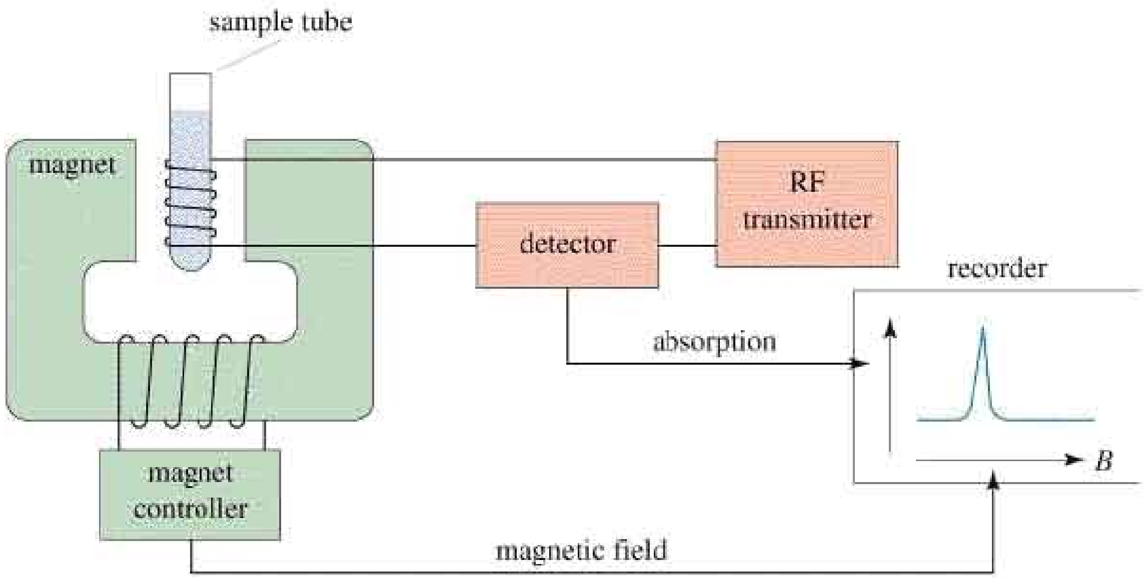
NUCLEAR MAGNETIC RESONANCE (NMR) SPECTROSCOPY

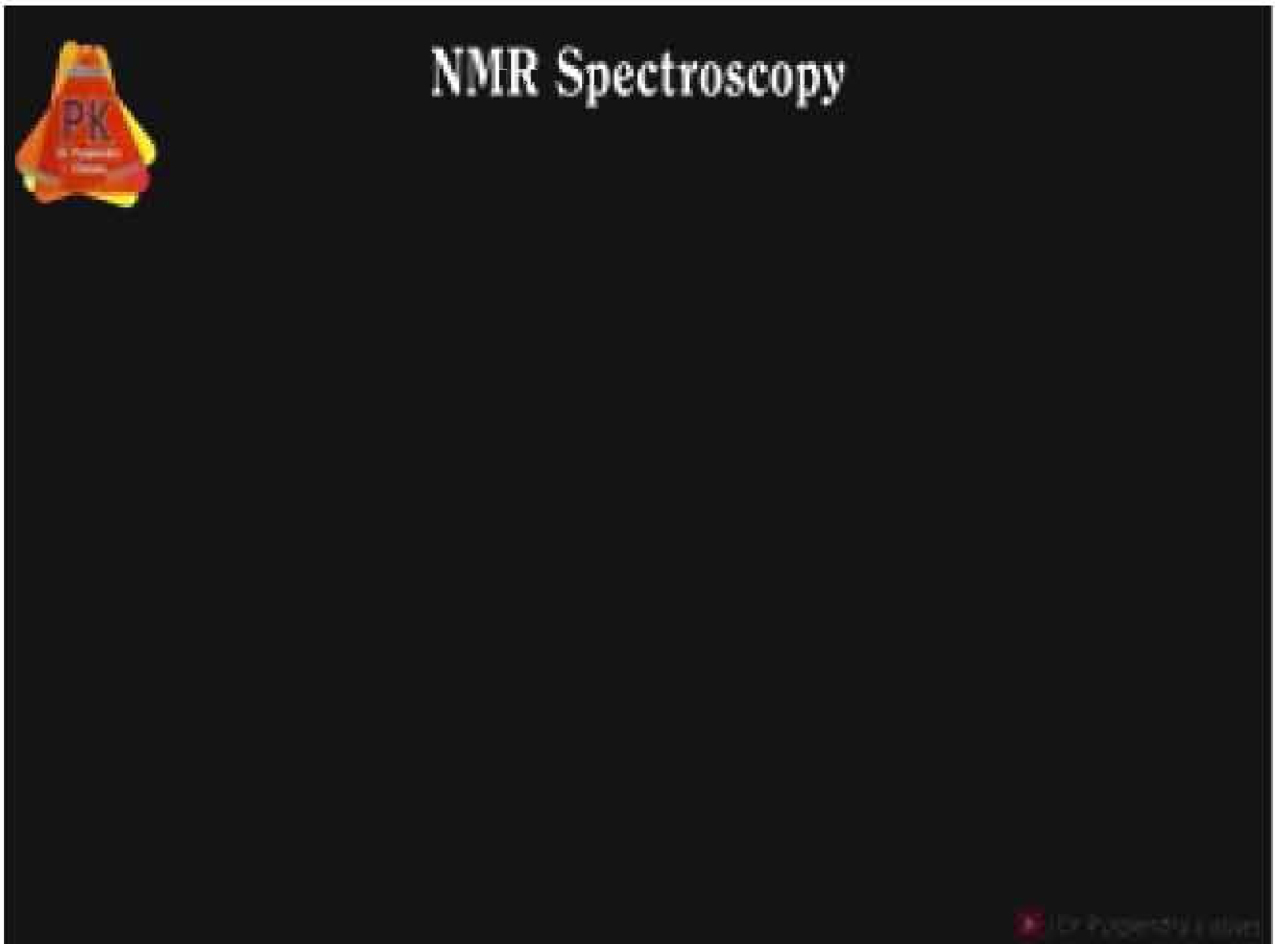


By: Dr Nikhil kumar Kaushik

Nuclear Magnetic Resonance (NMR) Spectroscopy

- The **principle** behind **NMR** is that many nuclei have spin and all nuclei are electrically charged. If an external magnetic field is applied, an energy transfer is possible between the base energy to a higher energy The nuclei of all elements carry a charge. When the spins of the protons and neutrons comprising these nuclei are not paired, the overall spin of the charged nucleus generates a magnetic dipole along the spin axis, and the