

Pulse and FT NMR

In practice bulk magnetization is observed

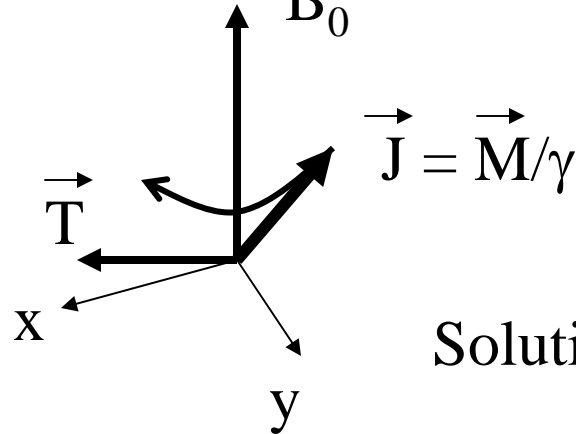
For isolated spins behavior is according to classical Bloch equations

$$\frac{d\vec{M}}{dt} = \gamma \vec{M} \times \vec{B} - (M_z - M_0) \frac{1}{T_1} \hat{z} - M_{x,y} \frac{1}{T_2} \hat{r}_{xy}$$

Precession in a Static Field

Torque on system with angular momentum (\vec{J}) causes precession of the momentum vector.
 $\frac{d\vec{J}}{dt} = \vec{T}$. Torque is given by $\vec{J} \times \vec{B}_0$ and $\vec{M} = \gamma\vec{J}$.
 Bloch equations give precession at $\omega = -\gamma B_0$.

$$\frac{d\vec{M}}{dt} = \gamma \vec{M}(t) \times \vec{B}_0$$



$$\frac{d\vec{M}}{dt} = \gamma \begin{vmatrix} \vec{i} & \vec{j} & \vec{k} \\ M_x & M_y & M_z \\ 0 & 0 & B_0 \end{vmatrix}$$

$$\frac{dM_x}{dt} = \gamma M_y B_0$$

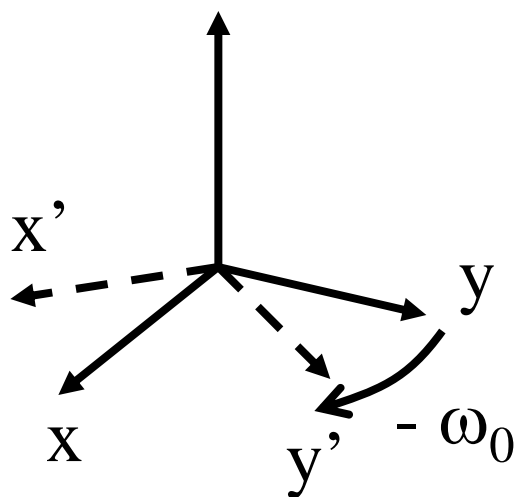
$$\frac{dM_y}{dt} = -\gamma M_x B_0$$

$$\frac{dM_z}{dt} = 0$$

Solution: $M_x(t) = M_{0x} \cos(-\gamma B_0 t) - M_{0y} \sin(-\gamma B_0 t)$
 $= M_0 \exp(-i \gamma B_0 t) = M_0 \exp(i \omega_0 t)$

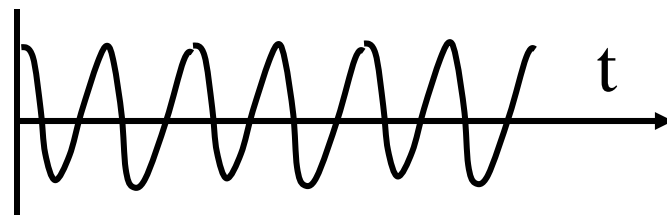
The Rotating Frame Simplifies Analysis of RF Pulses and Small Frequency Offsets

ω_0 is very high ($500 \text{ MHz} \times 2\pi$) – differences due to chemical shifts etc. are small ($\text{ppm} \times 500 \text{ Hz} \times 2\pi$)
Therefore, use reference frame moving near ω_0 .

