

Spectroscopy Techniques for Pharmaceutical & Biopharmaceutical Industries

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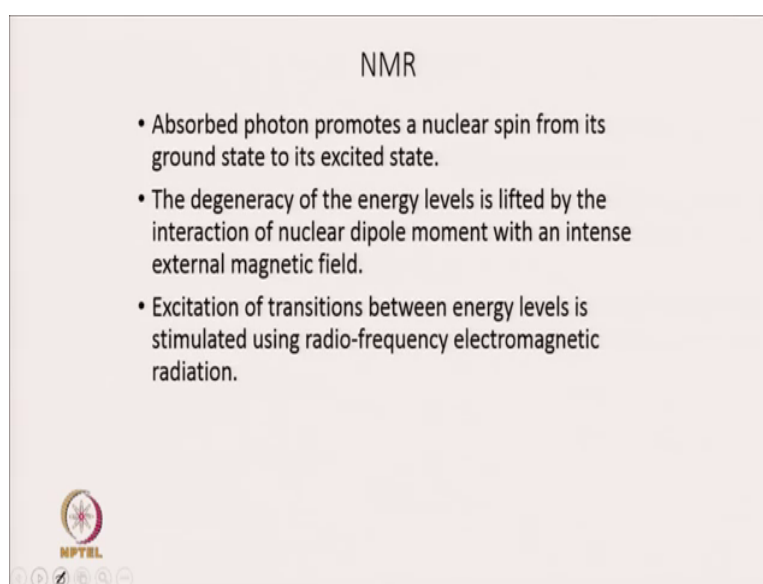
Indian Institute of Technology Delhi

Lecture 30

Principle of NMR

Hello students, in the last lecture I discussed about fluorescence and fluorescence microscopy. In this lecture I will start to discuss about one of the most important technique for chemical molecule characterization and biomolecule is NMR. And in this lecture I am going to discuss about principles of NMR spectroscopy.

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NMR

- Absorbed photon promotes a nuclear spin from its ground state to its excited state.
- The degeneracy of the energy levels is lifted by the interaction of nuclear dipole moment with an intense external magnetic field.
- Excitation of transitions between energy levels is stimulated using radio-frequency electromagnetic radiation.

NPTEL

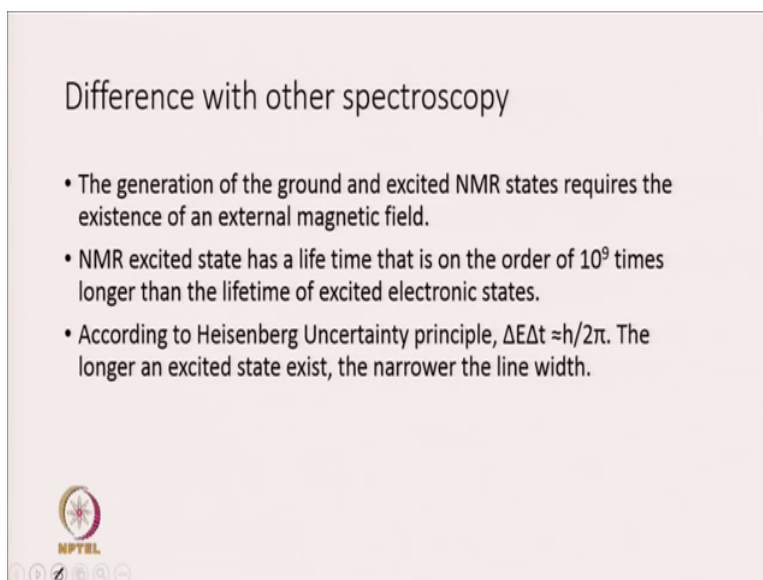
In NMR when sample is irradiated with light the absorbed photon promotes a nuclear spin from its ground state to its excited state. So, here basically radio frequency pulse is applied and which promotes a nuclear spin from its ground state to excited state. The degeneracy of energy levels is lifted by the interaction of nuclear dipole moment with an intense external magnetic field.

So, initially all the nuclear levels are degenerate and their degeneracy is lifted by the interaction of nuclear dipole moment with an intense external magnetic field. Now you need radiofrequency-electromagnetic radiation to excite nuclear spin from ground state level to the excited state. So, transition between different energy levels is done by using radio frequency electromagnetic radiation.

So, two, three things are important, one is that the levels are degenerate, levels are degenerate, their degeneracy is lifted by external magnetic field. So you require an external

magnetic field to remove the degeneracy. And then transition between the energy levels will be stimulated using radio frequency electromagnetic radiation.

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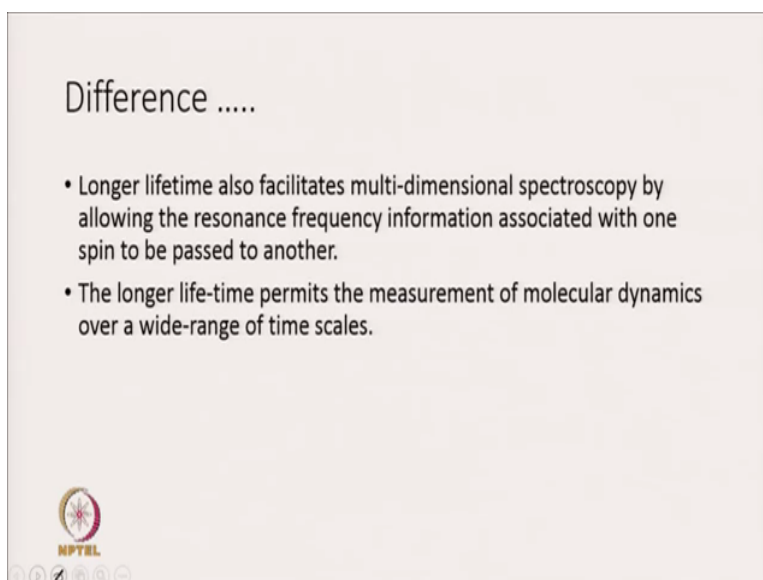
Difference with other spectroscopy

- The generation of the ground and excited NMR states requires the existence of an external magnetic field.
- NMR excited state has a life time that is on the order of 10^9 times longer than the lifetime of excited electronic states.
- According to Heisenberg Uncertainty principle, $\Delta E \Delta t \approx h/2\pi$. The longer an excited state exist, the narrower the line width.

NPTEL

So, what does that mean is that the generation of the ground and excited NMR states requires for the existence of an external magnetic field. Already I have talked about life time and now you know what is the importance of life time. NMR excited state has a life time that is on the order of 10 to power 9 times longer than the lifetime of excited electronic states. So, if you remember when I talked about Heisenberg Uncertainty principle, it tells you that the longer and excited state, the longer and excited state exist, the narrower the line width. And so NMR is a very high resolution technique.

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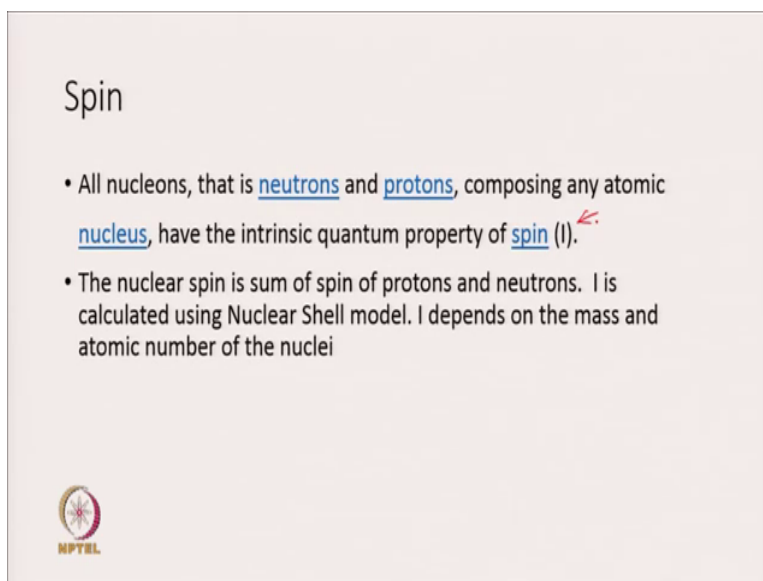
Difference

- Longer lifetime also facilitates multi-dimensional spectroscopy by allowing the resonance frequency information associated with one spin to be passed to another.
- The longer life-time permits the measurement of molecular dynamics over a wide-range of time scales.

NPTEL


Longer lifetime not only ensures a better resolution, it also facilitates multidimensional spectroscopy by allowing the resonance frequency information associated with one spin to be passed to another. And that is why you see 2D, 3D, 4D NMR. The longer life time permits measurement of molecular dynamics over a wide range of time scales. These are the few of the advantage associated with NMR measurements.

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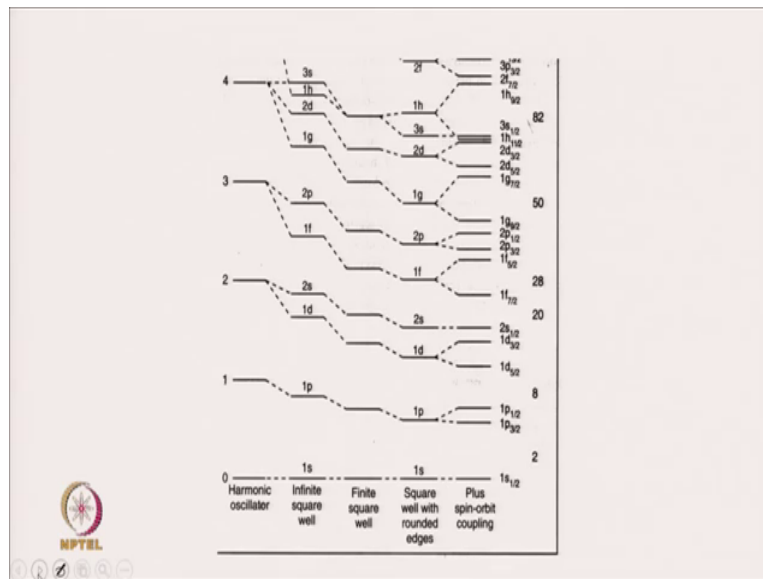
Spin

- All nucleons, that is neutrons and protons, composing any atomic nucleus, have the intrinsic quantum property of spin (I).
- The nuclear spin is sum of spin of protons and neutrons. It is calculated using Nuclear Shell model. It depends on the mass and atomic number of the nuclei

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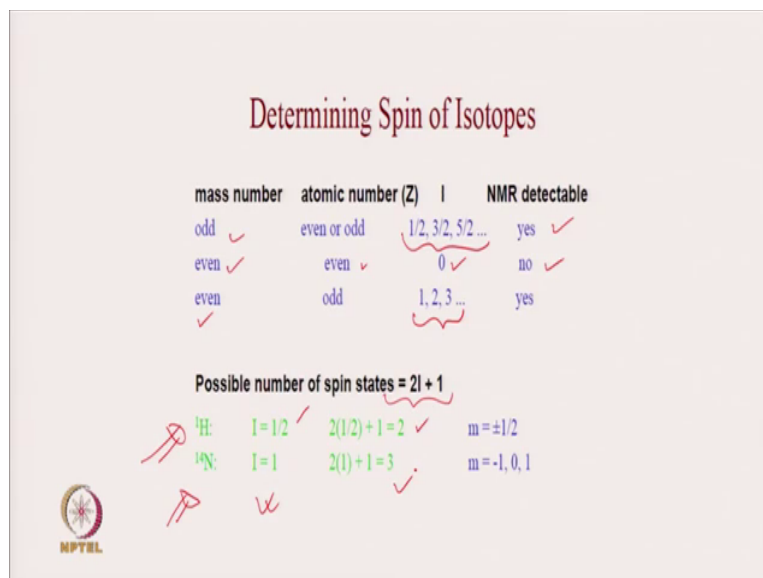
Now, let us come back to basic. So you must be knowing that all nucleons, which consist of neutrons and protons have intrinsic quantum property of spin, which is shown by I . Nuclear spin is sum of spin of protons and neutrons, since nucleus consist of protons and neutrons and so nuclear spin is sum of spin of protons and neutrons. It can be calculated using nuclear shell model, it can be calculated using nuclear shell model. It depends on mass and atomic number of the nuclei.

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And these are the different energy levels associated with different orbitals, some of them I have already discussed in the atomic spectroscopy, so I am not going to go into detail. But filling of nucleons in these levels gives you the value of I.

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In general if the mass number is odd, atomic number is even or odd, I will going to have value half, 3 by 2, 5 by 2. So it will going to have fraction values and they are detectable by NMR. If mass number is even, and atomic number is even, then I is going to have value 0, so the nuclei with even mass number and even atomic number is not NMR active. A nuclei with even mass number and odd atomic number is going to have value of I equal to an integer 1, 2,

3 and it is NMR active. So a nuclei with even mass number, odd atomic number is going to be NMR active.

So for example, if you take proton ^1H nuclei it is going to have I equal to half and for a nuclei ^{14}N I is going to be 1. And you can see that it has N has your even mass number and odd atomic number 14 is even and its atomic number is 7 and so it is going to have I equal to 1 or I value which is an integer. So these two are NMR active nuclei, NMR active nuclei and the possible number of spin state is going to be $2I + 1$, $2I + 1$.

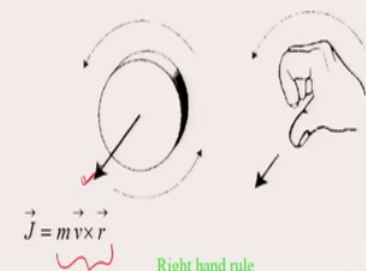
And what does that mean is proton is going to have two spin states, whereas ^{14}N going to have three spin state. But they are degenerate states only when you apply magnetic field the degeneracy is removed.

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All nucleons, that is [neutrons](#) and [protons](#), composing any atomic [nucleus](#), have the intrinsic quantum property of [spin](#).

Angular Momentum

A rotating object possesses angular momentum

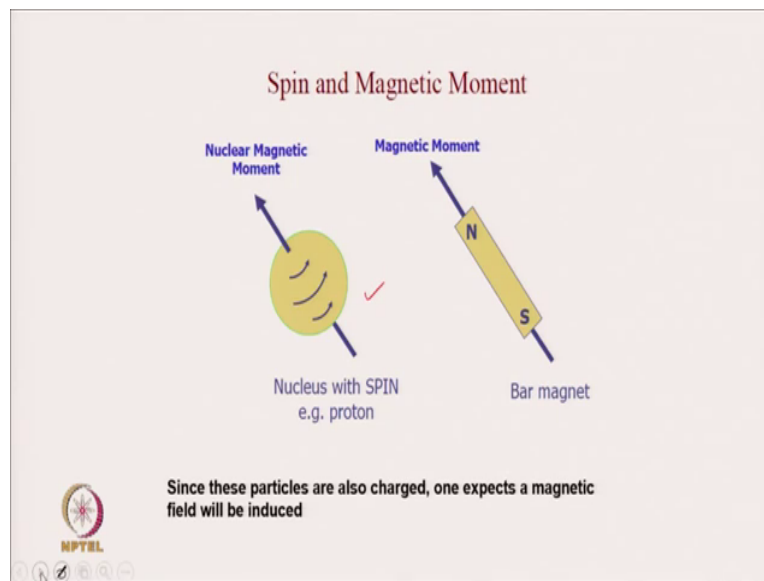


As the name suggests, spin was originally conceived as the rotation of a particle around some axis. This picture is correct so far as spin obeys the same mathematical laws as [quantized angular momenta](#) do.

 $\vec{J} = m \vec{v} \times \vec{r}$ Right hand rule

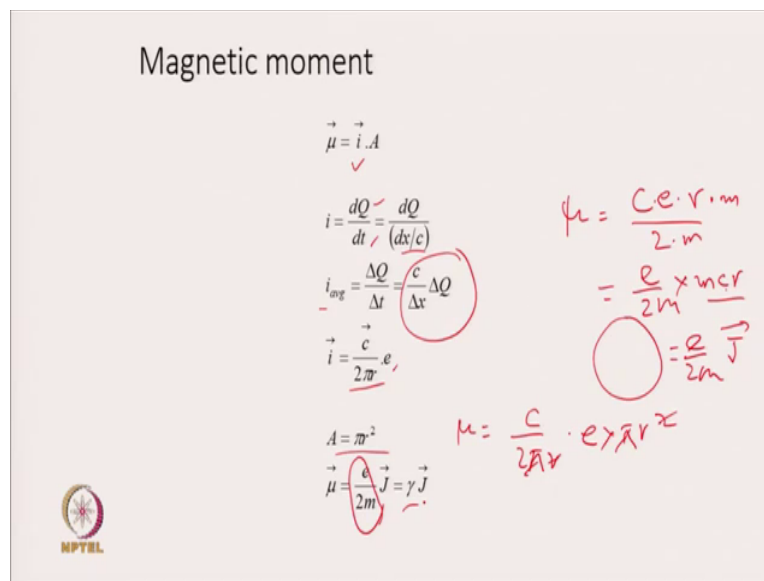
As we know that a rotating object versus angular momentum again this I have discussed in spin orbit coupling that a rotating object processes an angular momentum is given by mvr and its direction can be known from the right hand rule, known from the right hand rule. So if suppose the rotating direction is this side, then your momentum will be towards this axis.

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Now Spin is rotating and it is also charged, what does that mean is that a magnetic field will be induced. So, nucleus with spin is going to have nuclear magnetic moment as a bar magnet has a magnetic moment.

