Nuclear Magnetic Resonance (NMR)

Atkins, Chapter 19

Many nuclei possess a spin angular momentum (depending on the number of protons and neutrons)

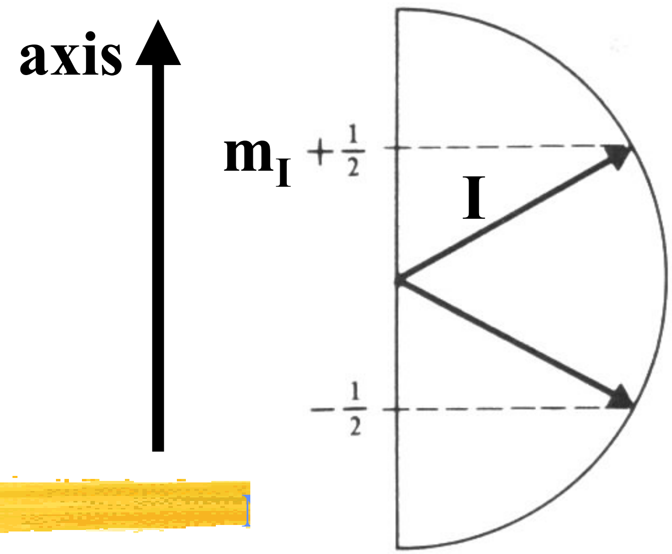
⇒ they behave like magnets with spin quantum number I; their spins may have different orientations

$$m_I = -I,\ldots,+I$$

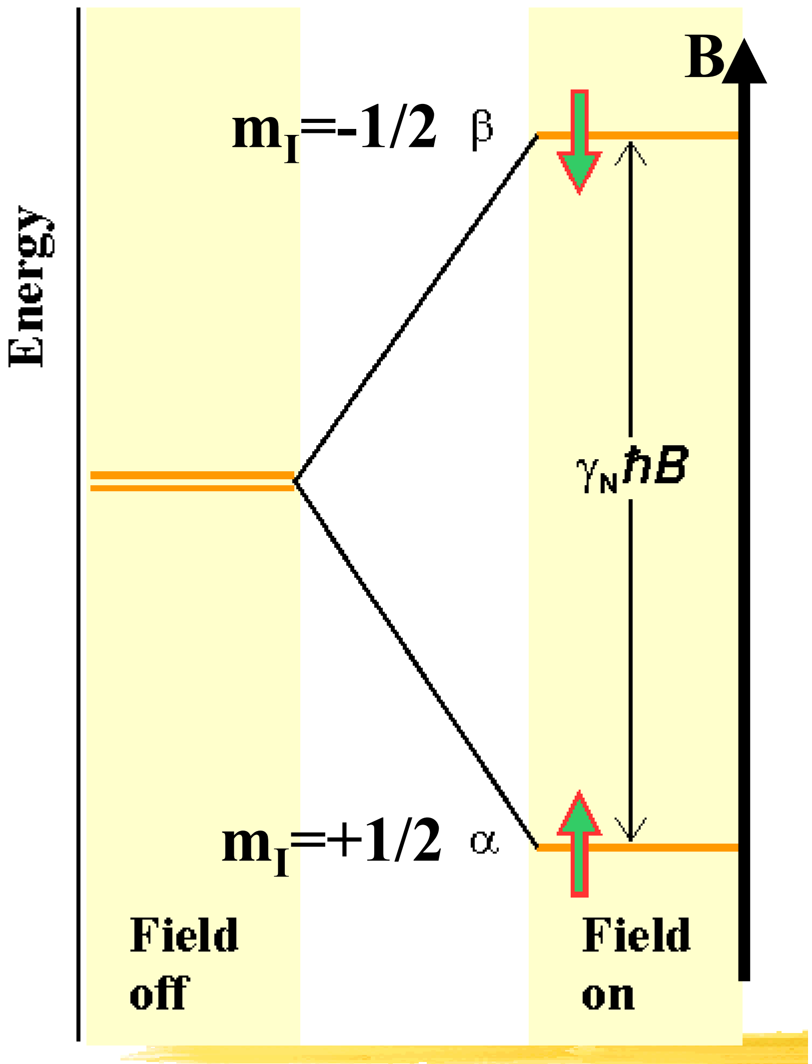
with respect to an outside axis, e.g., I = 1/2 ⇒ two orientations

