



CHEM F111 : General Chemistry

Semester II: AY 2017-18

Lecture 19 (26-02-2018)

Summary of Lecture 18

$$\frac{N_{\beta}}{N_{\alpha}} = e^{\frac{-\Delta E}{kT}} = e^{\frac{-h\nu}{kT}} = e^{\frac{-\gamma_N \hbar B_0}{kT}}$$

- Intensity of absorption (I) $\propto B_0^2/T$
- Decreasing T or Increasing B, \Rightarrow Population increases in α -state.
- Increase the population difference \Rightarrow increase sensitivity.
- Absolute resonating frequency (ν) depending upon the external applied magnetic field. Chemically different proton resonate at different frequency, whereas chemically similar protons resonate at the same frequency.

$$\nu = \gamma_N B_{\text{eff}} / 2\pi = \gamma_N B_0(1-\sigma)/2\pi$$

- Absolute chemical shift (δ) is independent to the applied external magnetic field or field strength of the instrument.

$$\text{Chemical shift: } \delta = \{(\nu - \nu_0) / \nu_0\} \times 10^6$$

- The electron density around the ^1H -nucleus have direct influence on the local magnetic field or *shielding factor* (σ) exerted by the nucleus in a magnetic field, thus more electron density around nucleus means more shielding.

Shielding vs. Deshielding



- Chemically different protons resonate at different δ -value

$$\text{Shielding factor: } \sigma = \sigma_{\text{local}} + \sigma_{\text{neighbour}} + \sigma_{\text{solvent}}$$

σ_{local} : due to the shielding from the electrons immediately surrounding the nucleus. (Electron density around the nuclei).

$\sigma_{\text{neighbour}}$: due to the shielding from the neighboring environment.

σ_{solvent} : the contribution from solvent molecules.

What is Shielding? “A nucleus whose chemical shift has been decreased due to addition of electron density, magnetic induction, or other effects.”

What is Deshielding? “A nucleus whose chemical shift has been increased due to removal of electron density, magnetic induction, or other effects.”

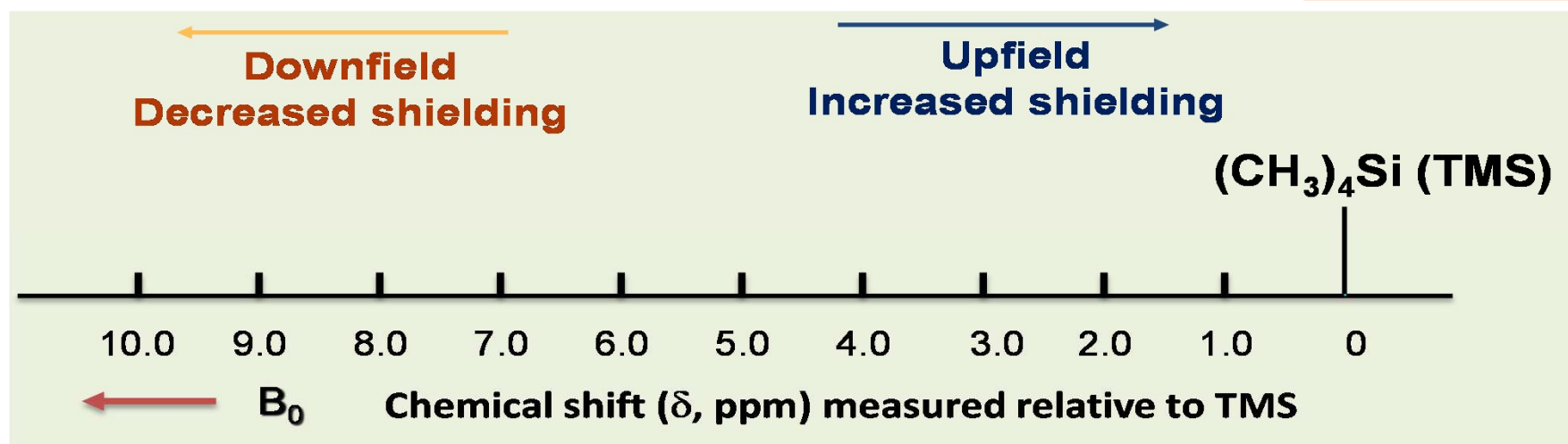
Nuclei in a region of high electron density are more shielded from the applied field than those in regions of lower electron density.

Chemical shift: Shielding vs. Deshielding

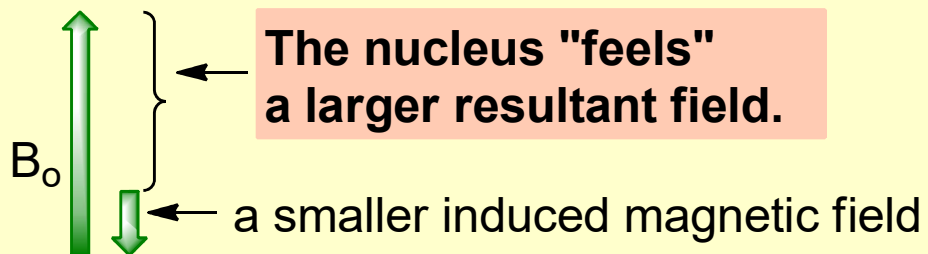


- **The Chemical Shift:** The resonance frequency depends on the “effective” magnetic field that a proton feels. This can differ for different types of ^1H due to local electron currents that counteract the applied field. → **Shielding**

