# NMR Spectroscopy: Principles and Applications

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**Classical Description**

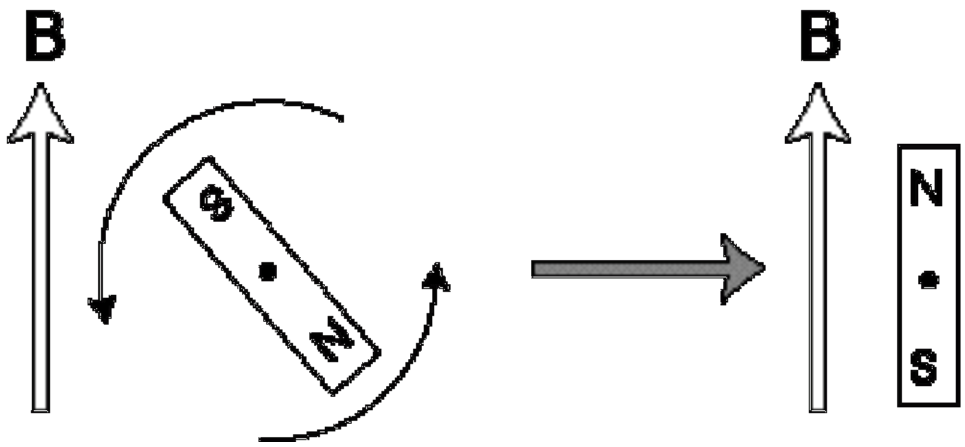
Lecture 2

# Classical Description

*We will first look at NMR Using a Vector model. Strictly speaking this applies only to uncoupled spins and thus precludes clean explanation of NMR spectrum or experiments involving real samples. Yet, quite a lot of insight can be gained in understanding RF pulses, free induction decay and some simpler experiments.*

# Nuclear Magnetic Moments in Magnetic Field

*Let us try to understand the forces and dynamics imposed on nuclear magnetic moments in a classical view. Suppose if a bar magnet on a friction less bearing is exposed to a magnetic field (a compass in earth field) the North and South pole align along the field.*



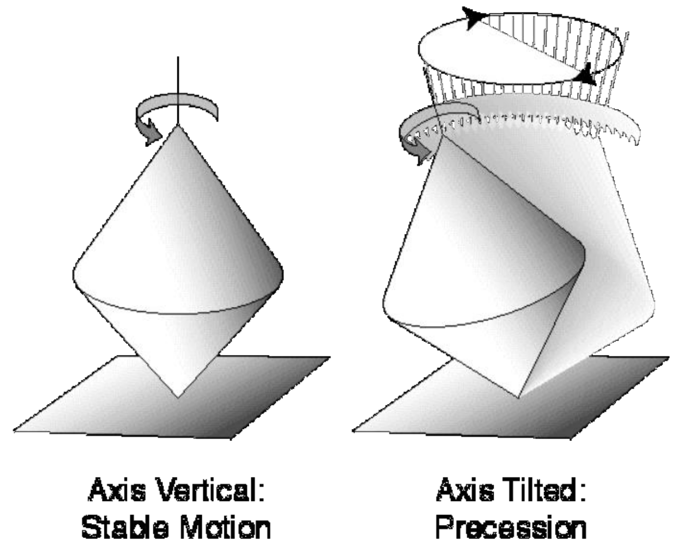
# Nuclear Magnetic Moments in Magnetic Field

*The applied magnetic filed impinges a torque on the nuclear magnetic moments. The moment itself is due to an angular momentum (**I**ħ) and the rate of change of angular momentum is then given by*

$$\frac{d(\boldsymbol{I}\hbar)}{dt} = \boldsymbol{\mu} \times \boldsymbol{B_0}$$

$$\frac{d\boldsymbol{\mu}}{dt} = \boldsymbol{\mu} \times \gamma \boldsymbol{B_0}$$

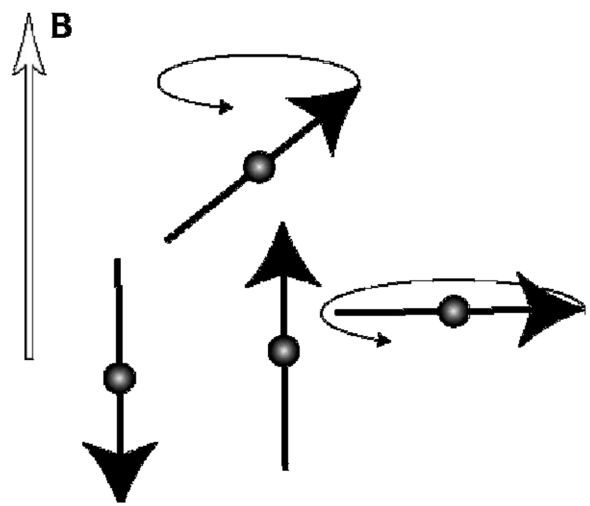
$$\because \boldsymbol{\mu} = \gamma(\boldsymbol{I}\hbar)$$

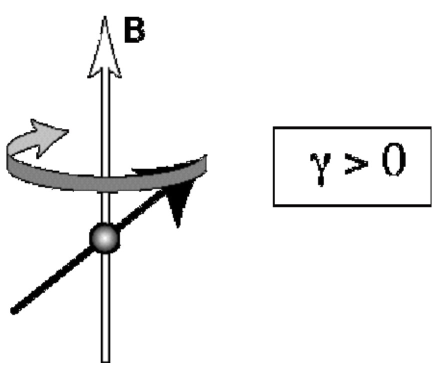


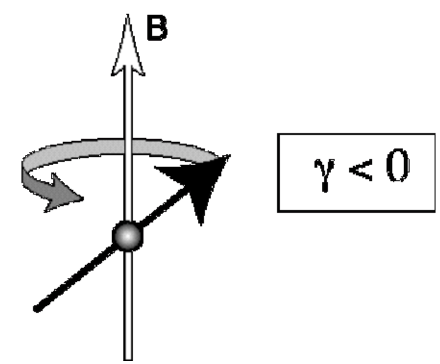

*Thus the effect of the torque is to induce a precession of the nuclear moment about the applied field as a top would precess in the earth's gravitational field*

# Nuclear Magnetic Moments in Magnetic Field

*Nuclear moments goes around the magnetic field sweeping a cone with the initial tilt angle of the nuclear moment with respect to the field direction.*



# Alignment of Nuclear Magnetic Moments

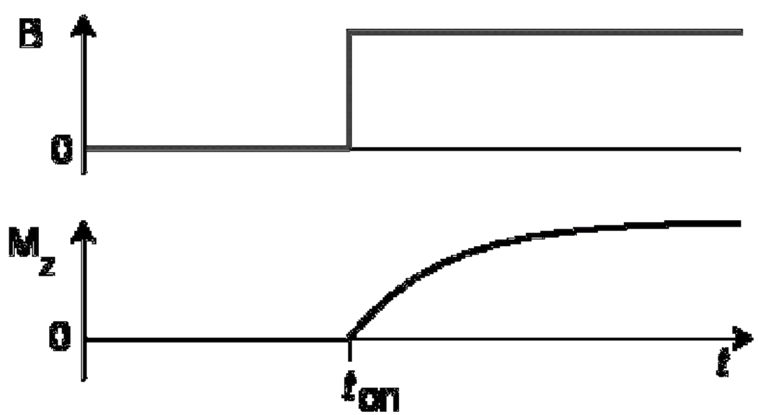
*When a sample is placed in a magnetic field the individual magnetic moments undergo the precession motion around the field and if this was just the case there won't be any bulk magnetization as there will be equal number of spins in opposite orientations and the net will vanish in any direction. But, each nuclei with its own spin is a magnetic system and interacts with each other. Moreover, they undergo incessant collisions, tumbling, and fluctuations due to the molecular motions and thus the local environment of magnetic field experienced fluctuate. This process is called interaction of spins with surroundings or spin-lattice relaxation. The relaxation process ultimately leaves some excess spin preferentially aligned along the applied field so that a net magnetization to builds up along the direction of the applied magnetic field direction – called* ***longitudinal magnetization****.*

# Alignment of Nuclear Magnetic Moments

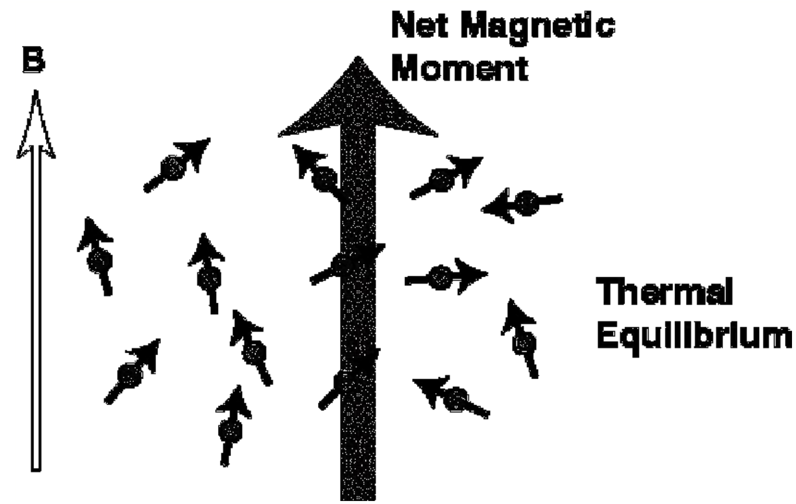
*What happens in the plane perpendicular to the applied field? There is no magnetization at equilibrium or the transverse magnetization is zero. This can be visualized as follows. The individual magnetic moments precess in a cone with its preferential tilt angle but spins with the same tilt angle can still have the starting phase different such that the net magnetization in the plane that is perpendicular to the field is zero. This situation can be termed as random phase dispersion. Such a feature is often represented, pictorially, as the individual magnetic moments spanning a cone at any given tilt angle as any of that phase is equally probable. The lack of transverse magnetization can thus be termed as a condition with no **phase coherence** between the spins.*

