Advanced NMR Techniques in Solution and Solid – State
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Module 3
NMR Concepts and Spin Physics - II
Lecture - 03

Welcome back. In the last class we discussed about the Zeeman interaction, we found out the population ratio between two energy states for protons, in different magnetic fields. dWe also calculated the sensitivity factor, and we also found out what happened to the sensitivity as we enhance the magnetic field; and we understood Larmor frequency varieites of things we discussed.

And as far as the sensitivity is concerned not only the magnetic field there are several other factors which govern the sensitivity of detection of the NMR signal. Today let us start with this and see what are the other factors which can give raise to enhanced sensitivity; there are several other factors that give raise to the sensitivity.

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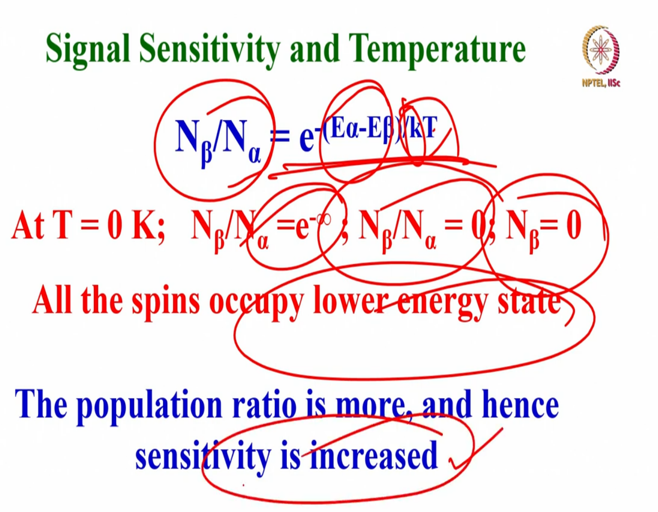

Signal Sensitivity and Temperature

$$N_\beta/N_\alpha = e^{-(E\alpha-E\beta)/kT}$$

At T = 0 K; $N_\beta/N_\alpha = e^{-\infty}$; $N_\beta/N_\alpha = 0$; $N_\beta = 0$

All the spins occupy lower energy state

The population ratio is more, and hence sensitivity is increased

Now signal sensitivity also depends upon temperature. Look at the this is a Boltzmann equation N beta divided by N alpha; we also worked out, it depends upon the energy separation divided by Boltzmann constant into T, which is the temperature. You cannot deal with this thing, the energy separation you can deal by the magnetic field. But what about the temperature? that is in your hands. Can you not vary the temperature? what happens? Let us say I go to low temperature. At 0 K, of course you cannot achieve absolute 0 K, I agree, assume T = 0, then what will happen? If you look at the N beta for N alpha ratio, it will become e to the power of minus infinity. So, N beta divided by N alpha becomes 0. That means N beta = 0, it means all the spins are in the lower energy state. And this gives rise to a lot of population difference as all the spins are in the lower energy state. In the higher energy state there are no spins at all.

That means be the population differenc is enormous at low temperature. So that means when the population difference is larger, the sensitivity is increased. That is one thing; thus the sensitivity gets increased with the reduced temperature.

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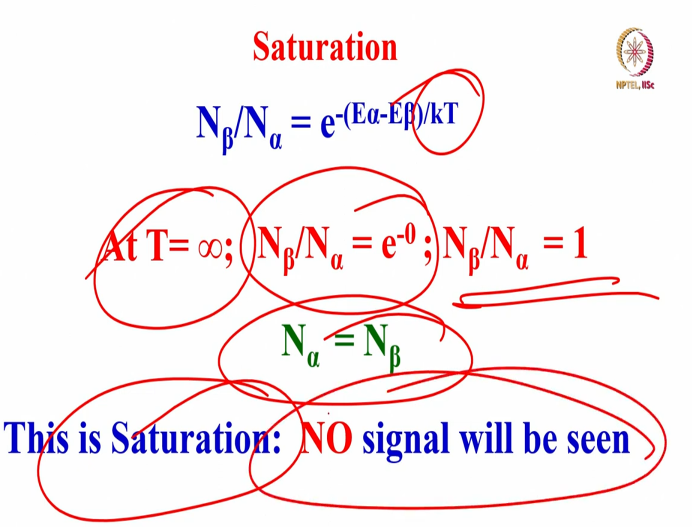

Saturation

$$N_\beta/N_\alpha = e^{-(E\alpha-E\beta)/kT}$$

At T= ∞; $N_\beta/N_\alpha = e^{-0}$; $N_\beta/N_\alpha = 1$

$$N_\alpha = N_\beta$$

This is Saturation: NO signal will be seen

Now you may ask me a question why should I go to low temperature, what happens if I increase the temperature? Increase to very high value, let us say I go to T which is equal to infinity. Put infinity here in this equation; infinity is in the denominator then what will happen? N beta / N alpha will become equal to e to the power -0 which is equal to 1. So that means N alpha becomes equal to N beta; that is, the population between both the spins states are equal.

In the alpha state and beta state the same number of spins are present. This is a condition called saturation in NMR. That way there is no population difference, the spin state energy levels are saturated, you do not see any signal at all; no signal will be seen, this is saturation condition.

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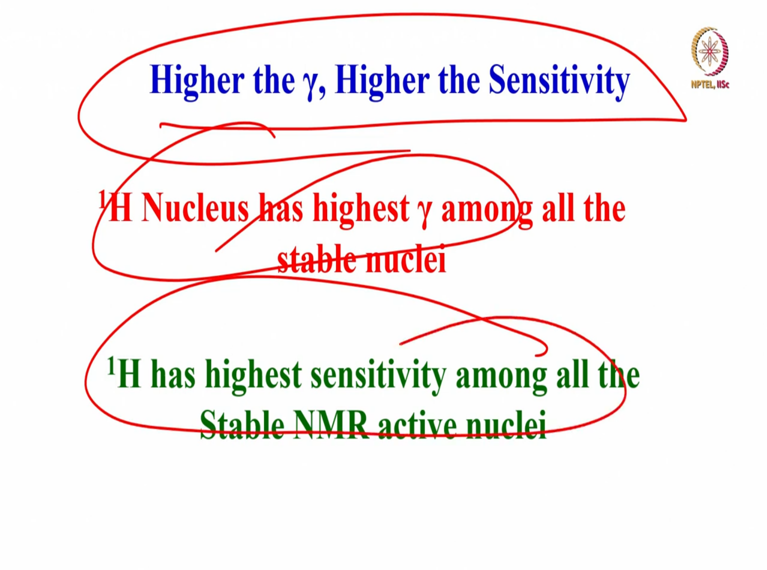

Higher the γ, Higher the Sensitivity

^{1}H Nucleus has highest γ among all the stable nuclei

^{1}H has highest sensitivity among all the Stable NMR active nuclei

I just introduced the saturation. Now let us see what happened to gamma, which is another factor which is responsible for sensitivity. Of course you cannot change the gamma, gamma is a constant for a given nucleus. It is not in your hands. But let us see what happens for different nuclei with the different gamma, how the sensitivity varies. Proton nucleus has highest gamma among all the stable nuclei. So, proton has the highest sensitivity among all is stable NMR active nuclei.

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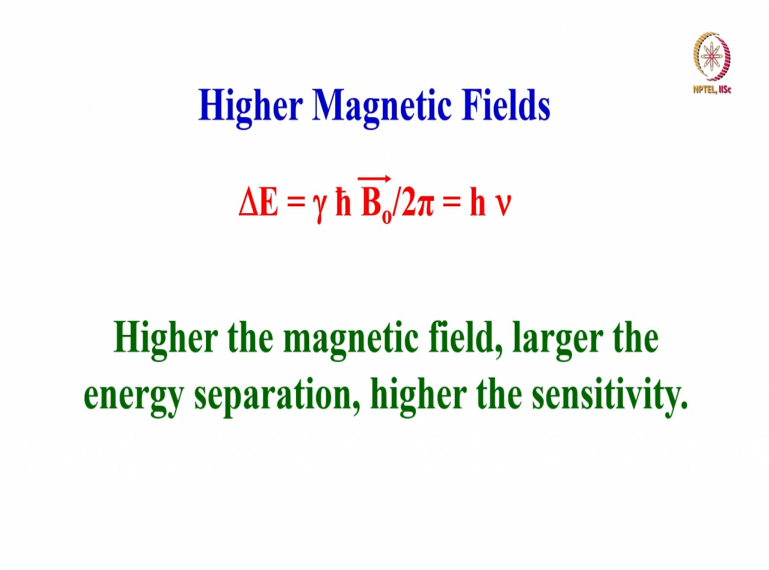

Higher Magnetic Fields

$$\Delta E = \gamma \hbar \overrightarrow{B_o}/2\pi = h\nu$$

Higher the magnetic field, larger the energy separation, higher the sensitivity.

And higher the magnetic field, the energy separation becomes larger and larger, higher the magnetic field, higher the separation and higher the sensitivity. This we understood.

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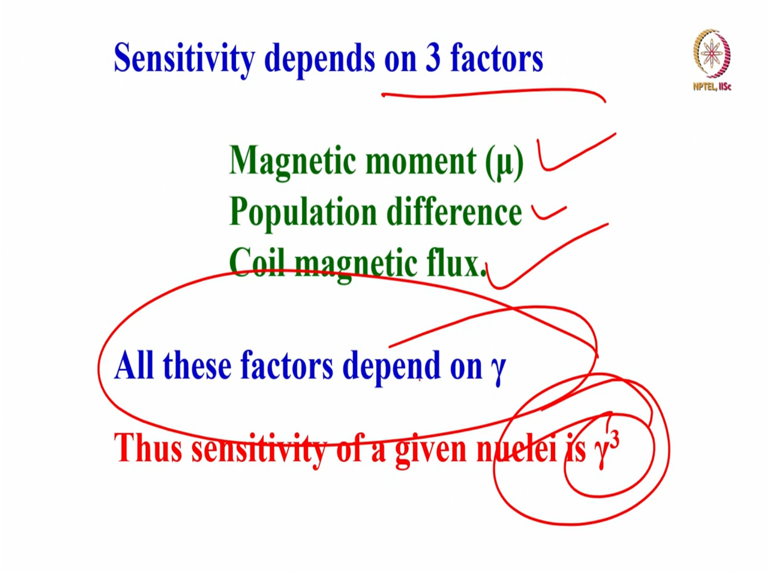

Sensitivity depends on 3 factors

Magnetic moment (μ)
Population difference
Coil magnetic flux.

