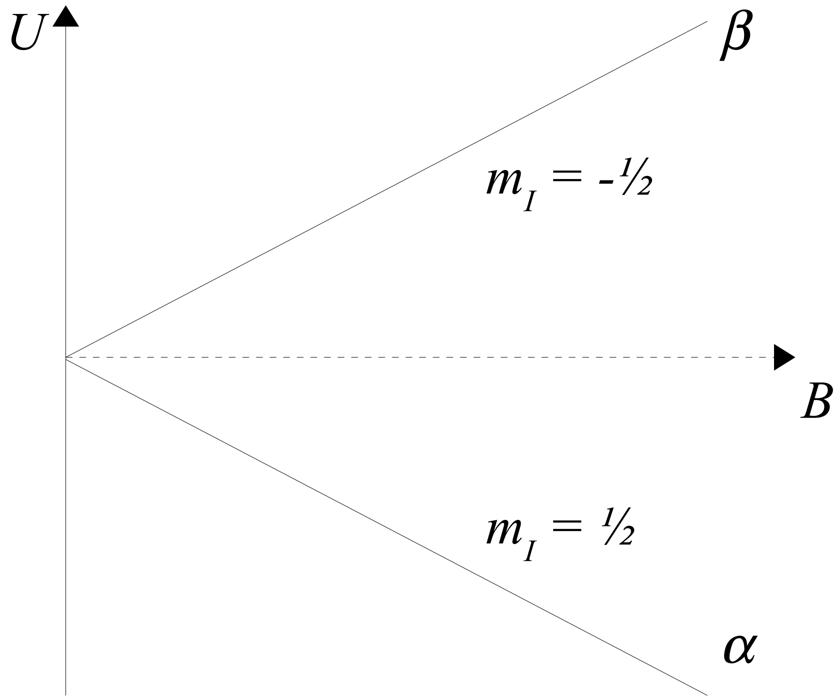
Effect of a magnetic field

The energy of interaction between a magnetic field *B* and a magnetic moment μ is given by:

$$U = -\boldsymbol{\mu} . \boldsymbol{B}$$

Now if *B* is applied in the *z* direction:

$$U = -\mu_z B_z$$
$$U = -\gamma \hbar m_I B_z$$



A spin of quantum number *I* has 2*I* + 1 states

2*I* + 1 separate non-degenerate energy levels corresponding to the 2*I* + 1 values for m_I.

Energy separation

The energy separation between the states can be easily found

$$\Delta U = -\gamma \hbar m_I^1 B - (-\gamma \hbar m_I^2 B)$$

$$\Delta U = \gamma \hbar \Delta m_I B$$

Induce transitions between these energy states by irradiating the sample with the appropriate electromagnetic radiation.

- **Resonance**

Frequency of radiation

$$h \nu = \gamma \hbar \Delta m_I B$$

$$\nu = \frac{\gamma}{2\pi} \Delta m_I B$$

What are the allowed values for Δm_I

- selection rule

Selection rule

$$\Delta m_I = \pm 1$$

Electromagnetic radiation must conserve angular momentum. Since a photon has one unit of angular momentum when a transition occurs the magnetic energy levels must compensate.

Two allowed transitions for a spin-1/2 nucleus:

α to β: absorption and β to α :emission.

Transition frequency:

$$\boxed{\nu = \frac{\gamma}{2\pi} B}$$

Resonance condition.

SI unit for a magnetic field is Tesla

Typical field for NMR	1.5 - 18.8 T.
Earth's magnetic field:	10^{-5} T.

For the proton, ^1H: $\gamma = 26.752 \times 10^7$ rad$T^{-1}s^{-1}$.
For a 10 T magnetic field we get

$$\nu = 425.8 \text{ MHz}$$

Choose magnetic field for certain ^1H resonant frequencies e.g. 60, 100, 200, 270, 300, 360, 400, 500, 600, 750, 800, 900 MHz

NMR transitions can be viewed as a rotational processes, so rather than the linear frequency ν it is much more common to see ω used in NMR expressions.

$$\omega = 2\pi\nu \quad \text{rad s}^{-1}$$

This gives the resonance condition as

$$\omega = \gamma . B \quad \text{rad s}^{-1}$$

Note

- 300 MHz or 400 MHz NMR spectrometer we are talking about the linear frequency.

Recap

The quantum mechanical picture of ^{1}H NMR
- two energy levels
- electromagnetic radiation inducing transitions between the two spin states.

NB The probability of a stimulated absorption and emission are the same.

Intensity of the NMR signal

Distribution of nuclear spins across the energy levels:

- dealing with ~10^{23} spins,

Boltzman distribution.

For the two energy levels of a spin-1/2 nucleus this can be written as:

$$N_\beta = N_\alpha \exp\left(\frac{-\gamma\hbar B_0}{kT}\right)$$

Can the thermal energy, kT, promote spins from a lower to a higher energy state, $\gamma\hbar B_0$.

NMR

- small energy differences ~2 x10^{-24} J for ^{1}H in a 10 T field
- thermal energy at room temperature, 300 K is ~ 4 x 10^{-21} J.

Consequence:

- α and β spin states have almost the same population.

One reason why NMR is an insensitive technique.

Put these numbers into the Boltzman equation we find:

$$N_\beta = N_\alpha \exp\left(-0.7 \times 10^{-4}\right)$$
$$N_\beta = N_\alpha \times 0.99993$$

a difference of only 7 in 105.

Compare with visible light of 500 nm (green light).

$$\Delta E = h\nu = h\frac{c}{\lambda} = \frac{6.6261 \times 10^{-34} \times 2.9979 \times 10^{8}}{500 \times 10^{-9}}$$
$$\Delta E \approx 4 \times 10^{-19} \text{ J / molecule}$$

$$N_\beta = N_\alpha \exp(-100)$$
$$N_\beta = N_\alpha \times 4 \times 10^{-44}$$

How to improve sensitivity

1. The lower the temperature

2. Work at the highest possible magnetic field B_0.

3. Study a nucleus with the highest possible magnetogyric ratio, γ.

4. Natural abundance of the nuclei

Nucleus	Abundance, %	Relative freq. MHz
^{1}H	100	100.0
^{13}C	1.11	25.144
^{15}N	0.37	10.133
^{19}F	100	94.077
^{29}Si	4.7	19.865
^{31}P	100	40.481

Proportionality

Important factor in NMR

- coefficient of absorption of the radiation is the same regardless of the nucleus and its environment.

The consequence of this is that NMR signal is directly proportional to the number of nuclei producing it. Take a couple of simple examples:

	Resonance	Intensity
1. Ethanol CH_3CH_2OH	Methyl	3
	Methylene	2
	Hydroxyl	1
2. Toluene	Methyl	3
	Aromatic	5

Relaxation

Can the nuclear spins change their spin state when no irradiation is present?

- Yes: build up in population difference
- Yes: return to thermal equilibrium after irradiation

Irradiation equalises the populations of the α and β spin states.

- saturation

Energy must come from somewhere

- lattice
- other nuclear spins

Must have fluctuating magnetic field to induce a transition

- dynamics: molecular tumbling, translation

Two types of relaxation

spin-lattice	:	net energy loss to the surroundings T_1 Restores thermal equilibrium
spin-spin	:	no net energy loss to the surroundings T_2 Loss of spin coherence