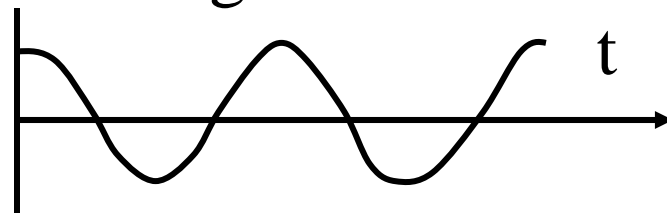


$$\omega_{\text{obs}} = \omega_0 - \omega'$$

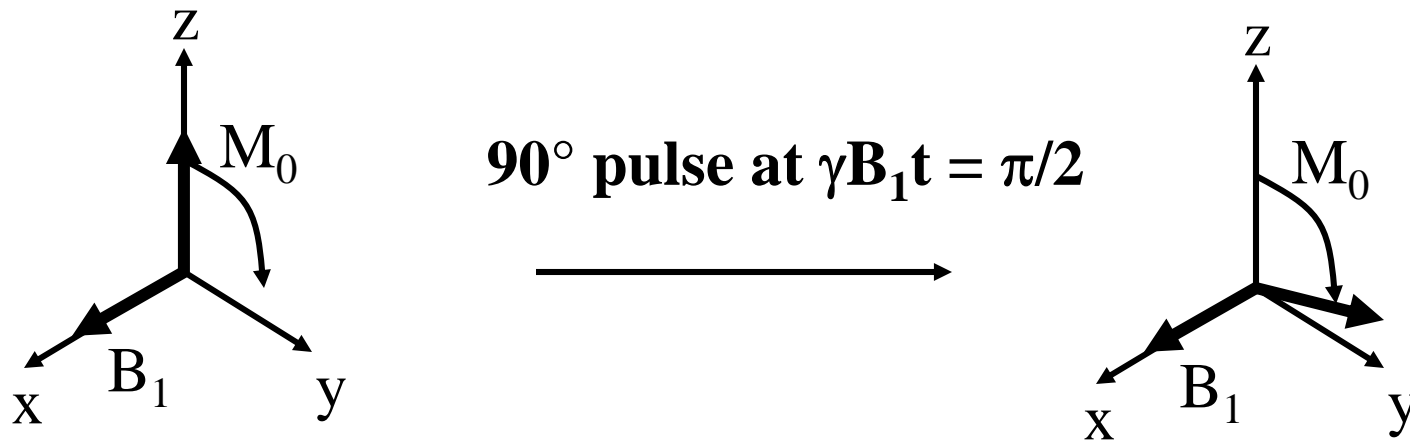
Signal in lab frame



Signal in rotating frame



RF Pulses are Required to Establish Initial Transverse Magnetization



Note: diagram is in the “rotating frame”

$B_1 = B_{01} \cos(B_0 \gamma t)$ to keep pace with precessing magnetization

Maximum signal is obtained with a 90° pulse $t_{90} = \pi/(2\gamma B_1)$

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

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

spin relaxation

Measurement of Chemical Shift

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

σ_i , a shielding constant dependent on electronic structure, is $\sim 10^{-6}$. Measurements are made relative to a reference peak such as TMS. Offsets given in terms of δ in parts per million, ppm, + downfield.