intrinsic magnitude of this dipole is a fundamental nuclear property called the nuclear magnetic moment, μ. level (generally a single energy gap).

Nuclear Magnetic Resonance (NMR) Spectroscopy



Nuclear Magnetic Resonance (NMR) Spectroscopy

NMR Sensitivity

But at a significant cost!

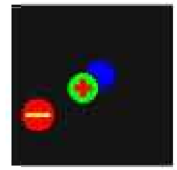
~$800,000

~$2,00,000

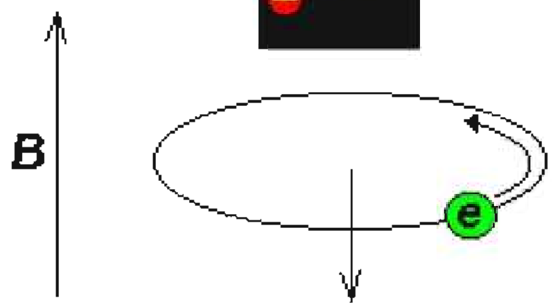
~$4,500,000

A Basic Concept in ElectroMagnetic Theory

A Direct Application to NMR

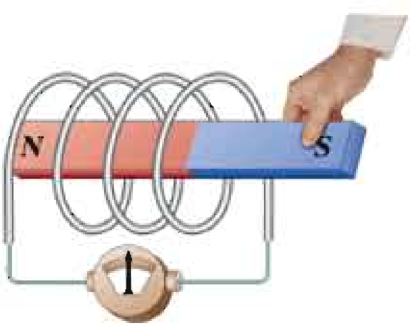


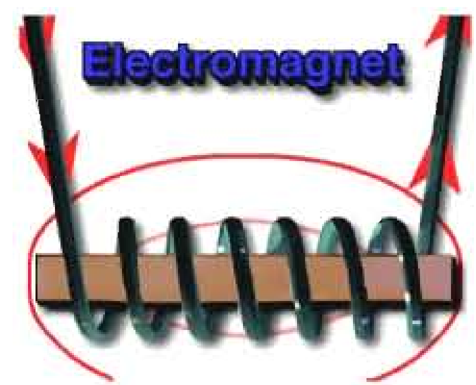
A moving perpendicular external magnetic field will induce an electric current in a closed loop



