# Shielding constant

Look at the transition frequency again

$$v = \frac{\gamma}{2\pi} B$$

Same for all <sup>1</sup>H nuclei!

What is the effect of the electrons around <sup>1</sup>H nucleus?



Magnetic field felt by the nucleus

$$B = B_0 + \delta B$$
$$B = B_0 - \sigma B_0$$
$$B = B_0 (1 - \sigma)$$

Resonance condition

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

Hence resonant frequency depends on the local electronic environment.

Do not measure absolute shielding constants

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- too difficult to measure B_0 accurately
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Measure relative frequencies with respect to a reference standard

- leads to the chemical shift,  $\boldsymbol{\delta}$ 

Chemical shifts

Reference compound for <sup>1</sup>H and <sup>13</sup>C - tetramethylsilane, TMS

Definition of the chemical shift,  $\boldsymbol{\delta}$ 

$$\delta = 10^6 \frac{(v_{sample} - v_{TMS})}{v_{TMS}}$$

Since  $v_{TMS} \sim v_0$ 

$$\delta = 10^6 \frac{(v_{sample} - v_{TMS})}{v_0}$$



Secondary references - eg in water

### DSS 2,2 dimethyl -2-silapentane-5 sulphonate



Example

What is the frequency difference between two resonances 1.0 ppm apart at 500 MHz?

 $v - v_0 = 500 \text{ x } 10^6 \text{ x } (1.0) \text{ x } 10^{-6} = 500 \text{ Hz}$ 

# Shielding

Two components: associated with the circulation of electrons



Special case - <sup>1</sup>H

- No p/d electrons
- Negligible paramagnetic term,  $\Delta E$  (1s-2s) large
- Depends just on ground state electron distribution

Changes in chemical shifts

- directly related to changes in the local electron distribution
- look at inductive/mesomeric effects

#### Electronegativity of the bonded atoms

СНзХ	бн	EX
SiMe3	0	1.9
Н	0.13	2.2
CN	1.97	2.6
NH2	2.36	3.05
OH	3.38	3.5

A) Substituted methanes CH<sub>3</sub>X

B) Halomethanes  $CH_3X$ 

СНзХ	бн	EX
F	4.26	3.9
Cl	3.05	3.15
Br	2.68	2.95
Ι	2.16	2.65

Aromatic rings

Variations in chemical shifts reflect o/p and m directing effects of substituents



- Increase in electron density in ortho and para positions
- Increase in the shielding
- Less positive chemical shift moves towards 0 ppm



## Similarly for other substituents



# Prediction of <sup>1</sup>H Chemical shifts

Generally limited accuracy

Quantum mechanical - GAUSSIAN

- COSMOS

Computer database

- SPECINFO, Chemical Concepts
- Spectral fragments

Older fragment methods - Shoolery Rules

CHXYZ

$$\delta = \delta_{methane} + \Delta \,\delta_X + \Delta \,\delta_Y + \Delta \,\delta_Z$$

 $\Delta \delta_{X,Y,Z} \text{ substituent constant,}$ -H: +0.58 $-C_6H_5: +1.84$ e.g. -CHO: +1.50-OH: +2.74 $<math display="block">\delta_{methane} = 0.23$ 

Similar rules for alkenes and aromatics

Anisotropic Effects

Non-local contributions

Compare



Why this difference in chemical shift?

Aromatic ring current

Electron circulation not just around one atom but around a number

- delocalised  $\pi$ - electrons of an aromatic ring



Above  $-B_{loc}$  opposes  $B_0$ : shielding Side  $-B_{loc}$  with  $B_0$ : deshielding

## Represent as a shielding cone



Cone angle  $\theta = 54.7^{\circ}$ 

#### Example

[10] – paracyclophane



Other anisotropic groups

- carbonyl, alkene, alkyne

Effect of hydrogen bonding

Consistent with changes in electron density

 $X^{\delta\text{-}}-H\;.....Y^{\delta\text{-}}$ 

- electron density removed

- deshields the nucleus
- higher values for  $\boldsymbol{\delta}$

The stronger the H-bond the more positive  $\boldsymbol{\delta}$ 

With intermolecular H-bonding e.g. in solvents Factors

- concentration
- solvent
- temperature

Break up in H-bond network, causes a shielding

Compare:

Neat C<sub>2</sub>H<sub>5</sub>OH C<sub>2</sub>H<sub>5</sub>OH/CCl<sub>4</sub>  $\delta = 5.28$   $\delta = 0.7$ 

Intramolecular H-bonding less affected by dilution