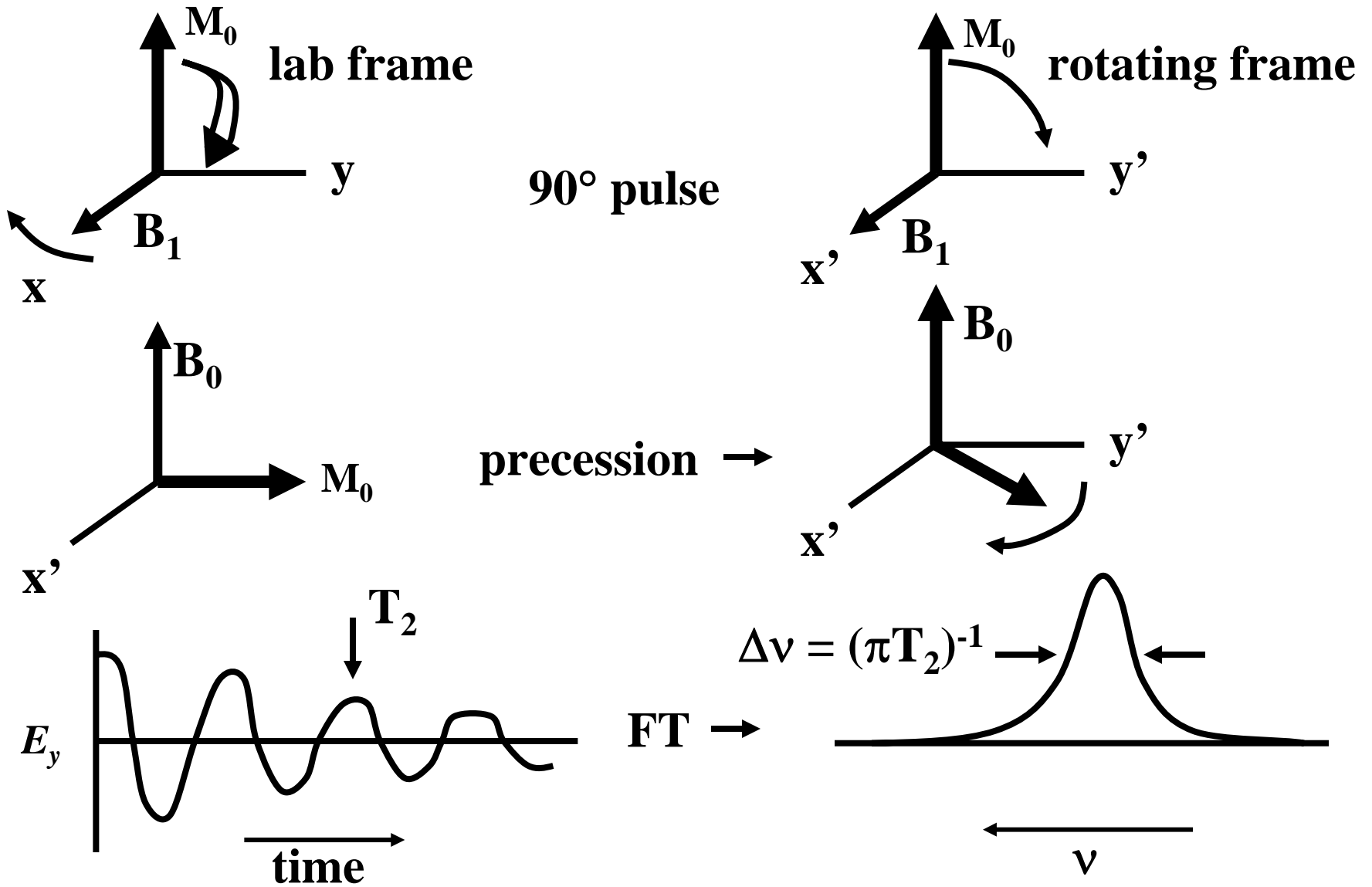
$$\delta_i = (\sigma_{\text{ref}} - \sigma_i) \times 10^6$$