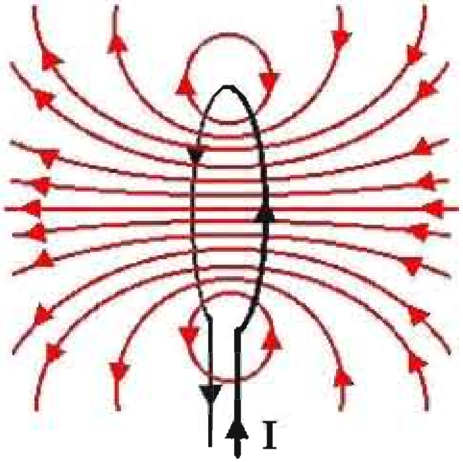
An electric current in a closed loop will create a perpendicular magnetic field

Magnetic field produced by circulating electron





A Basic Concept in ElectroMagnetic Theory



For a single loop of wire, the magnetic field, B through the center of the loop is:

$$B = \mu_o I / 2R$$

μ_o – permeability of free space ($4\pi \times 10^{-7}$ T · m / A)
R – radius of the wire loop
I – current

Theory of NMR

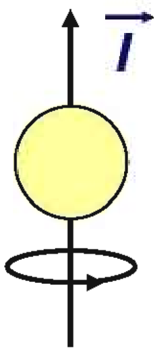
Quantum Description

Nuclear Spin (think electron spin)

- Nucleus rotates about its axis (spin)
- Nuclei with spin have angular momentum (p) or spin

