Classical Behavior of Net Magnetic Moments from Nuclear Spins: Bloch Equations

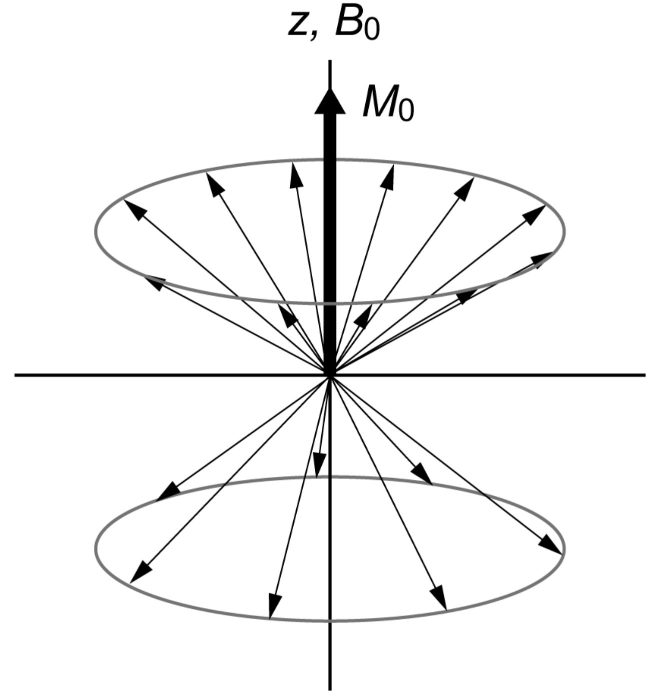
BCMB/CHEM 8190

Review of Spin Properties

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

$$M_0 = \gamma\hbar \sum_{m=-I}^{I} m N_m \quad (\text{recall } \mu_z = m\gamma\hbar)$$

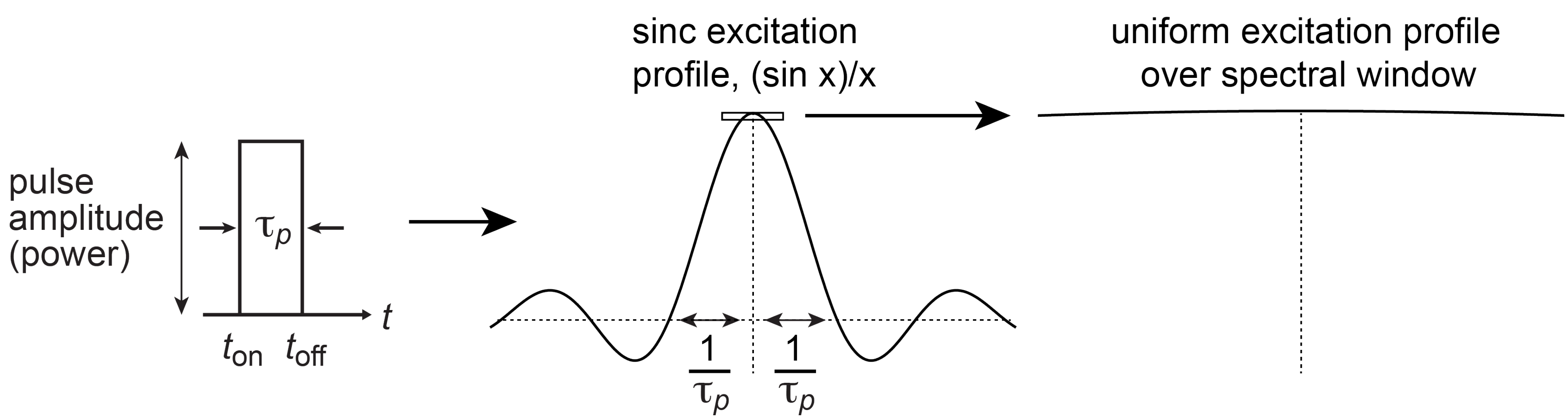
$$M_0 \approx \frac{N\gamma^2\hbar^2 B_0}{k_B T(2I+1)} \sum_{m=-I}^{I} m^2 \approx \frac{N\gamma^2\hbar^2 B_0 I(I+1)}{3k_B T}$$



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

RF Pulses are Required to Establish Initial Transverse Magnetization

- Old NMR instruments used a magnetic field or radiofrequency "sweep" to "find" Larmor frequencies (continuous wave, CW)
- Modern NMR uses short (μs) high power radiofrequency pulses to simultaneously excite a broad frequency bandwidth
- Short pulses ($\tau_p = t_{off} - t_{on}$) give broad excitation bandwidths (proportional to $1/\tau_p$), and uniform excitation over spectral width
  - example: At 400 MHz (^{1}H), a 5 μs rf pulse gives a bandwidth of 400,000 Hz ($2/\tau_p$, first lobe of sinc) or 1000 ppm. A typical ^{1}H sweep width is 4000 Hz, or 10 ppm

