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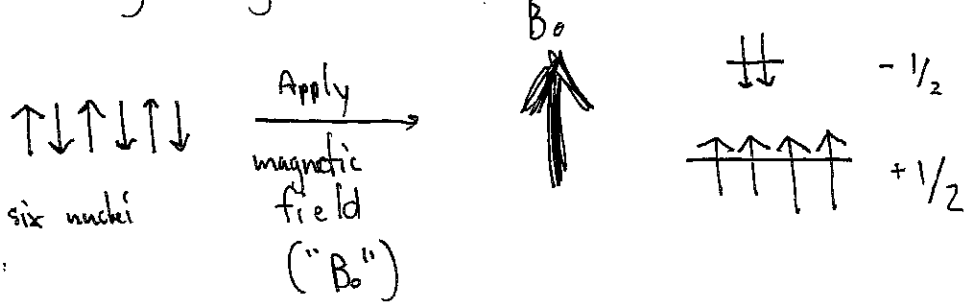
Recall: physical basis of NMR measurement - focus on nuclear spin

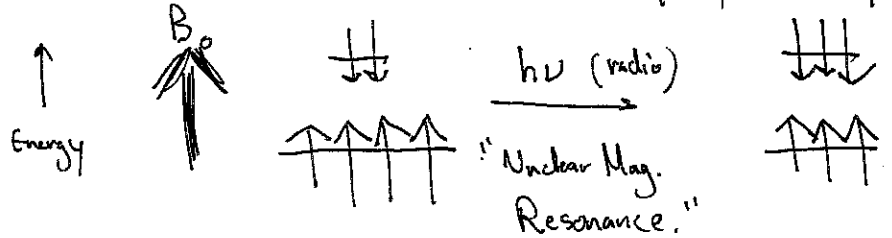
- For $^1H$, 2 spin states $+1/2$ (↑) vs. $-1/2$ (↓)

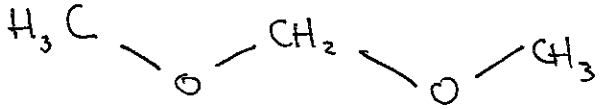
Need strong magnetic field to differentiate nuclear spin states.

Ex.




Induce "spin flip" w/ radio frequency energy:




Example: 


2 kinds of H

6 on $2\times CH_3$

2 on $CH_2$

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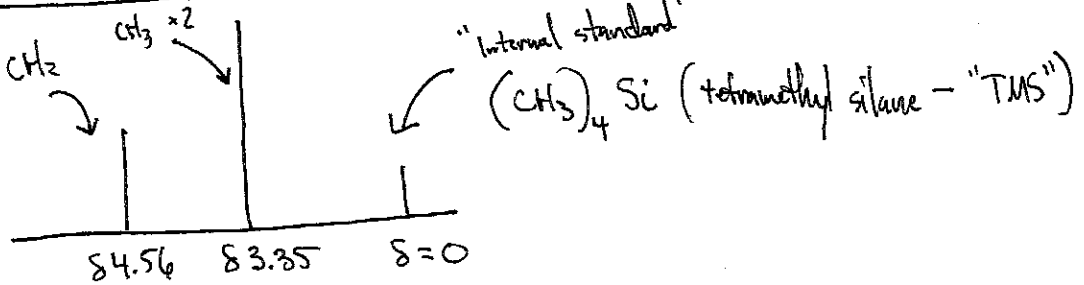
$^1H$-NMR spectrum:




Making sense of the spectrum:

Horizontal scale:

-normalized to "remove" variations in magnetic field strength (i.e., need a universal scale).

2 steps to generate "universal" horizontal scale:

1) Measure difference in a signal (from sample) & the internal standard.
2) Divide the difference by a value characteristic of spectrometer ("operating frequency")

Result: Horizontal scale has no physical units. We use two different and equivalent designations for horizontal scale values; termed "chemical shift" values; "parts per million" (ppm) or δ.

· Thus, in our example, for $CH_2$, δ = 4.56 -or- 4.56 ppm.

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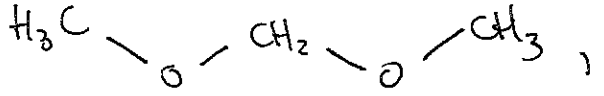
Vertical scale - none in an NMR plot.

However, the intensities of NMR signals ("integrations") indicate proportions of different types of $^1H$ nuclei.

∴ Integration ratio = ratio of # of H's

For: 

| | Relative integration |
|---|---|
| $\delta$ 4.56 ($CH_2$) | 1 |
| $\delta$ 3.35 (2×$CH_3$) | 3 |

Interpretation of chemical shift values:

- The chemical shift ($\delta$) for a particular H is characteristic of that H's local environment w/in a molecule.
- Many factors contribute to local environment. → influence chemical shift.
- Making maximum use of chemical shift data involves 2 skills.

1) General understanding of types of molecular features that influence $\delta$.

2) Practice solving NMR problems using tables of $\delta$ values. (Appendix III)

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One major influence on $\delta$ is the electronegativity of nearby atoms. More local eN $\Rightarrow$ larger $\delta$.

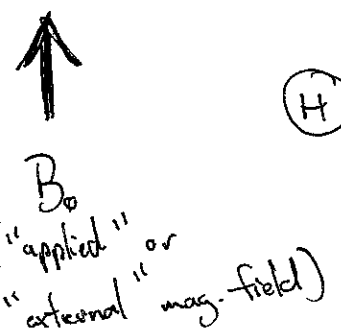
See Table 13.1 in textbook.

| | $\delta$ | |
|---|---|---|
| $H_3C-F$ | 4.26 | Don't memorize these number! |
| $H_3C-Cl$ | 3.05 | Do understand the trend! |
| $H_3C-C(CH_3)_3$ | 0.86 | |
| $H_3C-Si(CH_3)_3$ | 0 | → know that this is defined as zero. |

Physical origin of this trend.

Influence of nearby electrons on magnetic field that is "felt" by H nuclei.

- External magnetic field causes motion of electrons to generate a secondary magnetic field that opposes the applied field.




↓ 2° magnetic field, induced by $B_0$ & opposite

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This H "feels" a magnetic field slightly smaller than $B_o$
→ "shielding" effect

- More $e^-$ density around a given H ⇒ more shielding.
- Shielding causes $\delta$ to move to the right (i.e. small $\delta$ value)