

# Spin

Just what does that 4th quantum number represent?

- \* Introduced empirically to explain certain features of atomic spectra (1925).
- \* Theory developed by **Pauli** and shown to be a consequence of the **Dirac equation**.
- \* It is the intrinsic, characteristic and irremovable angular momentum of a particle.

You can visualize it as the rotation of a body about its own axis, but... what about **point** particles?

- \* It is a **non-classical phenomenon!**

In contrast, orbital angular momentum → classical behaviour at high enough  $l$  values.

- \* All matter can be classified according to spin:

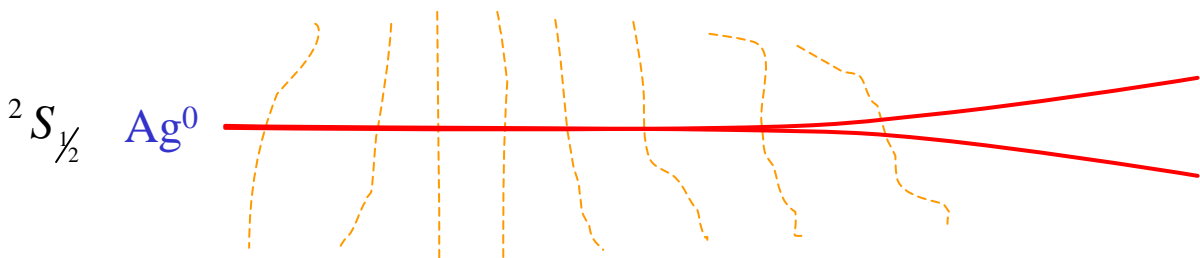
**Fermions** have half-integral spins ( $\frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \dots, n + \frac{1}{2}$ ) and satisfy **Fermi-Dirac** statistics.

**Bosons** have integral spin (0, 1, 2, ... ) and satisfy **Bose-Einstein** statistics

# Experimental Evidence for Spin

- ❖ Fine structure
  - ❖ Zeeman effect
  - ❖ Hyperfine structure
- } in atomic spectra
- ❖ Alternating intensities in the rotational structure of vibration bands of centrosymmetric molecules.
  - ❖ Magnetic resonance spectroscopy – ESR and NMR
  - ❖ The Stern-Gerlach Experiment:

In an inhomogeneous magnetic field



The beam of silver atoms splits into two.

The first experiment gave the classical result of an even distribution. The beam intensity was high enough that collisions between atoms scattered the beam.

# Magnetic Moments in Atoms and Molecules

Angular momentum can arise from:

- ♦ orbital motion of electrons  $\vec{L}$
- ♦ electron spin  $\vec{S}$
- ♦ nuclear spin  $\vec{I}$

In general, for an angular momentum quantum number  $j$

$$\text{magnitude} = [j(j+1)]^{1/2} \hbar$$

$$z\text{-component} = m_j \hbar \quad m_j = j, j-1, \dots, -j$$

The interaction of the orbital or spin angular momentum with a magnetic field is characterized by the **magnetic moment**.

