Pulse and FT NMR

In practice bulk magnetization is observed

For isolated spins behavior is according to classical Bloch equations

\[
\frac{dM}{dt} = \gamma M \times B - (M_z - M_0) \left(\frac{1}{T_1}\right) - M_{x,y} \left(\frac{1}{T_2}\right)
\]
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 $\dot{\vec{M}} = \gamma \vec{J}$. This leads to the Bloch equations.

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

$$\vec{J} = \vec{M}/\gamma$$

$$
\begin{vmatrix}
\vec{i} & \vec{j} & \vec{k} \\
M_x & M_y & M_z \\
0 & 0 & B_0
\end{vmatrix}
$$

$$
\begin{align*}
\frac{dM_x}{dt} &= \gamma M_y B_0 \\
\frac{dM_y}{dt} &= -\gamma M_x B_0 \\
\frac{dM_z}{dt} &= 0
\end{align*}
$$
Solutions to Bloch Eq.
(time 0 on x axis)

\[ M_x(t) = M_0 \cos(\gamma B_0 t) = M_0 \cos(-\omega_0 t) \]
\[ M_y(t) = -M_0 \sin(\gamma B_0 t) = M_0 \sin(-\omega_0 t) \]

Larmor freq.
\[ \omega_0 = 2\pi f_0 \]

In complex notation:
\[ M(t) = M_x + iM_y = M_0 \exp(-i\omega_0 t) \]
The Rotating Frame

\( \omega_0 \) is very high. (500 MHz). Differences due to chemical shift etc. are in ppm. (kHz).

\[ \omega = \Delta \omega = \omega_0 - \omega' \]

Signal in lab frame:

Signal in rotating frame:
Not all nuclei see $B_0$. It is modified by electronic structure.

$B_{\text{eff}} = (1-\sigma)B_0$

$\kappa$ shielding constant.

$\omega = \omega_0 + \Delta \omega$, $\Delta \omega = +\kappa \chi B_0$

Could choose a reference line (TMS) to represent $\omega_0$ and measure relative frequencies.

$\delta_i = \frac{\omega_i - \omega_{\text{TMS}}}{\omega_i} \times 10^6$ (in ppm)
RF Pulses: Creating an Initial State

Z component is defined by pop. diff.

\[ M_{z0} = N_0 \gamma^2 \hbar^2 B_0 I(I+1)/3kT \]

but x + y projections sum to zero

solution: move \( M_z \) to x or y axis

- apply field on x or y in rotating frame

\[ t_{90} = \frac{\pi}{2\gamma B_1} \]
3. **The $B_1$ Field**

- $B_1$ is a radio frequency field, which creates a linearly polarized oscillating magnetic field.

- The $B_1$ field can be decomposed in 2 equal fields of half intensity. For $B_1$ along $x$:

$$B_{\text{rf}} = 2B_1 \cos(\omega_{\text{rf}} t)$$

$$B_{\text{rf}} = B_1 \left( e^{+i\omega_{\text{rf}} t} + e^{-i\omega_{\text{rf}} t} \right)$$

where $B_1$ is the amplitude and $\omega_{\text{rf}}$ is the frequency related to $B_{\text{rf}}$
3. The $B_1$ Field (cont’d)

Linearly polarized oscillating magnetic field

Two counter-rotating magnetisation vector

$2B_1 \cos(\omega t)$
3. **The $B_1$ Field** (cont’d)

- Only the field rotating in the same sense as the magnetic moment interacts significantly with the magnetic moment (resonance effect).

$$B_{\text{rf}} = B_1 e^{i\omega_{\text{rf}} t}$$

- In the rotating frame:

$$\omega_{\text{rot}} = \omega_{\text{rf}}$$

$$B_{\text{eff}} = (B_1, 0, \Delta B_o)$$

where $B_1 = -\omega_{\text{rf}}/\gamma$ and $\Delta B_o = -\Delta/\gamma$; $\Delta = \omega_o - \omega_{\text{rf}}$
4. 90° Pulse : Pulse Length

