HNMR

NMR

- Spectroscopy is the study of the interaction of electromagnetic radiation with matter. **Nuclear magnetic resonance spectroscopy** is the use of the NMR phenomenon to study physical, chemical, and biological properties of matter.

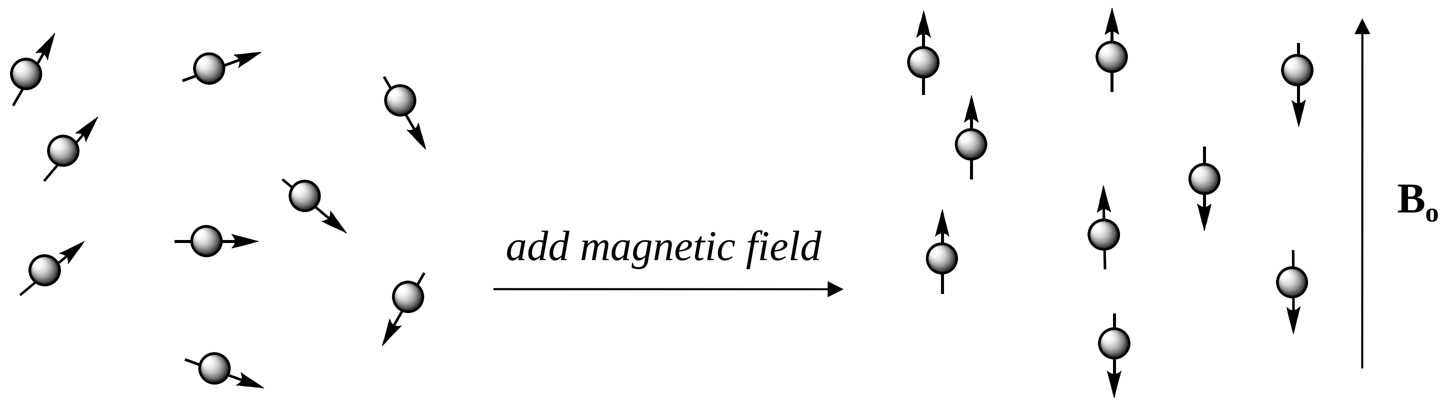
What it can measure:
Chemical structure of molecules
Diffusion coefficients
Relaxation time

Application areas:
Petroleum Exploration
Food
Pulp and Paper Industry
Medicine

^{1}H-NMR Spectroscopy

Background and Theory

•Protons has “spin” (*I*)
•Rotation of charged particle creates magnetic field
•In absence of external influence, magnetic poles (spin axis) randomly oriented
•Add external magnetic field ($\mathbf{B_o}$): spins align



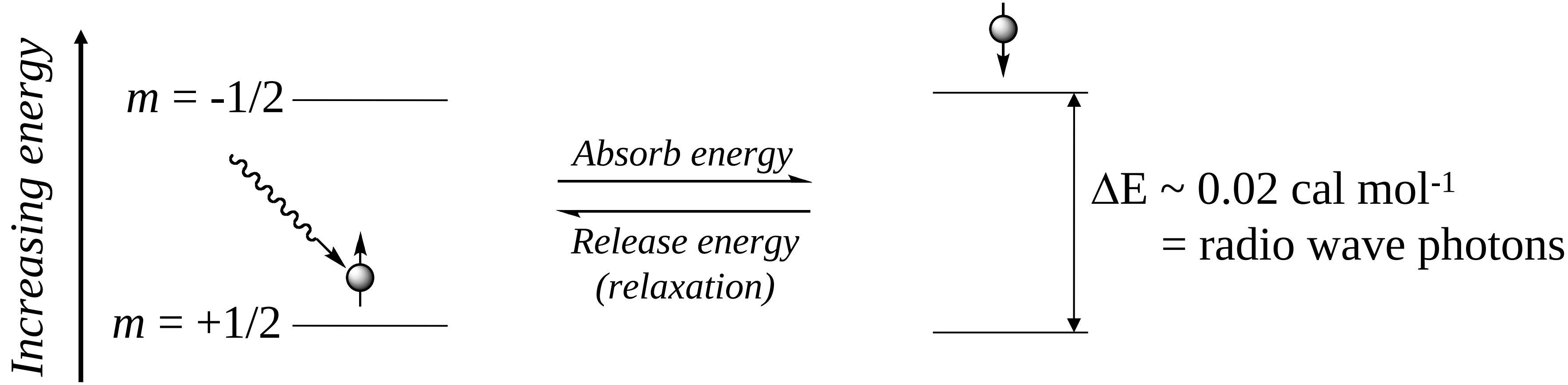
No external magnetic field
Spin alignment random

With external magnetic field
Spins aligned

Background and Theory

Nuclear Spin Flip

- *m* = +1/2 parallel to $\mathbf{B_o}$ (lower energy); *m* = -1/2 antiparallel to $\mathbf{B_o}$ (higher energy)
- Addition of energy results in nuclear spin flip



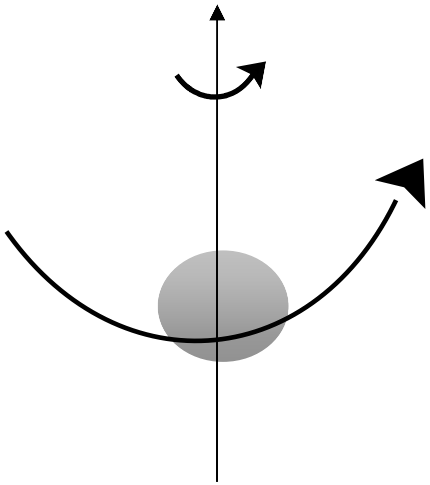
<u>Ground state</u>
Nuclear spin parallel to $\mathbf{B_o}$
Lower energy

