Magnetic properties of nuclear spins!

Classical Mechanical Roots:

Nuclei of atoms are characterized by a ***nuclear spin quantum number***, **I**, which can either be equal to zero, or to multiples of ½. For atoms with **I = 0** there is no nuclear spin and therefore, they cannot have a nuclear magnetic resonance. These atoms are called NMR silent. All other values of **I** (i.e., **I ≠ 0**) yield nuclear spin.

I = 0 (^{12}C, ^{16}O, etc.)
Even mass # & Even atomic #
No Nuclear spin

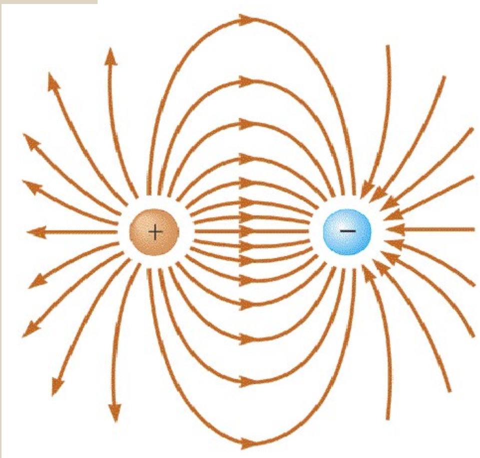
I = ½ (^{1}H, ^{13}C, ^{15}N etc.)
Spherical charge distribution in nucleus

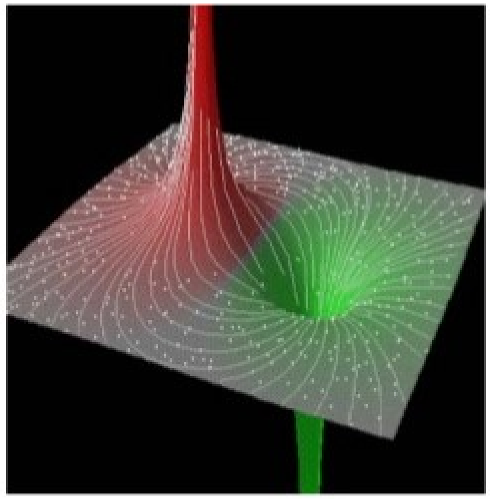
Magnetic dipole moment

I > ½ (^{2}H, ^{11}B, ^{23}Na etc.)
Odd mass # & Odd atomic # (I = ½ integer, i.e., 3/2, 5/2, 7/2)
Even mass # & Odd atomic # (I = whole integer, i.e., 1, 3)
Ellipsoidal charge distribution in nucleus gives ***quadrupolar electric field.***