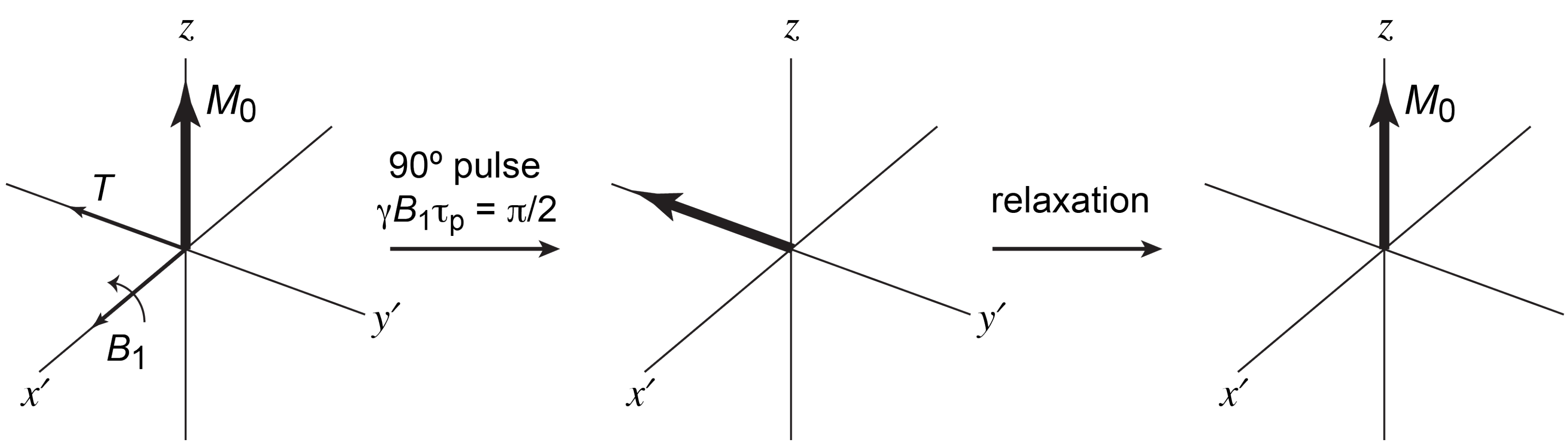


RF Pulses are Required to Establish Initial Transverse Magnetization

- An RF pulse (B_1) in the transverse plane exerts a torque on M_0 that moves it through some angle (Θ) toward the transverse (x-y) plane according to

$$\Theta = \gamma B_1 \tau_p$$

- By definition, Θ is 90° degrees ($\pi/2$ radians) for a 90° pulse



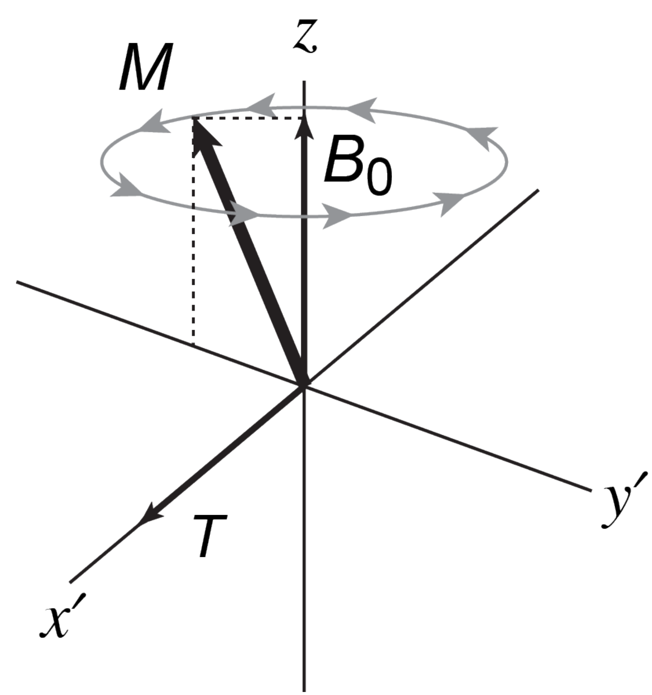
- With time, normal relaxation processes return the system to thermal equilibrium, and M_0 returns to the $+z$-axis

Precession

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

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

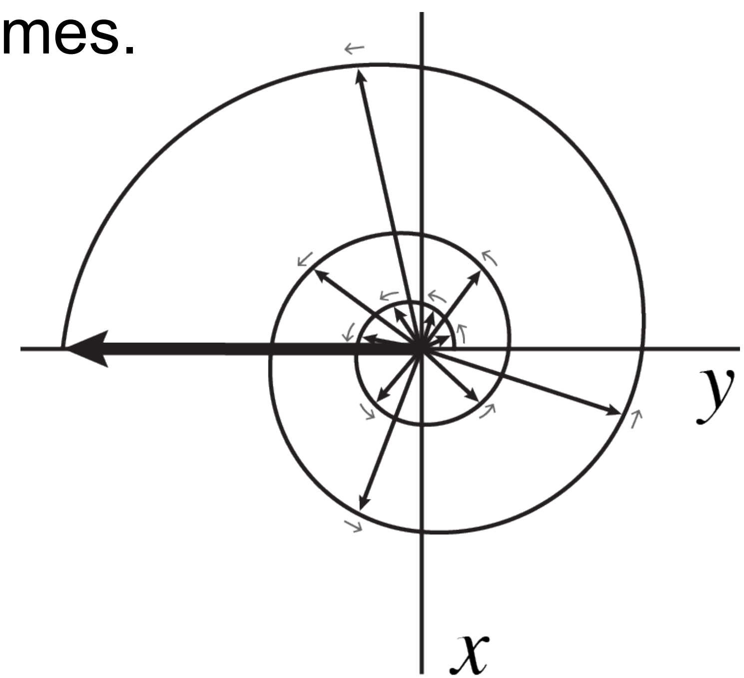
- The B_0 field also exerts a torque on the bulk magnetization vector (M). When displaced by an RF pulse from its equilibration position (along the z-axis), B_0 causes M to precess about z (at $\omega_0 = \gamma B_0$) until relaxation processes return it to its equilibrium position on z