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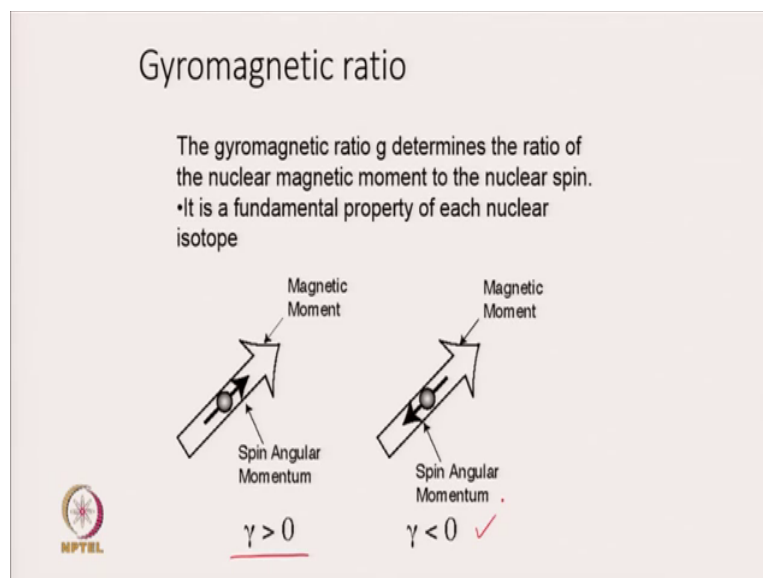


So, let us see what will be the value of magnetic moment. This I have already discussed I will again discuss that magnetic moment is simply equal to current multiplied by area and as we know current is dQ by dt and dt is your distance divided by velocity, we have velocity of light and then i average can simply be written as ΔQ by Δt or in this term you can write simply c by Δx into ΔQ .

So, i is equal to c divided by $2\pi r$, πr because you are talking about parameter of a circle and so Δx is $2\pi r$ and ΔQ is charge which is equal to e , charge which is equal to e . So an area of circle is πr^2 . So we can get μ , μ is equal to i , i is your c divided by $2\pi r$ into e , this is your μ . And multiplied by area is πr^2 , πr^2 and you can see that π π cancels out, r^2 cancels out. And so μ is equal to c into e into r by 2 .

Now multiply and divide by m , multiply and divide by m . And now you can look at this is e by $2m$ into mcr , so mass into velocity into r and this is equal to angular momentum, this is equal to angular momentum and that is what is written here. And e by $2m$ is known as gyromagnetic ratio. So magnetic moment is simply given by gyromagnetic ratio multiplied by angular momentum.

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Gyromagnetic ratio determines the ratio of nuclear magnetic moment to the nuclear spin, it is a fundamental property of each nuclear isotope and the sign of gyromagnetic ratio tells you about the, tells you about the direction of magnetic moment. So, if gyromagnetic ratio is greater than 0, then magnetic moment and spin angular momentum has same direction, whereas if gamma is less than 0 it means magnetic moment and spin angular momentum is going to be in opposite direction.

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Magnetic Properties of Selected Nuclei

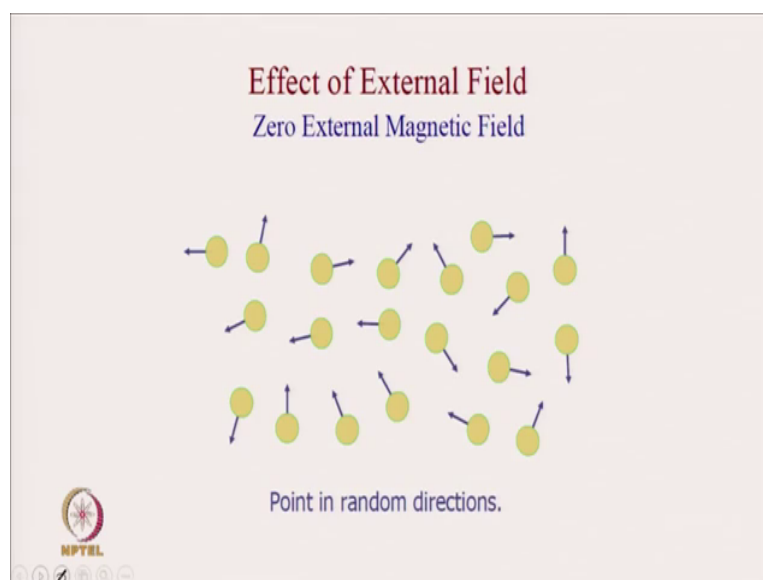
Nucleus	Abundance %	Spin, I	$\gamma_N = \frac{2\pi g_N \mu_N}{h}$ ($/10^7$ Ts)
^1H	99.98	1/2	26.75
^2H , (D)	0.02	1	4.10
^{13}C	1.1	1/2	6.73
^{14}N	99.64	1	1.93
^{15}N	0.365	1/2	-2.7116
^{19}F	100	1/2	25.1665
^{31}P	100	1/2	10.8289
^{35}Cl	75.4	3/2	2.6210
^{37}Cl	24.6	3/2	2.1718



This is the magnetic property of selected nuclei, these nucleus are given and their I value is also given and this is your gyromagnetic ratio. Now you can also look at the abundance this is important if you want to look at the signal to noise ratio, if you want to look at the signal to noise ratio. One of the thing which you will notice is proton has gyromagnetic ratio 26.75 and if you look at 13 carbon it is 6.73.

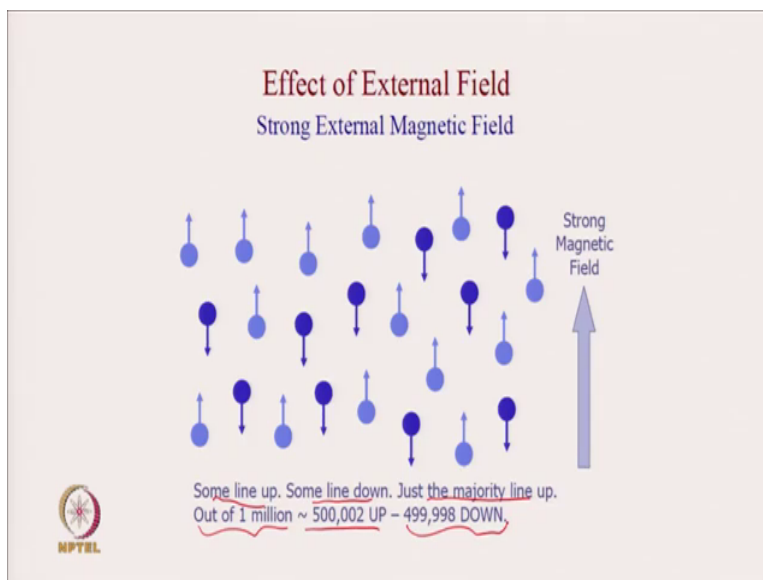
So as you know that the okay, so let us I will talk about this in the next slide because still I have not talked about magnetic field. Now, we have already discussed spin, now think about what is the effect of external magnetic field.

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When there is a zero external magnetic field spin points in random direction, so what happens is that your combined spin or combined magnetization is your zero or resultant magnetisation is zero.

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When you apply strong external magnetic field what it does is that some line up and some line down in the direction of a strong magnetic field. Majority of them line up and does there is a net magnetization in the direction of magnetic field, net magnetization in the direction of magnetic field.

However, since the gap between two energy levels in NMR states are very small and so out of 1 million this much goes up and this much goes down and there is very small difference in the population between excited state and your ground state and that is why NMR is a low sensitive technique, this is one of the problem with NMR. NMR high resolution technique but the intensity you get is very small, so sensitivity is small.

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Effect of an External Magnetic Field

- **No magnetic field:**
(2I+1) spin states are degenerate (*i.e.* they all have the same energy).
- **With magnetic field:**
Spin states separate in energy (larger values of m have lower energy)
- The separation of energy levels in a magnetic field is called the **nuclear Zeeman effect**. The energy of a spin state is given by:


$$E = -\vec{\mu} \cdot \vec{B}; \quad \vec{\mu} = \gamma \vec{I}$$

(Handwritten red annotations: a circle around the second equation, an arrow pointing to the vector I, and a bracket under the first equation)

So, in a nutshell if there is no magnetic field that 2I plus 1 spin states are degenerate 2I plus 1 spin states are degenerate, what does that mean? They are going to have same energy. When only you apply magnetic field, then degeneracy of spin states are removed and now they differ in energy.

Separation of energy levels in a magnetic field is called nuclear Zeeman Effect. The energy of a spin state is given by this equation E equal to minus mu dot B and we have already discussed mu is equal to gamma into I or J, sometime some books refer it as J, some book refers it as I which is angular momentum, angular momentum.

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Magnetic moment

$$\vec{\mu} = i \cdot A$$

$$i = \frac{dQ}{dt} = \frac{dQ}{(dx/c)}$$

$$i_{avg} = \frac{\Delta Q}{\Delta t} = \frac{c}{\Delta x} \Delta Q$$

$$\vec{i} = \frac{c}{2\pi} \vec{e}$$

$$A = \pi r^2$$


$$\vec{\mu} = \frac{e}{2m} \vec{J} = \gamma \vec{J}$$

$$\mu = \frac{c \cdot e \cdot r \cdot m}{2 \cdot m}$$

$$= \frac{e}{2m} \times mcr$$

$$\text{Circle} = \frac{e}{2m} \vec{J}$$


$$\mu = \frac{c}{2A} \cdot e \gamma \pi r^2$$



All nucleons, that is [neutrons](#) and [protons](#), composing any atomic [nucleus](#), have the intrinsic quantum property of [spin](#).


Angular Momentum

A rotating object possesses angular momentum




$$\vec{J} = m \vec{v} \times \vec{r}$$

Right hand rule




As the name suggests, spin was originally conceived as the rotation of a particle around some axis. This picture is correct so far as spin obeys the same mathematical laws as [quantized angular momenta](#) do.



