What is magnetic resonance and why bother?

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What exactly is spin?

A quantum of magnetic material: a single spin is the smallest permanent magnet possible.

A property of elementary particles: quarks and leptons all have spin.

The reason why things take space: only one fermion at a time can occupy a particular quantum state; elementary fermions all have spin 1/2.

Spin is a relativistic symmetry that gives charged particles a magnetic moment.
Magnetic resonance industry

“By 2020, nuclear magnetic resonance (NMR) spectrometry is likely to lead the spectroscopy market in terms of annual revenue, which is expected to reach approximately $1.7 billion worldwide.”


NMR statistics, worldwide

Number of instruments at research organizations: ~16,000
Number of instruments at industrial companies: ~7,000
Market capitalization of the three major vendors: $78.5B
Number of academic publications in 2014: ~55,000

MRI statistics, worldwide

Number of instruments at research organizations: ~3,000
Number of instruments at medical institutions: ~31,000
Market capitalization of the five major vendors: $4.65T
Number of academic publications in 2014: ~59,000

Every major Chemistry Department has at least five NMR instruments.
Much or modern quantum technology involves spin or its mathematical lookalikes.
Magnetic moments of nuclei

Magnetic Properties of Nuclei
- Nuclei have a spin quantum number, just like electrons.
- The spin quantum number of a nucleus is a physical constant.
- A nucleus of spin \( S \) has \( 2S+1 \) energy levels.
- There are three types of nuclei:
  - No spin (\(^{12}\)C, \(^{16}\)O): spherical, but not NMR active (no magnetic moment).
  - Spin \( \frac{1}{2} \) (same as electron): \(^{1}\)H, \(^{13}\)C, \(^{15}\)N, \(^{19}\)F, \(^{31}\)P – spherical, easy to observe.
  - Spin \( >\frac{1}{2} \): \(^{2}\)H, \(^{11}\)B, \(^{14}\)N, \(^{17}\)O, \(^{33}\)S, \(^{35}\)Cl – not spherical, hard to observe.

Magnetogyric ratio
- Theory of Relativity requires charged spins to have magnetic moments.
- The magnetic moment of a nucleus is proportional to its spin:

\[
\vec{\mu} = \gamma \vec{S}
\]

\[
E = -\vec{\mu} \cdot \vec{B}
\]

\( \gamma \) is the magneto-gyric ratio.

Spin is mathematically similar to angular momentum, but physically distinct.
Energies and frequencies

- NMR people hate Joules and record all energies as frequencies. When spin and field are both along Z:
  \[
  \omega = -\gamma \left( \vec{S}_\uparrow - \vec{S}_\downarrow \right) \cdot \vec{B} = -\gamma B_Z
  \]

- The energy difference between spin-up and spin-down (tiny, hard to detect) may be obtained from the frequency:
  \[
  \Delta E = \hbar \omega
  \]

- For a hydrogen nucleus in the magnetic field of 11.7 Tesla:
  \[
  \gamma = 2.675 \cdot 10^8 \text{ (rad/s)/T} \\
  \omega/2\pi = -498 \text{ MHz} \\
  \Delta E = -0.199 \text{ J/mol}
  \]

\[
\frac{p_\downarrow}{p_\uparrow} = \exp\left( -\frac{\Delta E}{RT} \right) = 0.999920
\]

<table>
<thead>
<tr>
<th>Isotope</th>
<th>Net Spin</th>
<th>( \gamma / \text{ MHz T}^{-1} )</th>
<th>Abundance / %</th>
</tr>
</thead>
<tbody>
<tr>
<td>(^1\text{H})</td>
<td>(\frac{1}{2})</td>
<td>42.58</td>
<td>99.98</td>
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<tr>
<td>(^2\text{H})</td>
<td>1</td>
<td>6.54</td>
<td>0.015</td>
</tr>
<tr>
<td>(^3\text{H})</td>
<td>(\frac{1}{2})</td>
<td>45.41</td>
<td>0.0</td>
</tr>
<tr>
<td>(^{31}\text{P})</td>
<td>(\frac{1}{2})</td>
<td>17.25</td>
<td>100.0</td>
</tr>
<tr>
<td>(^23\text{Na})</td>
<td>3/2</td>
<td>11.27</td>
<td>100.0</td>
</tr>
<tr>
<td>(^{14}\text{N})</td>
<td>1</td>
<td>3.08</td>
<td>99.63</td>
</tr>
<tr>
<td>(^{15}\text{N})</td>
<td>(\frac{1}{2})</td>
<td>4.31</td>
<td>0.37</td>
</tr>
<tr>
<td>(^{13}\text{C})</td>
<td>(\frac{1}{2})</td>
<td>10.71</td>
<td>1.108</td>
</tr>
<tr>
<td>(^{19}\text{F})</td>
<td>(\frac{1}{2})</td>
<td>40.08</td>
<td>100.0</td>
</tr>
</tbody>
</table>

11.7 Tesla requires a large and expensive superconducting magnet.
Introduction to NMR spectroscopy

\[ \Delta E_k = \hbar \omega_k \]

- **Source** → **Physical System** → **Detector**

  - Energy levels
  - Transitions

  *Line position provides information about the chemical environment*

  *Line splitting depends on inter-atomic distances, bond angles and types*

  *Line integral is proportional to concentration*

  ![NMR Spectrum Diagram]

  - Linear frequency / Hz
  - Frequency range: 1000 Hz to 1300 Hz

  N.B. The term “spectrum” in physical sciences refers to the set of Hamiltonian eigenvalue differences corresponding to the energies of the allowed transitions under electromagnetic irradiation.
The anatomy of an NMR spectrometer
Ways of improving sensitivity

Isotope labelling
- Feeding bacteria $^{13}$C glucose and $^{15}$N urea (expensive)
- Synthesis from isotopically enriched precursors (very expensive)

Cryogenically cooled electronics and samples
- Johnson-Nyquist noise power is proportional to temperature
- Boltzmann law has temperature in the denominator

Monstrous superconducting magnets
- All things considered, the sensitivity goes as $B^{3/2}$ (very expensive)

Quantum mechanical tricks
- Dynamic nuclear polarisation
- Algorithmic cooling
- Quantum optimal control

Even in the strongest magnet, the energy level population difference for $^1$H is tiny.
Rapid structure determination is essential in chemical and biological sciences.

**NOESY spectrum of strychnine**

Cartesian coordinates of every atom in a few hours.
The anatomy of an MRI scanner

- The duration of a typical scan is 5-10 minutes.
- A superconducting magnet can exert a massive force on ferromagnetic objects.
A full-body scan is a rare luxury because instrument time is expensive.
Functional MRI

1. Two states of haemoglobin have very different magnetic properties.
2. Local neuron activation creates de-oxygenated haemoglobin.
3. The effect is nearly instant and may be used in difference imaging.
4. Local levels of brain activity may be monitored.

Figure 7.5 Changes in oxygenated and deoxygenated hemoglobin following neuronal stimulation. This figure shows that the concentration of deoxygenated hemoglobin increases rapidly at stimulus onset, peaking at about 2 s, and then declines to a minimum value about 6 s after onset. The oxygenated hemoglobin signal shows no decline, but begins rising shortly after stimulus onset and reaches a peak at about 5 to 6 s, with a slow decline to about 10 s. (Data from Malonek and Grinvald, 1996.)