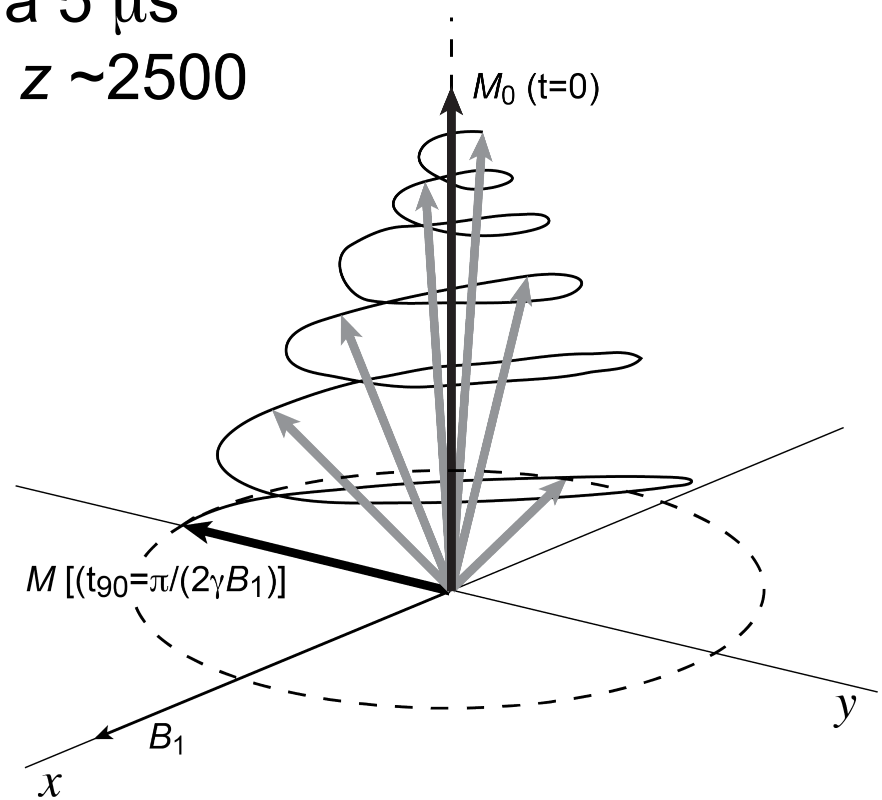


Precession

- *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

- For individual spins and bulk magnetization, the relationships between magnetization and angular momentum are

$$\vec{\mu} = \gamma \vec{I} \qquad \vec{M} = \gamma \vec{L}$$

- Torque (T) is the change in the bulk angular momentum with time

$$\vec{T} = \frac{d\vec{L}}{dt} = \frac{1}{\gamma}\frac{d\vec{M}}{dt}$$

- The torque applied to the bulk magnetization by the static magnetic field is given by the cross product

$$\vec{T} = \frac{d\vec{L}}{dt} = \frac{1}{\gamma}\frac{d\vec{M}}{dt} = \vec{M} \times \vec{B} \qquad \text{so,}\ \frac{d\vec{M}}{dt} = \gamma \vec{M} \times \vec{B}$$

- The latter equation describes the time dependence of the bulk magnetization vector in a static magnetic field. It can be used to describe *free precession* under the influence of B_0.
- This is the basis of the Bloch equations

Bloch Equations of Motion

- The cross product of the bulk magnetization vector (*M*) and the magnetic field (*B*) vector can be shown to be (see "Appendix")

$$\vec{M} \times \vec{B} = \left[M_y B_z - M_z B_y \quad M_z B_x - M_x B_z \quad M_x B_y - M_y B_x \right]$$

- This leads to the three component equations, which are the Bloch equations for *free precession* in a static magnetic field (*ignoring relaxation*).

$$\frac{dM_x}{dt} = \gamma\left(M_y B_z - M_z B_y\right) \qquad \frac{dM_y}{dt} = \gamma\left(M_z B_x - M_x B_z\right) \qquad \frac{dM_z}{dt} = \gamma\left(M_x B_y - M_y B_x\right)$$

- These can be simplified knowing $B_x = B_y = 0$, and $B_z = B_0$

$$\frac{dM_x(t)}{dt} = \gamma M_y(t) B_0 \qquad \frac{dM_y(t)}{dt} = -\gamma M_x(t) B_0 \qquad \frac{dM_z(t)}{dt} = 0$$