# Bulk Magnetization

*It takes a finite time to induce the magnetization by the external field and* ***the time constant $T_1$ is known as longitudinal relaxation time****.*




*External Field induces net magnetization*

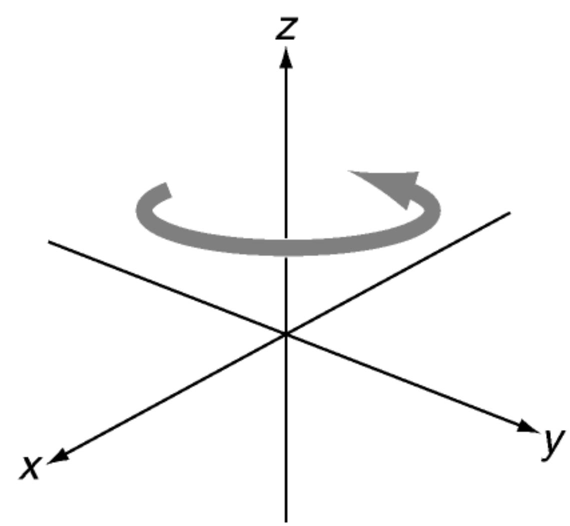



$$M_0 = \mu_0 \frac{N\gamma^2\hbar^2 I(I+1)B_0}{3k_B T}$$

*At equilibrium the net magnetization is along the direction of the B field and is taken as z-axis. There is, however, no net transverse magnetization (i.e. in the x-y plane).*

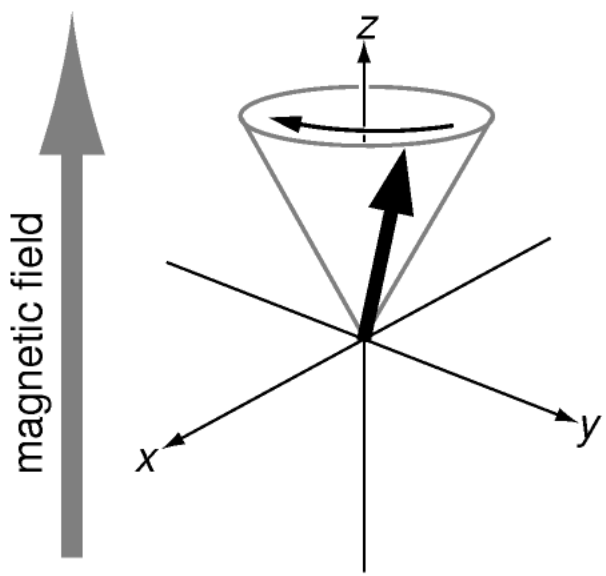
# Vector Model and Axis System

*We will represent the nuclear magnetization as a vector in a 3 dimensional space and describe its motion in this space. The axis system is a right handed system in that a positive rotation is given by the curl of the right hand when the right thumb is pointing up.*



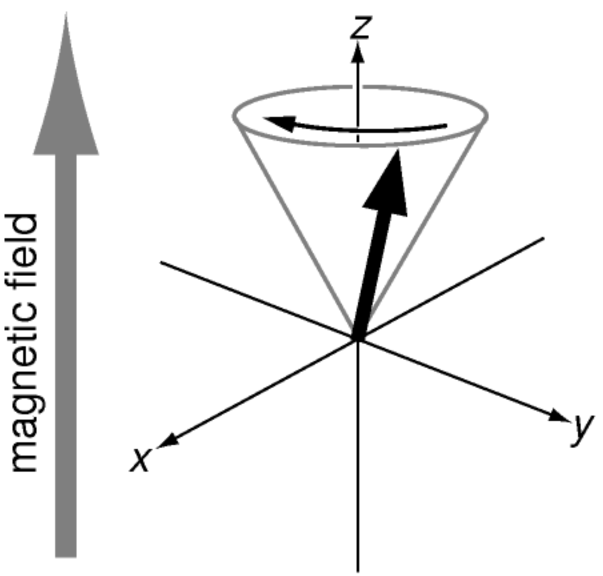
# Larmor Precession

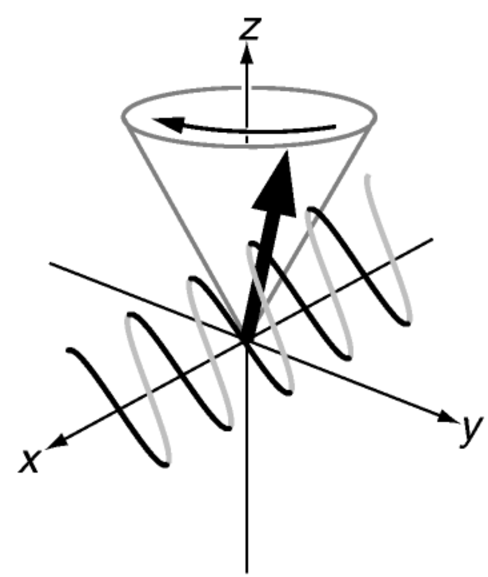
*The equilibrium magnetization vector is aligned along the z-axis and is fixed in size and direction. If by some means the magnetization vector is tipped away from the z-axis such that it makes angle $\beta$ with the z-axis then the magnetization vector starts rotating about the direction of the magnetic field sweeping a cone around. This kind of motion is called Precession. The precession frequency is Larmor frequency.*



# NMR Signal Detection

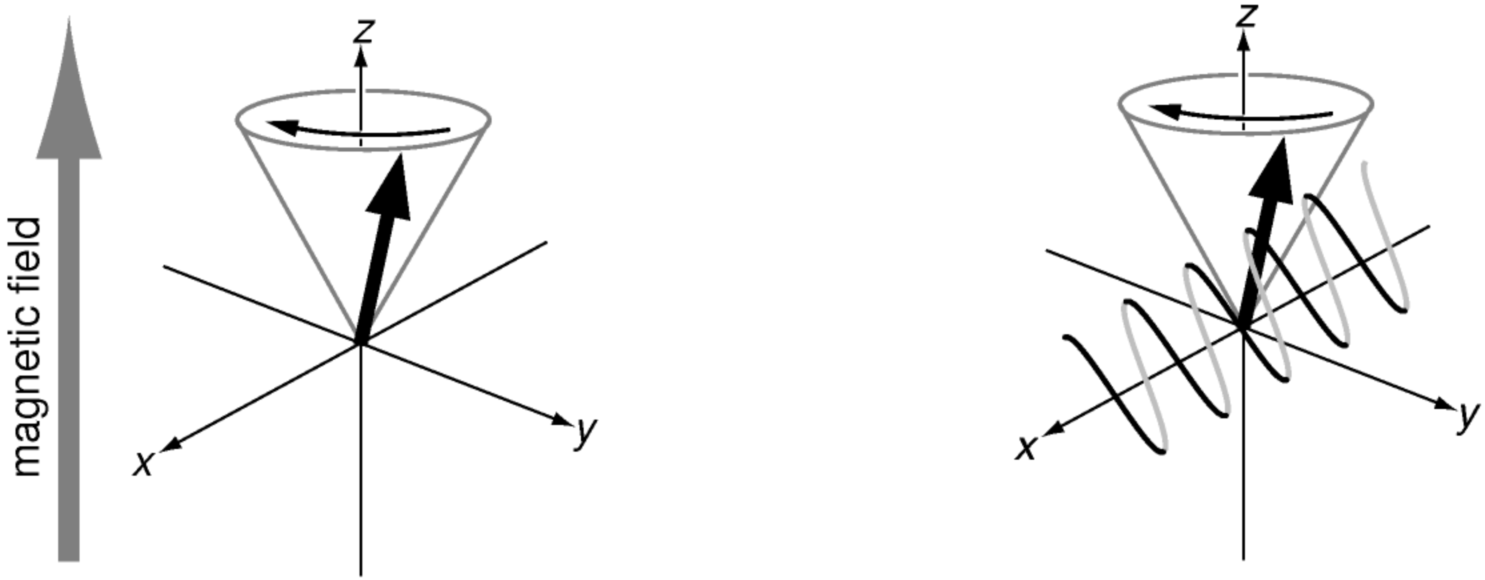
*If we mount a small coil of wire around the sample with its axis aligned in the xy-plane then as the precessing magnetization vector cuts through the coil a current is induced. This signal is called **free induction** and as it would decay with time it is known as **free induction decay** (**FID**)*



