Pulse and FT NMR

In practice bulk magnetization is observed

For isolated spins behavior is according to classical Bloch equations

\[
\frac{d\mathbf{M}}{dt} = \gamma \mathbf{M} \times \mathbf{B} - (M_z - M_0) \left(\frac{1}{T_1}\right) - M_{x,y} \left(\frac{1}{T_2}\right)
\]
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 $\omega = -\gamma B_0$.

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

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

\[
\begin{align*}
\frac{dM_x}{dt} &= \gamma M_y B_0 \\
\frac{dM_y}{dt} &= -\gamma M_x B_0 \\
\frac{dM_z}{dt} &= 0
\end{align*}
\]

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

$\omega_0$ is very high (500 MHz x $2\pi$) – differences due to chemical shifts etc. are small (ppm x 500 Hz x $2\pi$) Therefore, use reference frame moving near $\omega_0$.

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

\[ \nu_i \text{ (Hz)} = \frac{\gamma B_0}{2\pi} (1-\sigma_i) \]

\[ \sigma_i \text{, a shielding constant dependent on electronic structure, is } \sim 10^{-6}. \]

Measurements are made relative to a reference peak such as TMS. Offsets given in terms of \( \delta \) in parts per million, ppm, + downfield.

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

or

\[ \delta_i = \left(\frac{\nu_i - \nu_{\text{ref}}}{\nu_{\text{ref}}}\right) \times 10^6 \]

Ranges: \( ^1H, ^2H, 10 \text{ ppm} \); \( ^{13}C, ^{15}N, ^{31}P, 300 \text{ ppm} \); \( ^{19}F, 1000 \text{ ppm} \)
Pulse FT NMR

lab frame

90° pulse

precession

Δν = (πT₂)⁻¹

FT

B₀

B₁

M₀

x

y

x′
y′

B₀

B₁

M₀

x′
y′

x′
y′

E_y

time

time

ν
Inversion-Recovery Measures $T_1$s
Using a 180° Pulse

$$M(x, y, z)_{B1}$$

180 x $\tau$ 90 x $t$

FT and observe as a function of $\tau$

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