- These can be solved to give the following

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

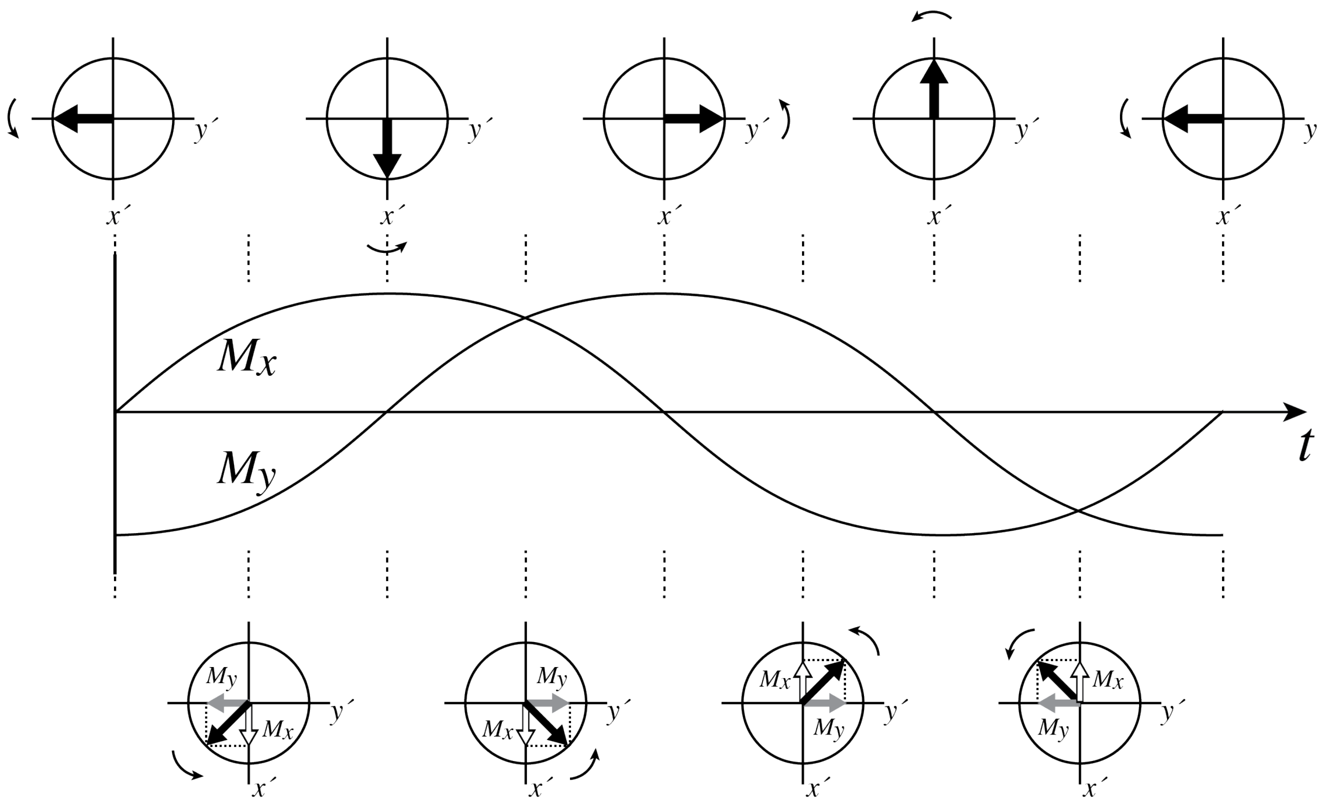
$$M_y(t) = M_{y,0}\cos(-\gamma B_0 t) + M_{x,0}\sin(-\gamma B_0 t) = M_{y,0}\cos(\omega_0 t) + M_{x,0}\sin(\omega_0 t)$$

Bloch Equations of Motion

- 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

- 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 $B_z = B_0$

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

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

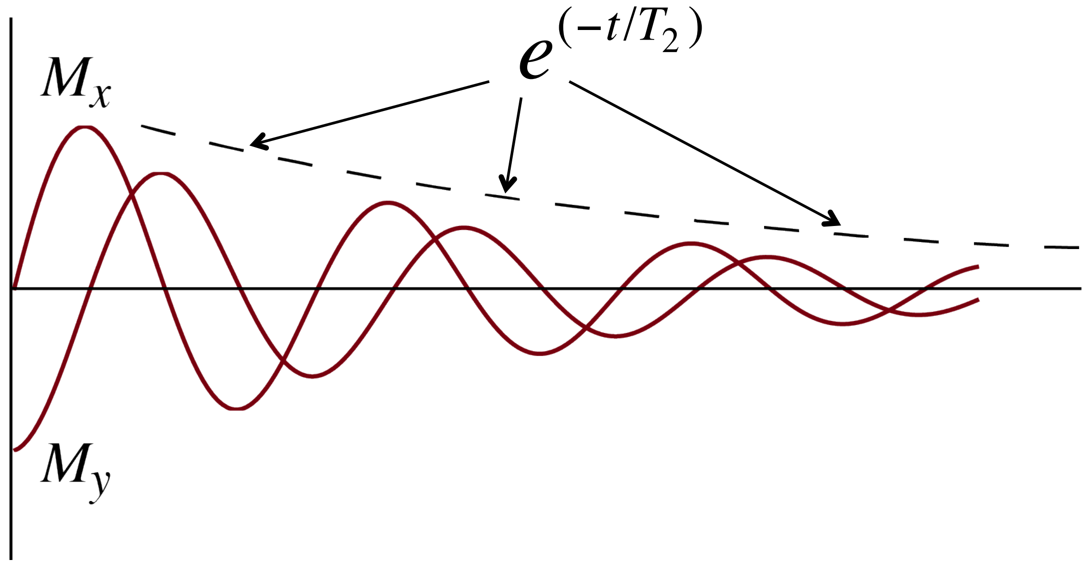
$$\frac{dM_z}{dt} = \gamma\left(M_x(t)B_y - M_y(t)B_x\right) - \frac{M_z(t) - M_0}{T_1} = -\frac{M_z(t) - M_0}{T_1}$$

