Modern Methods in Heterogeneous Catalysis Research

Electron Paramagnetic Resonance

*November 21st, 2014*

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Outline

1. Basic Principles

2. Electron-Nucleus Interactions (Hyperfine Coupling)

3. Anisotropy

4. Electron-Electron Interactions (Fine Coupling)

5. Linewidths

6. Literature

1. Basic principles

- ➤ **Electron paramagnetic** resonance (EPR) = **Electron spin** resonance (ESR) spectroscopy
- ➤ Same underlying physical principles as in **nuclear magnetic** resonance (NMR)

One unpaired (free) electron:
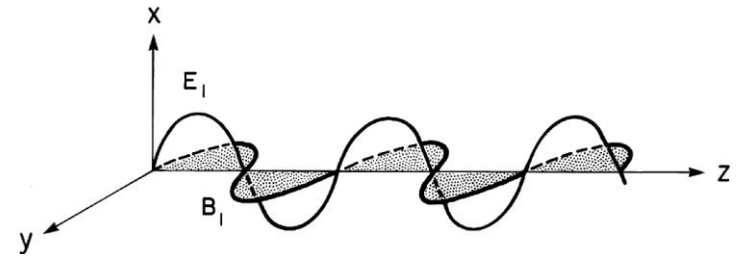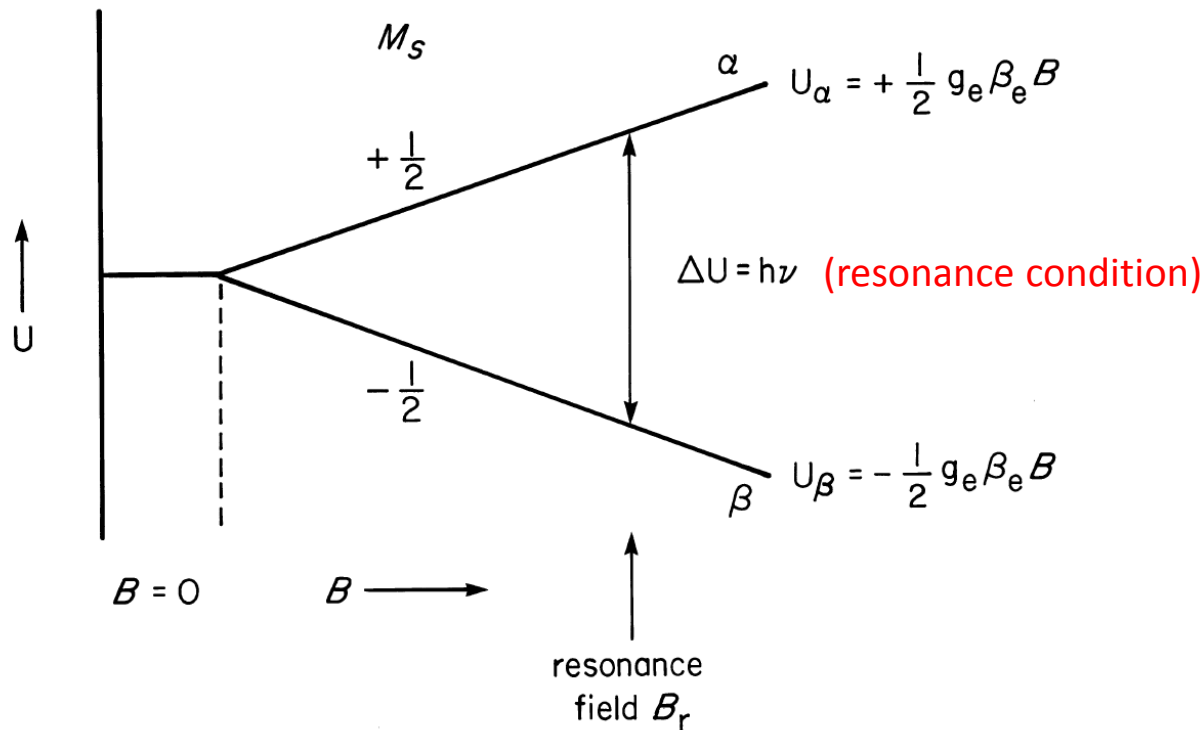
Zeeman effect:

Selection rule: $\Delta M_s = \pm 1$

$$\Delta U = g\beta_e B$$
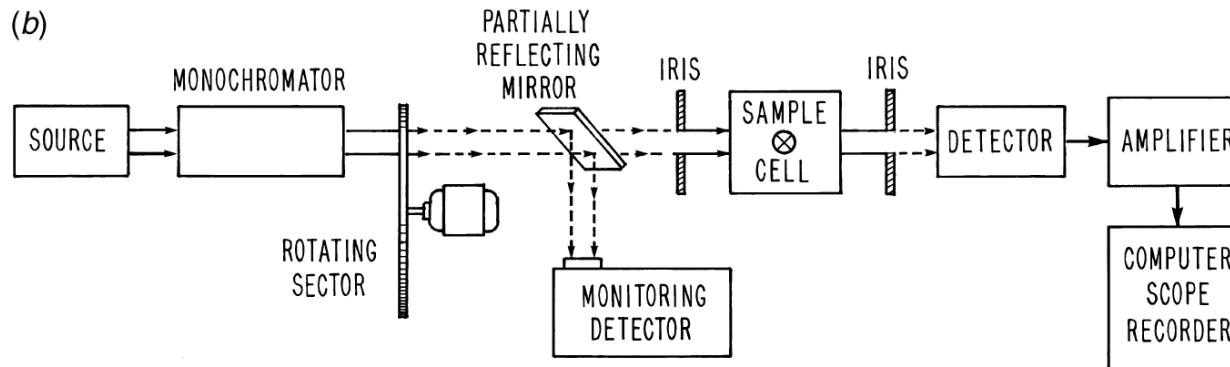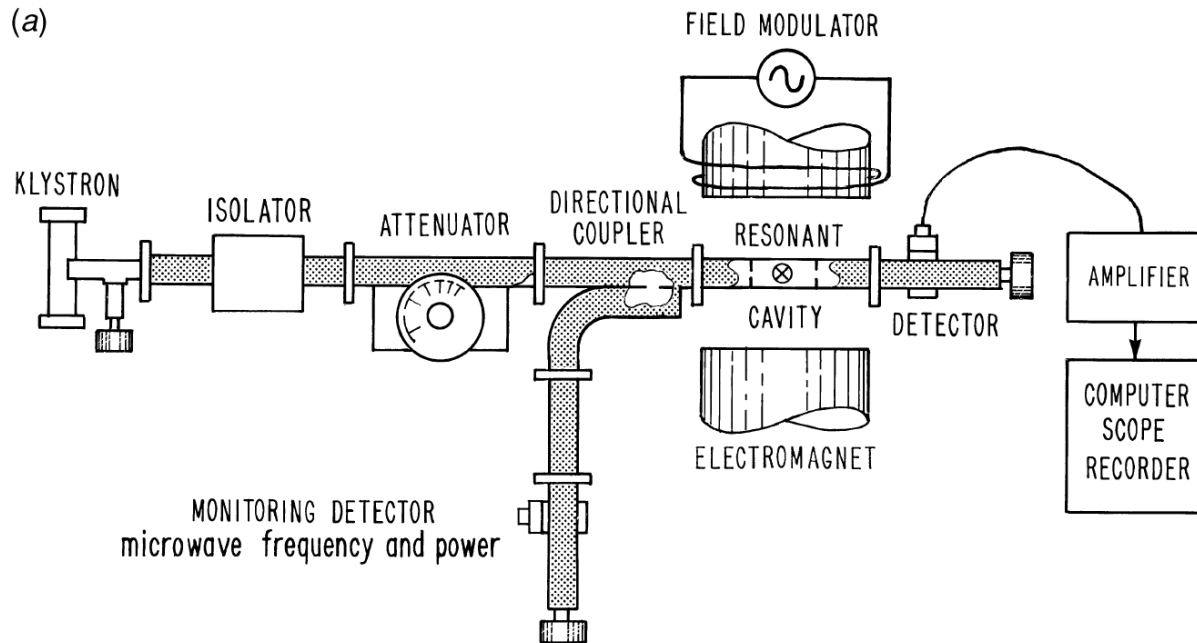$$g = \frac{h\nu}{\beta_e B}$$

$g:$ g factor
for free electron: $g_e = 2.0023$
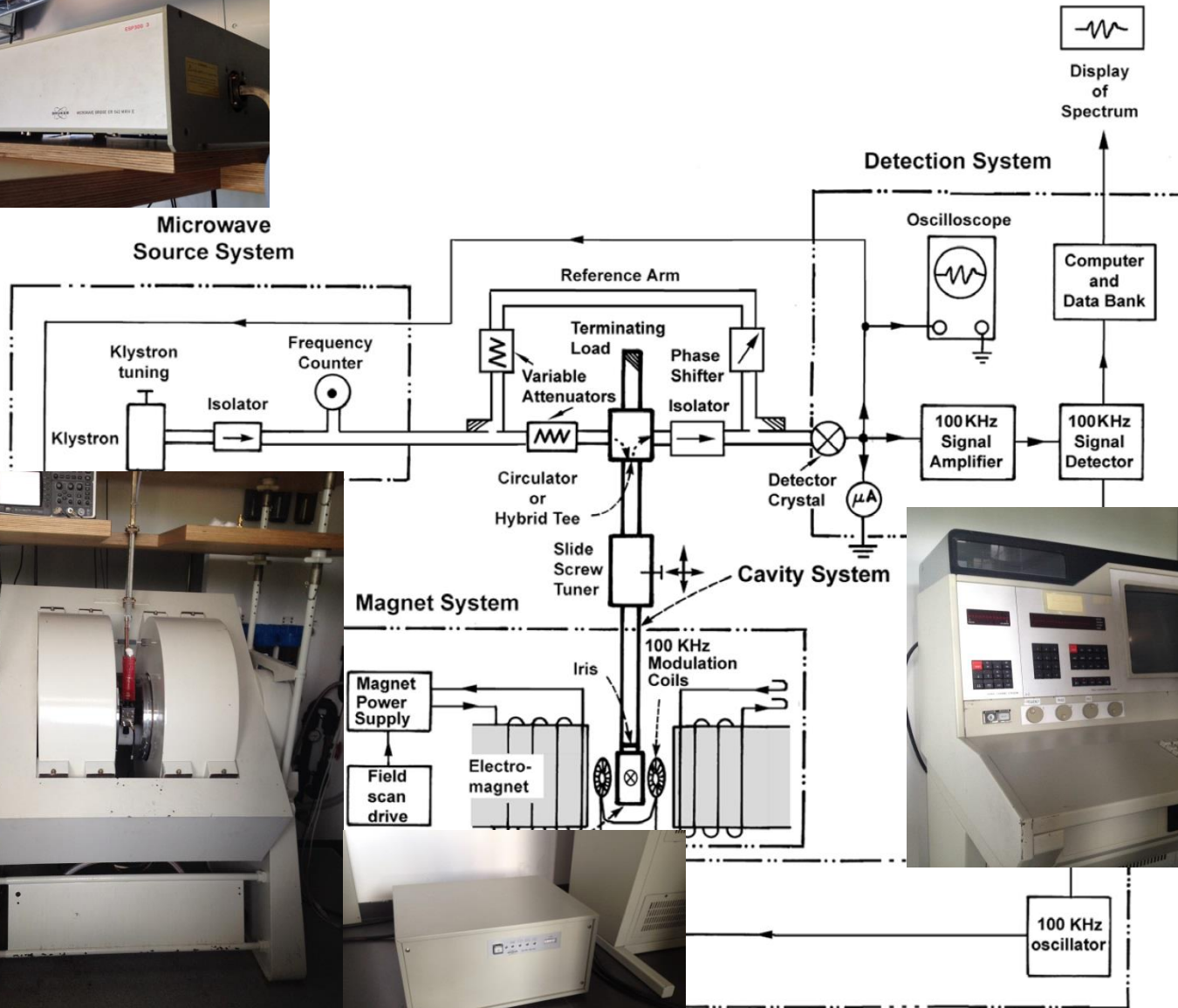β_e: Bohr magneton

$\Delta U = h\nu$ (resonance condition)