or

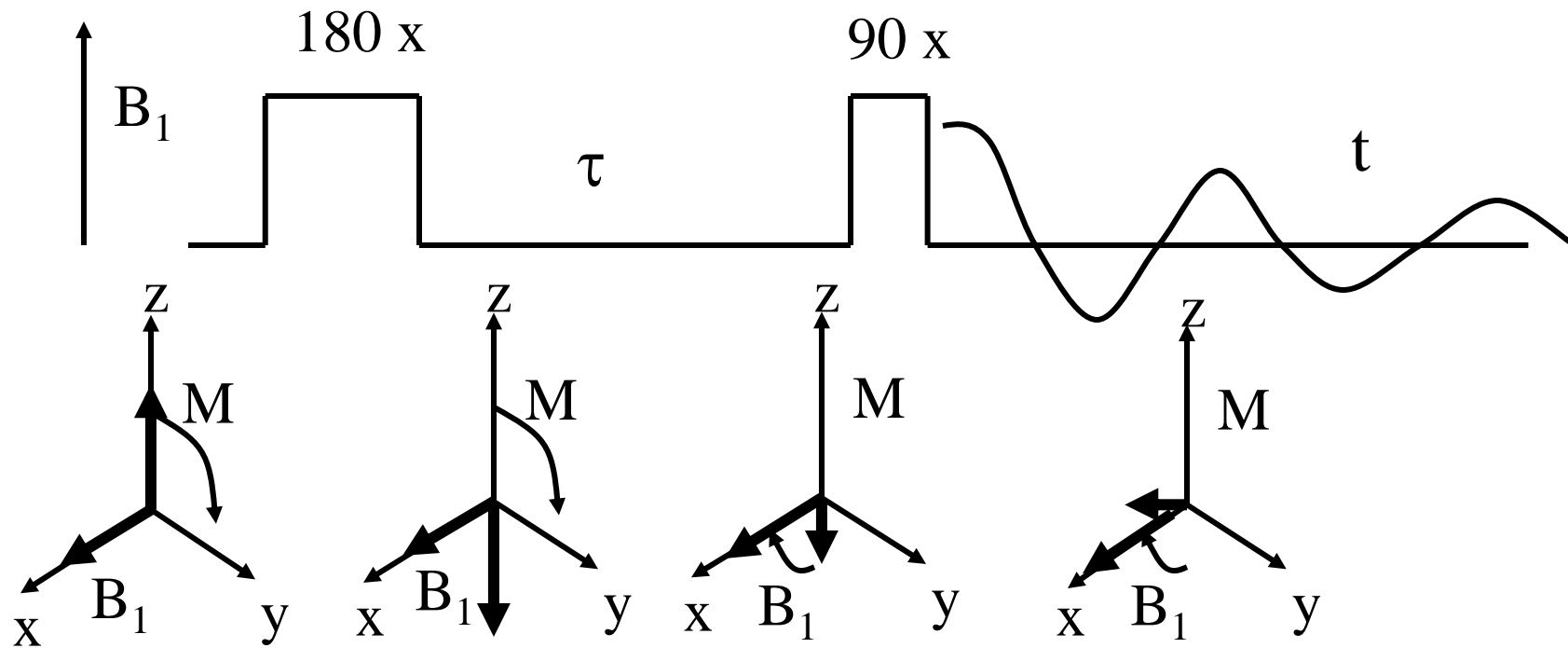
$$\delta_i = ((\nu_i - \nu_{\text{ref}}) / \nu_{\text{ref}}) \times 10^6$$

Ranges: ^1H , ^2H , 10 ppm; ^{13}C , ^{15}N , ^{31}P , 300 ppm; ^{19}F , 1000 ppm

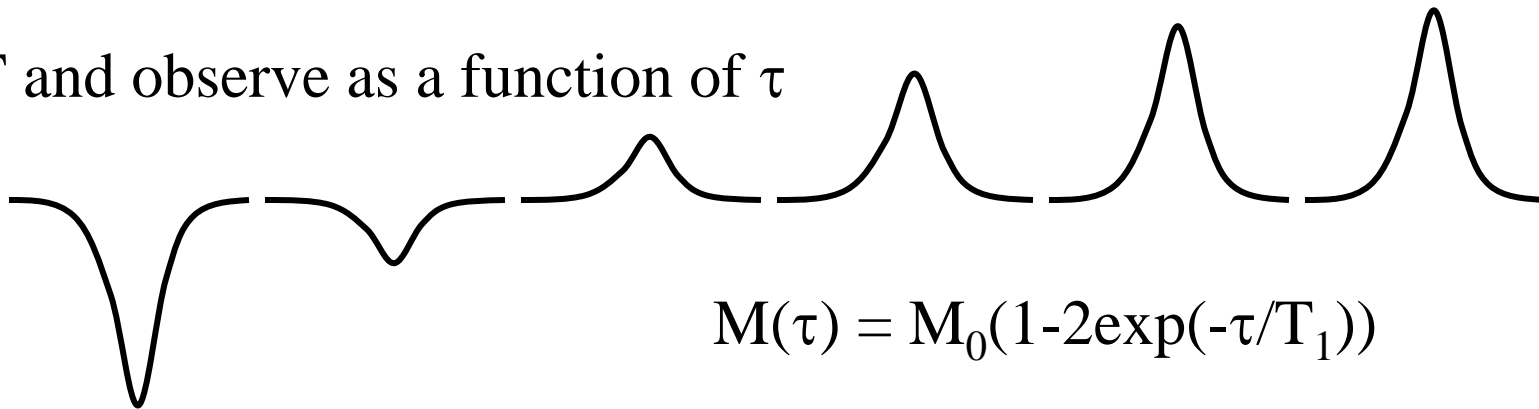
Pulse FT NMR



Inversion-Recovery Measures T_1 s Using a 180° Pulse



FT and observe as a function of τ



$$M(\tau) = M_0(1 - 2\exp(-\tau/T_1))$$