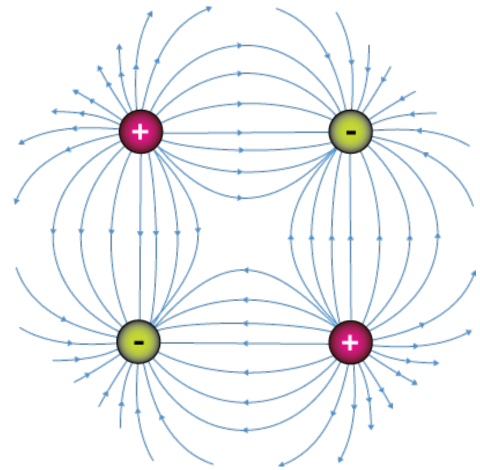
Magnetic quadrupole moment

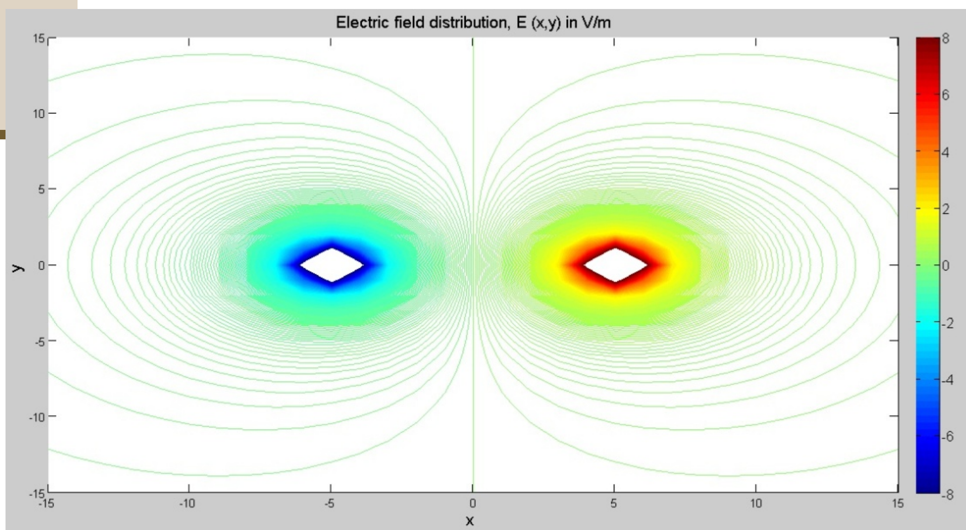
Dipole Moment *VS* Quadrupole Moment

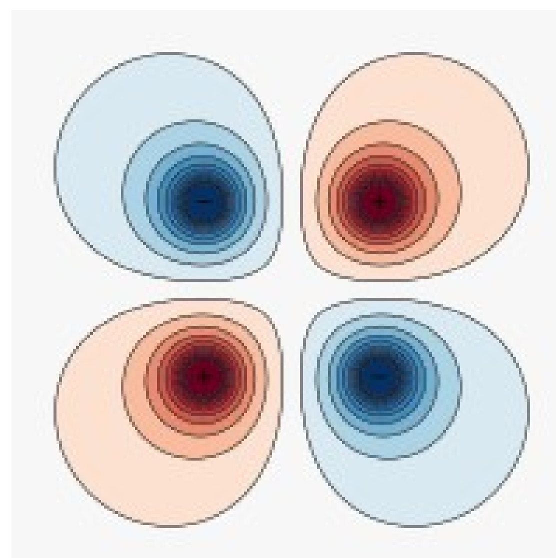




3D plot of the field intensity in the *x*-*y* plane





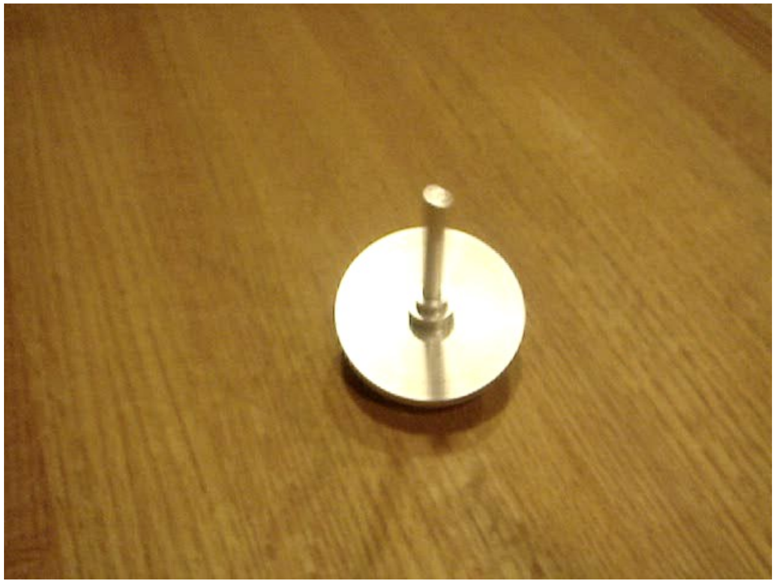


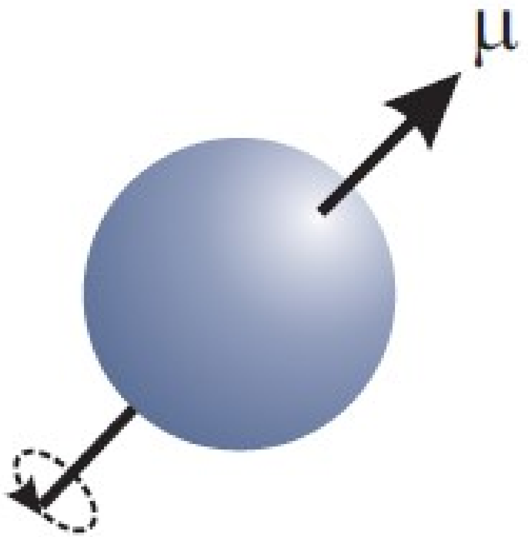
Angular momentum!

Nuclear spin results in *angular momentum* (p). Since the nucleus is charged, spin will produce a *magnetic moment* (μ):

$$\mu = \gamma p$$

Where γ is the proportionality constant called the *magnetogyric ratio*.





Larmor Frequency!

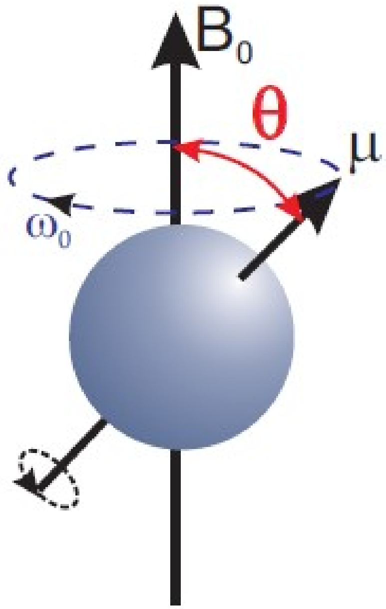
Placed in an external magnetic field B_0 the spin precesses at a specific frequency:

$$\omega_0 = -\gamma B_0 \text{ rad s}^{-1}$$

or (in Hz)

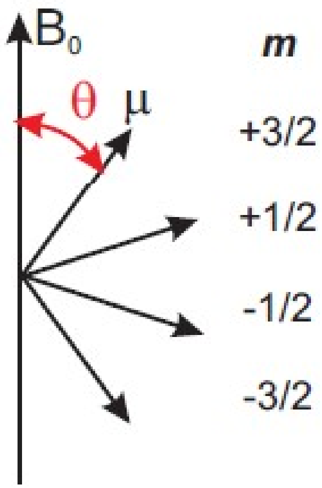
$$\upsilon = -\gamma B_0 / 2\pi \quad \{\text{Larmor Frequency}\}$$

The relative orientation of the magnetic moment (θ) is dependent on the value of I. This can be determined using quantum mechanics.



