Pulsed FT NMR

Two features

- Pulses of radiofrequency radiation
- Fourier transform methods

Why pulses?

- Allows fourier transform methods
  - improves S/N ratio
- Extremely versatile
  - sophisticated pulse sequences

For spectral assignment and spatial correlation

Multi-dimensional NMR
COSY, NOESY

CW NMR

- Measure absorption of rf energy
- NMR spectrum in the frequency domain
- Excite each resonance individually

Pulsed NMR

- Measure free induction decay
- NMR signal in the time domain
- Pulse excites all the spins at the same time

How?

- Uncertainty principle
  Short pulse means spread in excitation frequencies

$$\Delta t . \Delta E > \frac{1}{2}\hbar$$

- Look at fourier transform of a pulse
  Pulse contains all the frequency components in the corresponding frequency domain

$$\frac{\sin x}{x}$$

Signal-to-noise ratio (S/N)

Signal adds coherently :

$$Signal \propto N$$

where N is the number of scans

Noise adds incoherently :

$$Noise \propto \sqrt{N}$$

Signal-to-noise ratio defined as

$$S/N = Signal/Noise$$

$$S/N = \sqrt{N}$$

To improve *S/N* by a factor x takes x^2 more scans and x^2 more time

Pulsed NMR

Descriptions

- classical
- quantum mechanical

Only consider the classical picture
Explains simple one-dimensional NMR

- inadequate when magnetisation transferred between spins

Key concepts

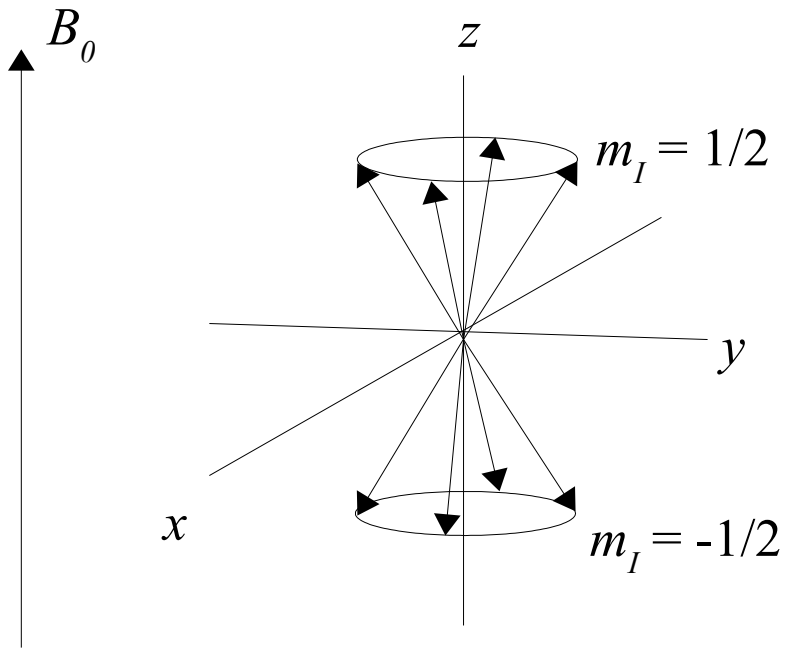
- Bulk magnetisation
- Rotating frame
- Vector diagrams
- Rf pulses as rotations

