

Nuclear Magnetic Resonance

CHEM 361B: Introduction to Physical Chemistry

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Lecture 18

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Learning Objectives:

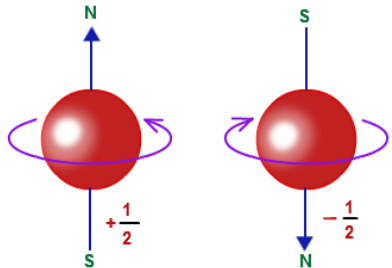
- Qualitatively interpret NMR spectroscopy

References:

- Atkins and de Silva Topic 13A and 13B
- LibreText §5.1 to 5.5

Nuclei Have Spin

- Nuclei are charged entities
- Like electrons, they have intrinsic spin
- The magnitude of this spin depends on the number of protons and neutrons in the nucleus:



# protons	# neutrons	Spin
Even	Even	0
Odd	Odd	Integer (1, 2, 3, ...)
Even	Odd	Half-Integer ($\frac{1}{2}$, $\frac{3}{2}$, ...)
Odd	Even	Half-Integer ($\frac{1}{2}$, $\frac{3}{2}$, ...)

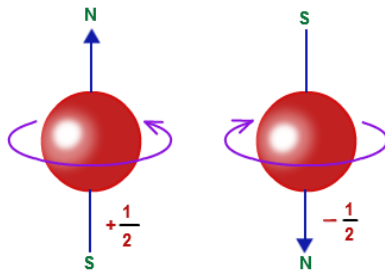
Nuclei In Magnetic Fields

- Spinning charges have magnetic moments. For a hydrogen nucleus (a proton):

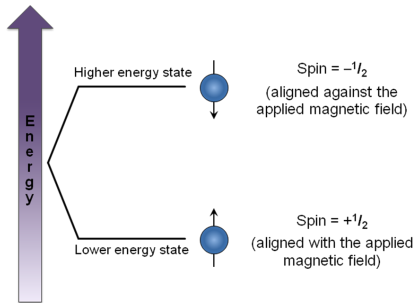
$$\begin{aligned}\mu_N &= \frac{e\hbar}{2m_p} \\ &= 5.051 \times 10^{-27} \text{ J T}^{-1}\end{aligned}$$

- Just like electrons, nuclei in a magnetic field split the $2I + 1$ degenerate states into discrete energy levels given by

$$E_{m_I} = -\gamma_N \hbar B_0 m_I$$



Energy Splitting in Hydrogen



- An alternative way to express this is

$$E_{m_I} = -g_I \mu_N B_0 m_I$$

where

$$g_I = \frac{\gamma_N \hbar}{\mu_N}$$

- Nuclear g-factors are experimentally determined dimensionless quantities with values typically between -6 and 6.

Nuclear Spin Properties

Nucleus	Natural abundance/ (per cent)	Spin, I	$\gamma_N/(10^7 \text{ T}^{-1} \text{ s}^{-1})$
^1H	99.98	$\frac{1}{2}$	26.752
^2H (D)	0.0156	1	4.1067
^{12}C	98.99	0	—
^{13}C	1.11	$\frac{1}{2}$	6.7272
^{14}N	99.64	1	1.9328
^{16}O	99.96	0	—
^{17}O	0.037	$\frac{5}{2}$	-3.627
^{19}F	100	$\frac{1}{2}$	25.177
^{31}P	100	$\frac{1}{2}$	10.840
^{35}Cl	75.4	$\frac{3}{2}$	2.624
^{37}Cl	24.6	$\frac{3}{2}$	2.184

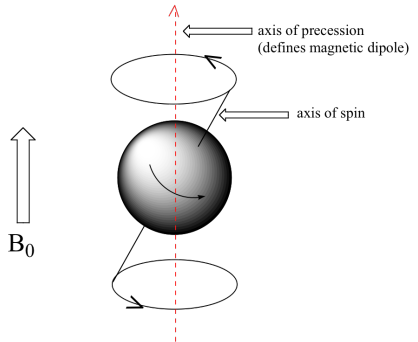
Larmor Precession Frequency

- If the magnetic moment is not aligned with the B-field, the nucleus precesses.
- The frequency of that precession (for spin- $\frac{1}{2}$ particles) is given by