Energy levels and transitions (I = 3/2)!

General rule: The *number of orientations* of the precessing spin is equal to **2I+1**. Therefore a nucleus with I = 3/2 there are four possible orientations of the magnetic moment :



Angular momentum vector (m).

Energy

levels

The *allowed transitions* are across unit differences i.e., $\Delta m = 1$. For I = 3/2 there are three (degenerate) transitions:

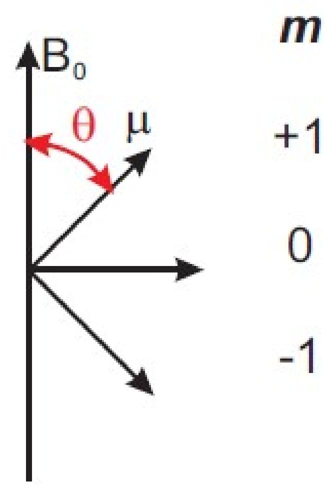
$-3/2 \leftrightarrow -1/2$,
$-1/2 \leftrightarrow +1/2$
$+1/2 \leftrightarrow +3/2$

Energy levels and transitions (I = 1 and ½)!

For I = 1 there are three orientations:

There are two allowed transitions across the three states:

$-1 \leftrightarrow 0$
$0 \leftrightarrow +1$

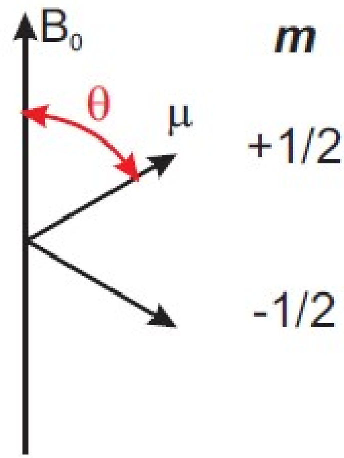


Energy levels

For I = ½ there are two orientations:

This is the simplest case because there is only one transition across the two states.

$-½ \leftrightarrow +½$



Block equations, spin-relaxation!

When Bloch published his first observation of NMR in 1946 he separately published a paper with a physical description of the phenomenon. His theory uses a series of equations of motion for the net magnetization vector M of a sample of spins placed in a magnetic field (B_0). The components of M are M_x, M_Y and M_z with initial equilibrium value of M_0.

The Bloch Equations:

$$dM_Z/dt = \gamma(M\ B)_Z - (M_Z - M_0)/T_1$$

$$dM_X/dt = \gamma(M\ B)_X - M_X/T_2$$

$$dM_Y/dt = \gamma(M\ B)_Y - M_Y/T_2$$

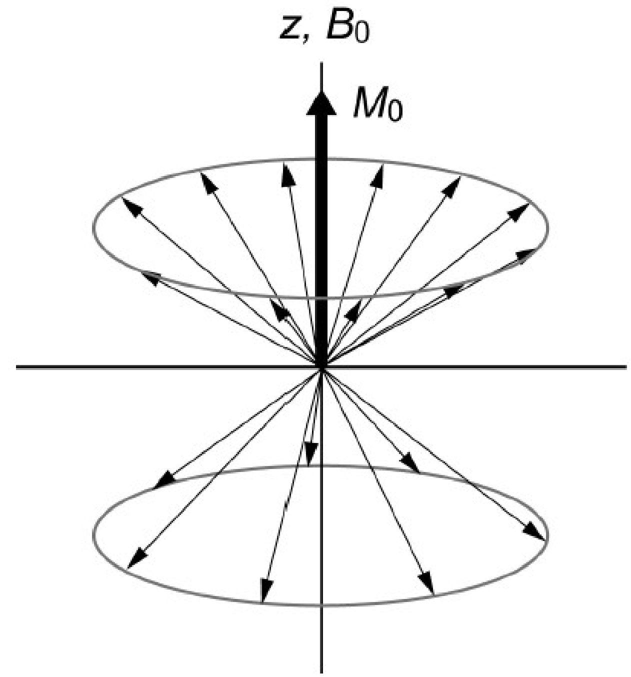
T_1 is the ***Spin-Lattice*** relaxation time constant. It is the process that dictates how fast magnetization builds up along the z-axis.

T_2 is the ***Spin-Spin*** relaxation time constant. It is the process that dictates how fast magnetization is lost in the x-y plane.