1) total magnitude

$$\hbar\sqrt{I(I+1)}$$



1) quantized, spin quantum number I

2) $2I + 1$ states: $I, I-1, I-2, \ldots, -I$

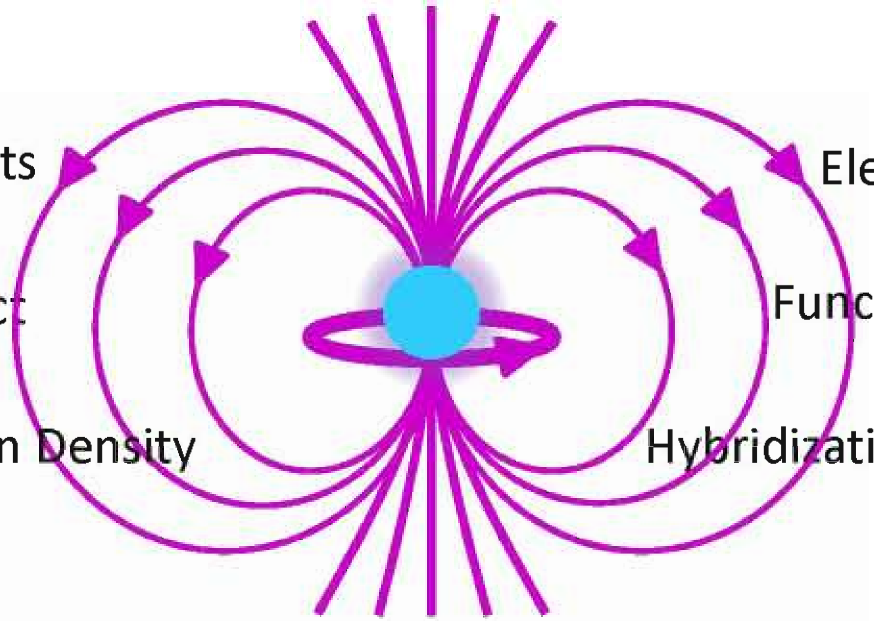
$I=1/2$: $-1/2, 1/2$

3) identical energies in <u>absence</u> of external magnetic field

Learning Module #3

Chemical Shift and Multiplicity

3.1 Chemical Shifting



Chemical Environments

Electronegativity

The Shielding Effect

Functional Groups

Electron Density

Hybridization

3.2 Multiplicity

Multiplicity

Equivalent Protons

Coupling Constant

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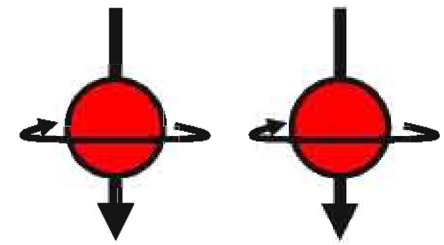
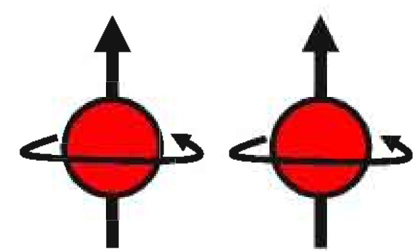
NMR Spectroscopy

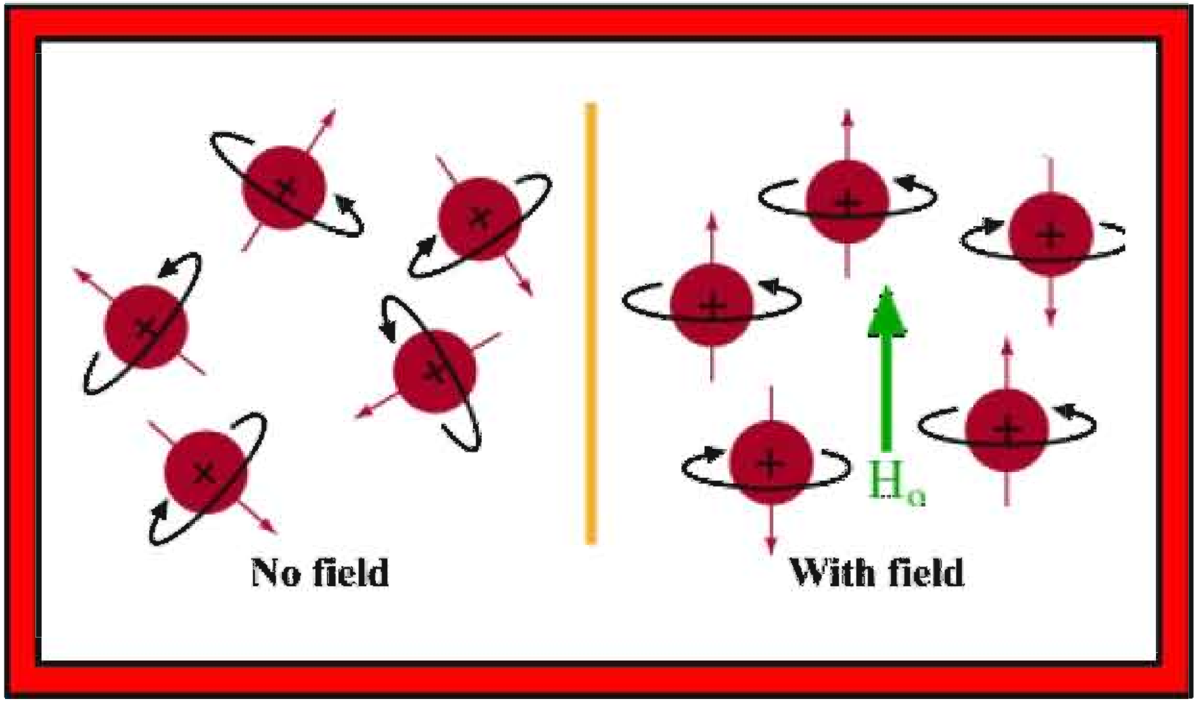




NUCLEAR SPIN

How does nuclear spin relate to quantum numbers learned in general chemistry?

