Introduction to 1D and 2D NMR Spectroscopy

(2) Vector Model and Relaxations

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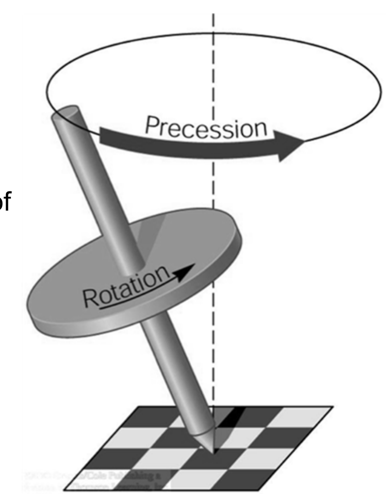
Rules of Electromagnetism (1): Behaviors of the Magnetic Moments

1. In the field of gravity, a stationary object would simply fall, while a spinning object (a *moment*) would <u>precess</u>
   – Precession is around the direction of gravity
2. Precession of the magnetic moment on the horizontal plane (around the z-axis) emits signal
3. Signal intensity ∝ amplitude of horizontal component



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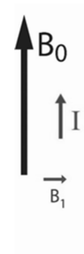
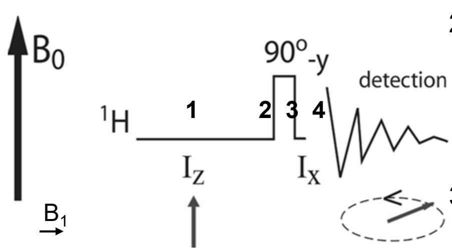
Rules of Electromagnetism (2): Resonance

- When the frequency of the pulse satisfies the Larmor Equation ("resonance"), the oscillation of the pulse and the external field B_0 cancels each other, resulting in a static horizontal magnetic field B_1
  - i.e., during pulsing, B_0 can be considered non-existent, and only B_1 is at play
  - B_0 and B_1 are the magnetic fields, which influence the magnetic moments
  - I is the magnetic moments, i.e., the object to be manipulated by the fields



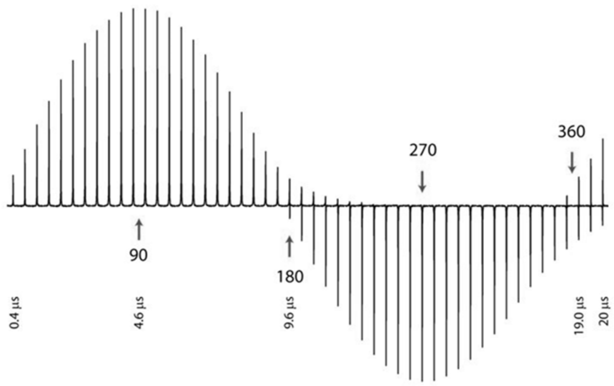
Vector Model of NMR **



1. Magnetic moments are aligned along z direction
2. A pulse creates a horizontal magnetic field B_1 along -y direction, which (1) cancels B_0; (2) causes the magnetic moments to precess around B_1
3. The pulse stops when the magnetic moments turns 90° , toward x
4. Magnetic moments precess around B_0, generating signal

- Two precessions:
  - 1. during pulsing, on a vertical circle, around the horizontal field B_1 created by the pulse
  - 2. after pulse stops, on a horizontal circle, around the vertical big field B_0
- Angle turned by the pulse $\propto$ pulse length
- Signal strength $\propto$ horizontal component of the magnetic moment

Signal strength at imcrementing pulse length



- Increment step = 0.4 µs
- First maximum of signal appears at ca. 4.6 µs
- First null point appears at 9.6 µs 5

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Use These Questions to Familiarize Yourself with Vector Model

- Suppose a pulse of 10 µs turns the vector by 90°, generating a signal with intensity of 1. What would signal intensity be for pulses of
  - 20 µs?
  - 30 µs?
  - 40 µs?
  - 5 µs?
  - 3.33 µs?

