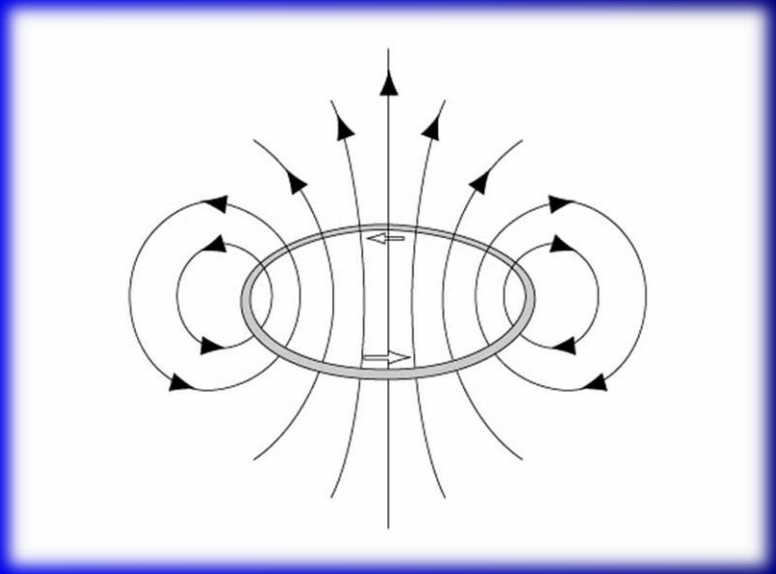
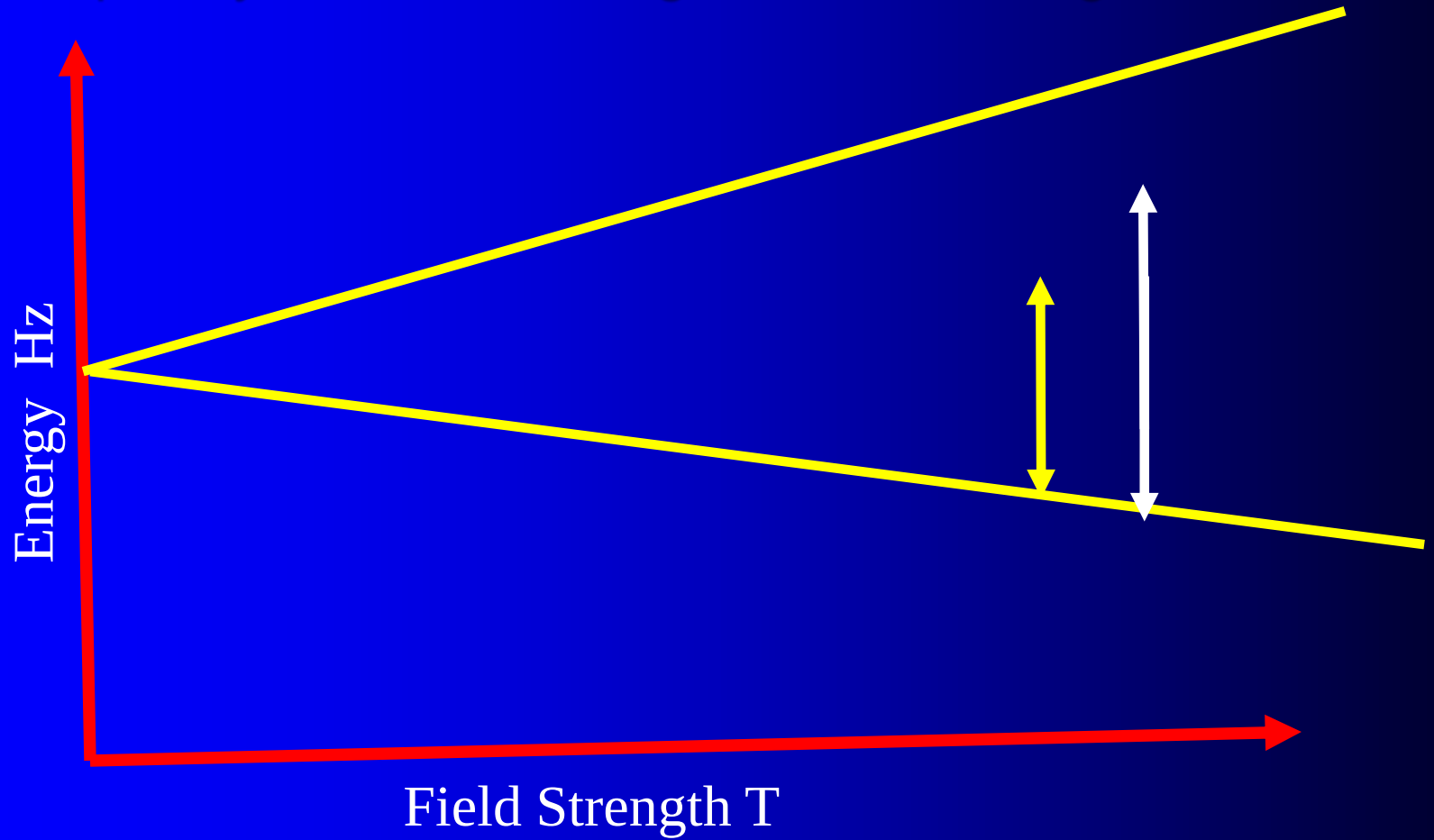
Lecture 4
Some More nmr