Bloch Equations of Motion

- 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

- 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

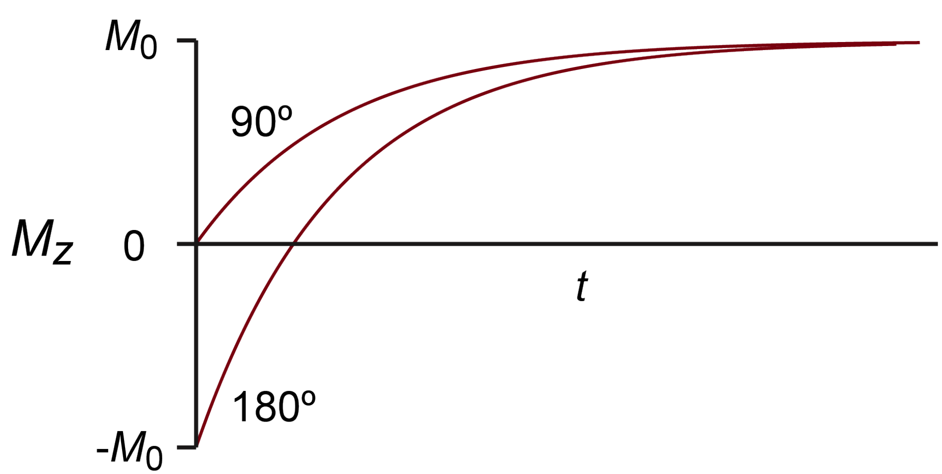
$$M_z(t) = M_0 + \left[M_{z,0} - M_0\right]e^{(-t/T_1)} = M_{z,0}e^{(-t/T_1)} + M_0(1 - e^{(-t/T_1)})$$

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

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

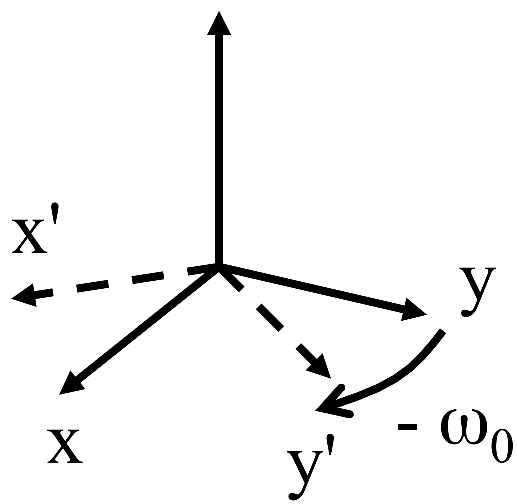
  - examples: following a 180° pulse ($M_{z,0}$= -M_0)

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

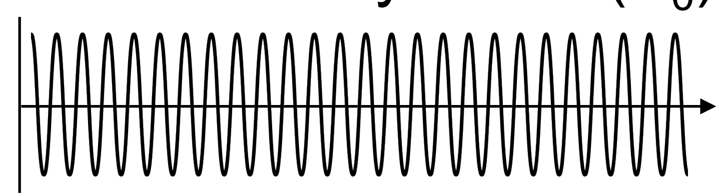


The Rotating Frame Simplifies Analysis of RF Pulses and Small Frequency Offsets

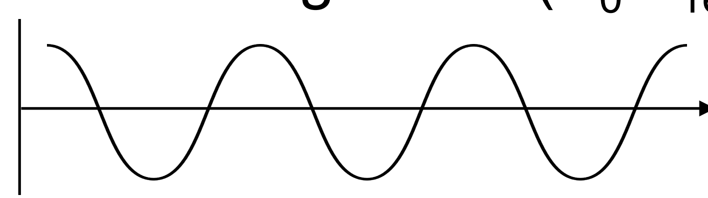
- For a given type of nucleus (i.e. ^1H), Larmor frequencies (ω_0) are very high (~500 MHz for ^1H @ 11.74T)
- However, differences in Larmor frequencies are comparatively small (Hz, tens of Hz, kHz)
- It is convenient to subtract a reference (ω_{ref}) frequency from NMR signals similar in magnitude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



Signal in laboratory frame (ω_0)



