Electron Paramagnetic Resonance (EPR)

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Theory

- <u>Angular Momentum and Magnetic Moment</u>

  Electrons that perform a circular movement with an angular momentum *l* have a magnetic dipol moment μ_l:

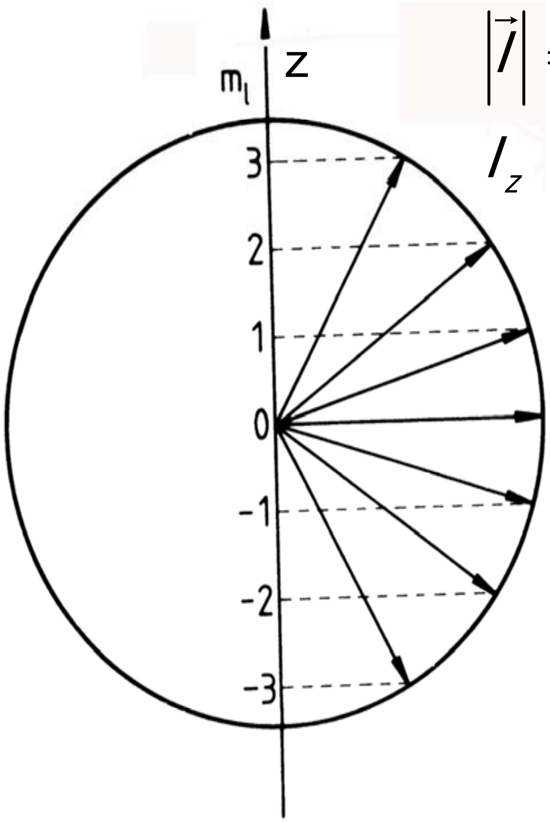
$$\mu_l = -\gamma l \quad \text{where } \gamma = e/2m_e$$

γ is called the gyromagnetic constant. The magnetic moment is usually refered to in units of Bohr's magneton μ_B:

$$\mu_l = -\frac{\mu_B l}{\hbar} \qquad \mu_B = 9.27402 * 10^{-24}\ \text{J/T}$$

Schroedinger Equation

- **Quantization** of Spin and Angular Momentum

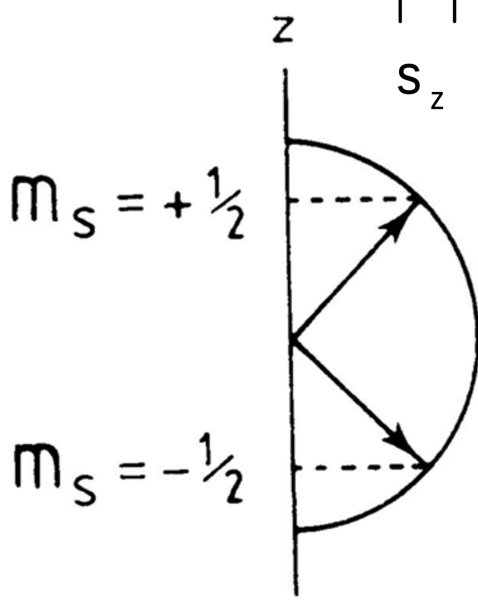


$$\left|\vec{l}\right| = \hbar\sqrt{l(l+1)}$$

$$l_z = m_l\hbar \quad m_l = 0, \pm1, \pm2, \ldots, \pm l$$

$$\left|\vec{s}\right| = \hbar\sqrt{s(s+1)}$$

$$s_z = m_s\hbar \qquad m_s = \pm s$$



$$\mu_s = -\frac{g_e \mu_B s}{\hbar}$$

g_e = 2.00232
Landé factor

Theory

- <u>Interaction of the Electron with an External Magnetic Field</u>

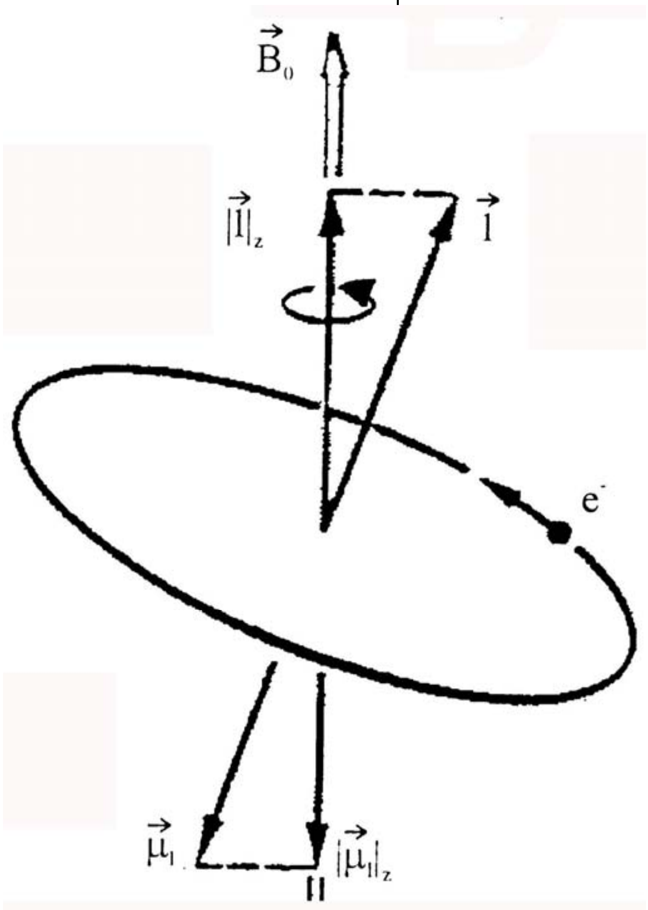
$$E = -\mu_l B \cos\alpha$$

μ_l aligns with respect to the axis of the external magnetic field (z)