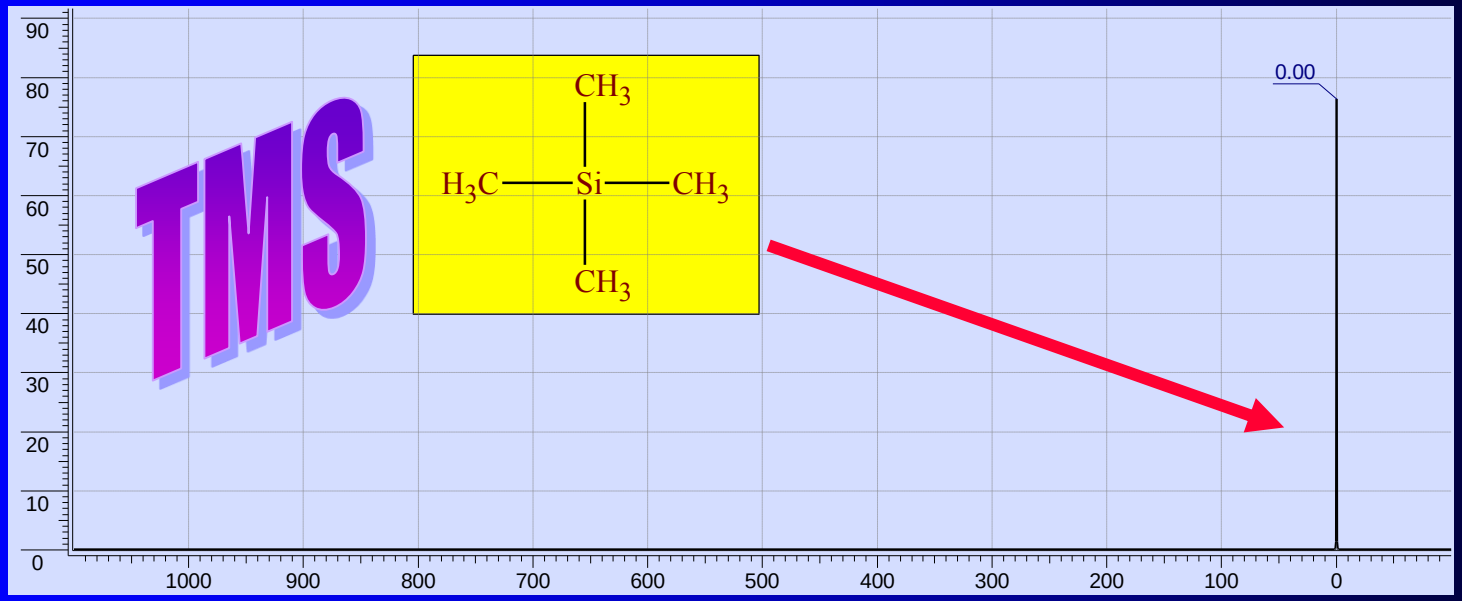
Conducting loops and magnetic fields
"conventional" current??

http://www.mi.mun.ca/users/cchaulk/eltk1100/ivse/ivse.htm

Resonance can be achieved by changing the magnetic field strength at constant frequency …or by changing frequency at constant magnetic field strength



The 100MHz nmr Chart

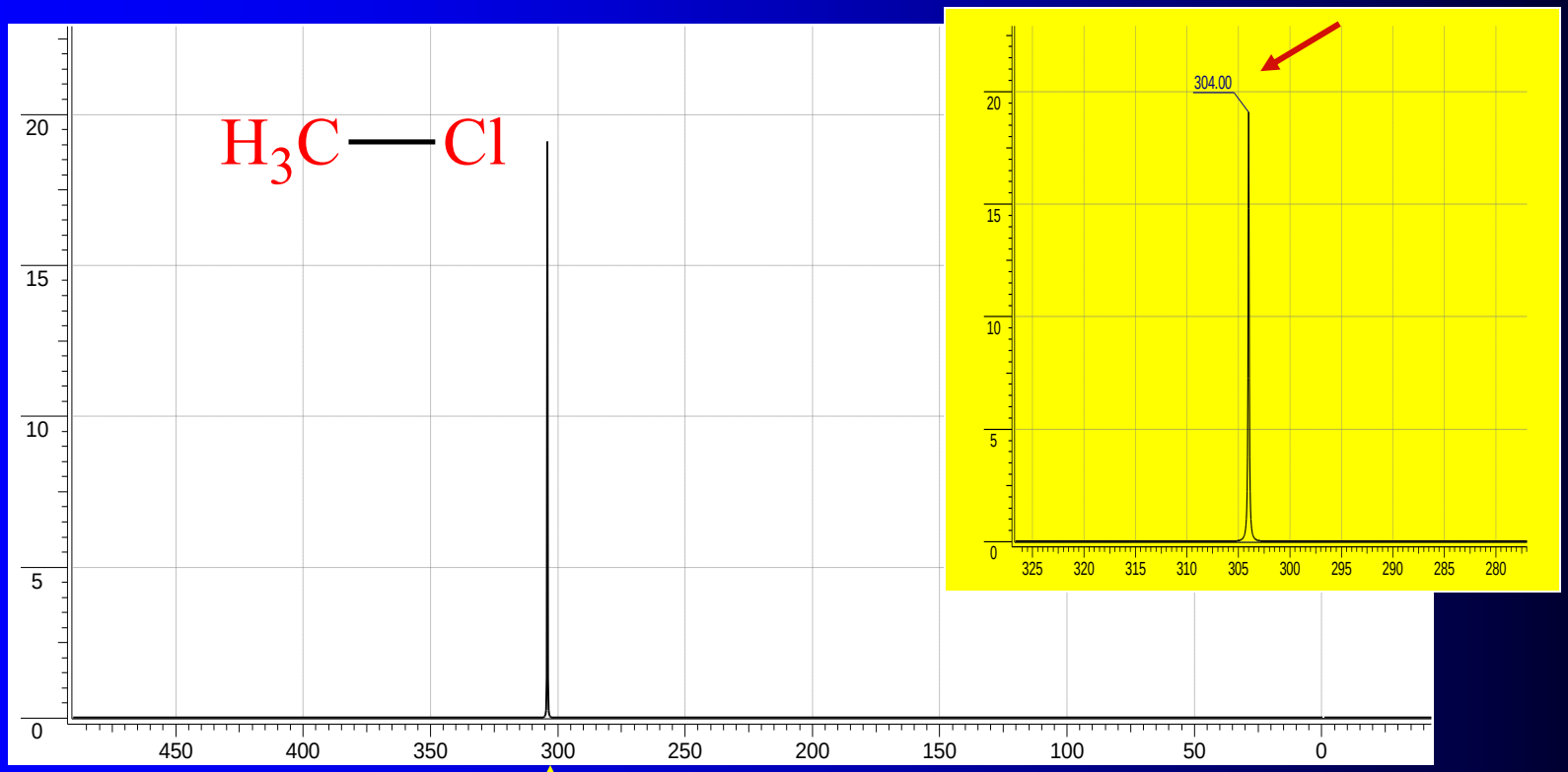


Frequency

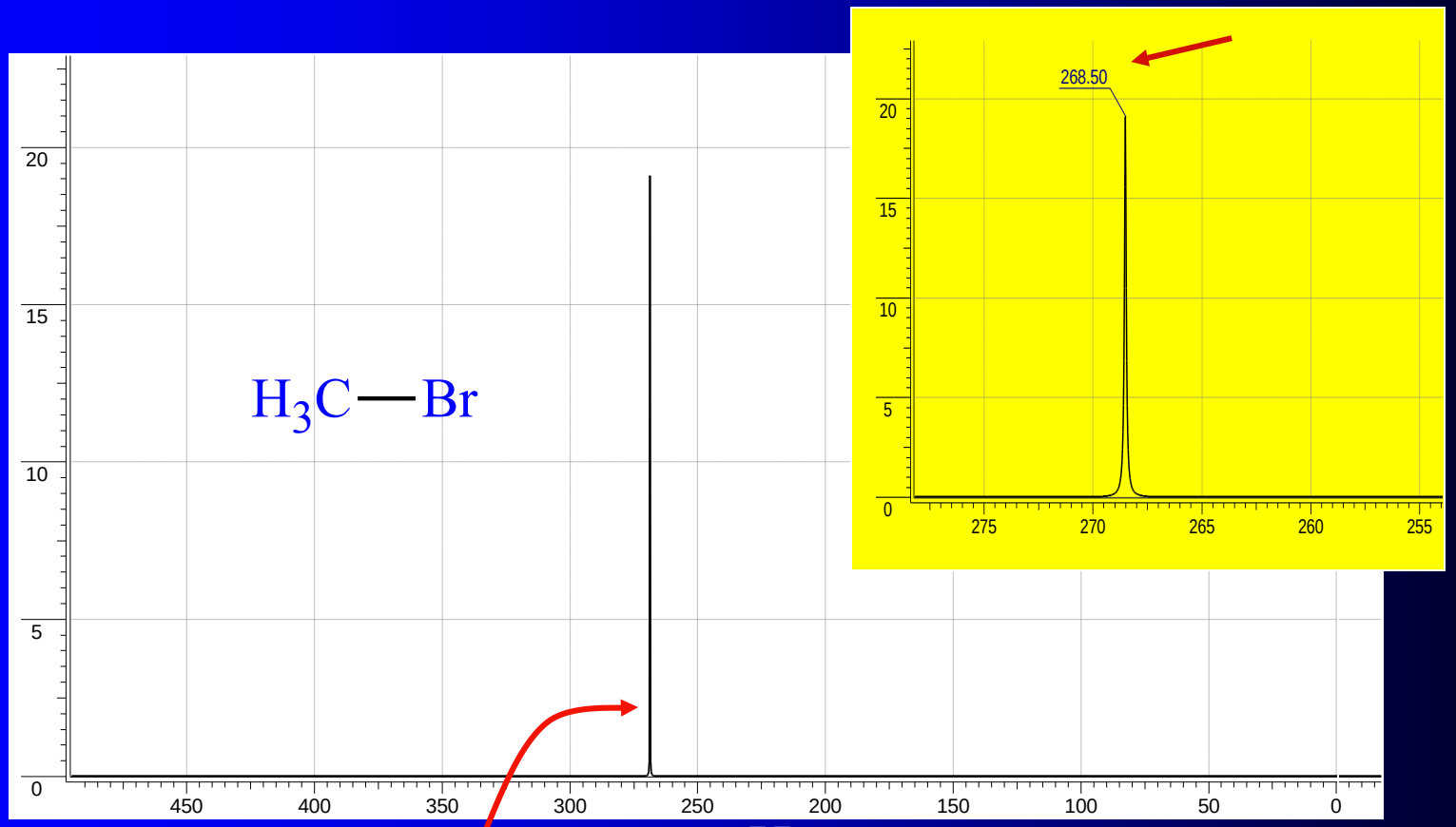
field

The TMS resonance is defined as having “0” frequency

100MHz Spectrum



100MHz nmr Spectrum



Chemical Shift

- The difference in resonance frequencies for hydrogens in CH_3Cl compared to CH_3Br under an applied field of 2.34T is only 35.5Hz, which is 0.35 parts per million (ppm) compared with the irradiating frequency

$$\frac{35\ \text{Hz}}{100 \times 10^6\ \text{Hz}} = \frac{0.35}{10^6} = 0.35\ \text{ppm}$$

Here, 35Hz is the difference in resonance frequency and 100MHz is the ^{1}H resonance frequency for B=2.34T and γ = 42.58 MHz / Tesla

Calculating Chemical Shift

At 7.05 T, a resonance is at 715 Hz (from TMS)

1. What is the spectrometer frequency?

$\nu = \gamma B = (42.5\text{MHz/T})(7.05\text{T}) = 300\text{MHz}$

2. What is the chemical shift in ppm???

$$\frac{715\ \text{Hz}}{300 \times 10^6\ \text{Hz}} = \frac{2.38}{10^6} = 2.38\ \text{ppm}$$

Chemical Shift

- Depends on several things (1) electronegativity of nearby atoms, (2) the hybridization of adjacent atoms, and (3) magnetic induction within an adjacent pi bond
- (1) Electronegativity

CH_3-X	Electronegativity of X	δ of H
CH_3F	4.0	4.26
CH_3OH	3.5	3.47
CH_3Cl	3.1	3.05
CH_3Br	2.8	2.68
CH_3I	2.5	2.16
$(CH_3)_4C$	2.1	0.86
$(CH_3)_4Si$	1.8	0.00 (by definition

Chemical Shift

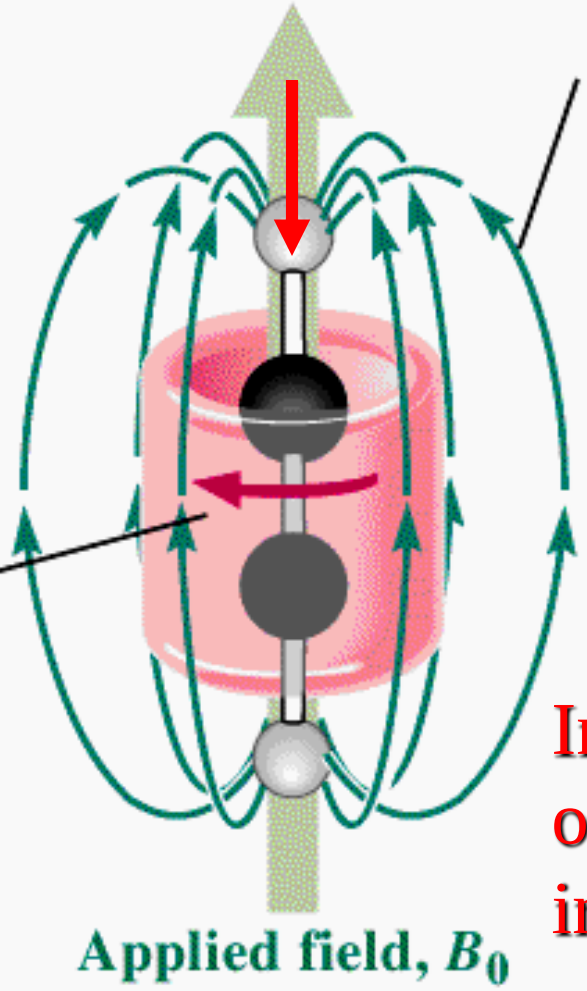
- (2) The Hybridization of C Effects ^{1}H chemical Shift

Hybrid	Type of H	Name	δ
sp^3	RCH_3	alkyl	0.8- 1.0
sp	$RC{\equiv}CH$	acetylenic	2.0 - 3.0
sp^2	$R_2C{=}CH_2$	vinylic	4.6 - 5.7

This seems like a Mystery!!

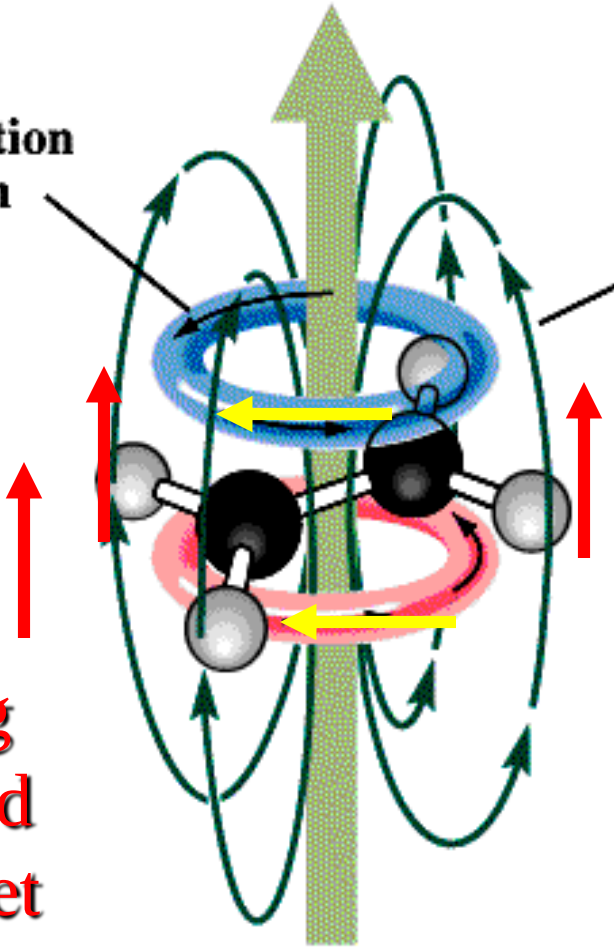
Magnetic field induced in the pi bonds if a carbon-carbon triple bond

is this arrow correct for electron flow???



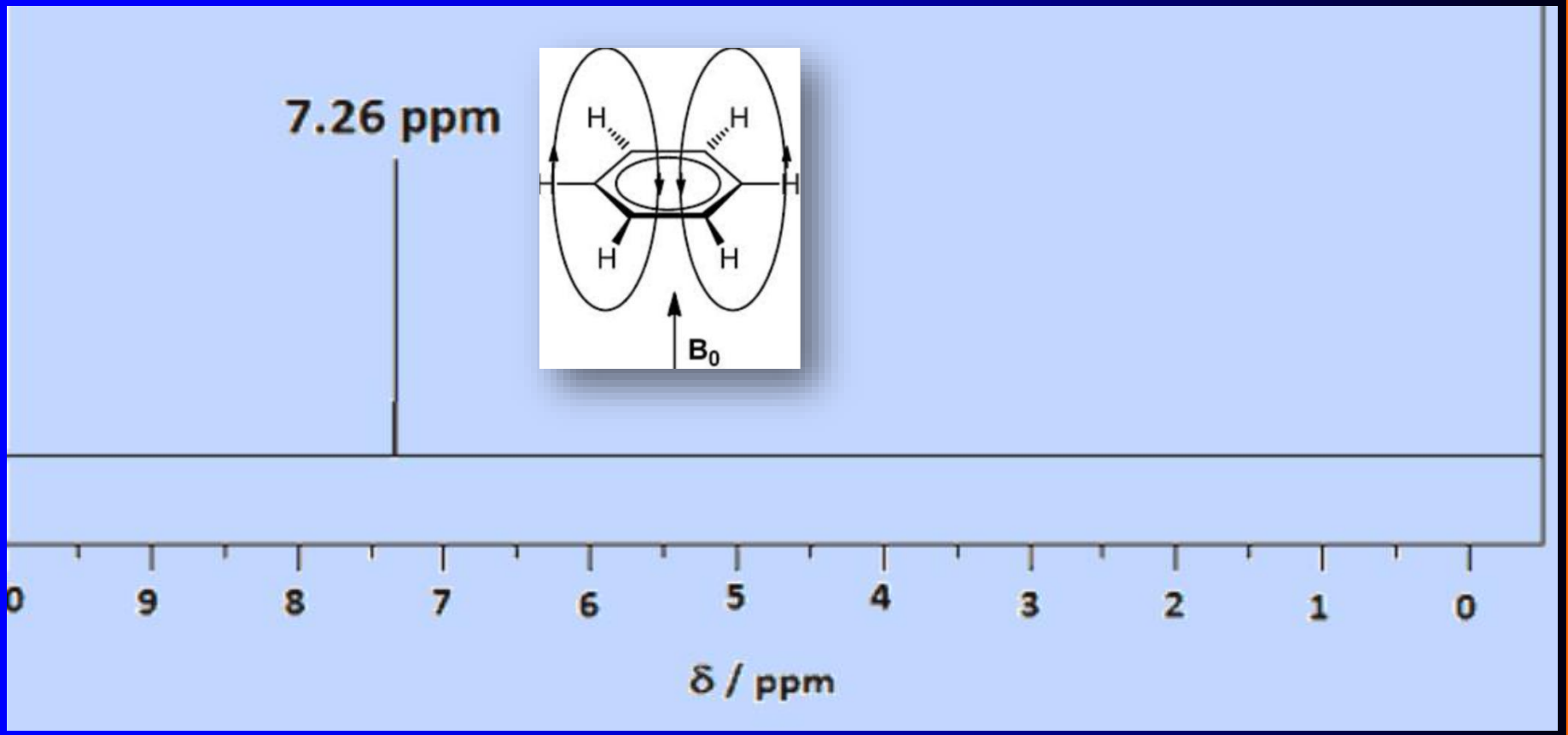
Induced field opposes big magnet inside the ring