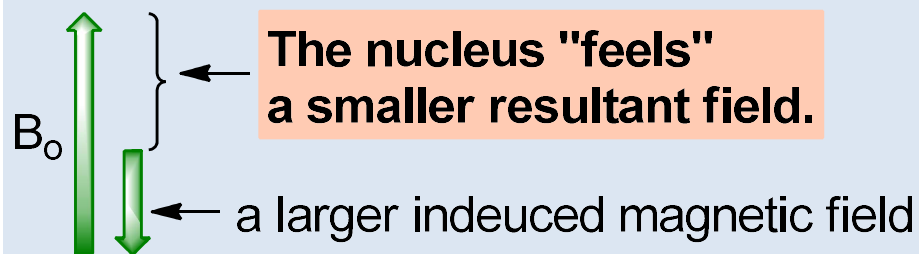
$$B_{\text{eff}} = B_0(1-\sigma)$$



A deshielded nucleus



A shielded nucleus



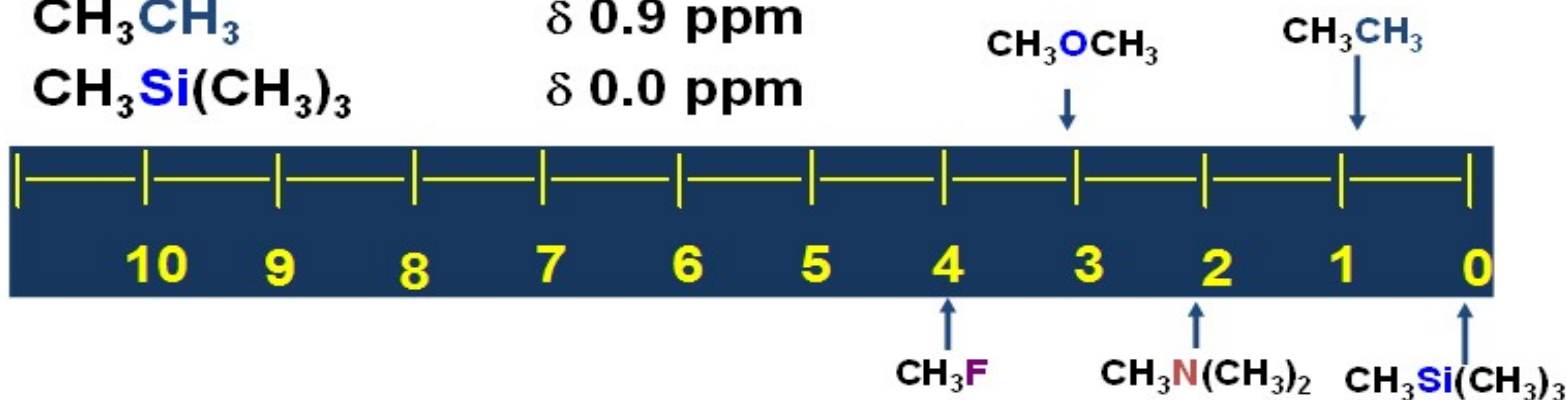
Shielded = more e⁻ density = peak shifts upfield = lower ppm
Deshielded = decreased e⁻ density = peak shifts downfield = higher ppm

How does electronegativity affect chemical shift?

- Protons in different environments experience different degrees of shielding and have different chemical shifts

CH_3F	δ 4.3 ppm
CH_3OCH_3	δ 3.2 ppm
$\text{CH}_3\text{N}(\text{CH}_3)_2$	δ 2.2 ppm
CH_3CH_3	δ 0.9 ppm
$\text{CH}_3\text{Si}(\text{CH}_3)_3$	δ 0.0 ppm

Electronegative substituents decrease the shielding of methyl groups



Electronic effect is cumulative:

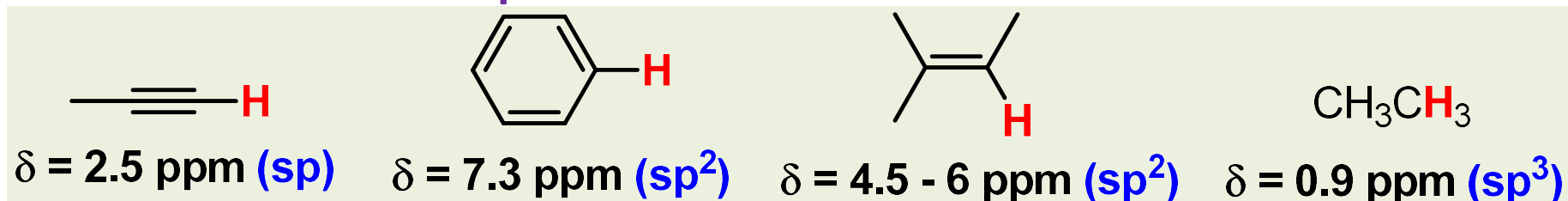
$\text{CH}_3\text{CH}_2\text{I} \sim \delta$ 2.10; $\text{CH}_3\text{CH}_2\text{Br} \sim \delta$ 2.70; $\text{CH}_3\text{CH}_2\text{Cl} = \delta$ 3.05; $\text{CH}_3\text{CH}_2\text{F} = \delta$ 4.30.

$\text{CH}_3\text{Cl} = \delta$ 3.1 ppm, $\text{CH}_2\text{Cl}_2 = \delta$ 5.3 ppm, $\text{CHCl}_3 = \delta$ 7.3 ppm.