# NMR Signal Detection

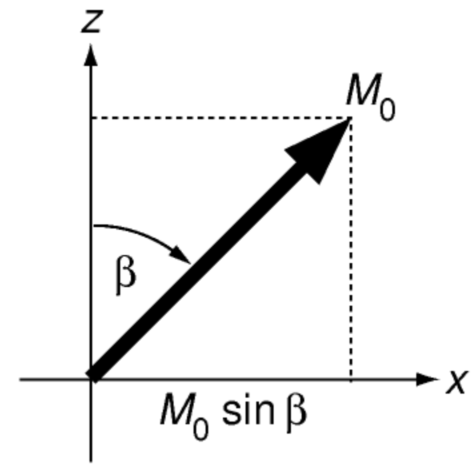
*The signal in the xy-plane (FID) implies that now there is a net magnetization in the transverse plane. We know that at equilibrium (i.e. when magnetization was aligned along the applied field) there was no transverse magnetization or phase coherence. Once the magnetization is tilted by some means the transverse magnetization or, in other words, a phase **coherence** between the individual magnetic moments is generated.*



# NMR Signal Detection

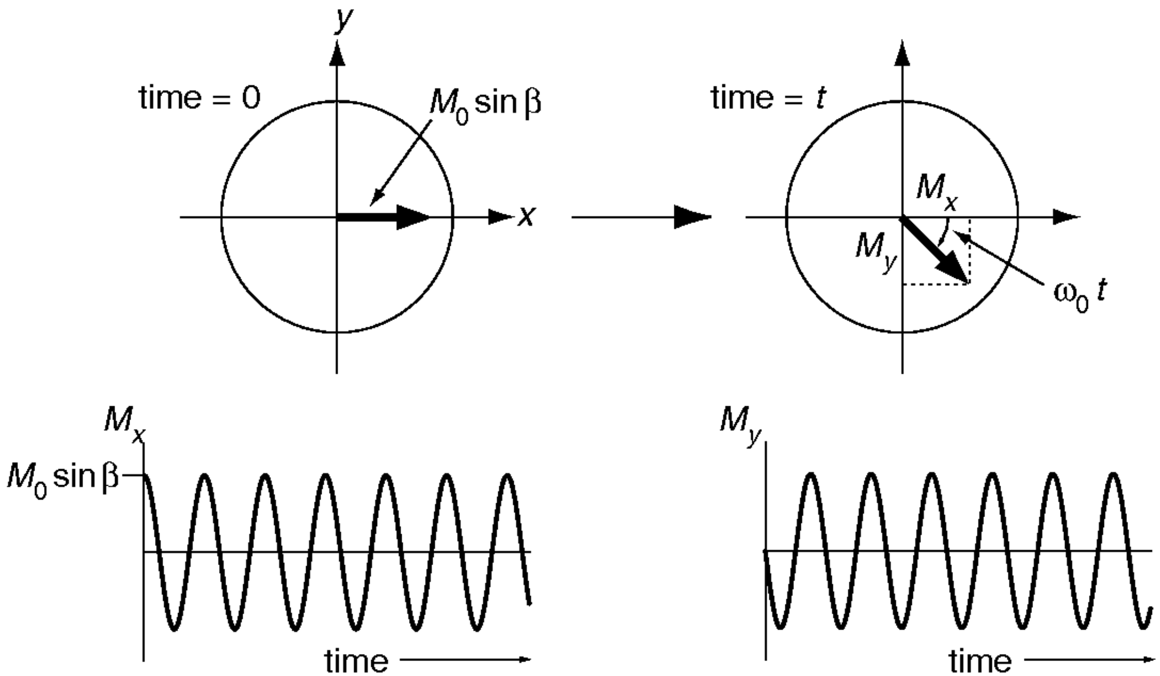
*If we just focus on projection of the magnetization on the xy- plane then the precession of the vector at the Larmor frequency can be written as:*

$$M_x = M_0 \sin\beta \cos\omega_0 t$$
$$M_y = M_0 \sin\beta \sin\omega_0 t$$



# NMR Signal Detection

*At time t=0 the transverse magnetization is along x- axis and as time progresses it rotates at the Larmor frequency about the z-axis along which $B_0$ field is applied.*

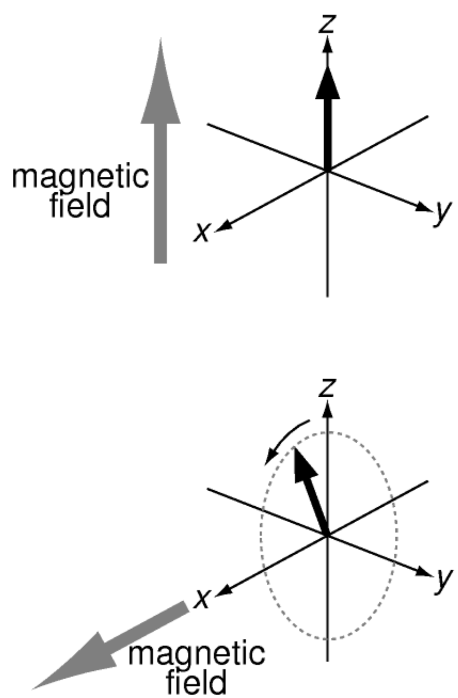



$$M_x = M_0 \sin\beta \cos\omega_0 t$$

$$M_y = M_0 \sin\beta \sin\omega_0 t$$

# How to Tilt $M_0$ ?

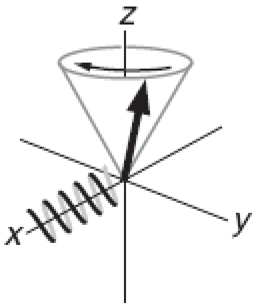
*Now Let us focus on how we tilt the magnetization away from z-axis. We could suddenly switch the magnetic field that is along z- axis to say x- axis and then the magnetization would precess about this axis. But it is impossible to switch field suddenly, instead, we will apply a radiofrequency (RF) field with frequency of oscillation at (or near) the Larmor frequency (resonance condition).*

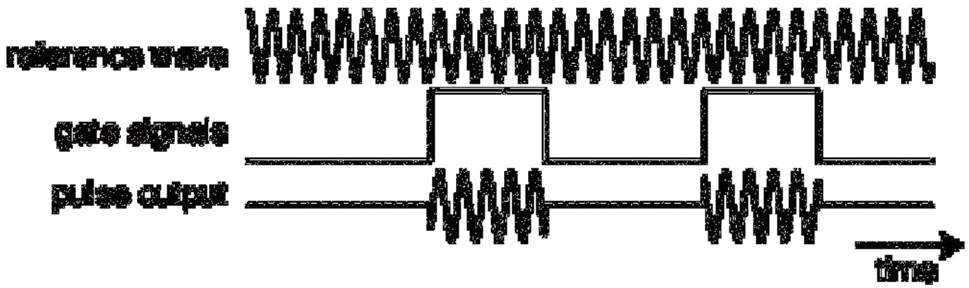


# Pulses

*We will apply a radiofrequency (RF) field of amplitude $2B_1$ with frequency of oscillation at (or near) the Larmor frequency (resonance condition) using the same coil that helped detect the FID.*

$$B_1(t) = 2B_1 \cos \omega t$$
$$\omega \cong \omega_0$$




*Usually the RF field will be applied only for a few microseconds and is thus aptly referred that a RF pulse is applied.*

# Nuclear Magnetic Moments in Magnetic Field and RF Field

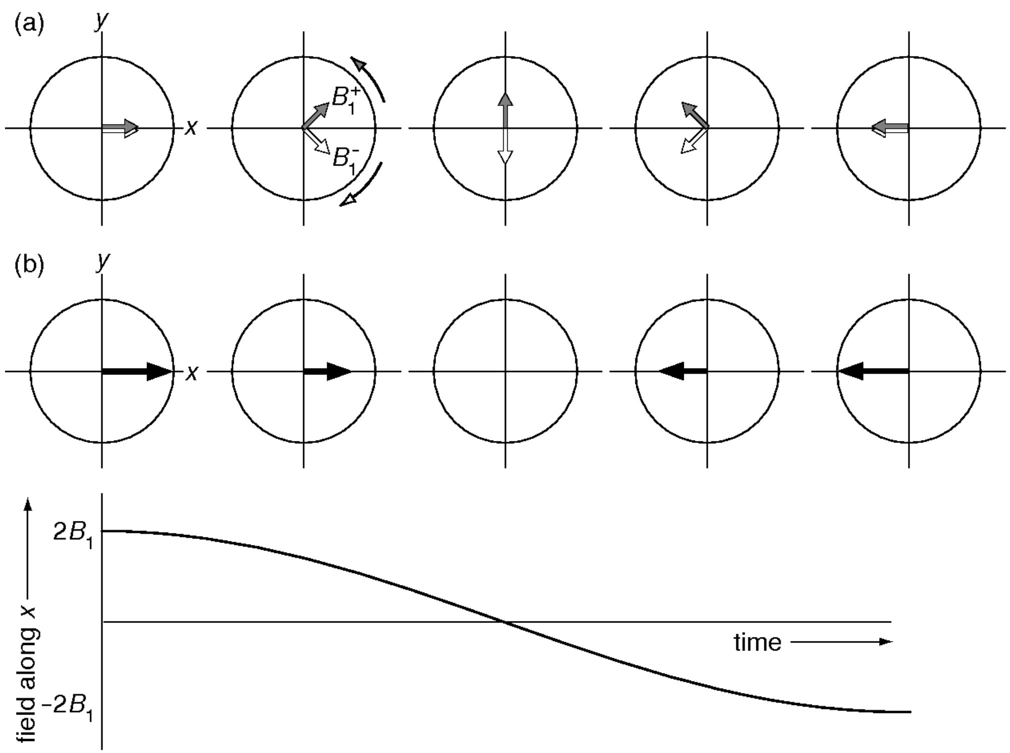
*The nuclear magnetic moments are now subjected to not only a static field along z-axis but also to an oscillating field in the transverse axis.*

$$\frac{d\boldsymbol{\mu}}{dt} = \boldsymbol{\mu} \times \gamma(\boldsymbol{B_0} + \boldsymbol{B_1}(t))$$