The Boltzmann distribution

- The sum of the *z*-components of the nuclear dipoles in an ensemble gives the macroscopic (bulk) magnetization, M_0

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

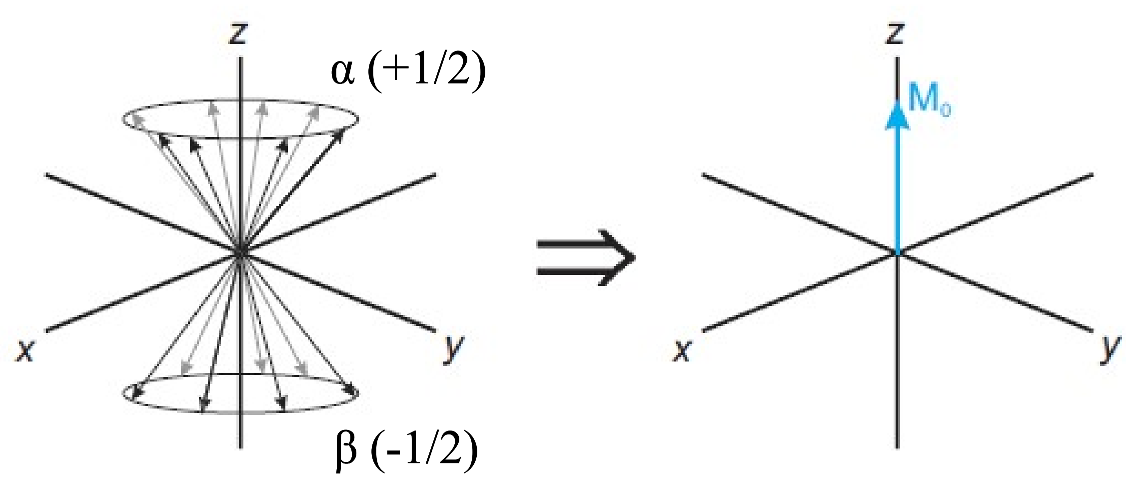


- Note: dependence on γ^2, linear dependence on B_0, dependence on isotopic abundance (N)

The bulk magnetization with B_0

A collection of like spins (*ensemble*) will align themselves either parallel or anti-parallel to the orientation of the applied field B_0 (commonly labeled the **z**-axis).

The ***bulk magnetization vector*** $\mathbf{M_0}$ represents the **z**-axis component of the excess lower energy spins.

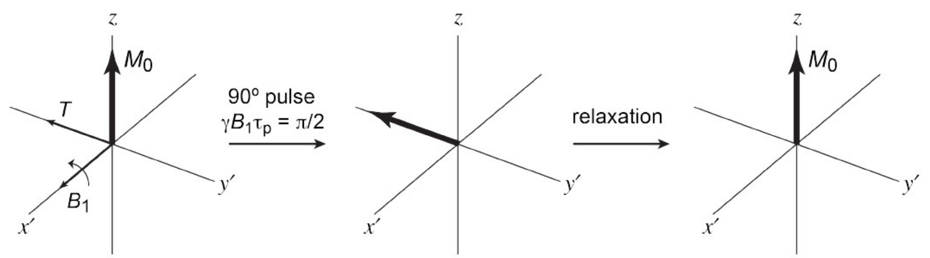


This rationale forms the basis for the ***Vector Model,*** which we will explore in detail later.

- RF Pulses are Required to Establish Initial Transverse Magnetization
- T_1 spin-relaxation moves M_0 back to +z axis

An RF pulse (B_1) *in the transverse plane exerts a torque on M_0* that moves it through some angle (90^o or π/2) toward the transverse (*xy)* plane

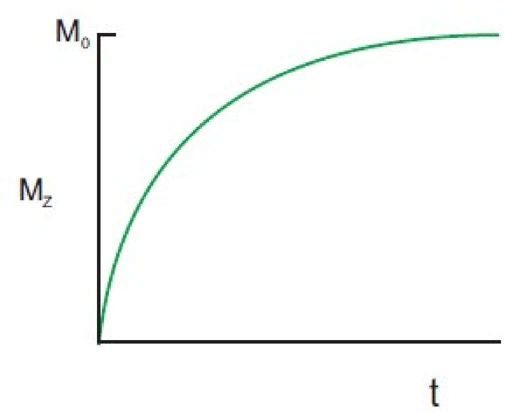
In these forms the Bloch equations show how magnetization reaches equilibration after a perturbation:



With time, normal relaxation processes return the system to thermal equilibrium, and M_0 returns to the +*z*-axis

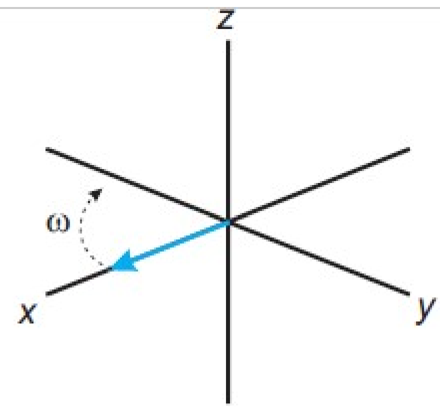
The Z-component:

$$M_z = M_0 (1 - e^{(-t/T_1)})$$

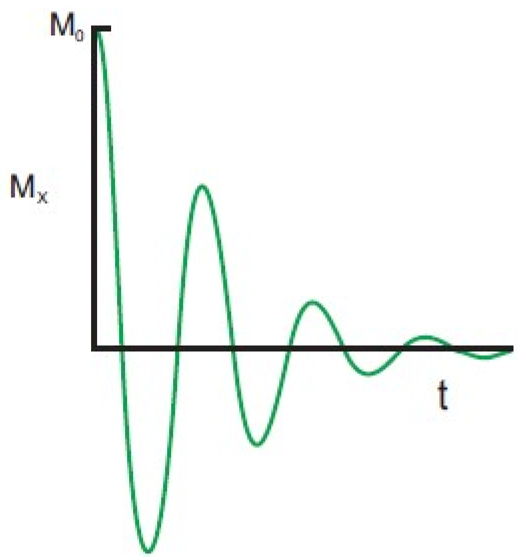


Free induction Decay (FID) on x-y plane

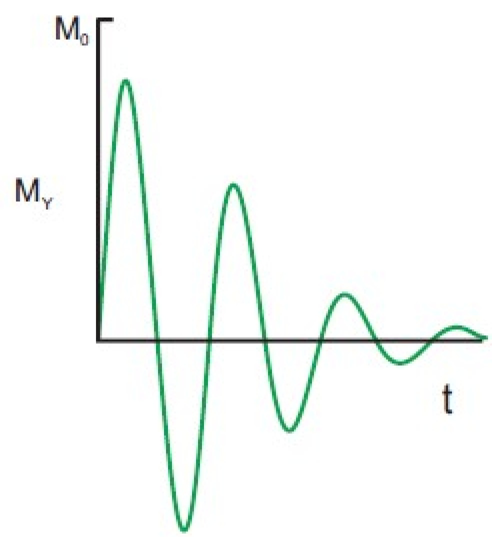
The X & Y components
(*Free Induction Decay*):



$M_X = M_0 \cos \omega t \, e^{(-t/T_2)}$



$M_Y = M_0 \sin \omega t \, e^{(-t/T_2)}$

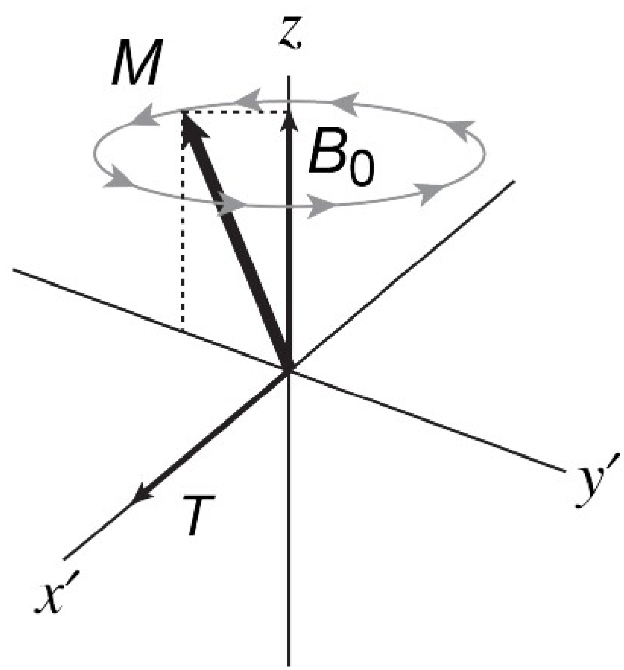


Precession

- The torque exerted by B_0 on the magnetic moments/dipoles promotes precession about the *z*-axis at a frequency given by

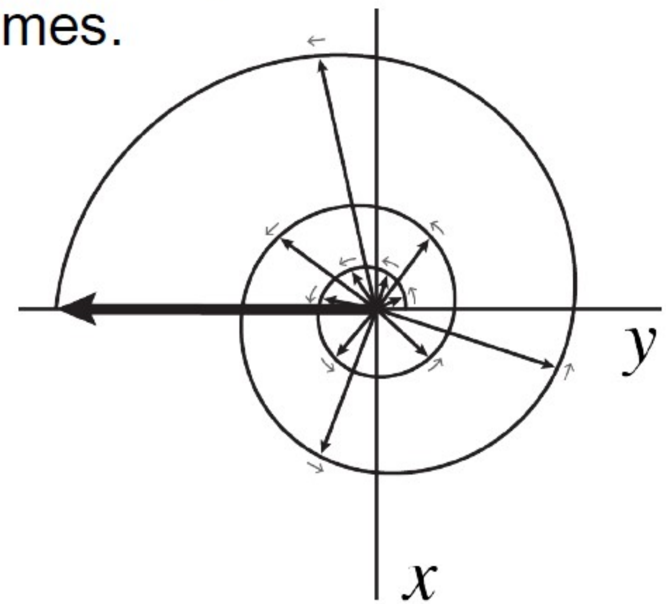
  $\upsilon_L = \gamma B_0 / (2\pi)$ (in Hz) $\omega_0 = \gamma B_0$ (in radians/sec)