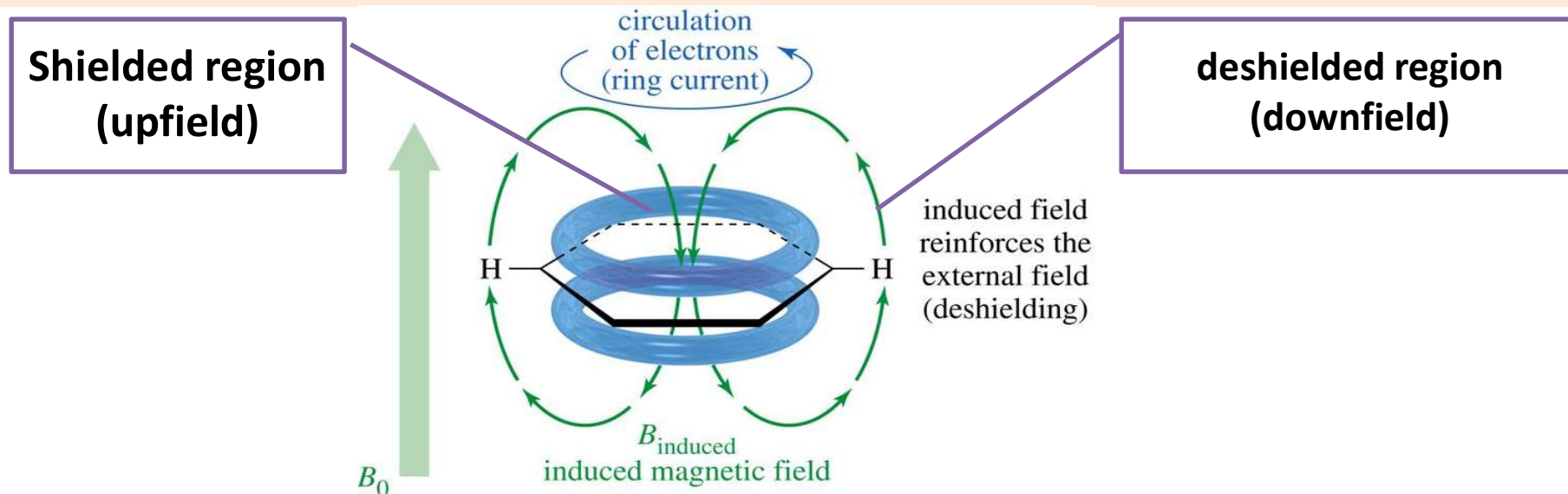
$\sigma_{neighbour}$ effect of neighboring environment: Anisotropic effect



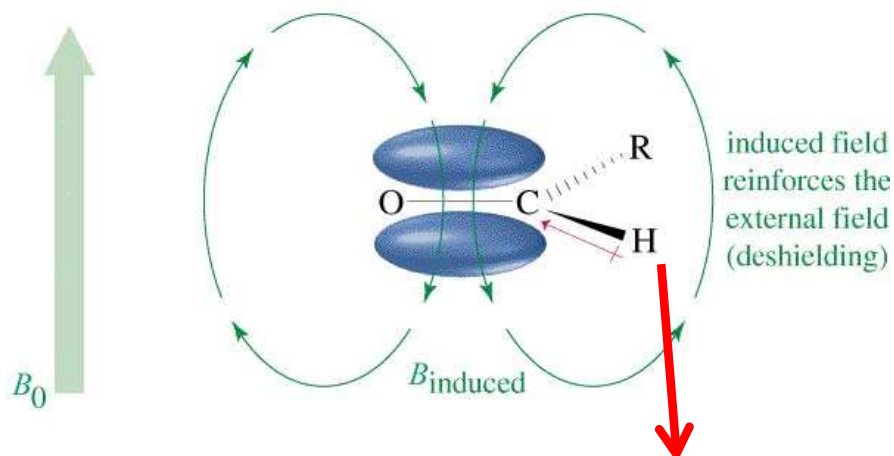
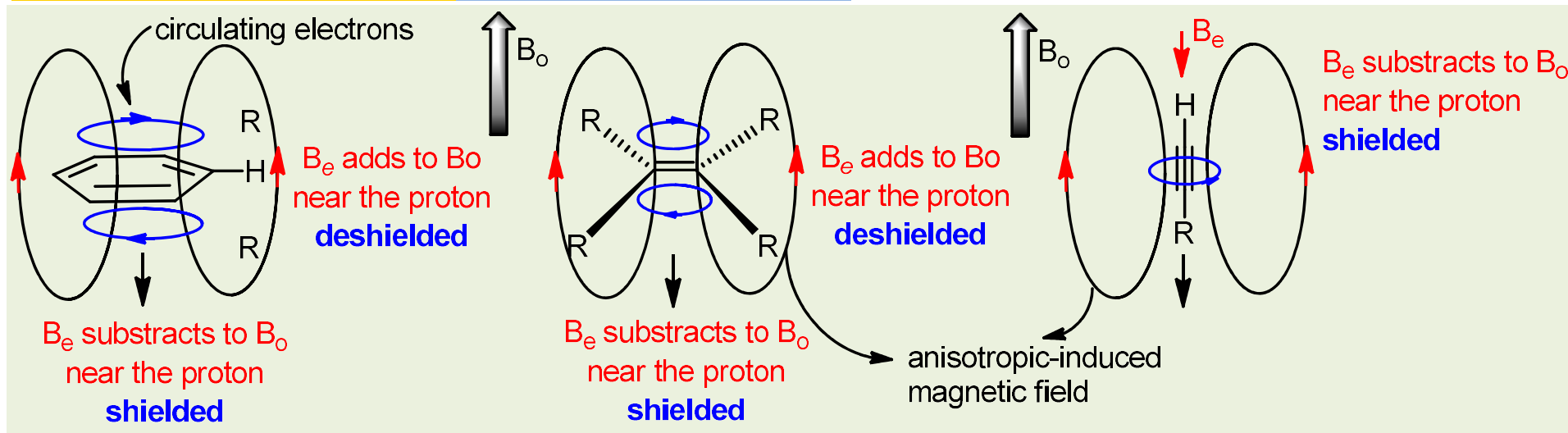
Magnetic anisotropy of bonds: Chemical bonds are anisotropic in space: they have different properties along different axis. When a chemical bond is placed in a external magnetic field, it will generate a local field around itself that will also be anisotropic.



