1/8/18

NMR

- Nuclear Magnetic Resonance (Spectroscopy)
- Some nuclei are magnets!
- "Intrinsic" nuclear magnetism is due to "spin", which is a quantum mechanical form of angular momentum (see notes)
- The spin of a particular nucleus may be zero (not a magnet) or $\pm 1/2$, or $+1, 0, -1$, or even more complex
- For example

1) Isotopes w/ odd mass numbers have $m_s = 1/2$
2) " " even " " " $m_s = \emptyset$

→ or m_s = integer

3) If # neutrons (n) and # protons (p) are *both* even, then $m_s = \phi$

4) If n + p are both odd, then m_s = integer

- Spin is a quantum mechanical phenomenon – this means that the behavior of individual spins can only be explained using quantum mechanics...

- But – we do not need Q.M. to explain most (simple) NMR experiments!

How can this be?!

- We first recognize that NMR is a kind of spectroscopy that is averaged both in time, and over a large # particles.

Now about spin ...

- Spin ≡ intrinsic angular momentum
- 1st postulated by W. Pauli in ~ 1925
- The notion that spin was actually a rotation was dreamed up by Goudsmith, Kronig & Uhlenbeck — although these guys were (generally) v.good physicists, they were off in the weeds w.r.t. spin.
- A mathematical model for spin was worked by Pauli (Pauli matrices) in 1927.
- P. Dirac created a Q.M. formalism that included spin explicitly - Dirac Eq

$$\left(\left(\beta mc^2 + c\left(\sum_1^3 \alpha_n p_n\right)\right)\right) \Psi(x,t) = i\hbar \frac{\partial \Psi(x,t)}{dt}$$

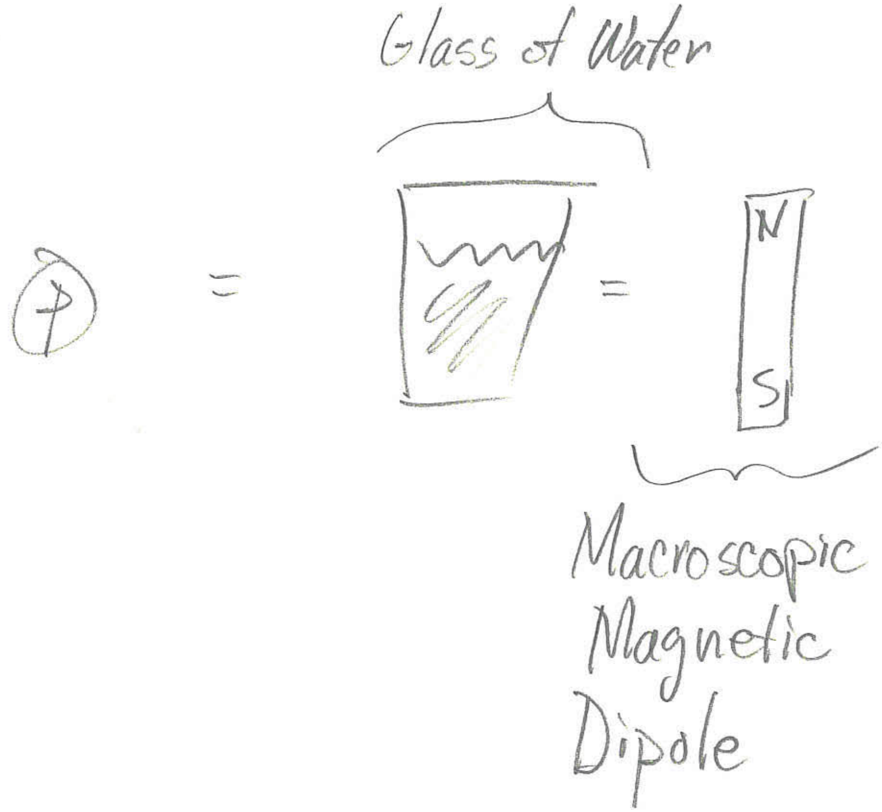
Hint: Magnetism is a relativitist effect

- This sort of double average is called a "time and ensemble average".

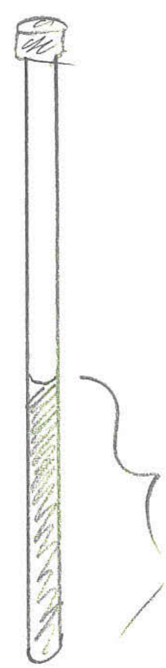
It turns out that if you have a large number of QM systems - spins - and if you monitor their behavior for a long time, seconds, then the overall behavior can be described using classical mechanics!

