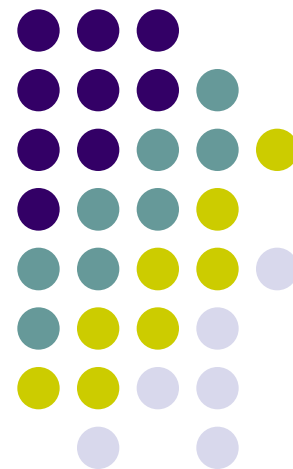
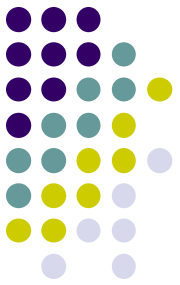


Nuclear Magnetic Resonance Spectroscopy

(NMR)





What is NMR?

Nuclear Magnetic Resonance is a phenomenon that a nuclei transits between different **magnetic energy levels** after absorbing certain frequency of irradiation when it locates in the magnetic field.

Molecular structures can be determined via the **position, intensity** and **fine structures** of the peak signals on the NMR spectrum.



1. Mechanism of NMR

- NMR Phenomenon
- Relaxation
- Chemical Shift
- Spin-Spin Coupling



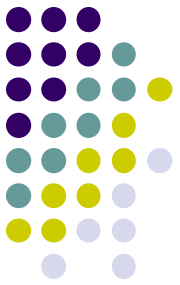
1) NMR Phenomenon

Nucleus Spin

Table 1 Nucleus Spin Quantum Number (I)

Mass	Proton	Neutron	I	Example
Even	Even	Even	0	^{12}C , ^{16}O
Even	Odd	Odd	$n/2 (n=2,4,\dots)$	^2H , ^{14}N
Odd	Even Odd	Odd Even	$n/2 (n=1,3,5,\dots)$	^1H , ^{13}C , ^{19}F , ^{31}P , ^{15}N

$I \neq 0$, NMR Active; $I = 0$, NMR Inactive



- Each nucleus has its constant spin quantum numbers ,
e.g. ^1H $I=1/2$;
- $I=0$, no spin , NMR inactive ; $I \neq 0$, NMR active.
- **$I = 1/2$** : ^1H , ^{13}C , ^{19}F , ^{31}P

uniformly distribution of charges on the surface of the nucleus , mostly targeted in NMR analysis.

- **For other nucleus $I \neq 0$**

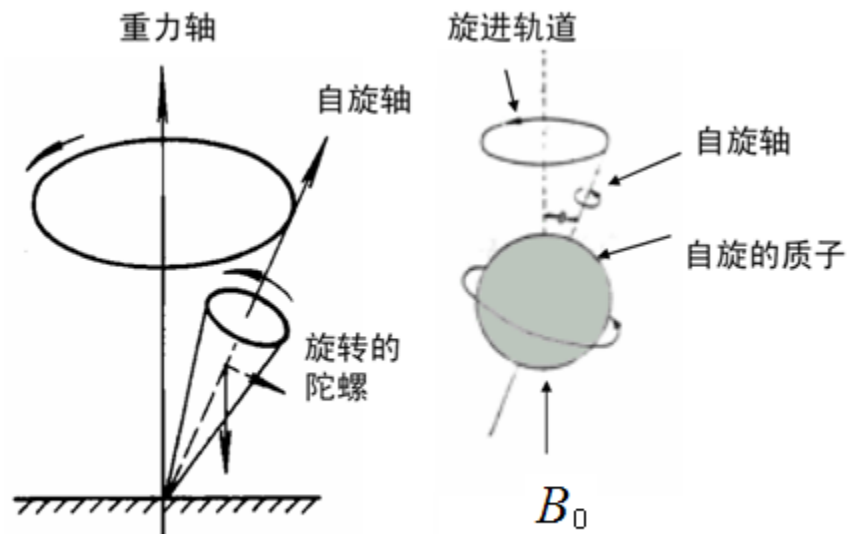
uneven distribution of charges on the surface of the nucleus,
complex NMR.

Nucleus Precession

The nucleus rotates around the direction of the external magnetic field subjecting to the action of the magnetic force, and meanwhile keeps spinning. This kind of motion is defined as Nucleus Precession.