Protons attached to sp^2 hybridized carbon are less shielded than those attached to sp^3 hybridized carbon

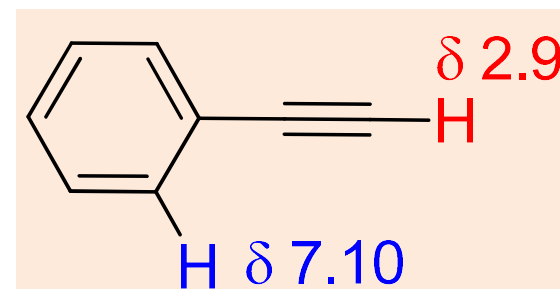
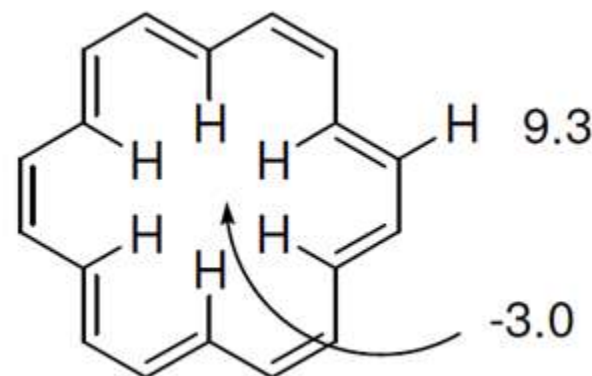


$\sigma_{neighbour}$ effect of neighboring environment: Anisotropic effect



O=CR-H, approx. δ 9-10

Highly Deshielded



σ_{Solvent} = Effect of Solvent



$$\text{Shielding factor: } \sigma = \sigma_{\text{local}} + \sigma_{\text{neighbour}} + \sigma_{\text{solvent}}$$

- A solvent may influence the local magnetic field experienced by a nucleus in a variety of ways.

Solute –Solvent interactions:

Minor effects

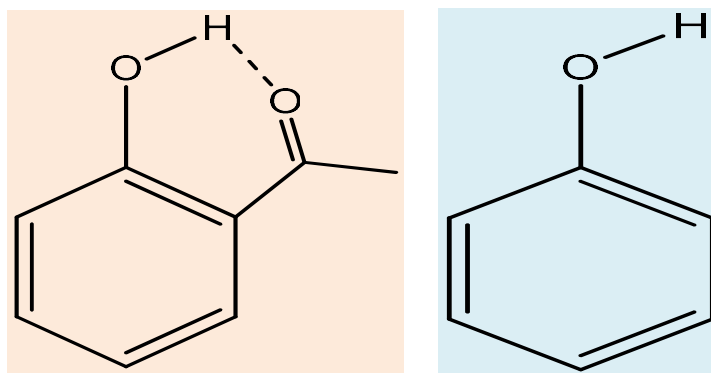
- Hydrogen Bonding
- Lewis acid base complex formation
- Solvents such as benzene having magnetic susceptibilities can provide shielding or deshielding effects.
- Steric interactions.

- Deuterium labeled Solvents: Chloroform-d (CDCl_3),
deuterium oxide (D_2O),
benzene-d₆ (C_6D_6),
acetone-d₆ (CD_3COCD_3)

Chemical Shift: O-H and N-H Signals



- Chemical shift of O-H & N-H depends on concentration & the solvent used for recording NMR.
- Hydrogen bonding in concentrated solutions deshield the protons. Hydrogen bonding involves electron clouds transfer from hydrogen atom to neighboring electronegative atoms.