*It is very complicated to follow the motion of the magnetic moment vector in such a situation and it is useful to transform our reference frame called* ***rotating frame*** *so that the applied fields will appear static and we can follow the motion of* $\boldsymbol{\mu}$ *vector easily. It will also bring out the usefulness of resonance condition (i.e. frequency at or near Larmor frequency) and the requirements on the amplitude of the RF field.*

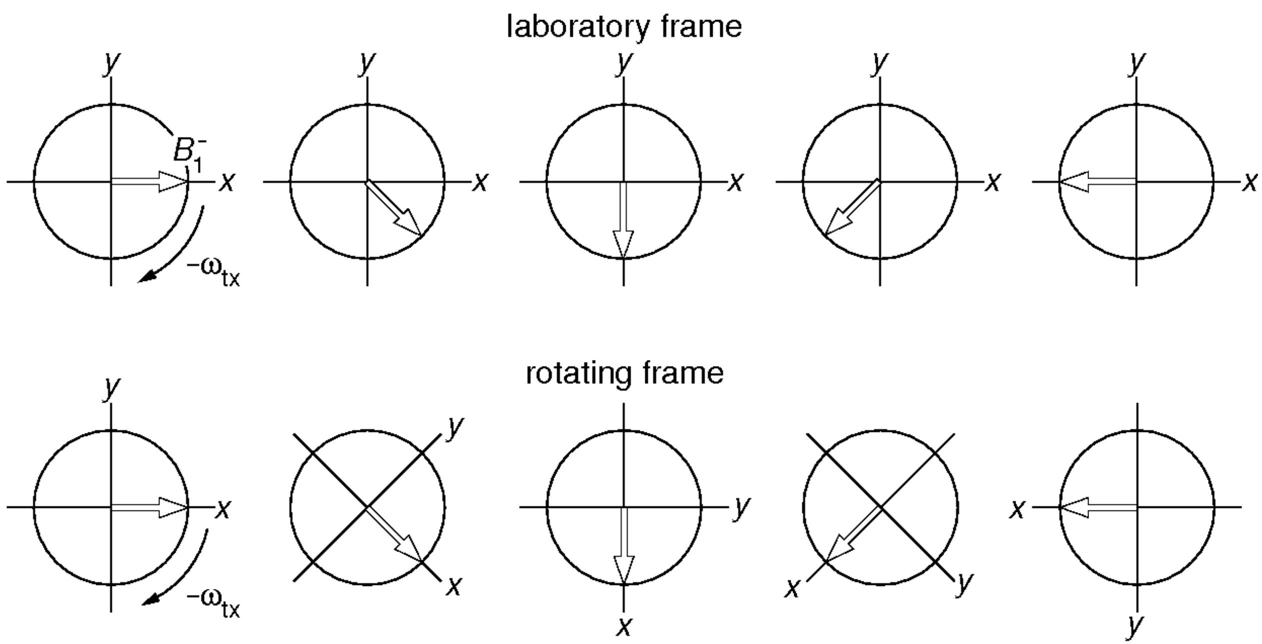
# Rotating Frame

*In Lecture 1 we noted that a linear oscillation of vector can be expressed as sum of two rotations in which the vector in one rotate clock wise and in the other counter-clock wise. The field $2B_1\cos\omega t$ can thus be represented as two rotating fields rotating in opposite direction (a) and the result appear like a filed oscillating on x- axis (b).*

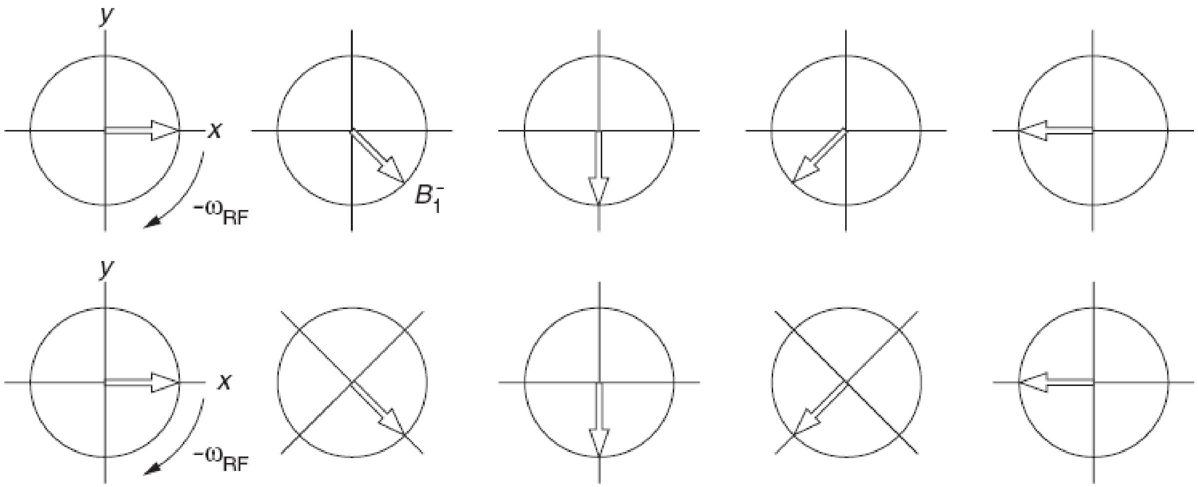


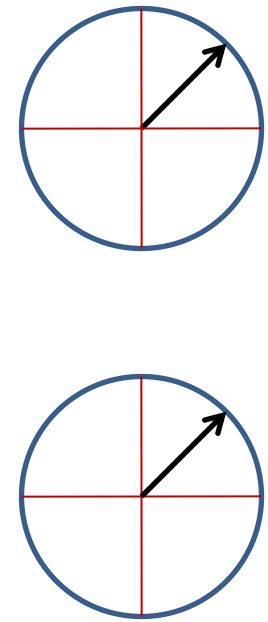
# Rotating Frame

*Let us focus on one of the rotating component* $B_1^-$ *and say we have a coordinate system that rotates about z-axis at the same frequency then this component appears static.*



# Rotating Frame

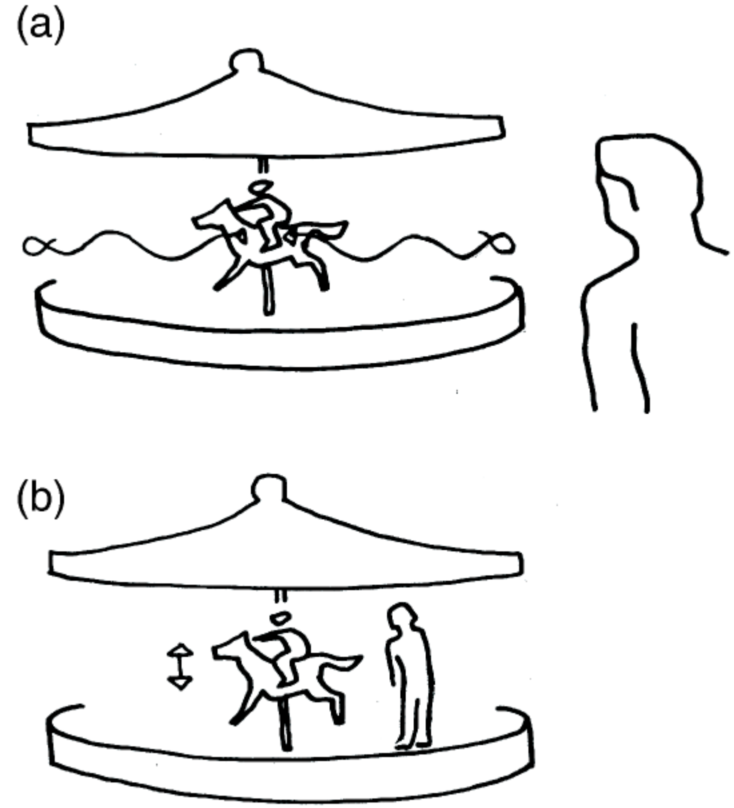


*In the top figure a vector rotates in x-y plane, in bottom figure the x-y axes system is rotating and the vector is always along x-axis*

# Rotating Frame

*A good analogy would be a child on a merry-go-round in which the horse that the child is riding going up and down. For an observer standing outside (a) there are two motions to see – the spinning of the merry-go-round and the up and down motion. But if the observer hops on to the merry-go-round (b) then* ***the spinning motion is subtracted*** *and only the up and down motion is observed – simplifying the details of the motion.*



# Rotating Frame

*The purpose of the rotating frame is to remove the time dependence of the applied field arising from the RF and in rotating frame rotating at the RF frequency, the RF field appear static. In general if the rotating frame frequency is slightly different from the resonance condition then there is a slow apparent precession frequency (called **offset frequency**) given as*

$$\Omega = \omega_0 - \omega_{rot.\,frame}$$

*Since we know $\omega$=-$\gamma$B, we can write the apparent precession frequency in terms of a **residual magnetic field** as*

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

*In the rotating frame the static $B_1$ field is along x-axis and the residual magnetic field along z- axis.*