- This ↑ means that if we talk about a glass of water - many ^1H nuclei - that the behavior of the system may be treated classically, e.g. using classical electromagnetism...

- Thus,

$N_{av} \times$ 

- Our "glass of water" is actually a tube of high-class borosilicate:

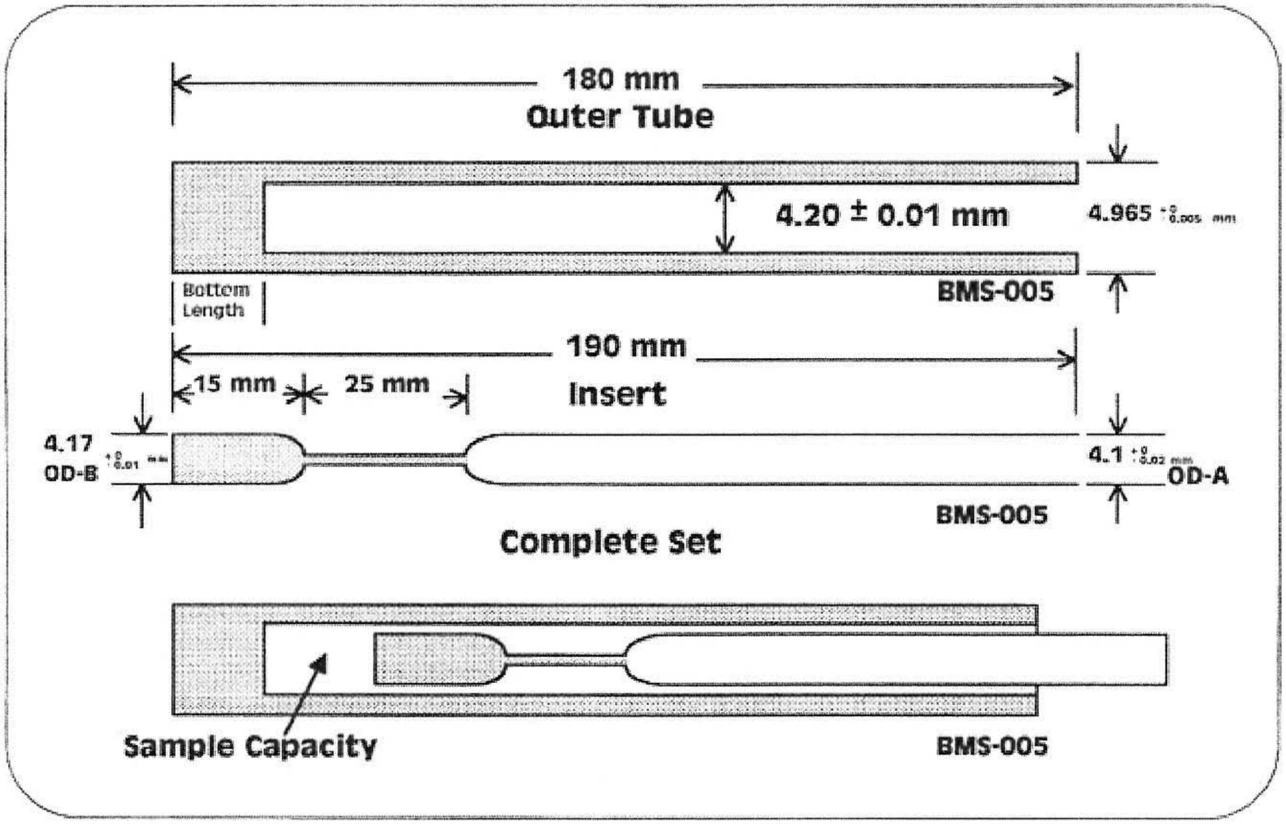


7" length
5mm outer diameter (OD)
3-4mm inner diameter (ID)

Sample height ~ 40mm
Sample Volume ~ 800μL

Alternative NMR Cell Design

Shigemi Microcell



Sample Volume = 350µL

- Consider 1 mg of compound-X dissolved in 0.8 mL

$$[X]_{800\mu L} = \frac{\left(\frac{1\times10^{-3}\,g}{1000\,g/mol}\right)}{0.8\times10^{-3}\,L} \cong \overset{1.25\,mM}{0.00125\,\frac{mol}{L}}$$

$\underbrace{}$ Close to limit of detection!

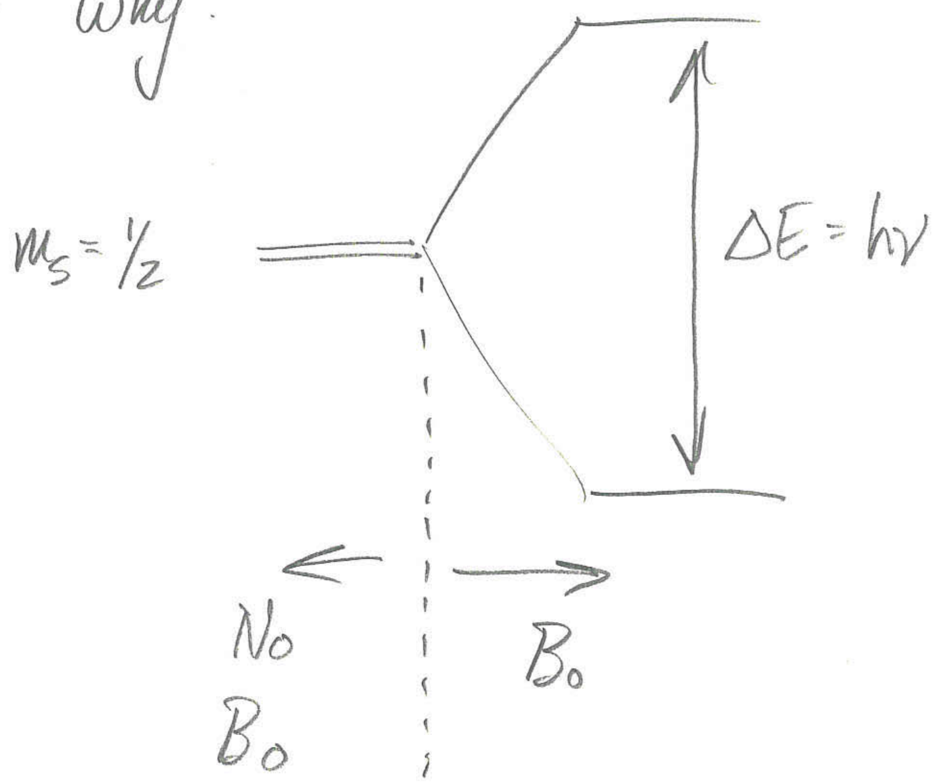
— versus —

$$[X]_{350\mu L} = \frac{\left(\frac{1\times10^{-3}\,g}{1000\,g/mol}\right)}{0.35\times10^{-3}\,L} \cong 2.85\ mM$$

$$\frac{[X]_{350\mu L}}{[X]_{800\mu L}} = \frac{2.85}{1.25} \simeq 2.3 \text{ (more conc'd)}$$

But... $(2.3)^2 = 5.2$ times more sensitive in time!

- Central fact: Sensitivity is everything
- Why?



- Sensitivity is measured as the ratio:

$$\frac{\text{Signal}}{\text{Noise}} = \frac{S}{N}$$

S : depends on [ ], B_0, γ, T (weak)

N : depends on electrical engineering

- $\Delta E = h\nu$ ...

To make things easy, let us set $h = 1$

Then $\Delta E = \nu$ } Energy in Hz?!

- In NMR, ν ranges from 300×10^6 Hz to 900×10^6 Hz

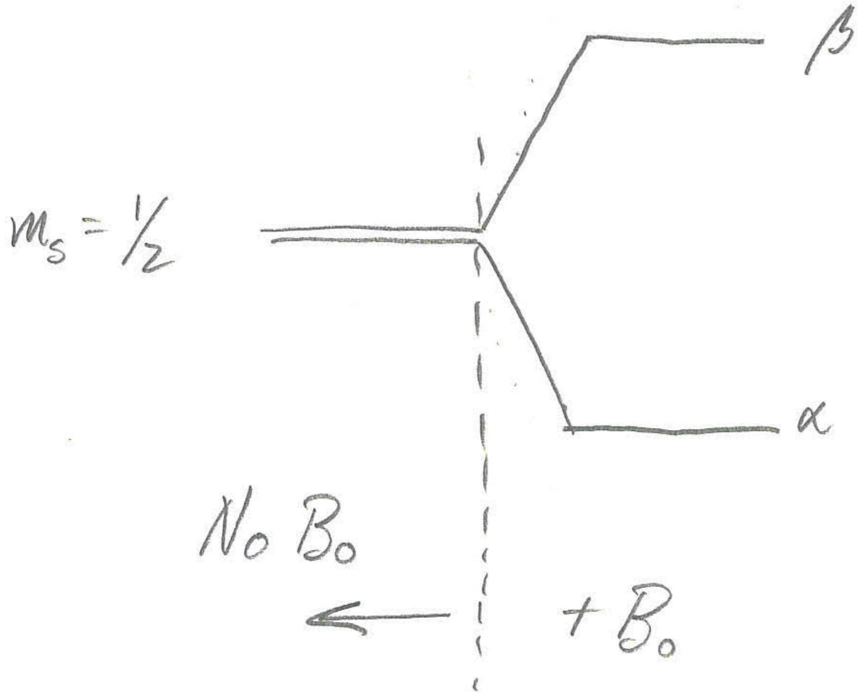
- In electro-optical spectroscopy, ν is in the range of 10^{14}-10^{16} Hz