Table 19.1 *Nuclear spin properties*

Nucleus	Natural abundance/ per cent	Spin, I	$\gamma_N/(10^7\ T^{-1}\ s^{-1})$
^{1}H	99.98	$\frac{1}{2}$	26.752
^{2}H (D)	0.0156	1	4.1067
^{12}C	98.99	0	—
^{13}C	1.11	$\frac{1}{2}$	6.7272
^{14}N	99.64	1	1.9328
^{16}O	99.96	0	—
^{17}O	0.037	$\frac{5}{2}$	−3.627
^{19}F	100	$\frac{1}{2}$	25.177
^{31}P	100	$\frac{1}{2}$	10.840
^{35}Cl	75.4	$\frac{3}{2}$	2.624
^{37}Cl	24.6	$\frac{3}{2}$	2.184



An outside magnetic field splits up the degenerate spin orientations

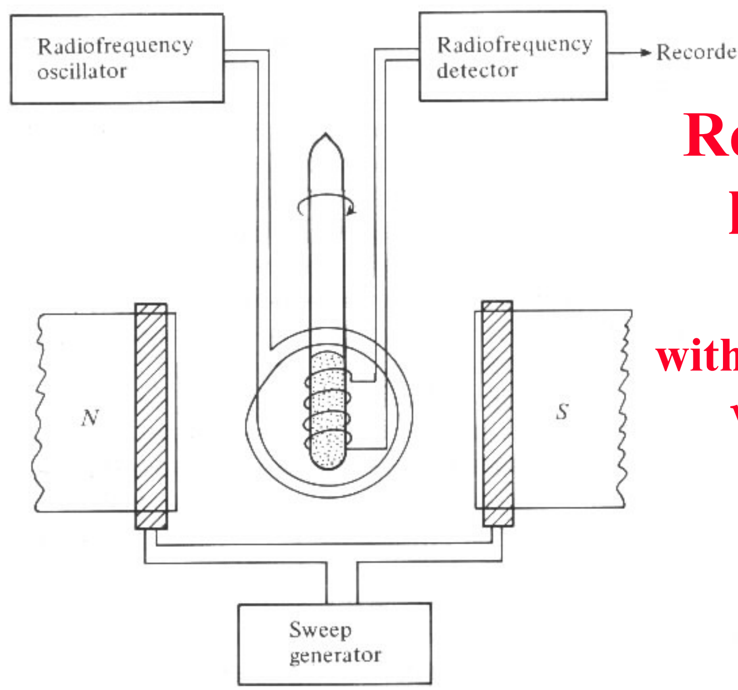


$$E_{m_I} = -\gamma_N \hbar B m_I = -g_I \mu_N B m_I$$