# Effective Field in Rotating Frame

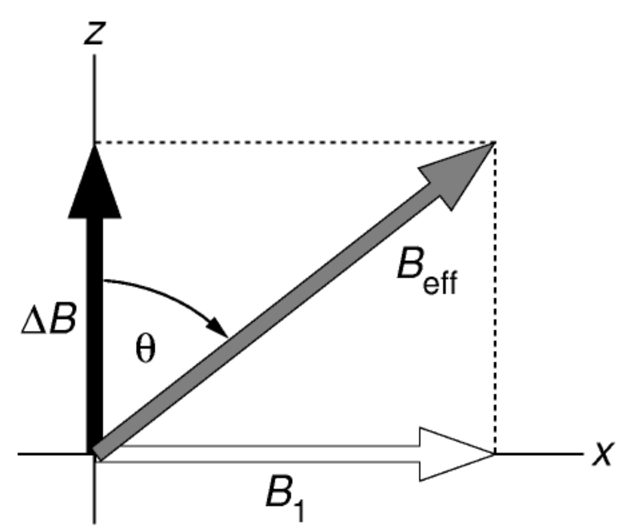
*In the rotating frame the reduced field along z-axis and the B1 field along x-axis add vectorially.*

$$B_{eff} = \sqrt{B_1^2 + (\Delta B)^2}$$

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

*Since the sign of $\gamma$ and frequencies are absorbed in the residual field definition $\omega_{eff}$ is always positive. We can also express the effective field tilt angle as*

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




*When the RF frequency and rotating frame frequency are at resonance the residual field is zero and $\theta = \pi/2$ and the effective field is along the x-axis of length $B_1$.*

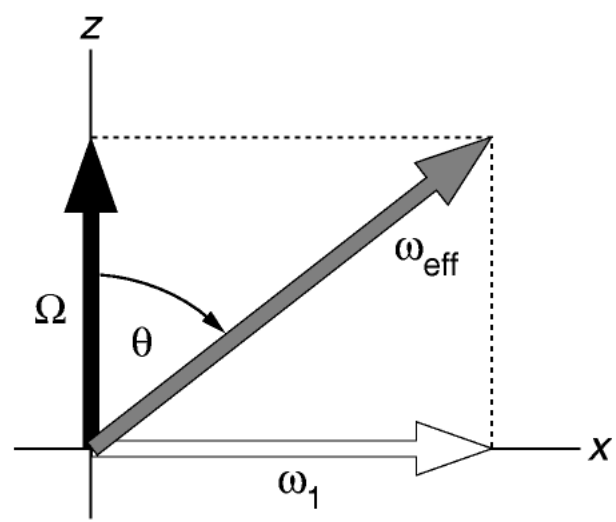
# Effective Field in Rotating Frame

*The same can be expressed in frequency representation also.*

$$\omega_{eff} = \sqrt{\omega_1^2 + \Omega^2}$$

$$\Omega = -\gamma \Delta B$$

$$\omega_1 = |\gamma| B_1$$



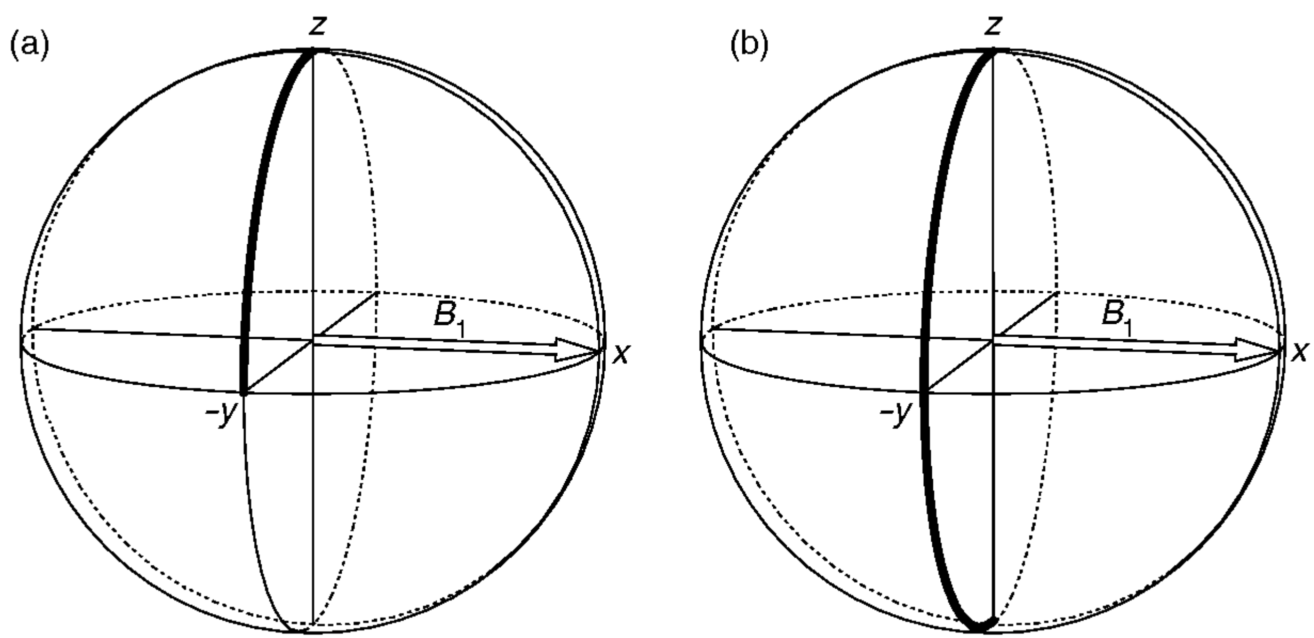

*Since the sign of $\gamma$ and frequencies are absorbed in the residual field definition $\omega_{eff}$ is always positive. We can also express the effective field tilt angle as*

$$\sin\theta = \frac{\omega_1}{\omega_{eff}} \qquad \cos\theta = \frac{\Omega}{\omega_{eff}} \qquad \tan\theta = \frac{\omega_1}{\Omega}$$

*When the RF frequency and rotating frame frequency are at resonance the offset frequency is zero and $\theta = \pi/2$ and the effective field is along the x-axis of length $\omega_1$.*

# On – Resonance Pulses

*When the RF frequency is exactly at the Larmor frequency it is straightforward to understand the motion of the magnetization in the rotating frame. Let us say the RF field is applied along x-axis for a duration* $t_p$ *such that the magnetization rotates by* $90^0$ *(*$\pi/2$ *radians) as in figure (a) and in figure (b)* $t_p$ *is long enough for a* $180^0$ *(*$\pi$ *radians) rotation.*



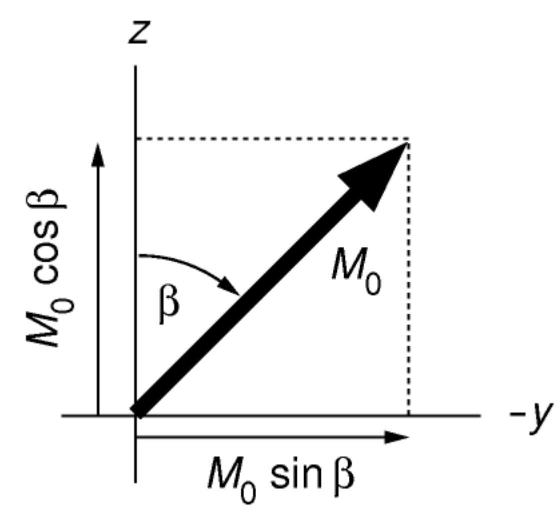
# On – Resonance Pulses

*In general for any duration $t_p$ the magnetization will rotate by an angle $\beta$ given by*

$$\beta = \omega_1 t_p$$

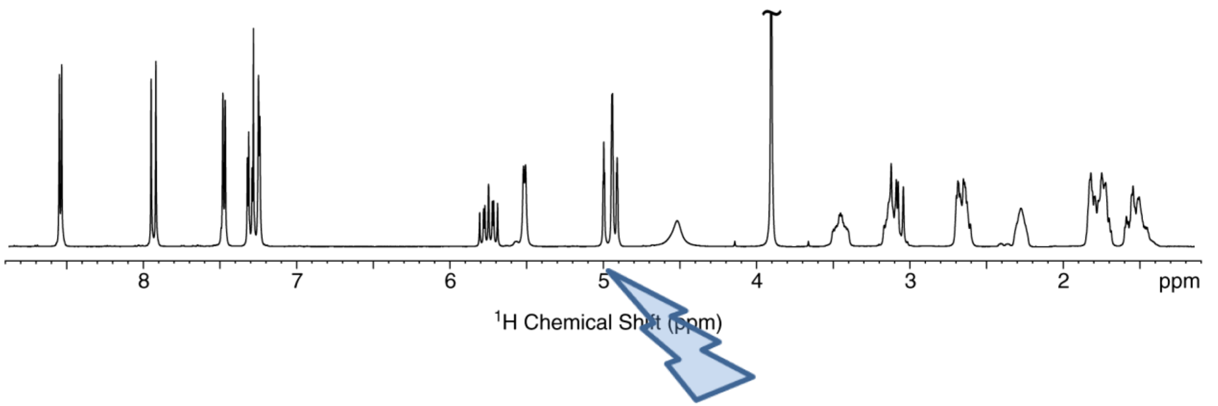
*If the pulse is applied along x- axis then the z and y component of the magnetization at the end of the pulse is given by*

$$M_z = M_0 \cos\beta \qquad M_y = -M_0 \sin\beta$$



# Hard Pulses

*A typical proton spectrum spans about 10ppm. It is critical to be able to emulate an on resonance rotation to all the spins.*