$$\Delta E = -\gamma_N \hbar B_0 \left(-\frac{1}{2} - \frac{1}{2} \right)$$

$$h\nu = \gamma_N \hbar B_0$$

$$\nu = \frac{\gamma_N B_0}{2\pi}$$



Nuclear Magnetic Resonance

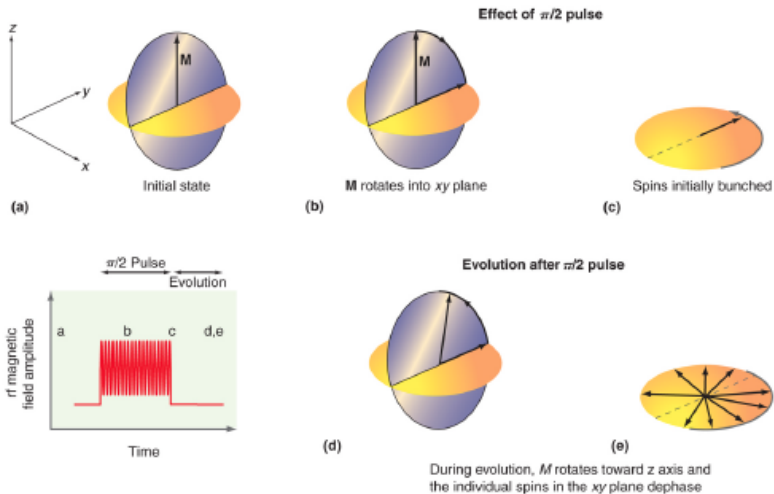
Fourier Transform NMR is a technique where a sample

- Is placed in a strong B-field and
- Exposed to brief bursts of radio frequency radiation

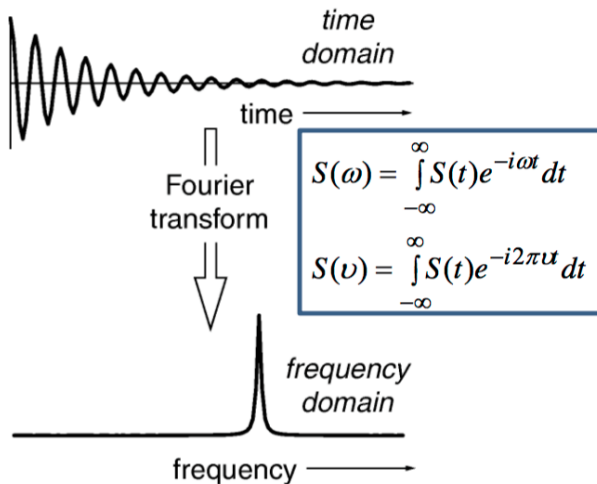
The RF bursts changes the orientation of the nuclear spins in a controlled way

- The radiation that is emitted by the sample as it returns to equilibrium is monitored and analysed
- The analysis includes applying a Fourier Transform to extract all frequencies simultaneously

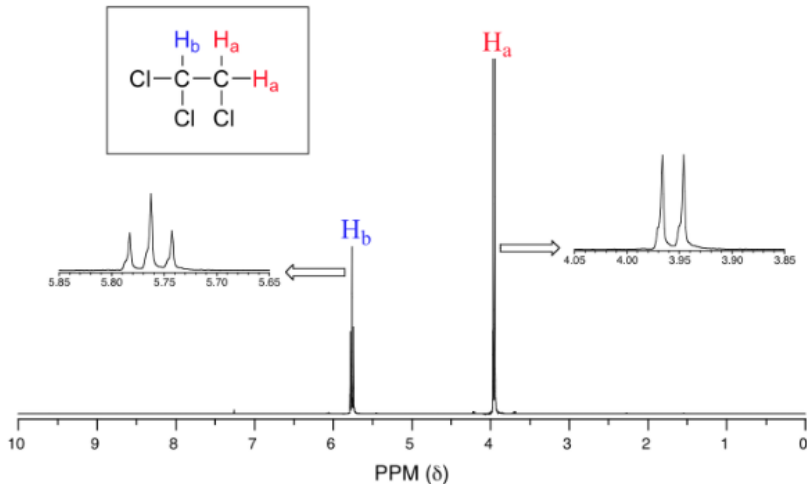
Illustration of FT-NMR Procedure



Where the Fourier Transform Comes In



A Sample NMR Spectra



Question: Why do we get peak shifts?