NMR spectroscopy employs an magnetic energy absorption process, which orients spinning nuclei in a strong external magnetic field. (1)

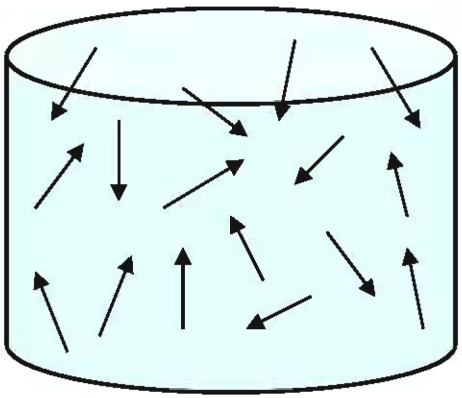


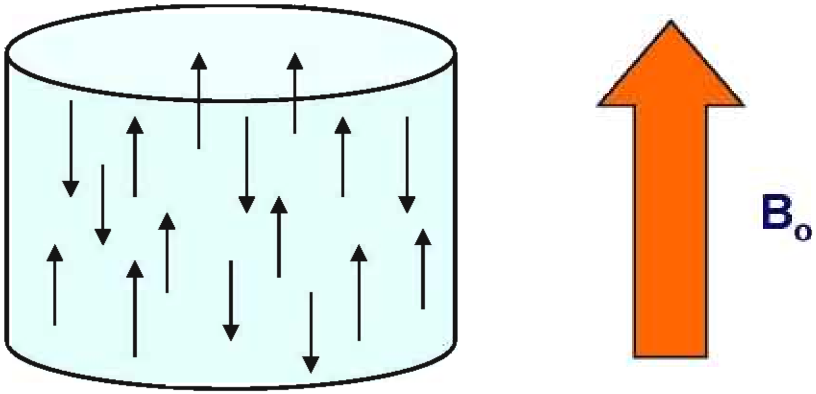
H^{1} C^{13} N^{14} F^{19} P^{31}

NMR spectroscopy observes isotopes having odd mass numbers and/or odd atomic numbers.*

Magnetic alignment

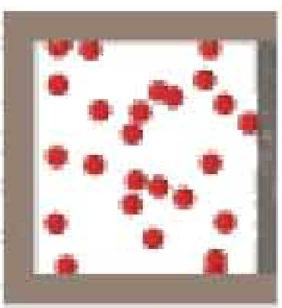
$\uparrow = \gamma h / 4\pi$

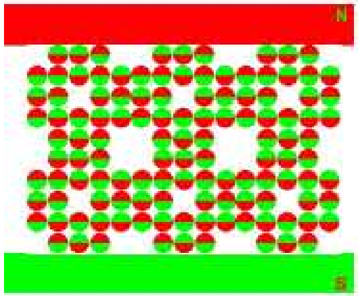




In the absence of external field,
each nuclei is energetically degenerate

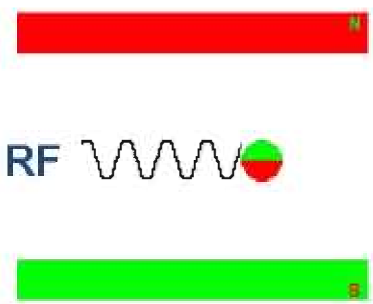
Add a strong external field (B_o) and the nuclear magnetic moment: aligns with (low energy)
against (high-energy)

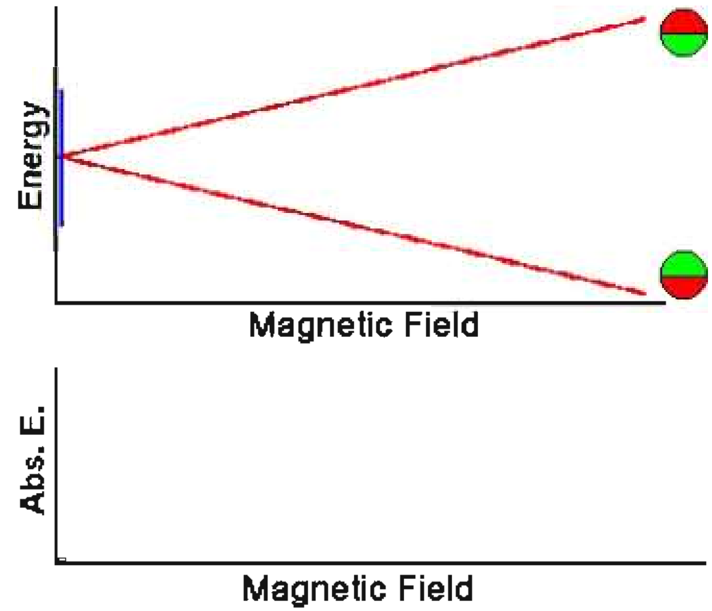




Spins Orientation in a Magnetic Field (Energy Levels)

