

University of Babylon  
College of Science  
Department of Chemistry  
Course No. Chsc 424



Undergraduate Studies  
Physical chemistry  
Fourth year - Semester 2  
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Scholar units: three units

Lectures of Molecular spectroscopy  
Second Semester, Scholar year 2018-2019  
Prof. Dr. Abbas A-Ali Draea

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**Lecture No. Seven: Nuclear Magnetic Resonance**  
**Spectroscopy**

- 1-Introduction.
  - 2- Energy level calculations.
  - 3-Spin Interaction with Magnetic field.
  - 4-The Chemical Shift.
  - 5- Couplings Interaction.
  - 6-Strong coupling.
  - 7-Application of Spin - spin coupling.
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**1-Introduction:**

The NMR experiment measures a large ensemble of spins derived from a huge number of molecules. The sum of the dipole moments of all nucleus is called **magnetization**. In equilibrium the spins of  $I=1/2$  nuclei are either in the  $\alpha$ - or  $\beta$ -state and precess about the axis of the static magnetic field. Application of a radiofrequency (RF) field perpendicular to the magnetic field (e.g. along the x- or y-axis), the so-called  $B_1$  field, creates a state in which the phases of the spins are partially correlated. This state is called coherence. (حالة الاقتران ما بين طاقتين).

## 2-Energy level calculations:

Energy levels of NMR are function for  $\mu$  &  $(H_0 \text{ or } B_0)$ , where they nuclear magnetic moment and intensity of magnetic field. The represented relation of radiation frequency (RF) with intensity of magnetic field onto following relation:-

$$\nu = \frac{\gamma H^0}{2\pi} \dots\dots 1$$

Since:-

$\gamma$  is magneto gyric ratio and is a fundamental nuclear constant which has a different value for every nucleus and  $h$  is Planck's constant.

The energy of a particular energy level is given by;

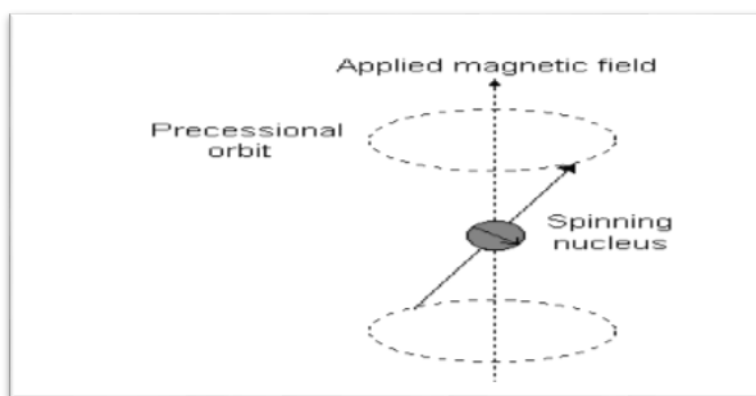
$$E = \frac{\gamma h m H^0}{2\pi}$$

It's very essential nuclear constant represented the ratio between  $\mu$  &  $I$

Due  $\gamma = \frac{2\pi \cdot \mu}{h \cdot I}$  so that  $\nu = \frac{H^0 \cdot 2\pi \cdot \mu}{2\pi \cdot h \cdot I}$  and then:

$$\nu = \frac{H^0 \cdot \mu}{h \cdot I} \dots\dots 2$$

Proton is small magnetic around under magnetic field effect. Axis of this magnetic preconcert along the axis of magnetic field as shown:-