So let us see this is the equation which I am talking about, this gamma into J and J is your angular momentum, J is your angular momentum.

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$$\hat{H} = -\gamma \hat{B}_0 \hat{I}_z$$

$$\hat{H} = -\omega_0 \hat{I}_z \quad (\text{in rad s}^{-1})$$

$$\hat{H} = -\mathcal{G}_0 \hat{I}_z \quad (\text{in Hz})$$

$$\hat{I}_z \psi_m = m \hbar \psi_m$$

$$E_m = -m \hbar \gamma B_0$$

$$= m \omega_0 \quad (\text{in rad s}^{-1})$$


$$= m \mathcal{G}_0 \quad (\text{in Hz})$$

Now, once you know that now you can write a Hamiltonian. So, Hamiltonian in the Z direction is equal to minus gamma into B naught into I J. So Hamiltonian operator is equal to minus gamma B naught into I J operator.

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Effect of an External Magnetic Field

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- The separation of energy levels in a magnetic field is called the **nuclear Zeeman effect**. The energy of a spin state is given by:




$$E = -\vec{\mu} \cdot \vec{B}; \quad \vec{\mu} = \gamma \vec{I}$$

$E = -\gamma I_z B$
 $E_z = -\gamma I_z B$

Energy is equal to minus mu into B where mu is equal to gamma into I, so E is equal to minus mu minus gamma into I into B, gamma I into B. So E J is equal to E Z direction is minus gamma into I J into B.

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$$\begin{aligned}\hat{H} &= -\gamma \hat{B}_0 \hat{I}_z \\ \hat{H} &= -\omega_0 \hat{I}_z \quad (\text{in rad s}^{-1}) \\ \hat{H} &= -\mathcal{H}_0 \hat{I}_z \quad (\text{in Hz}) \\ \hat{I}_z \psi_m &= m \hbar \psi_m \\ E_m &= -m \hbar \gamma B_0 \\ &= m \omega_0 \quad (\text{in rad s}^{-1}) \\ &= m \mathcal{H}_0 \quad (\text{in Hz})\end{aligned}$$

And if you remember quantum the energy is obtained by applying Hamiltonian operator. So, in this case Hamiltonian operator is equal to minus gamma B naught I J. So, Hamiltonian is also equal to minus omega naught I J, where gamma B naught is omega naught, so now it is in radian per second, radian per second unit. And it also can be expressed in hertz unit as minus nu naught I J operator.

If I apply I J, I Z operator into a wave function what I will get is mh cross psi m, mh cross psi m. So this is the way you can express energy of mth spin level, mth spin level, energy of mth spin level is minus mh cross gamma B naught, mh cross gamma B naught and this is in energy unit, but in radian per second unit it is m omega naught and in hertz unit is m nu naught.

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Magnetic Quantum Numbers

- l is quantized producing $(2l + 1)$ discrete values of angular momentum, m_l .
- $m_l = l, l-1, \dots, -l$

Em ??

$l = 1/2$ $l = 1$ $l = 3/2$

m =

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l is quantized and that gives you $2l + 1$ discrete value of angular momentum and angular momentum is between l to minus l . So, if l is equal to half, then there will be two values of m which is half and minus half, if l is equal to 1 then you have three values 1, 0, minus 1 and if l is equal to 3 by 2 then you have m value, m is equal to 3 by 2 so these all are different value of m . So now, if I want to go from this to this the ΔE can be calculated because we know energy of m th level, we know energy of m th level, so it can be calculated.

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$$E = m \hbar \gamma B_0$$

The nuclei with half spin has two energy levels (α and β) and their energies are given by

$$E_\alpha = \frac{1}{2} \hbar \gamma B_0 \quad E_\beta = -\frac{1}{2} \hbar \gamma B_0$$

For Nuclei with positive γ , E_β is lower in energy

$$\Delta E = \hbar \gamma B_0$$

$E_\alpha - E_\beta = \frac{1}{2} \hbar \gamma B_0 + \frac{1}{2} \hbar \gamma B_0$

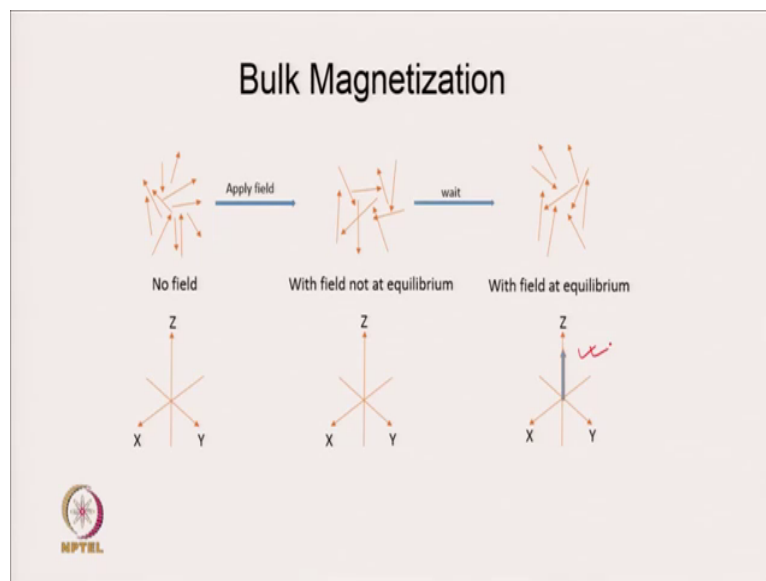
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So energy is this $m \hbar \gamma B_0$ that is what we looked at, if we take nuclei with half spin, for example, $l = 1/2$ it has two energy levels and we denote sometime by α and β and their energies are given by E_α is half $\hbar \gamma B_0$, so m is equal to

half, and for beta m is equal to minus half so E_{β} will be given by minus half h cross γB_0 .

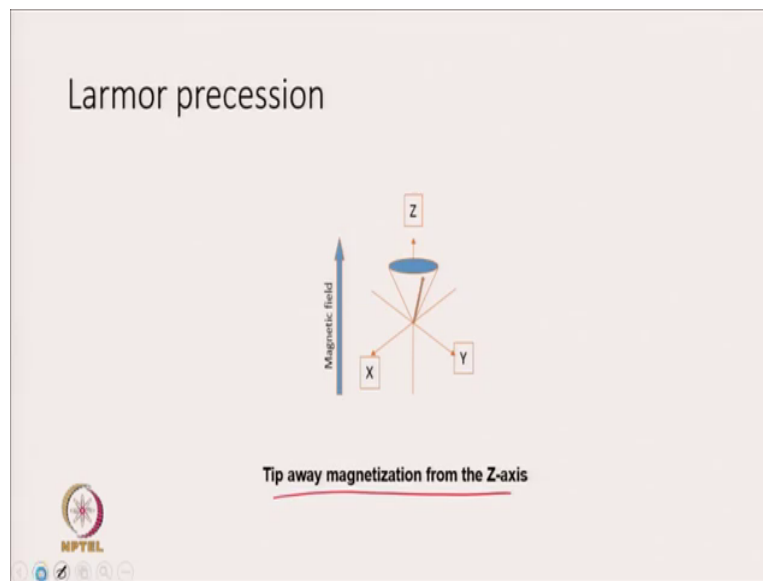
For nuclei with positive gyromagnetic ratio, E_{β} is lower in energy, E_{β} is lower in energy and so what does that mean is that if you take proton and this is E_{β} and this is E_{α} , E_{α} and ΔE will be equal to, ΔE will be equal to simply your half h cross γB_0 this is E_{α} minus minus h cross γB_0 . So E_{α} minus E_{β} , so this is basically E_{α} minus E_{β} is equal to this and this is equal to h cross γB_0 , h cross γB_0 .

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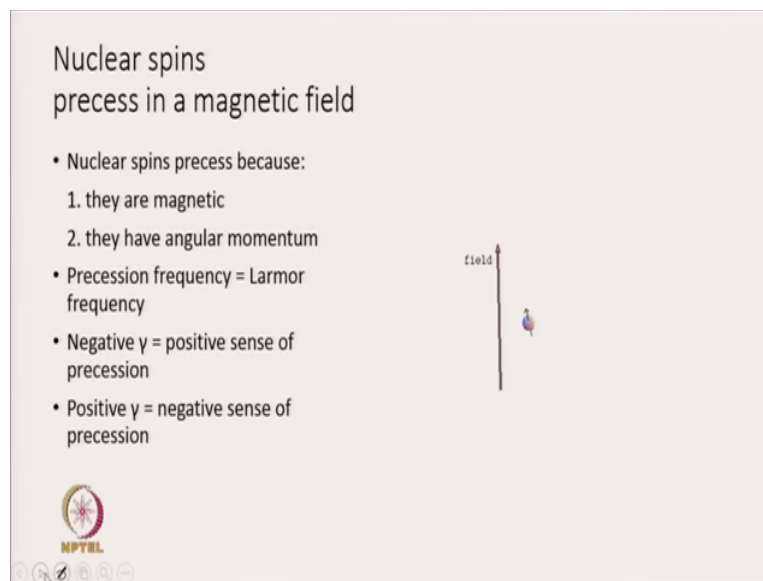
So what is happening is that if there is no field the magnets are, spin magnets are in random direction, but when you apply a field in Z direction then after sometime bulk magnetization will be in Z direction. Since these spins are in random state before application of magnetic field so bulk magnetisation is 0, but when you apply magnetic field in Z direction then you will get a bulk magnetization in Z direction, this is net effect of external magnetic field.