The frequency of the precession is

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

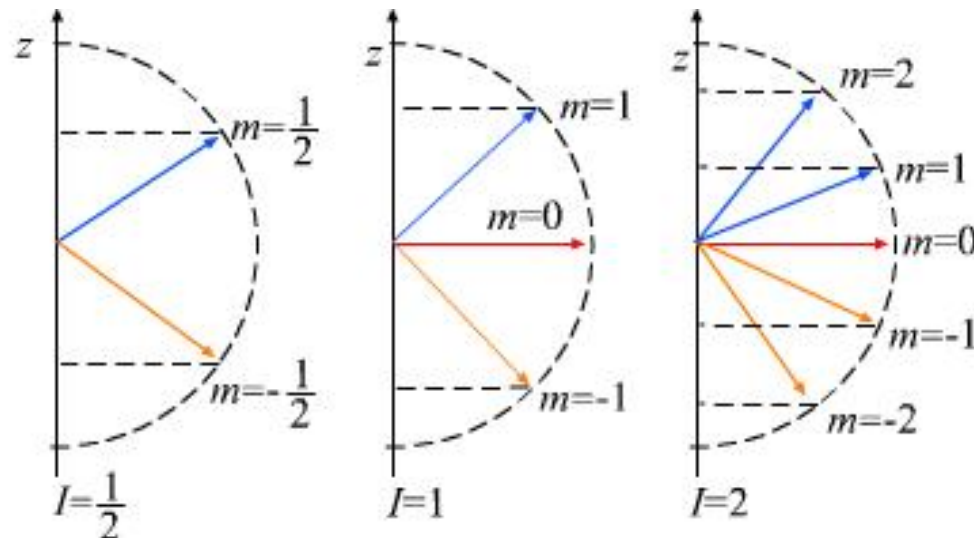
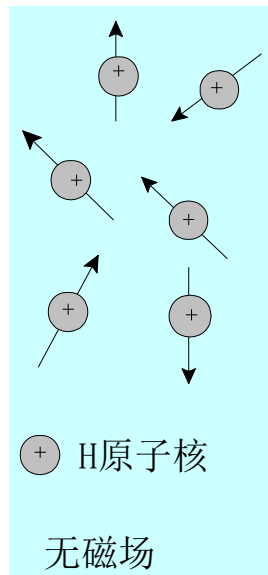




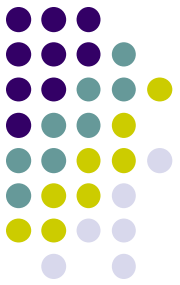
Nucleus Orientation and Energy Level Splitting

The orientation of the nucleus in the space direction is quantized under external magnetic field, which is depend on the magnetic quantum number (m can be one of the $2I+1$ discrete values of $I, I-1, I-2 \dots -I$).

For $I=1/2$ nucleus ($^1\text{H}, ^{13}\text{C}$) , only 2 orientations.



Spin Angular Momentum (P)

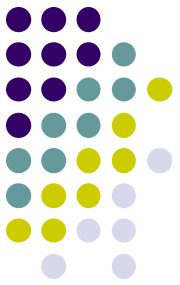


$$P = \frac{h}{2\pi} \sqrt{I(I+1)} = \hbar \sqrt{I(I+1)}$$

P is a vector, whose component on z-axis P_z is:

$$P_z = \frac{h}{2\pi} m = \hbar m$$

m is magnetic quantum number, which is total **$2I+1$** discrete values of $I, I-1, I-2 \dots -I$.



Nucleus Magnetic Moment (μ)

$$\mu = g_N \cdot \frac{e\hbar}{2m_p} \sqrt{I(I+1)} = g_N \mu_N \sqrt{I(I+1)}$$

g_N – Lande Factor

e – charges of nucleus

m_p – mass of the nucleus

μ_N – nuclear magneton

μ is also a vector, whose component on the z-axis μ_z is:

$$\mu_z = g_N \cdot \mu_N \cdot m$$



Nucleus Spin Magnetic Ratio (γ)

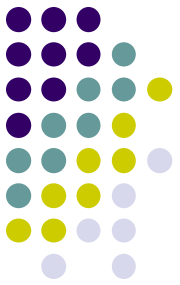
$\gamma = \mu / P$ is a nucleus depend constant , which is related to the nucleus mass, charge and Landes factor.

