Nuclear Magnetic Resonance (NMR)

A Brief Introduction and Applications

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Overview

1. Principles of NMR
2. Apparatus and Experimental Procedures

Setup

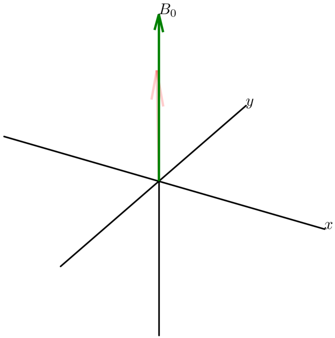


Figure: Typical $\vec{B}_0$ and vector aligned with field

- Spin 1/2 nuclei
- Strong magnetic field, denoted $\vec{B}_0$

Energy and Hamiltonian

Magnetic moment of nucleus

$$\vec{\mu} = \gamma \vec{S} \tag{1}$$

Yields energy and Hamiltonian of

$$E = -\vec{\mu} \cdot \vec{B}_0 \tag{2}$$

$$H = -\gamma \vec{B}_0 \cdot S \tag{3}$$

Larmor Precession

Evolving an arbitrary spin vector

$$|\psi\rangle = \cos\left(\theta/2\right)|+\rangle + e^{i\phi}\sin\left(\theta/2\right)|-\rangle$$

yields, [1]

$$\langle S_x\rangle = \frac{\hbar}{2}\sin(\theta)\cos(\gamma B_0 t)$$
$$\langle S_y\rangle = \frac{\hbar}{2}\sin(\theta)\sin(\gamma B_0 t)$$
$$\langle S_z\rangle = \frac{\hbar}{2}\cos(\theta)$$

with the characteristic **Larmor frequency**

$$\omega_0 = \gamma B_0 \tag{4}$$

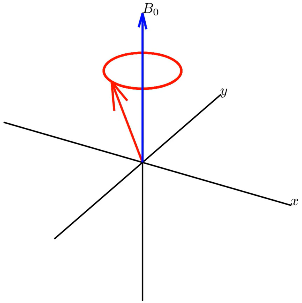


Figure: Larmor precession about $\vec{B}_0$

Net Magnetization and Relaxation

With many spins, any material can acquire a net magentization.
Along $\hat{z}$, statistical mechanics tells us that

$$\frac{N_+}{N_-} = \exp\left(\frac{\gamma \hbar B_0}{kT}\right) \tag{5}$$

with total **net magnetization**

$$M_z = \sum_i \gamma \hbar m_i = \frac{\hbar}{2}\gamma(N_+ - N_-) \tag{6}$$

Expect spins to eventually re-align with $\hat{z}$ direction.

Producing Transverse Magnetization

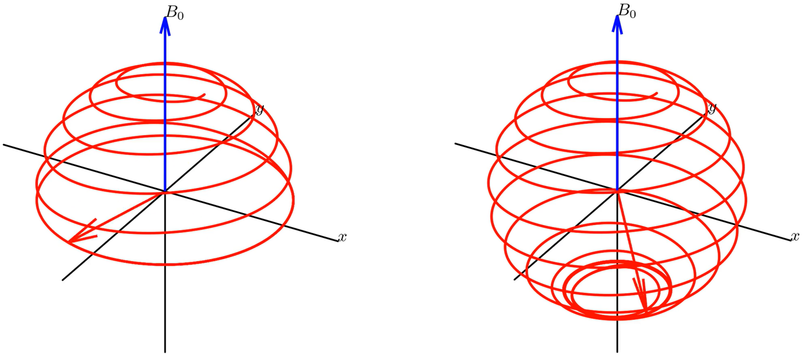
Circularly Polarized Field

$$\vec{B}_1(t) = B_1 \left[\cos(\omega_0 t)\hat{x} + \sin(\omega_0 t)\hat{y}\right] \tag{7}$$

To "tip" magnetization into xy plane, apply a circularly polarized $\vec{B}_1(t)$. Classical torque result in a rotating frame yields,

$$\vec{B}^* = \left(\left[\vec{B}_0 - \frac{\omega_0}{\gamma} \right] \hat{z}^* + B_1 \hat{x}^* \right) \tag{8}$$

$\frac{\pi}{2}$ and π pusles



(a) $\frac{\pi}{2}$ pulse produces transverse magentization (b) π pulse flips magentization from $+\hat{z}$ to $-\hat{z}$

Figure: $\langle\vec{S}\rangle$ over time during a $\frac{\pi}{2}$ and π pulse

Spin-Lattice Relaxation (T_1)

Time constant associated with decay of net magnetization back towards $+\hat{z}$.

$$\frac{d\vec{M}(t)}{dt} = \frac{\vec{M}(t) - \vec{M}_0}{T_1} \tag{9}$$

Referred to as the **Bloch equations**.