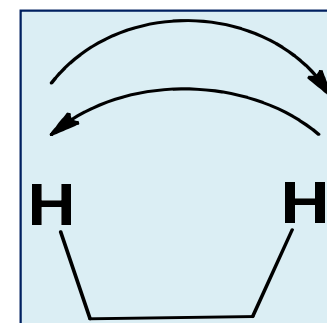
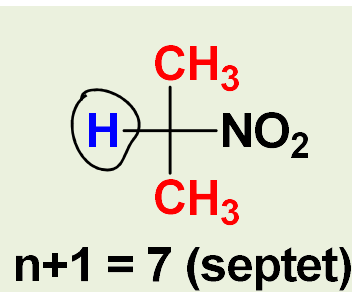
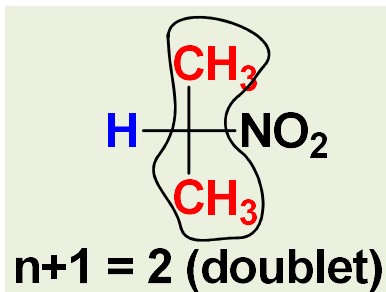
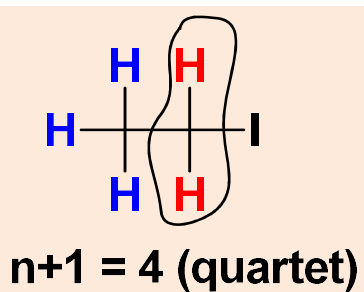
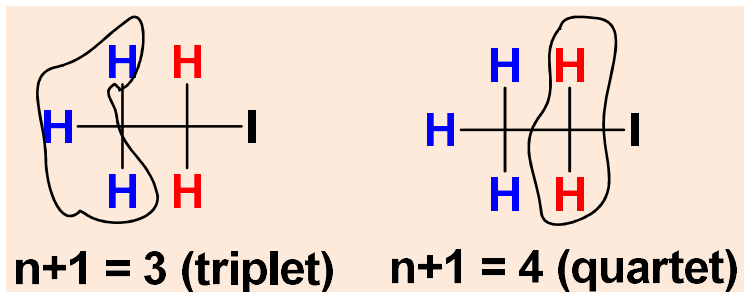
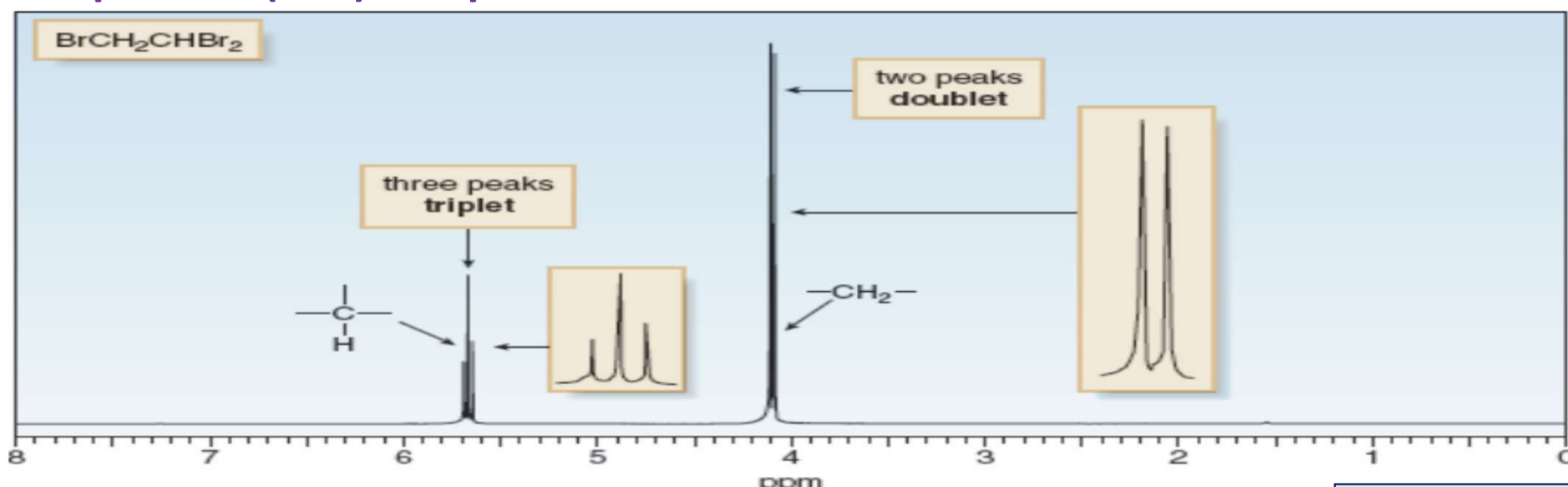


- δ (O-H) in *o*-hydroxyacetophenone is more deshielded than δ (O-H) in phenol
- However, δ value of OH/NH may vary in aliphatic or aromatic systems (no fixed region).
- O-H and N-H peaks are observed as broad peaks.

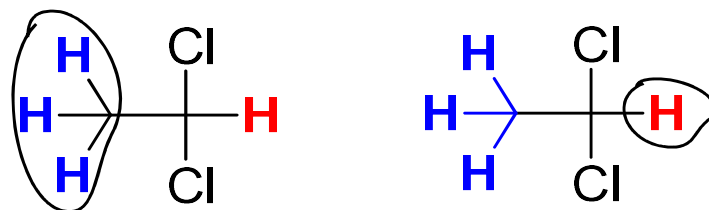
The fine structure: Spin-spin coupling



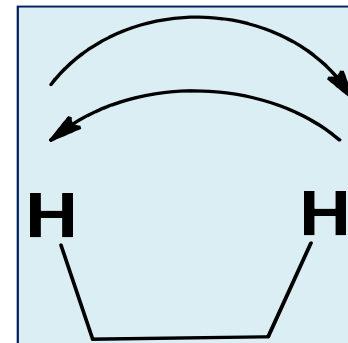
- The phenomenon of splitting of peaks into individual lines is called fine structure or spin-spin coupling, and can be explained through $(n+1)$ rule.
- Each type of proton senses the number of equivalent protons (n) on the carbon atom next to one to which it is bonded, and its resonance peak is split into $(n+1)$ components.



The fine structure: Spin-spin coupling



$\delta = 2.5$ ppm and 5.7 ppm (area ratio 3:1)
2.5 ppm (doublet), 5.7 ppm (quartet)

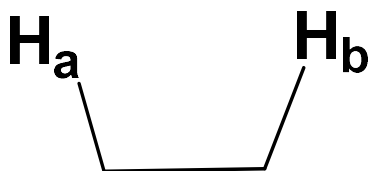


- Each ^1H nucleus in the molecule acts as a tiny magnet, and each hydrogen “feels” not only the very large applied magnetic field but also a tiny field due to its neighboring hydrogens.
- This coupling interaction between two nuclei occurs through chemical bonds, (and can typically be seen up to three bonds away) results in splitting of spectral lines, called the **multiplicity or splitting or coupling pattern of each signal**.
- The strength of interaction is expressed by **spin-spin coupling constant J (Hz)**: **J is independent of applied magnetic field (B_0)**.
- The spin-spin coupling gives a new type of structural information i.e. how many hydrogens are adjacent to each type of hydrogen that is giving an absorption peak.