Larger γ , stronger NMR signal.

$$^1\text{H} \quad \gamma = 26.752 \times 10^7 \text{ T}^{-1} \cdot \text{S}^{-1}$$

$$^{13}\text{C} \quad \gamma = 6.728 \times 10^7 \text{ T}^{-1} \cdot \text{S}^{-1}$$

(T—Tesla) ;



Energy of Magnetic Nucleus under B_0

$$E = -\mu \cdot B_0 = -\mu B_0 \cos \theta$$

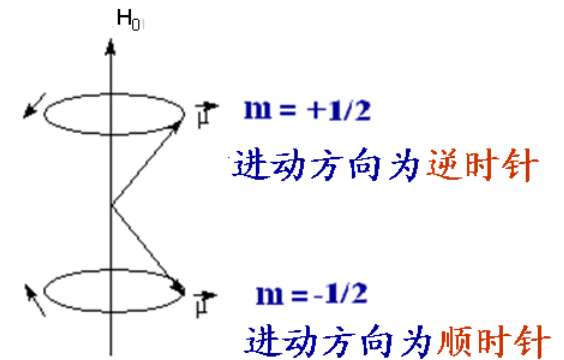
$$= -\mu_z B_0 = -g_N \mu_N m B_0 = -\frac{h}{2\pi} \gamma m B_0$$

$$I=1/2, m=+1/2$$

$$E_{+1/2} = -g_N \mu_N m B_0 = -1/2 g_N \mu_N B_0 = -h \gamma B_0 / 4\pi$$

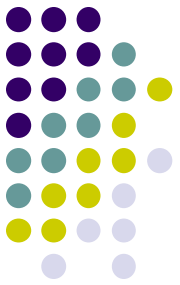
$$I=1/2, m=-1/2$$

$$E_{-1/2} = g_N \mu_N m B_0 = 1/2 g_N \mu_N B_0 = h \gamma B_0 / 4\pi$$



$$\Delta E = E_{-1/2} - E_{+1/2} = \frac{h}{2\pi} \gamma B_0 \quad \Delta E \propto B_0$$

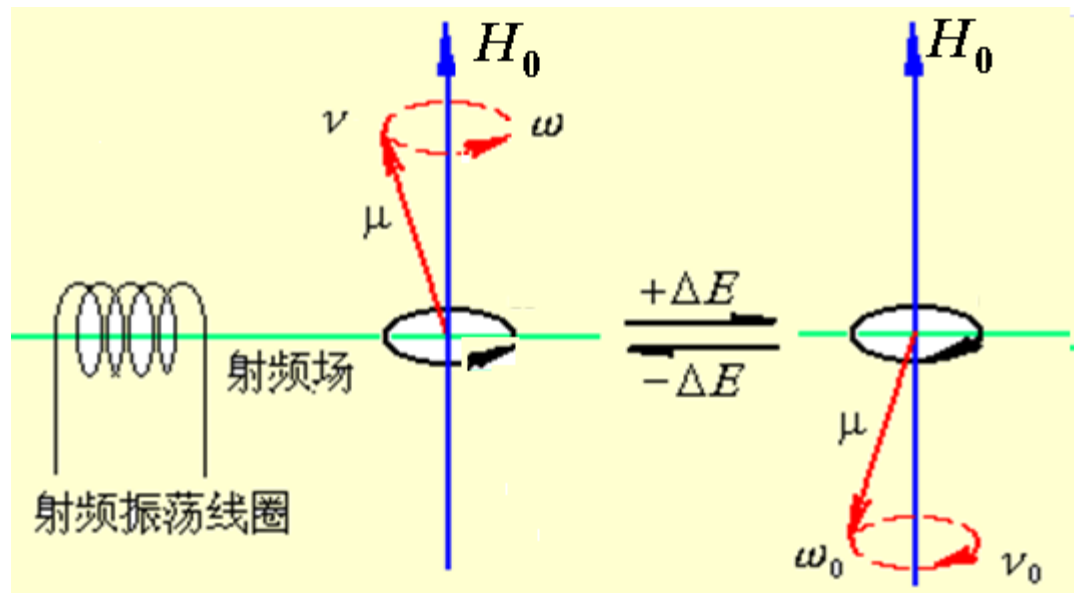
When $B_0 = 0$, the two energy levels are degenerated.