Bulk Magnetisation

Total magnetic moment, ***M***

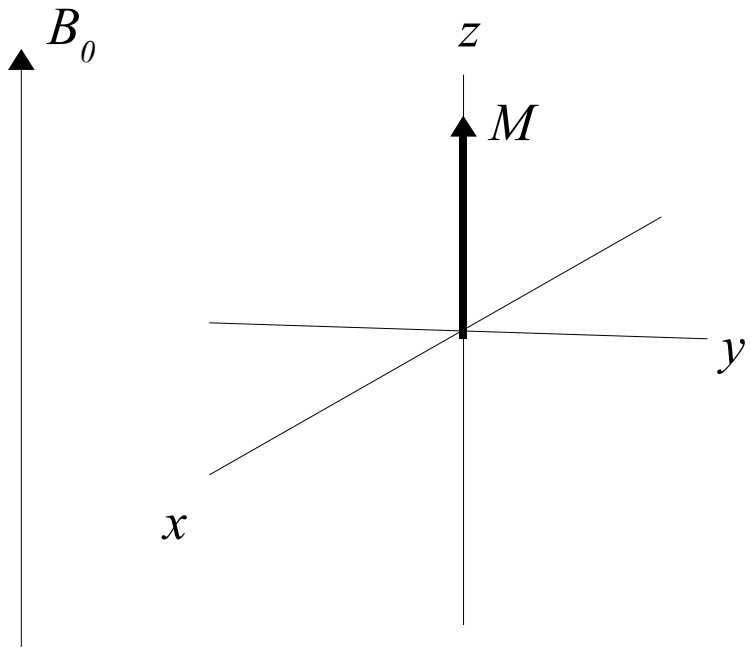
$$M = \sum_j \mu_j$$

Macroscopic property of the sample

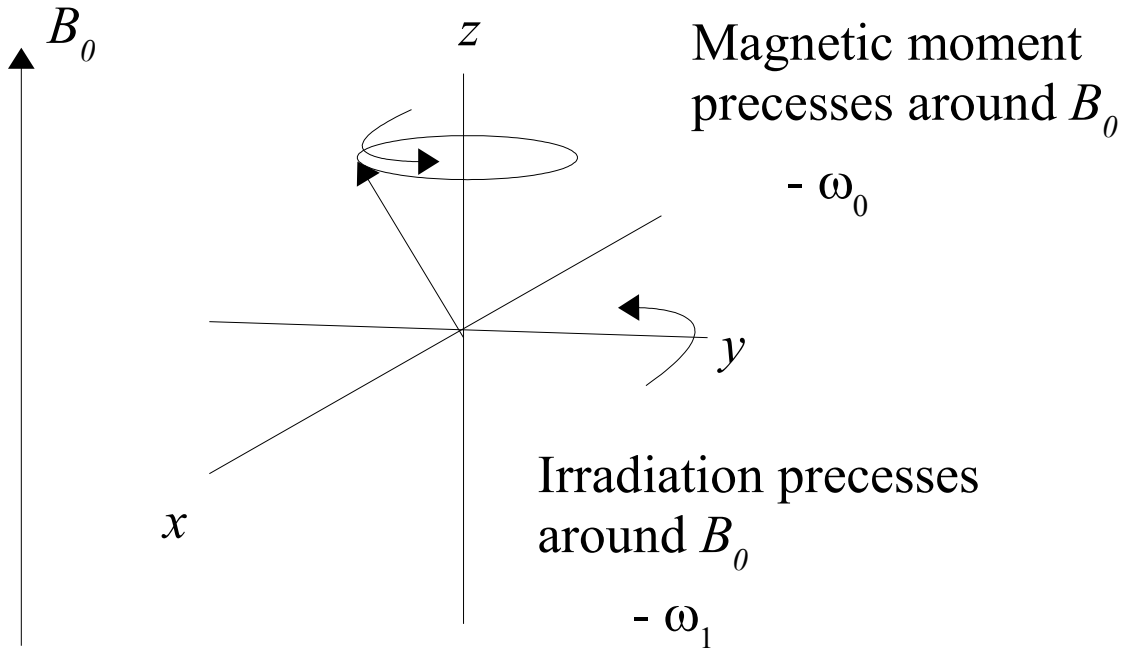


- Magnetic moments randomly oriented in precessional cone
- Slight excess in the upper $m_I = +1/2$ cone