$U_\alpha = +\frac{1}{2} g_e \beta_e B$

$U_\beta = -\frac{1}{2} g_e \beta_e B$

1. Basic principles

➢ **A continuous wave (cw) EPR spectrometer:**

1. Basic principles

1. Basic principles

➢ **The EPR resonator (cavity)**

Rectangular TE$_{102}$ cavity

(a) Sample Stack, Iris Tuner, Iris
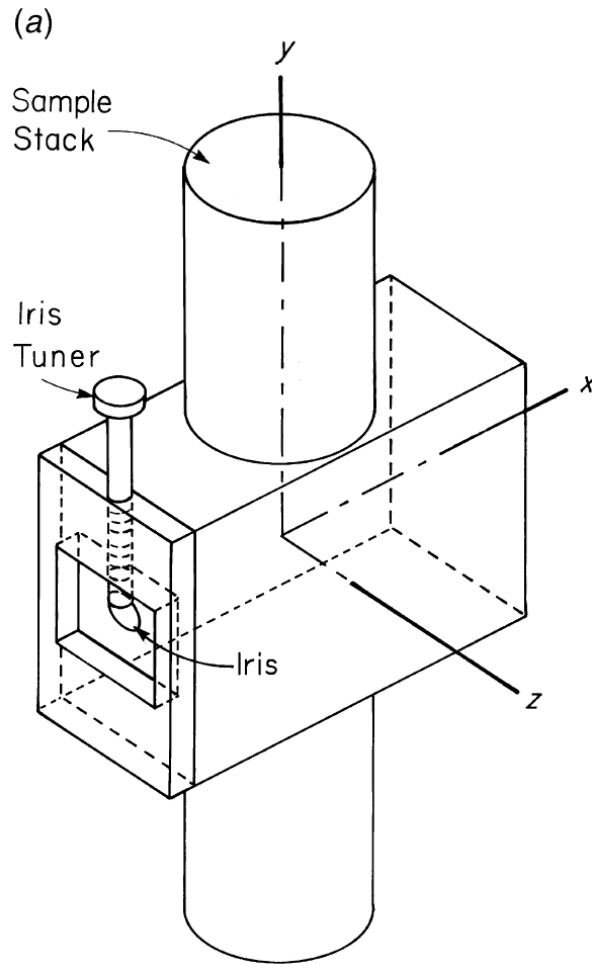
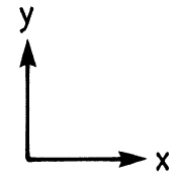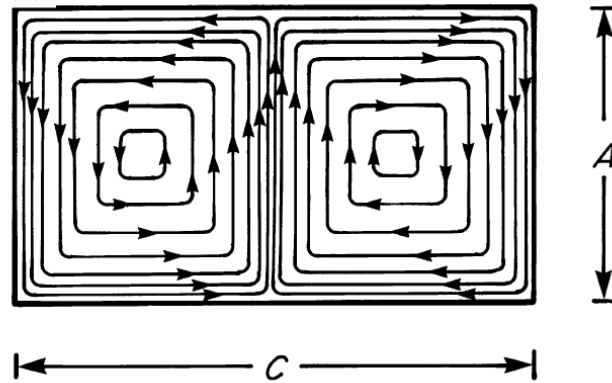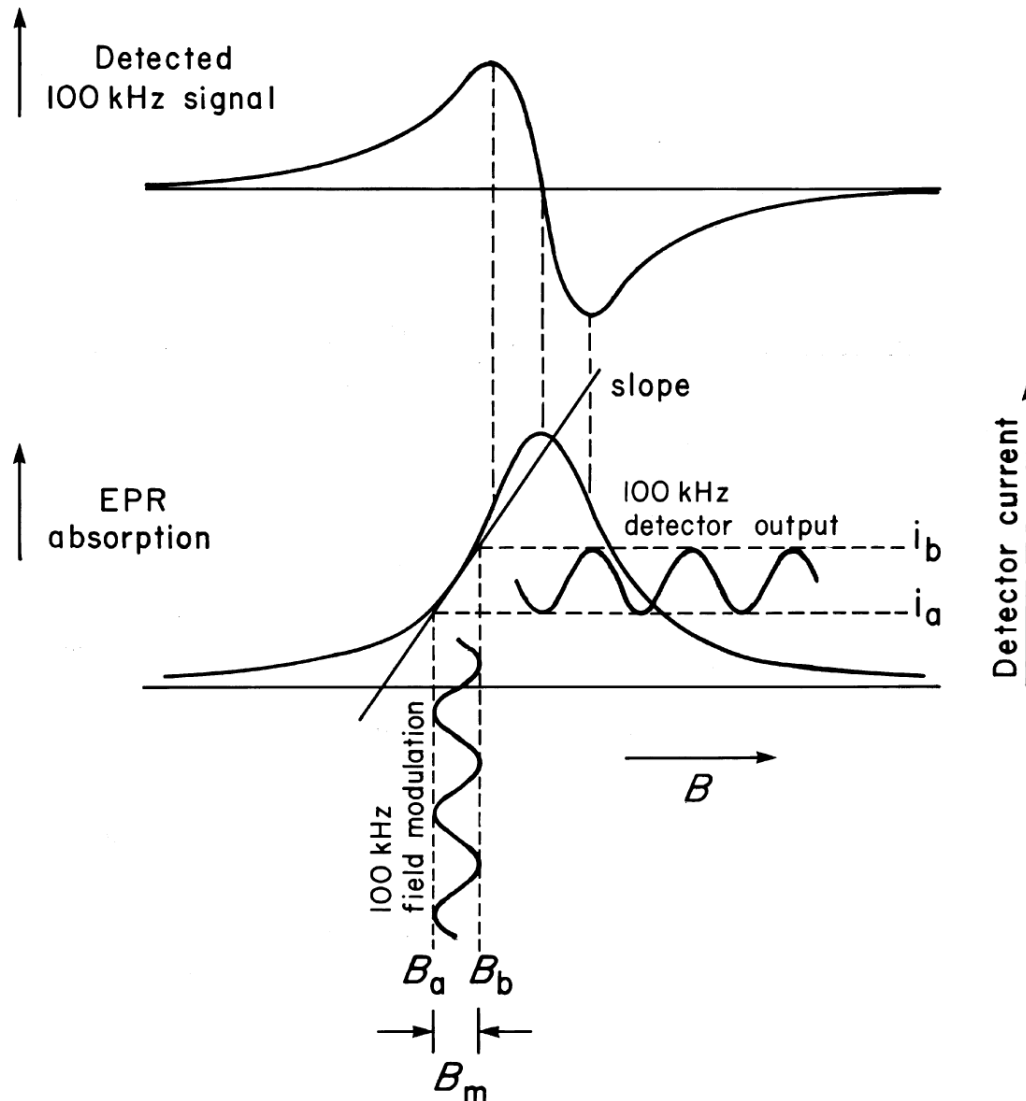(b) Electric field:
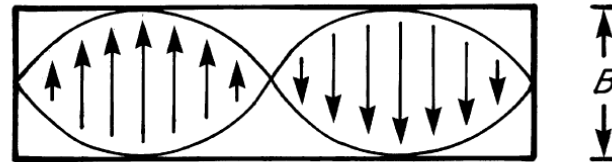
(c) Magnetic field:

1. Basic principles

➢ **Typical frequency and magnetic induction ranges in EPR**

Microwave band	Microwave frequency (GHz)	B_0 (for g = 2) gauss
L	1	390
S	3	1070
X	9	3380
K	24	8560
Q	35	12,480
W	94	33,600

1. Basic principles

> **(Phase) Sensitive detection by field modulation**

1. Basic principles

➢ **Samples that can be principally measured by EPR:**

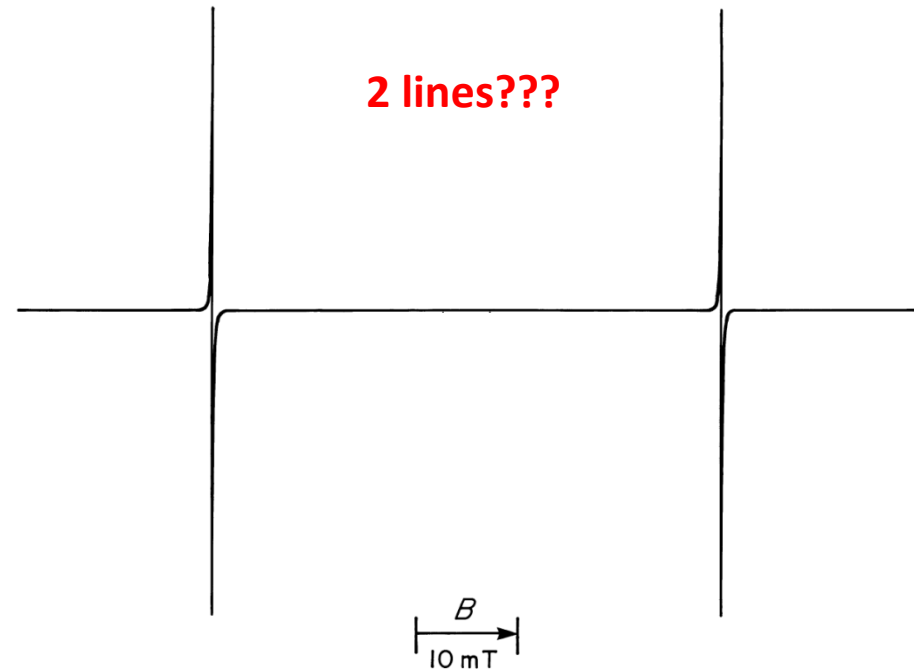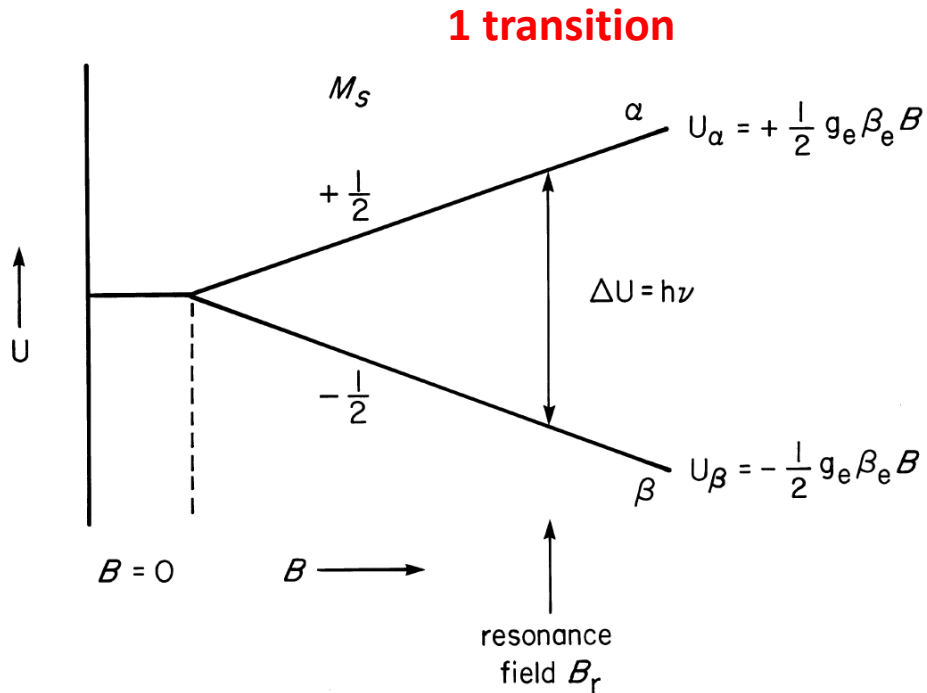✓ Free radicals in solids, liquids or in the gas phase

✓ Transition metal ions with unpaired electron(s)

✓ Point defects in solids

✓ Systems with more than one unpaired electrons, e.g. triplet systems, biradicals, multiradicals

✓ Systems that temporarily generate states with unpaired electrons by excitation with, e.g., light

✓ Systems with conducting electrons

2. Electron-Nucleus Interactions

2. Electron-Nucleus Interactions

Example: Hydrogen atom

➢ One unpaired electron → electron spin S = ½

1 transition

M_S

α $U_\alpha = +\frac{1}{2} g_e \beta_e B$

$+\frac{1}{2}$

$\Delta U = h\nu$

$-\frac{1}{2}$

β $U_\beta = -\frac{1}{2} g_e \beta_e B$

$B = 0$ $B \longrightarrow$

resonance field B_r

2 lines???

