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 \( \pm \frac{1}{2} \), or \( +1, 0, -1 \), or even more complex

- For example
  1) Isotopes with odd mass numbers have \( m_s = \frac{1}{2} \)
  2) "even" " " " " " " m_s = 0,

\( \pm \) or \( m_s = \text{integer} \)
3) If # neutrons (n) and # protons (p) are both even, then $m_s = 0$

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

\[
\left(\beta mc^2 + c \sum E_n \hat{p}_n \right) \psi(x,t) = i\hbar \frac{\partial \psi(x,t)}{\partial t}
\]

Hint: Magnetism is a relativistic 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 'H nuclei—that the behavior of the system may be treated classically, e.g., using classical electromagnetism...
Thus,

\[ N_{av} \times D = \text{Glass of Water} \]

Macroscopic Magnetic Dipole

- 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
Sample Volume = 350 μL

Alternative NMR Cell Design

Shigemi Microcell
• Consider 1 mg of compound-X dissolved in 0.8 mL

\[
[X]_{800\mu L} = \left( \frac{1 \times 10^{-3} \text{g}}{1000 \text{g/mol}} \right) \frac{1.25 \text{mM}}{0.8 \times 10^{-3} \text{L}} \approx 0.00125 \text{ mol/L}
\]

Close to limit of detection!

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-versus-

\[
[X]_{350\mu L} = \left( \frac{1 \times 10^{-3} \text{g}}{1000 \text{g/mol}} \right) \frac{2.85 \text{mM}}{0.35 \times 10^{-3} \text{L}} \approx 2.85 \text{ mM}
\]

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

But... \((2.3)^2 = 5.3 \) times more sensitive in time?
• Central fact: Sensitivity is everything

• Why?

\[ m_s = \frac{1}{2} \]

\[ \Delta E = h\nu \]

\[ \text{No} \quad \text{Bo} \quad \text{Bo} \]

• Sensitivity is measured as the ratio:

\[ \frac{\text{Signal}}{\text{Noise}} = \frac{S}{N} \]

\[ S \text{ depends on } E, B_0, \gamma, T/\text{weak} \]

\[ N \text{ depends on electrical engineering} \]
• \( \Delta E = h \nu \ldots \)

To make things easy, let us set \( h = 1 \)

Then \( \Delta E = \nu \) \} Energy in \( \text{Hz} \) ?

• In NMR, \( \nu \) ranges from \( 300 \times 10^6 \text{ Hz} \)
  
  to \( 900 \times 10^6 \text{ Hz} \)

• In electro-optical spectroscopy, \( \nu \) is in the range of \( 10^{14} - 10^{16} \text{ Hz} \)

• Hmmm...

\[
\frac{10^{16}}{10^{10}} = 10^6 \]  \} NMR is \( 10^6 \) less sensitive?

• In NMR we have figured out how to make \( N \) small...
- Let us now return to this picture

\[ m_s = \frac{1}{2} \]

\[ \text{No } B_0 \rightarrow +B_0 \]

- 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

\[ E = -\hbar m_s \gamma B_0 \]

\[ \hbar = \frac{\hbar}{2\pi} ; \quad m_s = \pm \frac{1}{2} \]

\( \gamma \) = gyromagnetic ratio

response of nucleus to unit \( B_0 \)

\( B_0 \) = magnetic flux density (field strength)

With \( m_s = -\frac{1}{2} \) \( \rightarrow \) \( \alpha \)-state

\( m_s = +\frac{1}{2} \) \( \rightarrow \beta \)-state

\( E_\alpha = -\frac{1}{2} \hbar \gamma B_0 \); \( E_\beta = +\frac{1}{2} \hbar \gamma B_0 \)

\[ \Delta E(\beta - \alpha) = \hbar \gamma B_0 \]
• Frequency Units?

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

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

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

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

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

• Polarization

\( \vec{M} = \sum_i \vec{m}_i \) \{ sum of \( \alpha, \beta \) states \}

\# in \( \beta \)-state = \( N_\beta = e^{-E_\beta/kT} \)

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\( \frac{N_\beta}{N_\alpha} = e^{\frac{\Delta E}{kT}} = e^{-\hbar \nu B_0/kT} \)
\[ \hbar = \frac{h}{2\pi} = 1.0546 \times 10^{-34} \text{ J} \cdot \text{s}^{-1} \]

\[ k = 1.3805 \times 10^{-23} \text{ J} \cdot \text{K}^{-1} \]

\[ \gamma (\text{H}) = 267.522 \times 10^6 \text{ s}^{-1} \cdot \text{K}^{-1} \]

\[ \frac{N_b}{N_a} = \exp \left\{ \frac{(1.0546 \times 10^{-34}) (267.522 \times 10^6) (2.3487)}{(1.3805 \times 10^{-23}) (298)} \right\} \]

\[ \frac{N_b}{N_a} = 0.999983 \]

\[ \gamma (\text{H}) = 21.49 \text{ K} \]

\[ \frac{N_b}{N_a} = 0.999853 \]