<u>Excited state</u>
Nuclear spin antiparallel to $\mathbf{B_o}$
Higher energy

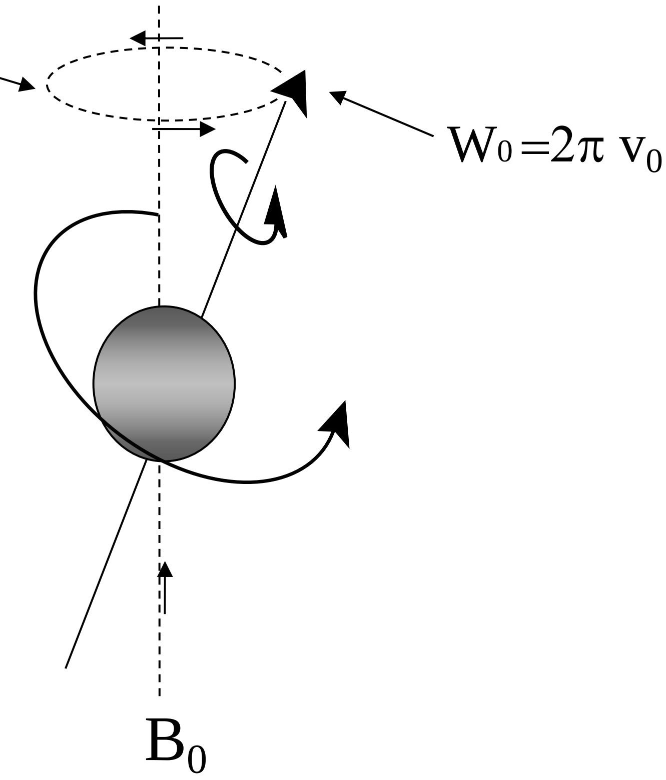
Background and Theory

Nuclear Spin Flip

Precession orbit of nuclear mass
(Precession angular velocity w_0)



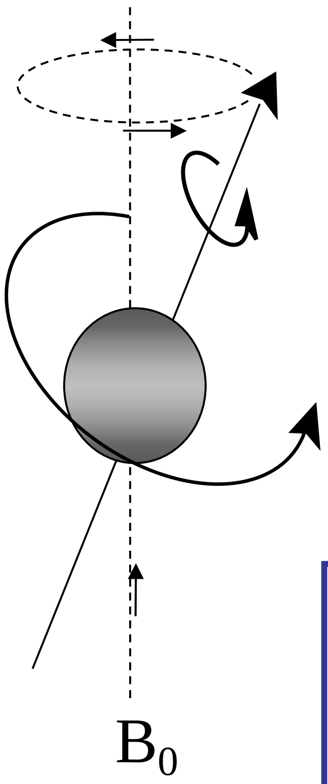
Spinning charge in proton generates magnetic dipole moment



Proton precess in a magnetic field B_0

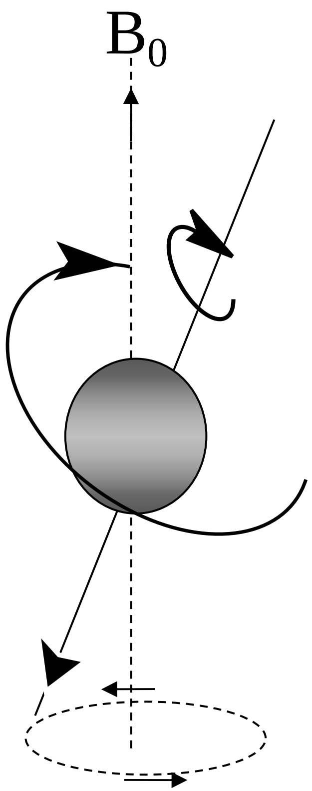
Background and Theory

Nuclear Spin Flip



Ground State

$$\xrightarrow{+\Delta E} \quad \xleftarrow[-\Delta E]{}$$



Excited State

$$\Delta E = h\nu_0 = \frac{h\gamma B_0}{2\pi}$$

γ is the magnetogyric ratio

v_0 is the frequency of electromagnetic radiation

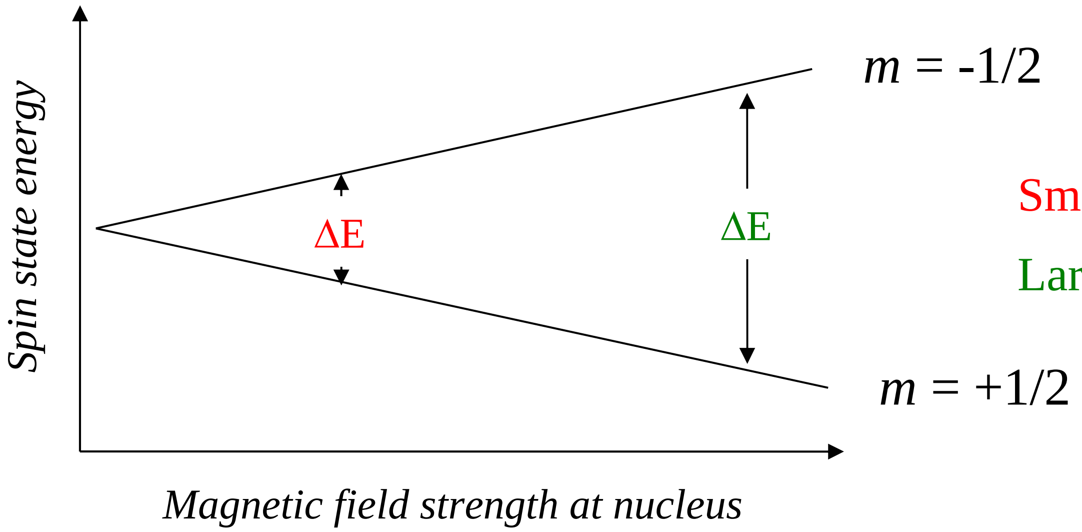
h is Plancks constant

Background and Theory

Magnetic Field Controls ΔE

- ΔE influenced by magnetic field strength at nucleus

$$\Delta E = h\nu_0 = \frac{h\gamma B_0}{2\pi}$$



Small magnetic field → small ΔE

Large magnetic field → large ΔE

Energy required for spin flip (ΔE)