Magnetic field induced in the pi bond of a carbon-carbon double bond



Outside the ring the induced field helps big magnet

^{1}H-nmr spectrum of benzene



Chemical Shift

- Magnetic induction in pi bonds of a….
  - a carbon-carbon triple bond shields an acetylenic hydrogen and shifts its signal upfield (to the right) to a smaller δ value
  - carbon-carbon double bond deshields vinylic a hydrogens and shifts their signal downfield (to the left) to a larger δ value

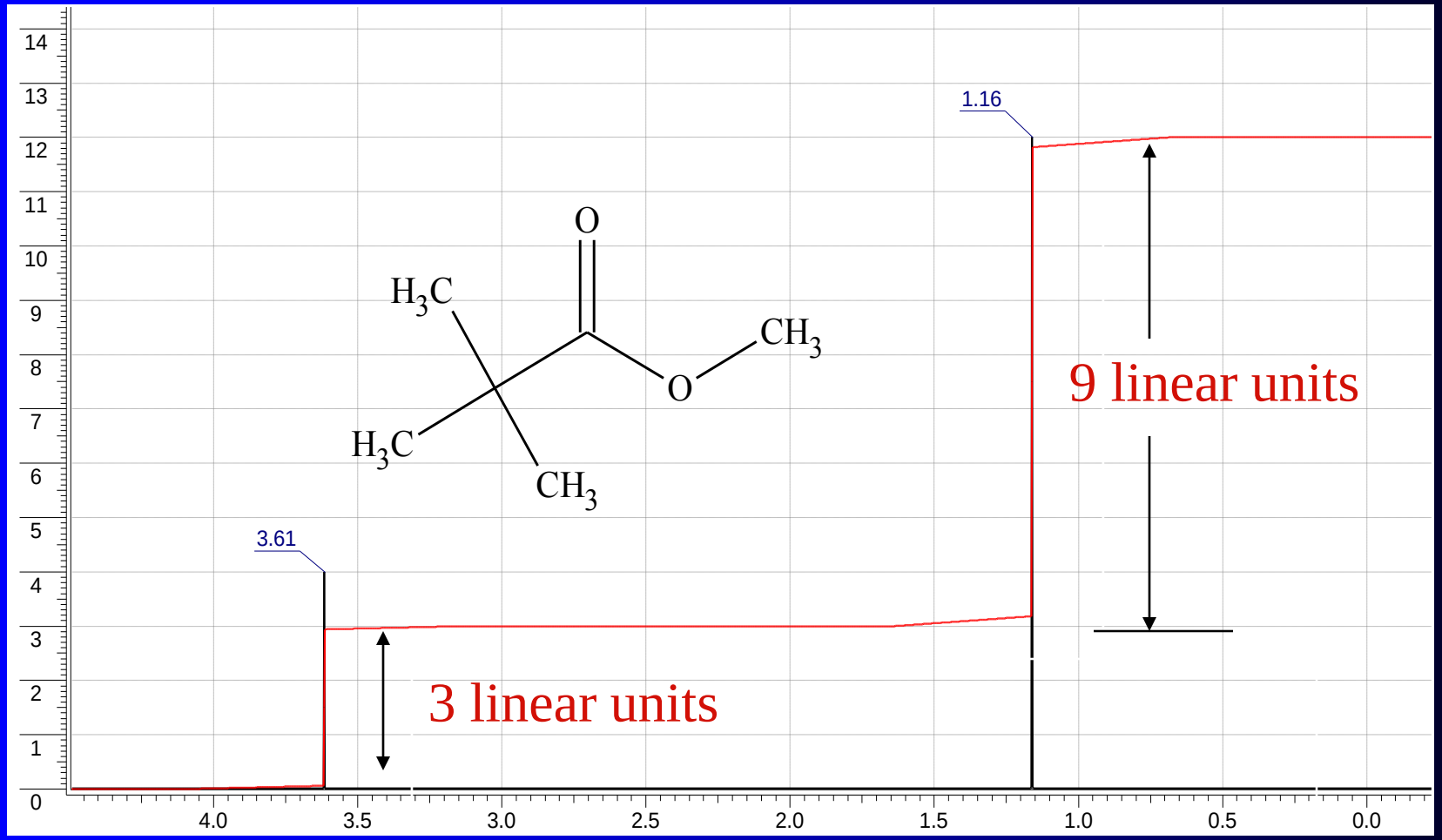
Chemical Shift - ^{1}H-NMR

Type of H	δ	Type of H	δ
$(CH_3)_4Si$	0	ROH	0.5-6.0
RCH_3	0.9	RCH_2OR	3.3-4.0
RCH_2R	1.2-1.4	R_2NH	0.5-5.0
R_3CH	1.4-1.7	$RC(=O)CH_3$	2.1-2.3
$R_2C{=}CRCHR_2$	1.6-2.6	$RC(=O)CH_2R$	2.2-2.6
$RC{\equiv}CH$	2.0-3.0		
$ArCH_3$	2.2-2.5		

Chemical Shift - ^{1}H-NMR

Type of H	δ	Type of H	δ
	3.5-3.9	$R_2C{=}CH_2$	4.6-5.0
	4.1-4.7	$R_2C{=}CHR$	5.0-5.7
RCH_2I	3.1-3.3	ArH	6.5-8.5
RCH_2Br	3.4-3.6		9.5-10.1
RCH_2Cl	3.6-3.8		10-13
RCH_2F	4.4-4.5		

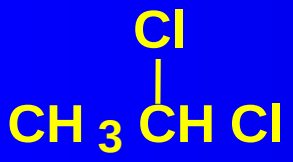
Integration



"up field"

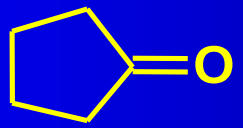
Equivalent Hydrogens

- Have exactly the same chemical environment



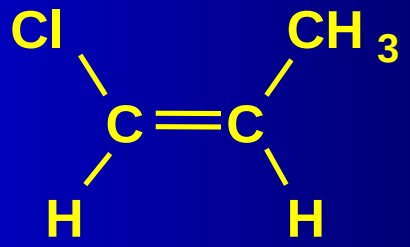
1,1-Dichloro-ethane

2 signals



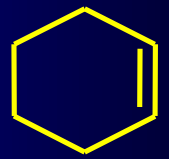
Cyclopentanone

2 signals



(Z)-1-Chloropropene

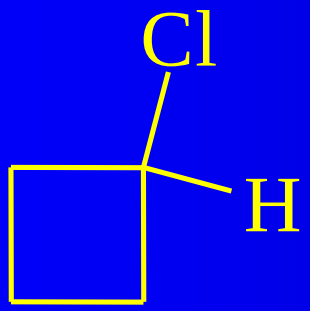
3 signals

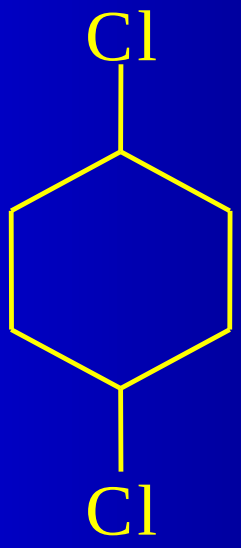


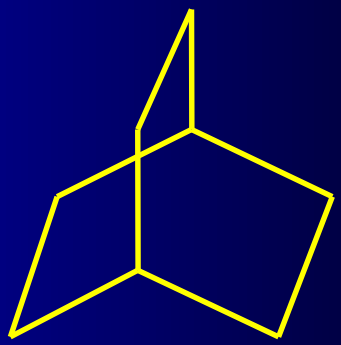
Cyclohexene

3 signals

How many equivalent hydrogens??





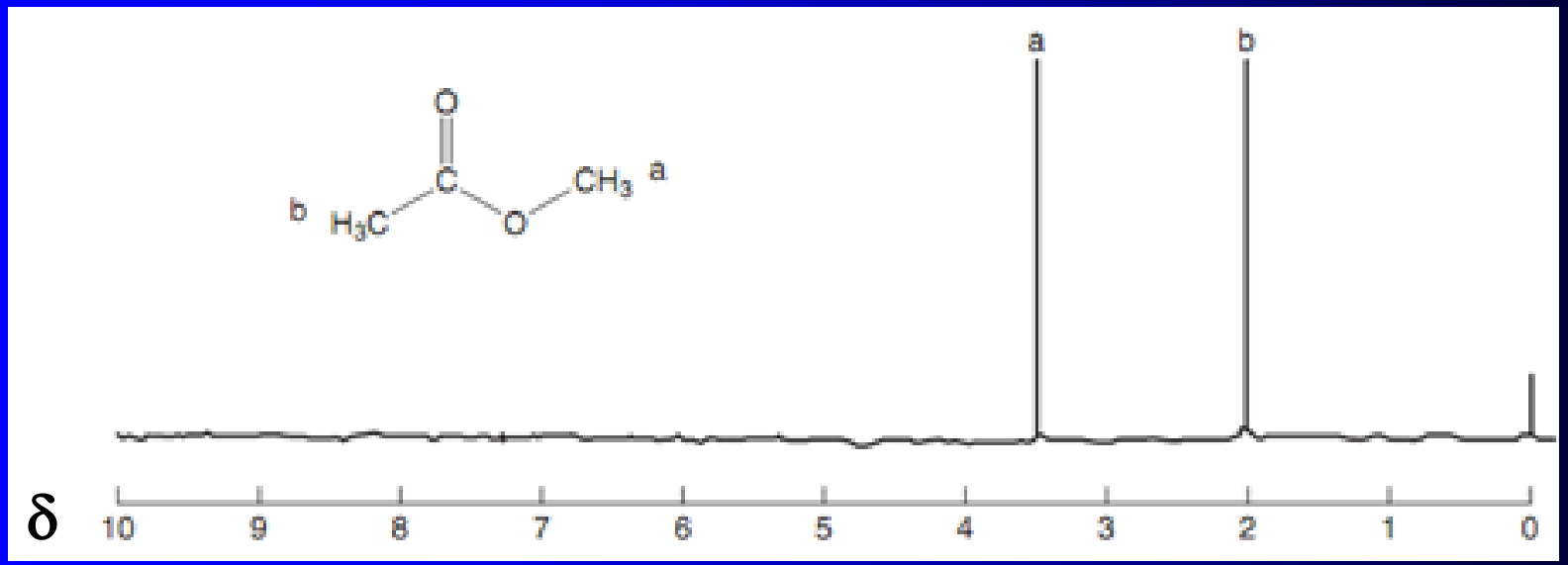


This looks “easy” but it is not!!

Changing Spectrometers

- If the resonance of the peak on a 7.05 T instrument is 715 Hz, what will the resonance frequency be at 23.5 T
- What is the resonance in ppm at 7.05 T ?
- What is the resonance in ppm at 23.5 T?

Chemical shift in ppm (δ) is independent of field strength!



