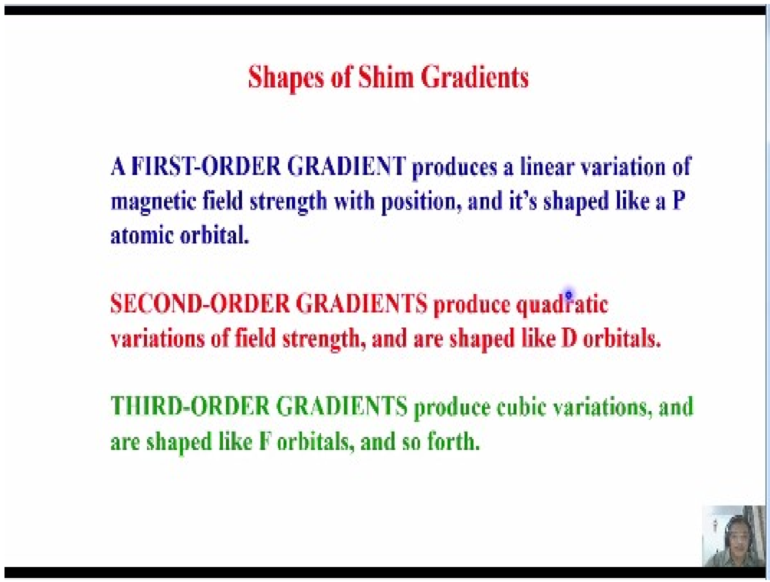

So the shapes of the shim gradients: we can consider, a FIRST-ORDER GRADIENT, it produces linear variation like a Z, X, Y. SECOND-ORDER is quadratic like x^2, y^2 etc. THIRD- ORDER is cubic variations. Okay.

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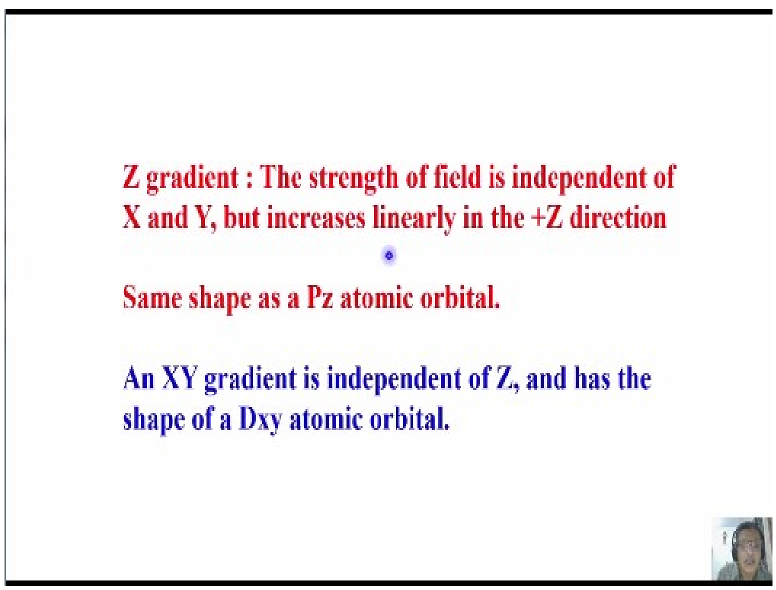

Z order, Z gradient is of course independent of x and y, increases linearly with the Z; and it can be treated like a Pz atomic orbital, okay. And XY gradient is independent of Z, and has a shape like Dxy atomic orbital. So for all these we can have a similarity with atomic orbitals, and inhomogeneity in the magnetic field, how the shim currents produce different magnetic fields with a different spatial profile with a different shim coils.