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Now next step in NMR is somehow we tell the bulk magnetization from Z axis. So, if you tip away magnetization from Z axis what will happen? It will start rotating it will start precession, so it will start precessing.

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So nuclear spin precess in magnetic field since they are magnetic and they have angular momentum. Precession frequency is equal to Larmor frequency and if the gamma value of or gyromagnetic value of the nuclei is negative it means it has positive sense of precision, if the value is positive then it has negative sense of precession.

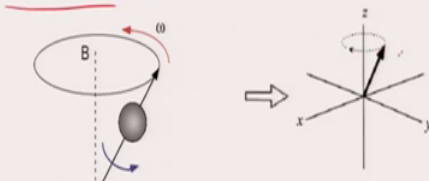
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The Larmor Frequency

A nuclear magnetic moment will precess about the axis of an externally applied field at a frequency proportional to the strength of the applied field, B_0 .

$$\omega = \gamma B_0 \text{ (rad/s)}$$
$$\nu = \gamma B_0 / 2\pi \rightarrow \text{Larmor Frequency}$$

The direction of motion can be clockwise or counterclockwise and is determined by the sign of γ . By convention, the field is applied along the z axis of a Cartesian co-ordinate frame.





So when you tip the magnetic field away from Z axis, the nuclear magnetic moment will precess about the axis of externally applied field at the frequency equal to the strength of the applied magnetic field. So omega will be gamma B naught in radian per second and nu will be gamma B naught by 2 pi and this is known as Larmor frequency.

The direction of motion can be clockwise or anticlockwise and it is determined by value of gamma. Generally the field is applied along Z axis of Cartesian co-ordinate frame, Cartesian co-ordinate frame. So you can see that now it is rotating this way, it can also rotate in this way.

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Larmor Precession

If the magnetic field strength is B_0 , then the frequency of the Larmor precession is ω_0 (in rad s^{-1})

$$\omega_0 = -\gamma B_0$$

or if we want the frequency in Hz, it is given by

$$\nu_0 = -\frac{1}{2\pi} \gamma B_0$$



So let us discuss about Larmor precession now. If the magnetic field strength is B , then the frequency of Larmor precession is ω , so ω is given by γB and if we want in hertz it will be $\frac{\gamma B}{2\pi}$ this I have already discussed.

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NMR nuclei frequency in different external magnetic field.

Magnetic Field	^1H Frequency (MHz)	^{13}C Frequency (MHz)	^{15}N Frequency (MHz)
9.36 T	400	100.8	40.8
11.7 T	500	126	51
14.04 T	600	151.2	61.2

Engineering Chemistry, Oxford University Press

Now this NMR nuclei frequency will be different in different external magnetic field. NMR nuclei frequency will depend on two different things, one is magnetic field and another is type of nuclei. Now let us see some of the values. If suppose magnetic field is 9.36 tesla, then proton frequency will be 400 megahertz or ^{13}C frequency will be 100.8 megahertz in 9.36 tesla magnetic field. It is almost 1 by 4 time of proton frequency.

And ^{15}N frequency in 9.36 tesla is 40.8 megahertz, 40.8 megahertz so whenever you have heard about that you are working on 400 megahertz, it is basically your frequency with respect to proton nuclei, it is not 400 megahertz with respect to ^{13}C frequency or with respect to ^{15}N nuclei, with respect to ^{15}N nuclei. So on 400 megahertz machine your ^{13}C frequency will be 100.8 megahertz, whereas ^{15}N frequency will be 40.8 megahertz. This is on a machine which has magnetic field 9.36 tesla.

If you change the magnetic field to 11.7 tesla then the frequency is 500 megahertz on for proton nuclei and 126 megahertz for ^{13}C nuclei and 51 megahertz for ^{15}N nuclei. On 14.04 tesla machine spectrometer you have proton frequency around 600 megahertz, ^{13}C frequency around 151.2 megahertz and ^{15}N frequency around 61.2 megahertz.

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Apply RF Field

Excitation of transitions between energy levels (or tipping of magnetization away from z-axis) is stimulated using radio-frequency electromagnetic radiation.

Now question is how to tilt your magnetic field, how to tilt magnetization, bulk magnetization away from the Z axis. That is done by applying a RF field along x or y direction. So unless you apply RF field the magnetization is going to be, is not going to be tilted and then there cannot be a transition. So excitation of transition between energy levels or in other way you can say that tipping of magnetization away from Z axis is stimulated using radio frequency electromagnetic radiation.

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Two counter-rotating field is equivalent to field oscillating along the x-axis (RF field)

(a)

(b)

Now, how does RF field does it, it is a bit difficult to understand, but you can think of RF field as a two counter-rotating field, what is RF field? RF field is like this, it starts from some

point and then it is like a wave, so it is like a wave, it is maximum it is going to 0 and then it is going to maximum in negative direction, this is the way RF field works.

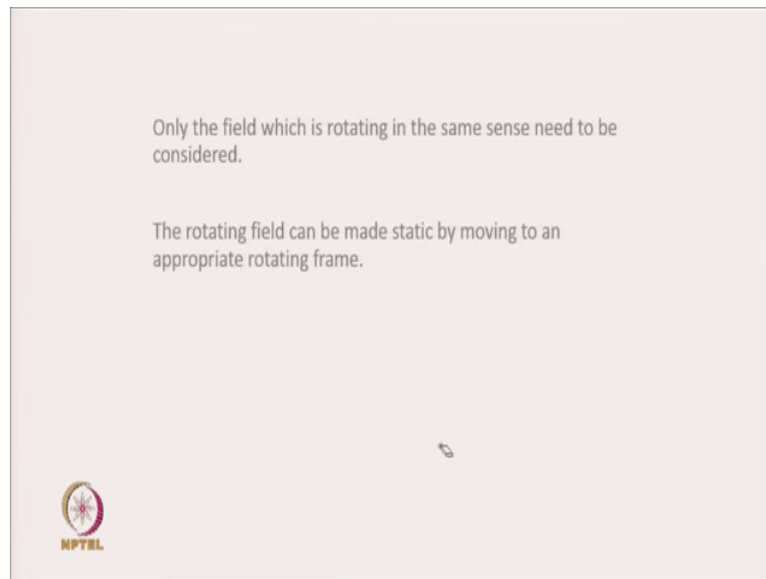
Now, if we want to look at the effect of RF field we need to take the RF field as two counter rotating field. Now, can we represent it by a two counter-rotating field? Answer is yes, now you think about there is two fields here at this point, if the two fields are in this direction X direction, positive X direction they will combine and give you maximum magnitude along X direction and that corresponds to this point.

Now, they started counter rotating, one is shown by B 1 plus, another is shown by B 1 minus, so what does that mean? That one field is rotating in minus direction, one field is rotating in plus direction, minus tells you about clockwise direction, plus talks about anti clockwise direction. If they are in this position then your, then your resulting along X axis will be smaller than this and that is what you get at this position, at this position.

Now it is going like this, this is going with this and so suppose if it is B 1 plus is at this position, B 1 minus is at this position then what will happen? The resultant along x direction is 0 and that corresponds to this point. Now, it moved further this way, it goes in this direction, when it is here then you have resultant along minus X axis and that is what is shown here.

And if it again rotates and comes to minus x direction both are coming to minus x direction and the resultant will be maximum but in minus x direction and that corresponds to this. So, what does that mean is a RF field can be thought of equivalent to two-counter rotating field, equivalent to two-counter rotating field.

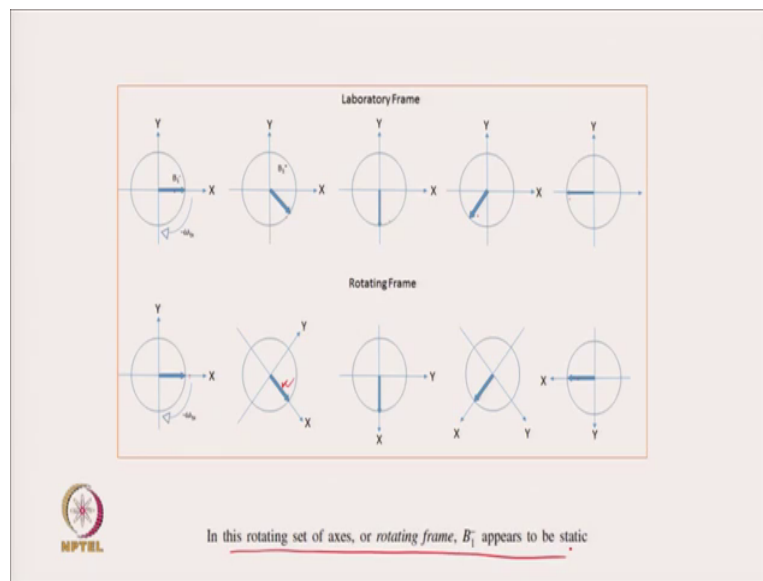
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So, only the field which is rotating in the same sense need to be considered, only the field which is rotating in the same sense need to be considered, so out of two field we have to look at the field which is the rotating in the same sense in which your magnetization is bulk magnetization is rotating. So, you can choose one of the field depending on the, depending on the sense of direction in which your sense of direction in which magnetization will move.