- Transition from the low energy to high energy spin state occurs through an absorption of a photon of radio-frequency (RF) energy

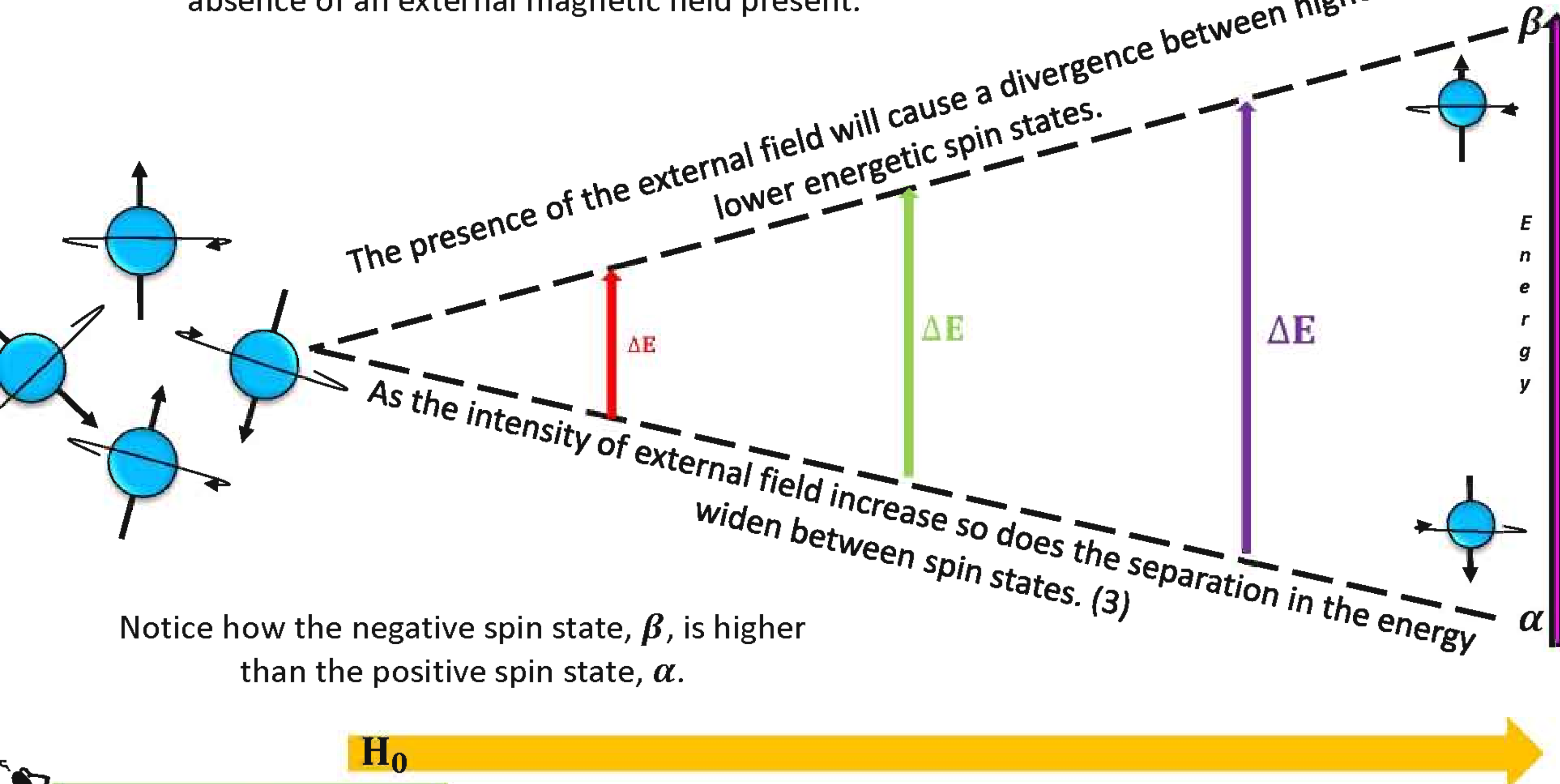




Frequency of absorption: $\nu = \gamma B_o / 2\pi$

Magnetic Resonance

Initially, there is no difference between spin states in the absence of an external magnetic field present.