The fine structure (Effect of X on A)



- Consider the protons H_a and H_b (in general spin $\frac{1}{2}$ nuclei) with 3 bond distance away.



Case I: Neglecting spin-spin coupling,

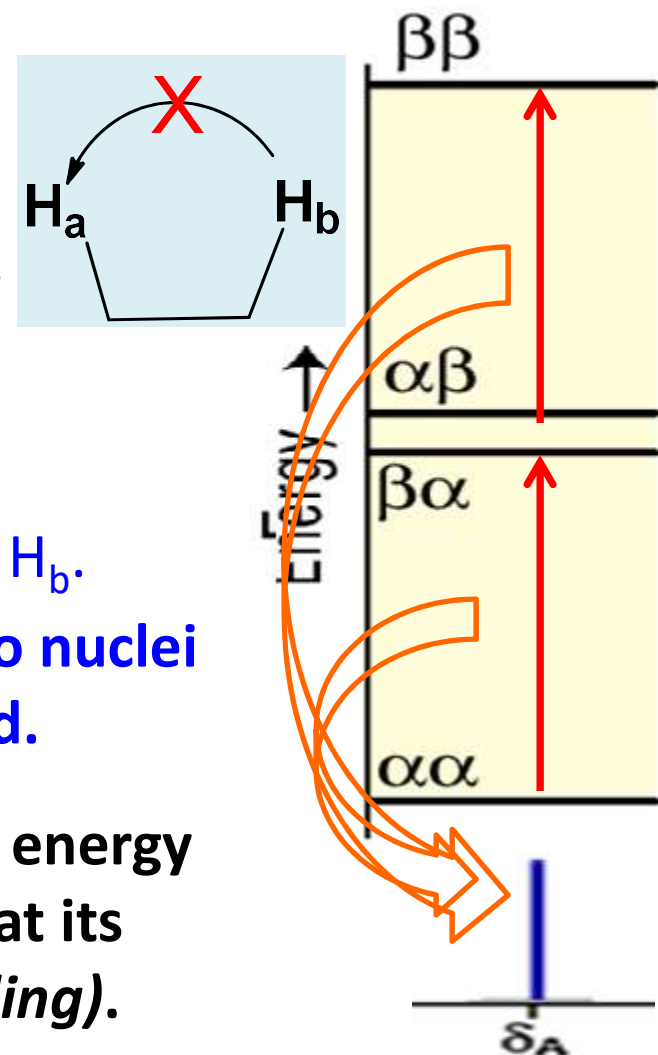
the total energy of two ^1H nuclei in a magnetic field B is the sum of their individual energies

$$E = -\gamma_N \hbar (1 - \sigma_a) B m_a - \gamma_N \hbar (1 - \sigma_b) B m_b$$

σ_a and σ_b are the shielding constants of H_a and H_b .

Assuming different orientations (α or β) of two nuclei possible: Four energy levels could be predicted.

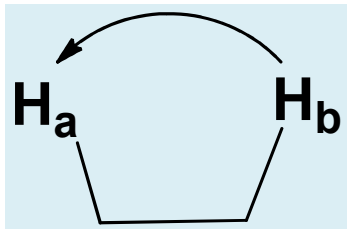
Nuclear transitions of a nuclei (a) are of same energy and only one peak should be observed for H_a at its respective δ value (*Neglecting spin-spin coupling*).



The fine structure (Effect of X on A)



Case II: Considering spin-spin coupling, \longrightarrow H_a and H_b are close enough such that their magnetic moments will perturb each other.



$$E_{\text{spin-spin}} = hJ_{ab}m_a m_b$$

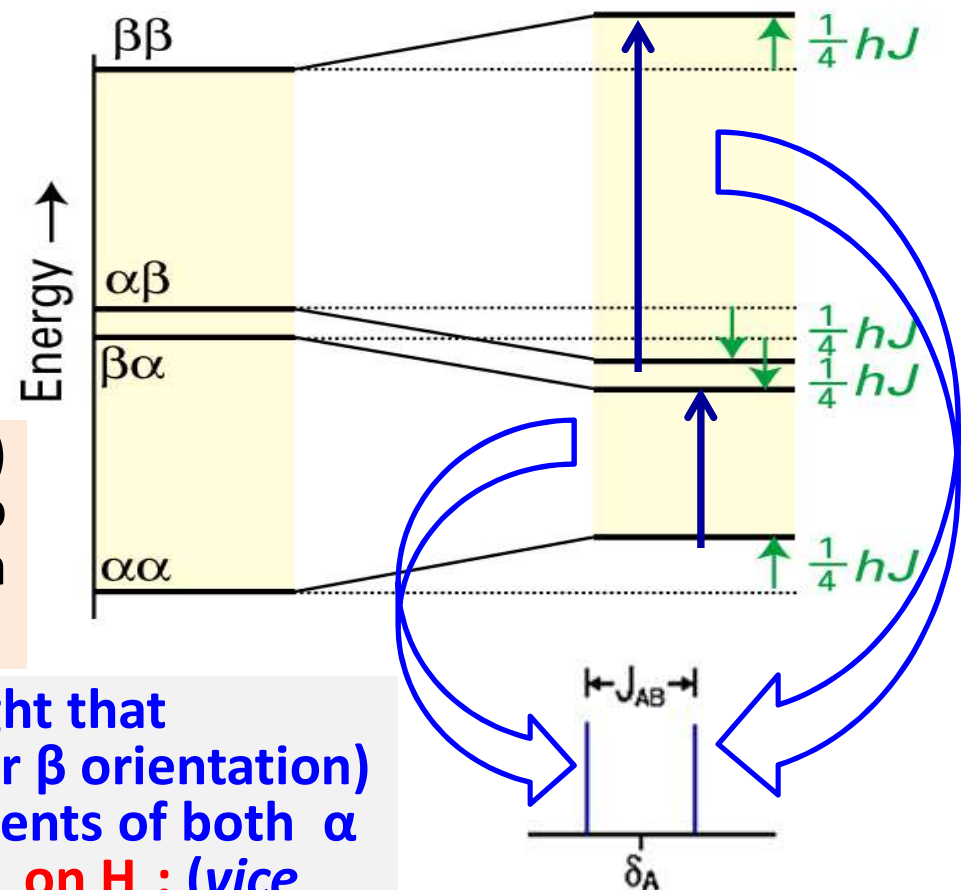
$$E_{\text{total}} = E + E_{\text{spin-spin}}$$