Why we are doing that? It is because only that field is going to affect your magnetization. Now your this thing is rotating, your magnetization is rotating and your field is also rotating and so it is a bit difficult to look at the affect. And so what we do is that we make rotating field static by moving to appropriate rotating frame. If you have studied in your Bachelor class about physics, you must have known the concept of rotating frame. Now, what we are going to do is from laboratory frame we are going to move to rotating frame.

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So let us see here, this is the way your field is moving in the laboratory frame B_1 minus is here, now it is going this way, it ends up here, then this and this position. So, one whole circle is completed. Now think of that if your field is moving like that, so your laboratory frame is here and here is your rotating frame also. If it comes at this position, I rotate my frame such that, I rotate my frame such that it is now at this position, so now you see it is still along X axis, so your frame is also rotating the way your magnetization is your field is rotating.


If they are here, it is here at this position, then your rotating frame is here, here then rotating frame is here. So, as field moves in the same direction you are moving your rotating frame, rotating frame and you are in the rotating frame and then your the magnetic field, the rotating magnetic field looks like a static magnetic field, looks like a. So in this rotating set of axis or rotating frame B_1 minus appears to be static.

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Larmor frequency in rotating frame

$$\Omega = \omega_0 - \omega_{\text{rot. fram.}}$$
$$\omega = -\gamma B.$$
$$\Omega = -\gamma \Delta B$$

hence $\Delta B = -\frac{\Omega}{\gamma}$.



This apparent magnetic field in the rotating frame is usually called the *reduced field, ΔB* .

So what will be the Larmor frequency in the rotating frame? It will be equal to omega naught minus omega rotating frame, alright, omega naught is the Larmor frequency in laboratory frame and now you are trying to look at Larmor frequency in rotating frame and so the chemical shift or the Larmor frequency in the rotating frame will be equal to omega naught minus omega rotating frame.

So, omega we know that omega is minus gamma B naught, so this Larmor frequency will be equal to minus gamma into delta B, so gamma into delta B, so delta B is corresponding to this difference. And hence, delta B will be minus Larmor frequency in rotating frame divided by gamma, Larmor frequency in rotating frame divided by gamma. This apparent magnetic field in rotating frame is usually called reduced field delta B.

So, one of the effect of considering rotating frame is that the effective magnetic field along z direction is no longer equal to B, it is now equal to delta B, delta B and that is your apparent magnetic field in the rotating frame. So, one thing you did is you rotated your frame so that magnetic field, radiofrequency field looks static that is good enough but that has effect on the effective magnetic field, that has effect on the magnetic field as such. And the reduced magnetic field is now given a symbol delta B.

(Refer Slide Time: 38:01)

The effective field in presence of RF field

$$\Omega = \omega_0 - (-\omega_{RF})$$

$$= \omega_0 + \omega_{RF}$$

$\omega_{\text{rot frame}} = -\omega_{RF}$

$$\omega_{\text{eff}} = \gamma B_{\text{eff}}$$

$$B_{\text{eff}} = \sqrt{B_1^2 + \Delta B^2} \quad \omega_{\text{eff}} = \sqrt{\omega_1^2 + \Omega^2}$$

$$\sin \theta = \frac{B_1}{B_{\text{eff}}} \quad \cos \theta = \frac{\Delta B}{B_{\text{eff}}} \quad \tan \theta = \frac{B_1}{\Delta B}$$

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So what we are looking at is what is the effect of RF field on the magnetization in presence of magnetic external magnetic field in the rotating frame in the rotating frame, so we know that your this chemical shift is equal to omega naught minus omega in rotating frame, rotating frame. So, what we do is, we take omega rotating frame is equal to minus omega of RF field under such condition your chemical shift is equal to omega naught minus minus omega RF and what does that mean is chemical shift is sum of omega naught and omega RF.

So now w effective will be given by gamma into B effective, w effective will be given by gamma into B effective and B effective is basically square root of B 1 square plus delta B square. So, let us understand here B 1 is your RF field and delta B is your, delta B is your the external magnetic field in rotating frame. So effective B will be given by B effective and as you can see that B effective can be given by square root of B 1 square plus delta B square, so omega effective is equal to square root of omega 1 square plus chemical shift square.

This angle theta can also be related to delta B and B effective, so cos theta will be equal to delta B divided by B effective, whereas sin theta will be equal to B 1 by B effective, tan theta is equal to B 1 by delta B, B 1 by delta B.

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On-resonance pulse


If the transmitter frequency is exactly the same as Larmor frequency

$$\Delta B = 0$$

$$B_{eff} = B_1$$

Pulse is exactly on Resonance, and tilt angle is 90°

Handwritten notes:
 $\omega_{tF} = \omega_{rot\ frame}$
 $\omega_{RF} = -\omega_{tF}$
 $\Omega = \omega_0 + \omega_{RF}$
 $= \omega_0 - \omega_{tF}$
 $= 0$



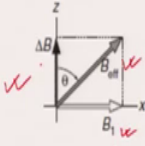
The effective field in presence of RF field


$$\Omega = \omega_0 - (-\omega_{RF}) = \omega_0 + \omega_{RF}$$

$$\omega_{eff} = \gamma B_{eff}$$

$$B_{eff} = \sqrt{B_1^2 + \Delta B^2} \quad \omega_{eff} = \sqrt{\omega_1^2 + \Omega^2}$$

Handwritten notes:
 $\Omega = \omega_0 - \omega_{rot\ frame}$
 $\omega_{rot\ frame} = -\omega_{RF}$



$$\sin \theta = \frac{B_1}{B_{eff}} \quad \cos \theta = \frac{\Delta B}{B_{eff}} \quad \tan \theta = \frac{B_1}{\Delta B}$$


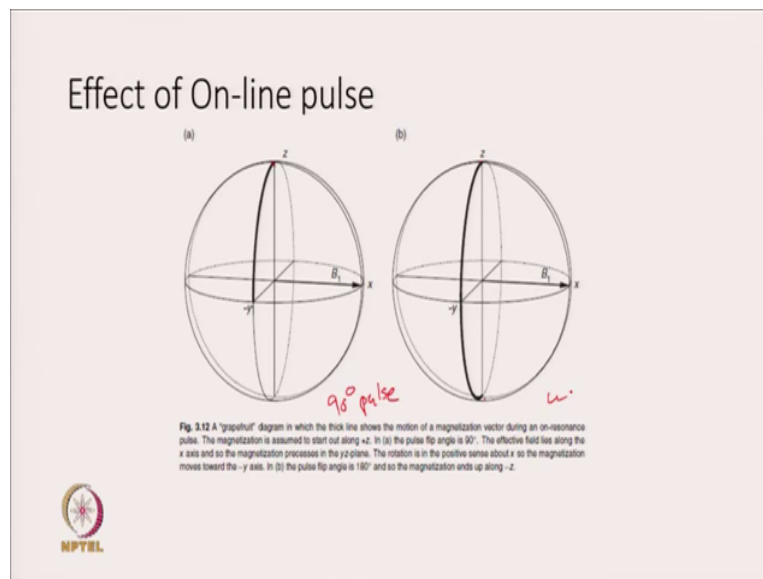
Now you must have heard about on resonance pulse, if you go and look at any manuscripts related to NMR, you will listen about this, you will come across on resonance pulse, what is on resonance pulse? On resonance pulse, a pulse is called on resonance pulse, if the transmitter frequency is exactly the same as Larmor frequency, exactly the same as Larmor frequency.

And transmitter frequency is basically equal to transmitter frequency tF is basically equal to frequency of rotating frame, rotating frame it means RF is equal to minus tF and we know that this is equal to omega minus omega if you look at the formula, this is omega naught minus omega naught plus omega RF and omega naught minus omega tF and if this is equal

then this will be 0, this will be 0. And so ΔB is equal to 0 and $B_{\text{effective}}$ is simply B_1 , $B_{\text{effective}}$ is simply B_1 .

So ΔB is 0 means $B_{\text{effective}}$ is B_1 square, square root of B_1 square and that means it is equal to B_1 , ΔB is 0, then effective field will be equal to B_1 . So pulse is exactly on resonance in that case pulse is exactly on resonance. And tilt angle will be 90 degree and you can see from here, if $B_{\text{effective}}$ is here then θ is equal to 90 degree, so tilt angle is 90 degree.