γ_N = magnetogyric ratio

g_I = nuclear g-factor

$$\mu_N = \frac{e\hbar}{2m_P} = \text{nuclear magneton}$$



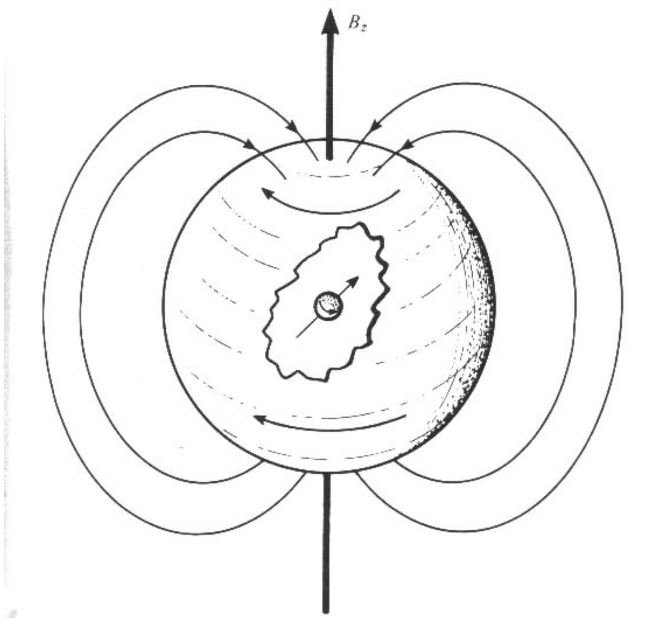
Resonance at
$h\nu = \gamma_N \hbar B$

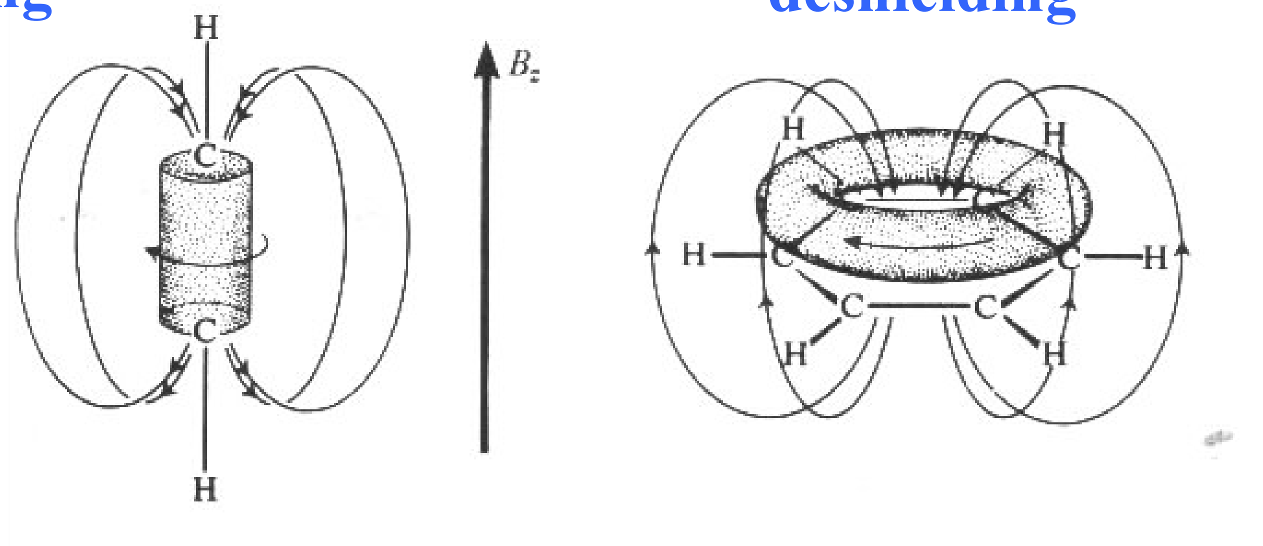
with B = 9.4T for ^{1}H
ν = 400 MHz

Shielding and deshielding

A magnetic field will induce a circulating motion in the electrons, giving rise to a small additional magnetic field at the nucleus

shielding | **deshielding**





(a) (b)

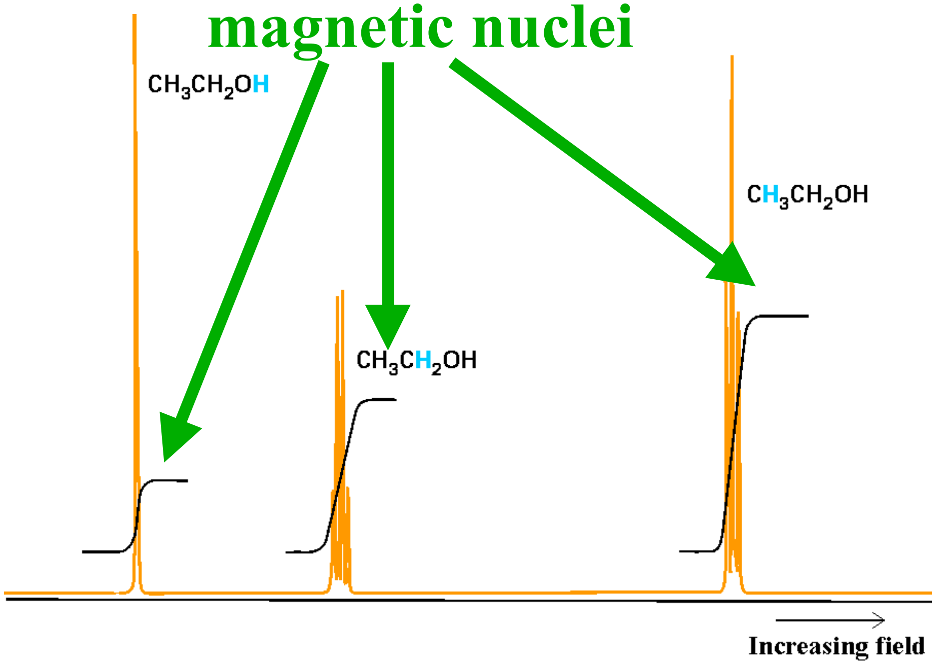
$$B_{effective} = B_{applied} - B_{induced} = B_{applied}(1-\sigma)$$