→ Precission of μ_l along z

→ Quantization of α

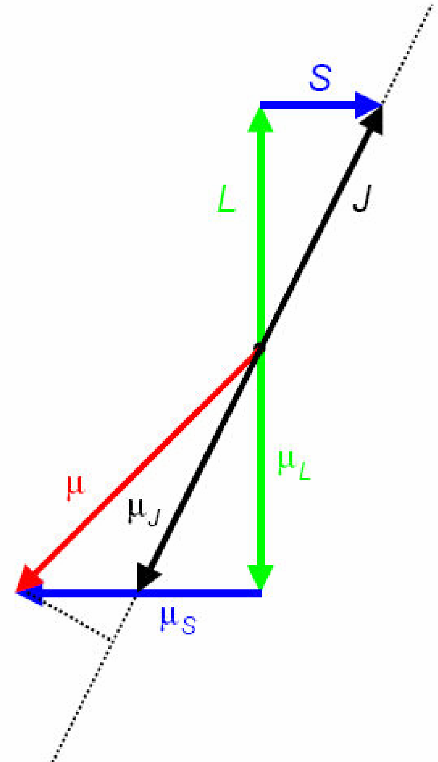
(α = angle between μ_l along z)



Russel-Saunders (LS) Coupling

- Fine Structure of Atoms

  For atoms in the gas phase of light elements, the total angular (*L*) and spin (*S*) momenta couple to give a total momentum (*J*) and a corresponding magnetic moment μ_J:



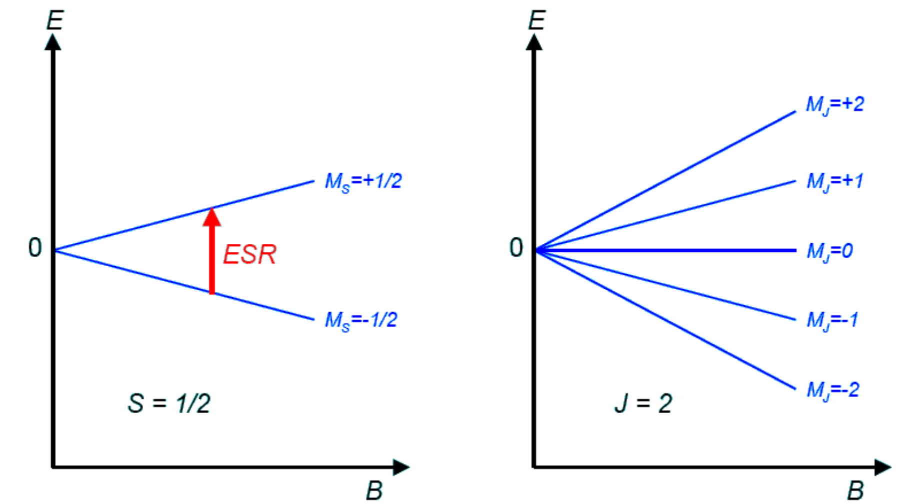
$$\mu_J = -g_J \frac{e}{2m_e} J$$

where $J = |L+S|, \ldots, |L-S|$

This generates the so-called fine structure in the electronic spectra of atoms.

Zeeman Effect

- Interaction of the magnetic moment μ_J with the external field lifts the energetic degeneracy of the (2J + 1) electronic M_J states



- Magnitude of energetic splitting depends linearly on the magnetic field strength

  → Electron Paramagnetic Resonance: transitions between the magnetically split M_J levels

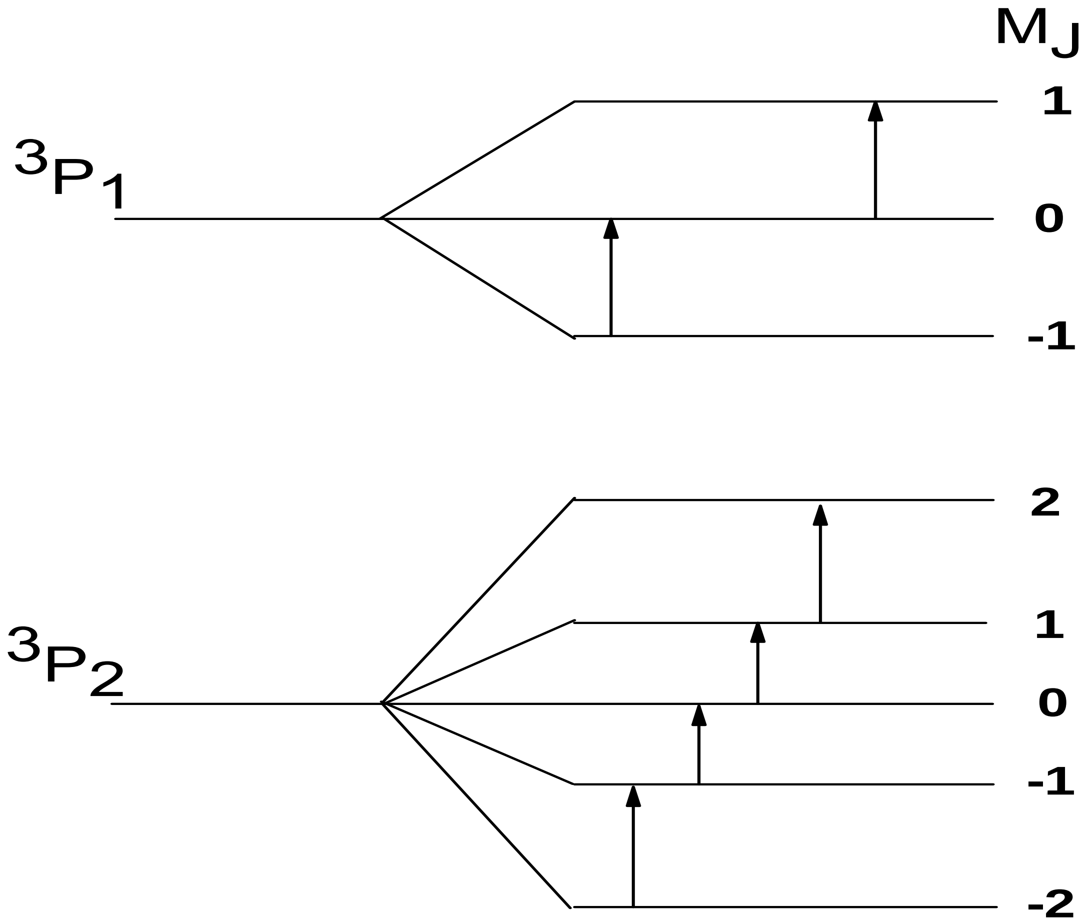
  → frequencies in the microwave region

  → selection rule: $\Delta J=0$, $\Delta M_J = \pm 1$)