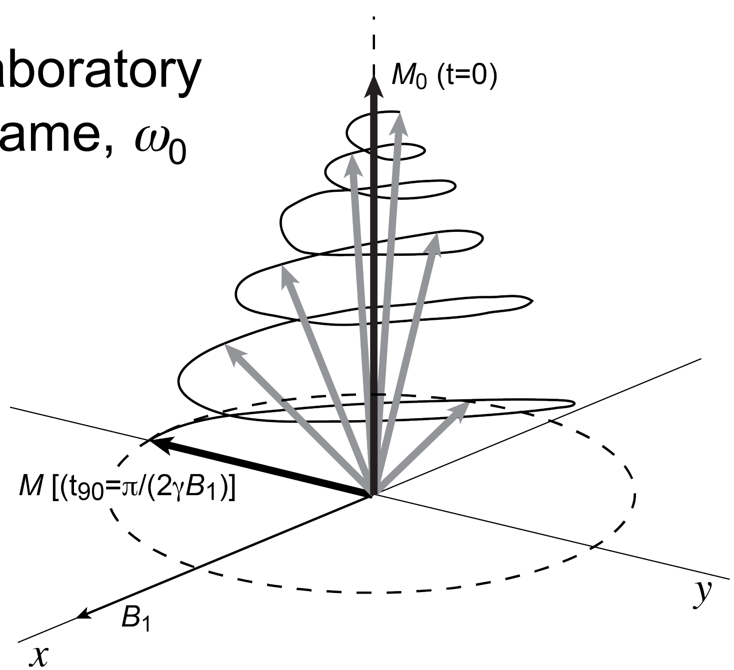
Signal in rotating frame (ω_0-ω_{ref})

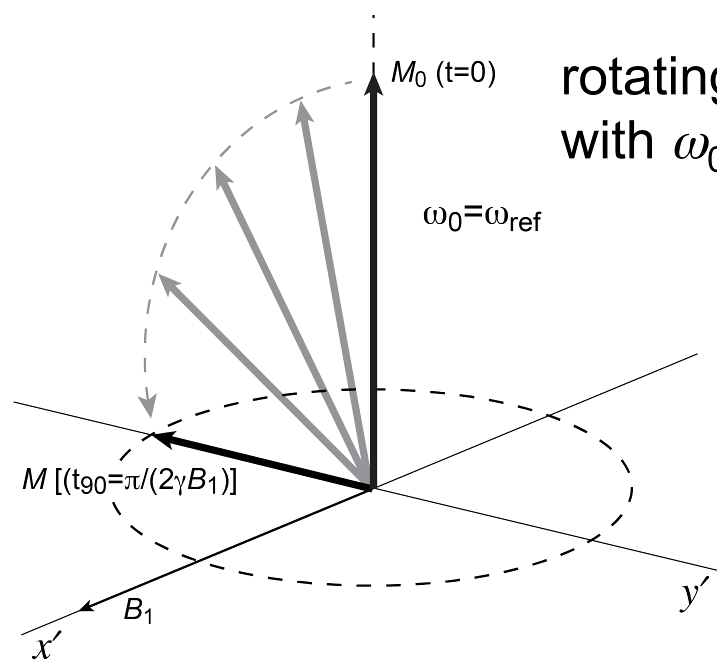


The Rotating Frame Simplifies Analysis of RF Pulses and Small Frequency Offsets

- Example:
  - in the *laboratory frame*, 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
  - in the *rotating frame* (with $\omega_0 = \omega_{ref}$) there is no apparent precession

laboratory frame, ω_0





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

Small Modifications in Precession Frequency (or decay of magnetization) are Primary Observables in High Resolution NMR

$$H = -\gamma B_0 \sum_i (1-\sigma_i) I_{Zi} + \sum_{j>i} 2\pi\, J\, I_i \cdot I_j + \sum_{j>i} 2\pi\, I_i \cdot D \cdot I_j$$

chemical shift   scalar coupling   dipolar coupling

$$1/T_{1,2} = \sum_{ij} J_i(\omega_i)\, |D_{ij}|^2 , \qquad J_i(\omega_i) = 2\tau_c/(\omega_i^2 \tau_c^2 + 1)$$

spin relaxation

Measurement of Chemical Shift

$$\upsilon_i\ \mathbf{(Hz)} = \gamma \mathbf{B_0/2}\pi\ \mathbf{(1-}\sigma_i\mathbf{)}$$

σ_i: shielding constant dependent on electronic structure, ~10^{-6}.
Measurements are made relative to a reference peak: TMS.
Offsets given in terms of δ (parts per million, ppm, downfield).