NMR:

1. Magnetic Nucleus ($I \neq 0$)
2. External Magnetic Field (B_0)
3. Frequency of Electro-magnetic irradiation

$$\nu = \frac{1}{2\pi} \gamma B_0$$



$$\nu = \frac{1}{2\pi} \gamma B_0$$



(1) Same Nucleus , same γ , $\nu \propto B_0$

^1H : $B_0 = 1.409 \text{ T}$, $\nu = 60 \text{ MHz}$

$B_0 = 2.305 \text{ T}$, $\nu = 100 \text{ MHz}$

(2) Different Nucleus, different γ , same B_0 , $\nu \propto \gamma$

$B_0 = 2.35 \text{ T}$, ^1H **100 MHz, ^{13}C **25 MHz****

(3) Two methods :

A. Frequency sweeping methods

B. Field sweeping methods

(4) Commonly used NMR:

^1H NMR

^{13}C NMR

^{19}F NMR

^{31}P NMR

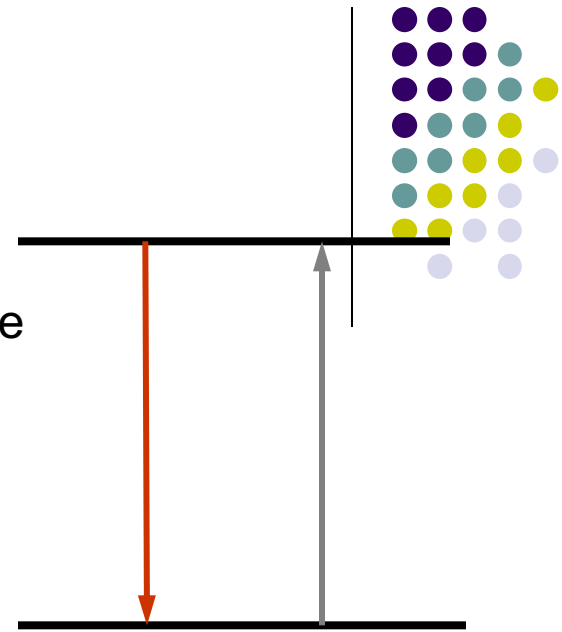
2) Relaxation

The process of returning from the excited state to the Boltzman equilibrium

$$\frac{N_l}{N_h} = e^{\Delta E / kT}$$

- Boltzmann equilibrium: particle numbers on the base level is more than excited level

$$\frac{N_{+1/2}}{N_{-1/2}} = e^{\Delta E / kT} = e^{(\gamma \hbar H_0) / kT} = 1.00000099$$

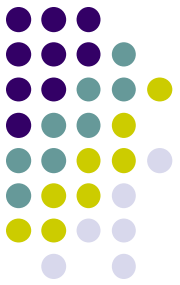




Spin-lattice relaxation

- Energy Transfer between **Spin Nucleus** and **Surrounding Molecules** (Solid: lattice; Liquid: solvent)
- Shorter relaxation time (T_1), higher relaxation efficiency: favors for NMR
- Shorter T_1 for liquid (\sim s); Longer T_1 for solid (\sim hr).

That's why liquid sample for NMR analysis.



Spin-spin relaxation

- Energy transfer between spin nuclei.
- No contribution to Boltzmann equilibrium
- Relaxation time (T_2): Longer T_2 for liquid (\sim s); Shorter T_2 for solid ($\sim 10^{-4}$ - 10^{-5} s)
- Width of NMR signal is reciprocal to T_2 .

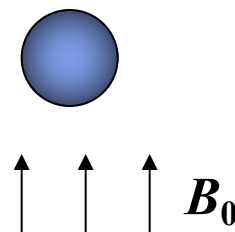
That's why liquid sample for NMR analysis.