B
$\overline{\text{10 mT}}$

2. Electron-Nucleus Interactions

Example: Hydrogen atom

➢ One unpaired electron → electron spin S = ½
➢ H atom has a **nuclear spin**: I = ½, M_I = ±½

Selection rule: ΔM_S = ±1; ΔM_I = 0

ΔM_I forbidden:

$+\frac{1}{2} \rightarrow -\frac{1}{2}$ $-\frac{1}{2} \rightarrow +\frac{1}{2}$

ΔM_I allowed: $+\frac{1}{2} \rightarrow +\frac{1}{2}$ $-\frac{1}{2} \rightarrow -\frac{1}{2}$

$$h\nu = g\beta_e B \pm 1/2 A_0$$
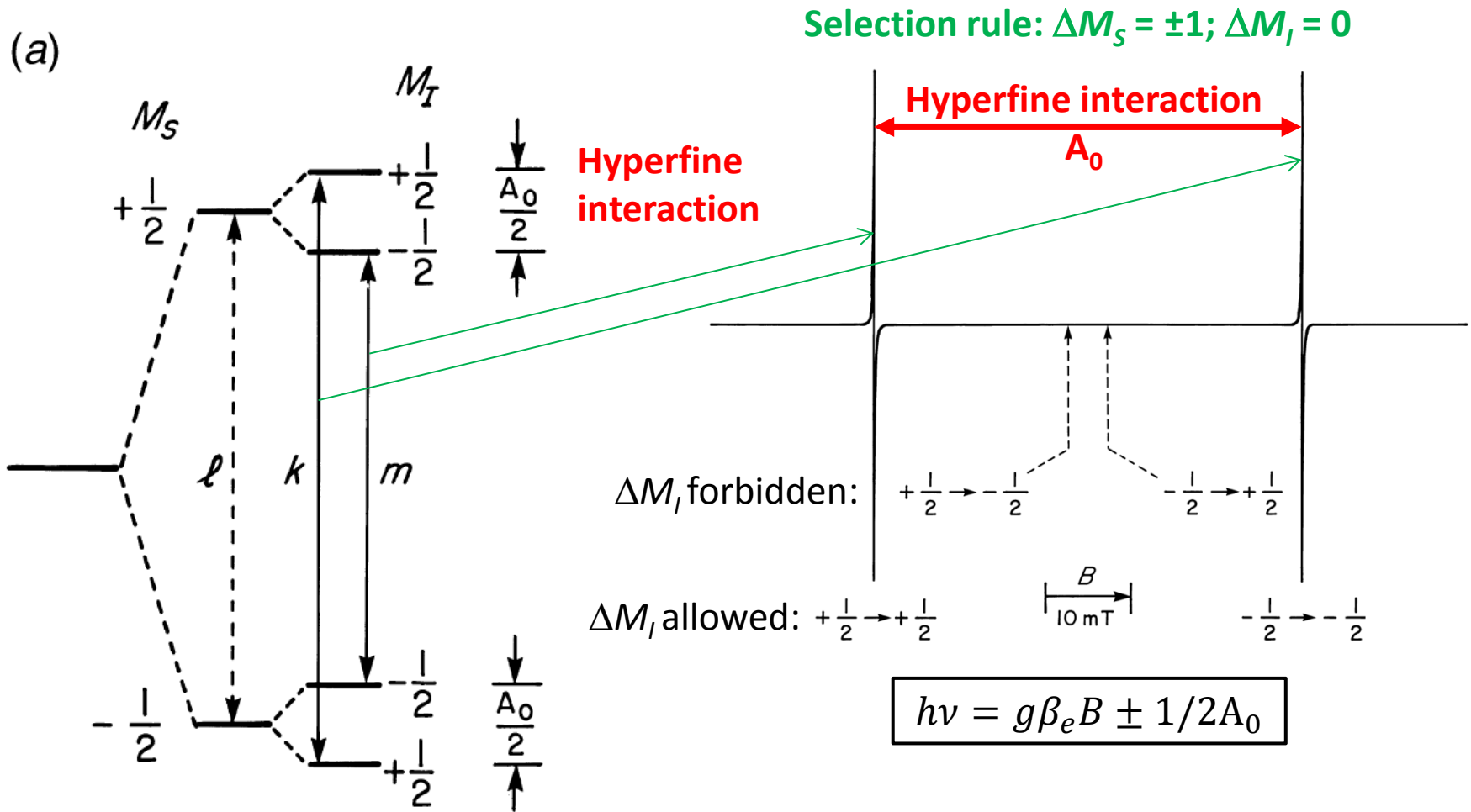
2. Electron-Nucleus Interactions

Example: Deuterium atom
➢ One unpaired electron → electron spin S = ½
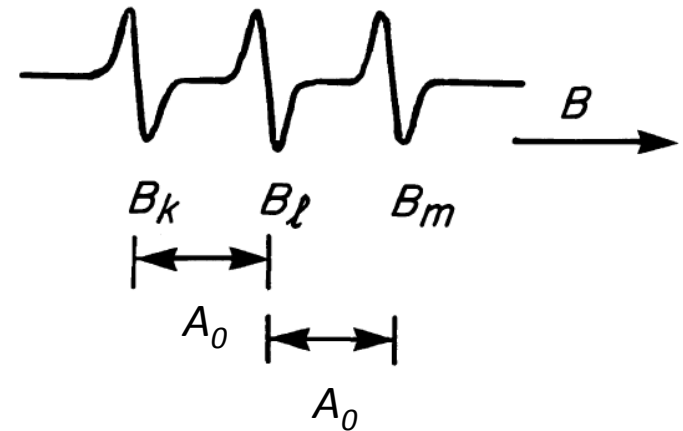➢ **Nuclear spin**: I = 1, M_I = -1, 0, +1
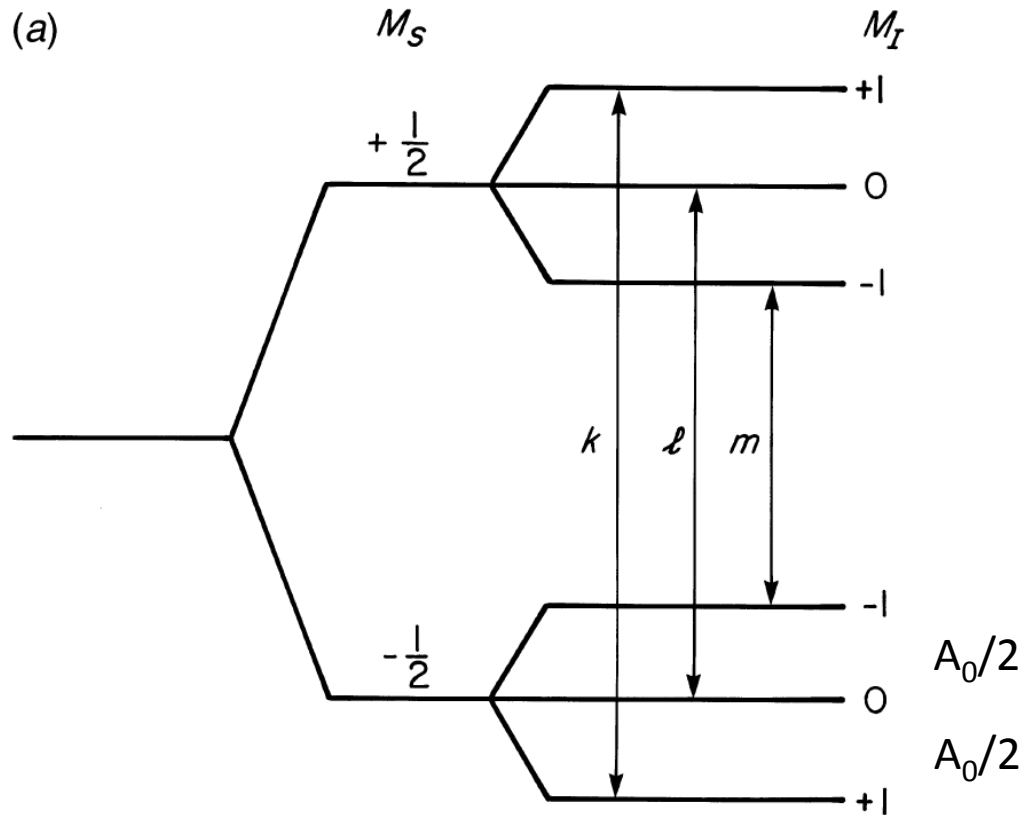
Selection rule: ΔM_S = ±1; ΔM_I = 0

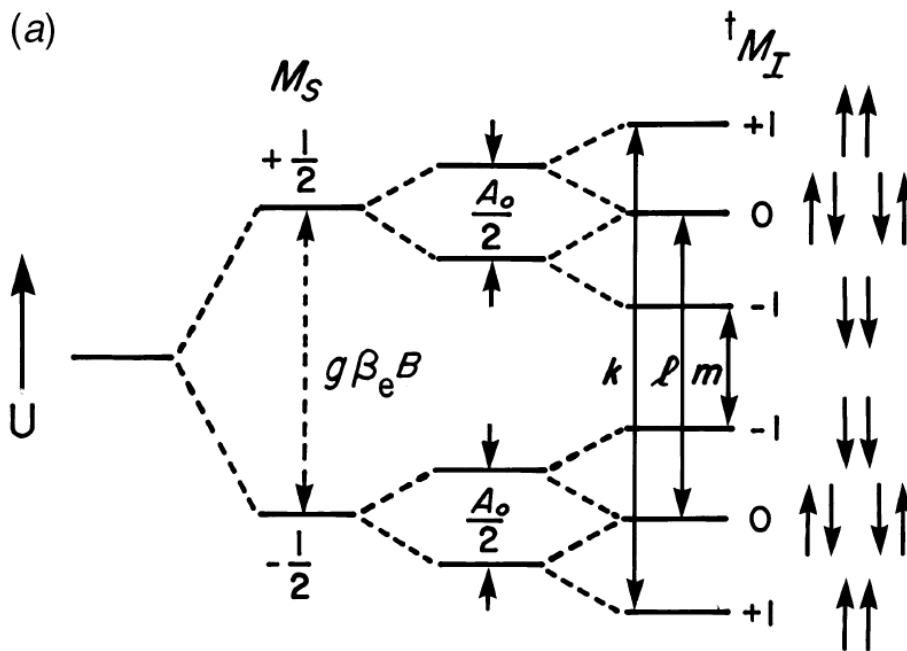**In general for single nucleus with spin I interacting with one electron: $2I+1$ lines of equal intensity, separated by hyperfine splitting A_0**

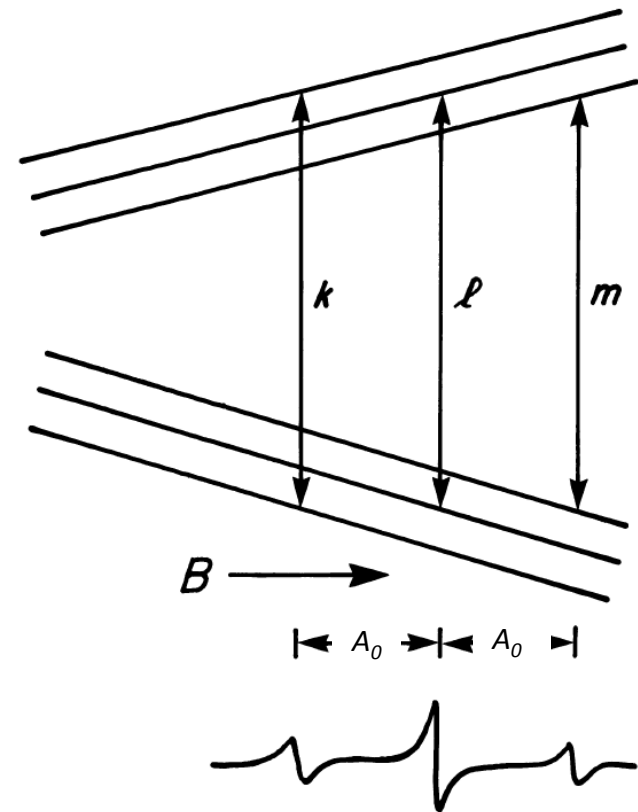# 2. Electron-Nucleus Interactions

Interaction of multiple nuclei with one electron

➢ One unpaired electron → electron spin S = ½
➢ **Two equivalent nuclei with I = ½, M_I = -½, +½**