↓

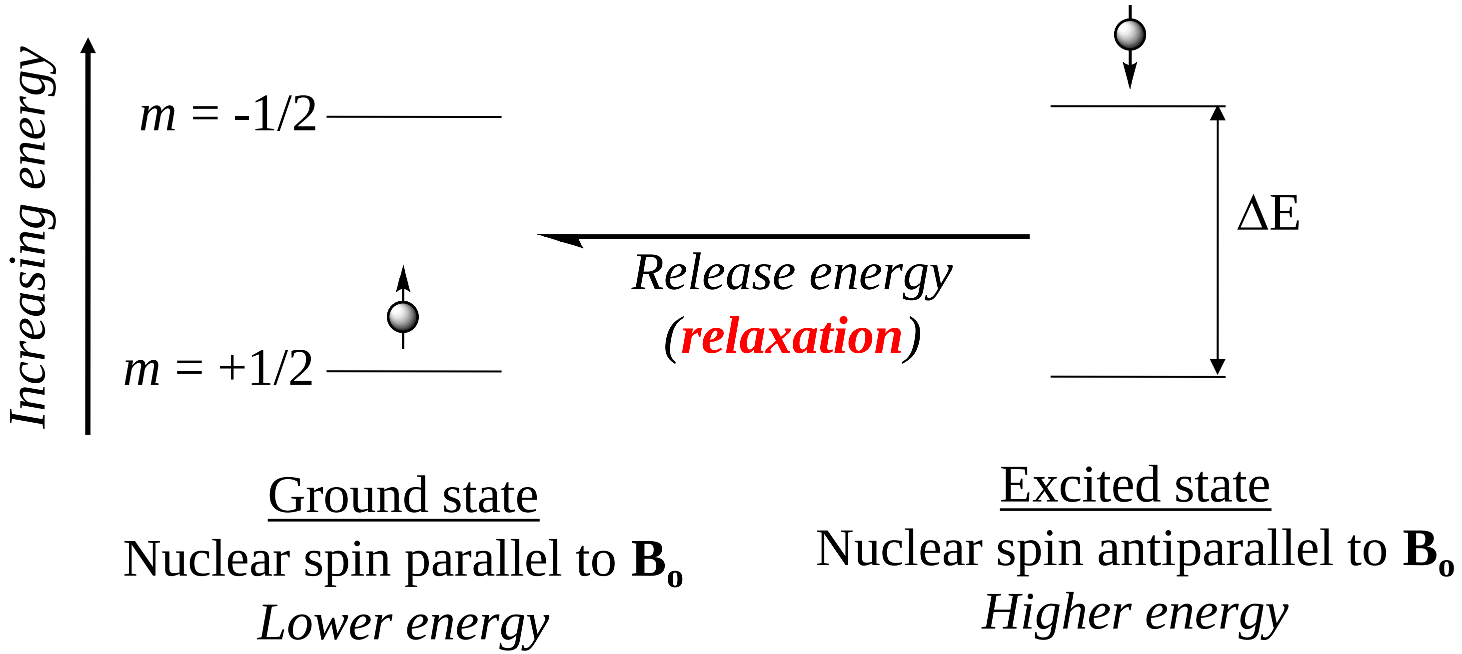
Information about magnetic field strength at nucleus

↓

Information about chemical structure

Relaxation Processes

•m = +1/2 parallel to $\mathbf{B_o}$ (lower energy); m = -1/2 antiparallel to $\mathbf{B_o}$ (higher energy)



Relaxation Processes

- **Spin-lattice relaxation**
- **Spin-spin relaxation**

Spin-lattice relaxation :

Energy is transferred to the molecular framework , the lattice, and is lost as vibrational or translational energy.

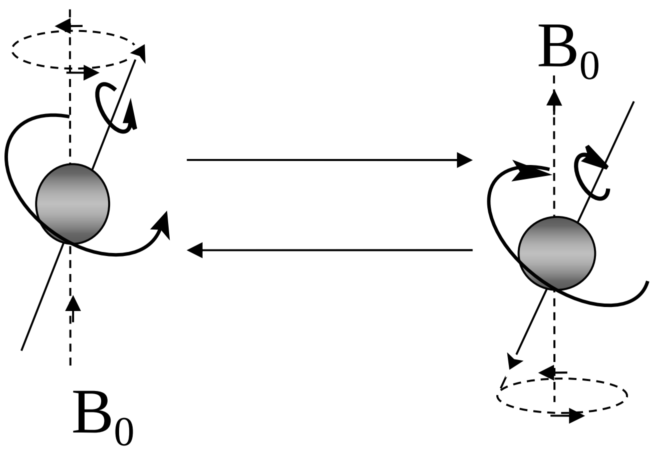
Contributing factors to this type of relaxation are **temperature**, **solution viscosity**, **structure**, and **molecular size**.

http://teaching.shu.ac.uk/hwb/chemistry/tutorials/molspec/nmr1.htm

Relaxation Processes

- **Spin-spin relaxation**

Energy is transferred to a neighboring nucleus, which have the identical precessional frequencies but differing magnetic quantum states.