*To achieve this we might choose the RF frequency at the center of the spectrum (~ 5ppm) and is usually called transmitter frequency. The largest possible offset then at 500 MHz system this translates to 2500 Hz or 1.57x10$^4$ rad s$^{-1}$.*

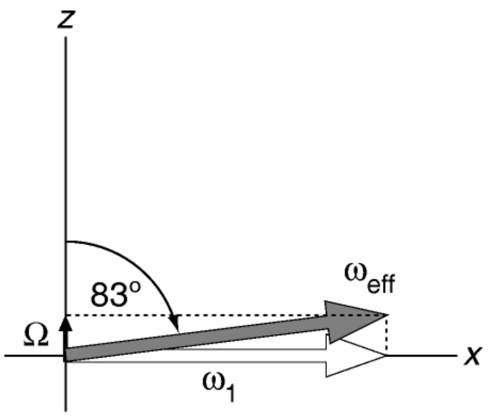
# Hard Pulses

*If we set the $\pi/2$ pulse width as 12 $\mu$s we can evaluate the required RF field strength.*

$$\beta = \omega_1 t_p \qquad \omega_1 = \frac{\beta}{t_p} \qquad \omega_1 = \frac{\pi/2}{12\times10^{-6}} = 1.31\times10^{5}\, rad \bullet s^{-1}$$

*Then the tangent of the tilt angle of the effective field is*

$$\tan\theta = \frac{\omega_1}{\Omega} = \frac{1.31\times10^{5}}{1.57\times10^{4}} = 8.34$$



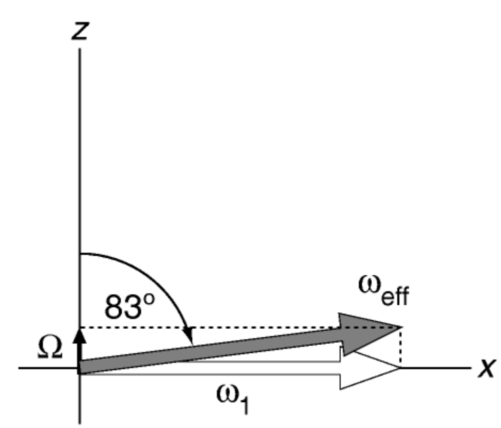

*Angle $\theta$ is $83^0$ as in figure. Do not confuse the angle $\theta$ with $\beta$; $\theta$ is the angle between z-axis and effective field and $\beta$ is the angle by which $M_0$ is rotated away from the z-axis.*

*Since $\omega_1$>> $|\Omega|$ the effective field is almost along x axis even for spins at 10 ppm resonance and such a pulse is known as a hard pulse.*

# Detection in Rotating Frame

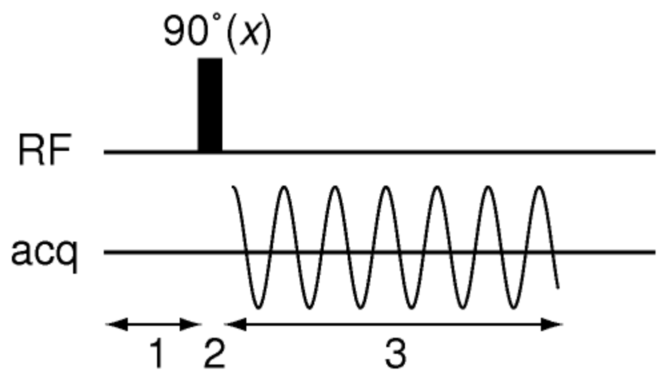
*Suppose after rotating the $M_0$ about x-axis so that it lines up with –y axis we switch of the RF field then in the rotating frame the only field that is present is the residual field or the offset $\Omega$ along the z-axis. Then the transverse magnetization will precess at a frequency $\Omega$ about the z-axis.*

$$M_x = M_0 \sin \Omega t \qquad M_y = -M_0 \cos \Omega t$$



# Pulse- Acquire Experiment

*The most familiar pulse acquire experiment is shown below*

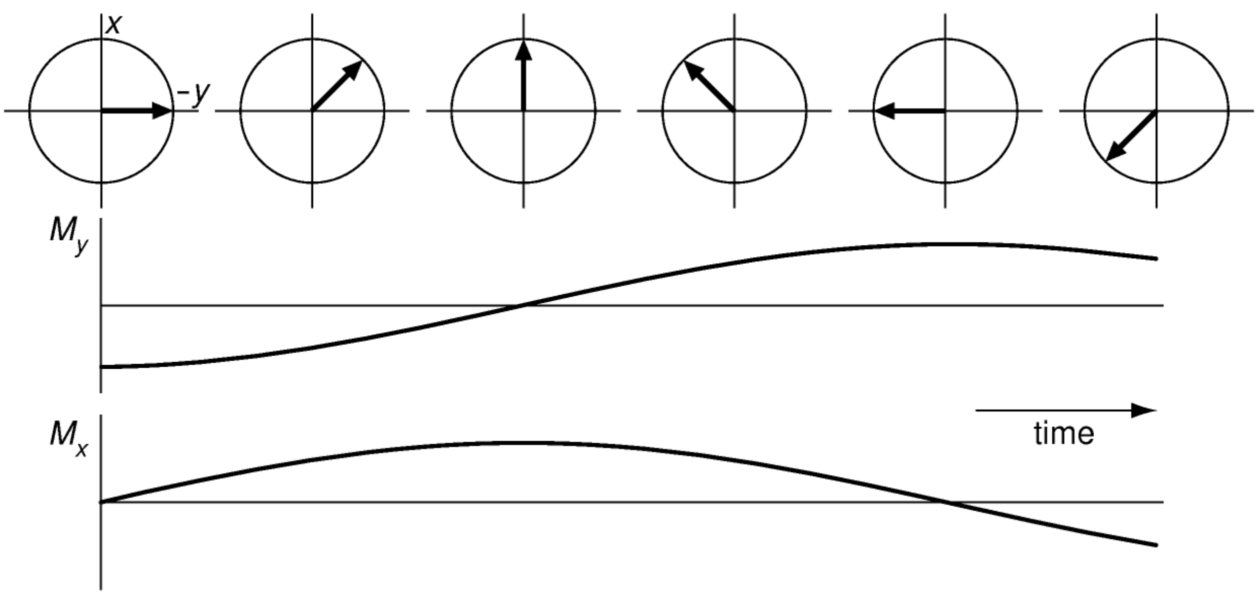


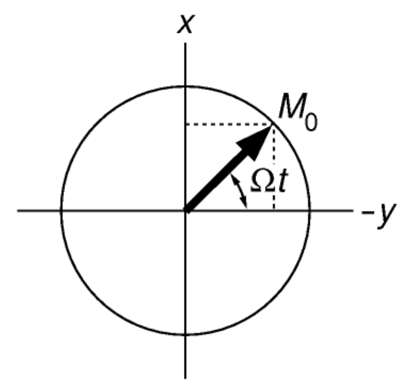

*During period 1 equilibrium $M_0$ builds up and period 2 the $90^o(x)$ hard pulse is applied. In priod 3 the signal is acquired in the rotating frame.*

# Pulse- Acquire Experiment

*The observed signal will be line at an offset* $\Omega$

$$M_x = M_0 \sin \Omega t \qquad M_y = -M_0 \cos \Omega t$$



# Pulse- Acquire Experiment

*If the spectrum has more than one line, then we can associate a separate $M_0$ vector with each one of them and then they will al bee rotated to –y axis and precess with their specific offset frequencies* $\Omega$.

$$M_y = -M_{0,1}\cos\Omega_1 t - M_{0,2}\cos\Omega_2 t - M_{0,3}\cos\Omega_3 t\ldots$$

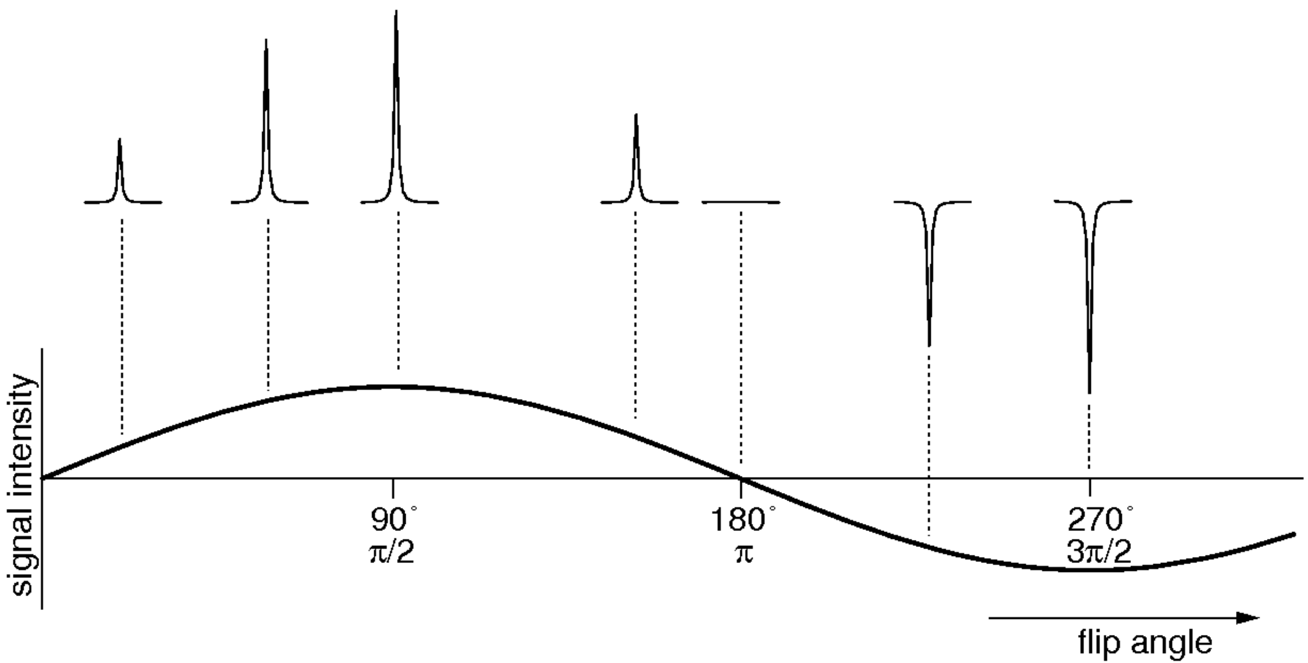
*This will result in a spectrum with lines at* $\Omega_1$, $\Omega_2$, $\Omega_3$… frequencies.