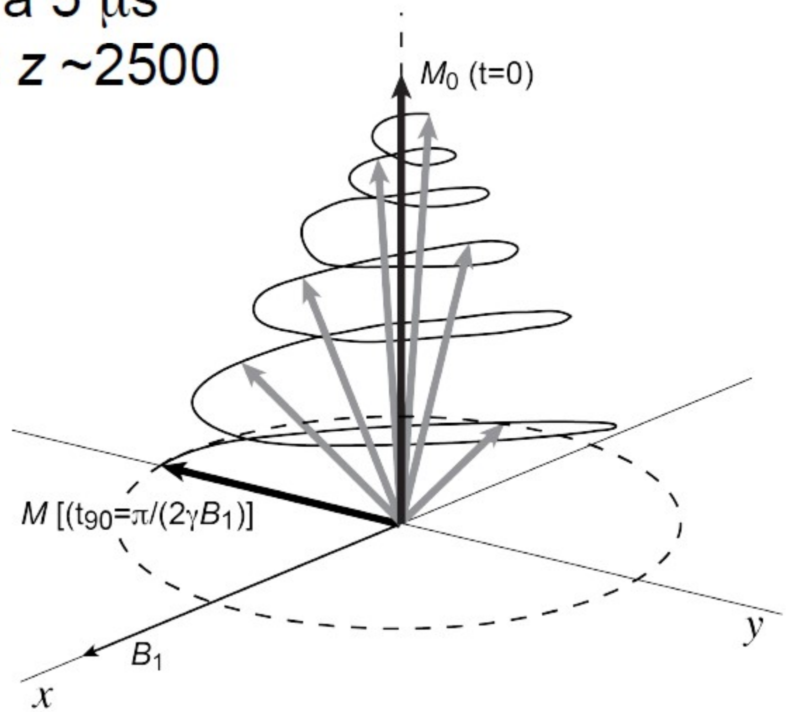
- The B_0 field also exerts a torque on the bulk magnetization vector (*M*). When displaced by an RF pulse from its equilibration position (along the *z*-axis), B_0 causes *M* to precess about *z* (at $\omega_0 = \gamma B_0$) until relaxation processes return it to its equilibrium position on *z*



Precession

- *During* an RF pulse, simultaneously B_1 moves M towards the transverse plane, and the torque exerted by B_0 on M causes M to precess about z at its Larmor frequency ($\omega = \gamma B_0$)
- For a ^{1}H nucleus with a Larmor frequency of 500 MHz, during a 5 μs 90° pulse, the M vector circles z ~2500 times.



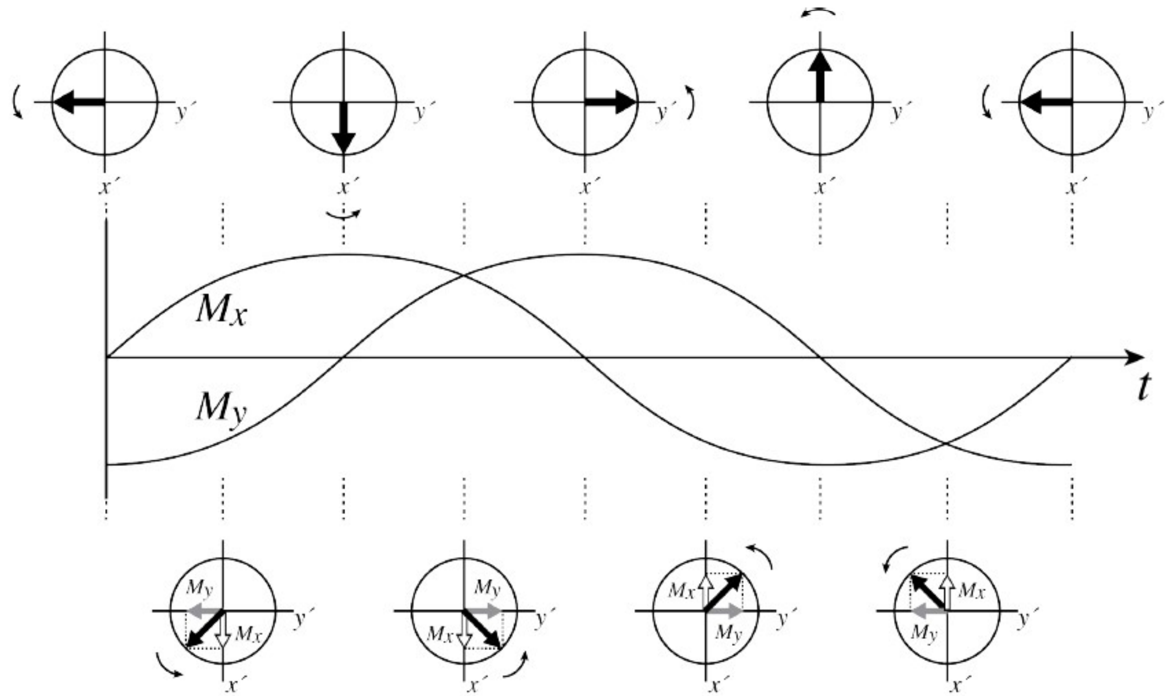


Bloch equations of motion (x-y plane)

- These equations give us the familiar result that a vector rotating in an *x*-*y* plane has projections on the *x*- and *y*-axes, the magnitudes of which exchange with time (ignoring relaxation)

$$M_x(t) = M_{x,0}\cos(-\gamma B_0 t) - M_{y,0}\sin(-\gamma B_0 t) = M_{x,0}\cos(\omega_0 t) - M_{y,0}\sin(\omega_0 t)$$

$$M_y(t) = M_{y,0}\cos(-\gamma B_0 t) + M_{x,0}\sin(-\gamma B_0 t) = M_{y,0}\cos(\omega_0 t) + M_{x,0}\sin(\omega_0 t)$$