$$E = -\vec{\mu} \cdot \vec{B} = -\mu_z \cdot B_z \quad \vec{B} = (0, 0, B_z)$$

**orbital**  $\mu_z = \gamma_e m_l \hbar = -\beta m_l$

**electron spin**  $\mu_z = g_e \gamma_e m_s \hbar = -g_e \beta m_s$

**nuclear spin**  $\mu_z = \gamma_N m_I \hbar = g_N \beta_N m_I$

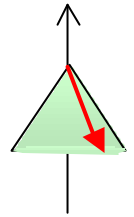
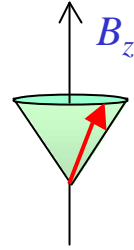
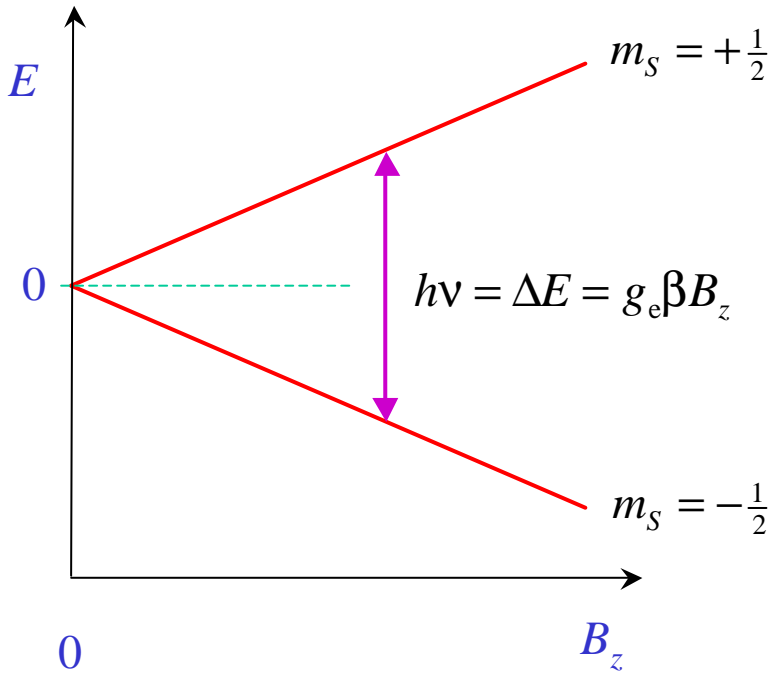
**magnetogyric ratio**  $\gamma_e = -\frac{e}{2m_e}$  **g-value** = 2.0023