Selection rule: ΔM_S = ±1; ΔM_I = 0

2. Electron-Nucleus Interactions

Interaction of multiple nuclei with one electron
- ➢ One unpaired electron → electron spin $S = \frac{1}{2}$
- ➢ n equivalent nuclei with

(a) $I_i = 1/2 \quad (i = 1, 2, \dots, n)$

No. of nuclei n	No. of lines $2I+1$	First-order line positions/a_0 M_I	Binomial intensity ratios
0	1	0	1
1	2	$\overline{1/2}$ $1/2$	1 1
2	3	$\overline{1}$ 0 1	1 2 1
3	4	$\overline{3/2}$ $\overline{1/2}$ $1/2$ $3/2$	1 3 3 1
4	5	$\overline{2}$ $\overline{1}$ 0 1 2	1 4 6 4 1
5	6	$\overline{5/2}$ $\overline{3/2}$ $\overline{1/2}$ $1/2$ $3/2$ $5/2$	1 5 10 10 5 1
6	7	$\overline{3}$ $\overline{2}$ $\overline{1}$ 0 1 2 3	1 6 15 20 15 6 1
⋮	⋮	⋮	⋮

(b) $I_i = 1 \quad (i = 1, 2, \dots, n)$

| No. of nuclei n	No. of lines $2I+1$	First-order line positions/a_0 M_I	Multinomial intensity ratios
0	1	0	1
1	3	$\overline{1}$ 0 1	1 1 1
2	5	$\overline{2}$ $\overline{1}$ 0 1 2	1 2 3 2 1
3	7	$\overline{3}$ $\overline{2}$ $\overline{1}$ 0 1 2 3	1 3 6 7 6 3 1
4	9	$\overline{4}$ $\overline{3}$ $\overline{2}$ $\overline{1}$ 0 1 2 3 4	1 4 10 16 19 16 10 4 1
⋮	⋮	⋮	⋮

In general for n equivalent nuclei with spin I interacting with one electron: $2nI+1$ lines with multinomial intensity ratios ("Pascal`s triangle"), separated by hyperfine splitting A_0
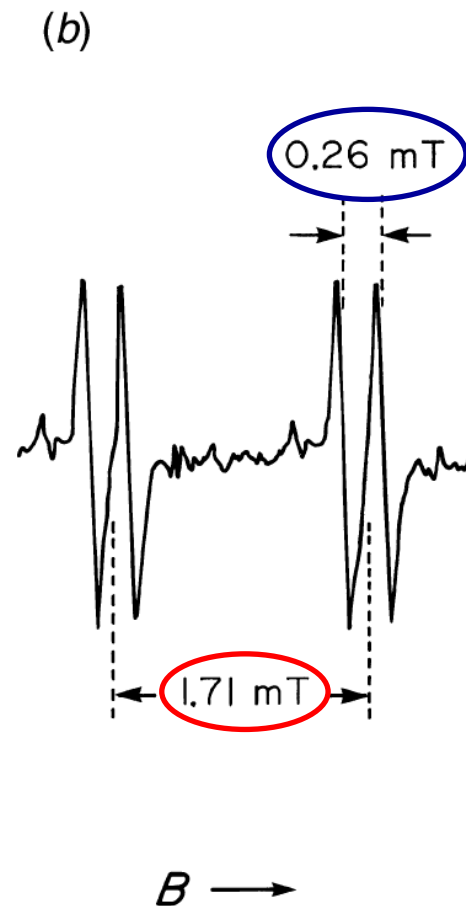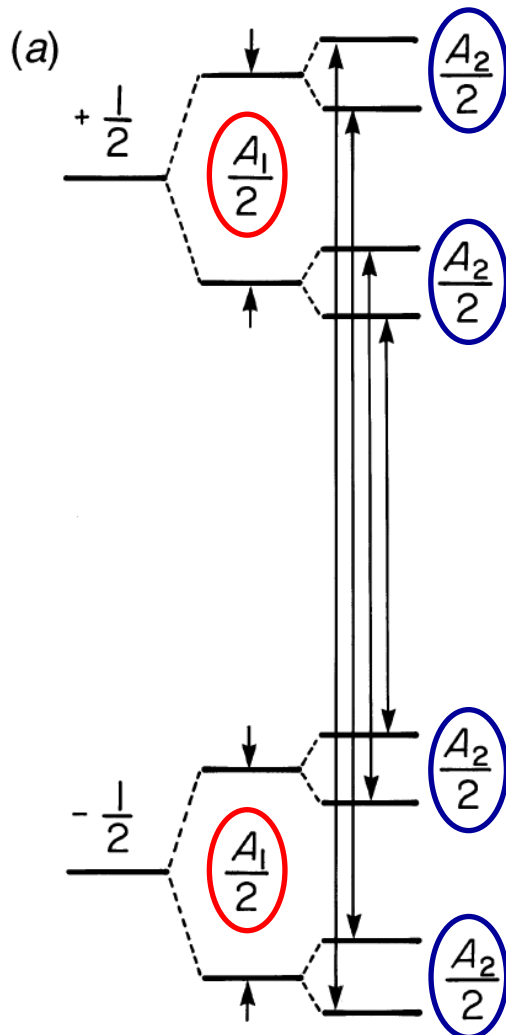
2. Electron-Nucleus Interactions

Interaction of multiple nuclei with one electron
➢ One unpaired electron → electron spin S = ½
➢ n equivalent nuclei with I = ½

2nI+1
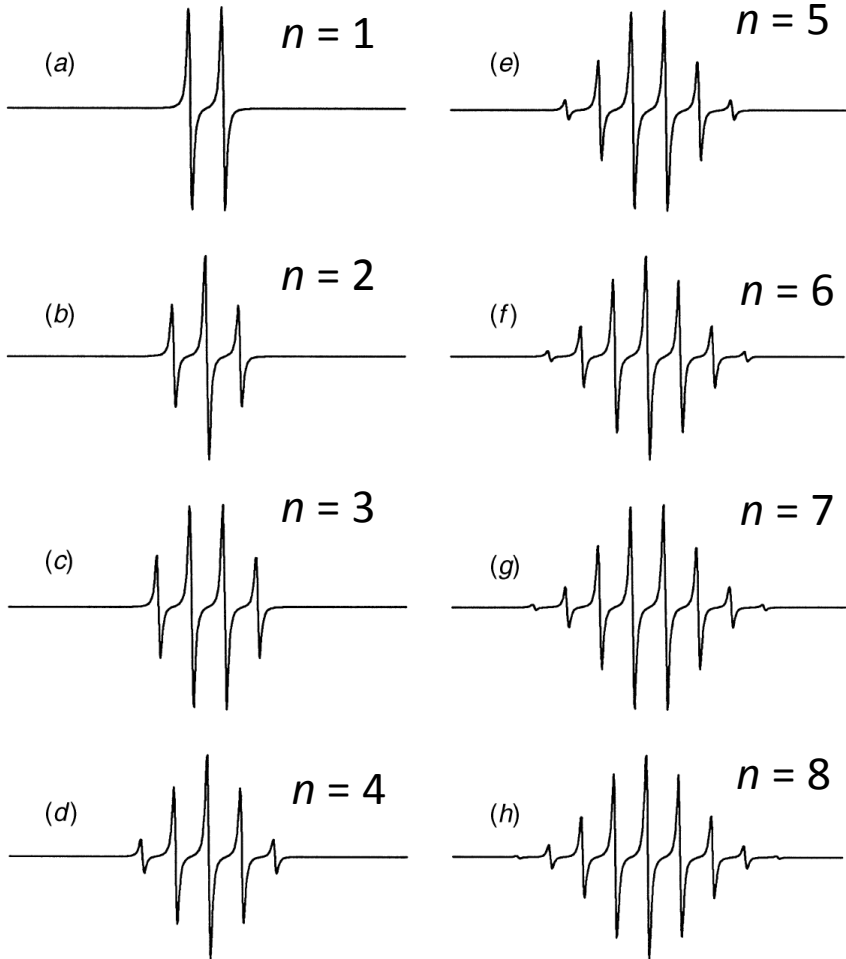
Interaction of multiple nuclei with one electron

➢ One unpaired electron → electron spin S = ½

➢ **Two *in*equivalent nuclei with I = ½**

(a)

$+\dfrac{1}{2}$

$\dfrac{A_2}{2}$

$\dfrac{A_1}{2}$

$\dfrac{A_2}{2}$

(b)

0.26 mT

HO-Ċ-COOH

H

$-\dfrac{1}{2}$

$\dfrac{A_2}{2}$
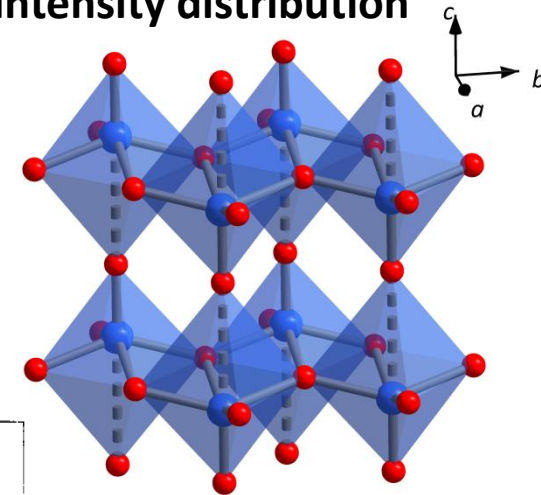
$\dfrac{A_1}{2}$

$\dfrac{A_2}{2}$

1.71 mT

$B \longrightarrow$
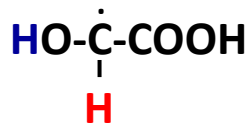
2. Electron-Nucleus Interactions

EPR spectrum of V_2O_5 single crystal

➢ One unpaired electron → electron spin S = ½ (V^{4+} defect)

➢ n (?) equivalent nuclei with I = 7/2

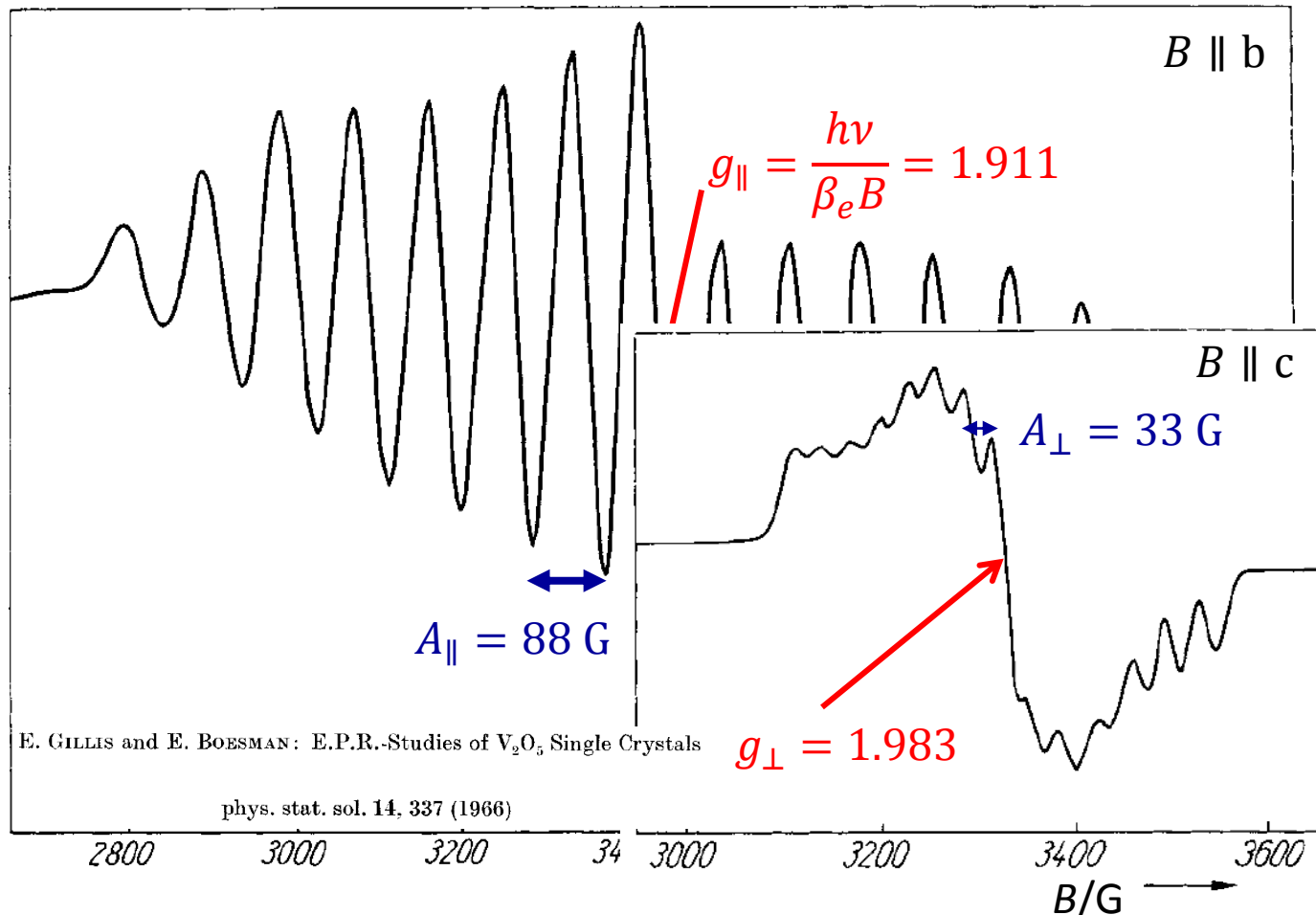**Number of lines = $2nI+1$ = 2x2x7/2+1 = 15 equally spaced lines with intensity distribution**