Lower energy

m = + 1/2

Higher energy

m = - 1/2

Contributing factor:

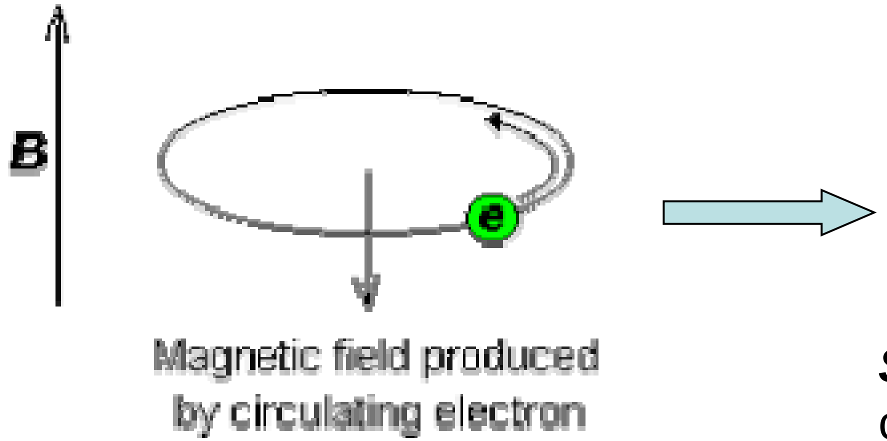
Inhomogeneity of the magnetic field

The presence of paramagnetic materials

Chemical shift

Resonance Condition: $\omega_0 = 2\pi v_0 = \gamma B_0$

v_0 Larmor frequency



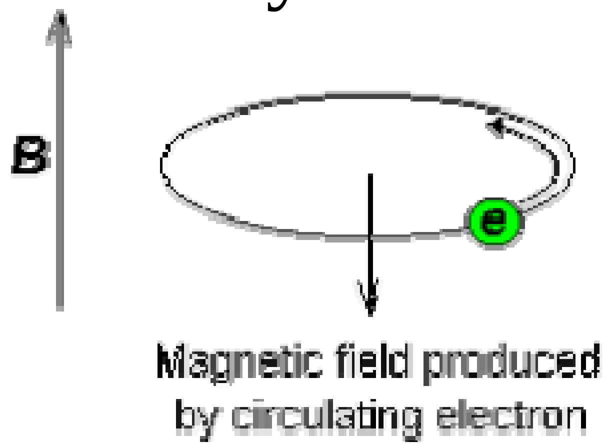
$$\omega_0 = \gamma(B_0 - S)$$

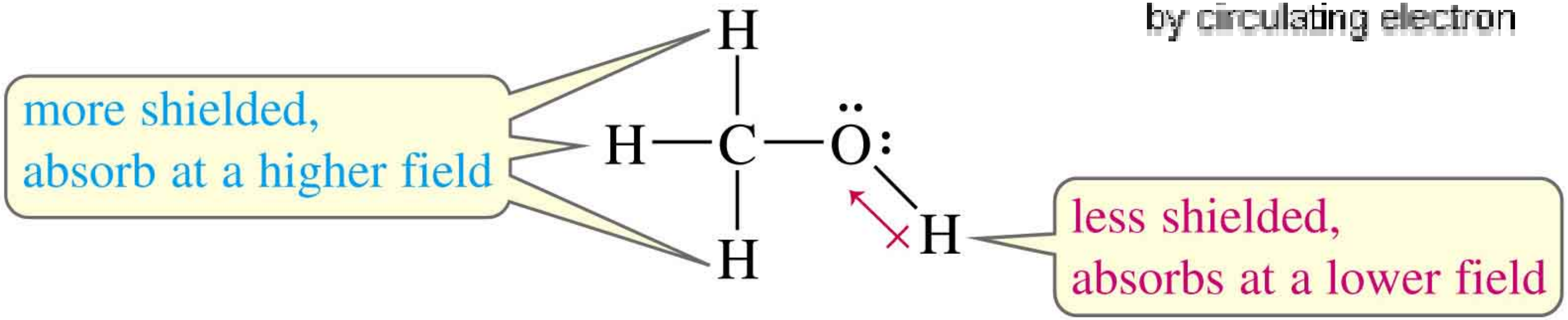
S: the change in magnet field caused by the opposing electron magnetic moment