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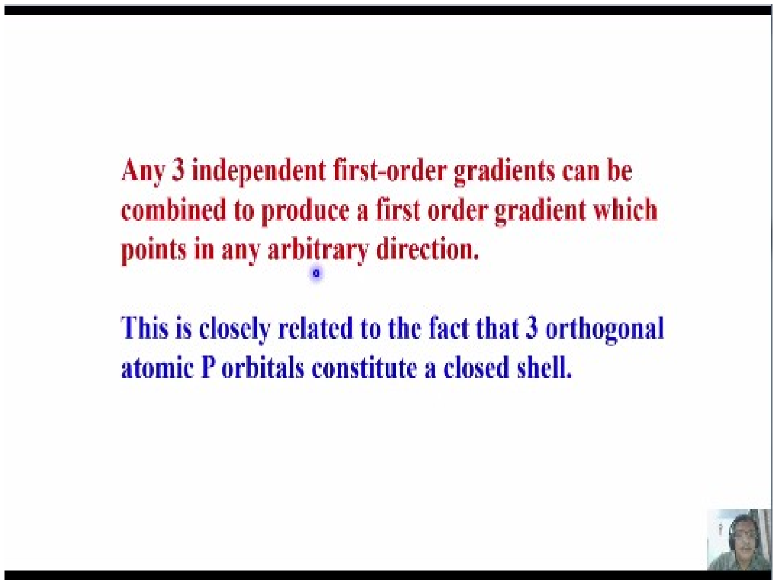

So you can keep on changing it. You can have three independent shim coils combined together. You can produce magnetic field gradients in any direction you want. You all know, since it is a chemistry course you know that, if I have three orthogonal three atomic orbital it can constitute a closed shell. It is an analogy. If I have three independent first-order gradients, I can combine them in various fashions and produce a first-order gradient, which can point in any arbitrary direction of my choice. That is how all 36 shim gradients can be designed, okay.

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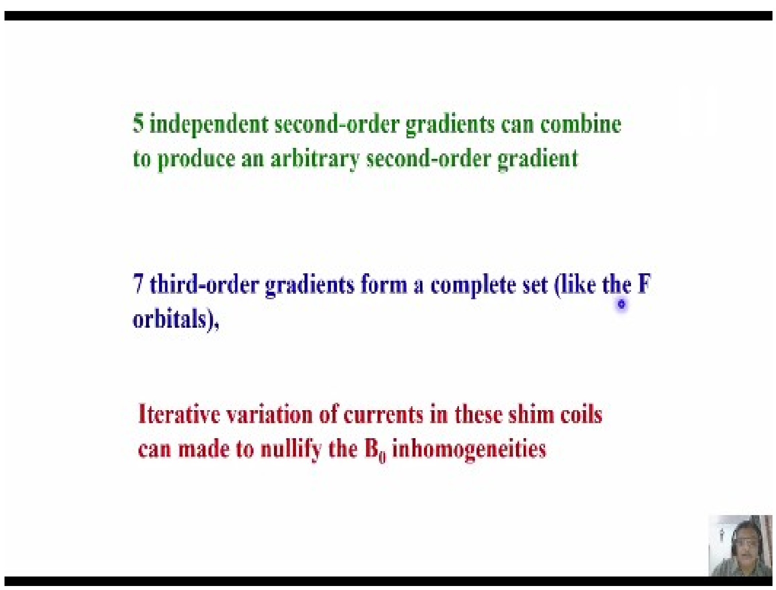

Similarly, 5 independent second-order gradients can combine give a second-order gradient arbitrary; third-order can give F like orbital shape. Like this you can have many things to talk about it.

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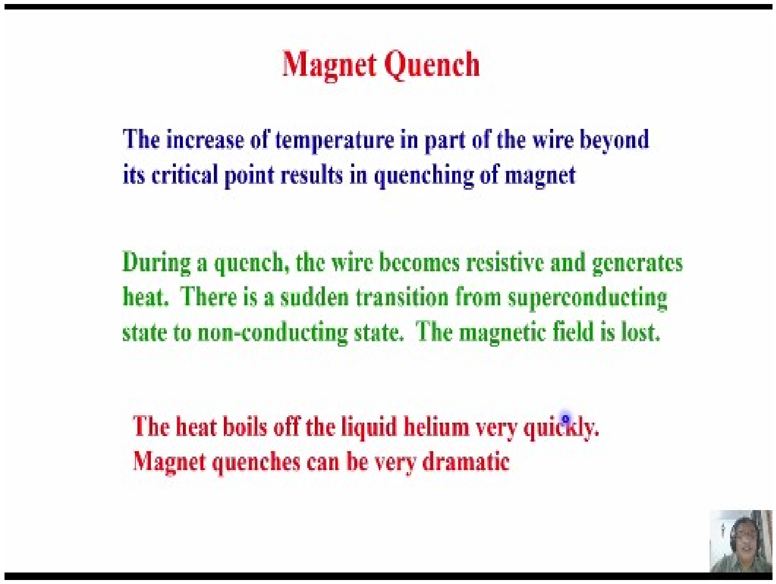

So this is how you get a magnet, you can tune the magnet and everything. This magnet has to be maintained in a persistent current mode. That means, you need to keep on filling liquid helium and liquid nitrogen. If liquid helium evaporates, magnet will suddenly achieve at room temperature; or at any instant of time a small resistance is generated in the superconducting coil or a superconducting material, by some reason, it generates heat. Remember what will happen to liquid helium. Liquid helium is at 4.2k, 4.2 degree Kelvin. To make you more familiar room temperature is 300k, remember that is at 4.2k. It is -269 degrees or 269 k lower than the room temperature, such a very low temperature. Small amount of heat when it is generated in the superconducting material, the entire helium gets evaporated, that is called quench.

It can happen for various reasons. Okay, magnet can quench without we doing anything, we have seen magnet quenching while filling liquid helium, while charging many times we have seen magnet quench. And magnet quenches because of the increase in the temperature, when it happens suddenly superconducting material enters into a non-conducting state; from the superconducting state.

It loses all superconducting state and gains the resistance which was zero before; and whole magnetic field is lost, okay. So the helium boils off very rapidly and if you really see the magnet quench, it looks very dramatic.

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See here you can see; this is the quench which happened in our lab one or two years back, while charging the magnet. You see entire helium is boiling off and is very dangerous remember. When one liter of helium evaporates it will evaporate into 27 liters of helium gas, it occupies the entire space. It can deplete oxygen. You see the point. Entire helium is getting evaporated now, it is coming out of the nasal like this. You have to be extremely careful. This is called a quench, okay. Now with this we will go further.

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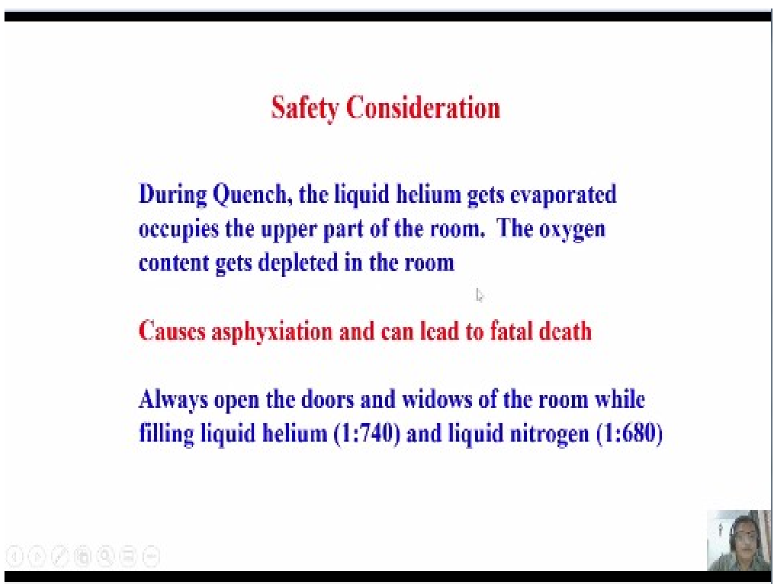

The safety consideration; the magnet quenches when helium get evaporated, as I said, oxygen may get depleted in the room. It may cause asphyxiation, can lead to fatal death also. Always open the doors and windows of the room while filling liquid helium and liquid nitrogen. Okay. Do not try to do; try to do the experiment by closing the doors and windows, while filling the helium. If by some reason, you have bad luck, if there is a quench it can be very dangerous. So this one of the safety warning I am giving you.