1 : 2 : 3 : 4 : 5 : 6 : 7 : 8 : 7 : 6 : 5 : 4 : 3 : 2 : 1

$B \parallel$ b

$$g_\parallel = \frac{h\nu}{\beta_e B} = 1.911$$

$B \parallel$ c

$A_\perp = 33$ G

$A_\parallel = 88$ G

$g_\perp = 1.983$

E. GILLIS and E. BOESMAN: E.P.R.-Studies of V_2O_5 Single Crystals

phys. stat. sol. **14**, 337 (1966)

Orthorhombic space group:
a=3.564(2) Å b=11.519(6) Å
c=4.373(2) Å

Conclusion: electron localized at two vanadium atoms

2800   3000   3200   34 3000   3200   3400   3600

B/G

3. Anisotropy

3. Anisotropy

Electron in environment with:

➤ **Cubic symmetry (cubal, octahedral, tetrahedral coordination)**

➤ **(Uni)Axial Symmetry**

➤ **Orthorhombic Symmetry**

Spin Hamiltonian:

$$\hat{\mathcal{H}} = \beta_e \left(g_x B_x \hat{S}_x + g_y B_y \hat{S}_y + g_z B_z \hat{S}_z \right) = \beta_e [B_x \quad B_y \quad B_z] \cdot \begin{bmatrix} g_x & 0 & 0 \\ 0 & g_y & 0 \\ 0 & 0 & g_z \end{bmatrix} \cdot \begin{bmatrix} \hat{S}_x \\ \hat{S}_y \\ \hat{S}_z \end{bmatrix} = \beta_e \mathbf{B}^{\mathrm{T}} \cdot g \cdot \hat{\mathbf{S}}$$
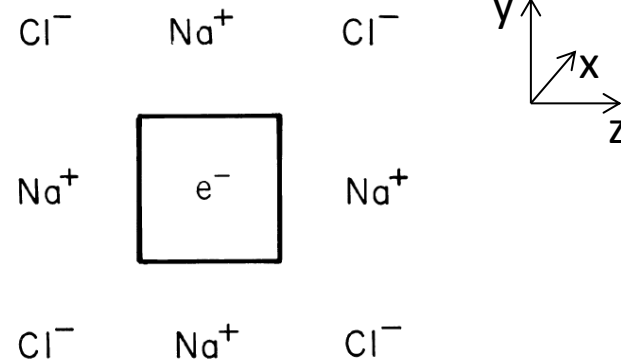
Row vector   *square matrix*   *column vector*

➤ **Cubic Symmetry:**

Isotropic g factor (independent on magnetic field direction): $g_x = g_y = g_z$

→ *g* is a scalar constant

$$\hat{\mathcal{H}} = \beta_e g (B_x \hat{S}_x + B_y \hat{S}_y + B_z \hat{S}_z)$$

F center in NaCl:

Cl^- Na^+ Cl^-

Na^+ e^- Na^+
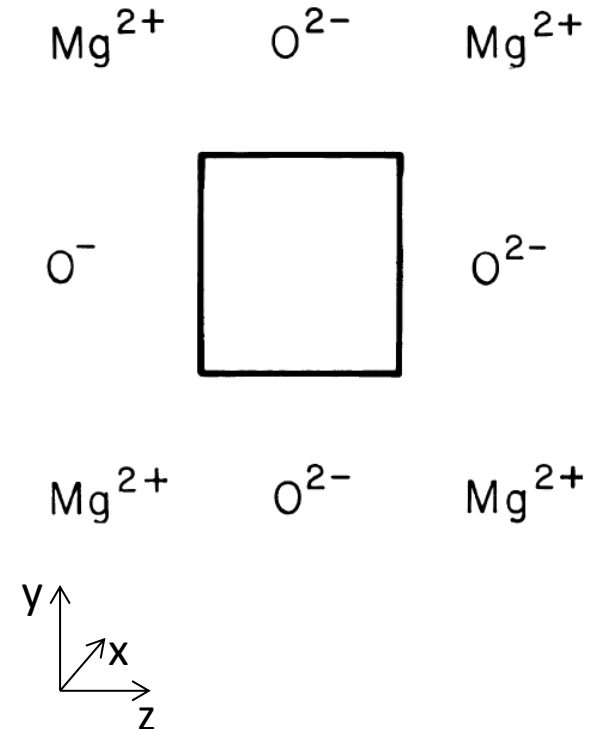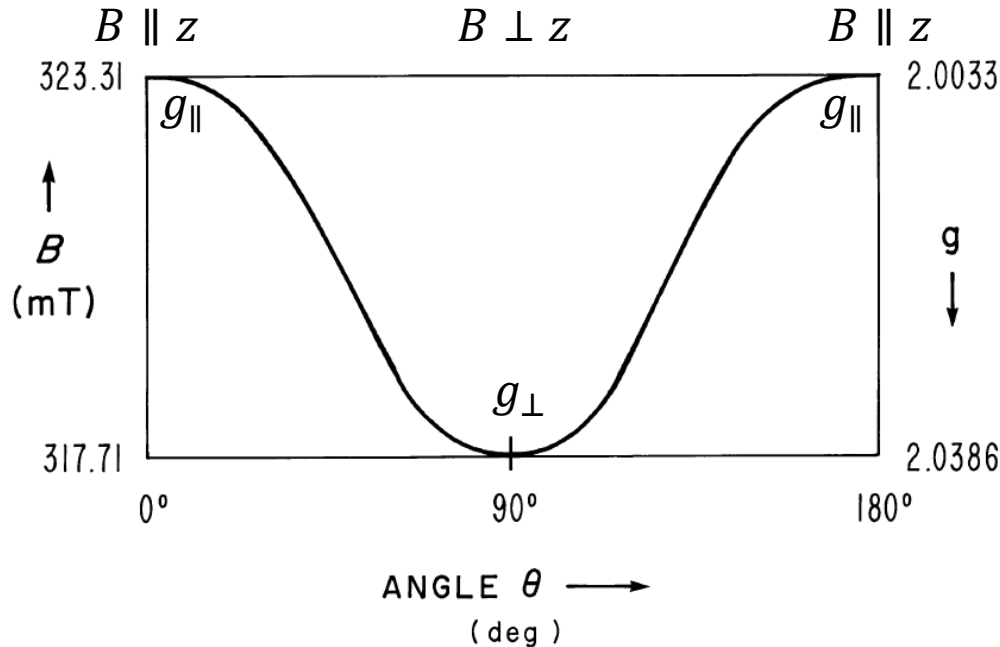
Cl^- Na^+ Cl^-

3. Anisotropy

➤ (Uni)Axial Symmetry

Anisotropic g factor (dependent on
magnetic field direction): $g_x = g_y = g_\perp \neq g_z = g_\parallel$

Spin Hamiltonian: $\hat{\mathcal{H}} = \beta_e(g_x B_x \hat{S}_x + g_y B_y \hat{S}_y + g_z B_z \hat{S}_z)$
$$= \beta_e[g_\perp(B_x \hat{S}_x + B_y \hat{S}_y) + g_\parallel B_z \hat{S}_z]$$
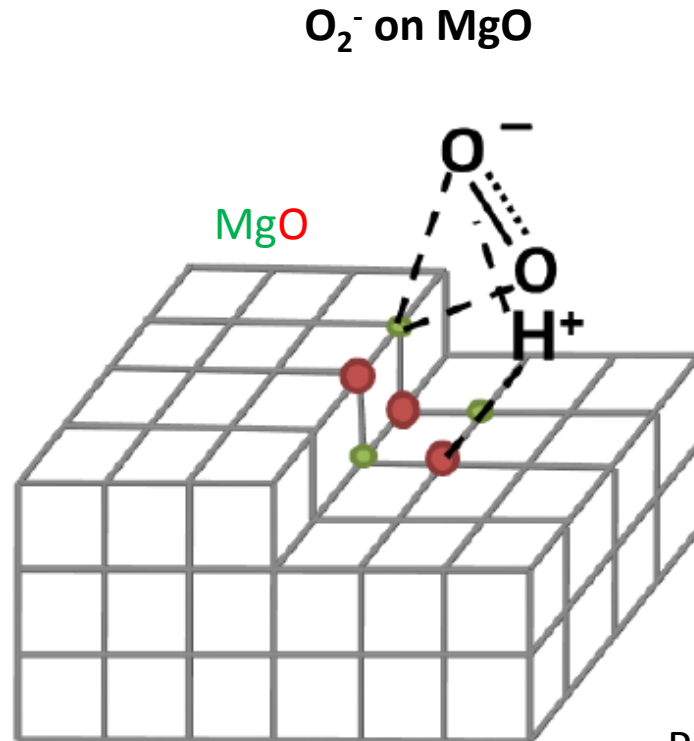
V^- center in MgO

Mg^{2+} O^{2-} Mg^{2+}

O^- O^{2-}

Mg^{2+} O^{2-} Mg^{2+}

$B \parallel z$ $B \perp z$ $B \parallel z$

$g_\parallel$ $g_\parallel$

$g_\perp$

B (mT)

g

323.31   2.0033

317.71   2.0386

0°   90°   180°

ANGLE θ ⟶
(deg)