Bloch equations of motion (T_1 and T_2)

- Relaxation processes occur during precession, so the Bloch equations are typically written to account for relaxation

$$\frac{d\vec{M}}{dt} = \gamma \vec{M}(t) \times \vec{B} - (M_z - M_0)(1/T_1) - M_{x,y}(1/T_2)$$

- The component equations are then written as shown, and simplified assuming $B_x = B_y = 0$, and $B_z = B_0$

$$\frac{dM_x}{dt} = \gamma\left(M_y(t)B_z - M_z(t)B_y\right) - \frac{M_x(t)}{T_2} = \gamma M_y(t)B_0 - \frac{M_x(t)}{T_2}$$

$$\frac{dM_y}{dt} = \gamma\left(M_z(t)B_x - M_x(t)B_z\right) - \frac{M_y(t)}{T_2} = -\gamma M_x(t)B_0 - \frac{M_y(t)}{T_2}$$

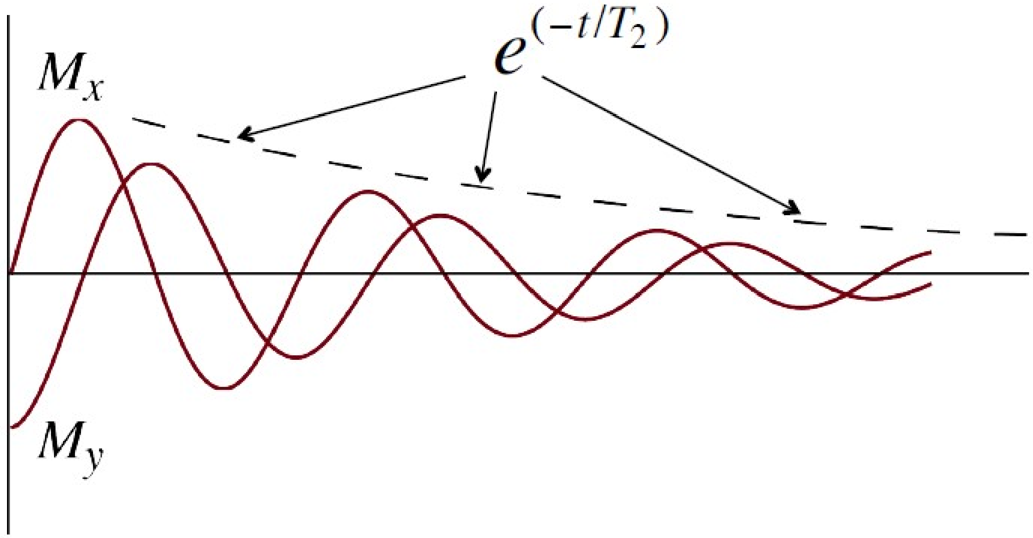
$$\frac{dM_z}{dt} = \gamma\left(M_x(t)B_y - M_y(t)B_x\right) - \frac{M_z(t) - M_0}{T_1} = -\frac{M_z(t) - M_0}{T_1}$$

Bloch equations of motion (T_2)

- The solutions for M_x and M_y describe the exponential decay, as a function of T_2 (i.e. T_2*), of the magnitude of the projection of the bulk magnetization vector in the transverse (*x*-*y*) plane

$$M_x(t) = \left[M_{x,0} \cos(\omega_0 t) - M_{y,0} \sin(\omega_0 t) \right] e^{(-t/T_2)}$$

$$M_y(t) = \left[M_{y,0} \cos(\omega_0 t) + M_{x,0} \sin(\omega_0 t) \right] e^{(-t/T_2)}$$



Bloch equations of motion (T_1)

- The solution for M_z describes the exponential growth, as a function of T_1, of M_z along the +*z* axis, returning to its equilibrium value of M_0 following an RF pulse

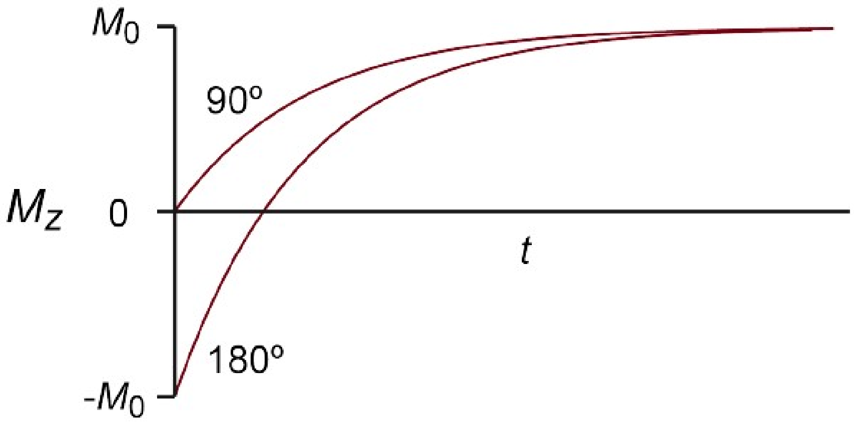
$$M_z(t) = M_0 + \left[M_{z,0} - M_0\right]e^{(-t/T_1)} = M_{z,0}e^{(-t/T_1)} + M_0(1 - e^{(-t/T_1)})$$