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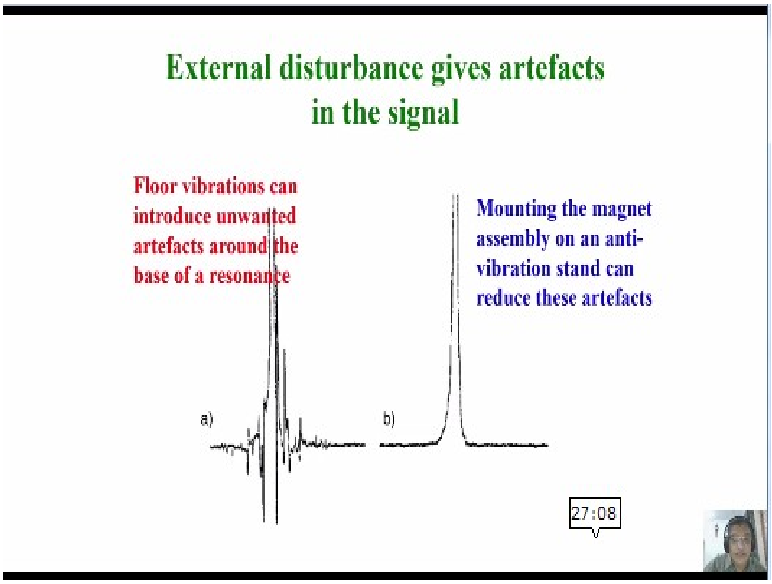

And sometimes magnet is so high, our homogeneity has to be so precise, we require such a good homogeneity. You may not know, you housed the magnet and charged completely, and the magnet is kept on the floor. Some vehicle, truck will be moving, let us say, in a main road far away, some 30 or 40 feet away or 50 feet away. The vibration, that is felt on the floor because of the movement of the vehicle can be seen by the spectrometer, the magnetic field start fluctuating; these are vibrations due to the external disturbance.

Floor vibration can cause problems. As a consequence you see NMR spectrum get distorted. So you have to ensure the magnet is put in a place which is free from floor vibration. You will not see sometimes the difference. You can check, in case if it is not put on a vibration free stand or anti-vibration stand, if it is put on the floor. If somebody is doing a work in a lathe or somewhere which is a far away or a heavy truck is moving just 30-40 feet away.

Your spectrum will have lot of disturbance. You will start interpreting as due to sinc function artifacts, etc. But this is due to external disturbance. Okay. So you have to mount it on an anti-vibration stand.

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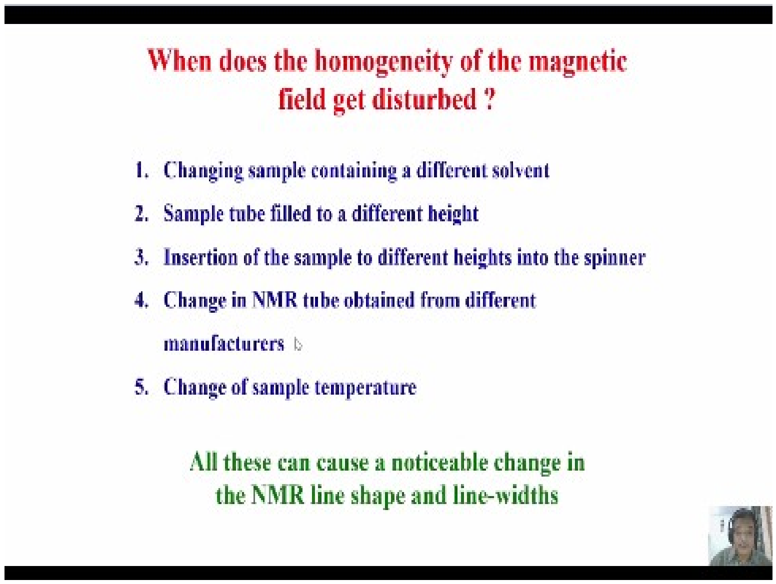

Now the question you may ask me. Okay, I will tune the homogeneity andf everything. But why should homogeneity get disturbed? I charge the magnet, tune once and keep quiet. I shim the magnet, make the field homogenous and keep quite. Why should it get disturbed again? Why should I do it again and again? That is the question you may ask. Remember, the magnetic field homogeneity microscopically even if you disturb, it get disturbed, it will be reflected in the spectrum.

See changing of the sample containing a different solvent. I have sample prepared in chloroform, I tune it, because it has one diamagnetic susceptibility for that sample. I change that sample put a different sample, with a different solvent; again you will see the susceptibility for that sample is different and because of that field will be different, homogeneity will be different. If you have a sample tube with a different height, if you do not take perfect height of the sample in the tube you may get into problems.

And you have to have the perfect height of the sample also; insert the spinner which should completely fit into the RF coil in the probe; otherwise you may get distortions. And NMR tube from different manufactures can be bad, sometimes. You check yourself. Purchase NRM tubes from different manufacturers and do the experiments, there could be slight inhomogeneities. It may be different from different manufacturers.