  → $\Delta E = h\upsilon = g_J \mu_B B$

Example

- ^{16}O-Atom: l = 1, s = 1 (J = 2, 1)

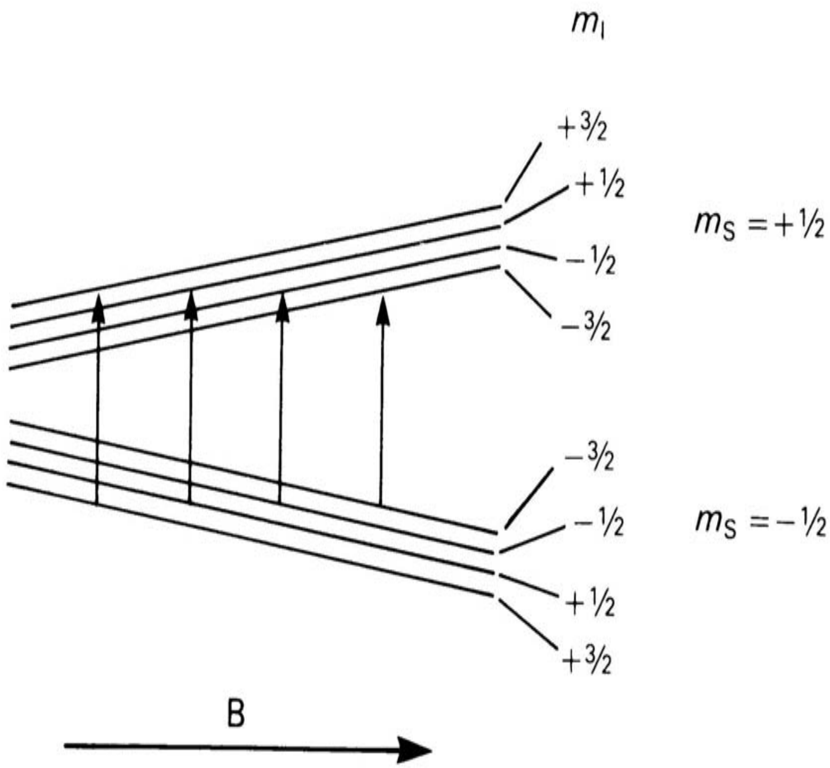


Hyperfine Splitting

- Interaction of the magnetic moment of the electron with that of the nucleus (angular momentum: I). Requirement: $I \neq 0$.

  The hyperfine splitting constant a is easily obtained from the spectra:

$S = 1/2$
$I = 3/2$



$$a = \frac{\Delta B g_J \mu_B}{h}$$

g shifts

- For atoms in the gase phase, the g value is simply defined as:

$$g = 1 + \frac{[J(J+1) + S(S+1) - L(L+1)]}{2J(J+1)}$$

- Experimentally, this value is accessible from the spectra:

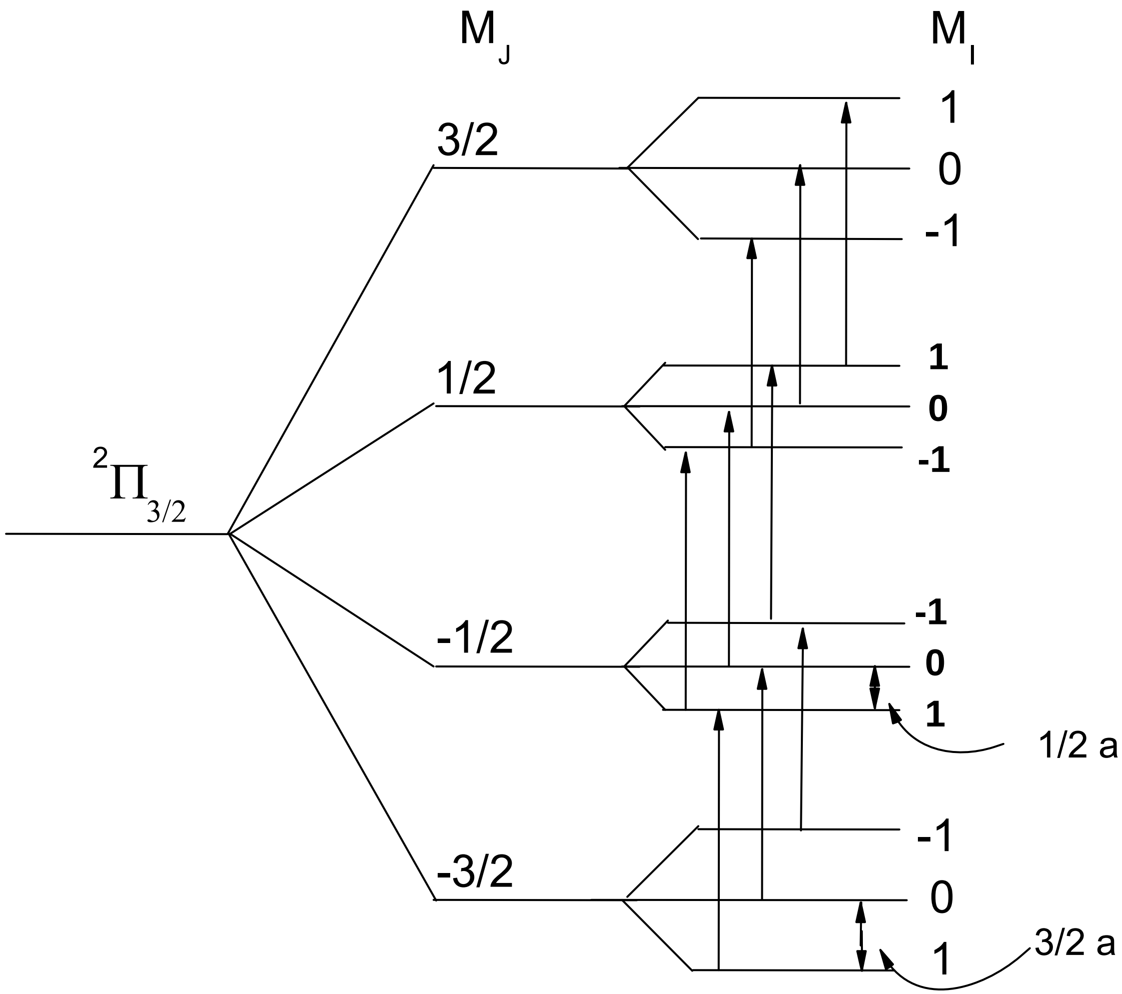
$$B = \frac{h\nu}{\mu} . \frac{1}{g}$$

- g factors are characteristic for the angular momentum J of the atom and hence, allow for the easy determination of this value experimentally (compare to d in NMR)

Example

Spectrum von NO.