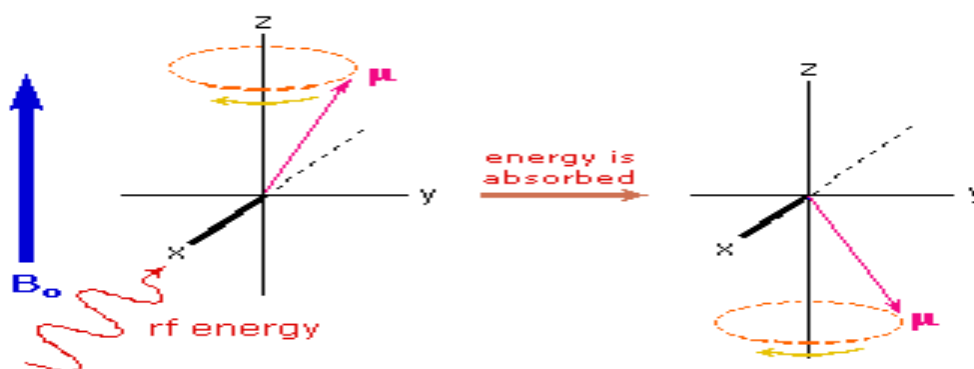
The frequency of precession is termed the *Larmor frequency*, which is identical to the transition frequency. The potential energy of the processing nucleus is given by;

$$E = - m B \cos q$$

Where  $q$  is the angle between the direction of the applied field and the axis of nuclear rotation. If energy is absorbed by the nucleus, then the angle of precession,  $q$ , will change. For a nucleus of spin  $1/2$ , absorption of radiation "flips" the magnetic moment so that it **opposes** the applied field (the higher energy state).

Spinning nuclei excited by absorption energy radiation with suitable frequency into higher energy levels with another orientations under magnetic field .the required energy equal to  $4.18 \times 10^{-12} \text{ kJ mol}^{-1}$ , that's smallest than UV- energy of excitation by 20 billion times.

If Radio frequency energy having a frequency matching the Larmor frequency is introduced at a right angle to the external field (e.g. along the x-axis), the processing nucleus will absorb energy and the magnetic moment will flip to its  $I = -1/2$  state. This excitation is shown in the following diagram. Note that frequencies in radians per second may be converted to Hz (cps) by dividing by  $2\pi$ .



Energy absorption.

The energy difference between nuclear spin states is small compared with the average kinetic energy of room temperature samples, and the +1/2 and -1/2 states are nearly equally populated. Indeed, in a field of 2.34 T the excess population of the lower energy state is only six nuclei per million. Although this is a very small difference, when we consider the number of atoms in a practical sample (remember the size of Avogadro's number), the numerical excess in the lower energy state is sufficient for selective and sensitive spectroscopic measurements.

### 3-Spin Interaction with Magnetic field:

The charged particles are spinning onto axis constitutes circular electric current which in turn produces a magnetic dipole. Spinning particle behave as a tiny bar magnetic placed along the spin axis. The size of dipole (strength of the magnet) for point charge can be shown to be :

$$\mu = \frac{q}{2m} \cdot I = \frac{q\sqrt{I(I+1)}}{2m} \cdot \frac{h}{2\pi} = \frac{qh \cdot \sqrt{I(I+1)}}{4\pi m}$$

by A.m<sup>2</sup> units, Since  $q$  and  $m$  are the charge and mass of particle.

The magnetic moment is here expressed in the appropriate fundamental SI units Ampere square meter. To express the magnetic moment in terms of magnetic flux density (colloquially magnetic field strength), the SI units of which is tesla (symbolized by T, units kg s<sup>-2</sup>.A<sup>-1</sup>) where 1T=10000gauss. The conversion is A.m<sup>2</sup>=(kg.s<sup>-2</sup>T<sup>-1</sup>)m<sup>2</sup>=J T<sup>-1</sup>(Joules per tesla). Can be writing then

$$\mu = \frac{qh \cdot \sqrt{I(I+1)}}{4\pi m} \quad (JT^{-1})$$

#### 4-The Chemical Shift:

More than a single line is observed for protons in an organic molecule such as ethanol. In liquid (isotropic) phase, this splitting of lines is caused by the chemical shift due to the Zeeman interaction and to scalar spin, spin couplings. As we have seen before, the resonance frequency depends on the strength of the applied static field and on the gyro magnetic ratio of the nucleus:

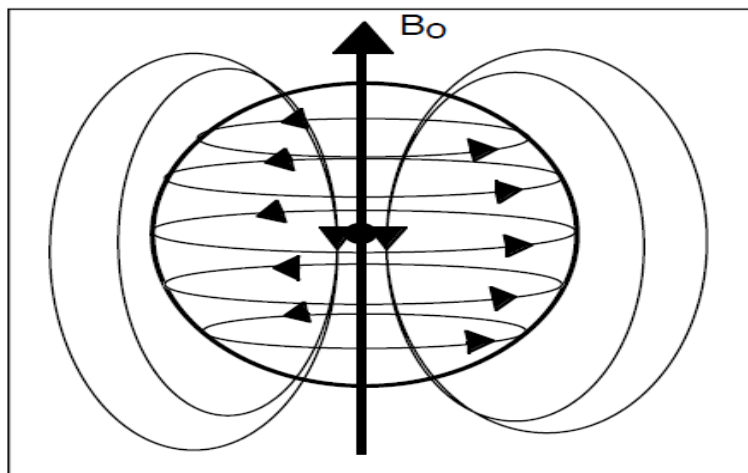
$$\omega = \gamma B$$

The field strength to be considered is not exactly the strength of the applied magnetic field **in vacuous** but is locally modified by the electronic environment of the nucleus. The **effective field strength** is very important at the nucleus site. Many different mechanisms are known that may influence the exact strength of field at the nucleus, which is  $\sigma$  that's consisted from several factors:

1.  $\sigma_{\text{dia}}$ . the diamagnetic contribution.
2.  $\sigma_{\text{para}}$ . the paramagnetic contribution.
3.  $\sigma_{\text{m}}$ . the neighbor anisotropy effect.
4.  $\sigma_{\text{rc}}$ . the ring-current contribution.
5.  $\sigma_{\text{ef}}$ . the electric field effect.
6.  $\sigma_{\text{solv}}$ . the solvent effect.

##### The diamagnetic effect

The nucleus are surrounded by an electron cloud. The static magnetic field  $B_0$  causes the electrons to process about the axis of the magnetic field. Thereby, a current is created that itself builds up a magnetic field. The direction of the induced field is opposed to the static field and acts to decrease the strength of the latter:

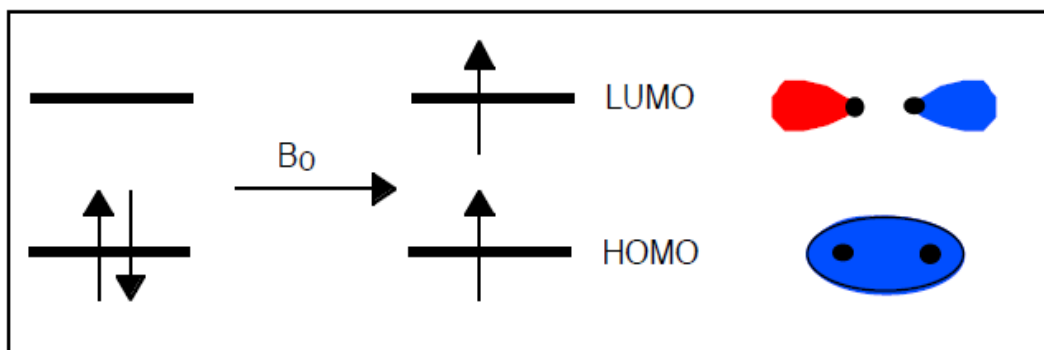


Diamagnetic force lines.

The diamagnetic shielding describes the behavior of spherically distributed electrons such as electrons from the s-orbital of protons. It is therefore the dominant term for proton shifts but less important for the heavier nuclei.