Chemical shift

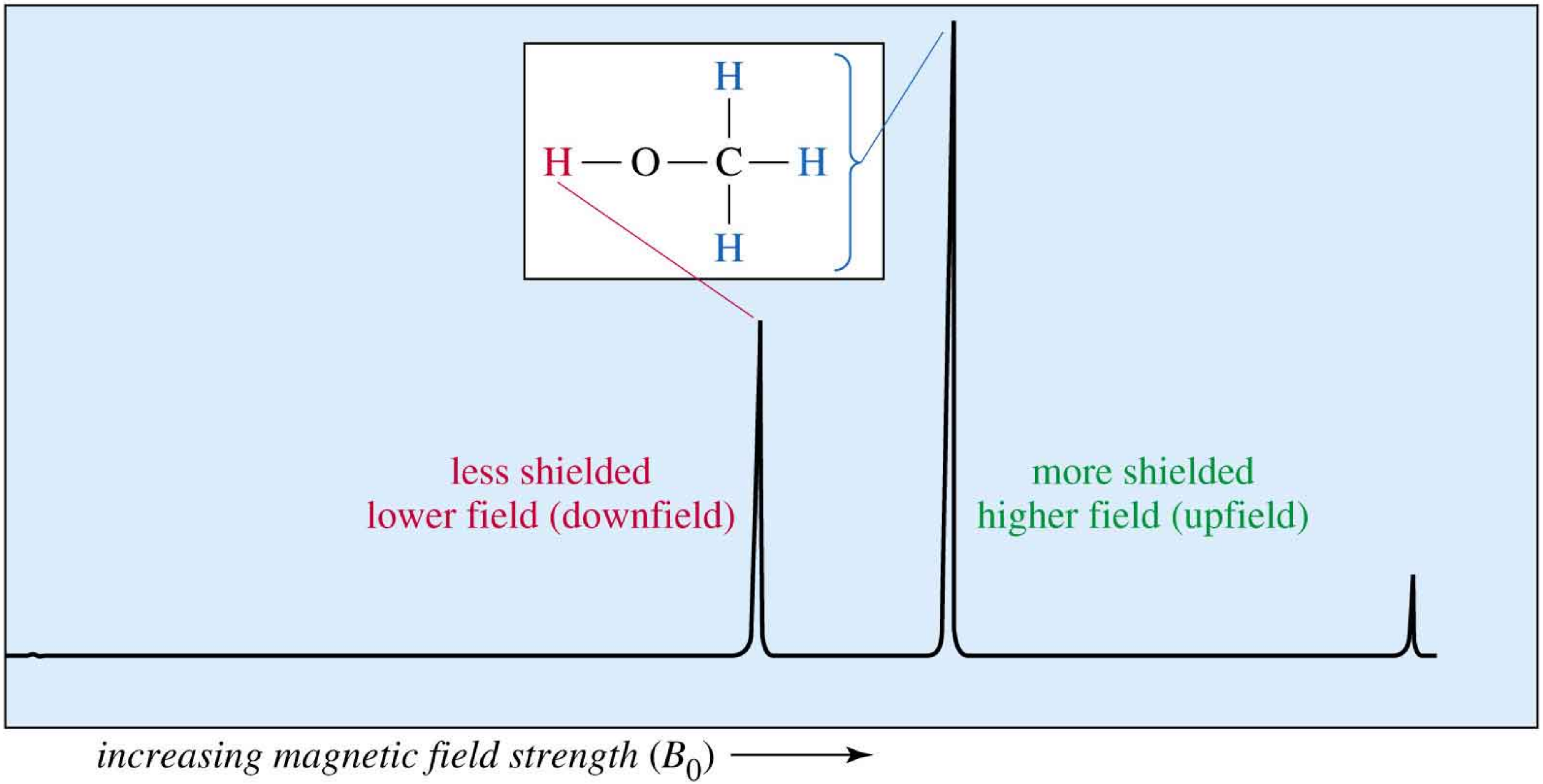
1.electronegativity

Depending on their chemical environment, protons in a molecule are shielded by different amounts.