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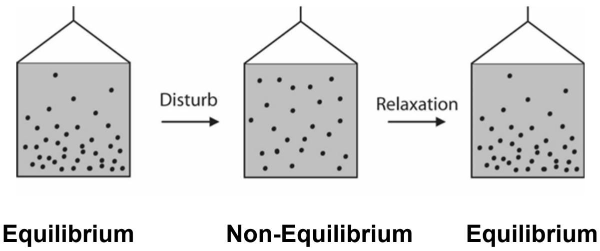
T_1 and T_2 Relaxations



- Relaxation: process from high-energy (excited) state to low-energy (equilibrium) state
- The higher the energy gain upon relaxation, the easier the relaxation is to occur

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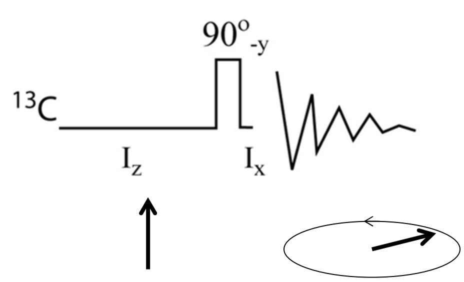
Relaxations in Vector Model **



- T_1: coming back to I_z = 1 (with no concern about $I_{x,y}$)
- T_2: coming back to $I_{x,y}$ = 0 (with no concern about I_z)
- T_1 and T_2 are independent processes
  - Vertical and horizontal components recover at different rates
- Don't confuse T_1 / T_2 relaxation with molecular relaxation

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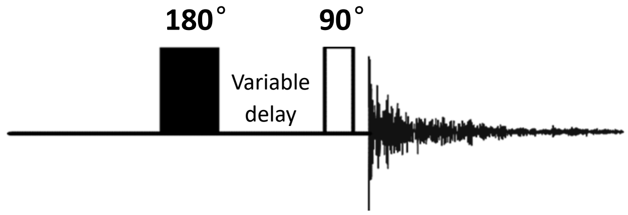
T_1 Measurement: Inversion Recovery



- What does the 180° pulse do?
- The 90° pulse: read out the signal

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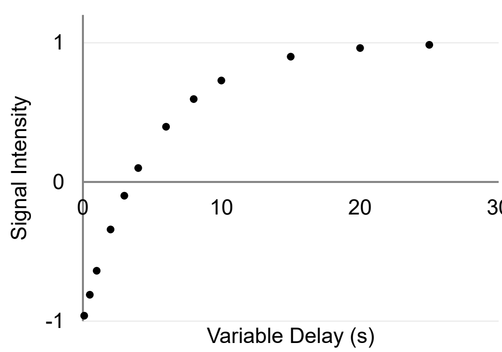
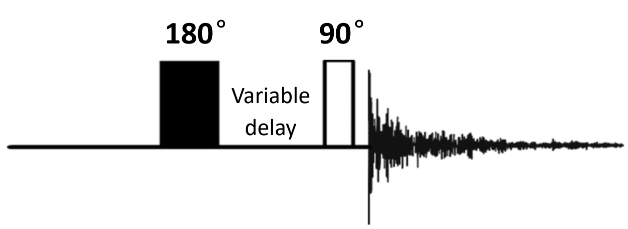
A Typical Inversion Recovery Curve





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- Why should I care about T_1 and T_2?
  - Is my spectrum quantitative?
  - Is everything in my sample showing up on the spectrum?
  - What are my molecule's physical behaviors?
- T_1 relaxation time affects signal intensity
  - Why?
- T_2 relaxation time affects signal width
  - $\Delta\nu = \frac{1}{\pi T_2}$

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Important Concepts

- Nuclear magnetic moments follow the rules of classical electromagnetics
  - Magnets will "precess" in an external magnetic field
  - Only horizontal component of magnetic moments gives out signal
- A 90° pulse, a 180° pulse, and what they do
- What are T_1 and T_2 relaxations, and what NMR properties that they affect

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