All these factors depend on γ

Thus sensitivity of a given nuclei is γ^3

And sensitivity also depends upon 3 more factors; the magnetic moment, population difference and coil flux. All these 3 factors depend upon gamma. That means sensitivity is given by gamma cube. I told you proton is the nucleus which has highest gamma, highest gamma means gamma cube; that means you will understand; which is the most sensitive nuclei? Protons, protons are the most sensitive nuclei for detection because this is the one nucleus which has highest gamma among all the stable NMR active nuclei. So, detection of protons is high sensitivity.

Remember I said NMR is insensitivity for detection. The sensitivity which I am talking is relative, relative to other nuclei proton is highly sensitive.

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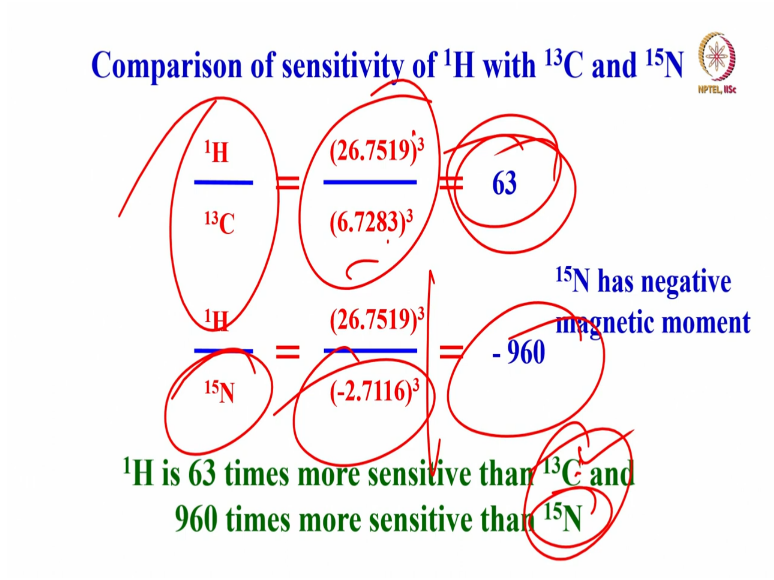

Comparison of sensitivity of ^{1}H with ^{13}C and ^{15}N

$$\frac{^{1}H}{^{13}C} = \frac{(26.7519)^3}{(6.7283)^3} = 63$$

$$\frac{^{1}H}{^{15}N} = \frac{(26.7519)^3}{(-2.7116)^3} = -960$$

^{15}N has negative magnetic moment

^{1}H is 63 times more sensitive than ^{13}C and 960 times more sensitive than ^{15}N

Let us compare the sensitivity of proton, carbon and nitrogen. Take the ratio of the proton and carbon sensitivity. That goes with the ratio of gamma. See in this equation here we can see B_0; 2 pi, gamma everything will be there. But if you take the ratio most of the things gets cancelled out and only gamma will be left. gamma cube of proton and the gamma cube of carbon if you consider, take the ratio it is 63.

I told you the ratio of gamma of proton and carbon is 4; carbon is 4 times smaller than proton. So, gamma cube; 4 cube is 64. So, it is approximately 64 you are getting 63 something. If you take nitrogen-15, it is 10 times lower gamma. But remember nitrogen has a negative magnetic moment. Does not matter, but if you consider the ratio it is almost 1000 times smaller. So, nitrogen is even more less sensitive compared to that of carbon-13.

Further, another important thing is, if you consider the ratio between these 2, compared to proton carbon is less sensitive; compared to carbon, nitrogen 15 even less sensitive; 960 times lower sensitive compared to proton.

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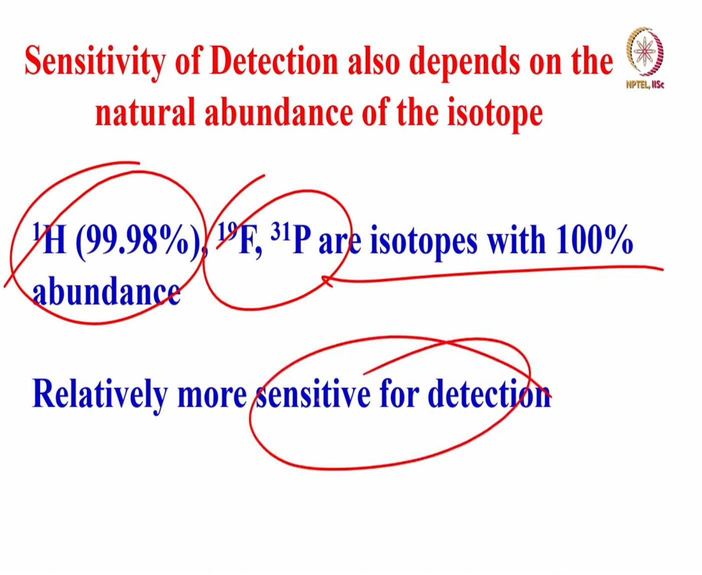

Sensitivity of Detection also depends on the natural abundance of the isotope

^{1}H (99.98%), ^{19}F, ^{31}P are isotopes with 100% abundance

Relatively more sensitive for detection

Now also sensitivity depends upon natural abundance of the isotope. For example you take proton, it has 100% abundant, almost 99.98%, fluorine, phosphorus 31, they are all isotopes with 100% abundance., They are more sensitive for detection; detection of these nuclei are much more sensitive compared to other nuclei.

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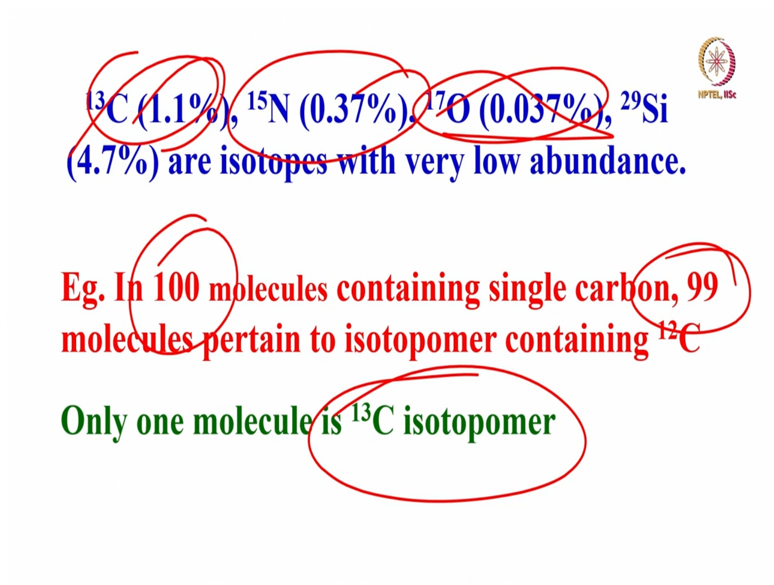

^{13}C (1.1%), ^{15}N (0.37%), ^{17}O (0.037%), ^{29}Si (4.7%) are isotopes with very low abundance.

Eg. In 100 molecules containing single carbon, 99 molecules pertain to isotopomer containing ^{12}C

Only one molecule is ^{13}C isotopomer

When I look at carbon-13, it is 1.1%, nitrogen-15 it is actually even smaller 0.037 and these are isotopes with a very low natural abundance. These are all natural abundance I am talking, and what does it mean? take carbon if I take 100 molecules containing carbon, 99 of them are in carbon 12; only one of them correspond to carbon 13 isotopomer. So, you have to detect among 100 molecules only one molecule which has carbon in carbon 13 state, that is going to give you the signal, you understand? That is the reason why the sensitivity of detection becomes more difficult as gamma and also natural abundance become smaller and smaller.

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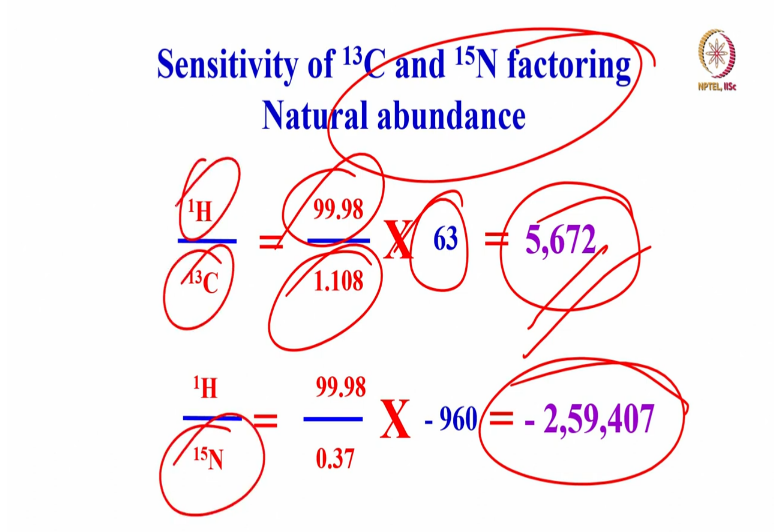

Sensitivity of ^{13}C and ^{15}N factoring Natural abundance

$$\frac{^{1}H}{^{13}C} = \frac{99.98}{1.108} \times 63 = 5,672$$

$$\frac{^{1}H}{^{15}N} = \frac{99.98}{0.37} \times -960 = -2,59,407$$

Let us consider sensitivity taking into account the natural abundance also. Earlier we calculated 63 taking into account only gamma cube. Now proton abundance is 100% almost, carbon is 1.1% take the ratio. Now taking natural abundance into account, it is nearly 5600 times less sensitive. What about nitrogen 15? my god, look at it, it is 260000 times much less sensitive compared to that of proton. So, if you take sensitivity, taking into account the natural abundance and also gamma, nitrogen 15 is least sensitive than carbon 13, compared to proton.

