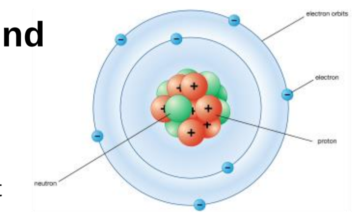
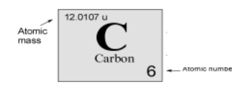
NMR Spectroscopy: Basic Theory
Lecture 2

Dr. Mohamed Abdul Aal

Background



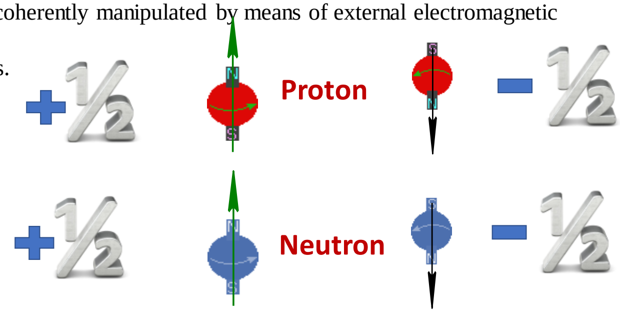


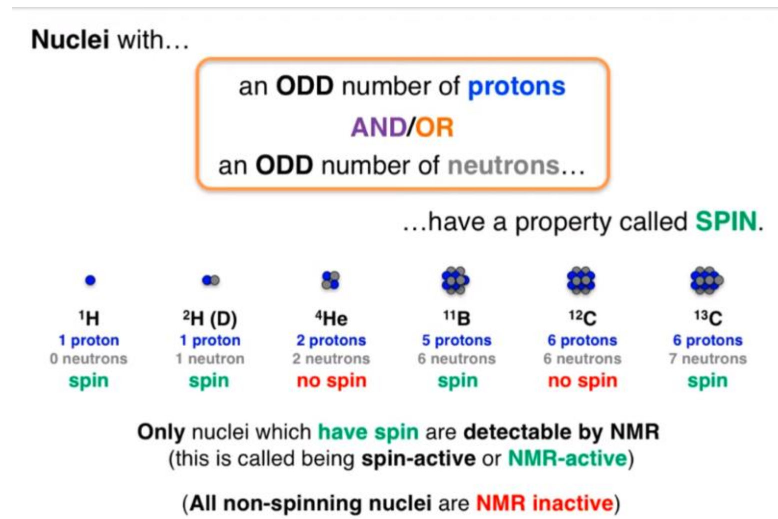
- Atoms are made up of electrons and ***nuclei***.
- Each atomic nucleus has four important physical properties: ***mass***, ***electric charge***, ***magnetism*** and ***spin***.
- The *atomic number* specifies the number of protons inside the nucleus.
- The *mass number* specifies the number of nucleons in the nucleus, i.e. the total number of protons and neutrons. Nuclei with the same atomic number but different mass numbers are called *isotopes*.
- Nuclear magnetism and nuclear spin have almost no effect on the normal behavior of substances. **But they are important in NMR spectroscopy**.

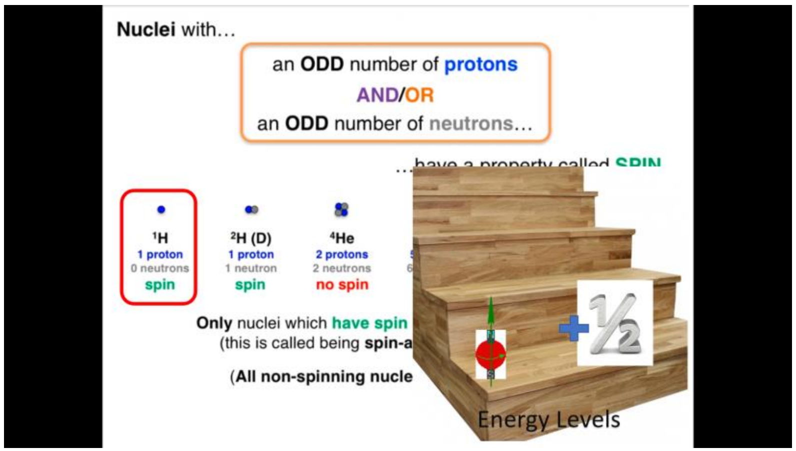
5

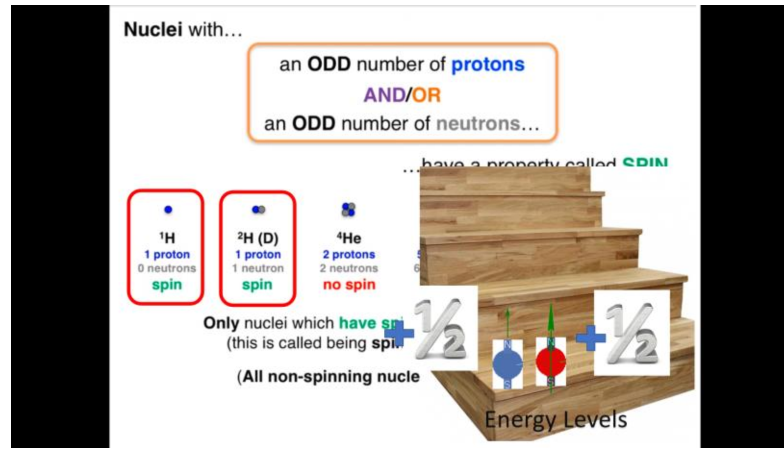
Molecular Spin theory?????!!!!!!

- Spins in solids or in molecules creates a magnetic flux and possess discrete energy levels, and the associated quantum states can be tuned and coherently manipulated by means of external electromagnetic fields.






Nuclei with…
an ODD number of protons
AND/OR
an ODD number of neutrons…
¹H
1 proton
0 neutrons
spin
²H (D)
1 proton
1 neutron
spin
⁴He
2 protons
2 neutrons
no spin
Only nuclei which have spin
(this is called being spin-a
(All non-spinning nucle
½
Energy Levels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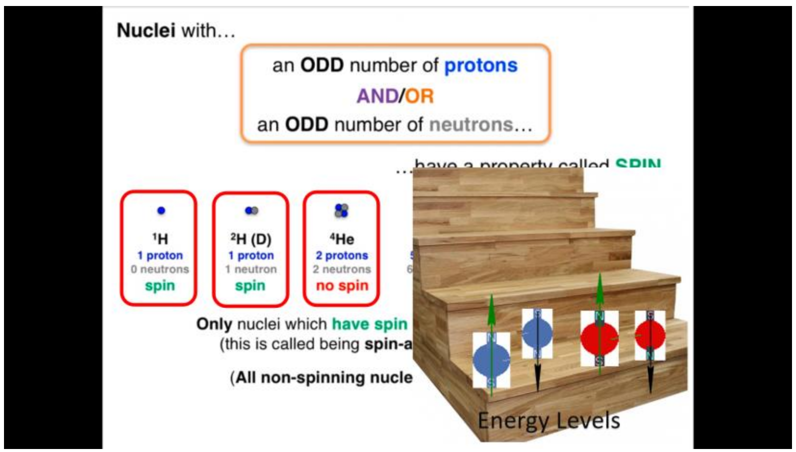
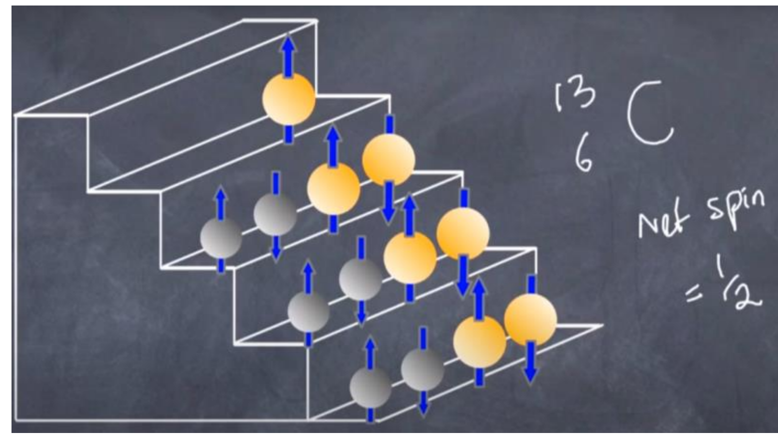




Can you tell me why the ^{12}C has no Spin?????

Spin has a **value (** I **)**, which can either be an **integer** or a **half-integer.**

Nuclei with…

an **ODD** number of **protons**
AND
an **ODD** number of **neutrons**…

…have **INTEGER** spins.

There are **only a handful** of **integer-spin** nuclei:

^{2}H = **1** ^{6}Li = **1** ^{10}B = **3** ^{14}N = **1** ^{50}V = **6** ^{138}La = **5**

Spin has a **value (** I **)**, which can either be an **integer** or a **half-integer.**

Nuclei with…

an **ODD** number of **protons**
OR
an **ODD** number of **neutrons**…

…have **HALF-INTEGER** spins.

There are **many half-integer-spin** nuclei, some examples:

^{1}H = **1/2** ^{13}C = **1/2** ^{15}N = **1/2** ^{19}F = **1/2** ^{31}P = **1/2**

^{11}B = **3/2** ^{17}O = **5/2** ^{43}Ca = **7/2** ^{209}Bi = **9/2**

The **total number** of **spin states** available to a nucleus **in an applied magnetic field** is given by:

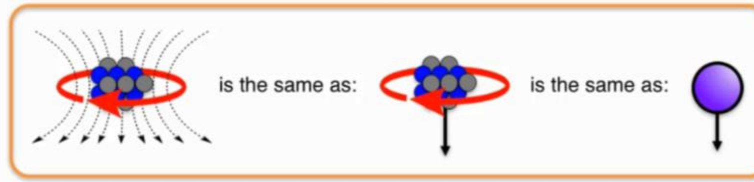
Number of spin states = $2I + 1$

(where I is the **spin** value)

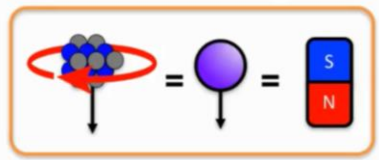
^{1}**H** ($I = 1/2$) = **2**	^{10}**B** ($I = 3$) = **7**
^{2}**H** ($I = 1$) = **3**	^{11}**B** ($I = 3/2$) = **4**
^{13}**C** ($I = 1/2$) = **2**	^{209}**Bi** ($I = 9/2$) = **10**

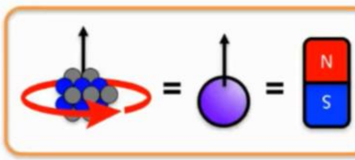
The **vast majority of the time**, we use **spin 1/2 nuclei** (**^{1}H and ^{13}C**)

We can represent the **magnetic moment of our nucleus** using a **single arrow**:



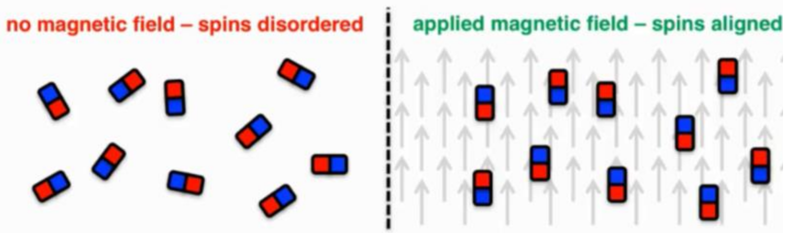
So, using our **bar magnet analogy**…





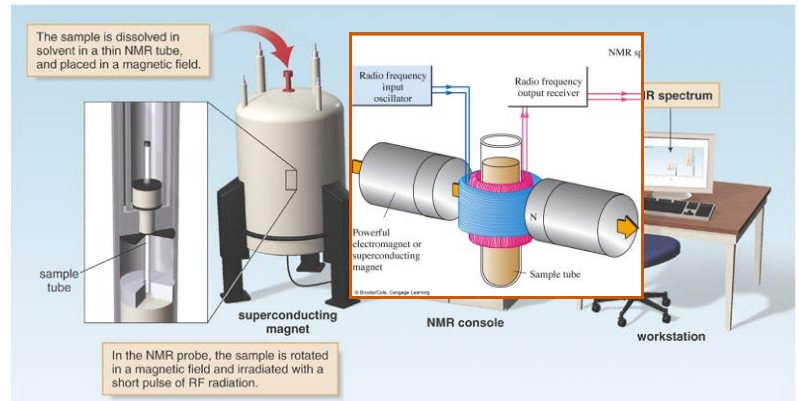
Under **normal conditions**, nuclei are free to orient their spin **however they like**.

There is **no energy difference** from one orientation to another (they are **degenerate**) and the **spins** of any given group of nuclei will be **disordered**.



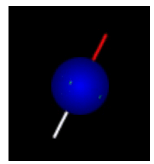
When you **place spinning nuclei in an** external (applied) magnetic field, they will **align their spins** in specific ways called spin states**:**

NMR Spectroscopy... Spectrometer



14

The Main Terms you must know for the NMR?



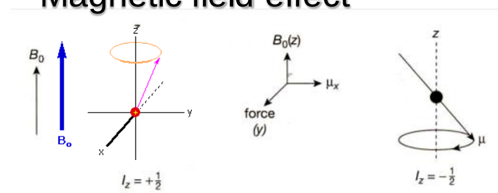
- Precessional motion : A form of motion that occurs when a torque is applied to a rotating body in such a way that it tends to change the direction of its axis of rotation.
- Larmor frequency: refers to the rate of precession of the magnetic moment of the proton around the external magnetic field
- Magnetic moment, also known as magnetic dipole moment, is the measure of the object's tendency to align with a magnetic field
- Gyromagnetic ratio of a particle or system is the ratio of its magnetic moment to its angular momentum

Magnetic Field

No magnetic field - all nuclei of the same isotope have the same energy

Magnetic field effect

B (magnetic field)
Larmor frequency:
o

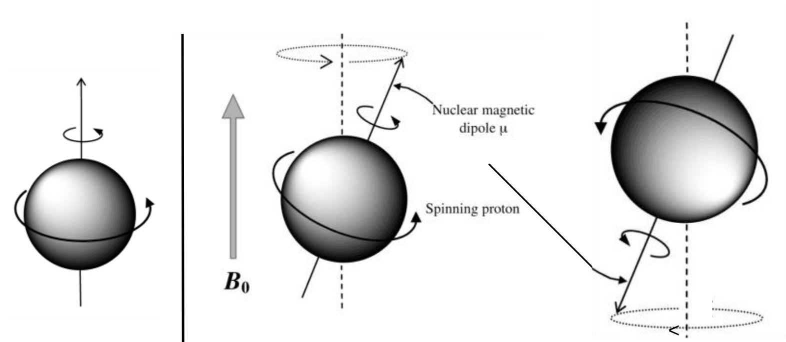


-The magnetic field $\mathbf{B_0}$ attempts to align the magnetic moment μ of particle spin with the field direction, but its angular momentum causes instead a **precessional motion of μ around the field axis**.

-Resonance phenomenon: absorption of energy by a spinning nucleus.

-NMR exploits magnetic properties of nuclei to provide the structure.

A Proton Precessing in a Magnetic Field B_0



No B_0

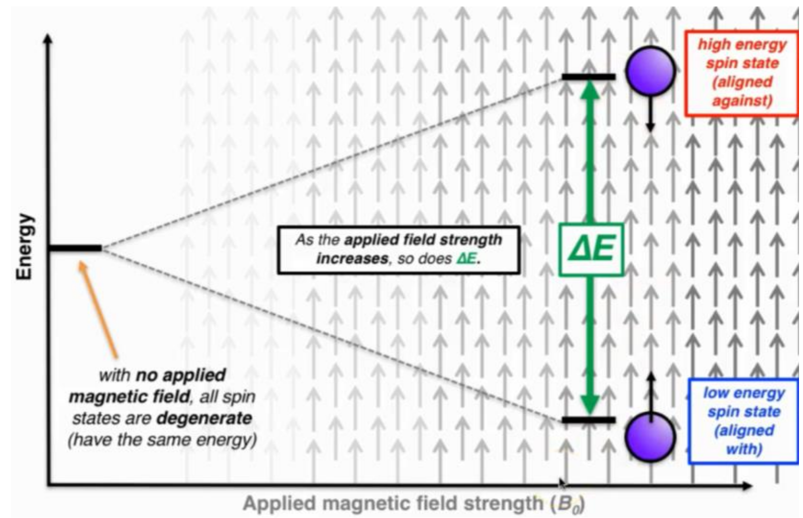
I = +1/2

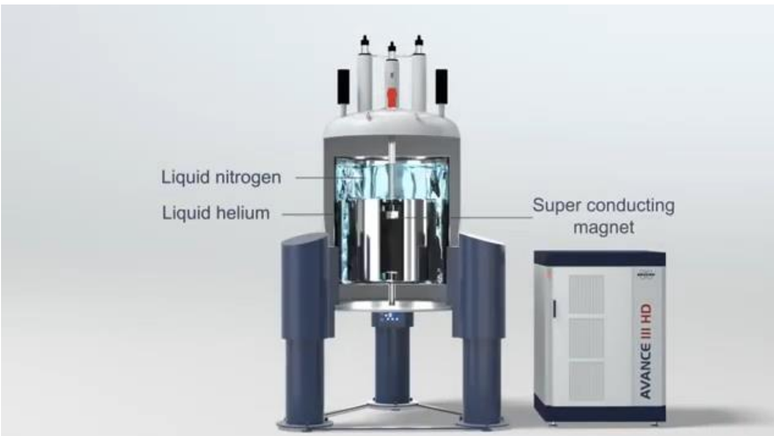
Lower energy state E_1

I = -1/2

Higher energy state E_2

9

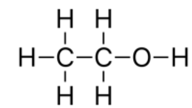


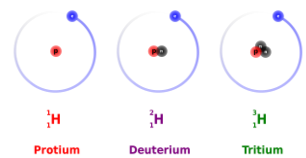


https://www.youtube.com/watch?v=Sn3dNMv-67k

What is the Molecule?

1. Atomic Number (P)
2. Mass Number (P+N)
3. Nuclear Magnetism





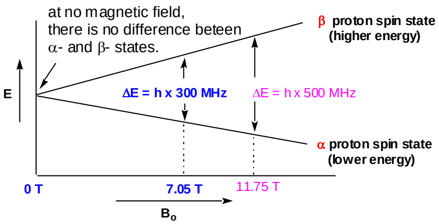
What is NMR?

Nuclide[3]	Z	N	Isotopic mass (Da)[4] [n 1]	Half-life [resonance width]	Decay mode [n 2]	Daughter isotope [n 3]	Spin and parity [n 4][n 5]	Natural abundanc
								Normal proportion
^{12}C	6	6	12 exactly[n 11]	Stable			0+	[0.9884, 0.9904][5]
^{13}C[n 12]	6	7	13.003 354 835 336(252)	Stable			1/2−	[0.0096, 0.0116][5]

NMR Spectroscopy... Effect of Magnetic Field B_0

Stronger magnet means **greater energy difference** between the α- and β- state of the protons.

Graphical relationship between magnetic field (B_o) and frequency (ν) for ^{1}H NMR absorptions



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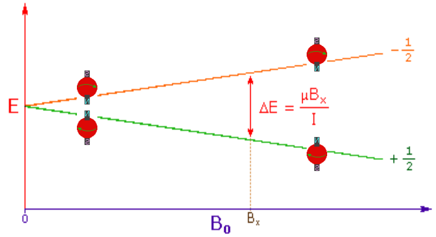
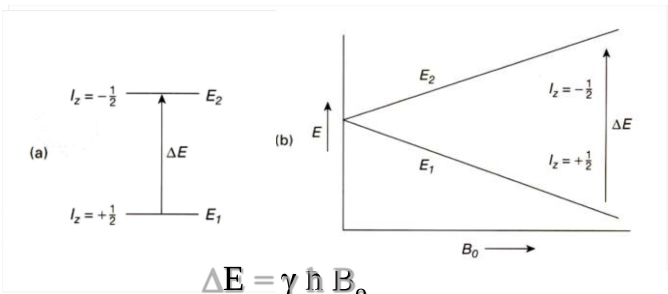


Nuclear Spin Transition



$$\Delta E = \gamma \hbar B_o$$

gyromagnetic ratio — Planck's constant/2π — magnetic field

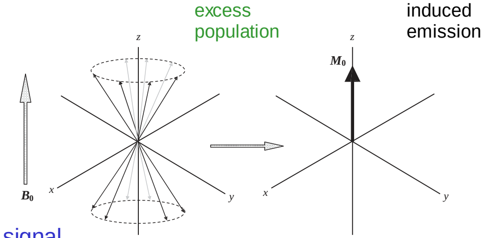
- Energy separation depends on B_0
- The absorbed energy causes the nuclear spin to move to a higher energy state

2

POPULATION AND SIGNAL STRENGTH

The strength of the NMR signal depends on the Population Difference of the two spin states

Radiation induces both upward and downward transitions.



For a net positive signal there must be an excess of spins in the lower state.

Saturation = equal populations = no signal

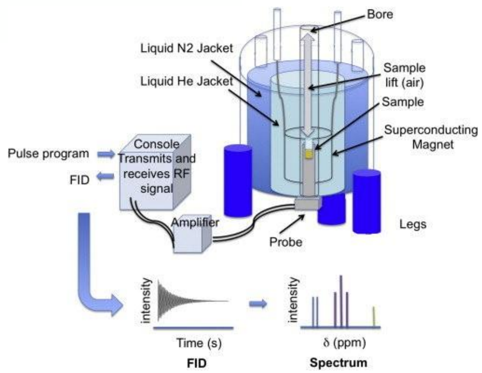
3

NMR Instrument

Bruker installs world's first 1.2 GHz NMR

by Craig A. Bettenhausen
May 15, 2020 | A version of this story appeared in Volume 98, Issue 19

Cost $17.8 million



- Schematic diagram of a Fourier transform NMR spectrometer with a superconducting magnet.
-
- The widely used instruments are of 300 MHz to 900 MHz instruments.

4

NMR Solvents

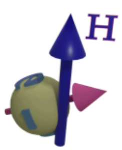
- The ideal solvent should contain **no Protons and be inert, low boiling**, and **inexpensive**.
- **Deuterated solvents** are necessary for NMR instruments.
- Deuterated chloroform ($CDCl_3$) is used as the solvent most of the time for organic compounds.
- A routine sample for ^{1}HNMR on a 300 MHz instrument consists of about 5 mg to 10 mg in about 0.5 ml solvent.

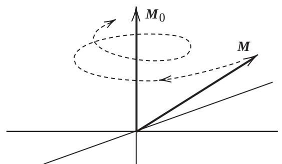
NMR Tube

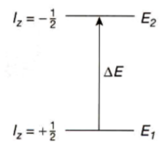
5

Relaxation

- Relaxation refers to the **establishment or re-establishment** of the equilibrium state of the nuclear spin magnetization.
- Equilibrium is achieved when $\boldsymbol{M}_0$ returns to the z-axis after a pulse.
- **Faster spin–spin relaxation** leads to **shorter FIDs** and **broader NMR peaks**; **slower spin–spin relaxation** results in **longer FIDs** and **sharper NMR peaks**.



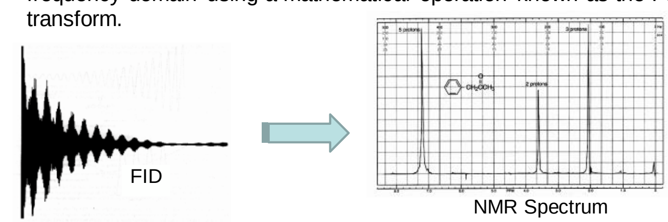




NMR relaxation is the processes by which an excited magnetic state returns to its equilibrium distribution

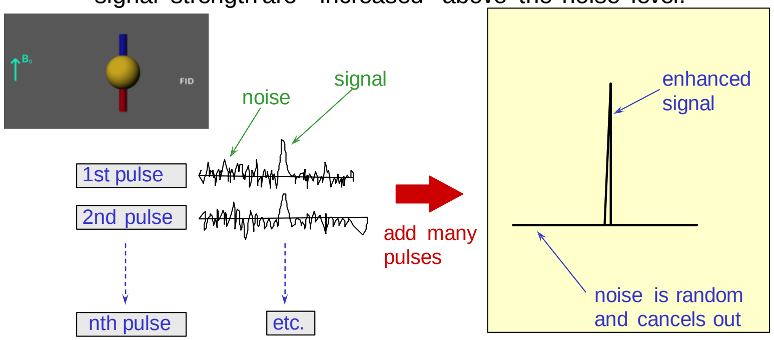
Free Induction Decay (FID)