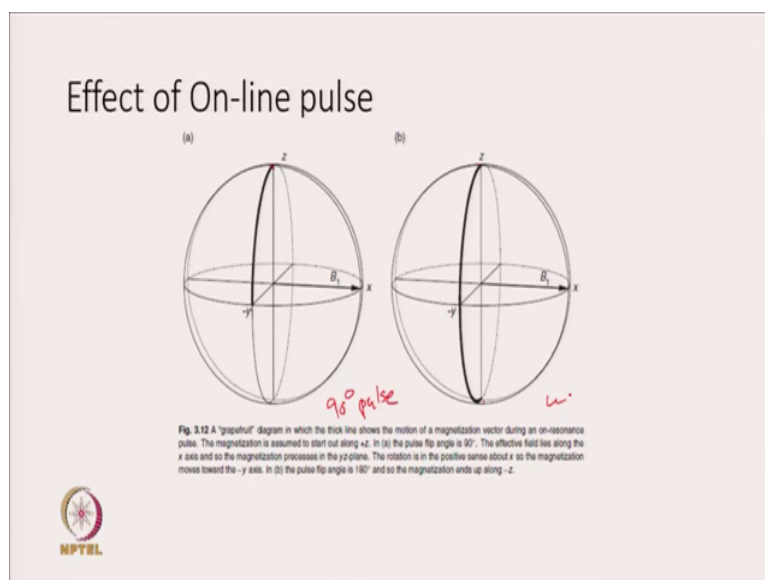
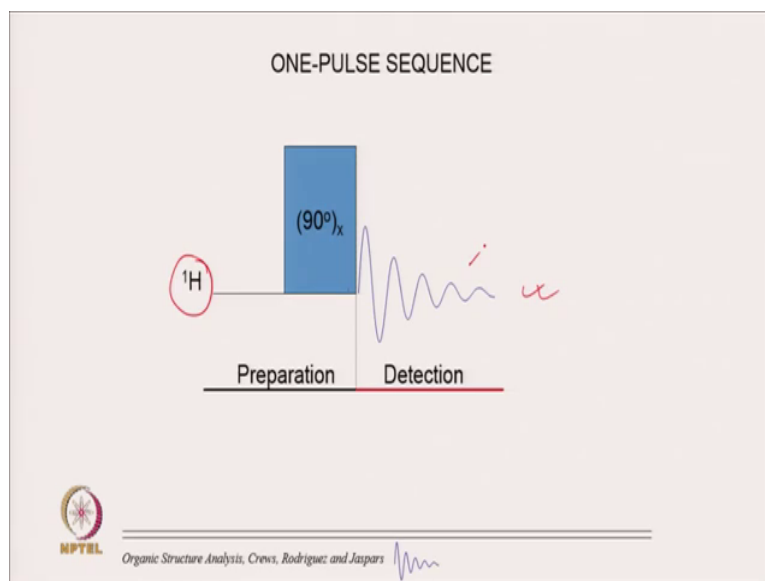
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Now let us look at the effect of on-line pulse, effect of on-line pulse. So this is given by this effect of on-line pulse is shown by a right hand rule, shown by a right hand rule. So think about this is your magnetization Z axis you have a magnetization and this is along the axis in which you have applied your magnetic field, then your magnetization will comes towards you, this magnetization will go from Z direction to this direction and that is what is shown here.

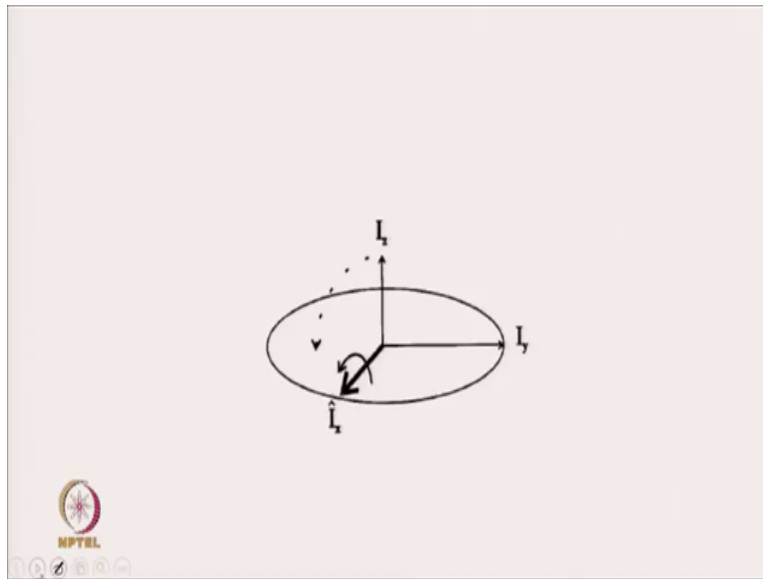
So, if you apply B_1 field along this, magnetization is going from Z axis to minus Y axis if you apply 90 degree pulse, this is for 90 degree pulse, this is for 90 degree pulse. And if you apply 180 degree pulse it will go from this point to this point, this point to this point. So this is your effect of on-line pulse when you understand this it is very easy to understand your the effect of pulses on the magnetization.

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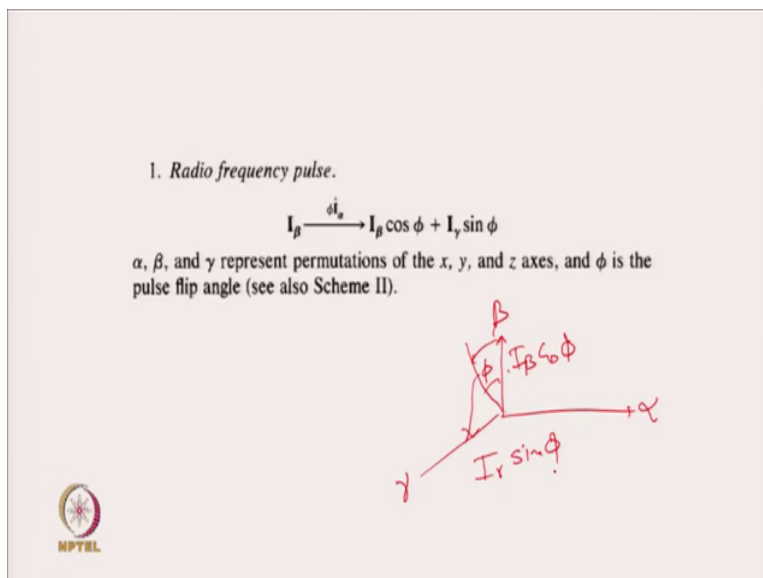
So, one-pulse sequence if you talk about a simple NMR spectra and that is basically one pulse sequence, what you do at proton nuclei you are applying 90 degree pulse, 90 degree pulse and so this seem as this and then you remove the pulse it will again go back to its position and it is shown here and I will discuss now how you get this kind of curve, this is known as FID which you are going to detect in a normal NMR in a typical NMR experiment.

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So this is very important, this rule is very important or this scheme is very important to understand the effect of a pulse on effect of pulse on magnetization or effect of RF pulse on magnetization. So think about if I apply so right hand rule so please remember right hand rule, if I apply magnetic field along y direction, so this is your y direction suppose then this is positive x direction and this is IZ magnetization is towards this and I apply then it goes to your IX and this side is IX.

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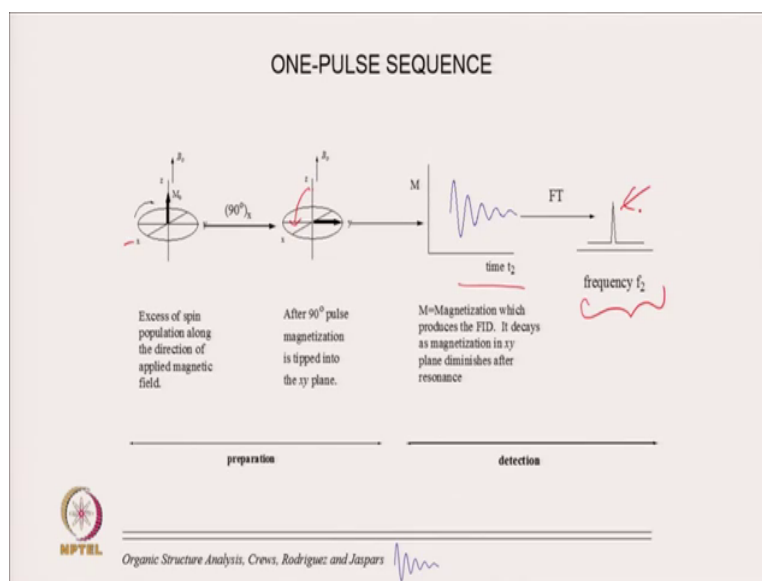


So, what you can write is I beta if I apply a pulse phi in alpha direction and what I will get is I beta cos phi because it is going from I beta and plus I gamma sin phi. So, what we did is, just take like this, this is your beta magnetization and you are applying alpha pulse and this is

your gamma. So, if I apply phi pulse, so means it will come from here move to this position, and this angle is phi.

And so its component along this axis, beta axis is going to be $I \beta \cos \phi$ and its component along this direction is going to be $I \gamma \sin \phi$. Now this is, if you understand this, it is not very difficult to understand the effect of pulses on the magnetization.