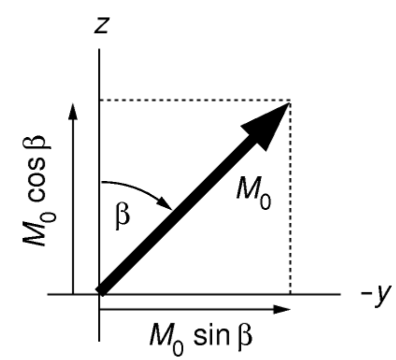
# Pulse Calibrations

*In general for any duration $t_p$ the magnetization will rotate by an angle $\beta = \omega_1 t_p$. If the pulse is on-resonance and applied along x- axis, then the z and y component of the magnetization at the end of the pulse is given by*

$$M_z = M_0 \cos\beta \qquad M_y = -M_0 \sin\beta$$

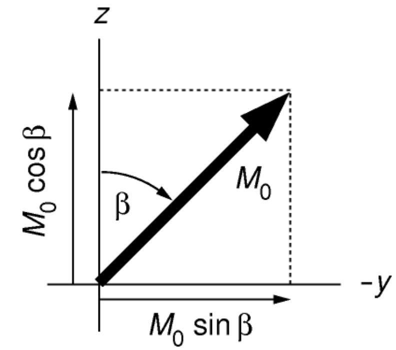
*If we monitor the NMR signal by only varying the pulse flip angle by varying the duration then we can calibrate the hard pulse for any rotation angle.*



# 180° Pulse

*For simplicity let us assume our pulse is on resonance and applied along x-axis. Suppose just before the pulse the Magnetization is along z- axis then at the end of the pulse it will align along the negative z-axis*




$$M_z(t_p) = M_z \cos\pi = -M_z$$

*It is then said that the magnetization has been inverted.*

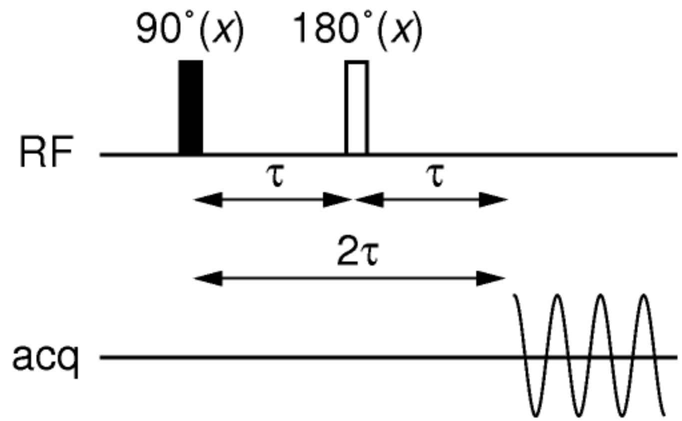
*If at the beginning of the pulse the magnetization was along the end of the pulse it will align along +y axis*

$$M_y(t_p) = -M_y \cos\pi = M_y$$

*Note: rotation is always about the RF pulse axis. The magnetization that is perpendicular to the RF pulse axis rotates in perpendicular plane. For example when RF pulse is along x-axis the magnetization rotates in the zy plane.*

# Spin Echo Experiment

*The spin echo sequence is a very important segment in many NMR experiments and as a stand alone experiment it involves application of two pulses:*

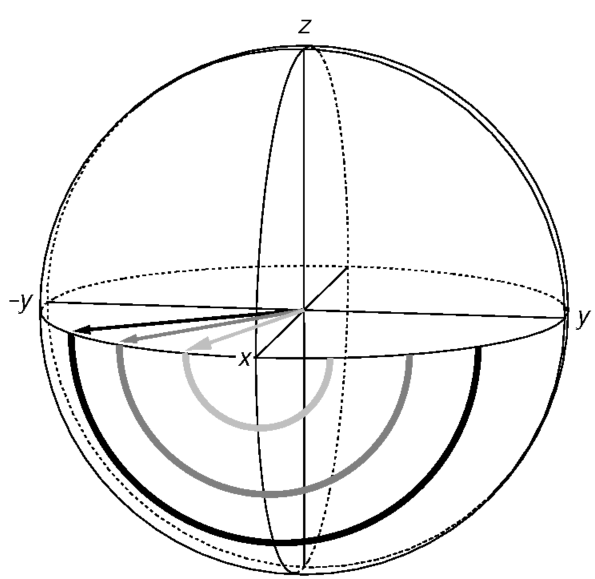


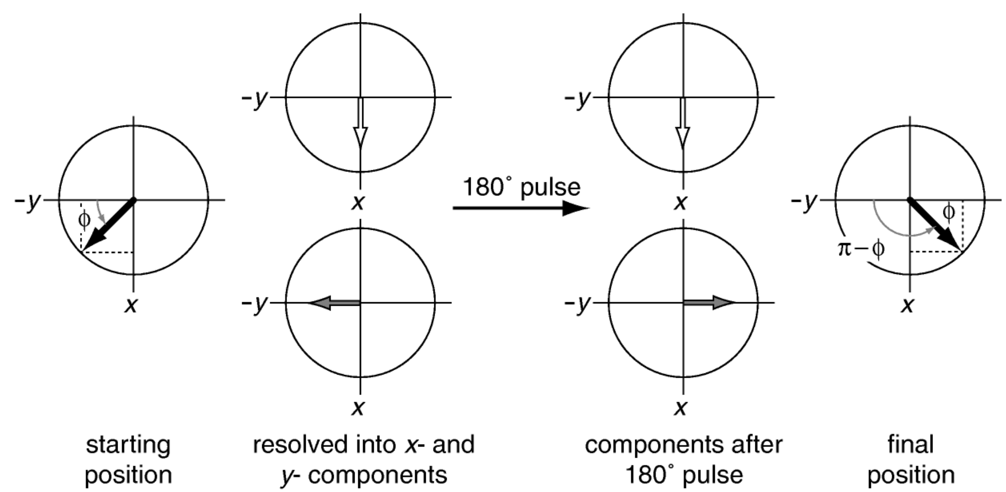

*At the end of the second $\tau$ delay the magnetization ends up along the same axis regardless of the offset frequency $\Omega$. It is said that the offsets have been refocused. The 180$^{o}$(x) pulse in this case is named a **refocusing pulse**.*

# Spin Echo Experiment

*The first 90$^o$(x) pulse rotate the magnetizations from z-axis to –y axis and the magnetizations precess in the xy plane according to their offset frequencies for a time $\tau$ and then the 180$^o$(x) pulse flips them to the opposite direction and further precession happens during the second $\tau$ delay and at the end of the second $\tau$ delay the magnetizations align along +y axis.*