Notice how the negative spin state, $\boldsymbol{\beta}$, is higher than the positive spin state, $\boldsymbol{\alpha}$.

Why is the negative spin state higher than the positive spin state?

The process of nuclear magnetic resonance occurs in a spectrometer in the following method:

1) Specific magnetic field strengths are generated on the z axis by a powerful magnet.

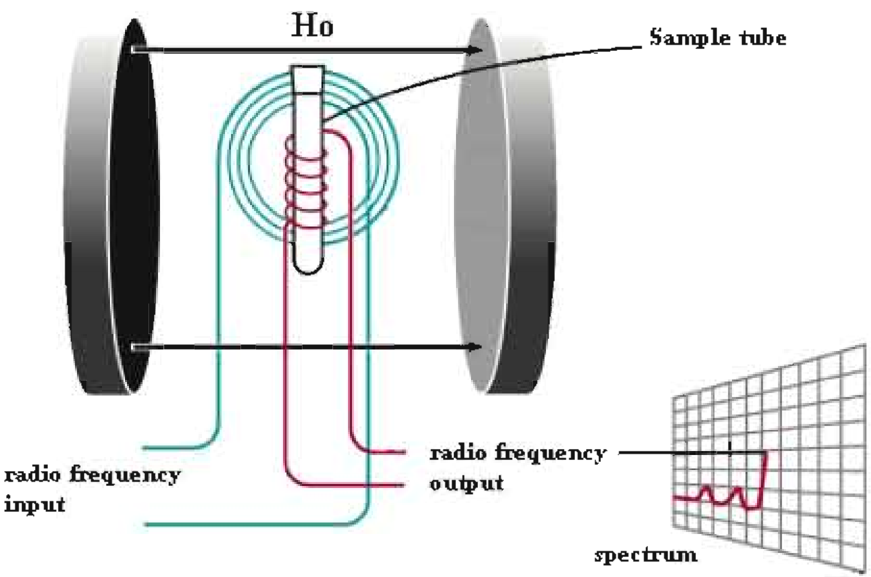
2) A sample is placed in the spectrometer and is bombarded with RF at a constant pace along the x axis.

3) When the external applied field establishes the correct intensity, resonance occurs as the nuclei of the sample absorb the supplied RF.

4) Resonance causes the nuclei to absorb a small current of electricity, which is noted by the receiver coil encompassing the sample.

5) The spectrometer amplifies the current from the receiver into a display of signals, known as an NMR spectrum.

The resulting illustration of an NMR spectrum can be deciphered into the sample's structure.



The Spectrometer

Larmor precession

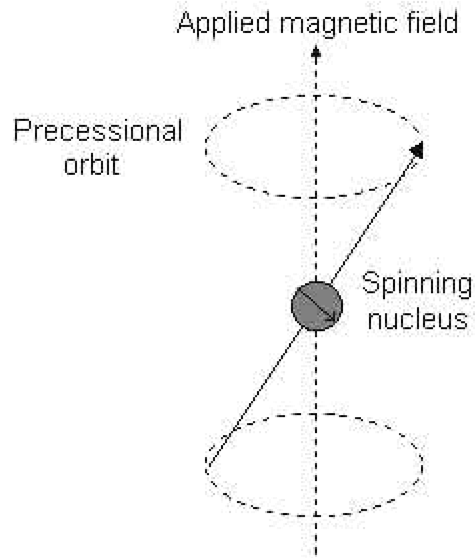
- In physics, **Larmor precession** (named after Joseph Larmor) is the precession of the magnetic moment of an object about an external magnetic field. Objects with a magnetic moment also have angular momentum and effective internal electric current proportional to their angular momentum; these include electrons, protons, other fermions, many atomic and nuclear systems, as well as classical macroscopic systems. The external magnetic field exerts a torque on the magnetic moment,