3) Chemical Shift



■ Exposed Nucleus

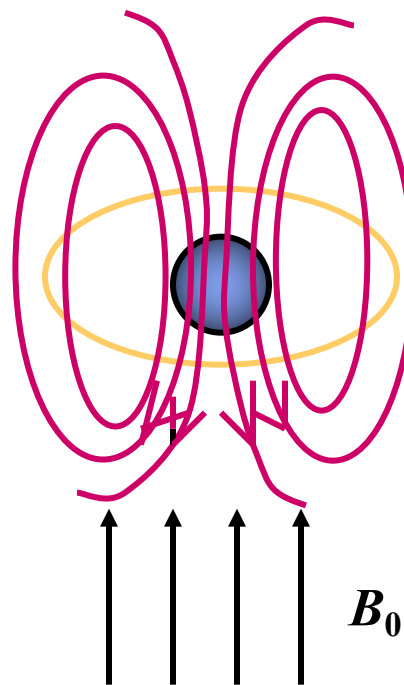
$$\nu = \frac{1}{2\pi} \gamma B_0$$



■ Nucleus with Electron Clouds

$$\nu = \frac{1}{2\pi} \gamma B_0 (1 - \sigma)$$

σ - Shielding Constant

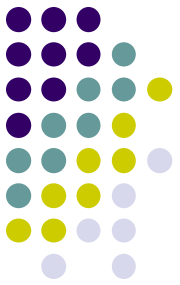


The density of electron cloud depends on the nucleus environment. Resonance changes due to the variation of nucleus chemical environment is defined as **chemical shift**.



$$\sigma = \sigma_d + \sigma_p + \sigma_a + \sigma_s$$

- σ_d anti-magnetic shielding Shielding from magnetic field produced by s electrons with spherical symmetry, mainly for H.
- σ_p para-magnetic shielding Shielding from magnetic field produced by other electrons with non-spherical symmetry, mainly for other nucleus.
- σ_a Shielding from anisotropy from adjacent groups.
- σ_s Shielding from solvent and other medium.



Chemical Shift Constant (δ)

Frequency Sweeping :

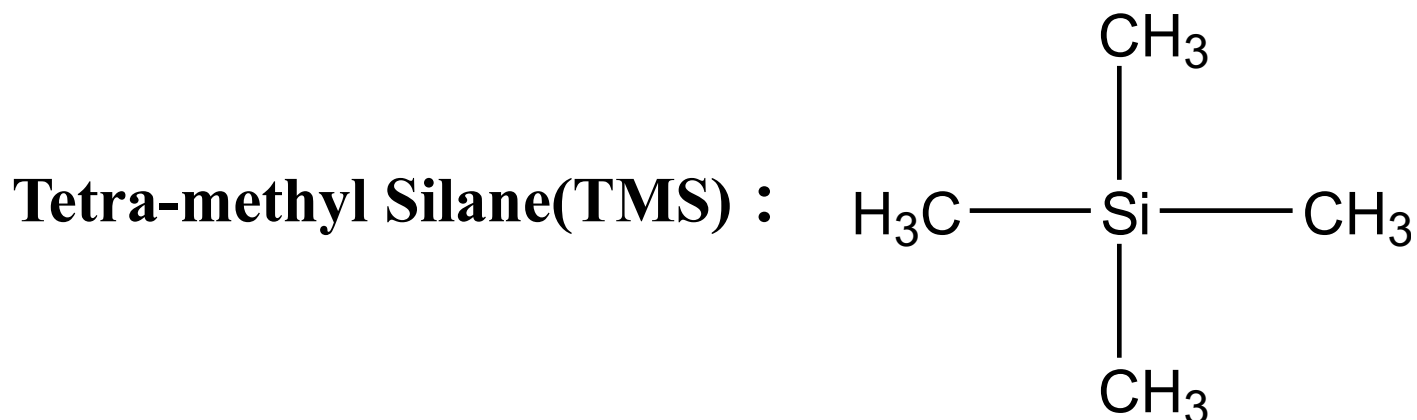
$$\delta = \frac{(\nu_{\text{样}} - \nu_{\text{标}})}{\nu_{\text{标}}} \times 10^6 = \frac{\Delta \nu}{\text{振荡器频率}} \times 10^6$$

Field Sweeping :

$$\delta = \frac{B_{\text{样品}} - B_{\text{标准}}}{B_{\text{标准}}} \times 10^6$$



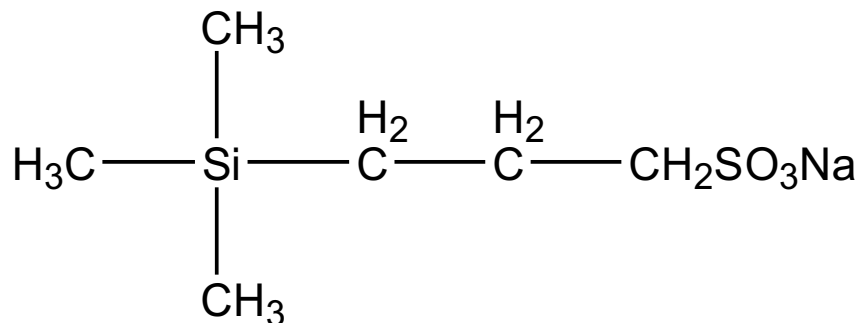
Reference Materials :



- ❖ Chemically inert
- ❖ Same chemical environment for all methyls, only 1 peak as $\delta=0$
- ❖ Lower electronegativity of Si(1.9) than C(2.5) , much more lower chemical shift constant than common organic compounds
- ❖ Low boiling point (27°C)



Sodium 2,2-dimethyl-2-pentasilyl-5-sulfonate (DSS) :



For water soluble samples.