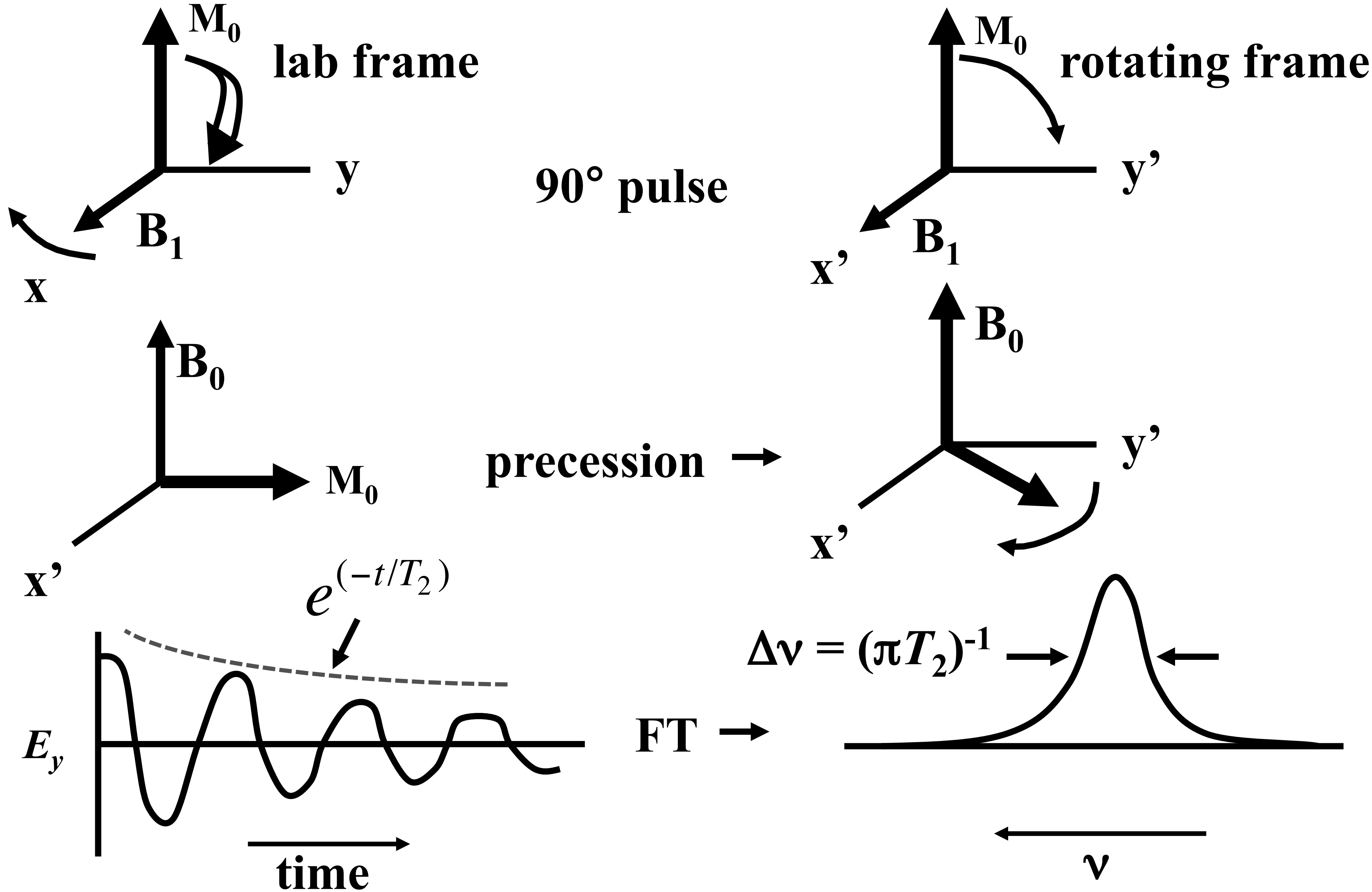
$$\delta_i = (\sigma_{ref} - \sigma_i) \times 10^6$$

or

$$\delta_i = ((\upsilon_i - \upsilon_{ref})/\upsilon_{ref}) \times 10^6$$

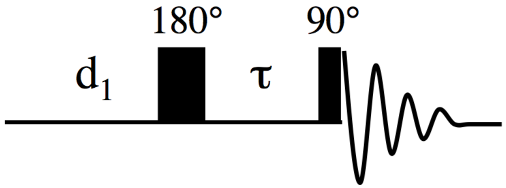
Ranges: ^1H, ^2H, 10 ppm; ^{13}C, ^{15}N, ^{31}P, 300 ppm; ^{19}F, 1000 ppm
-larger for heavier atoms due to deshielding effects associated with circulation of electrons between ground and excited states in low lying energy levels (proportional to $1/\Delta E$; ΔE is large for ^1H)