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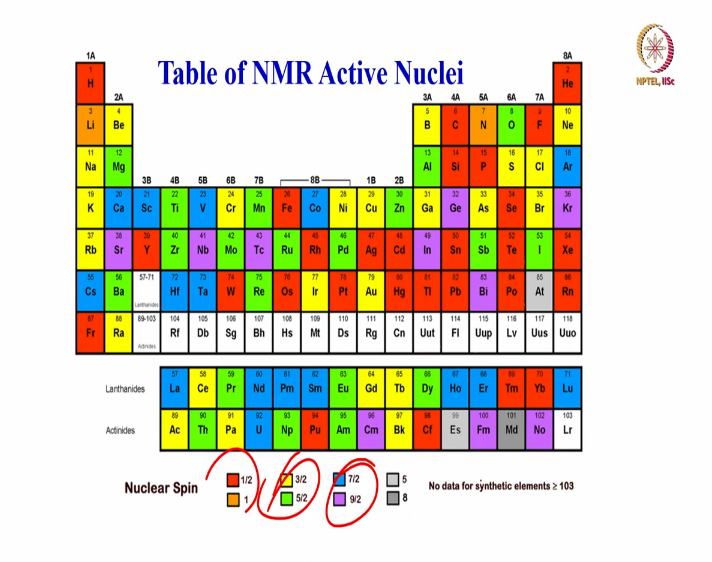

Table of NMR Active Nuclei

1A	2A	3B	4B	5B	6B	7B	8B	8B	8B	1B	2B	3A	4A	5A	6A	7A	8A
H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	57-71 Lanthanides	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	89-103 Actinides	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn	Uut	Fl	Uup	Lv	Uus	Uuo

Lanthanides	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Actinides	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

Nuclear Spin: 🟥 1/2, 🟧 1, 🟨 3/2, 🟩 5/2, 🟦 7/2, 🟪 9/2, ⬜ 5, ⬛ 8

No data for synthetic elements ≥ 103

Now if you go to the table of NMR active nuclei you can see so many nuclei are there. You can see different colours here, different colours correspond to different spins here; like what is written here; spins it means spin half, spin 1, 3/2, 5/2 etcetera. You can see in the entire periodic table at least there is one element or one isotope of an element which has spin. That means you can study almost all elements of the periodic table by NMR.

This is the beauty every element in the periodic table can be studied by NMR. That means any material you consider be it organic molecule, bio molecule or inorganic molecule or any material for that matter, they are all made up of one of these elements. That means you can utilize NMR to study anything. Material science you can do, biophysics, biochemistry chemistry, inorganic chemistry; in all branches of science NMR can be utilized. That is the beauty of NMR.

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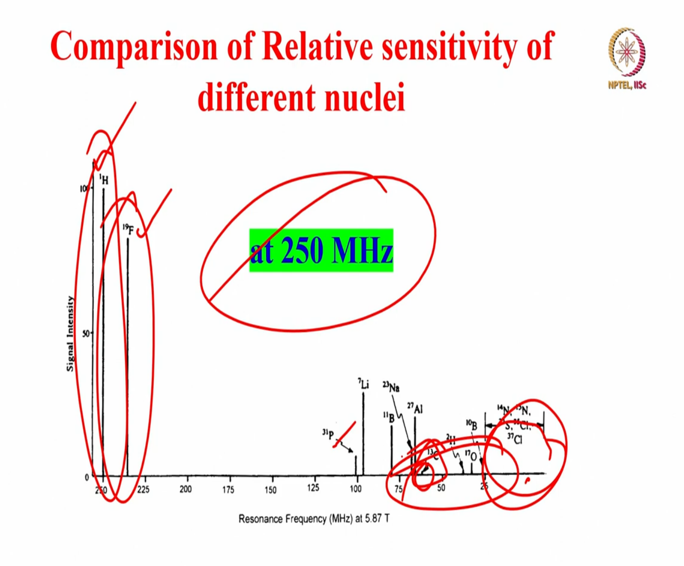

Comparison of Relative sensitivity of different nuclei

at 250 MHz

Now let us compare the relative intensity of different nuclei. These are the spectra obtained at 250 megahertz; just a stick plot. You can see that the proton is 100% abundant; that is taken as a standard with 100% abundance natural, highest gamma. Then comes fluorine, as you see here if you come near this region carbon 13 is very, very small. If you see in this region nitrogen-15 and others; they are not even seen here, very low sensitive. we calculated also nitrogen 15 has very low gamma and very low natural abundance. These are the least sensitive nuclei in this region.

So, the proton, fluorine, phosphorus, carbo,n these are generally common nuclei studied. Among them these are highly sensitive. Carbon and nitrogen are very least sensitive. Now we will induce the resonance. So far we understood the concept of NMR and varieties of things. How do you see the resonance? for this to understand we have to ensure the spins in the lower energy state should go to higher energy state and spins in the higher energy state should come to the lower energy state, and vice versa both should happen.

And remember if I have to see that in radio frequency region, only stimulated absorption or stimulated emission is possible. Spontaneous emission is practically ruled out in the radio frequency region.

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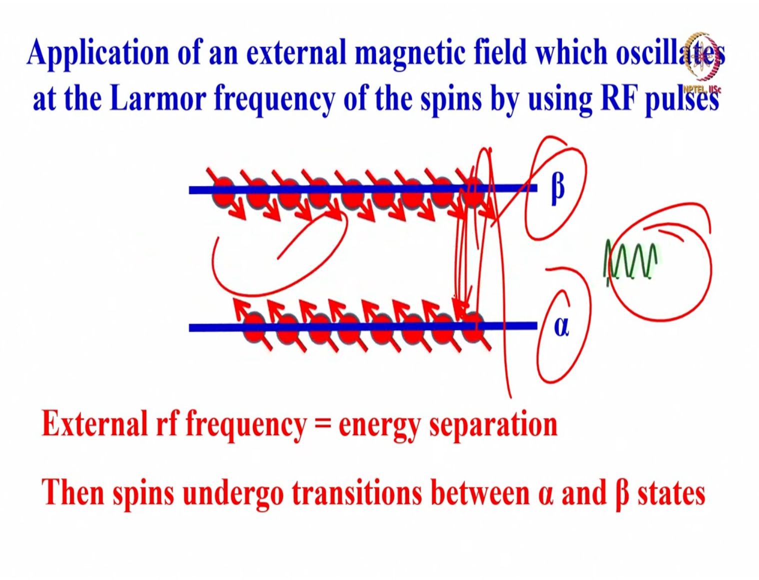

Application of an external magnetic field which oscillates at the Larmor frequency of the spins by using RF pulses

External rf frequency = energy separation

Then spins undergo transitions between α and β states

So, what we do is put the samples in a magnetic field. There is a small population difference between these 2; alpha state and beta state, and apply a radio frequency pulse like this, external from outside. And this should match with the energy separation between these two, this frequency. Then the spins undergo transition from alpha to beta and beta to alpha. And then we are going to see the signal.

Remember when the spins undergo transition, I told you a long back, the difference in the spins populations is what we are going to detect; and we are going to get the signal. And the only thing is the external radiofrequency pulse we are going to apply, RF radiation here should exactly match with the frequency separation between alpha and beta states. With this now I am going to introduce another term called random phase approximation and the concept of bulk magnetization.

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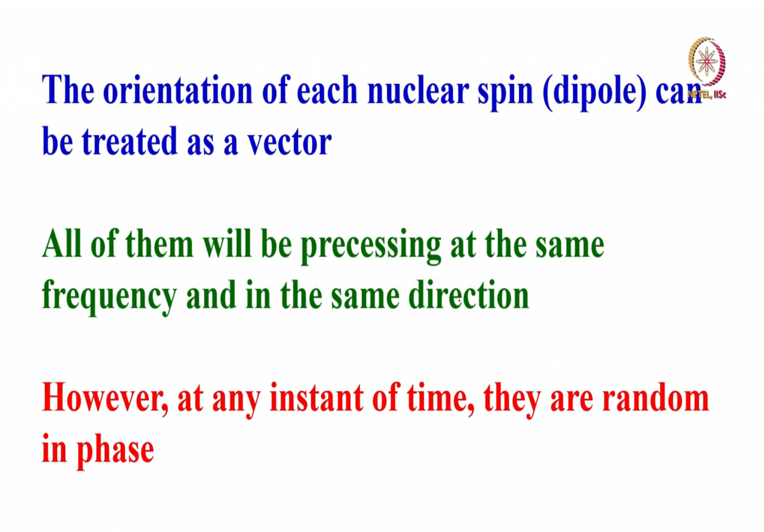

The orientation of each nuclear spin (dipole) can be treated as a vector

All of them will be precessing at the same frequency and in the same direction

However, at any instant of time, they are random in phase

Consider the orientation of each nuclear spin. I said it is a dipole; we can treat it as a vector. If you take ensemble of nuclear spins, millions and millions of nuclear spins are there. All of them are precessing at the same frequency, in the same direction; those which are in the direction of the magnetic field, they all will be rotating in the same frequency in the same direction. However, at any given instant of time, they are random in phase.

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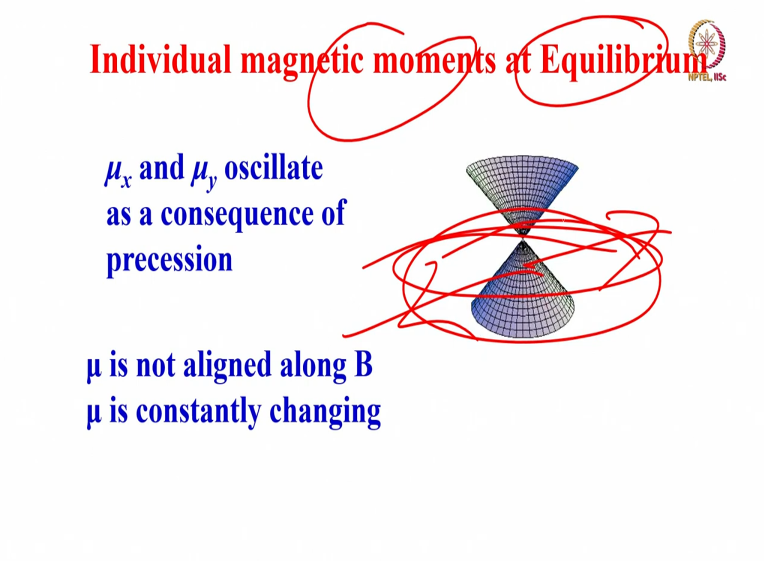

Individual magnetic moments at Equilibrium

μ_x and μ_y oscillate as a consequence of precession

μ is not aligned along B
μ is constantly changing

Especially, if you look at this individual magnetic moments at equilibrium. They are all oscillating, if I consider the magnetic moment, the x and y component when they are undergoing rotation like this the x, y components see here they all oscillate, as a consequence of the precession and μ is not aligned along B. μ is constantly getting changed like this. If you look at this, the x, y component if you consider here; the x, y components at any given instant of time, you see one vector here, other vector in the opposite direction. The ensemble average if you take, the orientation of nuclear spins in the XY plane, get averaged out. It becomes 0, the vector addition is 0.

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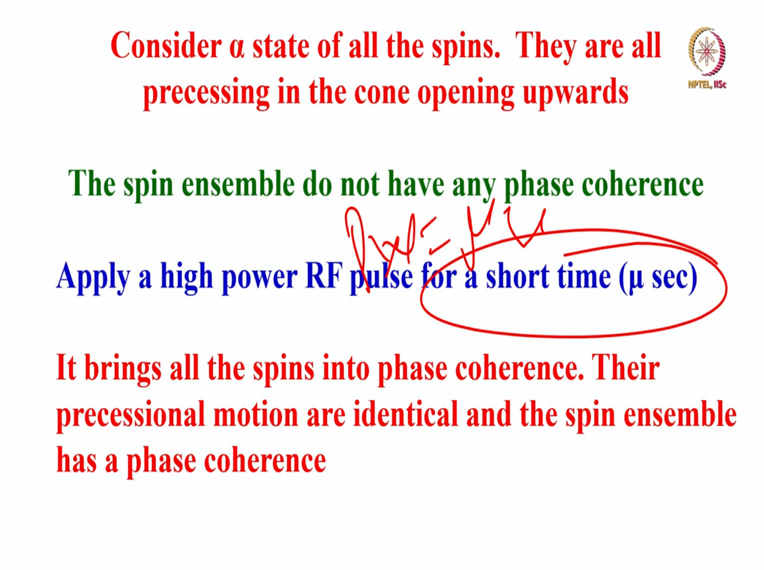

Consider α state of all the spins. They are all precessing in the cone opening upwards

The spin ensemble do not have any phase coherence

$P_w = \mu s$

Apply a high power RF pulse for a short time (μ sec)

It brings all the spins into phase coherence. Their precessional motion are identical and the spin ensemble has a phase coherence

Whereas now consider an example like this; all the alpha spin states you consider they are all precessing in a cone opening upwords like this. We saw that; and the spin ensemble do not have any phase coherence, they will be rotating. Now apply a high power radiofrequency pulse. Generally radiofrequency pulses are applied for a short time, we call it a 90 pulse, 180 pulse etcetera. The pulse width are of the order of microseconds. Remember the pulse width are of the order of microseconds. Once you apply radiofrequency pulse it brings all these spins into the phase coherence. That means all the nuclear spins, when you apply rf, conceptually from the Z orientation you are bringing it to the XY plane. The precision motions are identical and the spins ensemble has a phase coherence.

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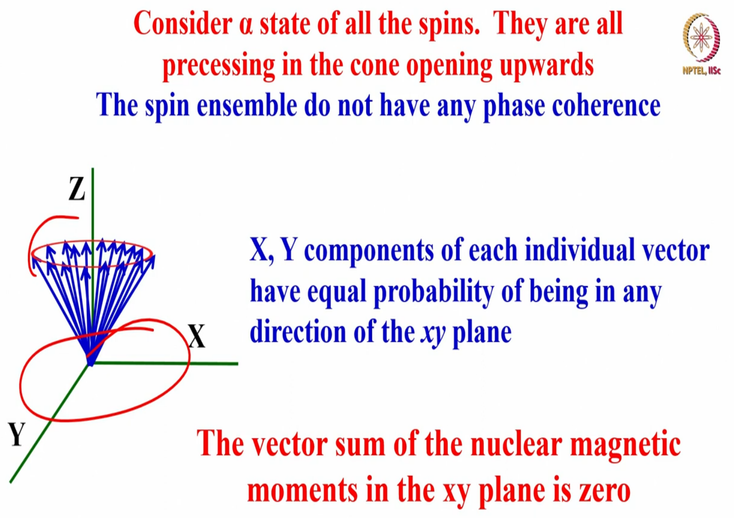

Consider *α* state of all the spins. They are all precessing in the cone opening upwards

The spin ensemble do not have any phase coherence

X, Y components of each individual vector have equal probability of being in any direction of the *xy* plane

The vector sum of the nuclear magnetic moments in the xy plane is zero

And then x, y components of each individual vectors have equal probability of being in any direction in the XY plane, I told you. The spins ensemble do not have any phase coherence here. But x, y component if we take, the vector sum of them will be 0; nuclear magnetic moments in the XY plane, vector sum if we take, is 0.

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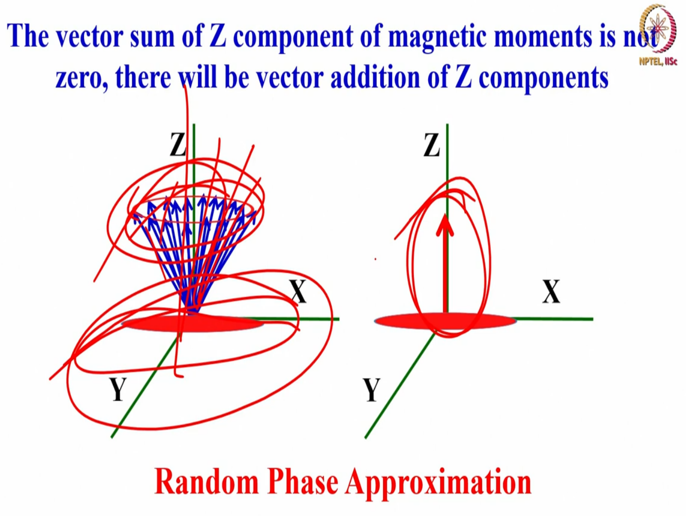

The vector sum of Z component of magnetic moments is not zero, there will be vector addition of Z components

Random Phase Approximation

Now what will happen is Z component? the vector sum of the Z component magnetic moment is not 0, only the x, y component are random in phase. Here they are all rotating in the same Larmor frequency simultaneously. Although the phases are different here, no problem. You take the vector addition of all of them, then that is nonzero. There is a component in the Z direction, given by vector addition, this is called a random phase approximation.

Because of random phase approximation, the x, y components, the vector sum is 0; but not along Z axis. In the Z axis there is a residual magnetization you can see which comes because of the orientation along Z axis.

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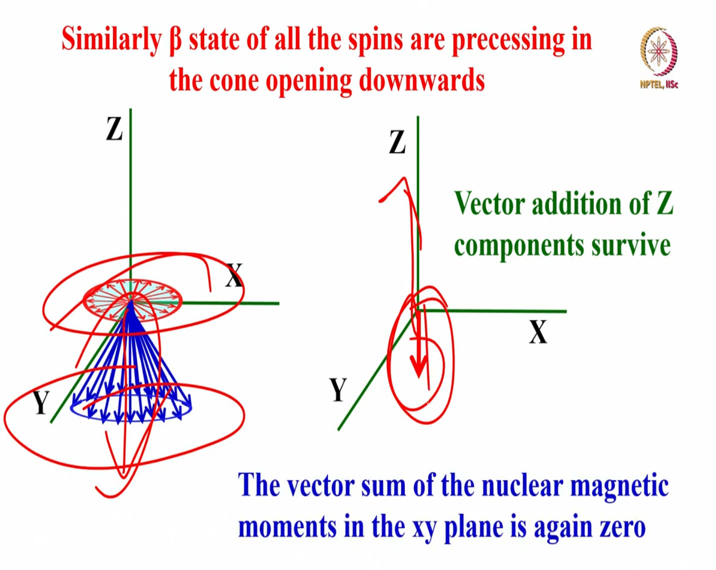

Similarly β state of all the spins are precessing in the cone opening downwards

Vector addition of Z components survive

The vector sum of the nuclear magnetic moments in the xy plane is again zero

What happened if I consider these spins which are in the beta state, they are all rotating in the direction opposite the magnetic field with a cone opening downwards. Again the x, y component if you take in the plane, the x, y components, the vector addition of all the components are 0. But not in the Z direction; here -Z direction because there is some residual magnetization here and the vector addition is not 0. So, there is some magnetization along Z axis, there is some magnetization along positive Z axis some along –Z axis.

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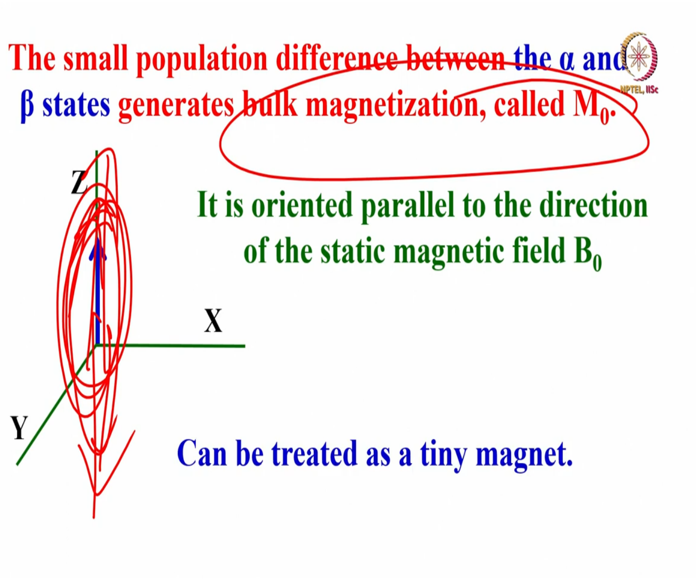

The small population difference between the α and β states generates bulk magnetization, called M_0.

It is oriented parallel to the direction of the static magnetic field B_0

Can be treated as a tiny magnet.

Now what did I say? there is a small population difference between the alpha states, beta states; they generate bulk magnetization. This is called M_0; M_0 is a bulk magnetization. Because it is the difference between the magnetization, now I am using the term magnetization; the bulk magnetization which is the Z component, which is a vector addition of all of them along this axis and along this axis. Because there are more spins in this direction than this one it is nonzero. The difference between these 2 vectors which turns out to be some value; which is along Z axis.

And it is oriented parallel to the magnetic field, the static magnetic field. This is called bulk magnetization M_0. So, this bulk magnetization can be treated as a tiny bar magnet; it is like a tiny magnet

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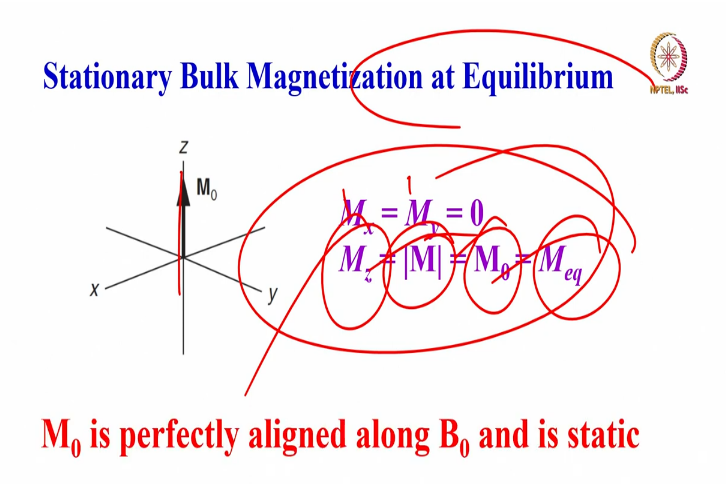

Stationary Bulk Magnetization at Equilibrium

$M_x = M_y = 0$

$M_z = |\mathrm{M}| = \mathrm{M}_0 = M_{eq}$

M_0 is perfectly aligned along B_0 and is static

Now the stationary bulk magnet at equilibrium; what happens? If you take at equilibrium; Mx is 0, My is 0, the Z component of the magnetization M refers to magnetization. If we take the magnitude of M which is nothing but equal to M_0 and which is equal to $M_{\text{equilibrium}}$. So, it is stationary. The magnetization, the bulk magnetization at equilibrium is stationary. It is not changing at all. But as individual nuclear magnetic moments were changing; remember they are rotating in cone.

Whereas when I consider to the random phase approximation and took bulk magnetization then it is stationary at equilibrium and it is perfectly aligned along B_0 and also it is static; is not changing. Now I will create a non equilibrium state. How do I create non equilibrium state? I said magnetization is in thermal equilibrium along Z axis and it is stationary. How do I disturb it? Now what I am going to do is, I am going to create a non equilibrium situation of this thing by applying what is called an oscillating field, an oscillating which field?

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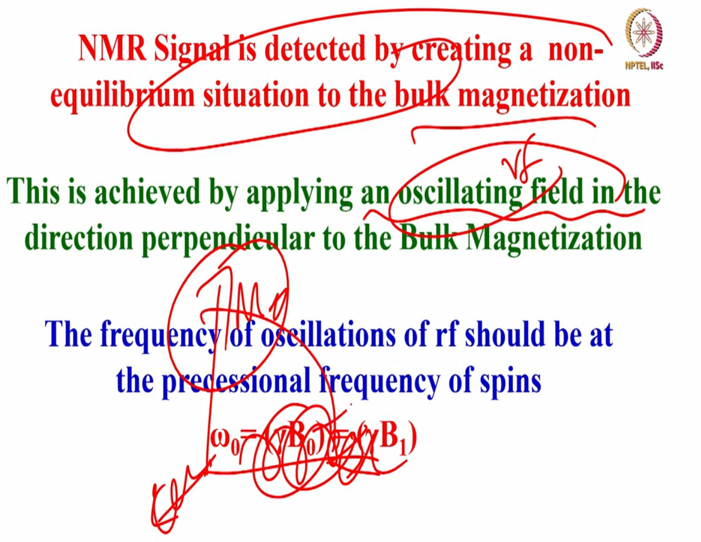

NMR Signal is detected by creating a non-equilibrium situation to the bulk magnetization

This is achieved by applying an oscillating field in the direction perpendicular to the Bulk Magnetization

The frequency of oscillations of rf should be at the precessional frequency of spins

$$\omega_0 = (\gamma B_0) = (\gamma B_1)$$

Radio frequency field; oscillating RF field if I apply in a direction perpendicular to the bulk magnetization, because this is M_0 I am going to apply radio frequency in this direction or in this direction, in one of these 2 directions. So, if you apply a radio frequency here, the RF pulse, this thing then I am disturbing this. I am creating a non equilibrium state and disturbing this equilibrium.

Then the frequency of oscillation rf should be at the precessional frequency. Remember the external frequency which we are going to apply here should be equal to precessional frequency of the spins, the Larmor precessional frequency then you can tilt it.

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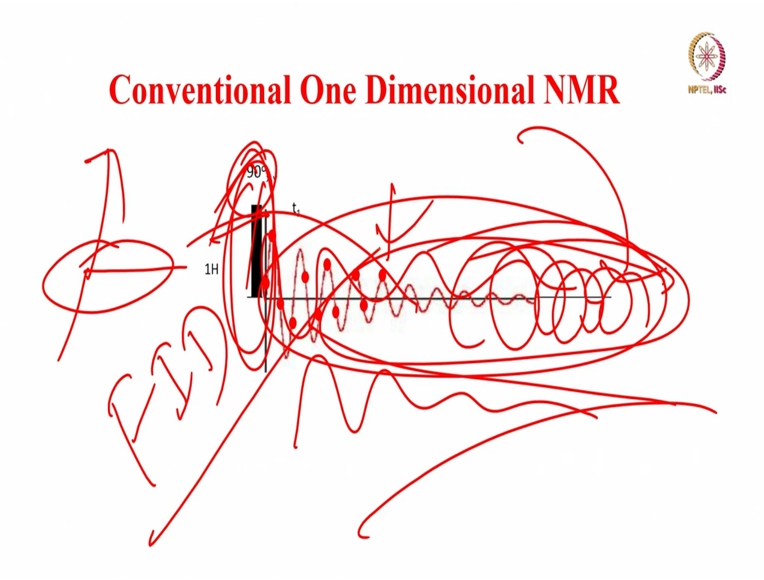
Conventional One Dimensional NMR

And then create non equilibrium situation. So, what? What will happen? Now I introduce a term called the free induction decay and the NMR spectrum. It is a conventional one dimensional NMR. What I said? by applying a radiofrequency pulse spins undergo transitions and you see the population difference; or by using the concept of bulk magnetization. What is happening is; you apply a small radio frequency pulse which is 90 degrees. In the previous course I have already explained what is that?

Magnetization which is along Z axis is brought to the XY plane. Exactly if you tilt from Z axis to X axis or Y axis; that is called a 90 degree pulse. Which you can control by using a pulse width and the power of the pulse. Apply your pulse keep quiet do not do anything. Then you have disturbed the magnetization. All the nuclear spins are brought back to the XY plane from Z axis it will come to the XY plane, here.

Then it will not stay there, it will start decaying, it will go back to Z axis. It is now disturbed, but it wants to go back to equilibrium. So, it wants to go back to equilibrium by inducing EMF. When I bring to X axis I keep the RF coil here for detection. So, while going back it induces EMF in this RF coil. I am going to detect that; and that detected signal follows an exponential path like this, it is an exponential pattern; it decays exponentially.

And this is what I am going to detect as a function of time. This is inducing voltage at the same time it is decaying, while inducing EMF in the coil, it is decaying freely. That is why it is called FID; means free induction decay.

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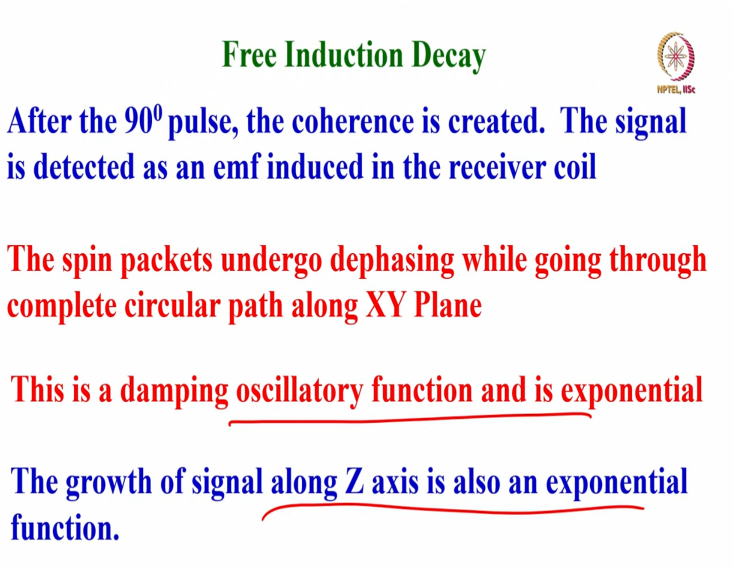

Free Induction Decay

After the 90^0 pulse, the coherence is created. The signal is detected as an emf induced in the receiver coil

The spin packets undergo dephasing while going through complete circular path along XY Plane

This is a damping oscillatory function and is exponential

The growth of signal along Z axis is also an exponential function.