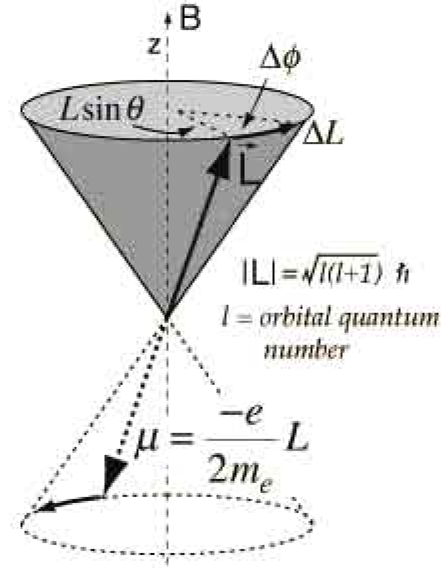
larmour procession

Theory of NMR

- *Spinning particle precesses around an applied magnetic field*

A Spinning Gyroscope in a Gravity Field





$$\cos\varphi = \sqrt{\frac{m}{I(I+1)}}$$

Classical Description

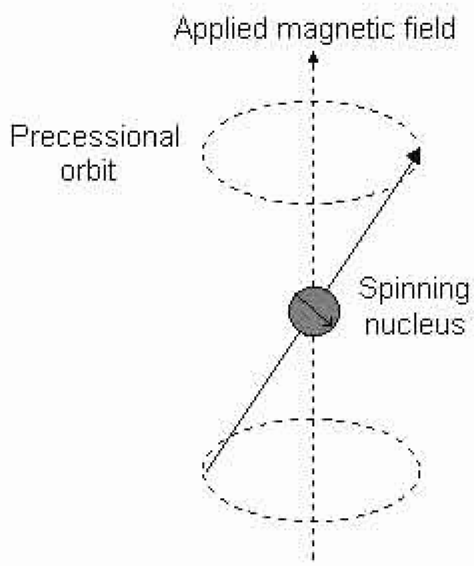
- *Angular velocity of this motion is given by:*

$$\omega_o = \gamma B_o$$

where the frequency of precession or **Larmor** frequency is:

$$\nu = \gamma B_o / 2\pi$$

Same as quantum mechanical description



different scales (δ and τ),

- Chemical shift is measure in three major spectra.
  - Delta(δ)
  - Tau scale(τ)
  - Hertz (H_z)

Up field shielding

Down field shielding

5	**4**	**3**	**2**	**1**	**0**	δ scale
5	6	7	8	9	10	T scale
1000	800		400		100	H_z

Spin-Spin Splitting in ^{1}H NMR Spectra

- Peaks are often split into multiple peaks due to *magnetic interactions* between nonequivalent protons on adjacent carbons, The process is called spin-spin splitting.
- The splitting is into one more peak than the number of H's on the adjacent carbon(s), This is the "n+1 rule"
- The relative intensities are in proportion of a binomial distribution given by Pascal's Triangle
- The set of peaks is a multiplet (2 = doublet, 3 = triplet, 4 = quartet, 5=pentet, 6=sextet, 7=heptet…..)

SPIN–SPIN COUPLING (SPLITTING): (*n* + 1) Rule

- **NMR Signals:** not all appear as a single peak.
- **Peak:** The units into which an NMR signal appears: singlet, doublet, triplet, quartet, etc.
- **Signal splitting:** Splitting of an NMR signal into a set of peaks by the influence of neighboring nonequivalent hydrogens.
- **(*n* + 1) rule:** If a hydrogen has *n* hydrogens nonequivalent to it but equivalent among themselves on the same or adjacent atom(s), its ^{1}H-NMR signal is split into (*n* + 1) peaks.

Origins of Signal Splitting

- **Signal coupling:** An interaction in which the nuclear spins of adjacent atoms influence each other and lead to the splitting of NMR signals.
- **Coupling constant (J):** The separation on an NMR spectrum (in hertz) between adjacent peaks in a multiplet.
  - A quantitative measure of the influence of the spin-spin coupling with adjacent nuclei.