$$\nu = \frac{\gamma_N}{2\pi} B_{applied}(1-\sigma)$$

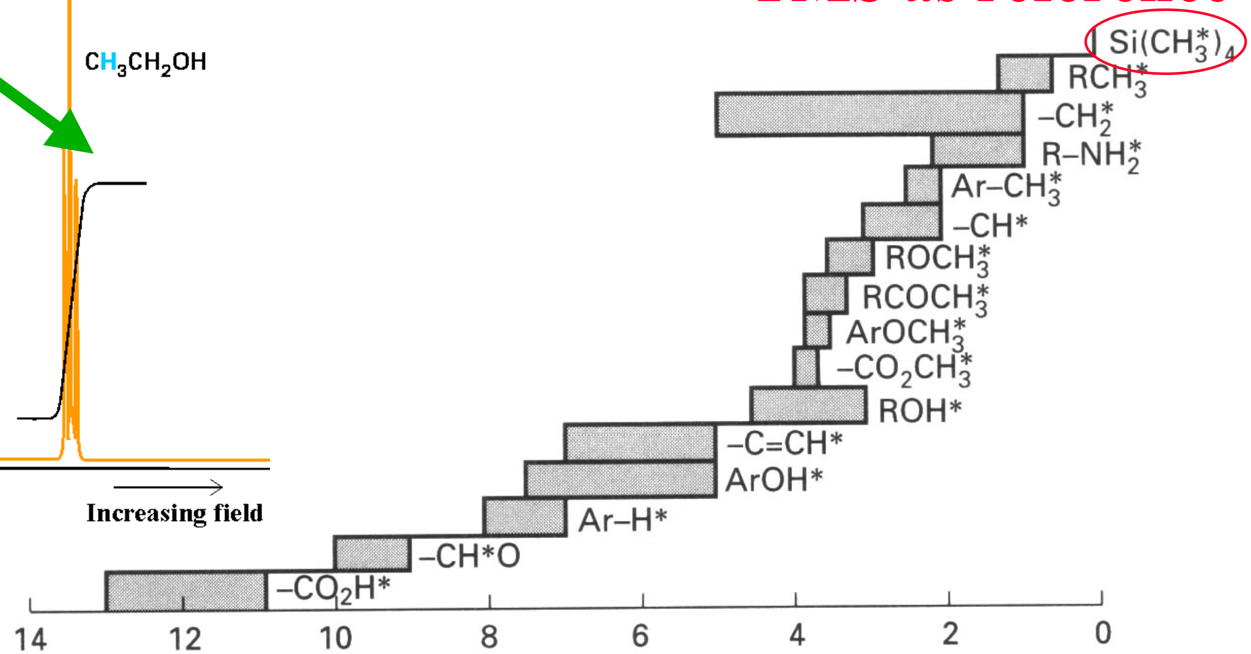
Chemical shifts vary with environment: Assignment of resonances

Relative signal intensities reflect number of identical magnetic nuclei

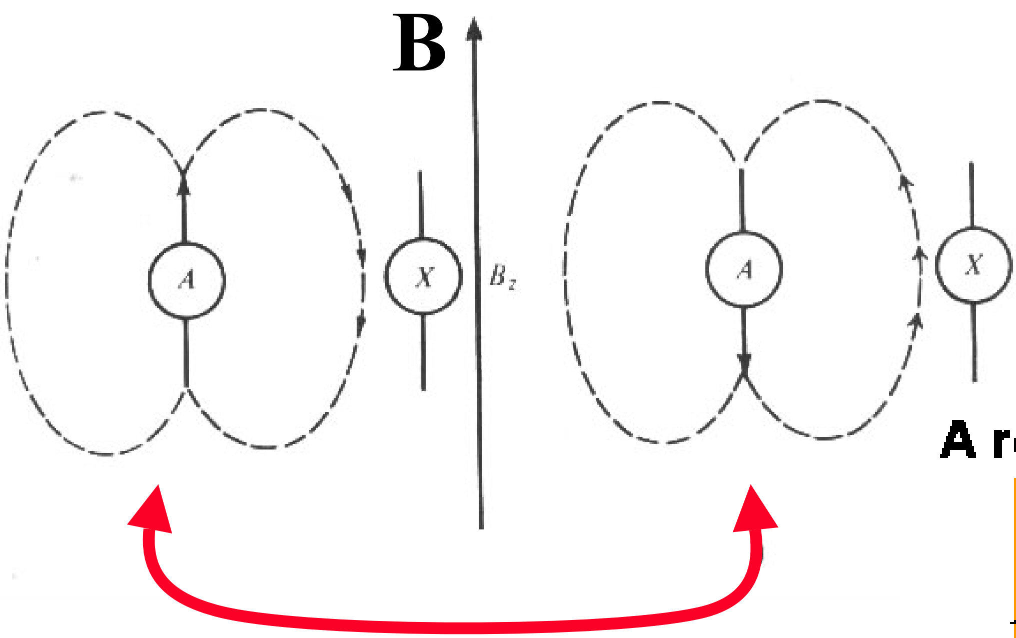
$$\delta \text{ scale } \delta = \frac{\nu - \nu^0}{\nu^0} [ppm]$$



TMS as reference



The fine structure: Spin-spin coupling



Energy difference J: Spin-spin coupling efficiency depends on distance (max. 4 bonds)

X and A exert effects on each

A resonance ← other → X resonance