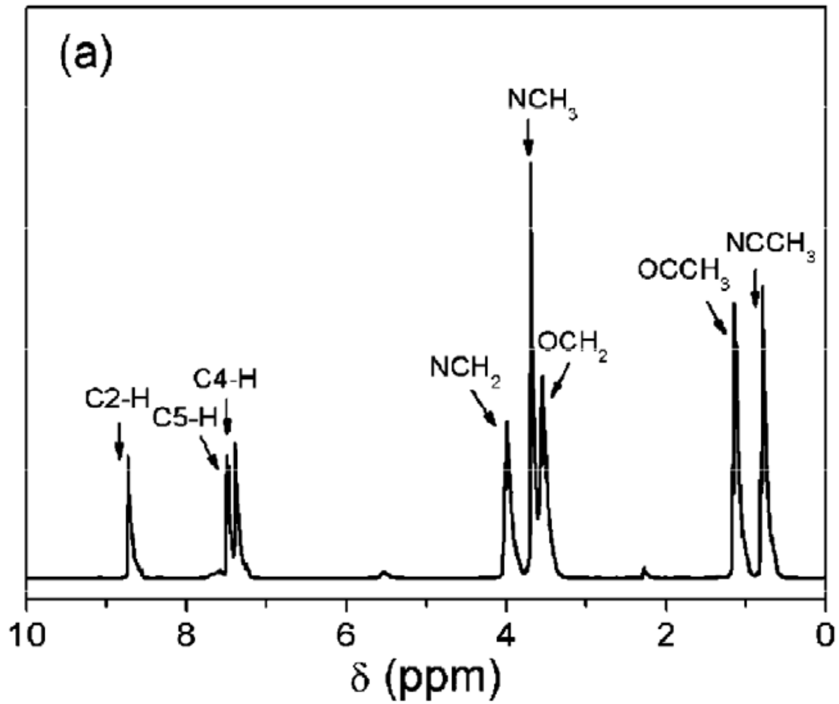


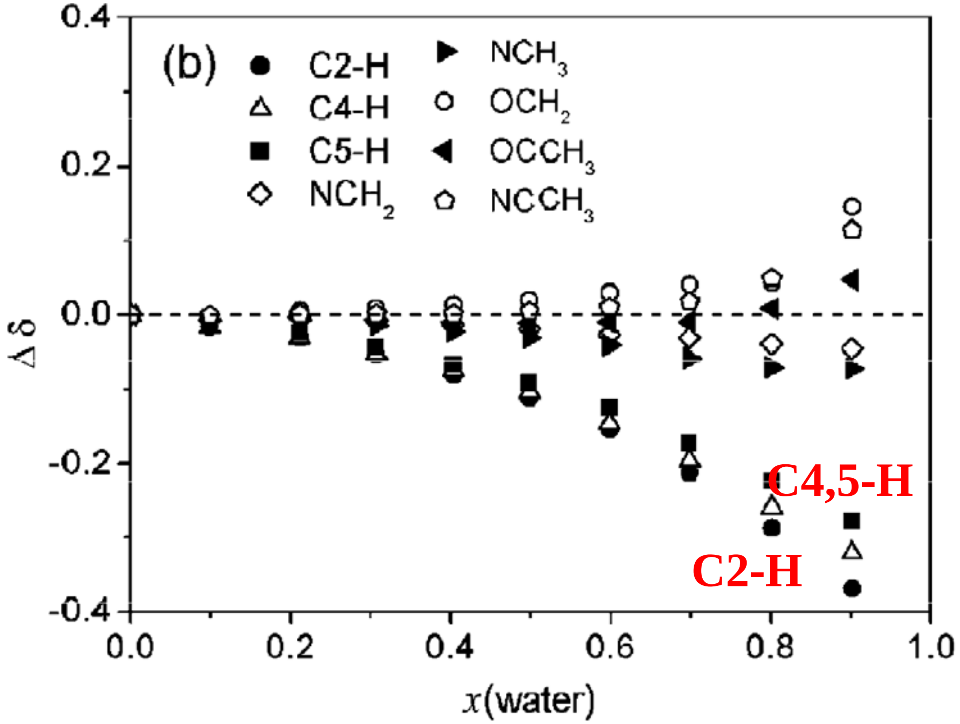


The NMR Graph



HNMR



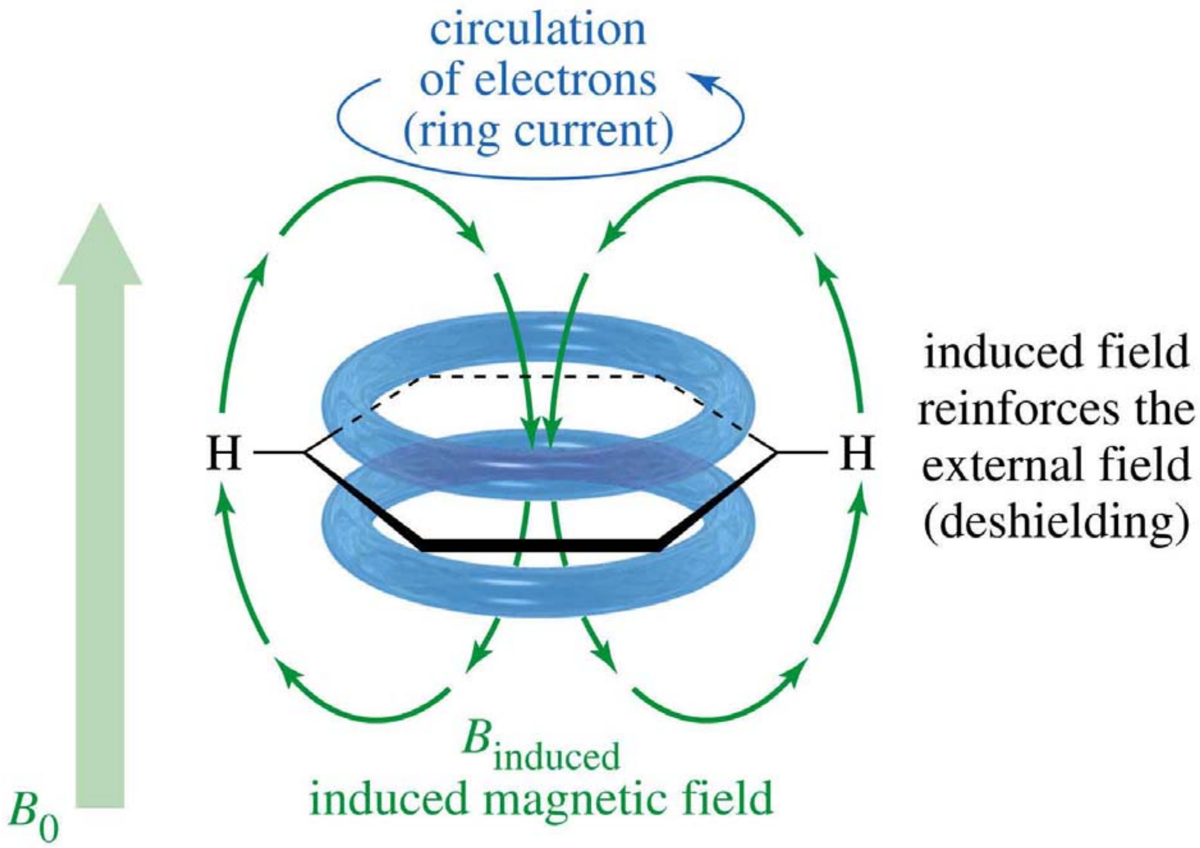


Hydrogen bonds in imidazolium ring are weakened with increasing water concentration