**Bohr magneton**  $\beta = \frac{e\hbar}{2m_e}$  **nuclear magneton**  $\beta_N = \frac{e\hbar}{2m_p}$

# Electrons and Nuclei in a Magnetic Field

**Electron spin**  $E_{m_S} = g_e \beta B_z m_S$   $m_S = \pm \frac{1}{2}$

selection rule:  $\Delta m_S = \pm 1$



X band 9.5 GHz ↔ 3.4 kG

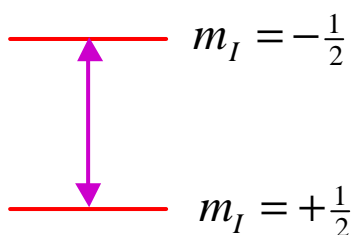
0.34 T

Q band 35 GHz ↔ 12.5 kG

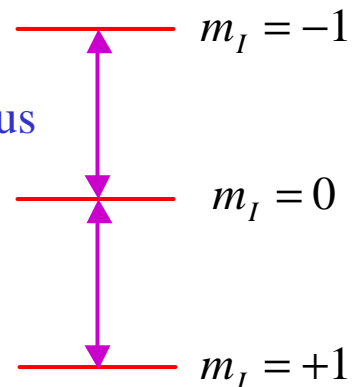
1.25 T

**Nuclear spin**  $E_{m_I} = -\gamma_N \hbar B_z m_I$  selection rule:  $\Delta m_I = \pm 1$

spin 1/2 nucleus

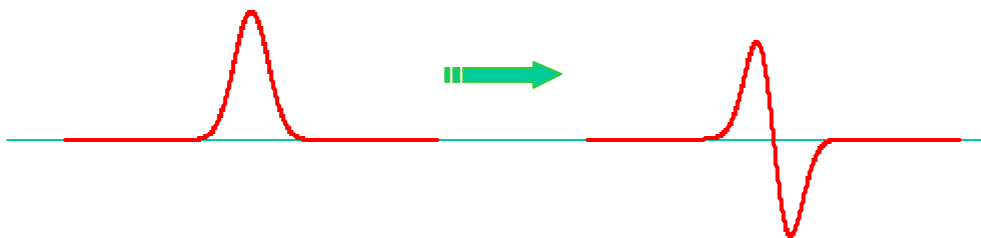


spin 1 nucleus



# ESR – Experimental Aspects

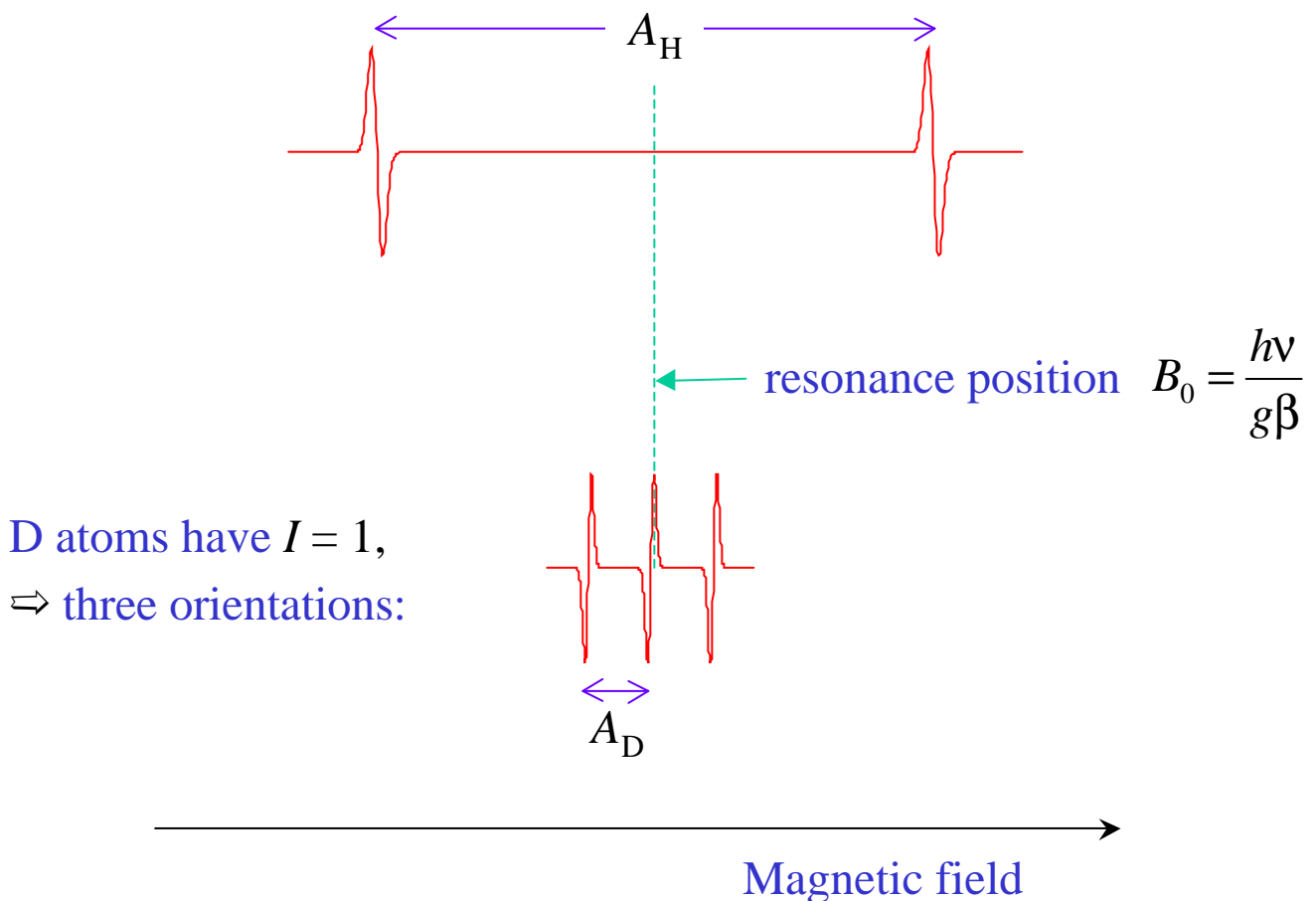
- \* Microwaves: generated by klystron oscillators, Gunn diodes conducted by waveguides
- \* Sample mounted in a **resonant cavity** – a metal box of precise dimensions tuned to be part of a microwave bridge and designed to favour a particular standing wave pattern.
- \* Absorption of microwaves by the sample at resonance unbalances the bridge, changing the output of a rectifying crystal detector in another arm of the bridge.
- \* Resonance found by sweeping field and keeping frequency constant. The spectrum is recorded as a function of field (in gauss), but spectral features *should* be described in MHz.
- \* Signal-to-noise (S/N) is improved by **field modulation** with phase sensitive detection. For a modulation amplitude smaller than the line width, the recorded spectral lineshape has a derivative-like shape:



# ESR Hyperfine Splitting

Interaction of the unpaired electron of a radical with magnetic nuclei (H, N, ...) results in **hyperfine** splitting of ESR resonances.

Each nuclear spin contributes a local magnetic field depending on its  $m_I$  value. Thus, the protons in H atoms can have  $m_I = \pm\frac{1}{2}$  resulting in two different local fields in addition to  $B_0$ .