- The standard method of recording NMR spectra is the pulsed-Fourier transform (FT) method.
- The sample is placed in an NMR probe in the magnetic field and irradiated with a **short pulse of high power radiofrequency energy**.
- This pulse simultaneously excites all of the nuclei of a given type (e.g., ^{1}H) in the sample.
- The resulting signal, known as the free induction decay (**FID**), is recorded and digitized by a computer.
- The information in the FID is converted to a readable spectrum in the frequency domain using a mathematical operation known as the Fourier transform.



Main advantage of FT-NMR is Improved Signal-to- Noise Ratio

By adding the signals from many pulses together, the signal strength are increased above the noise level.



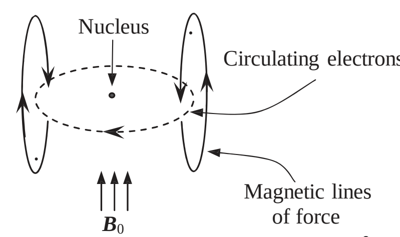
THE CHEMICAL SHIFT

- The nuclei is *shielded* by the local electronic structure of the molecule; the amount of shielding *varies with the* ***chemical environment***.
- This variation gives rise to differences in resonance frequencies, which are commonly called ***chemical shifts***, *which* facilitate the discrimination among the **individual spectral resonances** (**peaks**).

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

σ (magnetic shielding)

$$n_{eff} = (g/2\pi)B_{eff} = (g/2\pi)B_0(1-\sigma)$$



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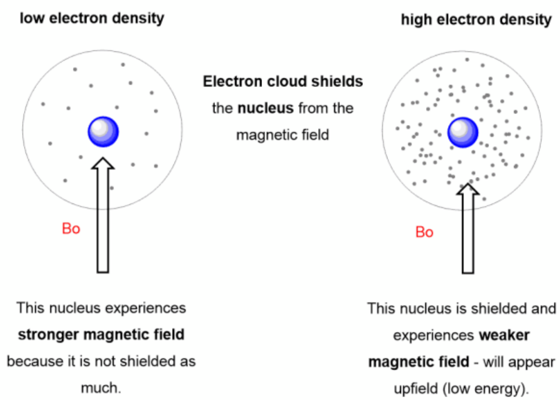
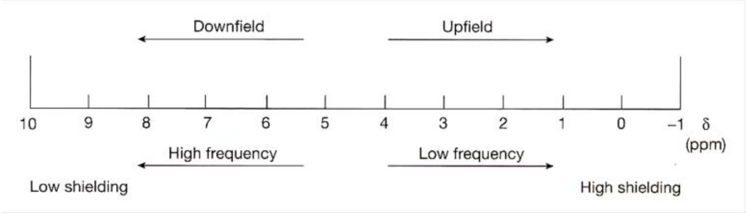


10

THE CHEMICAL SHIFT

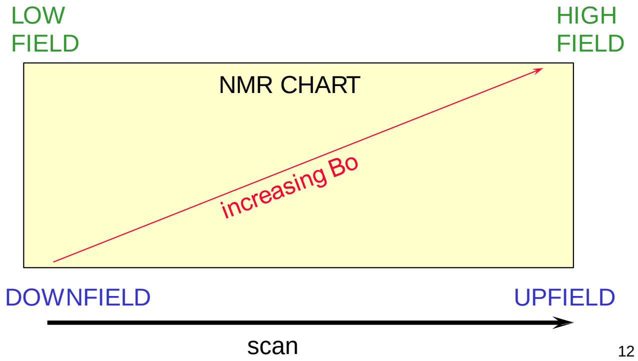
Chemical shift terms



11

Chemical shifts

IN THE CLASSICAL NMR EXPERIMENT THE INSTRUMENT SCANS FROM "LOW FIELD" TO "HIGH FIELD"



12