y
x
z

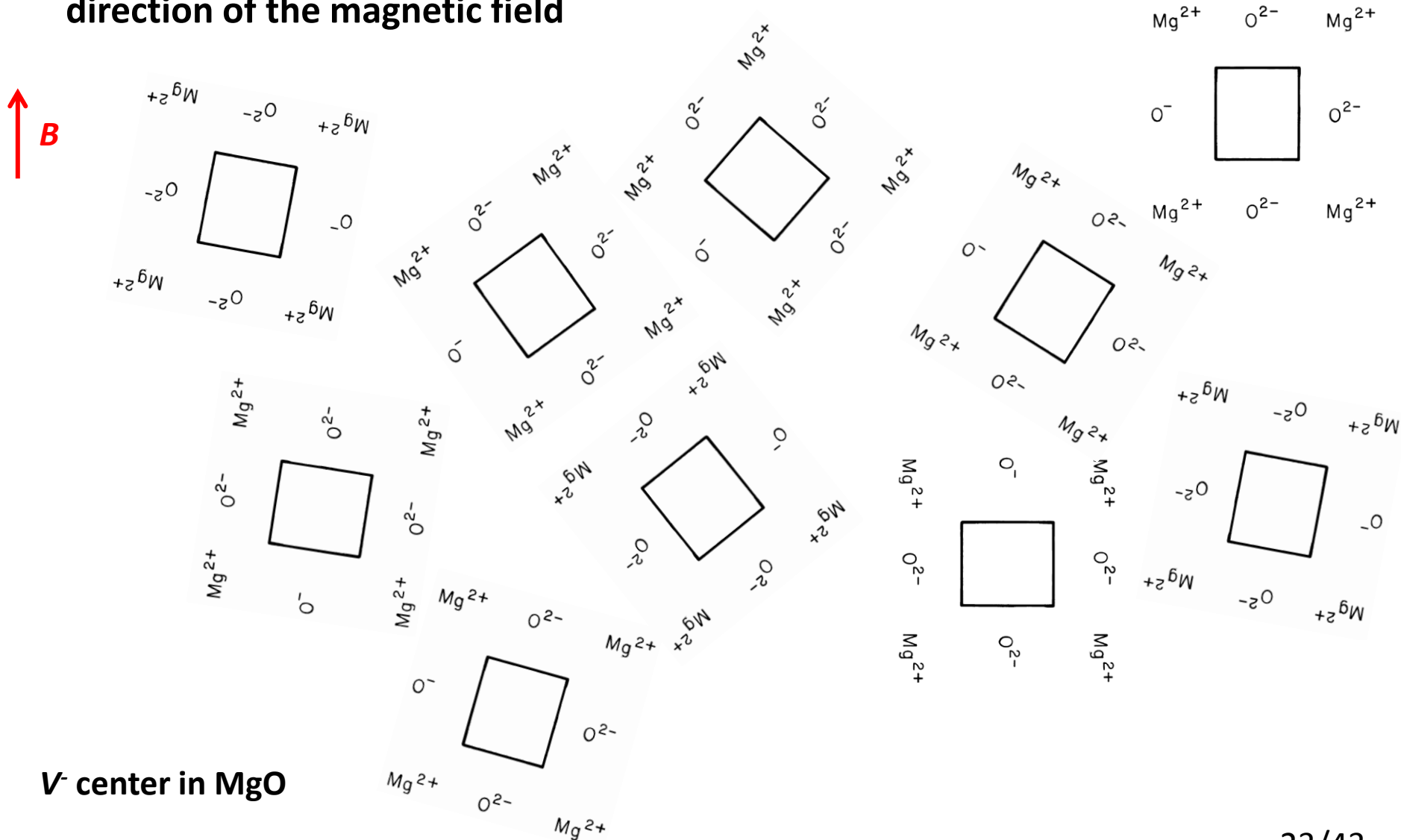# 3. Anisotropy

➢ **Orthorhombic Symmetry**

Spin Hamiltonian: $\hat{\mathcal{H}} = \beta_e(g_x B_x \hat{S}_x + g_y B_y \hat{S}_y + g_z B_z \hat{S}_z)$

Anisotropic g factor (dependent on magnetic field direction): $g_x \neq g_y \neq g_z$

O_2^- on MgO

P. Schwach

3. Anisotropy

➢ **Crystalline powders**: principal axis has all possible orientations relative to the direction of the magnetic field
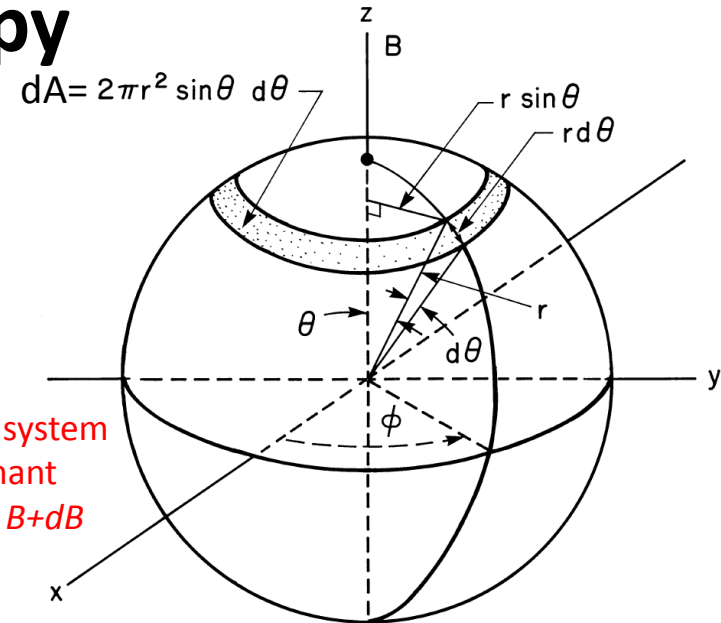

B

V^- **center in MgO**

3. Anisotropy

- **Crystalline powder**
- **S = ½, I = 0**
- **Uniaxial local symmetry**

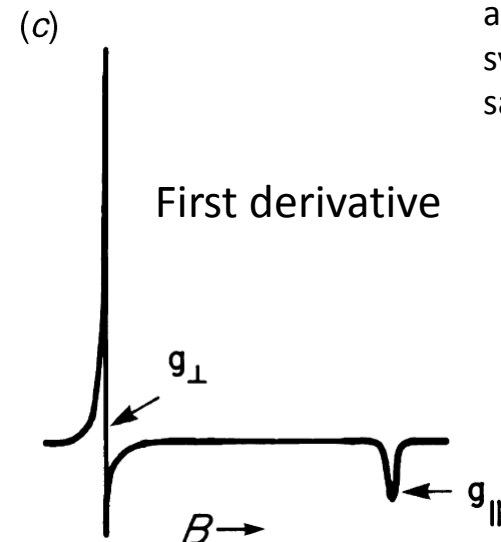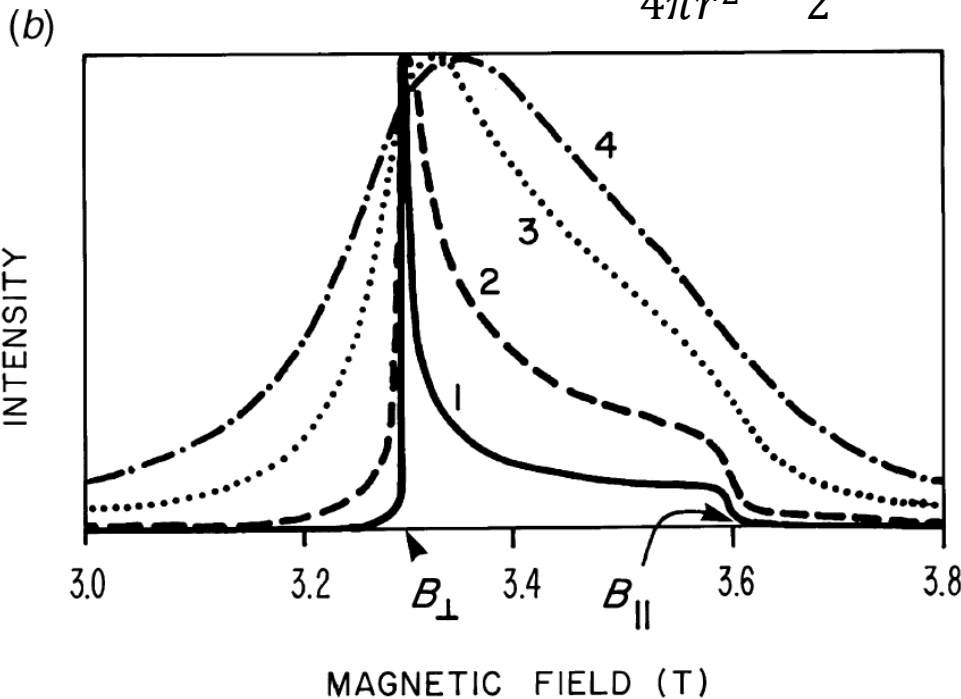Fraction of symmetry axes between θ and $\theta+d\theta$

$$P(\theta)\mathrm{d}\theta = \frac{dA}{A_{sphere}} \sim P(B)dB$$

Probability of a spin system experiencing a resonant field between *B* and *B+dB*

$$P(\theta)\mathrm{d}\theta = \frac{dA}{4\pi r^2} = \frac{1}{2}sin\theta \mathrm{d}\theta$$

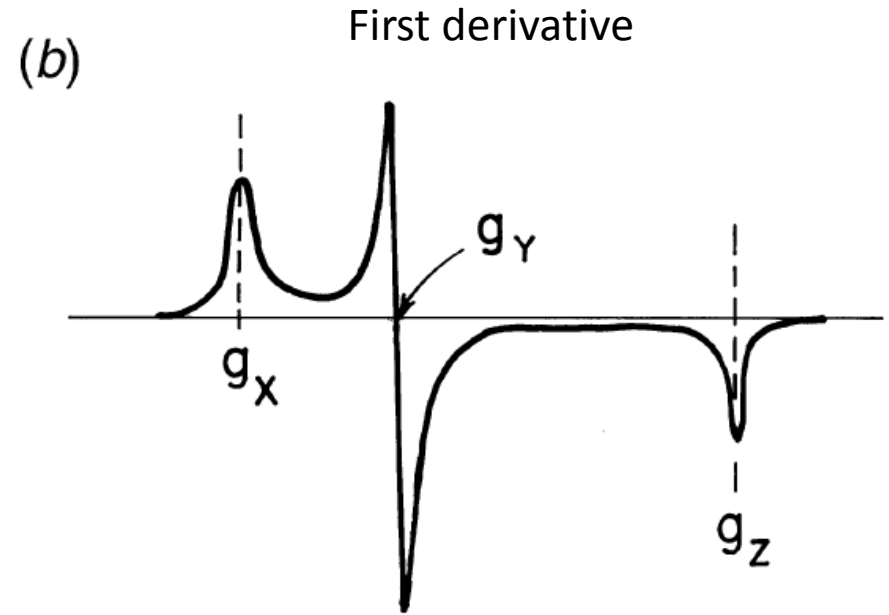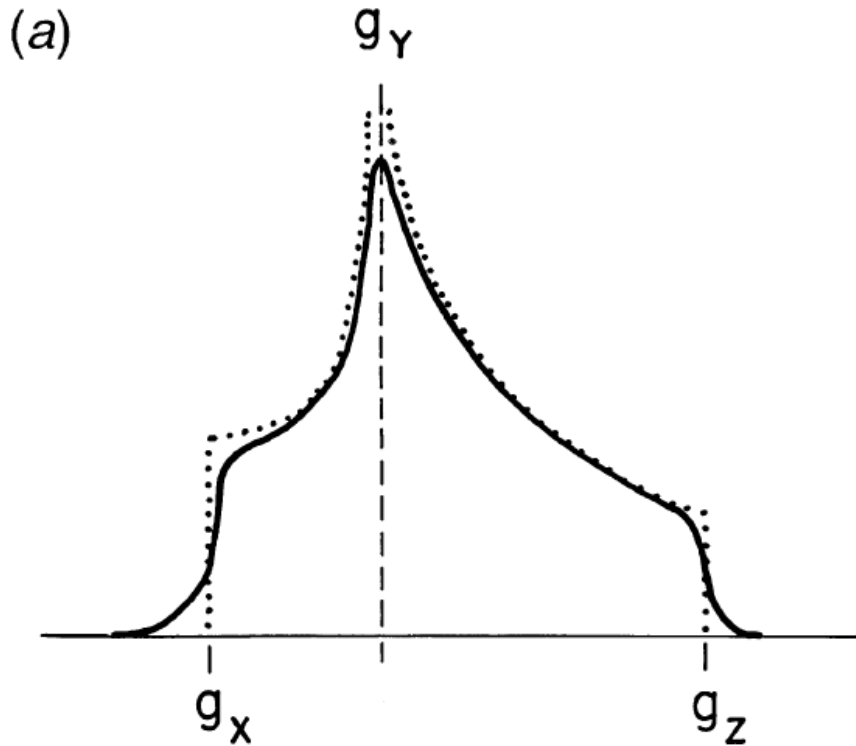$dA = 2\pi r^2 \sin\theta \, d\theta$

$r \sin\theta$

$r \, d\theta$

θ: Angle between magnetic field and principal symmetry axis of any spin system in the sample

(b)

INTENSITY

MAGNETIC FIELD (T)

$B_\perp$ $B_{||}$

(c)