The Local Magnetic Field is Key

The shifts in peaks (called the chemical shift) is due to

- The applied B-Field inducing a circulation of electrons in a molecule
- This gives rise to an additional B-field that either adds or subtracts from the externally applied one

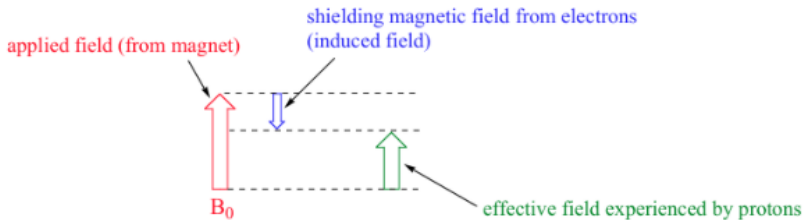
Therefore, the local B-Field seen by a given nuclei is

$$B_{local} = B_0 + B_{induced} = (1 - \sigma)B_0$$

The shielding constant, σ , takes into account effects on the local magnetic field from

- The atom's electrons
- The atom's neighbours
- The solvent

Range of Typical Chemical Shifts



The δ -scale

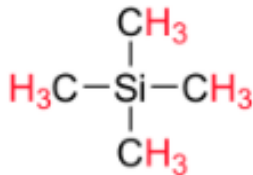
Chemical shifts are reported on the δ -scale

$$\delta = \frac{\nu - \nu_0}{\nu_0} \times 10^6$$

where

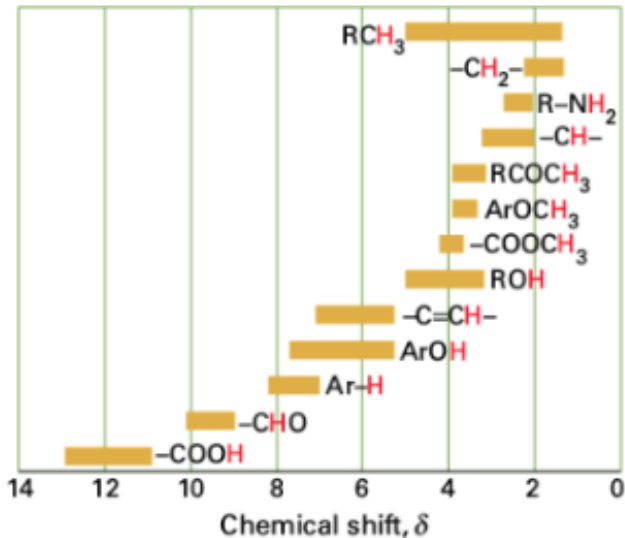
$$\nu = \frac{\gamma_N(1 - \sigma)B_0}{2\pi}$$

ν_0 comes from a reference. Typically this is from tetramethylsilane.

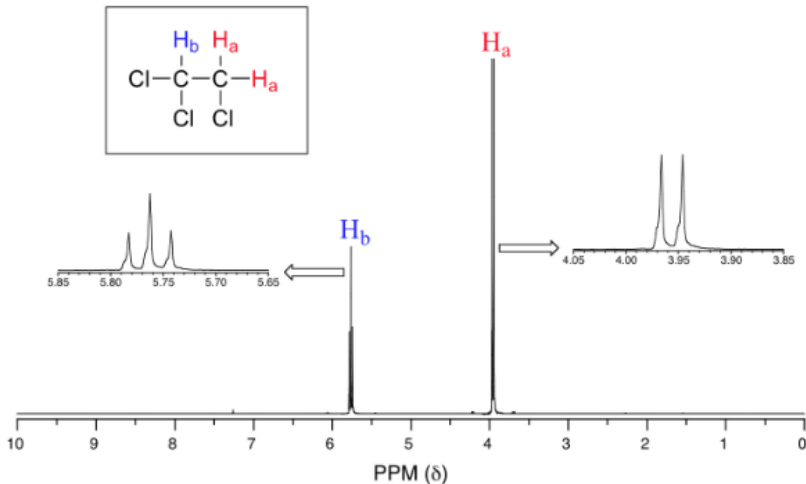


tetramethylsilane (TMS)

Range of Typical Chemical Shifts

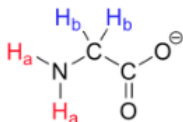


A Sample NMR Spectra

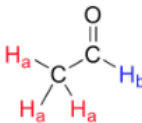


Question: Why do we get multiple peaks in each chemical shift?