- Hmmm...

$$\frac{10^{16}}{10^{10}} = 10^6 \quad \Bigg\} \text{ NMR is } 10^6 \text{ less sensitive!}$$

- In NMR we have figured out how to make N small...

- Let us now return to this picture



- Spin energy levels are redundant in the absence of an applied external magnet field, B_0

- Classical energy of a magnetic dipole in a magnetic field

$$E = -\mu B_0$$

magnetic moment = $q \cdot r$

- The QM statement is

$$E = -\hbar\, m_s \gamma B_0$$

$$\hbar = \frac{h}{2\pi} \;;\; m_s = \pm 1/2$$

$$\gamma = \underbrace{\text{gyromagnetic ratio}}_{\text{response of nucleus to unit } B_0}$$

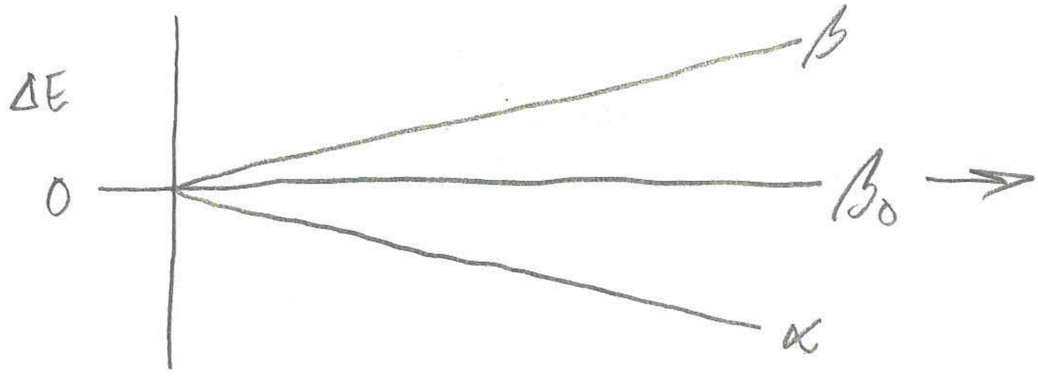
$B_0 \equiv$ magnetic flux density (field strength)

- With $m_s = -1/2 \longrightarrow \alpha$-state

  $m_s = +1/2 \longrightarrow \beta$-state

$$E_\alpha = -\tfrac{1}{2}\hbar\gamma B_0 \;;\; E_\beta = +\tfrac{1}{2}\hbar\gamma B_0$$

$$\Delta E(\beta - \alpha) = \hbar\gamma B_0$$



- Frequency Units?

Natural units: $\omega = 2\pi\left(\text{frequency in } \frac{1}{\text{sec}}\right)$

$= 2\pi(\text{frequency in Hz})$

$= 2\pi\left(\text{frequency in } \frac{\text{cycles}}{\text{sec}}\right)$

Convention: $[\omega] = \frac{\text{radians}}{\text{sec}}$

$[\nu] = \frac{1}{\text{sec}} = \text{Hz}$

- Polarization

$\vec{M} = \sum_i \vec{\mu_i}$ } Sum of α, β states

\# in β-state $= N_\beta = e^{-E_\beta/kT}$

\# in α-state $= N_\alpha = e^{-E_\alpha/kT}$

$$\frac{N_\beta}{N_\alpha} = e^{-\Delta E/kT} = e^{-\hbar\gamma B_0/kT}$$

$$\hbar = \frac{h}{2\pi} = 1.0546 \times 10^{-34}\ J \cdot s^{-1}$$

$$k = 1.3805 \times 10^{-23}\ J \cdot K^{-1}$$

@ 2.3487 T : $\gamma(^1H) = 267.522 \times 10^6\ s^{-1} \cdot T^{-1}$

$$\frac{N_\beta}{N_\alpha} = \exp\left\{-\frac{(1.0546\times10^{-34})(267.522\times10^6)(2.3487)}{(1.3805\times10^{-23})(298)}\right\}$$

$$\frac{N_\beta}{N_\alpha} = 0.999983$$

Note!

@ 21.49 T

$$\frac{N_\beta}{N_\alpha} = 0.999853$$