First derivative
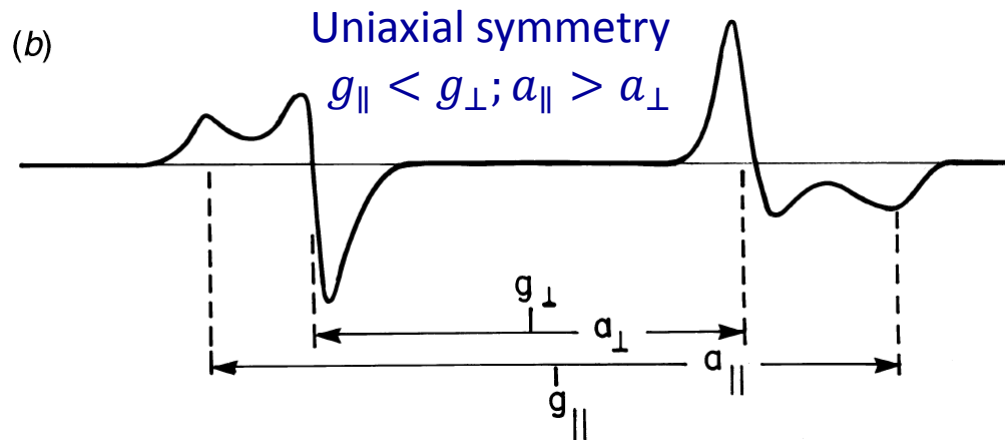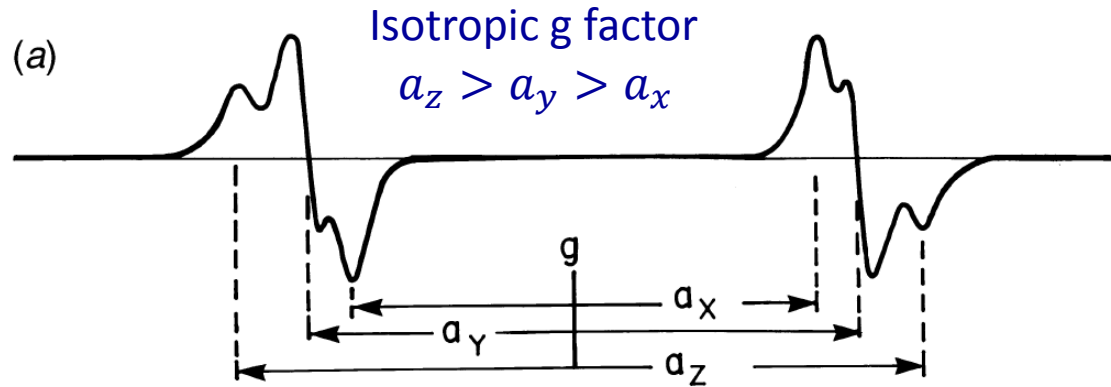

$g_\perp$

$g_{||}$

$B \rightarrow$

24/43

3. Anisotropy

- Crystalline powder
- $S = \frac{1}{2}$, $I = 0$
- Orthorhombic local symmetry

3. Anisotropy

- **Crystalline powder**
- **S = ½, I = ½**
- **Hyperfine anisotropy**

(a)

Isotropic g factor
$a_z > a_y > a_x$

g

a_X

a_Y

a_Z

(b)

Uniaxial symmetry
$g_\parallel < g_\perp; a_\parallel > a_\perp$

$g_\perp$

$a_\perp$

$a_\parallel$

$g_\parallel$

(c)

a_0

g_z

Isotropic hyperfine splitting
$g_z > g_y > g_x$

g_X

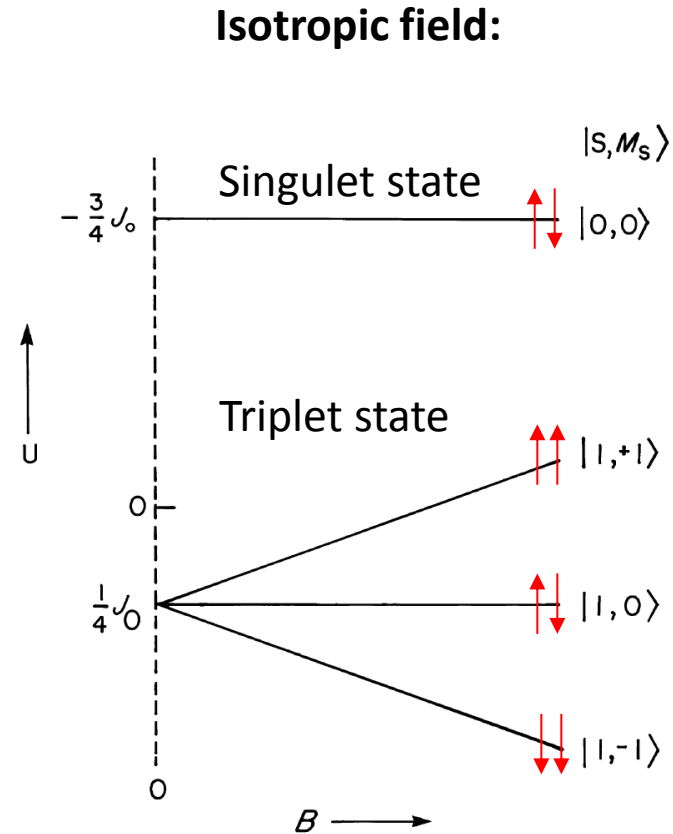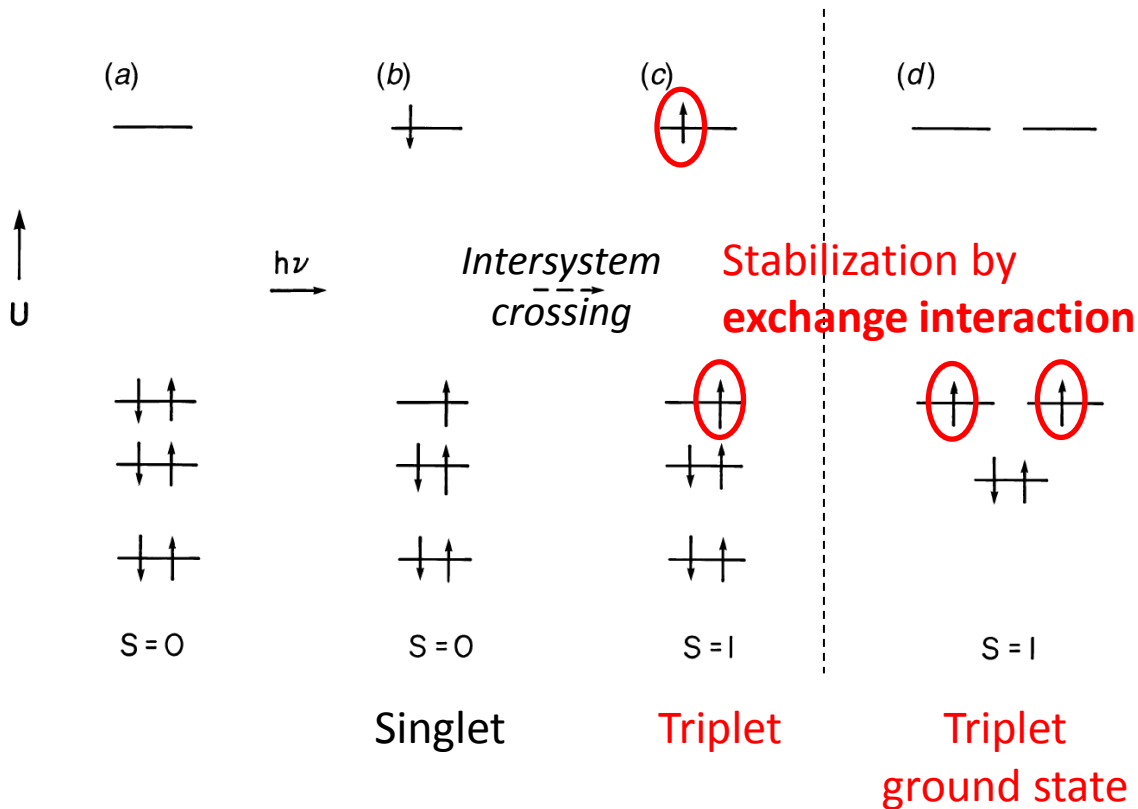a_0

a_0

g_Y
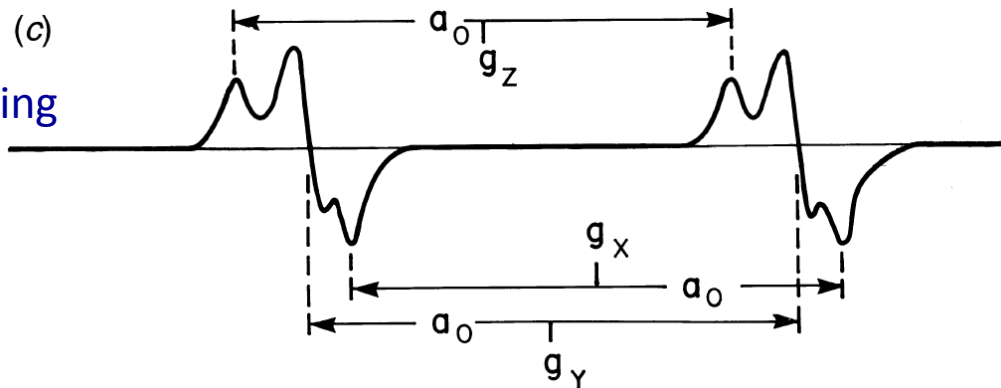
3. Anisotropy

- **MgO: H^+/O_2^-**
- **$S = \frac{1}{2}$, $I(H) = \frac{1}{2}$**
- **Orthorhombic:**

MgO
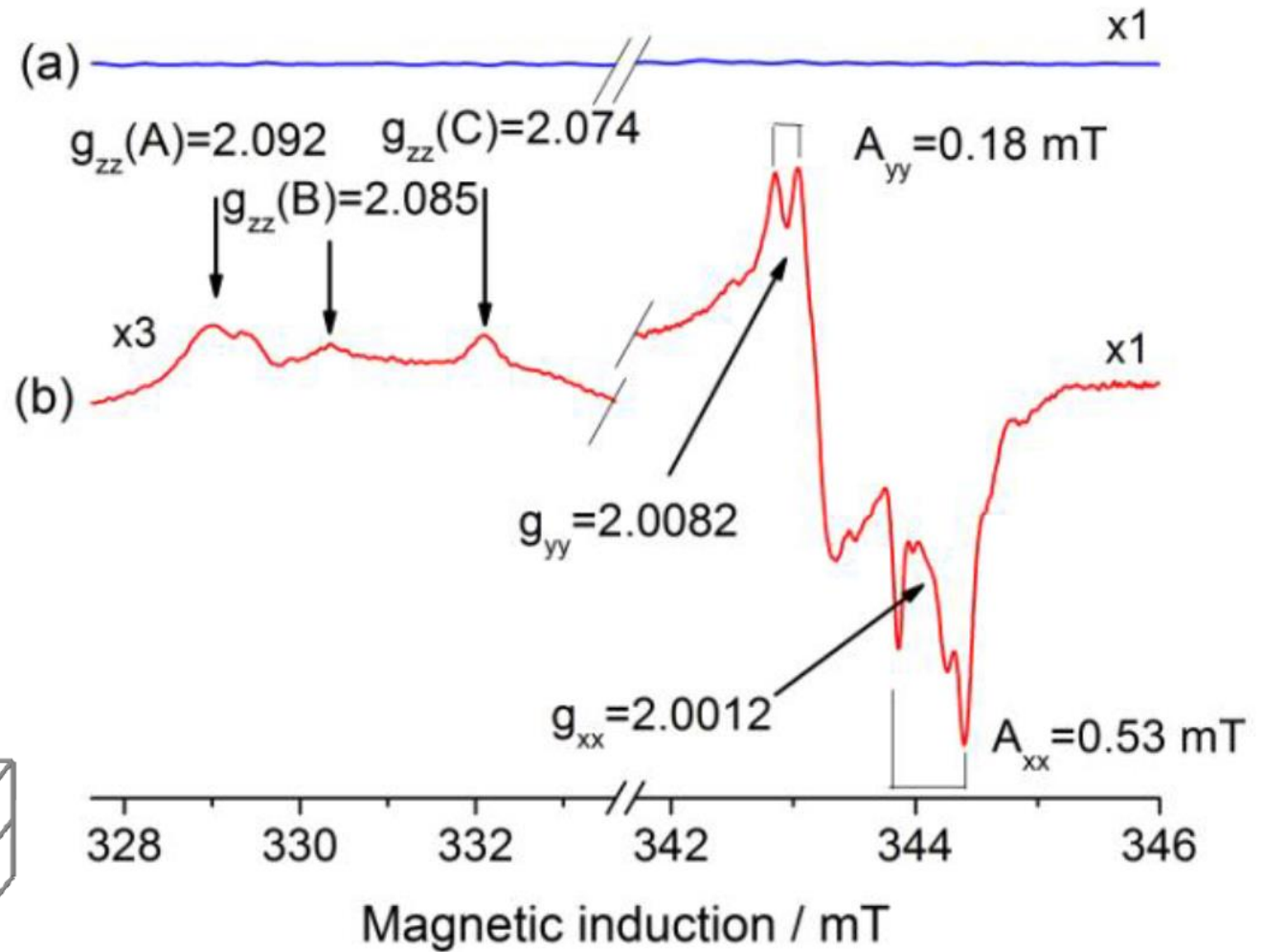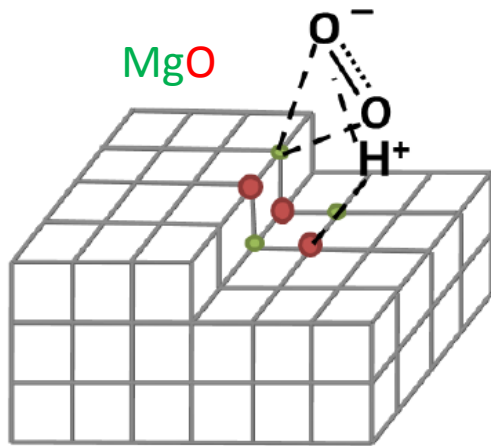
4. Electron-Electron Interactions