And if you can change the sample temperature, if you do not regulate, then inhomogeneity due to gradient of the temperature across the sample volume, can give rise to inhomogeneity. Many factors contribute like this. As a consequence, you take out the sample once, put the sample again, the same sample you may have to retune the field to some extent. If you change a different sample, of course no choice, you have to retune to get the better field homogeneity.

So all these effects can give a noticeable change in line-width and line shape. You have to take proper care, and every time you put a sample or you change a sample you have to tune the homogeneity, that is a important point. Okay.

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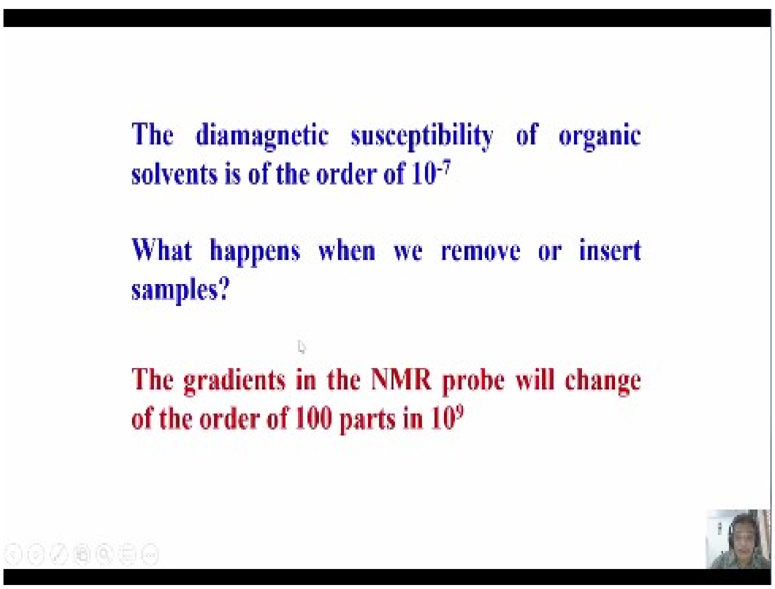

And how much it will change if I change the organic solvent? The diamagnetic susceptibility of organic solvents is of the order 10^{-7}. So what happens when you remove or insert samples? The changes by nearly 100 parts in 10^{9}, the gradients in the NMR probe will change of the order of 100 parts in 10^{9}. So as a consequence the field inhomogeneity will be developed, we need tune it.

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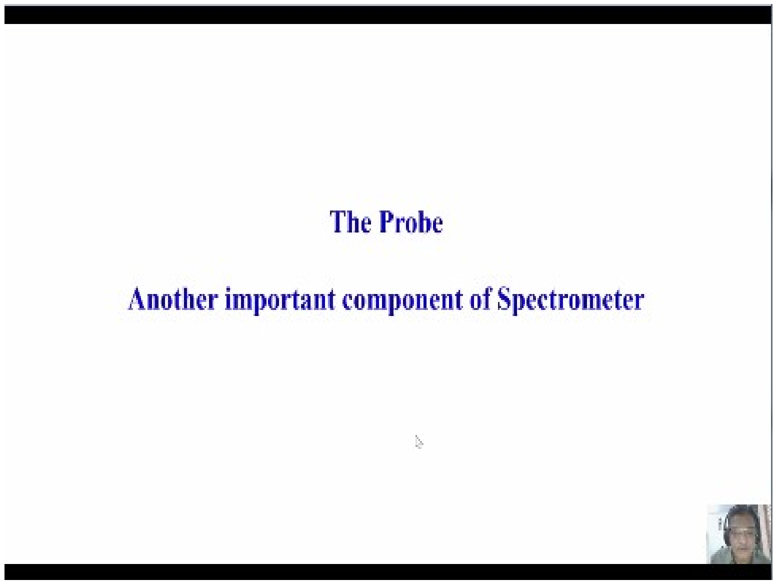

Okay. What I am going to do is next I will discuss something about the Probe which is another important component of the spectrometer and then we will talk about few other things and I do not want to go into the more details of other components. Probe is an important part. I will discuss that in the next class. So I am going to stop now. We will come back and continue on the instrument for some more time.