Spin-Spin Relaxation (T_2)

Time constant associated with the decay of the relative “coherence” of spins in xy plane, with associated Bloch equation [2],

$$\frac{d\vec{M}_{x,y}}{dt} = \frac{\vec{M}_{x,y}}{T_2} \tag{10}$$

Free Induction Decay and T_2^*

- Observations performed with a pickup coil detecting flux in transverse direction
- Magnetization becomes increasingly decoherent; produces **free induction decay (FID)** signal
- Combined effects of spin-lattice, spin-spin, and field inhomogeneities [2]

$$\frac{1}{T_2^*} = \frac{1}{T_1} + \frac{1}{T_2} + \gamma \Delta B_0 \tag{11}$$

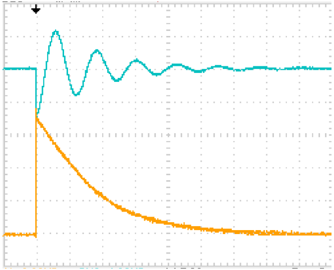


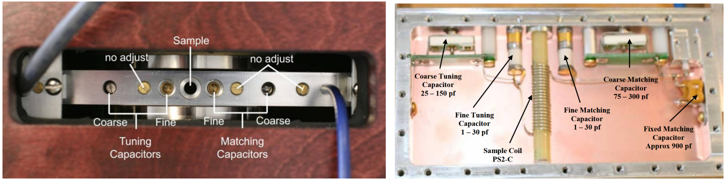
Figure: Basic FID signal of mineral oil [3]

Apparatus: TeachSpin NMR Set

Figure: Pulsed/CW NMR Spectrometer, PS2-B

Permanent Magnet

- .5 T magnetic field
- RF sample measurement coil
- Tuning capacitors (find resonance with RF coil)
- Thermal servo units/Field gradient coils



(a) Capacitors (b) RF Coil

Figure: Diagrams of RF coil and capacitors

PS2 Controller

- Field gradient coil control → Maximize homogeneity
- Magnet temperature control → Indicate reference temperature

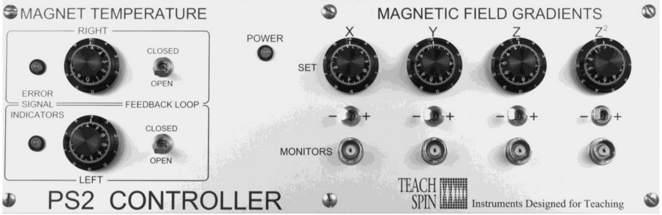


Figure: Temperature controller

Mainframe

- Receiver
  - Process RF sample signal
  - Tunable gain and filter
- Synthesizer
  - Generates RF excitation signal
- Pulse Programmer $\rightarrow$ Some Controls:
  - A and B length
  - A and B delay time

Some Notes on Pulse Sequencing

Recall,

$\frac{\pi}{2}$ pulse

- Flips net magnetization into xy plane
- Generates FID signal

π pulse

- Flips net magnetization along $-\hat{z}$ axis
- No FID signal

What happens after a $\frac{\pi}{2}$ pulse?

- FID signal decays primarily due to spin dephasing from field inhomogeneities*
- Spins decay back to the $+\hat{z}$-axis (even after FID signal disappears)

Dephasing due to field inhomogeneities

- Static magnetic field pointing in z produces a torque that causes the spin to rotate in the xy plane
- Different field magnitudes cause different rotation speeds
- If all the spins are aligned in the xy plane, FID signal is strong
- If they are misaligned (out of phase), FID signal is weak
- This makes it hard to measure T_2

What happens after a π pulse?

- FID does not form since spins are not in xy plane
- Spins decay back to the $+z$-axis (no FID signal forms)

T_1 Measurement Sequence: $\frac{\pi}{2} - \pi$

- Apply a $\frac{\pi}{2}$ pulse.
    - Magnetization enters xy plane and dephases Spins slowly decay to $+\hat{z}$
- Apply another $\frac{\pi}{2}$ pulse a little later
    - xy spins kicked to the $-\hat{z}$-axis (no FID signal)
    - $+\hat{z}$ spins kicked to the xy (FID signal)
- Gives an idea of how fast longitudinal spins decay

T_1 Measurement Sequence: $\pi - \frac{\pi}{2}$

- Apply a π pulse.
  - Net magnetization jumps to $-\hat{z}$ (no signal)
  - Spins slowly decay to $+\hat{z}$
- Apply a $\frac{\pi}{2}$ pulse a little later
  - Spins along $-\hat{z}$ are kicked to $-\hat{x}$
  - Spins along $+$z are kicked to $+\hat{x}$
  - If no FID signal is produced (half life)
- Much more elegant

T_2 Measurement Sequence: $\frac{\pi}{2} - \pi$

- Apply a $\frac{\pi}{2}$ pulse $\rightarrow$ Net magnetization enters the xy plane and dephases
- Apply a π pulse a little later
    - Spins remain in xy plane, but 'reverse' rotation direction
    - Spins rephase a little later
- The decay in rephasing signal follows T_2

Using More Pulses

- To better characterize the decay multiple π pulses are applied
- Must be close together to mitigate molecular diffusion
  - Spin dephases at one speed and returns at another
  - Will not rephase with the rest

Experimental Procedure: Resonance

- Tune RF frequency to proton resonance (21 MHz) $\rightarrow$ Minimize beats
- Use tuning capacitor to maximize FID signal

$\frac{\pi}{2}$ and π pulses

- Apply a single RF pulse and vary its length
- Find the length with maximum FID signal
- This is a $\frac{\pi}{2}$ pulse
- Double the length to find π pulse length

Sequencing

- Use adequate pulse sequences to measure decay times
- Record data for processing to calculate characteristic times T_1 and T_2

References

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Pulsed Nuclear Magnetic Resonance.