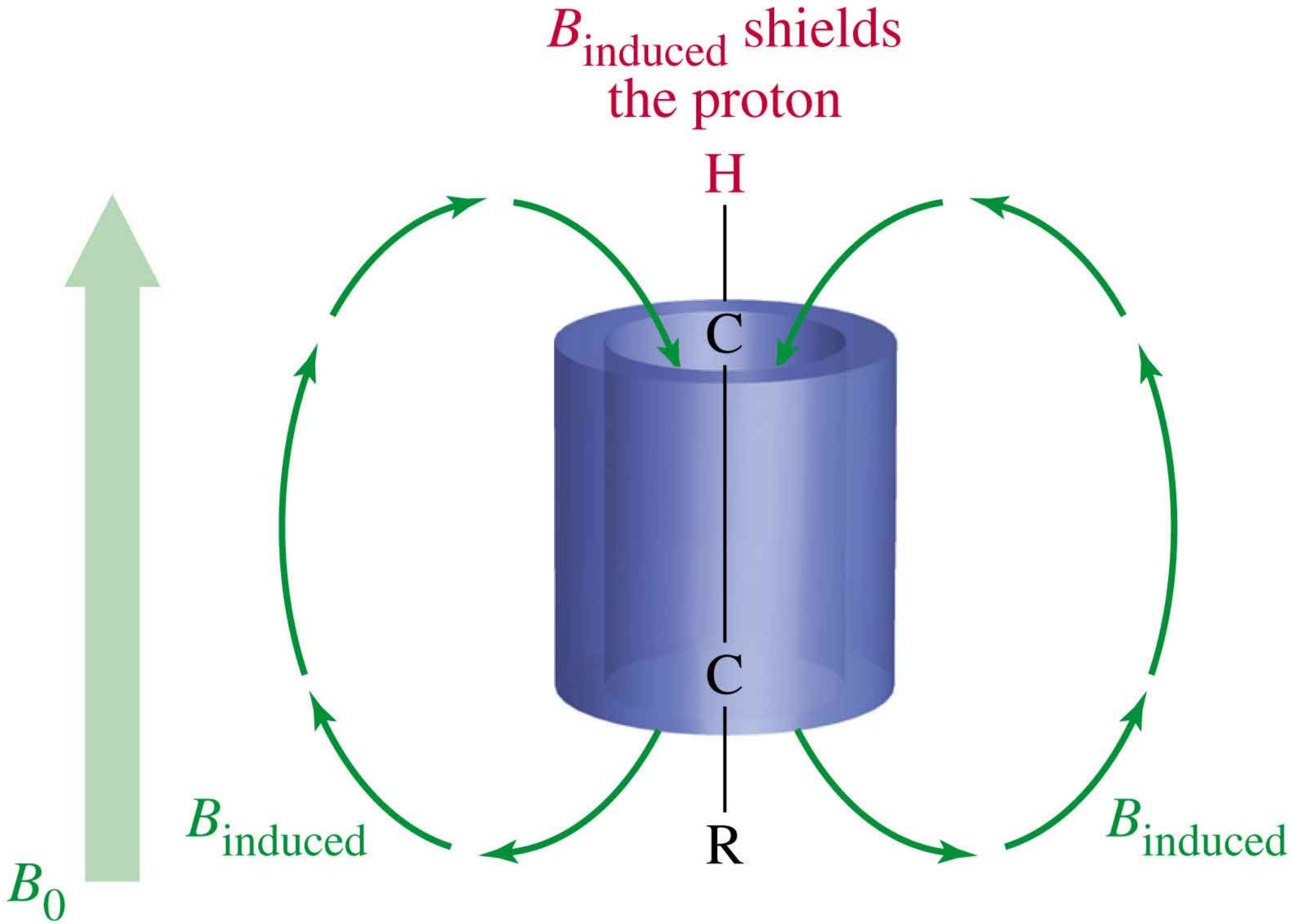
Chemical shift

2.Magnetic anisotropy

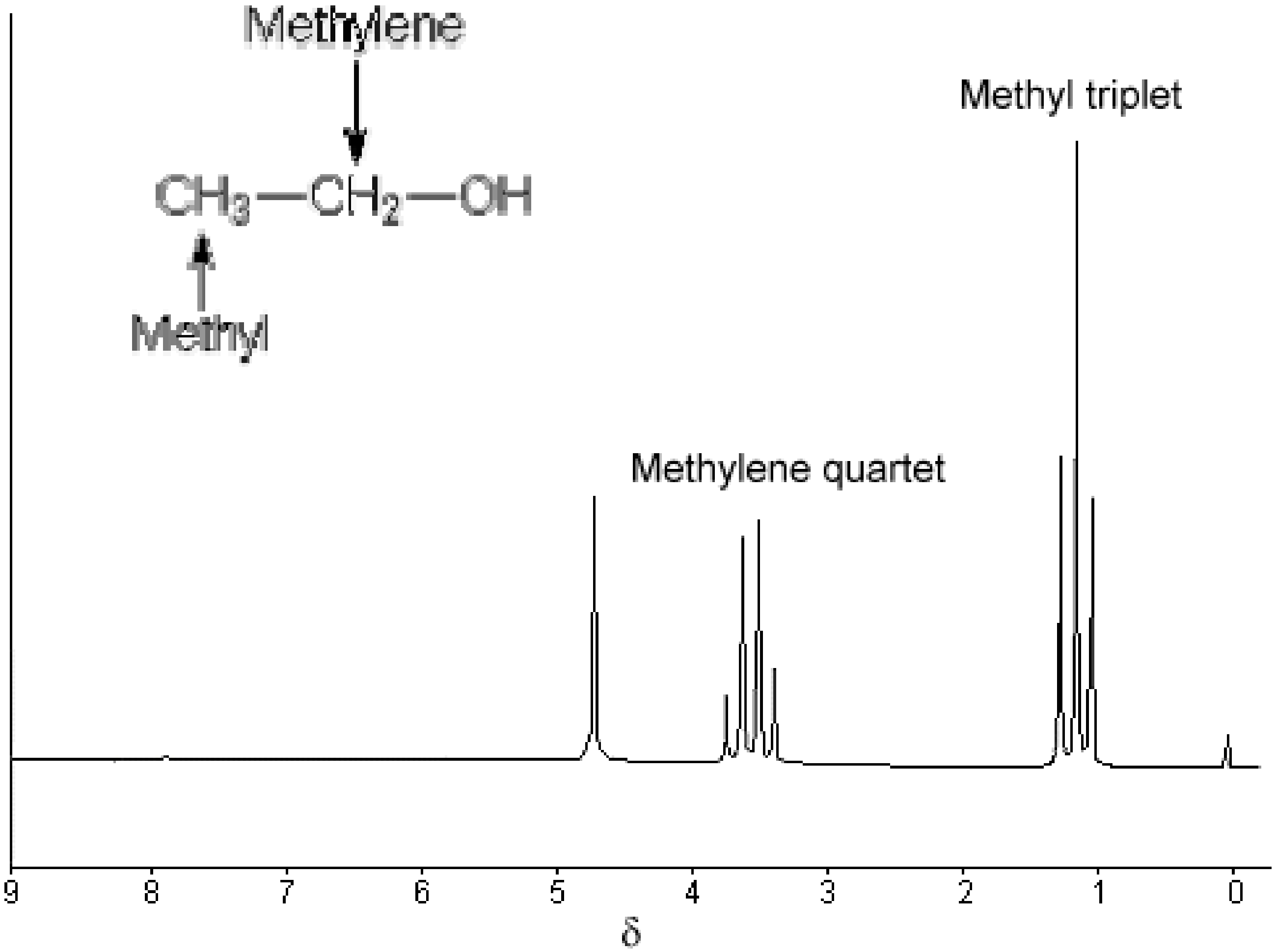
Aromatic Protons, δ7-δ8

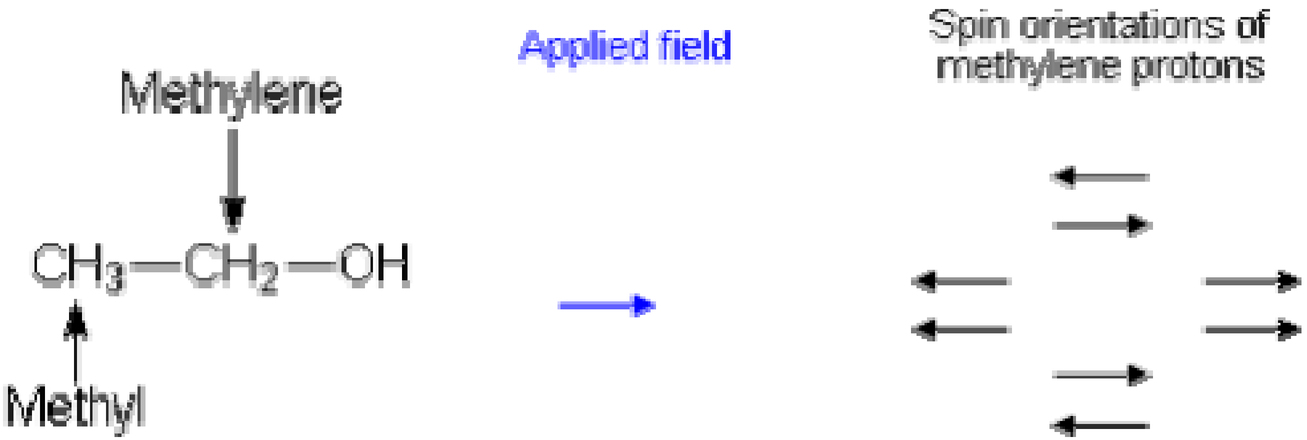


Acetylenic Protons, δ2.5