Net result



Rotating frame



Difficult to visualise with all rotating

Rotating frame

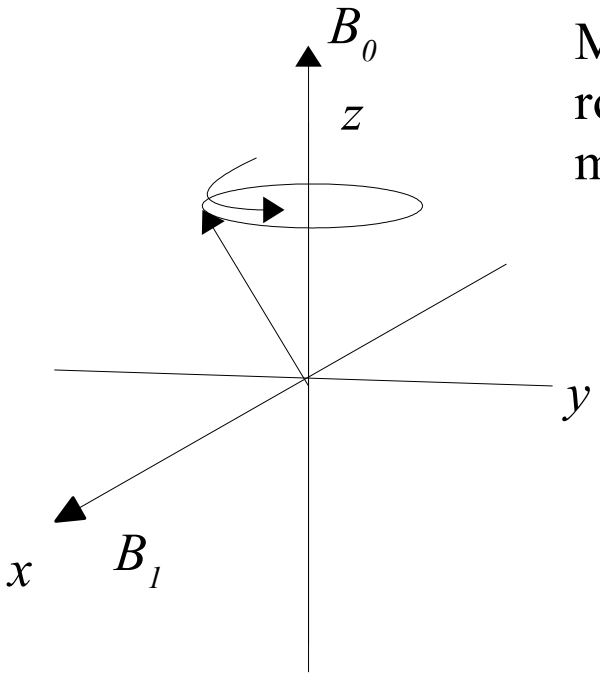
The Cartesian co-ordinate axes frame is considered to rotate about the z -axis at an angular frequency ω_0

Makes magnetisation stationary

Analogy

- distant observer of Earth *v.* us

Pulses as rotations



Magnetic moment rotates about a magnetic field

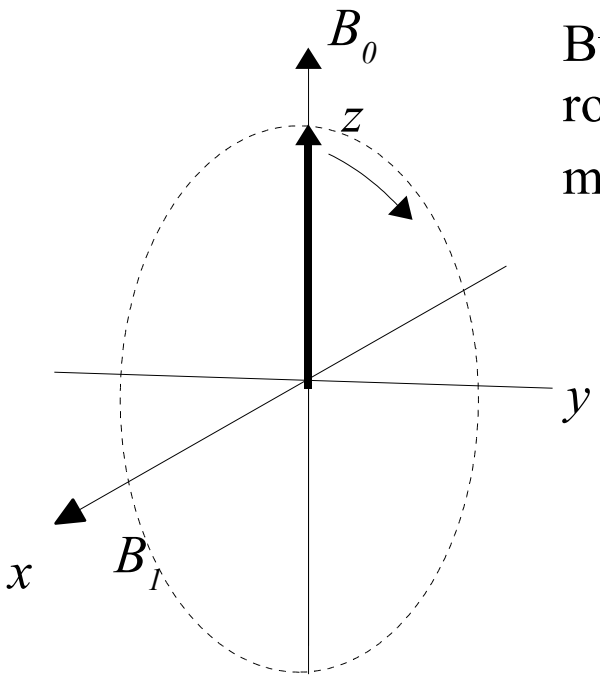
Radiofrequency pulse = electromagnetic radiation

Like a magnetic field pulse, B_1

- Apply in the *xy* plane
- Detect NMR signal through magnetisation in the *xy* plane
  - induced emf in a coil, μV

Magnetic moment will rotate for as long as the pulse is applied

Rotation of bulk magnetisation



Bulk magnetisation rotates about the B_1 magnetic field

Like angular transition frequency $\omega_0 = \gamma B_0$

So angular rotation frequency $\omega_1 = \gamma B_1$

- Pulse of duration τ_p will cause a rotation α (rad) ,also known as the flip angle

$$\alpha = \gamma B_1 \tau_p$$

- Intensity after a pulse

$$M_{x,y} = M \sin\alpha$$

$$M_z = M \cos\alpha$$

- Two special pulses

  90^0 or $\pi/2$: maximises signal in *xy* plane

  180^o or π : inverts the magnetisation, gives no signal

- Can apply pulse along other axes

  - rotation about x, -x, y and -y axes