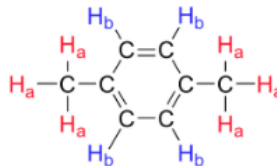
Chemical Equivalence



glycine



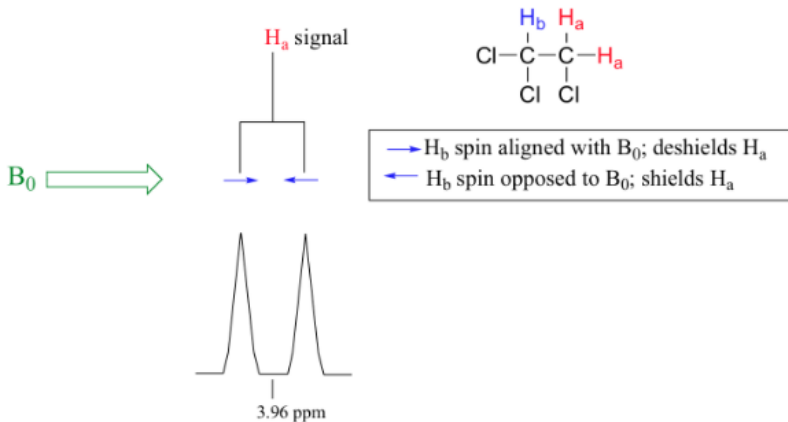
acetaldehyde

*para*-xylene

Nuclei in the same bonding environment are generally considered to be chemically equivalent

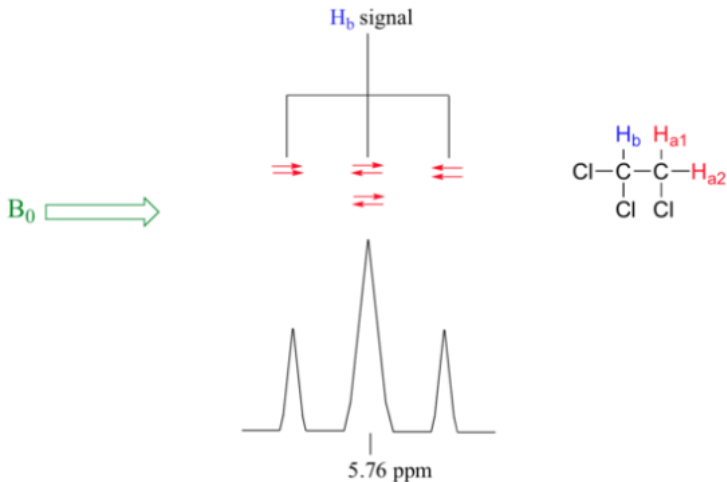
Spin-Spin Coupling - H_a

The spins of adjacent chemically inequivalent nuclei affect each other

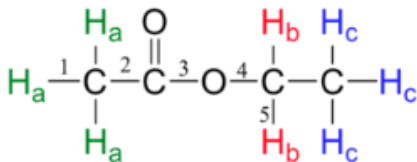
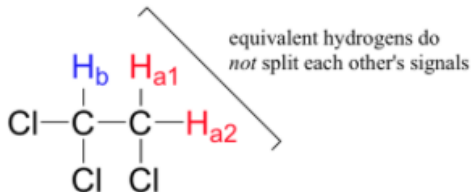


Spin-Spin Coupling - H_b

The spins of adjacent chemically inequivalent nuclei affect each other



Spin-Spin Coupling Notes

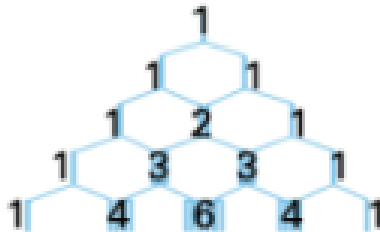


H_a protons are 5 bonds
away from H_b - no
coupling

Pascal's Triangle

N equivalent spin- $\frac{1}{2}$ nuclei split the resonance of a nearby group of equivalent spins into

- $N + 1$ lines
- With an intensity distribution given by Pascal's triangle



Summary

- Nuclei have spins and those spins are affected by B-fields
- By measuring how the magnetic moments relax when perturbed we can learn about the chemical make-up of a sample (NMR spectroscopy)
- Peak shifts relative to a reference are based on the local B-field at each nuclei. This is affected by
 - The chemical group around it and their electrons
 - The spin-spin coupling of nearby nuclei