Example: NO



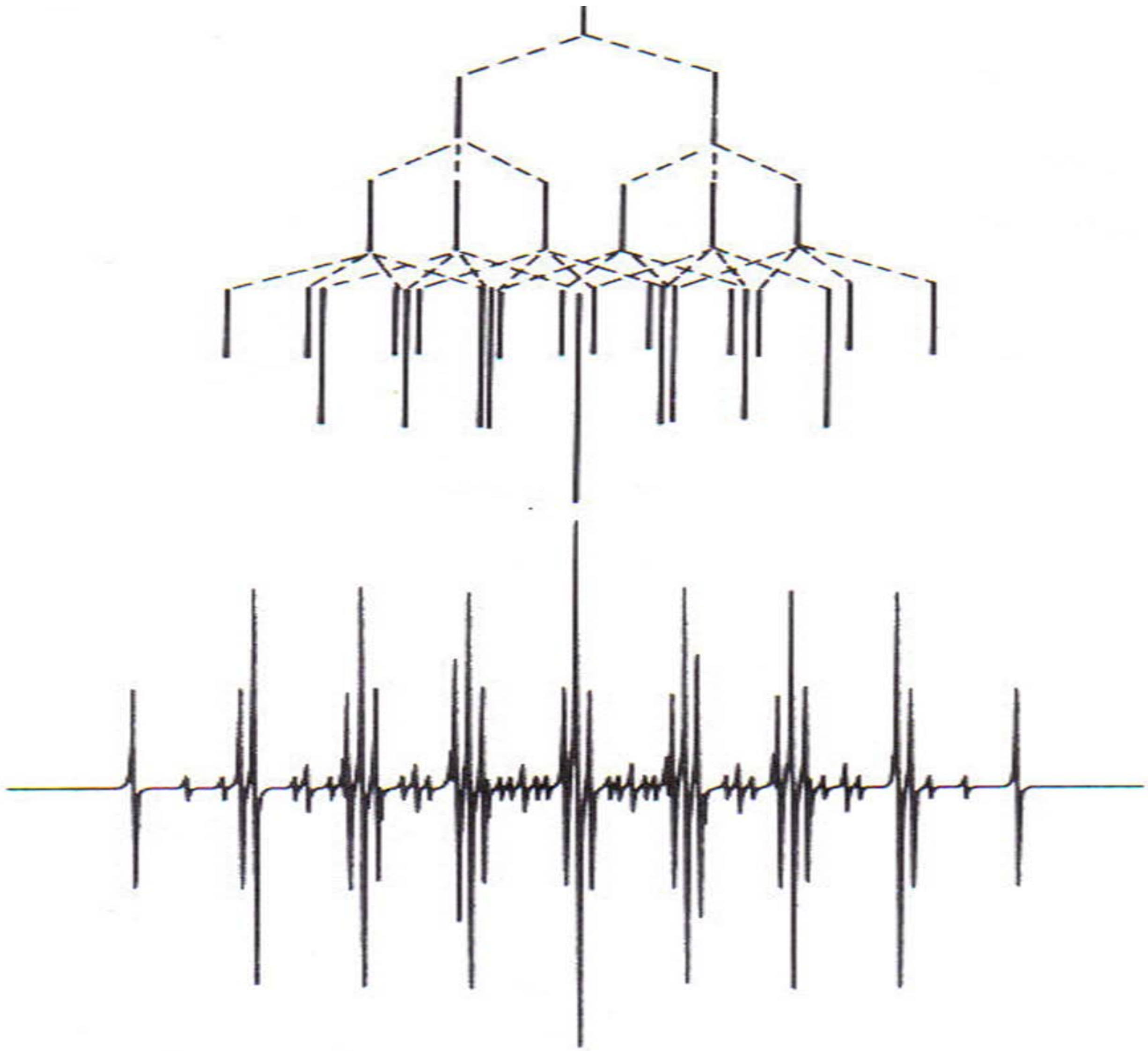
^{16}O, I=0
^{14}N, I=1

L=0
S=3/2
J=3/2

a=32,63 MHz
g_J=0,7759

$\Delta M_J = \pm 1$
$\Delta M_I = 0$

Example: Organic Radical



^{31}P, I=1/2
^{1}H, I=1/2
^{11}B, I=3/2

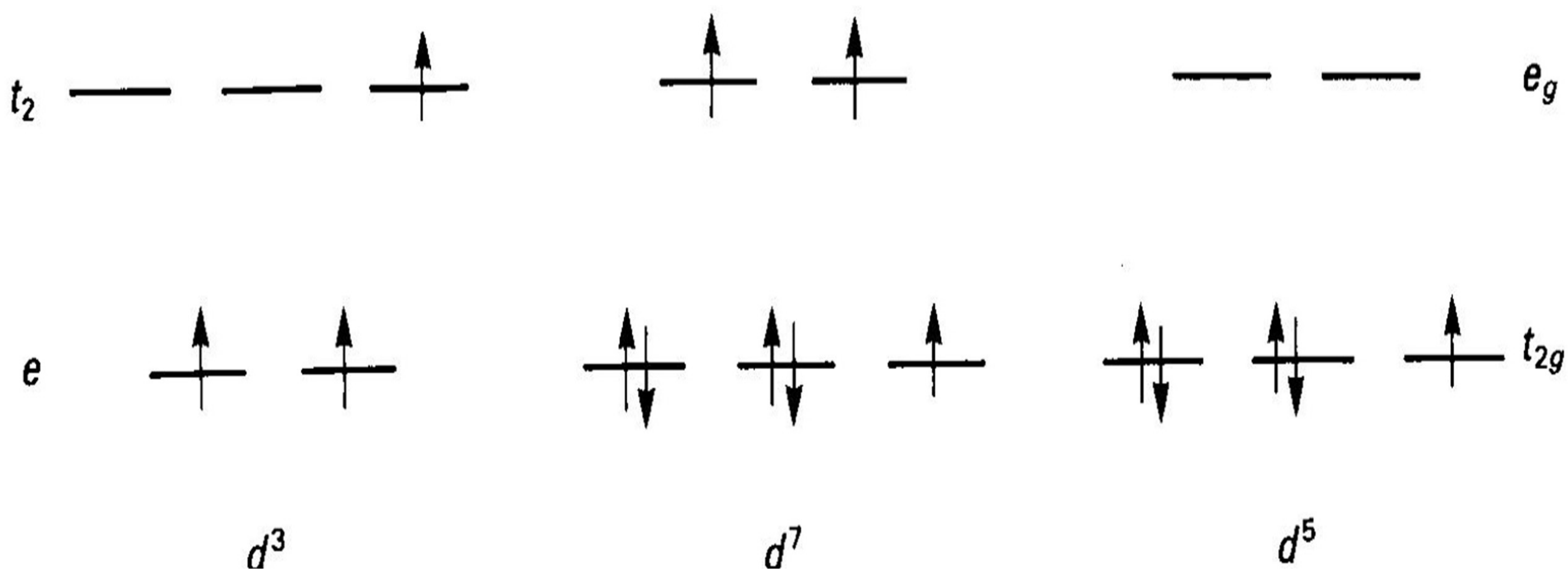
EPR spectrum of $(MeO)_3PBH_2$:
21 lines!!

Spin-Only Approximation

- In molecules with more than 2 atoms, especially in coordination compounds, the ground state is usually non-degenerate (Jahn-Teller Effect)

  → L = 0!! (but excited states can be degenerate)

Examples for Jahn-Teller active electron configurations:



g Anisotropy in Coordination Compounds

- The anisotropy of g values in coordination compounds is due to spin-orbit coupling

  $\rightarrow g_x \neq g_y \neq g_z$
- From perturbation theory, the g values are calculated:

$$g_i = g_e - 2\lambda \sum_{n \neq 0} \frac{\langle \Psi_0 | L_i | \Psi_n \rangle \langle \Psi_n | L_i | \Psi_0 \rangle}{E_n - E_0}$$

L_i: angular momentum operator

i = x, y, z

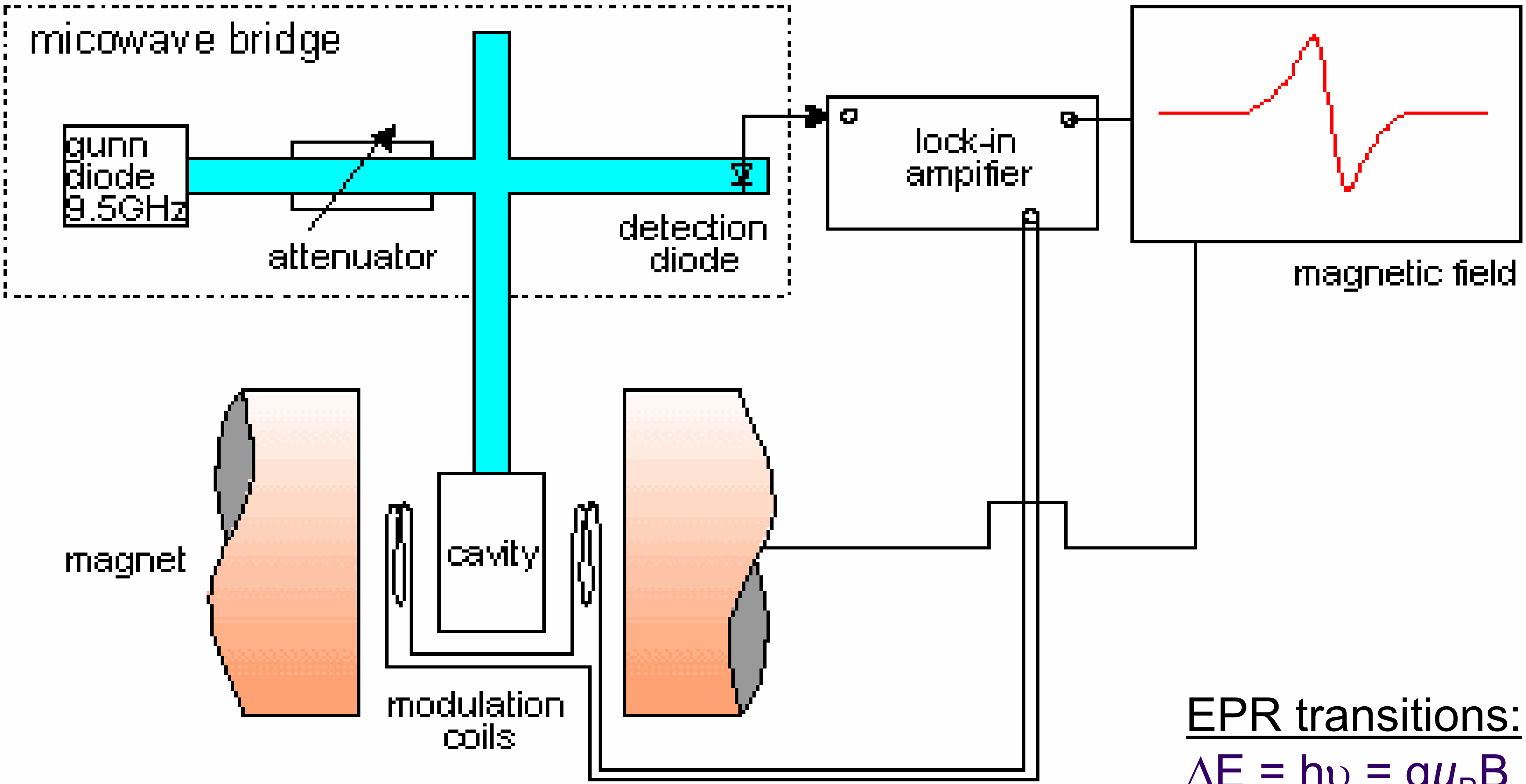
λ: spin-orbit coupling constant

- Example: spin-orbit coupling similar in x and y direction, but different in z:

  $\rightarrow g_x = g_y \; (g_\perp) \neq g_z \; (g_{//})$

The Instrument

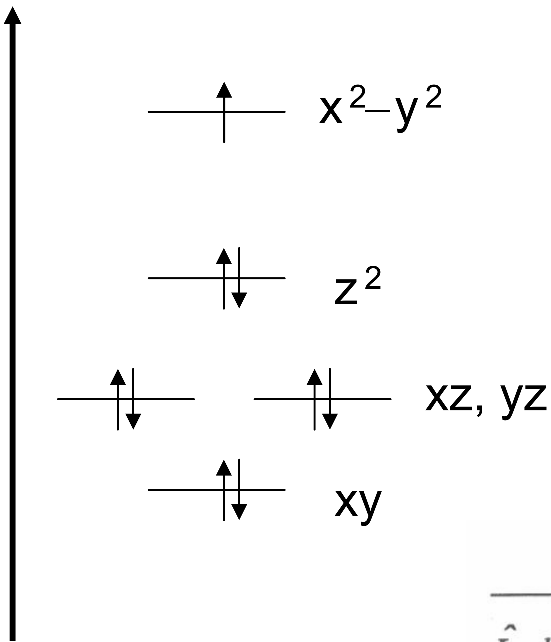
- <u>Design of an EPR Spectrometer</u>



EPR transitions:

$\Delta E = h\upsilon = g\mu_B B$

Example: tetragonal $[CuCl_4]^{2-}$



Ground State: $^2B_{1g}$

$$g_i = g_e - 2\lambda \sum_{n\neq 0} \frac{\langle \Psi_0 | L_i | \Psi_n \rangle \langle \Psi_n | L_i | \Psi_0 \rangle}{E_n - E_0}$$

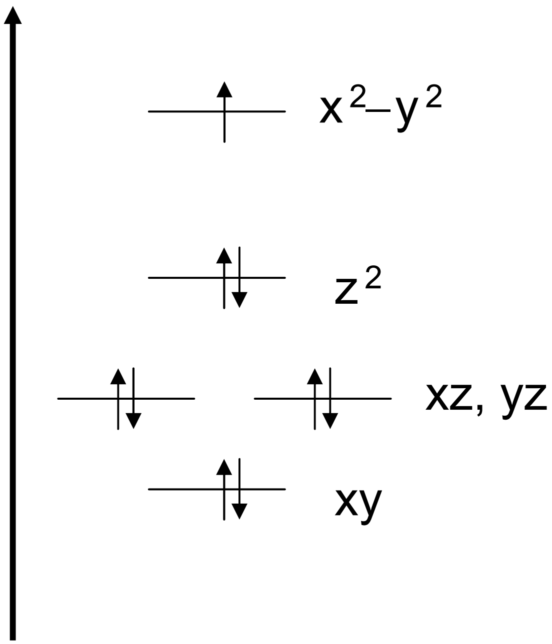
$g_z = ?$ ⟶ L_z

Effect of $\hat{L}_i$ on real d orbitals

$\hat{L}_x d_{xz} = -i\, d_{xy}$	$\hat{L}_y d_{xz} = i\, d_{x^2-y^2} - i\sqrt{3}\, d_{z^2}$	$\hat{L}_z d_{xz} = i\, d_{yz}$
$\hat{L}_x d_{yz} = i\sqrt{3}\, d_{z^2} + i\, d_{x^2-y^2}$	$\hat{L}_y d_{yz} = i\, d_{xy}$	$\hat{L}_z d_{yz} = -i\, d_{xz}$
$\hat{L}_x d_{xy} = i\, d_{xz}$	$\hat{L}_y d_{xy} = -i\, d_{yz}$	$\hat{L}_z d_{xy} = -2i\, d_{x^2-y^2}$
$\hat{L}_x d_{x^2-y^2} = -i\, d_{yz}$	$\hat{L}_y d_{x^2-y^2} = -i\, d_{xz}$	$\hat{L}_z d_{x^2-y^2} = 2i\, d_{xy}$
$\hat{L}_x d_{z^2} = -i\sqrt{3}\, d_{yz}$	$\hat{L}_y d_{z^2} = i\sqrt{3}\, d_{xz}$	$\hat{L}_z d_{z^2} = 0$

➡ Only one contribution!

Example: tetragonal $[CuCl_4]^{2-}$



Ground State: $^2B_{1g}$

$$g_i = g_e - 2\lambda \sum_{n \neq 0} \frac{\langle \Psi_0 | L_i | \Psi_n \rangle \langle \Psi_n | L_i | \Psi_0 \rangle}{E_n - E_0}$$

$g_z = g_{//} = 2.023 - 8\lambda \, / \, E(x^2\text{-}y^2) - E(xy)$

$g_{x,} = g_{\perp} = 2.023 - 2\lambda \, / \, E(x^2\text{-}y^2) - E(yz)$

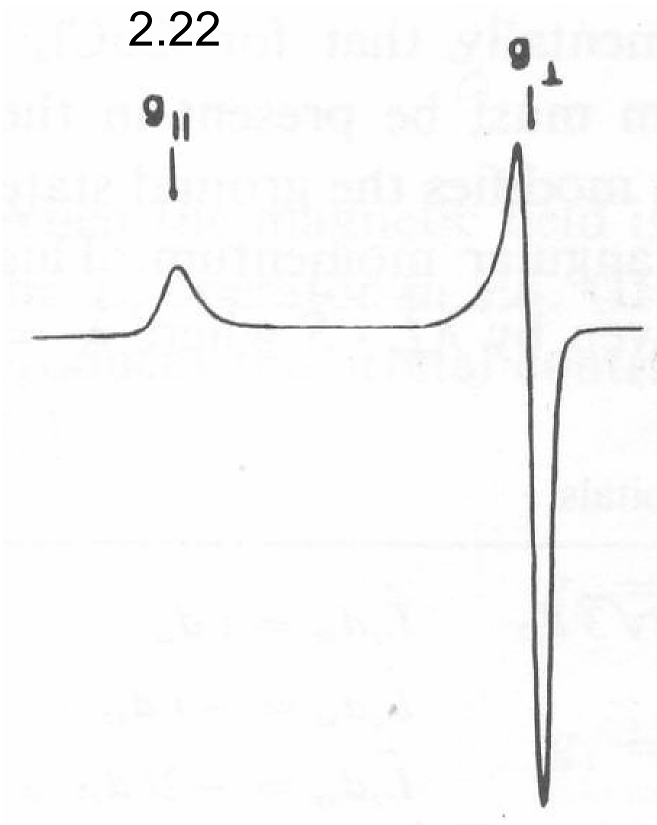
$g_{y,} = g_{\perp} = 2.023 - 2\lambda \, / \, E(x^2\text{-}y^2) - E(xz)$

→ Two transitions!