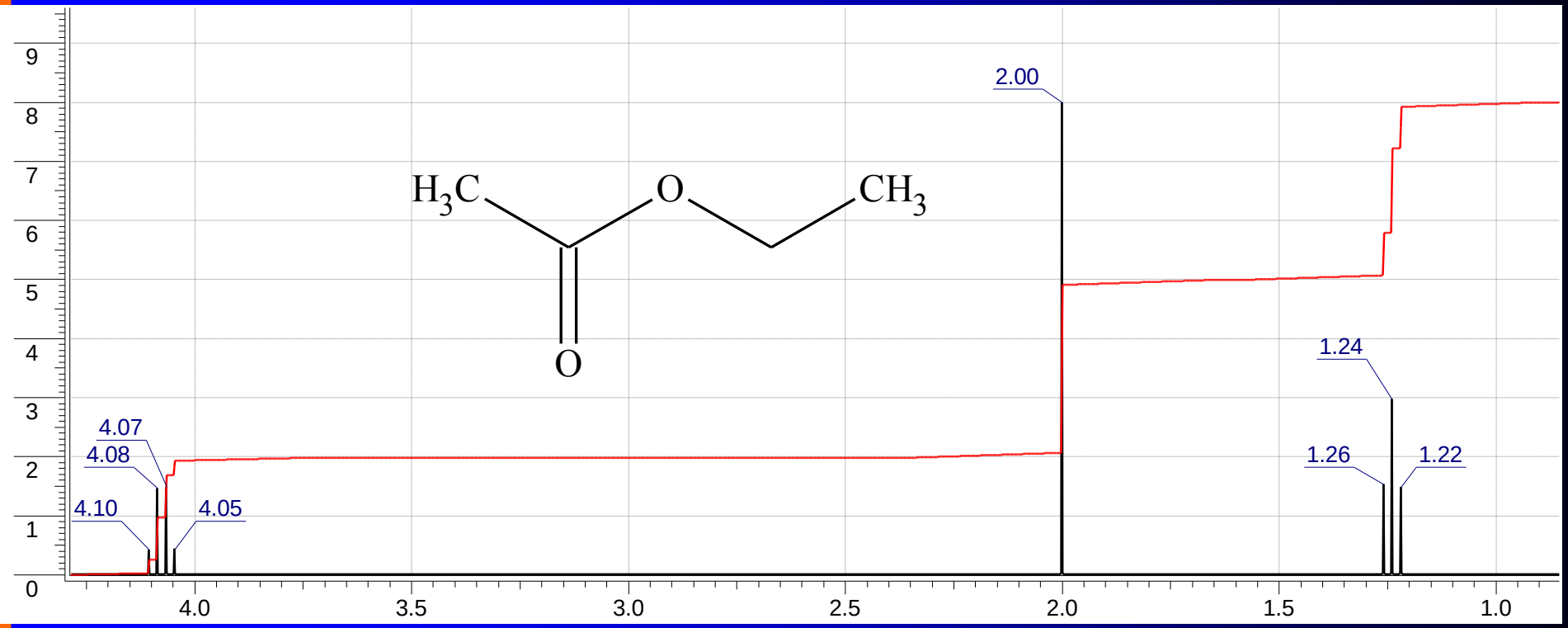
Frequency

Field

Up Field

Down Field

Ethyl Acetate



Signal Splitting

Huh?? Why??? What is going on here??

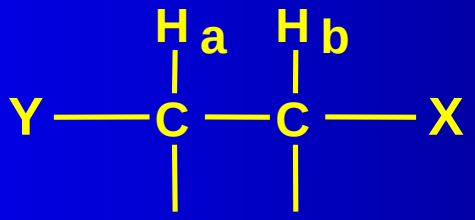
What a mess.

- Signal splitting: splitting of an NMR signal into a set of peaks by the influence of neighboring nonequivalent hydrogens

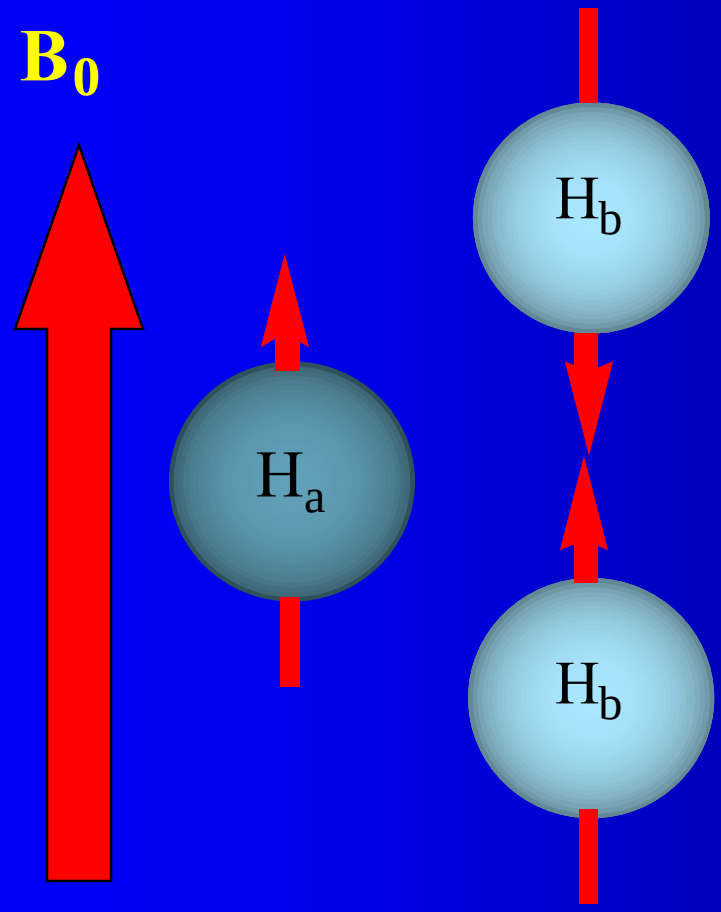
- This splitting business is actually rich in information…it is a wonderful thing!