Solvent for NMR

Deuterium solvent

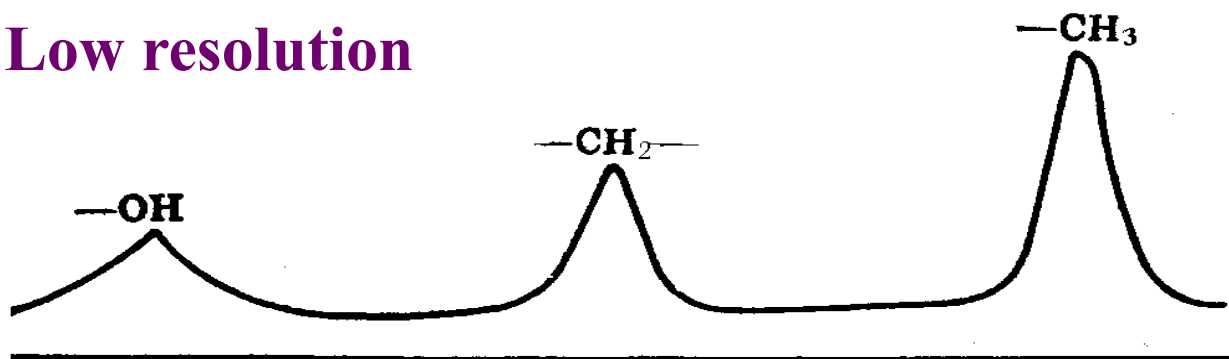
CDCl_3 , CD_3COCD_3 , CD_3OD , D_2O and etc.

4) Spin-Spin Coupling



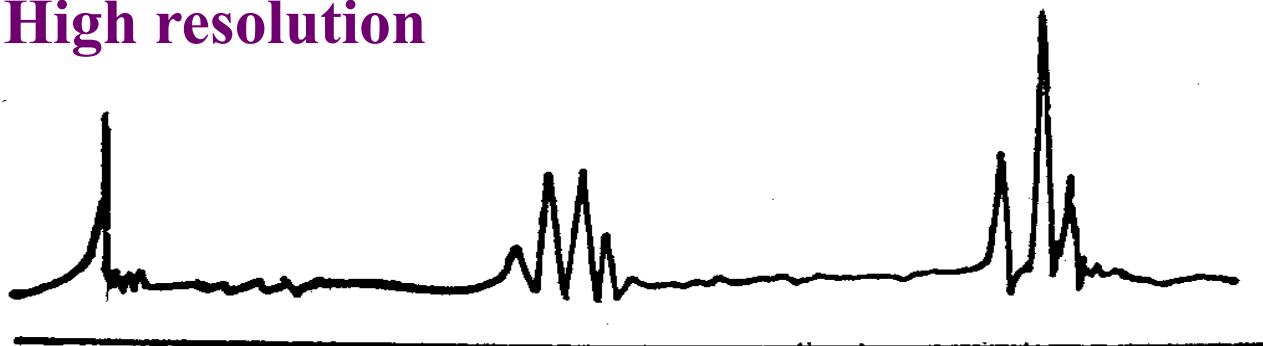
NMR of ethanol

Low resolution



化学位移 δ

High resolution



化学位移 δ



- Interactions between magnetic nuclei is defined as **spin-spin coupling**
- Multiple peaks caused by spin-spin coupling is defined as **spin splitting**