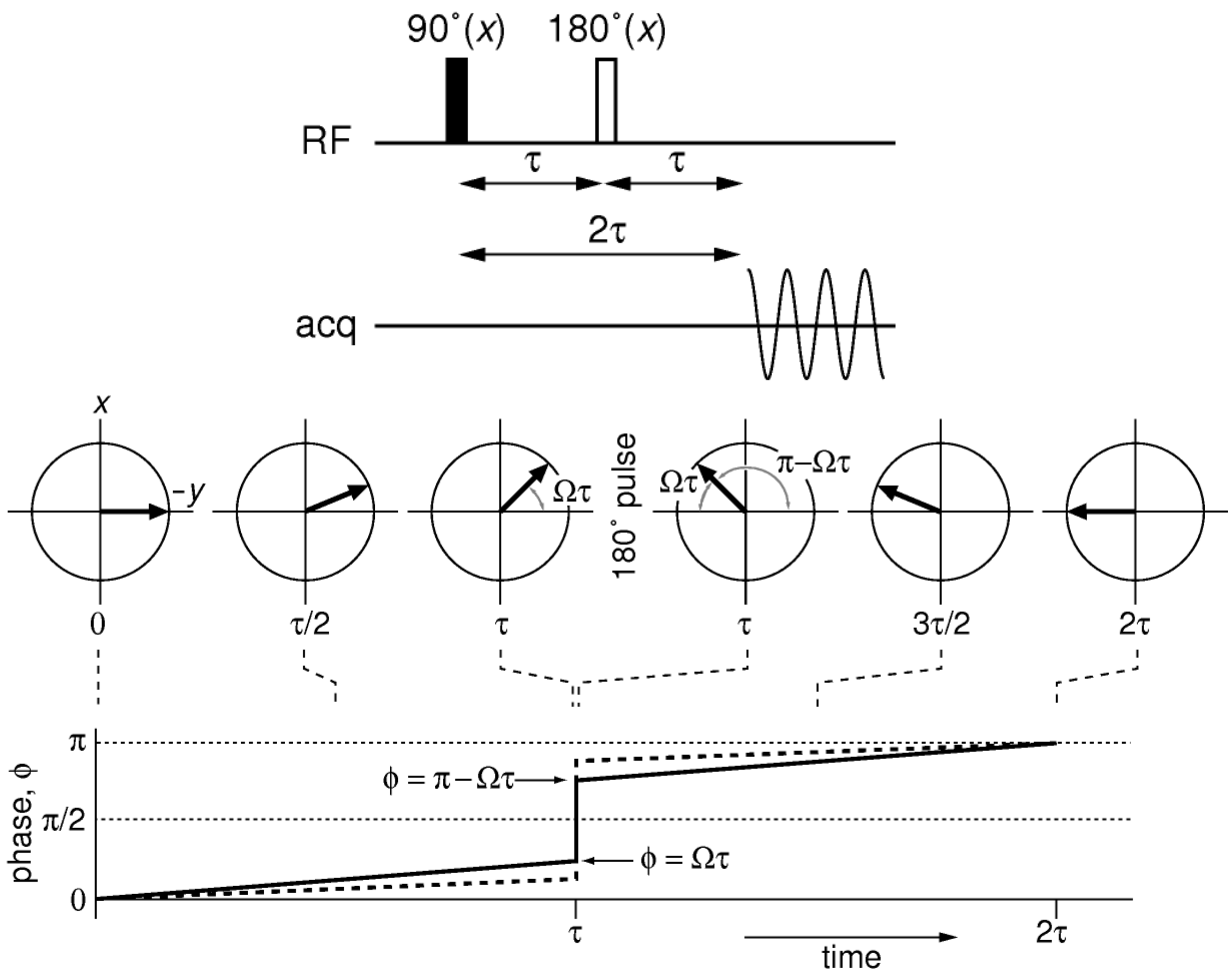
*Figures shows the refocusing effect of the 180$^o$ pulse*



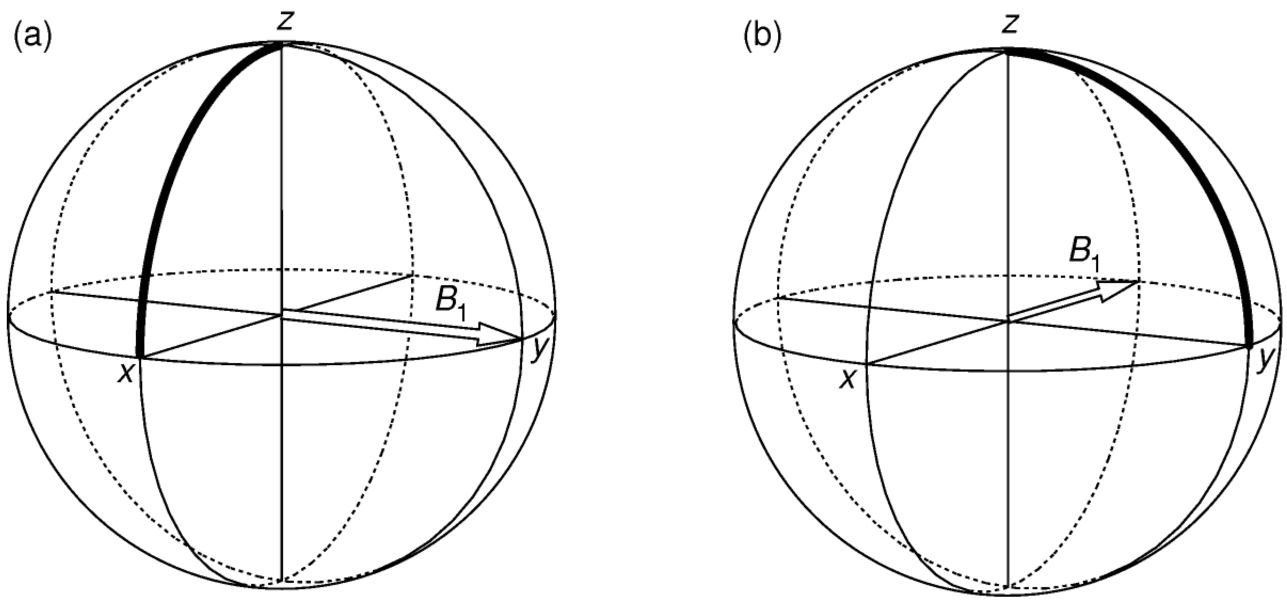
# Spin Echo Experiment

*It is now easy to understand the Spin Echo experiment in a pictorial way:*



# Pulses of Different Phases

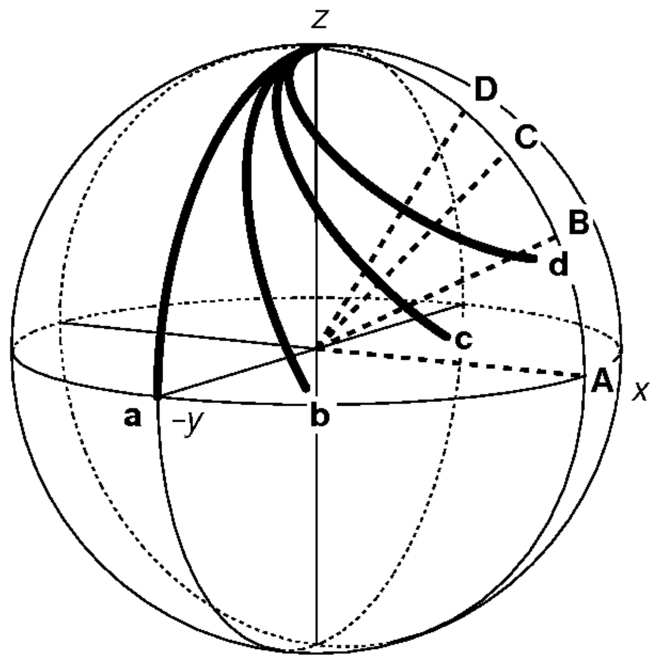
*Pulses don't have to be applied only along x axis. We can apply them on any axis in the plane perpendicular to z-axis. In (a) the pulse is along +y axis and $M_z$ goes to $M_x$ and in (b) pulse is along –x axis and $M_z$ goes to $M_y$.*




*Note: rotation is always about the RF pulse axis. The magnetization that is perpendicular to the RF pulse axis rotates in perpendicular plane. For example when RF pulse is along y-axis the magnetization rotates in the zx plane.*

# Off-Resonace Effects

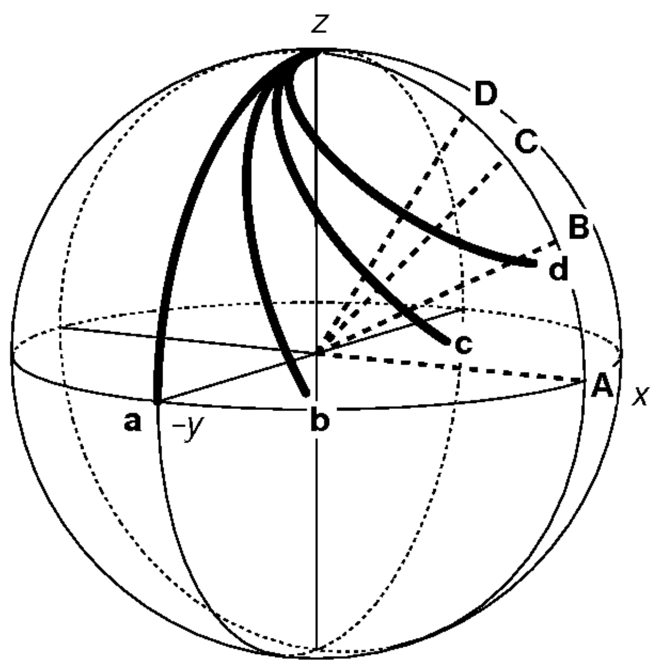
*Let's not impose the on resonance or the condition $\omega_1 >> |\Omega|$ and focus on situations when the offsets are comparable to the RF amplitudes.*




*As the offset increases the effective field moves from x-axis towards z-axis (A – effective field for on resonance and B,C, and D are the tilt of effective field as offset increases. The magnetization rotation is about the effective field (a, b, c, d are rotations about the axis A, B, C, D respectively). In such situations the lines in the NMR spectrum will show different phases.*

# Selective pulses

*It can be seen that if the effective rotation axis go closer to z-axis then the magnetization would not rotate away from z-axis. This can happen if either the offset is very large compared RF field amplitude or if we use very low RF amplitude. The later situation is called a soft pulse and such a pulse will rotate only the spin magnetization to which it is on resonance (for example just the case given by A and a).*



# Moving On

*In the two lectures we have progressed a lot in understanding the basic concepts in NMR. So far we only represented the final spectrum and talked about it without showing how we got it.* ***Fourier transform*** *techniques are applied to obtain the NMR spectrum from a detected signal. We will focus on that in the next lecture.*