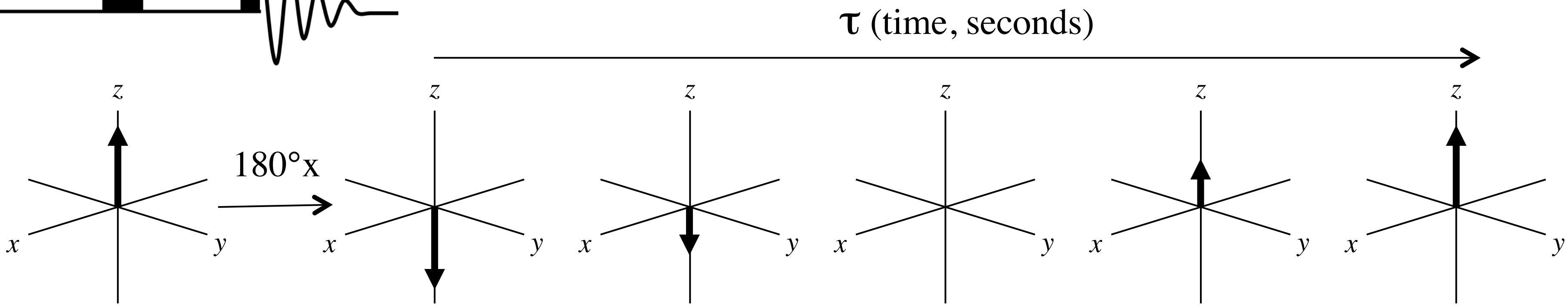
Pulse FT NMR



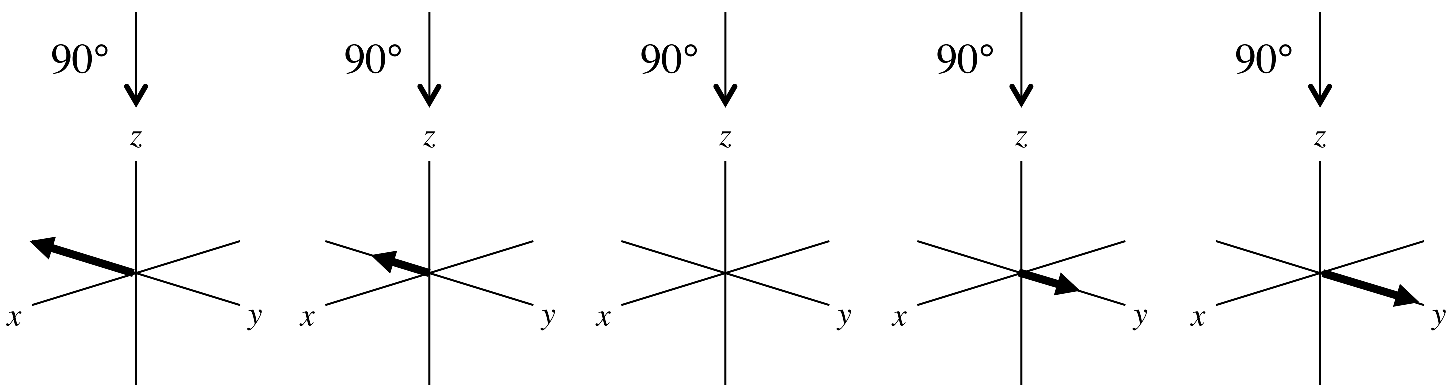
M0
lab frame
y
B1
x
90° pulse
M0
rotating frame
y’
x’
B1
B0
M0
x’
precession
B0
y’
x’
$e^{(-t/T_2)}$
$\Delta\nu = (\pi T_2)^{-1}$
E_y
FT
time
ν

Inversion-Recovery to Measure T_1

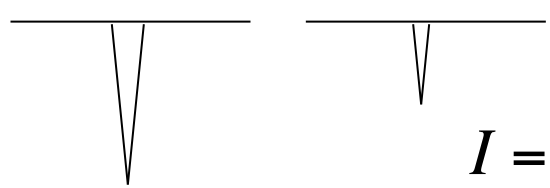


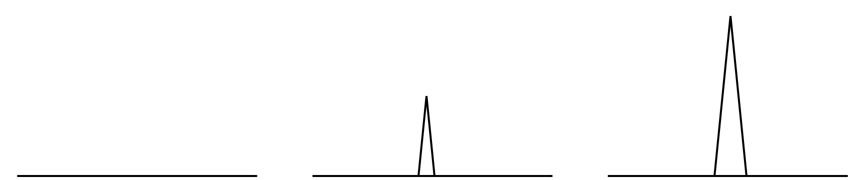


M_y is proportional to M_z following τ period



so, now ***signal intensity*** after FT is proportional to M_z following τ period





$$I = I_0(1 - \mathbf{2}e^{(-\tau/T_1)})$$

Appendix

The cross product of two vectors $\vec{M} = [M_x \;\; M_y \;\; M_z]$ and $\vec{B} = [B_x \;\; B_y \;\; B_z]$ is give by the following vector

$$\vec{M} \times \vec{B} = \left[M_y B_z - M_z B_y \quad M_z B_x - M_x B_z \quad M_x B_y - M_y B_x \right]$$

This formula can be derived based on the fact that the cross product is the determinant of a 3×3 matrix constructed as follows (Method of Cofactors, where $\vec{i}$, $\vec{j}$, and $\vec{k}$ are basis / unit vectors)

$$\vec{M} \times \vec{B} = \begin{bmatrix} \vec{i} & \vec{j} & \vec{k} \\ M_x & M_y & M_z \\ B_x & B_y & B_z \end{bmatrix} = \begin{bmatrix} M_y & M_z \\ B_y & B_z \end{bmatrix} \vec{i} - \begin{bmatrix} M_x & M_z \\ B_x & B_z \end{bmatrix} \vec{j} + \begin{bmatrix} M_x & M_y \\ B_x & B_y \end{bmatrix} \vec{k}$$

Recall

$$\begin{bmatrix} a & b \\ c & d \end{bmatrix} = ad - bc$$

So

$$\begin{bmatrix} M_y & M_z \\ B_y & B_z \end{bmatrix} \vec{i} - \begin{bmatrix} M_x & M_z \\ B_x & B_z \end{bmatrix} \vec{j} + \begin{bmatrix} M_x & M_y \\ B_x & B_y \end{bmatrix} \vec{k} = \left[\; (M_y B_z - M_z B_y)\vec{i} \quad (M_z B_x - M_x B_z)\vec{j} \quad (M_x B_y - M_y B_x)\vec{k} \; \right]$$