$$E_{\text{total}} = E + hJ_{ab}m_a m_b$$

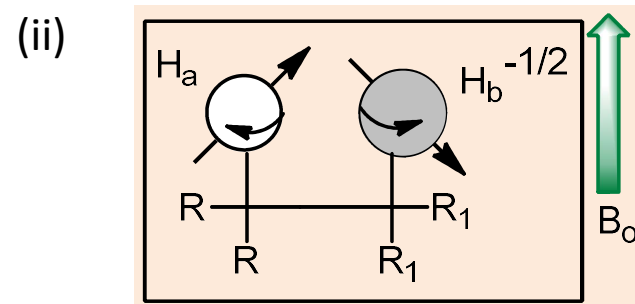
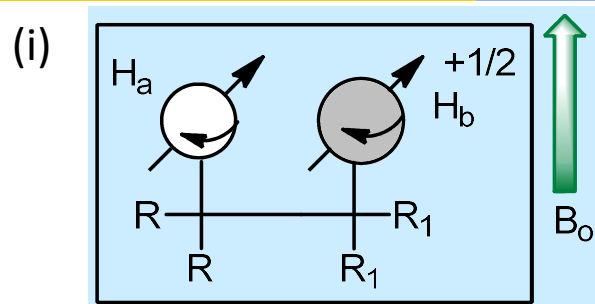
Different levels gets stabilized or destabilized by a factor of $E_{\text{spin-spin}}$

Nuclear transitions of a nuclei (H_a) will be of different energy and two peaks will be observed for hydrogen H_a at its respective δ value.

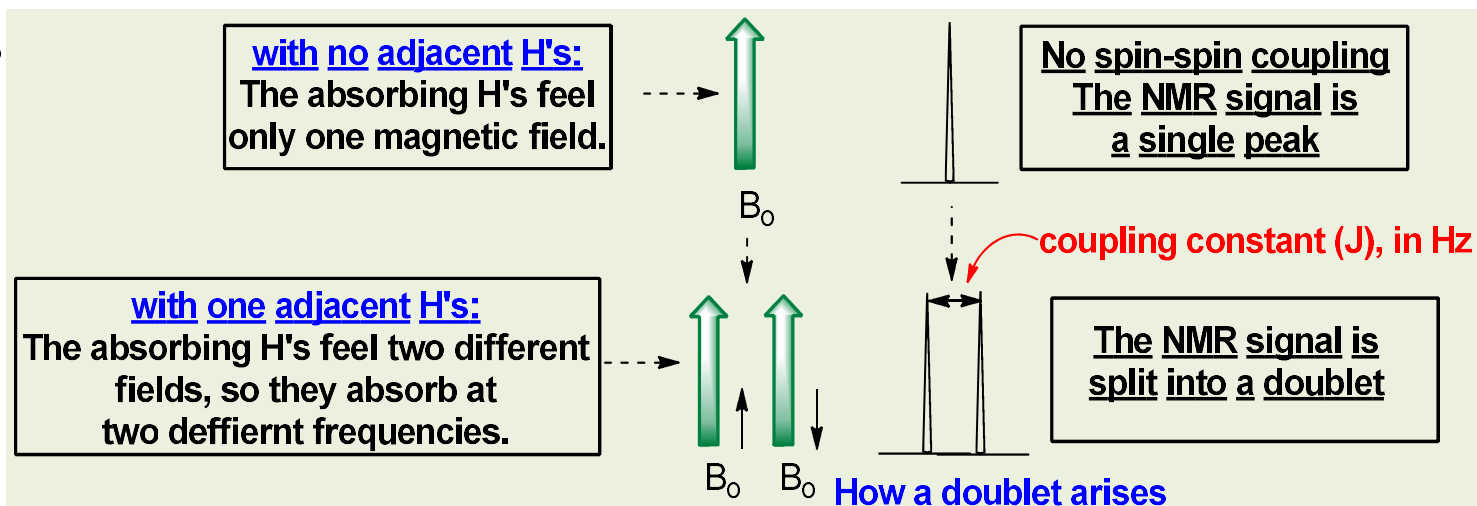
Effect of H_a on H_b : This could be thought that magnetic moment of H_a nuclei (in α or β orientation) will get perturb by the magnetic moments of both α or β states of nuclei H_b . **Effect of H_b on H_a :** (vice versa)



Effect of neighboring protons: Spin-spin coupling:



- The neighboring C-H is half the time aligned with the magnetic field and half the time aligned against the magnetic field.
- Due to this, the magnetic field of the nuclei whose peak is observed is perturbed slightly by the tiny fields of its neighboring ^1H nuclei
- H_a either feel a deshielding or a shielding effect from their neighbor (C- H_b), depending on whether its spin is aligned with or against the applied magnetic field.