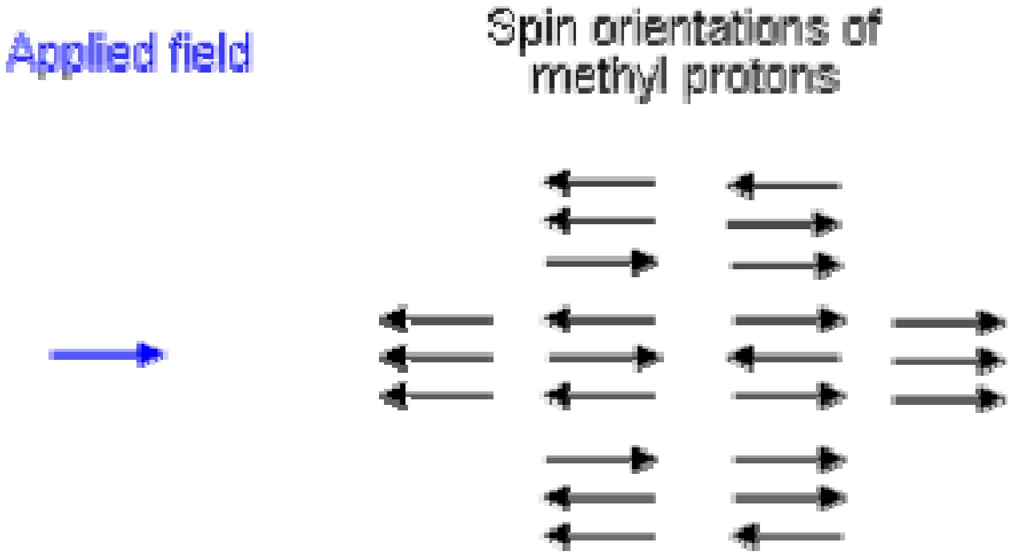


Spin-Spin Coupling





Methyl peak is split into three, with the ratio areas 1:2:1



Peaks number:

n + 1 rule

Methylene peak is split into four, with the ratio areas 1:3:3:1

The NMR Spectrometer