So, I applied 90 degree pulse and I created what is called a coherence? What do you mean by coherence? All the nuclear spins are brought to the XY plane; they are all at a given instant of time immediately, for a short time, they are all in coherence, that is for a short span of time; and after some time what will happen? they will start decaying. That is where the EMF is created and FID is going to be detected.

While they will go back to Z axis, by decaying in the XY plane while doing that, it induces EMF which is an exponential. We call it as free induction decay. This is a damped oscillatory function and is exponential. The growth of signal along Z axis is an exponential function. Please remember one thing I want to tell you here, you see here it is a damping oscillatory function and growth of signal along Z axis is also exponential. Decay is in the XY plane which is exponential while decaying, it goes back to Z axis. It is growth along Z axis. That is also exponential. These are the 2 phenomena which we will discuss later called the relaxation phenomena.

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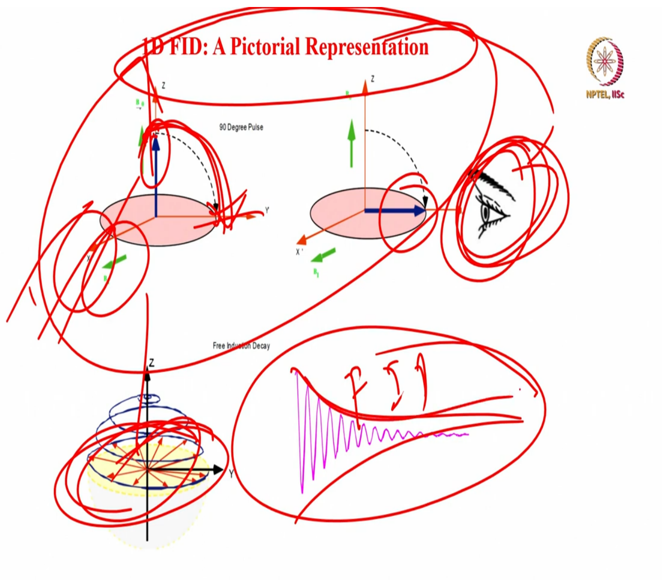

1D FID: A Pictorial Representation

So, this is what happens pictorially; a free induction decay is represented like this. It comes here bring your magnetization bulk magnetization which is along Z axis. Normally it is an equilibrium magnetization create a non equilibrium state by applying radiofrequency along the X axis the magnetization is brought to Y axis; all the 3 orthogonal to each other. I am sitting here watching in the Y axis. You apply pulse along the X axis, the magnetization which is the along z axis is brought to Y axis. And I am observing here; that is my receiver is here. I am seeing the signal here; instantaneously all the spin vectors are in phase; there is coherence. That is why it is called coherence. And with time this coherence decay is like this. At the same time, it starts going back to Z axis; it follows and a spiral path like this; decay is in the XY plane like this and simultaneously start going along Z axis.

And in the time function if you see that, it a decaying function we detect this signal as a function of time; this is a FID. This is a pictorial representation of one dimensional NMR. Magnetization is along Z axis, apply radiofrequency pulse in a direction perpendicular to it, disturb the spins and then bring it to another axis, Y axis. All the 3 orthogonal to each other. For a given instant of time there is instantaneous phase coherence; and the phase coherence is distorted. There is a decoherence and the spins start going back to Z axis while decaying in the XY plane ;and we collect the free induction decay as a function of time.

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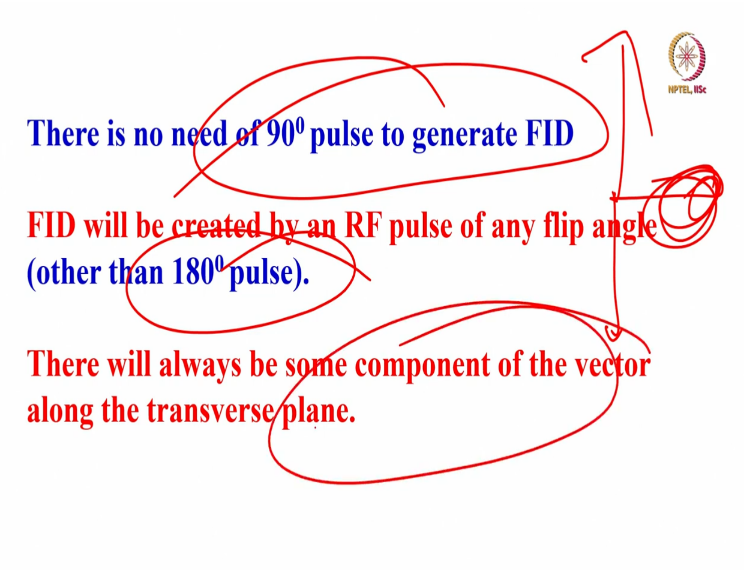

There is no need of 90^0 pulse to generate FID

FID will be created by an RF pulse of any flip angle (other than 180^0 pulse).

There will always be some component of the vector along the transverse plane.

And of course remember there is no need to apply 90 pulse. For explanation I showed you, I brought to the X axis or Y axis by applying an 90 degree pulse in a direction perpendicular. You can apply any angle also; there is no problem. Only thing you should not apply 180 pulse, because our magnetization is along Z axis and our receiver coil is here. If you apply a 180 pulse you bring it here, you will not see any signal. It is 0; this that we discussed in the last course. So, there will be always some component of the vector along the transverse plane you can resolve into a sin component and cosine component. You will see the signal even though it is not 90 degree pulse.

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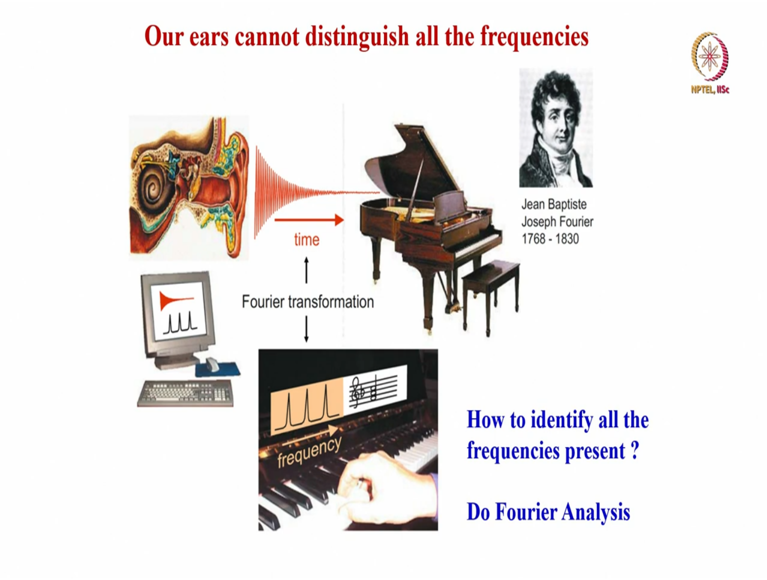

Our ears cannot distinguish all the frequencies

How to identify all the frequencies present ?

Do Fourier Analysis

Now you got the signal in time domain. But remember our ears cannot distinguish all the frequencies, it is an interferogram. All the frequencies are present. How to identify the frequencies present. There is mathematical operation called Fourier transformation; the Fourier transformation converts the time domain signal into frequency domain. The time domain signal and frequency domain signal, time and frequency are called Fourier pairs.

So, you can take the signal in time domain, do the Fourier transformation and take into frequency domain. Do the reverse Fourier transformation bring the frequency domain spectrum to time domain signal; both are possible. We will talk about Fourier transformation in one of the classes when we go ahead further.

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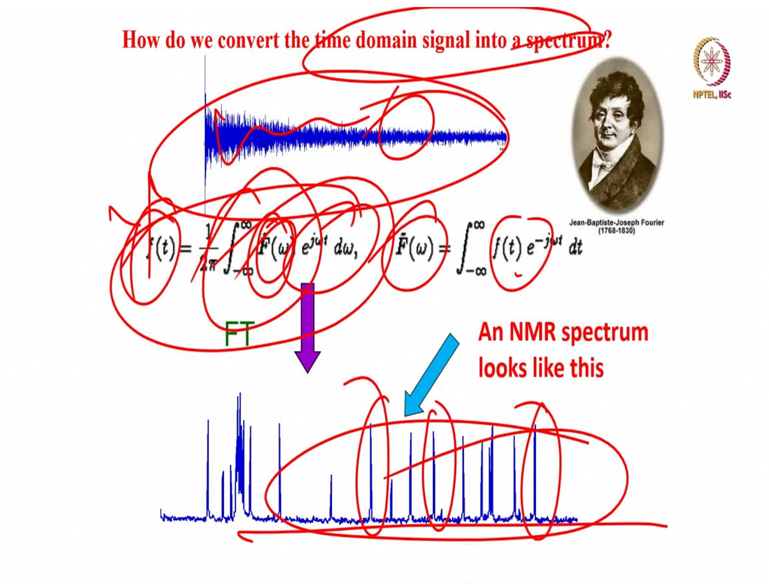

How do we convert the time domain signal into a spectrum?

$$f(t) = \frac{1}{2\pi}\int_{-\infty}^{\infty} \tilde{F}(\omega)\, e^{j\omega t}\, d\omega, \qquad \tilde{F}(\omega) = \int_{-\infty}^{\infty} f(t)\, e^{-j\omega t}\, dt$$

FT

An NMR spectrum looks like this

Jean-Baptiste-Joseph Fourier (1768-1830)

NPTEL, IISc

When we do the Fourier transformations, this is a time domain signal many frequencies are present here. We do not know, depending upon your sample of interest. So, how do we convert this time domain signal into spectrum? Do the Fourier transformation by using this equation. If I have a time domain signal I will integrate it from minus infinity to plus infinity for the frequency function, it is an exponential function i omega t into d omega and you will get the frequency.