# ESR Hyperfine Splitting – 2

Spin Hamiltonian

$$\hat{H} = g_e \beta B_z \hat{S} + a \hat{I} \cdot \hat{S}$$

$$\approx g_e \beta B_z \hat{S}_z + a \hat{I}_z \cdot \hat{S}_z$$

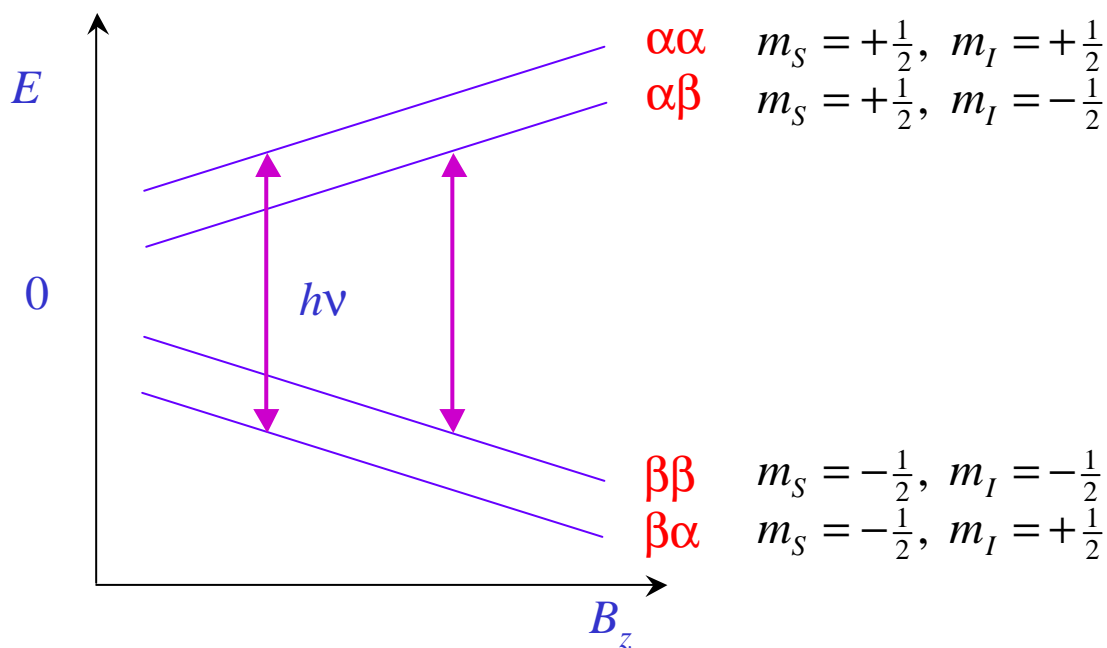
Zeeman      Hyperfine

$$E = g_e \beta B_z m_S + a m_S m_I$$

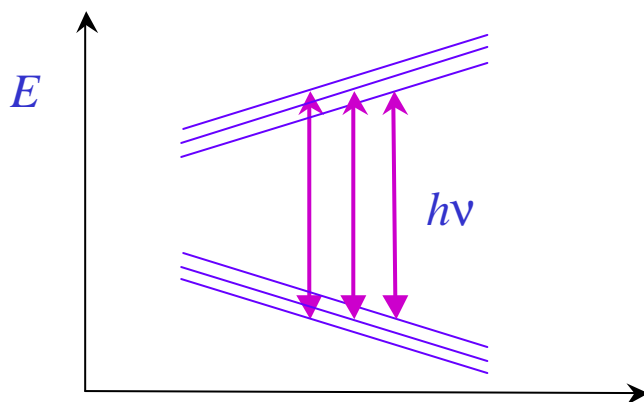
selection rules:  $\Delta m_S = \pm 1, \Delta m_I = 0$

$$h\nu = \Delta E = g_e \beta B_z \pm a m_I$$

H atom



D atom



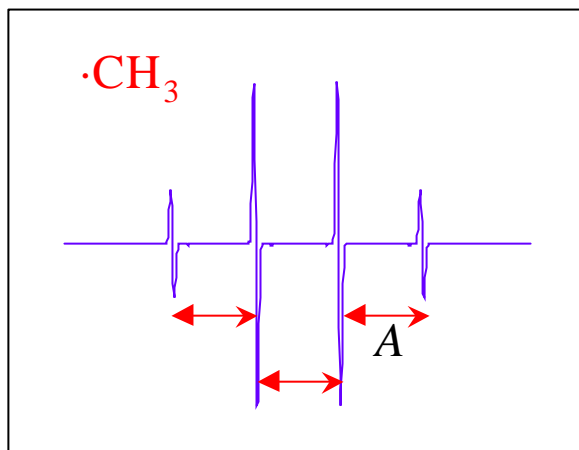
# Hyperfine Splitting by Many Nuclei

Most radicals contain more than one magnetic nucleus.