- Pulse length for 90° pulse ($\theta = \pi/2$):

\[ \theta = \omega_{rf} \cdot \tau_p = \pi/2 \]
\[ \tau_p = \theta / \omega_{rf} = \text{pulse length} \]

Example: Typical parameters for hard pulse on $^1\text{H}$

If $\tau_p = 10 \ \mu s$ for 90° pulse
($\theta = \pi/2 = 0.25 \ \text{radian}$)
\[ \omega_{rf} = \theta / \tau_p = 0.25 / 10 \ \mu s = 25 \ \text{kHz} \]
5. 90° Pulse: Phase of Magnetization

- So far we have omitted $\Delta$, but in reality $\Delta \neq 0$

- Solving for the Block equations and including $\Delta$, we get:

\[
M_x'(t) \approx \gamma^2 (\Delta B)B_1 M_z'(0)/\omega_{rf}^2; \quad \Delta B = - (\omega_i - \omega_{rot})/\gamma
\]

\[
M_y'(t) \approx (\gamma M_z'(0)B_1)/\omega_{rf}
\]

Note: $M_x'(t) \neq 0$ !!!
Sensitivity of the NMR Experiment

\[ \varepsilon \propto \frac{dM(t)}{dt} \]

\[ \frac{dM(t)}{dt} = \gamma M_0 B_0 = N\gamma^3 \frac{(h/2\pi)^2 B_0^2 I(I+1)}{3k_B T} \]
6. **$T_1$ and $T_2$ Relaxation**

- **$T_1$**: longitudinal or spin-lattice relaxation, return back to equilibrium

- **$T_2$**: transverse or spin-spin relaxation, dephasing in the x-y plane

- **$R_1 = 1/T_1$; $R_2 = 1/T_2$**
  $R_1$ and $R_2$ are rate constants

- **Let's consider some simplified cases i.e. after pulse ($B_1 = 0$) and on resonance ($\Delta B = 0$):**
6. \textbf{T}_1 \text{ and } \textbf{T}_2 \text{ Relaxation} (cont’d)

- \textbf{T}_2 \text{ relaxation}

\[
\begin{align*}
\frac{dM_x'(t)}{dt} &= -R_2 M_x'(t) \\
\frac{dM_y'(t)}{dt} &= -R_2 M_y'(t)
\end{align*}
\]

Solving for \( M_x' \):

\[
\int \frac{dM_x'(t)}{M_x'(t)} = \int -R_2 \, dt
\]

\[
\ln |M_x'(t)|_0^t = -R_2 \, t |_0^t
\]

\[
\ln \left| \frac{M_x'(t)}{M_x'(0)} \right| = -R_2 \, t
\]

\[
M_x'(t) = M_x'(0)e^{-R_2t}
\]

\[
M_y'(t) = M_y'(0)e^{-R_2t}
\]

\[
S = M_y'(0)*1/e
\]

t = T_2 \text{ when}

\[
t = T_2 \text{ when }
\]

\[
S = M_y'(0)*1/e
\]
6. \( T_1 \) and \( T_2 \) Relaxation cont’d

- \( T_1 \) relaxation

\[
dM_z'(t)/dt = R_1 \left[ M_0 - M_z'(t) \right]
\]

Solving for \( M_z' \):

\[
\int \frac{dM_z'(t)}{[M_z'(t) - M_0]} = -R_1 \int dt
\]

\[
\ln |M_z'(t) - M_0|_0^t = -R_1 t_0^t
\]

\[
\ln |(M_z'(t) - M_0)/(M_z'(0) - M_0)| = -R_1 t
\]

\[
M_z'(t) = M_0 - (M_0 - M_z'(0)) e^{-R_1 t}
\]
Measurement of $R_1$ - Inversion Recovery

A series of $T$ values: