

## Nuclear Magnetic Resonance

### Chapter 19

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## Theory of Magnetic Resonance

- Magnetic Resonance is based on the postulate by W. Pauli in 1924 that certain atomic nuclei should have properties of spin and magnetic moment, and exposure to a magnetic field would result in splitting of their energy levels
- This phenomenon can be described in two ways
  - Quantum mechanics - provides the relationship between absorption frequencies and nuclear energy states
  - Classical mechanics - yields a clear physical picture of the absorption process and how it is measured.

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## Quantum Description of NMR

- Certain nuclei spin about an axis:
  - This results in an angular momentum,  $p$
  - Maximum observable  $p$  is an integral or half-integral multiple of  $h/2\pi$
  - Spin Quantum Number,  $I$ , is the maximum number of components of  $p$ , and can have values of  $I, I-1, I-2, \dots -I$
  - All values of  $I$  are degenerate in the absence of a magnetic field.

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## Quantum Description of NMR (II)

- A spinning, charged nucleus creates a magnetic field and has a magnetic moment,  $\mu$ , proportional to the angular momentum,  $p$

$$\mu = \gamma p$$

$\gamma$  = magnetogyric ratio

- Interaction between nuclear spin and magnetic moment gives observable quantum states,  $m = l, l-1, l-2, \dots -l$ .

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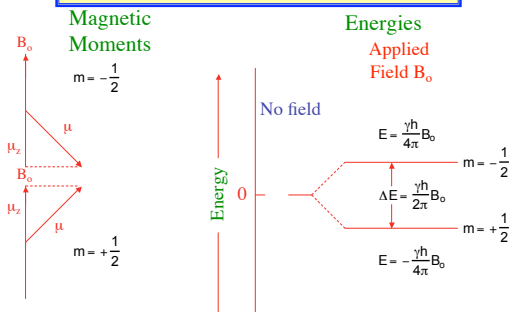
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### Magnetic Moments and Energy Levels $m = \pm 1/2$



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## Absorption of Radiation

The energy absorbed in the transition from the ground state to the excited state is derived from the energy difference between the two states.

$$\Delta E = h\nu = h \left( \frac{\gamma B_0}{2\pi} \right)$$

Thus the frequency of radiation absorbed is:

$$\nu_0 = \frac{\gamma B_0}{2\pi}$$

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## Distribution of Particles between Magnetic Quantum States

$$\frac{N_i}{N_o} = \exp\left(\frac{-\Delta E}{kT}\right)$$

Substituting for  $\Delta E$ :

$$\frac{N_i}{N_o} = \exp\left(\frac{-\gamma h B_o}{2\pi kT}\right)$$

- There are only a few more gs than es nuclei at room temperature
- The success of NMR depends on this excess
- It can be shown that the number of gs nuclei increases with  $B_o$ .

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## Classical Description of NMR

- A spinning nucleus precesses around a vector representing the magnetic field
- The frequency of precession is the Larmor Frequency, which is identical to the absorbed frequency in the quantum description
- Absorption of appropriate radiation will cause the spin to flip its orientation to the applied field
- This occurs in the radio frequency range.

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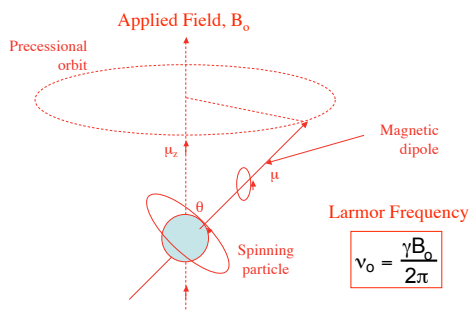
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## Precession of a Rotating Particle in a Magnetic Field



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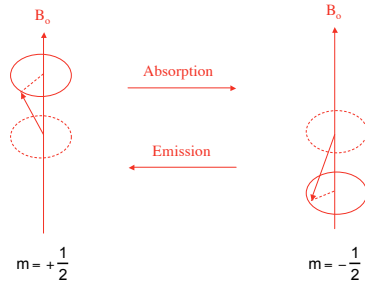
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## Absorption of Radiation By a Precessing Particle



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## Relaxation Processes

- Saturation occurs when # es = #gs and no further absorption can occur
- Relaxation must occur for NMR to remain viable
  - Relaxation should be fast so that an absorption signal can be detected
  - But, there is an inverse relationship between the lifetime of the e.s. and the width of the absorption line
- Two important relaxation processes exist
  - Spin-Lattice or Longitudinal Relaxationand
  - Spin-Spin or Transverse Relaxation

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## Spin-Lattice Relaxation

- Excited nuclei can relax by transferring energy to another nucleus in the lattice which has the same precessional frequency
  - 1st order process with a relaxation time,  $T_1$
  - $T_1$  is a measure of the average lifetime in the es
  - $T_1$  is strongly affected by the lattice mobility
    - Glasses and viscous liquids have large  $T_1$
  - $T_1$  can also increase in very mobile lattices.

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## Spin-Spin Relaxation

- Other relaxation processes can broaden NMR lines. These are called transverse or spin-spin relaxation,  $T_2$ 
  - $T_2$  values are very small for solids - difficult to run solid spectra
  - Neighboring nuclei with identical precession rates can exchange states - result is broadening
  - Many of these relaxation processes can be overcome by rapidly spinning the sample.

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## FT NMR

- Intense pulse saturates all nuclei
- Nuclei relax according to their spin-lattice interactions
- A Free Induction Decay, FID signal is detected by a radio receiver
- Summed data are converted to frequency domain by Fourier Transformation.

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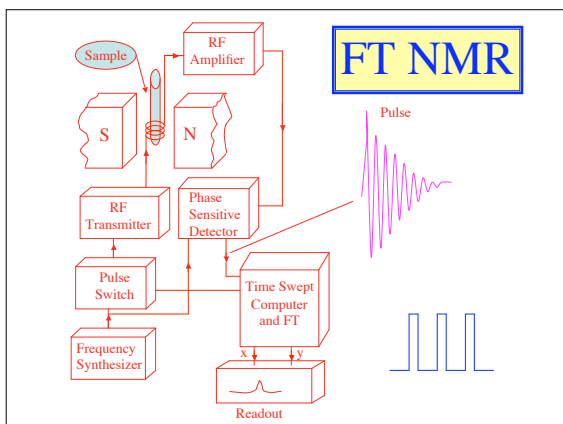
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## Magnets

- Sensitivity and resolution are critically dependent on quality of magnet
  - Both sensitivity and resolution increase with field strength
  - Superconducting magnets can achieve fields of 21T or proton frequencies of 900 MHz
  - Helium Dewar surrounded by N<sub>2</sub> Dewar
  - Field must be homogeneous to a few ppb in sample area. Difficult to obtain in practice.

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## Compensation for Drift and Homogeneity Variations

- Field/frequency lock: a reference nucleus is continually radiated and the signal monitored. Fluctuations are automatically compensated for by adjusting the field
- Shimming: small coils are provided a current to augment the field in various directions. Must be adjusted for each sample
- Sample spinning: corrects for sample inhomogeneities.

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## Types of NMR Spectra

- Wide-Line Spectra - Chemical structure is obscured by wide bandwidth of source lines
  - Quantitative identification of isotopes
  - Usually use low magnetic fields
- High-Resolution Spectra - Capable of differentiating frequencies of 0.01 ppm or less
  - Provide information about chemical environments of nuclei.

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## The Chemical Shift

- Caused by small magnetic fields generated by electrons - usually in opposition to the applied field

$$B_o = B_{\text{appl}} - \sigma B_{\text{appl}} = B_{\text{appl}}(1 - \sigma)$$

$\sigma$  is the screening constant

- For isolated protons  $\sigma$  is 0
- Different chemical environments will require different  $B_{\text{appl}}$  to bring protons into resonance

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## Spin-Spin Splitting

- Interaction of the magnetic moment of a nucleus with the magnetic moments of adjacent nuclei results in a splitting of the peak
  - Spin-spin splitting is independent of the applied field
  - Spin-spin effects are superimposed on the effects of the chemical shift.

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## Plotting Chemical Shifts

- TMS is used as an internal reference which has many equivalent protons, and exhibits a large screening constant
  - The chemical shifts of other protons are compared to those of TMS
  - The chemical shift parameter,  $\delta$  is defined as:
$$\delta = (\sigma_{\text{ref}} - \sigma_{\text{sample}}) \times 10^6$$
  - $\delta$  has the same value regardless of  $B_{\text{applied}}$ .

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## Rules for the Interpretation of First-Order Spectra

- Equivalent nuclei do not interact
- Coupling constants decrease with distance and coupling is seldom observed > 4 bonds
- Multiplicity of the splitting is n+1 splitting protons
- If more than one set of protons splits, the multiplicities are multiplicative
- Approximate relative areas of peaks is determined by the expansion  $(x+1)^n$
- Coupling is independent of applied field.

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