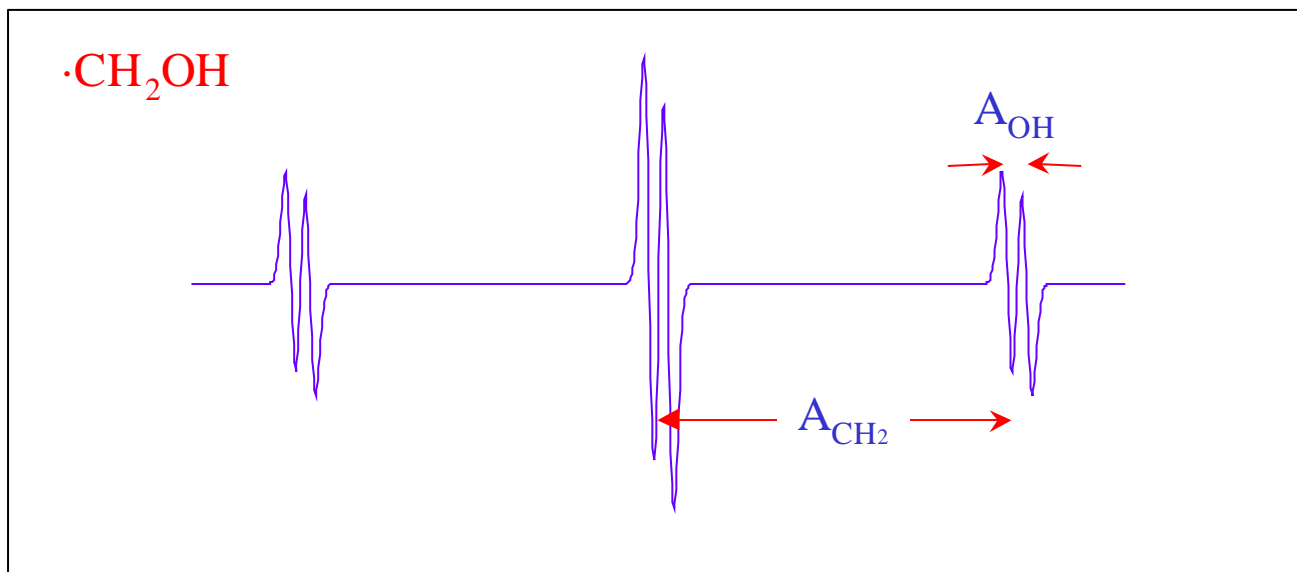
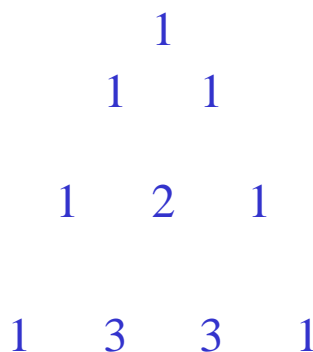
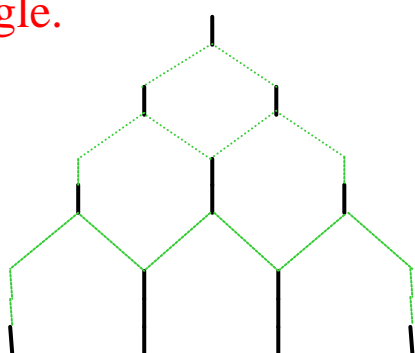
Each couples to the unpaired electron to produce its own splitting.

Equivalent nuclei with total spin  $I$  give  $2I+1$  lines.

Thus,  $n$  equivalent spin- $1/2$  nuclei (e.g. protons) couple to give a spectrum of  $n+1$  lines. Their relative intensities are given by the binomial coefficients of  $(1+x)^n$ .



Pascal's triangle.





# ESR of Organic Radicals – Examples