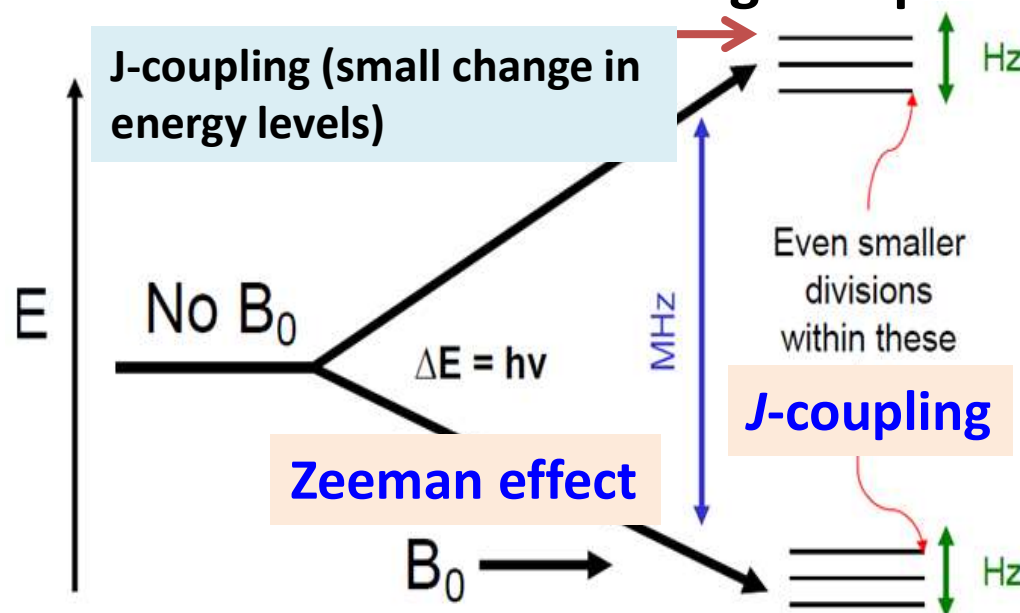


Spin-spin coupling:



(i) Chemical shift of proton H_a (deshielded- proton H_b has spin aligned with applied field)		(ii) Chemical shift of proton H_a (shielded- proton H_b has spin opposed with applied field)

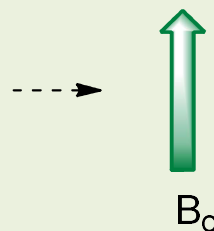
- This interaction is known as coupling and causes peaks to be split into a number of lines.
- When ^1H nuclei on one carbon is excited, the ^1H nuclei on neighboring carbons can be in either the lower or the higher spin state, with nearly equal probabilities.
- The spin state of one nucleus can create a slightly different B_{eff} in a Neighboring nucleus that gives us splitting of peaks.



Spin-spin coupling: For example $\text{CH}_3\text{CH}_2\text{Br}$



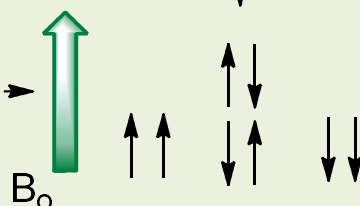
with no adjacent H's:
The absorbing H's feel only one magnetic field.



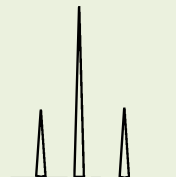
No spin-spin coupling
The NMR signal is
a single peak



with two adjacent H's:
The absorbing H's feel three different fields, so it absorb at three different frequencies.



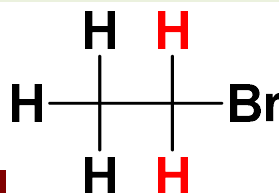
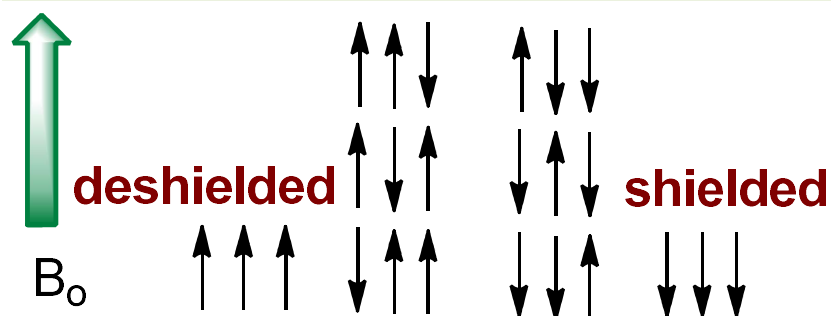
The NMR signal is
split into a triplet



three different magnetic field with intensity's ratio (1:2:1)

1. Both aligned with field
2. One aligned with the field and one against it (2 combinations); and
3. Both aligned against the field

- The two X nuclei may have the $2^2 = 4$ spin arrangements. The middle two arrangements are responsible for the coincident resonance of H_a .



There are $2^3 = 8$ arrangements of the spins of the three H nuclei, and their effects on the H nucleus gives rise to four groups of resonances.

four different magnetic field with intensity's ratio (1:3:3:1)

Chemical structure of ethyl bromide ($\text{CH}_3\text{CH}_2\text{Br}$) is shown above the spectrum. The spectrum displays two main signals: a quartet at $\delta = 3.4$ ppm (labeled in red) corresponding to the CH_2 group, and a triplet at $\delta = 1.7$ ppm (labeled in blue) corresponding to the CH_3 group. A TMS reference peak is visible at 0 ppm. The x-axis is labeled "Chemical shift (δ)" and ranges from 10 to 0 ppm. The y-axis is labeled "Intensity".



Effects of Molecular Structure on ^1H Chemical Shifts