Or you can take a time domain convert to frequency domain; take frequency domain convert to time domain, both are possible; either way it is possible. And when you do the Fourier transformation of this free induction decay you get a spectrum like this, this is what the NMR spectrum is, this is how it looks. All you have to do is if you want to analyze the spectrum, take the sample put it in a magnetic field, collect the time domain signal by doing by sending some RF pulse, collect the signal as a function of time, do the Fourier transformation you get an NMR spectrum like this.

Now your job is to interpret, analyze why these frequencies are her, what is this frequency, what is the peak corresponding to? Each of them is a characteristic of a particular functional group present in the molecule. If I say I have a frequency peak here, I know there is a particular functional group present. If I see a peak is here, I know there is a particular functional group present. So, this way many of the stalwarts in NMR have already worked out with decades and decays of research. They have already tabulated possible range of frequencies where we can see these peaks. We will discuss more when we go to the chemical shift and other things later.

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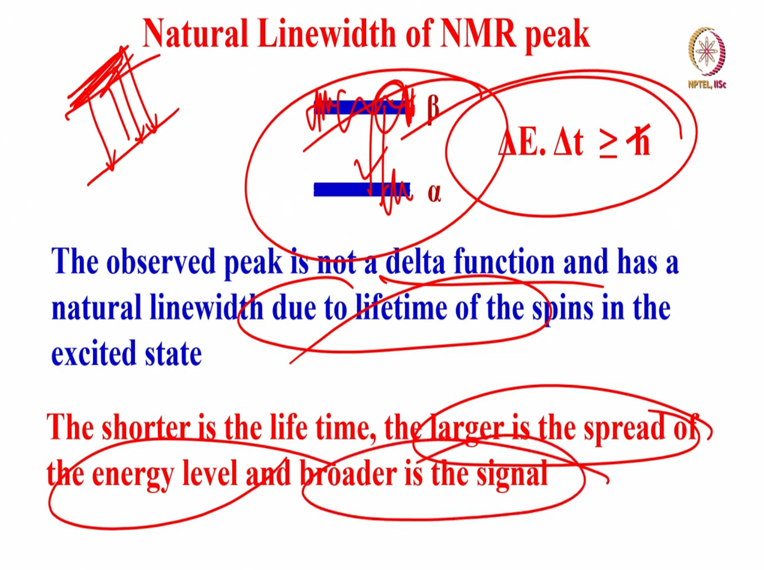

Natural Linewidth of NMR peak

$\Delta E . \Delta t \geq \hbar$

The observed peak is not a delta function and has a natural linewidth due to lifetime of the spins in the excited state

The shorter is the life time, the larger is the spread of the energy level and broader is the signal

With this now let me talk more about the NMR spectrum. I will talk something about natural linewidth. I consider two alpha and beta spin states; they are not well defined. There is a spread in the energy levels like this. Of course, you all know about Heisenberg uncertainty principle; I do not have to explain this. According to this deltaE and delta t should be greater than or equal to h cross. So, observed peak is not a delta function.

And has a natural linewidth due to lifetime of the nuclear spins in the excited state. The shorter the lifetime; the larger is the spread of the energy levels and broader the signal. When do we say lifetime is shorter, when the spins are coming back from excited state to the ground state faster; that is the relaxation is faster. I will talk more about it when we go to additional classes later. When the spins in the excited state stays only for a short time, it relaxes very fast.

Then what is going to happen there is a more spreading the energy level, here the is spread is more. As a consequence, you will not get short peak like this; there is the spread like this. You can get frequency from here to here, here to here, here to here; n number of frequencies will be present. As a consequence, they are going to get a broader signal, because of the spread in the energy levels. So, this is a natural linewidth you cannot avoid that because of the uncertainty principle. Now I am going to introduce a term called selection rule which is very important.

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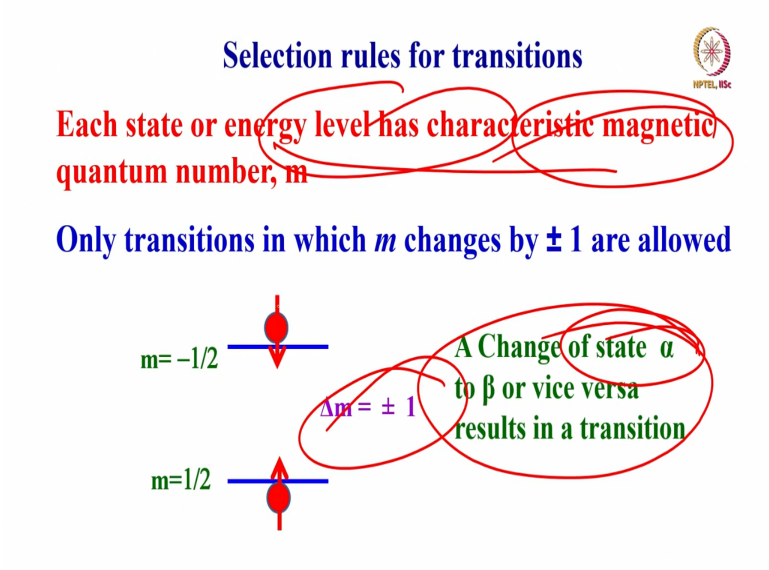

Selection rules for transitions

Each state or energy level has characteristic magnetic quantum number, m

Only transitions in which m changes by ± 1 are allowed

A Change of state α to β or vice versa results in a transition

What is the selection rule for the detection of the signal in NMR? We know the energy state between alpha and beta; m minus half and plus half. What is the difference in the magnetic quantum number between these two. m is equal to minus half, m is equal to plus half, difference if you go from here to here it is 1. If you come from here to here it is -1. Now if you take one spin, or n number of spins coupled to each other and they are interacting, we will see later and does not matter.

Each energy state can be given a particular magnetic quantum number m. For example, for spin of nuclei, for example you can see going from here to here or coming from here to here is going to a 1 or – 1. Then the change in the spin magnetic quantum number is 1 or – 1; that means delta m equal to plus or minus 1. They are called allowed transitions in NMR. The selection rule tells transitions between these two states are allowed. And that means when there is a transition taking place from alpha to beta; or beta to alpha, there is a change in the spin state. alpha spin goes to beta state, spin in the beta state comes to alpha state. So, one spin changing in state gives rise to one transition.

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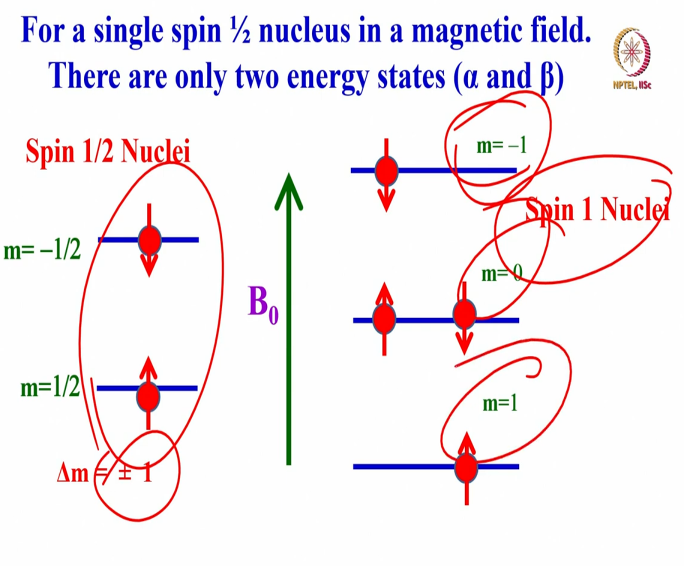

For a single spin ½ nucleus in a magnetic field. There are only two energy states (α and β)

These are all called single quantum transitions in NMR. We will discuss that later when we go ahead further. For spin half nuclei how many possible transitions we can think of? If we take delta m equal to 1 or – 1, only these 2 possibilities. So, for a single isolated spin half nucleus, if we take, you will get only one peak. For spin 1 nuclei there are 3 possible magnetic quantum numbers, I told you, from – I to I in steps of 1; then it would be– 1, 0 and 1; three states are there. Now transition of this to this is allowed transition; from this to this is also allowed.

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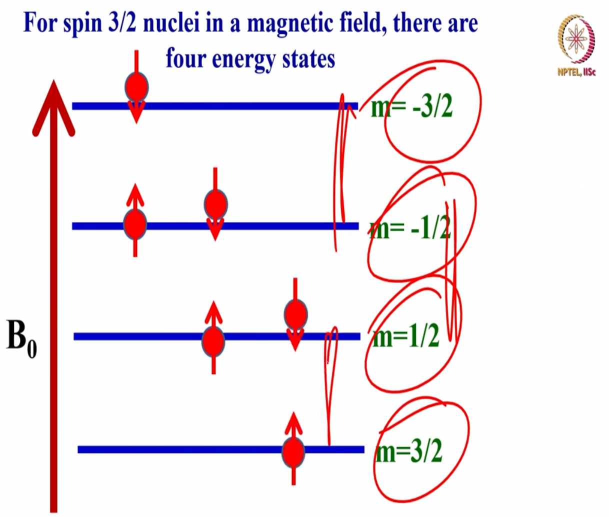

For spin 3/2 nuclei in a magnetic field, there are four energy states

For example, if you take 3/2 spin there are 4 energy states -3/2, minus half, plus half, 3/2. You work out m_i; it goes from – I to I in steps of 1. Now these are transitions allowed with this difference 1 or – 1; this difference is 1 or – 1; and this differences also 1 or -1. So, these are the allowed transitions.