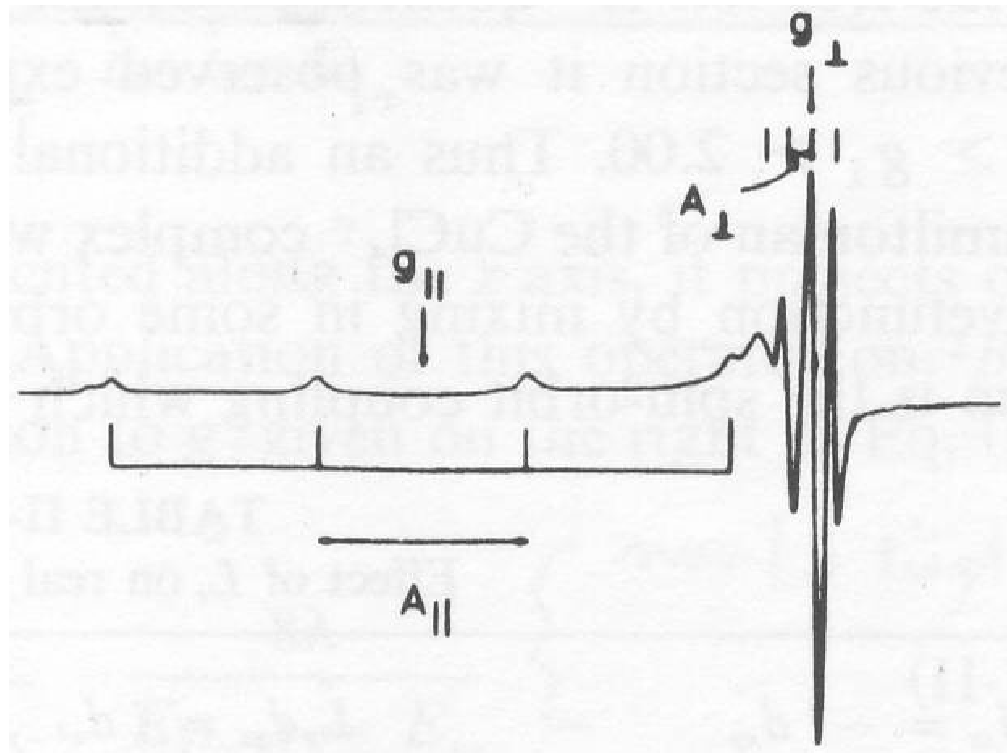
Example: tetragonal $[CuCl_4]^{2-}$

2.04

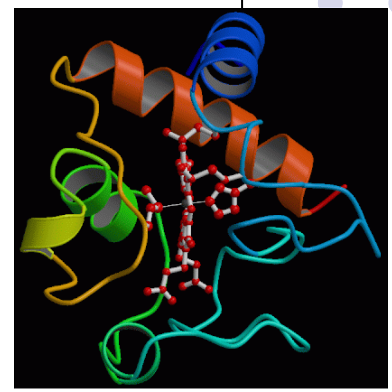
2.22



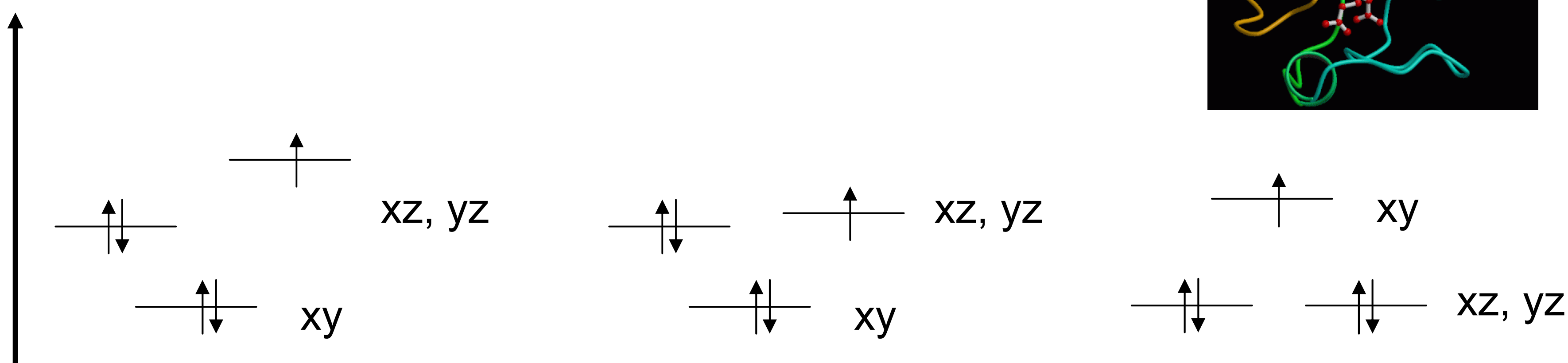
Cu: I = 3/2



Example: low-spin ferric heme



→ Relevant for Cytochrome C



Rhombic
g-values:
2.8, 2.3, 1.6

Parallel IM orientation

Large g_{max}
g-values:
3.4 (1.8, 0.9)