Mechanism of spin-spin coupling

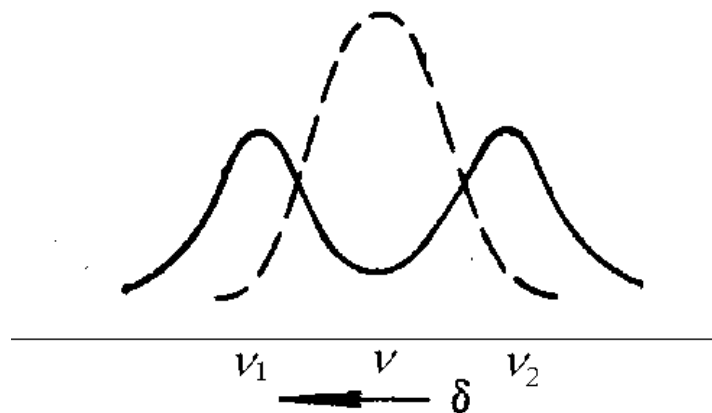
No adjacent nucleus : $\nu = \frac{\gamma}{2\pi} B_0 (1 - \sigma)$

If X is adjacent to A ($I=1/2$) X orientation: $\pm 1/2$

The magnetic field on A is now:

$$[B_0 (1 - \sigma) + \Delta B]$$

$$[B_0 (1 - \sigma) - \Delta B]$$





Two adjacent magnetic nuclei X_1 and X_2

X_1	↑	↑	↓	↓
X_2	↑	↓	↑	↓
	$+2\Delta B$	0	0	$-2\Delta B$

Magnetic field for A :

$[B_0 (1 - \sigma) + 2\Delta B]$	1
$B_0 (1 - \sigma)$	2
$[B_0 (1 - \sigma) - 2\Delta B]$	1

Triplet peak with intensity ratio 1 : 2 : 1



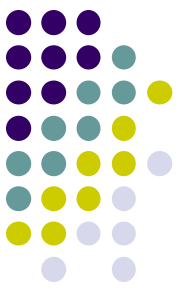
Coupling constant (J)

- Interference degree between coupled magnetic nuclei , Hz as the unit.
- Depend on the **chemical bonds** between each nucleus and **stereo-chemistry**
- Defined as $^1J_{\text{C} - \text{H}}$, $^3J_{\text{H} - \text{H}}$



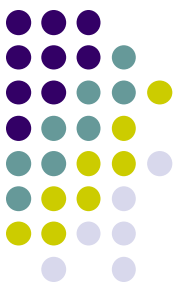
二、核磁共振谱仪简介

- 用于有机物结构分析的必须是**高分辨率仪器**
- **核磁共振仪的分类：**
 - **按外磁场强度不同而所需的照射频率分为：**
60MHz、100 MHz、200 MHz、300 MHz、400 MHz、500 MHz、600 MHz、800 MHz等型号，核磁共振仪的型号通常用H的共振频率来表示；
 - **按磁场的来源：**分为永久磁铁、电磁铁和超导磁体；
 - **根据射频的照射方式：**分为连续波核磁共振谱仪（CW - NMR）和脉冲傅里叶变换核磁共振谱仪（PFT - NMR）。



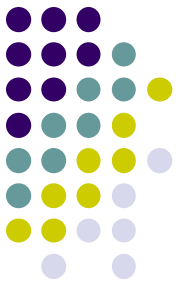
连续波核磁共振谱仪

- **磁体**：提供强的稳定均匀的磁场
- **射频振荡器**：产生一个与外磁场强度相匹配的射频频率，提供能量使磁核从低能级到高能级。
- **射频接受器**：用于接受携带样品核磁共振信号的射频输出,并将接收到的信号传送到放大器放大。
- **探头**:有样品管座、发射线圈、接受线圈、变温元件等。
- **扫描单元**：安装在磁极上的扫描线圈，提供一个附加可变磁场，用于扫描测定。



脉冲傅里叶变换核磁共振谱仪PFT-NMR

在外磁场保持不变的条件下，使用一个强而短的射频脉冲照射样品。这个射频脉冲包括所有不同环境的同类磁核的共振频率。各种核同时激发，发生共振，然后通过弛豫逐步恢复Boltzmann平衡。在这个过程中,射频接受器接受信号，得到随时间衰减的信号，称自由感应衰减信号（FID），通过计算机进行傅里叶变换转化为通常的NMR谱图。



FT-NMR谱仪特点：

- 扫描速度快，测定一张谱图只需要几秒-几十秒的时间。
- 不仅改善 ^1H 等天然丰度高的核种的谱图质量，而且使天然丰度小、绝对灵敏度低的同位素核的核磁共振测定得以实现。