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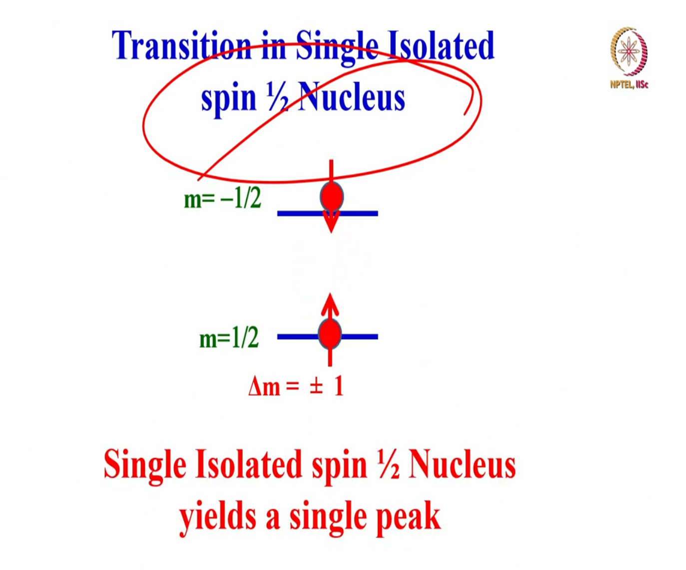

Transition in Single Isolated spin ½ Nucleus

Single Isolated spin ½ Nucleus yields a single peak

So, if I take a transition is single isolated spin half nucleus you get only one peak; what happens? If you have more number of spins we will come to that later.

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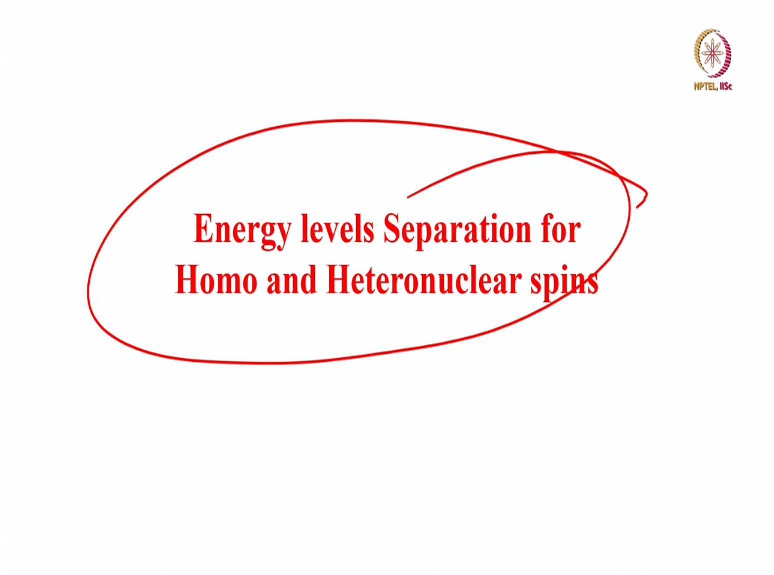

Energy levels Separation for Homo and Heteronuclear spins

But remember energy level separation depends upon gamma, I told you, which depends upon the nuclei of your interest. If I consider 2 nuclei which are interacting, if both are homo nuclear spins that is identical spins; like spins; the energy separation is different. If there are unlike spins, that is heteronuclei; the energy separation are different. So, we will see how much is different.

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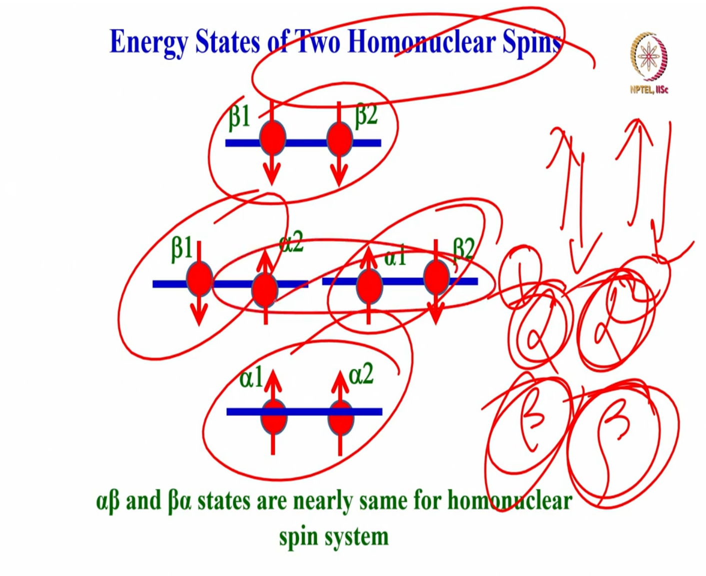

Energy States of Two Homonuclear Spins

αβ and βα states are nearly same for homonuclear spin system

We can see the energy state for 2 homonuclear spins if we take; homonuclear consider, if I have 2 spins one can be like this, it can be like this; other spins are like this, one can be like this; now various possible components you can think of; alpha and beta, alpha and beta for spin 1 and spin 2. Now this can be alpha this can be alpha; this can be alpha, this can be beta; and this can be beta this can be alpha; or this can be beta this can be beta.

So, there are 4 such possibilities beta beta, beta alpha, alpha beta and alpha alpha. So 4 such energy states are there corresponding to 4 possible magnetic quantum numbers when 2 homo nuclear spins are interacting. These are energy states, we will discuss more about this later and you remember alpha and beta states almost nearly same energy in homonuclear spin system. Now on the other hand instead of homonuclear if I consider heteronuclear what will happen?

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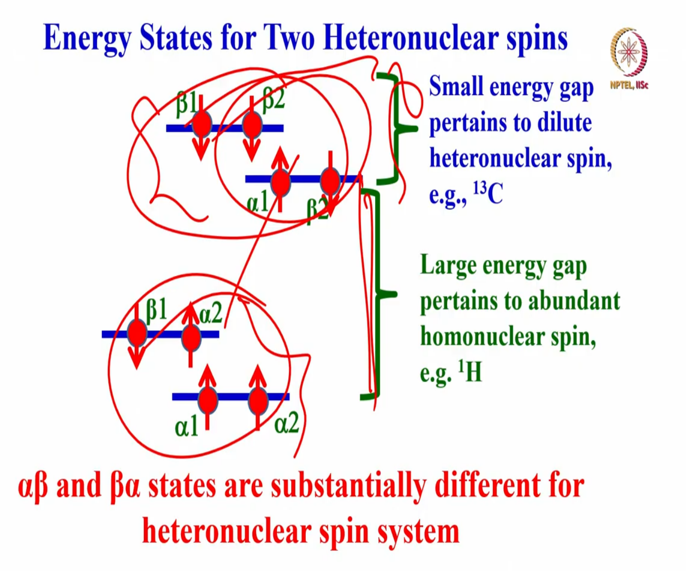

Energy States for Two Heteronuclear spins

Small energy gap pertains to dilute heteronuclear spin, e.g., ^{13}C

Large energy gap pertains to abundant homonuclear spin, e.g. ^{1}H

αβ and βα states are substantially different for heteronuclear spin system

See here, this is small energy gap between beta beta and alpha beta; similarly beta alpha and this one there is a small energy gap; whereas between this to this there is a large gap; because this corresponds to large gamma, this corresponds to small gamma. So this energy state correspond to dilute spin, a spin with lower gamma. This energy separation corresponds to spin with lower gamma. This energy state corresponds to spin with higher gamma. These are the energy states for 2 heteronuclear spins. So alpha beta states energy are substantially different here in heteronuclear spin system; whereas in the homonuclear spin systems you see the energy separation between alpha beta and beta alpha are nearly same. So, this is the thing which I wanted to tell you. So with this my time is also getting over.

What I told you today, in this class is, I covered lots of basics of spin physics. We discussed about the energy states, interaction of the magnetic moment with the magnetic field, we calculated what is sensitivity factor which are governing; we understood what is the coherence; we understood what is the saturation when the energy population between the alpha and beta spins states become equal.

What happens to the Boltzmann population ratio when I go to absolute 0; when the temperature is lowered; what happens when we go to the temperature infinity; let us say where the energy states are saturared, we discuss that. And we also understood what happens in the random phase approximation, we understood what is the bulk magnetization, bulk magnetization because of z magnification orientation of alpha spin and beta spin together. If we take the difference in the vector addition there is small magnetization which is along the direction of the magnetization in thermal equilibrium which is consider as the bulk magnetization. It can be treated like a tiny magnate, it is thermal equilibrium; it is stationary. whereas individual magnetic moments are undergoing motion; they will be undergoing precessions; whereas the bulk magnetization is stationary.

What we thought is, we can disturb this. How do you disturb? by applying a radio frequency pulse in a direction perpendicular to it; bring the magnetization to X axis or Y axis depending upon which direction you apply RF pulse; and this will induce EMF in the receiver coil. We collect signal as a function of time; we understood the time and frequency are related to each other by a term call Fourier transformation. By doing a mathematic operation we can convert time domain signal and find out the frequencies present and then we start interpretation. We also understood the selection rule. The selection rule is NMR is one where delta, the change in magnetic quantum number between 2 spins states must be either 1 or –1; anything be other then this 2 or –2 or 0 or anything other than plus or minus 1 are not allowed; there forbidden transaction. We understood that also.

And we understood also energy gap between homonuclear spin states and the heteronuclear spin states and we understood what are the possible of spins if we take 2 spins. This is the summary of today, so this covers more or less the fundamentals of spin physics and the concept of NMR, which in the previous course I covered this very extensively, for more than 1 or 2 weeks but this being advanced course lot of other topics I have to cover.

I went little faster, presuming that people already attending previous course. If not at least this should act as a starting point for you to learn; go back and refer to the previous course. and then from the next class I will introduce some interaction parameters in NMR and then continue further with other topics. Thank you.