The paramagnetic term:

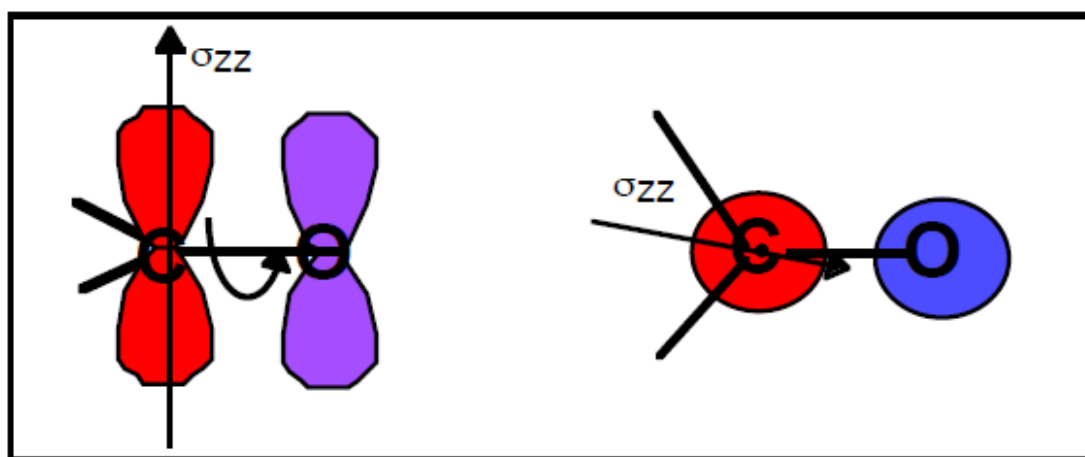
The paramagnetic term serves to correct for the disturbance of the spherical rotation of electrons. This may be caused by the formation of bonds. The electron distribution in such an excited state wave function is very different from that encountered in the ground state giving rise to a large change in the shielding:



Mixing of excited state wave function into ground-state wave functions through the  $B_0$  field.

## Chemical shift anisotropy:

The distribution of the electrons about the nucleus is usually non-spherically. The magnitude of the shielding therefore depends on the relative orientation of the nucleus with respect to the static field. For  $sp^3$  carbons the nuclei are tetrahedral coordinated and the electron distribution is almost invariant under rotation. For  $sp^2$  carbons such as aromatic or carbonyl nuclei the shielding highly depends on the orientation of the bond relative to the static field:

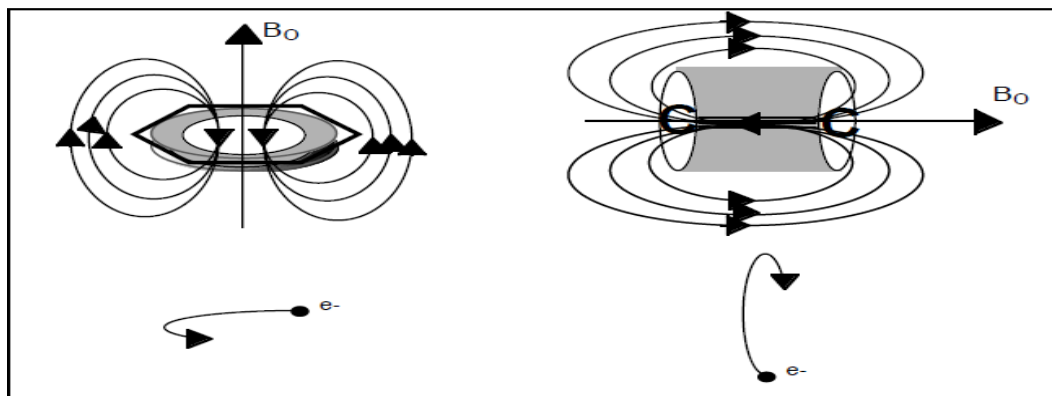


Shielding of carbonyl carbon independence of orientation.

## Magnetic anisotropy of neighboring bonds and ring current shifts:

Some types of neighboring bonds create an additional magnetic field which is anisotropic in space. An example is a triple bond. The  $\pi$  electrons of the triple bond form an electron cloud that extends around the bond axis in form of a tube. The magnetic field forces the electrons to rotate about the bond axis creating a magnetic field whose direction is along the bond axis and which again counteracts the static field. A similar counteracting field is formed in the  $\pi$ -cloud of aromatic systems. Such anisotropies can dramatically change the appearance of proton spectra. They usually increase the dispersion of proton spectra. However, in order to give substantial effects the influenced protons must be sterically fixed in relative

to the anisotropic group. This is the case for folded proteins that do adopt a unique structure. Therefore, one can sometimes judge from the signal dispersion of 1D proton spectra whether a protein is folded or random coil.



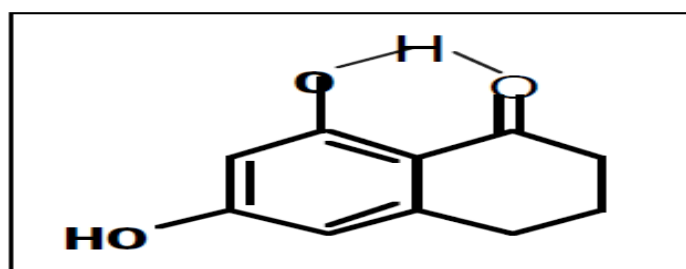
Left: Anisotropy from a benzene  $\pi$  system. Right: Anisotropy from a triple bond.

Electric field gradients:

Strongly polar groups create intermolecular electric fields. This has the effect of distorting electron density in the rest of the molecule and will hence influence the chemical shifts.

Hydrogen bonds:

Hydrogen bonds decrease the electron density at the involved proton site and hence lead to a high-frequency shift. The effect is especially pronounced for symmetric hydrogen bonds (those in which the distance of the proton is equal to both acceptors). Protons that are hydrogen bonded usually be easily recognized from their shift. Their shift is highly temperature, concentration and solvent dependent.



The hydroxyl group at the top of the molecule is part of a sym. H-bond and will therefore be down-field shifted.



Solvent effects:

Different solvents may have different effects on the chemical shifts. Quite often an overlapping signal can be resolved when changing the solvent. Suitable solvents for causing large changes in chemical shifts are benzene or acetone, which may completely change the appearance of a spectrum that has been acquired in chloroform. This effect is especially pronounced when benzene selectively complexes parts of the molecule due to the ring-current effect from the aromatic ring. Such selective effects may be the case when not all parts of the molecule can be accessed by the solvent.

Shifts due to paramagnetic species:

Paramagnetic compounds have unpaired electrons. When paramagnetic impurities are contained in the sample, the lines are usually considerably broadened for solvent excessible protons. However, the chemical shift can also be influenced. Paramagnetic reagents, also known as shift reagents, serve to disperse proton spectra. Thereby, a 2 ppm shift range for aliphatic protons can be dispersed over 6 ppm after addition of the shift reagent.

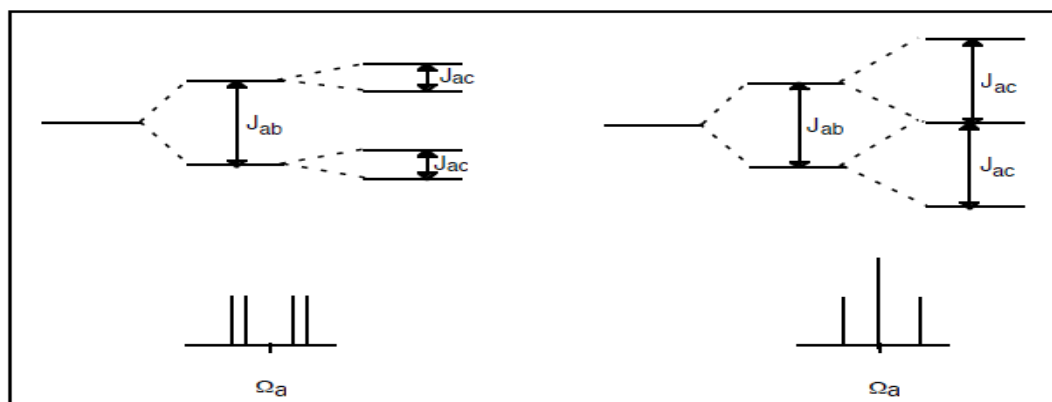
## **5- Couplings interaction:**

They found two types of interaction between spins are known as the dipolar coupling and scalar coupling. The contributions from dipolar coupling usually cannot be observed in isotropic (liquid) phase. This is so because the dipolar coupling depends on the orientation of the connecting vector to the static field. This orientation rapidly changes in solution due to molecular tumbling and the dipolar coupling therefore averages to zero. However, it can be observed in the solid state or in liquid crystals.

The scalar coupling leads to a splitting of resonance lines. The effect is mediated via the electrons and its magnitude therefore rapidly decreases when the number of intervening bonds increases. The basic mechanism that propagates the coupling is the Fermi-contact interaction. This effect describes the coupling between the nuclear and the electron spin.

#### 6-Spin couplings:

Each coupling doubles the numbers of lines. When couplings are of similar magnitude, some lines overlap. In open-chain compounds single bond dihedral angles are rotationally averaged so that all vicinal couplings are around 7 Hz. In this case the total number of lines of a single resonance due to the coupling with N neighboring protons is N+1. In cyclic or structurally well-defined compounds where the couplings may be much different the total number is  $2^{(N-1)}$ .

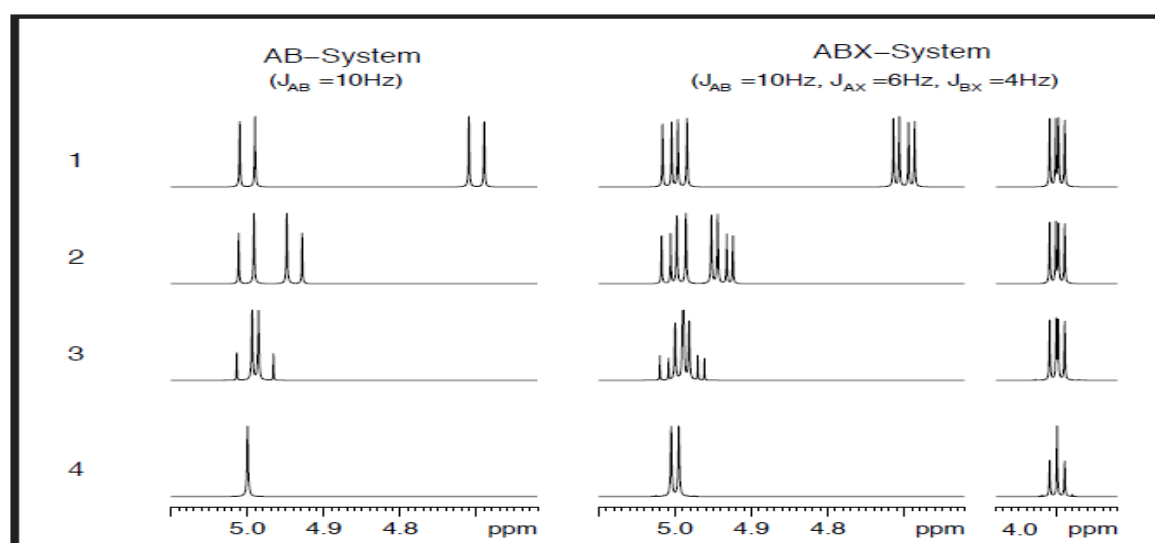


Coupling of a proton with two other protons b and c for the case of different (left) or similar (right) couplings. The intensities of the lines in the case of overlapping lines (similar magnitude of couplings) can be derived from the coefficient in the Pascal triangle.

Number of coupled nuclei		Number of lines	rel. intensities
$I=1/2$	$I=1$		
0		1 (singlet)	1
1		2 (doublet)	1:1
2		3 (triplet)	1:2:1
3		4 (quartet)	1:3:3:1
4		5 (quintet)	1:4:6:4:1
5		6 (sextet)	1:5:10:10:5:1
6		7 (septet)	1:6:15:20:15:6:1
	0	1 (singlet)	1
	1	3 (triplet)	1:1:1
	2	5 (quintet)	1:2:3:2:1
	3	7 (septet)	1:3:6:7:6:3:1

## 6-Strong coupling:

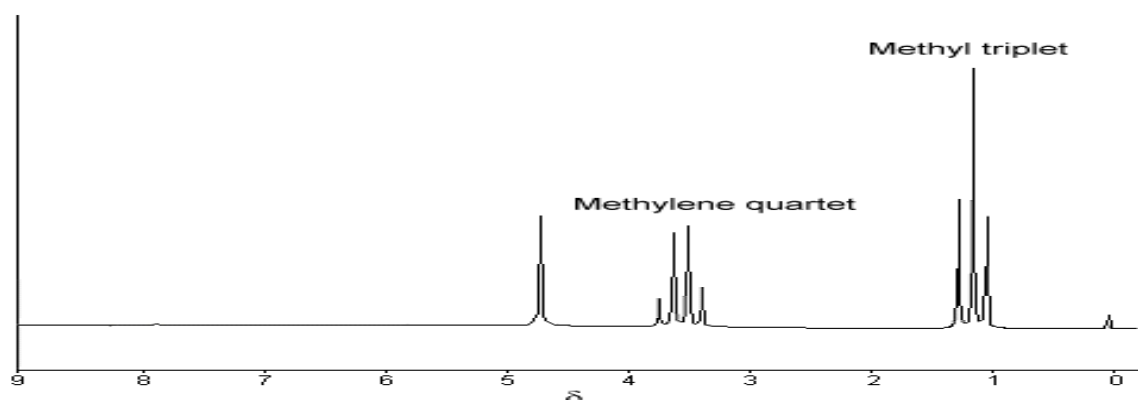
The rules for line multiplicities and intensities described above are only valid in the case of weak coupling. In the strong-coupling case spin properties are mixed. A practical consequence is that a resonance line cannot be referred to belong to a spin A or B, whereas in the limit of weak coupling a spin-flip of spin A does not cause spin B to flip there is a probability to do so in the strong coupling case. In order to derive coupling constants or chemical shifts from strongly coupled spins these parameters may not be extracted from the spectrum but have to be derived from a simulation and comparison to the measured spectrum.



Second order effects depending on the chemical shift difference

## 7-Application of Spin - spin coupling:

They Consider the structure of ethanol; methyl group  $\rightarrow \text{CH}_3$ -  
(OH) $\text{CH}_2$   $\leftarrow$  methylene group. The  $^1\text{H}$  NMR spectrum of ethanol (below) shows the methyl peak has been split into three peaks (a *triplet*) and the methylene peak has been split into four peaks (a *quartet*). This occurs because there is a small interaction (*coupling*) between the two groups of protons. The spacing between the peaks of the methyl triplet are equal to the spacing between the peaks of the methylene quartet. This spacing is measured in Hertz and is called the *coupling constant, J*.

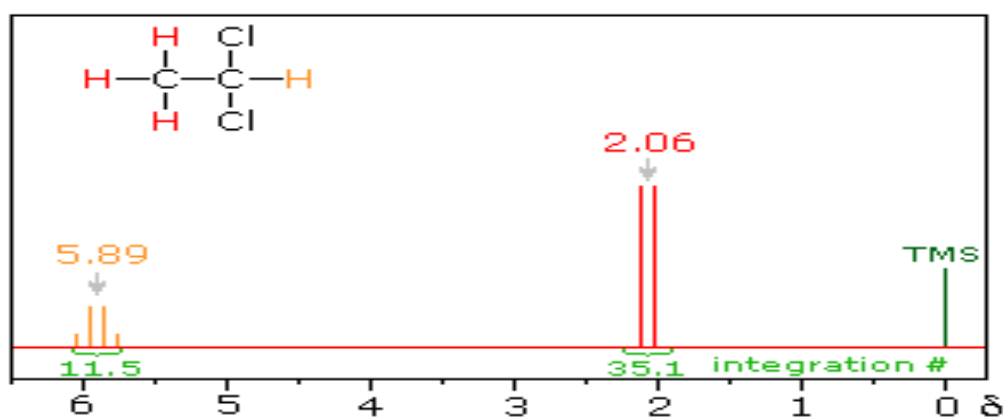


$^1\text{H}$ -NMR Chart of Ethanol.

In the first possible A combination, spins are paired and opposed to the field. This has the effect of reducing the field experienced by the **methyl** protons; therefore a slightly higher field is needed to bring them to resonance, resulting in an up field shift. Neither combination of spins opposed to each other has an effect on the methyl peak. The spins paired in the direction of the field produce a downfield shift. Hence, the methyl peak is split into three, with the ratio of areas 1:2:1. Similarly, the effect of the methyl protons on the methylene protons is such that there are eight possible spin combinations for the three methyl protons in B.

Out of these eight groups, there are two groups of three magnetically equivalent combinations. The methylene peak is split into a quartet. The areas of the peaks in the quartet have the ratio 1:3:3:1.

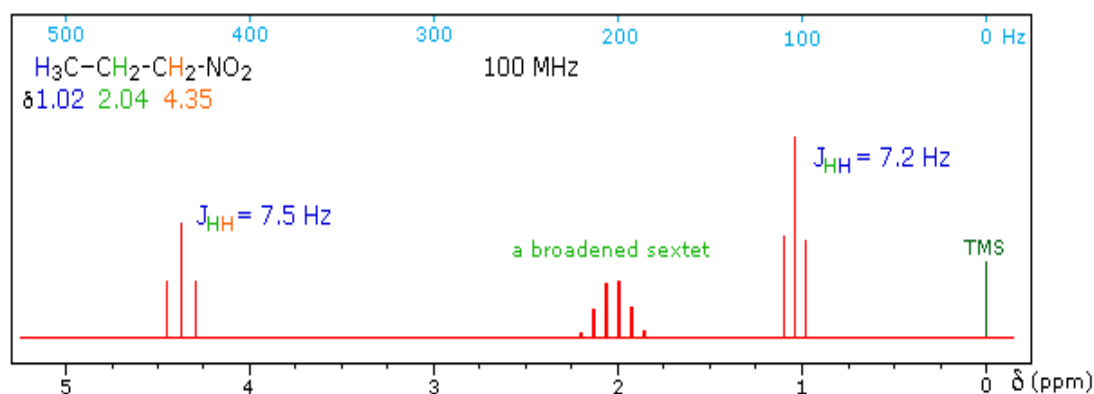
In the spectrum of 1, 1-dichloroethane shown on the right, it is clear that the three methyl hydrogens (red) are coupled with the single methyne hydrogen (orange) in a manner that causes the former to appear as a doublet and the latter as a quartet.



NMR chart of 1, 1-dichloroethane.

#### Spectrum of 1-nitropropane.

The three distinct sets of hydrogens in this molecule generate three resonance signals (two triplets and a broad sextet). A carefully tuned decoupling signal may be broadcast into the sample while the remaining spectrum is scanned. The region of the decoupling signal is obscured, but resonance signals more than 60 Hz away may still be seen. By clicking on one of the three signals in the spectrum, the results of decoupling at that frequency will be displayed.



NMR chart of 1-nitropropane.

In this example, the nuclei being decoupled and the nuclei being observed by the spectrometer are of the same kind (both protons). This phenomena is called homo nuclear decoupling. It is also possible to decouple different kinds of nuclei. For example, a compound having both hydrogen and fluorine as part of its molecular composition may exhibit spin-coupling between their nuclei, and one may be decoupled while the other is observed. This is termed hetero nuclear decoupling. Hetero nuclear decoupling is very important in  $^{13}\text{C}$ -NMR spectroscopy.

Fundamental Quantity	SI Unit Symbol	Units
Magnetization	M	A/m
Permeability of free space	$\mu_0 = 4\pi \times 10^{-7}$	Wb/A m
Gyromagnetic ratio	$\gamma$	(s A/m) $^{-1}$
Magnetic field strength	$H = NI$	A/m
Magnetic induction – Flux	$B = \mu_0(H + M)$	Wb/m $^2$ or Tesla (T)
Planck's constant	$h = 6.62 \times 10^{-34}$	J s
Plancks concstat/ $2\pi$	$\hbar = 1.055 \times 10^{-34}$	J s

*A – Ampere; m – meter, s – second; Wb – Weber; J – Joule; T – Tesla; N – number of turns per meter; I – current in Ampere units.*