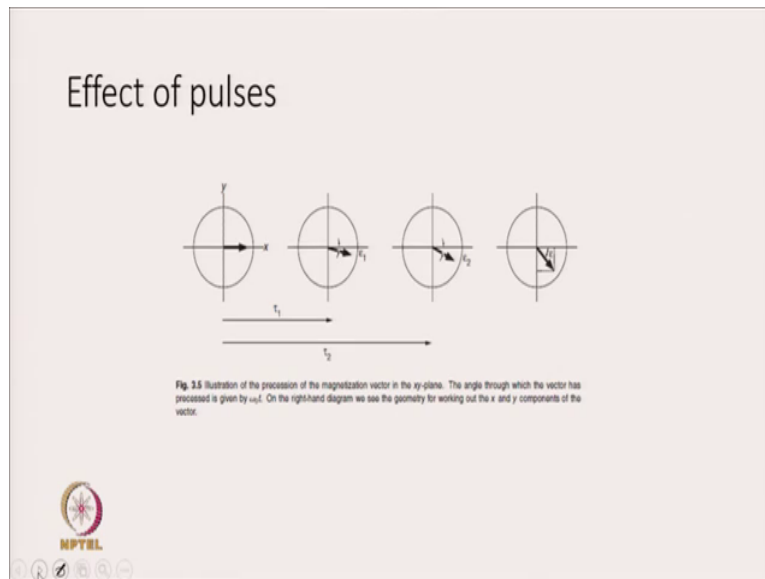
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So, let us talk about one-pulse sequence, this is magnetization along Z axis, I applied 90 degree along X axis, if I apply 90 degree then what will happen? 90 degree pulse along X axis, then what will happen is, this is right hand rule, so it is here, so it will go to this direction, so let us apply this is minus X axis suppose. If it is X axis then it will go like this, anyway it goes to y direction minus y or y. So it is basically tipped into x-y plane since 90 degree rotation is there, it can it will go towards this side basically.

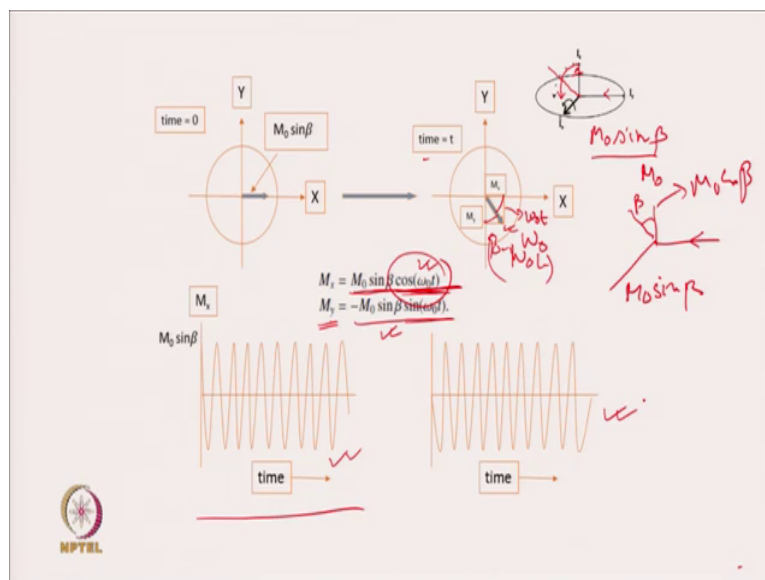
And then what will happen? It will come back to this point and so if you are looking magnetization along y direction it will decrease, this is the spectrum which you have obtained in, obtained in time domain and this is known as FID. And if you do Fourier transformation then you can get this kind of peak, which tells you about what is the frequency of that nuclei.

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Now, let us see the effect of pulses. So, what happens if I apply pulse and live it for some time? So, what does pulse do? Pulse tilts the magnetization away from Z axis and if you remove pulse then what will happen? It will start doing precession, start doing precession and that is what it is shown here, it is doing precession with time. So in tau 1 time it goes to this position, in tau 2 time it goes to this, so it is precessing, it is precessing.

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Now, let us think about, so what is happening? So it went to suppose here is the magnetization, you applied pulse, it goes to y direction and then this will start precessing slowly, slowly it will come back to z direction. This is the schematic of effect of, effect of chemical shift on the magnetization. Now, you see your chemical shift, so suppose you have a

magnetization here and you applied a magnetic field in this direction, your magnetization will come from Z axis to X axis, Z axis to X axis.

And suppose if I have applied beta degree pulse then magnetization will be equal to $M_0 \sin \beta$, $M_0 \sin \beta$. So this is your M_0 is here and if I applied pulse from this side, this angle is beta, so then this will be equal to $M_0 \sin \beta$ and this will be equal to $M_0 \cos \beta$. So, $M_0 \sin \beta$ is here on the X axis and now you remove the pulse and it start precessing and now we are going to see the effect of precessing.

So at time t it moved to this position with the frequency ω and if this angle is ωt then the component of the magnetization along the X axis will be $M_0 \sin \beta \cos \omega t$, so this angle is ωt , and this side you have a $\cos \omega t$, and since we have $M_0 \sin \beta$ here, so the total signal will be equal to total magnetization will be equal to $M_0 \sin \beta \cos \omega t$.

Magnetization in Y direction will be similarly given by minus $M_0 \sin \beta \sin \omega t$, $\sin \omega t$. And since it makes your $90 - \beta$, $90 - \omega t$ angle with the negative Y axis and so you will get this magnetization along Y axis. Here is a plot where M_x is plotted against time and as you see that this is, this magnetization along X axis depends on $\cos \omega t$ and so it will vary like a cosine function and that is what you see here.

Whereas, M_y is magnetization along Y axis is function of $\sin \omega t$ and if I M_y with time then it will be seen as a sin function, it will be seen as a sin function. What happen? That you applied the magnetic field, it came into x-y plane and now it is rotating, it is precessing, it is precessing and going towards your. So this is effect of only rotation and that is what is known as chemical shift evolution, this rotation after the pulse, after your pulse is known as chemical shift evolution.

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2. Chemical shift. The chemical shift has the effect of an "pulse" along the z axis.

Examples:

$$I_x \xrightarrow{\alpha_I t} I_x \cos(\Omega_I t) + I_y \sin(\Omega_I t)$$

$$I_y \xrightarrow{\alpha_I t} I_x \cos(\Omega_I t) - I_y \sin(\Omega_I t)$$

Ω_I is the chemical shift for spin I, and t is the time. With the exception

Now the chemical shift has the effect of an RF pulse along the Z axis, RF pulse along the Z axis. So, if you do not want to look at this picture, what you can do is, you can try to understand the effect of chemical shift by assuming that RF field by thinking that RF field is along the Z axis, RF field is along the Z axis. So, if I apply, so you see this I x, so magnetization is in the x direction, so x direction is suppose if you are taking like this.

So this is z direction and this is your, these are the three directions, so this is I y, this is I x and this is I z. Now, if you take I x, so this is I x magnetization if I apply z and then what will happen? It will move towards I y only. So movement if this is the magnetization, here is the magnetization, I apply chemical shift, it will move towards this direction, this direction. And so it is going from I x to I y and that is why I x has the cos component, I y has the sin component.

If you apply on I y direction, so you see this is I y direction and this is your field so it will move towards minus I x, so I y will move effect of I chemical shift is move I y towards minus I x magnetization from Y axis to minus X axis. And so this has cos component, this has minus this has sin component. So this is the effect of chemical shift.

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Fig. 4.3 The x and y components of the signal can be thought of as arising from the rotation of a vector S_0 at frequency Ω .

$$M_x = M_0 \cos \Omega t$$

$$M_y = M_0 \sin \Omega t$$

$$S(t) = S_x(t) + iS_y(t)$$

$$= S_0 \cos \Omega t + iS_0 \sin \Omega t$$

$$= S_0 \exp(i\Omega t)$$

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So first thing is this is the effect of chemical shift. M_x is given by $M_0 \cos$ this chemical shift multiplied by t , M_y is $M_0 \sin$ chemical shift multiplied by t . Here I have taken M_0 is basically $M_0 \sin \beta$, but now I am taking the $M_0 \sin \beta$ is suppose M_0 dash, M_0 dash. So M_x is M_0 dash \cos this frequency, this chemical shift multiplied by t , M_y is M_0 dash into \sin chemical shift multiplied by t . So signal will be sum of signal in x direction plus i multiplied by signal in y direction with time. So this is $S_0 \cos$ your chemical shift multiplied by t plus $i S_0 \sin$ chemical shift multiplied by t (56:05), so this is your total signal, this is your total signal.

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Decay of Signal with time

$$S(t) = S_0 \exp(i\Omega t) \exp(-R_2 t)$$

$S(t)$

time \rightarrow

FID

NPTTEL


Now signal will also decay with time, signal will also decay with time. And what will happen that with time it is going, it is going to decrease. So, why it is decreasing? Because it is, it will like, it will come back to finally z direction and so signal along x direction or y direction is going to be 0 after some time. And the rate of decay of this signal is given by R_2 , R_2 . So S_t is equal to $S_0 \exp(-R_2 t)$ and if you plot this S_t versus t , what you will get is this kind of curve. And thus it is typical your FID, typical FID, this is your typical FID.

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Fourier transformation (transformation of time-domain data to frequency domain)

Two key idea

- (i) Any time-domain function can be represented by the sum of cosine waves of different frequencies and amplitude.
- (ii) Cosine waves are orthogonal to each other, i.e. integral, taken between $t=0$ and $t = \infty$, of the product of any two cosine waves of different frequency is zero.



NPTEL

So you have obtained the signal in time domain, now you need to convert into, you need to convert into frequency domain to get the more accurate information and I have already discussed about what you do for this, you do Fourier transformation which transforms the time domain data to frequency domain data. So, I think now time is over, so I will stop here and I will discuss the other things about NMR in the next lecture, thank you very much.