Nuclear Magnetic Resonance (NMR) - Theory

1) Nuclear magnetism - NMR requires paramagnetic nuclei

Review: paramagnetic objects pulled toward magnetic field

unpaired \( e^- \) spins \( \Rightarrow S = \frac{\# \text{ of unpaired } e^-}{2} \)

n & p have weaker magnetic spins (< 0.001 spin of e^-)

\( \Rightarrow \) too weak to affect bulk magnetism

n & p isolated have spin \( \frac{1}{2} \) or \( \frac{3}{2} \)

nuclei - spins pair up. Nuclear spin \( \# = I = \frac{\# \text{ of unpaired spins}}{2} \)

Isotopic properties: mass, \( I, A, Z \), etc

\( ^99m \text{Tc} \xrightarrow{\gamma \text{ decay}} ^{99} \text{Tc} \)

'Cardulite' \( \gamma = 143 \text{ keV} \)

\( I = \frac{1}{2} \)

NMR \( \rightarrow \) almost always used w/ non-radioactive isotopes \( \Rightarrow \) MRI

Nuclei with \( A = \text{odd} \) are always NMR active, \( I > 0 \)

\( ^1H = \text{proton} \) \( (I = \frac{1}{2}) \)

\( I = \frac{1}{2}, \frac{3}{2}, \frac{5}{2}, ... \)

Nuclei with \( A = \text{even} \)

\( Z = \text{odd} \) (rare)

NMR active, \( I = 1, 2, 3, ... \)

\( ^{14} \text{N} = 99.6\% \text{ of } \text{N} - \text{NMR is weak & broad} \)

\( ^2 \text{H} = \text{D (deuterium)} < 0.02\% \Rightarrow \text{enriched to } 99.99\% \)

NMR solvents: \( \text{CDCl}_3, \text{acetone-d}_6, \text{D}_2 \text{O} \)

reasons: don't give 'H NMR signal

\( \text{lock signal} \) - keeps field strength constant

\( ^{12} \text{C}, ^{16} \text{O}, ^{32} \text{S} \)
p2) Theory of NMR for $I = \frac{1}{2}$ nuclei

most studied by NMR

5 most studied isotopes
($I = \frac{1}{2}$)

<table>
<thead>
<tr>
<th>Isotope</th>
<th>Magnetic Moment (μ)</th>
<th>$\Delta E$</th>
<th>Frequency for spin flip</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^1$H (proton)</td>
<td>2.79 μN</td>
<td>$3.31 \times 10^{-25}$ J</td>
<td>500 MHz</td>
</tr>
<tr>
<td>$^{19}$F</td>
<td>2.63 μN</td>
<td>$3.12 \times 10^{-25}$ J</td>
<td>471 MHz</td>
</tr>
<tr>
<td>$^{31}$P</td>
<td>1.13 μN</td>
<td>$1.34 \times 10^{-25}$ J</td>
<td>202 MHz</td>
</tr>
<tr>
<td>$^{13}$C</td>
<td>0.702 μN</td>
<td>$0.833 \times 10^{-25}$ J</td>
<td>126 MHz</td>
</tr>
<tr>
<td>$^{15}$N</td>
<td>-0.283 μN</td>
<td>$-0.336 \times 10^{-25}$ J</td>
<td>51 MHz</td>
</tr>
</tbody>
</table>

$\mu_N = 5.051 \times 10^{-27}$ J T$^{-1}$ Tesla = units of magnetic field

Nucl. in magnetic field:

$\mu = \text{magnetic field strength}$ (units = T)

$\Delta E = \mu B / I$

$m_I = -\frac{1}{2}$

$m_I = \frac{1}{2}$

our spectrometer: $B = 11.75$ T

* - for $^{15}$N, $m_I = \frac{1}{2}$ is lower $E$ than $m_I = -\frac{1}{2}$

Spin flips in NMR caused by radio waves

$E = h \nu \Rightarrow \nu = \frac{\Delta E}{h}$ (energy gap = $500,000,000$ s$^{-1}$ for H)

$h = 500,000$ MHz

"Resonance" = frequency and field matched to allow spin flips

$\nu$ is specific to 9 sig figs. Last 4 or 5 digits depend on chemical environment.
Two designs of NMR spectrometers

**1H spectrum of H$_2$O in acetone-d$_6$**

Goal of NMR: determine ratio of all atoms of element relative values, rel. to ref. comp.

for $^1$H and $^13$C, ref. comp. is tetramethylsilane (TMS), (CH$_3$)$_4$Si

Define chemical shift of $X$ as

$$\delta = \frac{(\text{Freq.})_X - (\text{Freq.})_{\text{TMS}}}{(\text{Freq.})_{\text{TMS}}} \times 10^6 \text{ ppm}$$

Modern NMR spectrometers

1) pulse very strong multiplex frequencies
2) excite nuclei
3) detect frequencies given off (FT)
4) analyze with Fourier transform techniques

Field is constant

Field Strength

increase by ~ 1 ppm per minute

Absorption

higher freq (modern NMR)

TMS

Sample (with TMS)

Transmitter

Receiver

Electromagnet

Upfield side

chemical shift = $\delta$

"up frequency shift"? No.