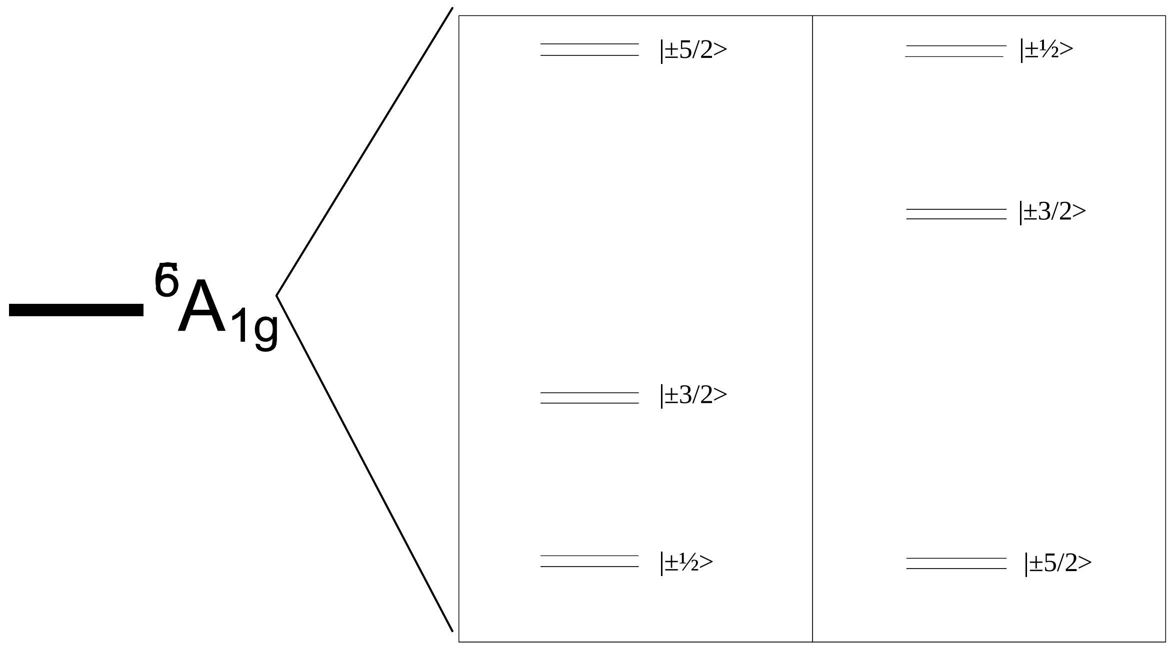
Perpendicular IM orientation

Axial
g-values:
2.2, 1.94

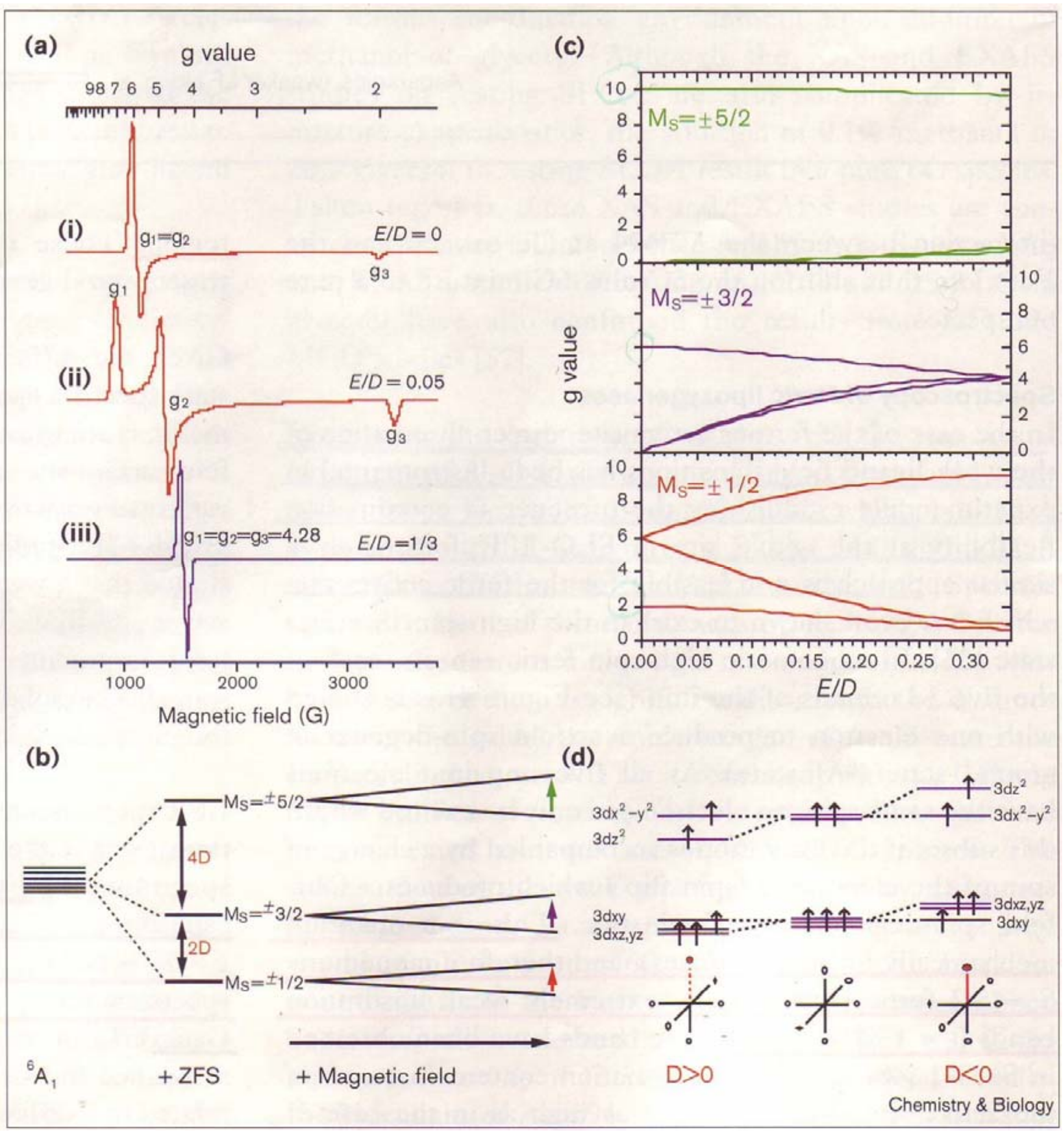
?

S > ½: Zero-field splitting

- Example: high-spin Fe(III)



S > ½: Zero-field splitting



Solomon et al., *Chemistry & Biology*, **1997**, *4*, 795-808