Origins of Signal Splitting

- When the chemical shift of one nucleus is influenced by the spin of another, the two are said to be *coupled*
- Consider nonequivalent hydrogens H_a and H_b on adjacent carbons
  - the chemical shift of H_a is influenced by whether the spin of H_b is aligned with or against the applied field



Origins of Signal Splitting

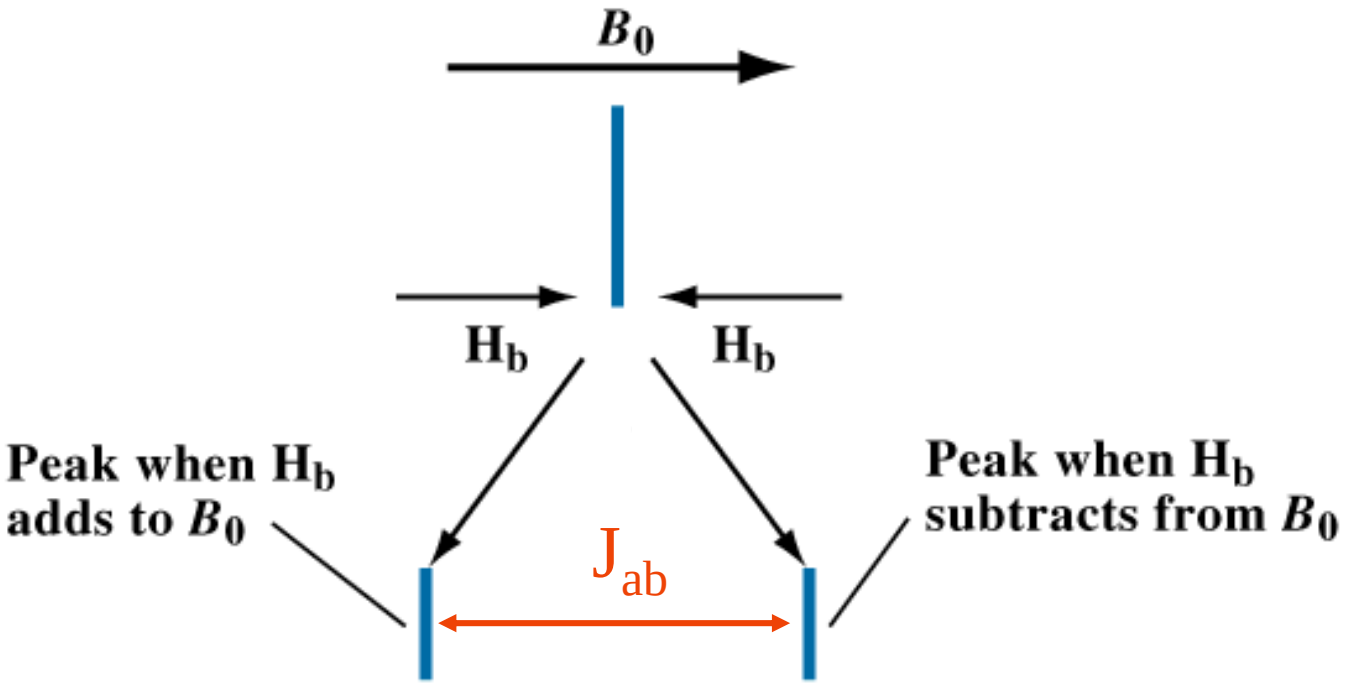


Magnetic field of H_b subtracts from the applied field; H_b signal appears at a higher applied field

Magnetic field of H_b adds to the applied field; H_a signal appears at a lower applied field

Remember…it is the NET field that counts

The signal of Ha is split into two peaks of equal area (a doublet)

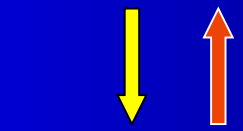


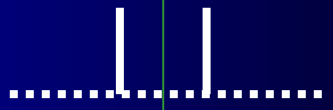
J_{ab}= coupling constant

Origins of signal splitting

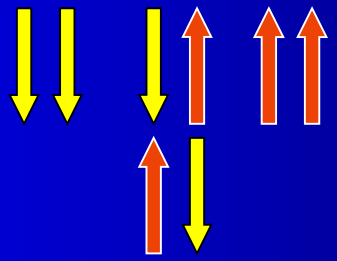
no neighbors

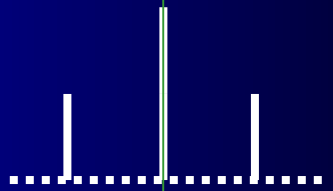
one spin



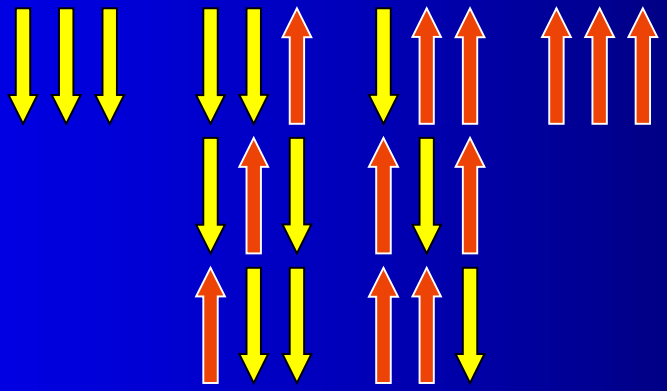


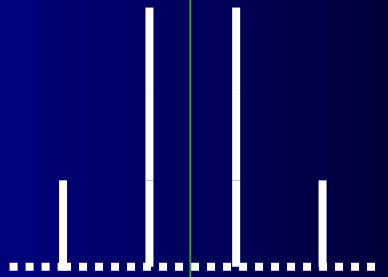
two spins





three spins





Relative Intensity of Peaks

singlet	1
double	1 1
triplet	1 2 1
quartet	1 3 3 1
quintete	1 4 6 4 1
sextete	1 5 10 10 5 1

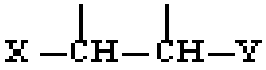
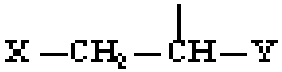
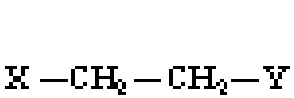
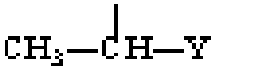
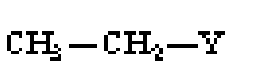
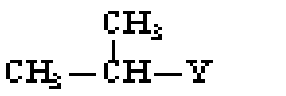
Pascal's triangle

The binomial coefficients

The "N+1 Rule"

- The ^{1}H-NMR signal of a hydrogen or set of equivalent hydrogens is split into (N + 1) peaks by a set of N equivalent neighboring hydrogens
  - All neighboring hydrogens in the analysis must have the same chemical shift (magnetically equivalent)
  - If this condition is not met, a graphical tree or second order analysis must be used to predict the splitting pattern. We will explore this condition later

NMR Splitting Patterns

n+1			n+1
2			2
2			3
3			3
2			4
3			4
2			7

Who needs DNA??