  - examples: following a 90° pulse ($M_{z,0}$= 0)

$$M_z(t) = M_0(1 - e^{(-t/T_1)})$$

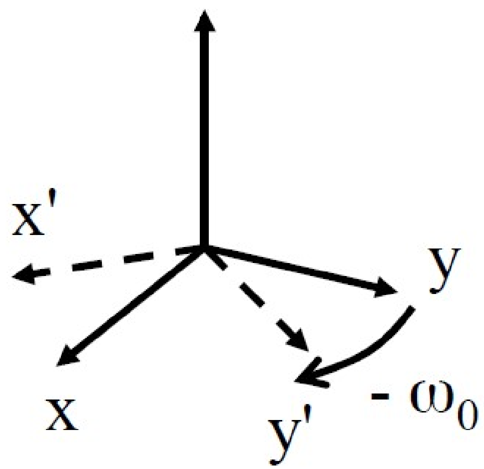
  - examples: following a 180° pulse ($M_{z,0}$= -M_0)

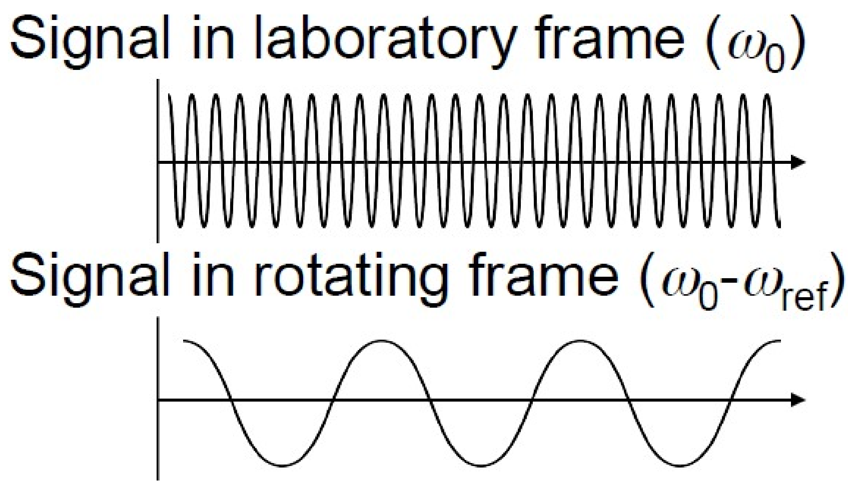
$$M_z(t) = M_0(1 - 2e^{(-t/T_1)})$$



The Rotating Frame Simplifies Analysis of RF Pulses and Small Frequency Offsets

- For a given type of nucleus (i.e. ^1H), Larmor frequencies (ω_0) are very high (~500 MHz for ^1H @ 11.74T)
- However, differences in Larmor frequencies are comparatively small (Hz, tens of Hz, kHz)
- It is convenient to subtract a reference (ω_{ref}) frequency from NMR signals similar in magnitude to the Larmor frequency. This is equivalent to rotating the cartesian axis system at this reference frequency (hence, "rotating frame")

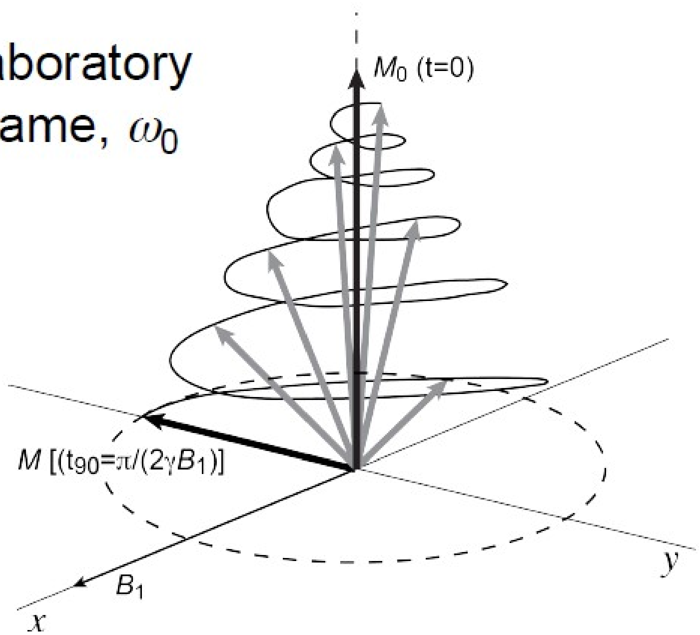




The Rotating Frame Simplifies Analysis of RF Pulses and Small Frequency Offsets

- Example:
  - <u>in the *laboratory frame*</u>, during an RF pulse, B_1 moves M towards the transverse plane, and the torque exerted by B_0 on M causes M to precess about z at its Larmor frequency ω_0
  - <u>in the *rotating frame*</u> (with $\omega_0 = \omega_{ref}$) there is no apparent precession

laboratory frame, ω_0



rotating frame with $\omega_0 = \omega_{ref}$