4. Electron-Electron Interactions

> E.g. O_2, V^{3+}, Ni^{2+}, Fe^{3+}
> Electron exchange interaction

Isotropic field:

4. Electron-Electron Interactions

➤ **Electron-electron dipole interaction**

Only Zeeman effect (S = ½, isotropic g factor, I = 0): $\quad \hat{\mathcal{H}} = g\beta_e(B_x\hat{S}_x + B_y\hat{S}_y + B_z\hat{S}_z)$

With electron-electron dipole (anisotropic) interaction (fine coupling) (S = 1, isotropic g factor, I = 0):

$$\hat{\mathcal{H}} = g\beta_e\big(B_x\hat{S}_x + B_y\hat{S}_y + B_z\hat{S}_z\big) + D_x\hat{S}_x^{\,2} + D_y\hat{S}_y^{\,2} + D_z\hat{S}_z^{\,2}$$

$$\hat{\mathcal{H}} = g\beta_e\mathbf{B}^{\mathrm{T}}\cdot\hat{\mathbf{S}} + D\big(\hat{S}_z^{\,2} - \frac{1}{3}\hat{S}^2\big) + E\big(\hat{S}_x^{\,2} - \hat{S}_y^{\,2}\big)$$
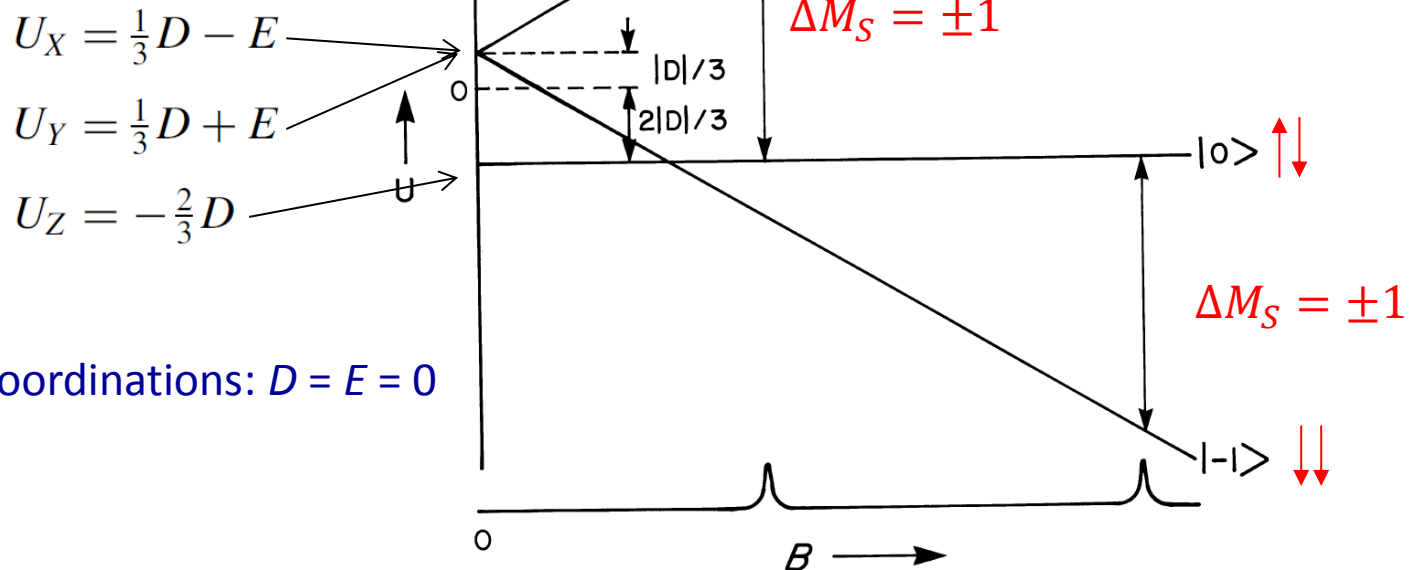
e.g. E = 0

Zero-field splitting

$U_X = \frac{1}{3}D - E$

$U_Y = \frac{1}{3}D + E$

$U_Z = -\frac{2}{3}D$

In cubic coordinations: *D = E = 0*

$|+1\rangle$ ↑↑

$\Delta M_S = \pm 1$

|D|/3

2|D|/3

$|0\rangle$ ↑↓

$\Delta M_S = \pm 1$

$|-1\rangle$ ↓↓

$B \longrightarrow$

4. Electron-Electron Interactions

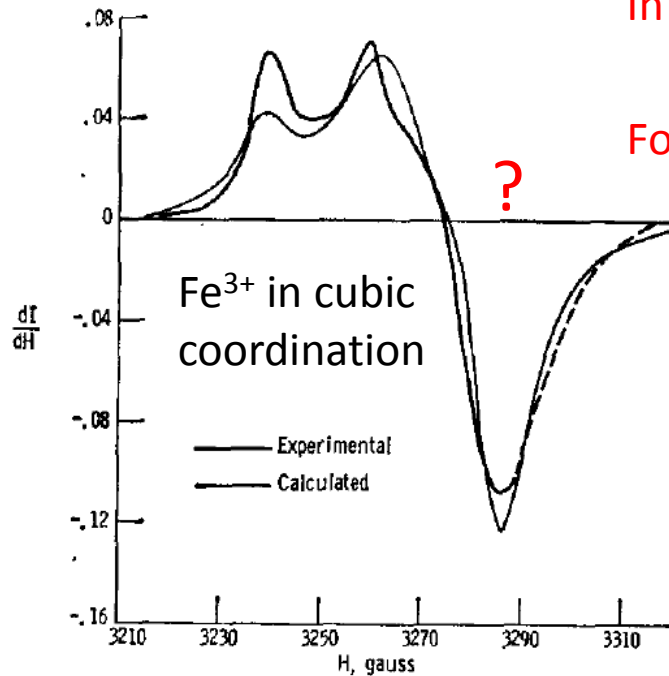> **Electron-electron dipole interaction**

With electron-electron dipole interaction (fine coupling) (S = 1, isotropic g factor, I = 0):

Second order term ~S²

$$\hat{\mathcal{H}} = g\beta_e \mathbf{B}^T \cdot \hat{\mathbf{S}} + D(\hat{S}_z^2 - \frac{1}{3}\hat{S}^2) + E(\hat{S}_x^2 - \hat{S}_y^2)$$

In cubic coordinations: *D = E = 0*

For high spin systems, e.g. Fe^{3+}: S = 5/2

?

Fe³⁺ in cubic coordination

$$\mathcal{H}_s = g\beta \mathbf{H} \cdot \mathbf{S}$$
$$+ \tfrac{1}{6}a[S_x^4 + S_y^4 + S_z^4 - \tfrac{1}{5}S(S+1)(3S^2+3S-1)]$$

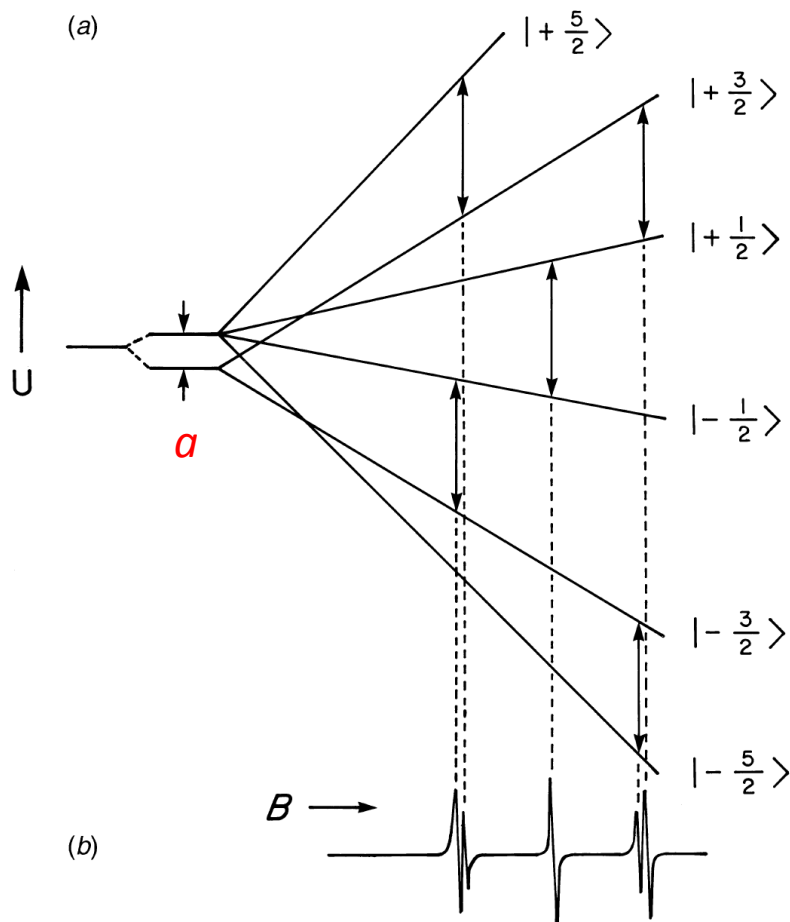*a: Fourth-order (high spin) parameter for cubic coordination*

FIG. 1. Experimental and calculated derivative spectra for Fe³⁺ ions in polycrystalline MgO. The experimental curve is for Fisher reagent-grade MgO powder and is extrapolated in the region of an overlapping Cr³⁺ spectrum (dashed portion).

4. Electron-Electron Interactions

➢ **Electron-electron dipole interaction**

With electron-electron dipole interaction (fine coupling) (S = 5/2, isotropic g factor, I = 0):

Single crystal d⁵ ion in octahedral (cubic) crystal field with B parallel to principal axis

(a)

$$\mathcal{H}_s = g\beta \mathbf{H} \cdot \mathbf{S}$$
$$+ \tfrac{1}{6}a[S_x^4 + S_y^4 + S_z^4 - \tfrac{1}{5}S(S+1)(3S^2+3S-1)]$$

$|+\tfrac{5}{2}\rangle$

$|+\tfrac{3}{2}\rangle$

$|+\tfrac{1}{2}\rangle$

$|-\tfrac{1}{2}\rangle$

$|-\tfrac{3}{2}\rangle$

$|-\tfrac{5}{2}\rangle$

U

a

B →

(b)

For (uni)axial symmetries: Axial fourth-order parameter _F_

➤ **The complete (simplified) Spin Hamiltonian**

$$\widehat{\mathcal{H}} = g\beta_e \mathbf{B}^{\mathrm{T}} \cdot \hat{\mathbf{S}} + \hat{\mathbf{S}}^{\mathrm{T}} \cdot \mathbf{D} \cdot \hat{\mathbf{S}} + \hat{\mathbf{S}}^{\mathrm{T}} \cdot \mathbf{A} \cdot \hat{\mathbf{I}}$$

Zeeman splitting: *g tensor*

Fine coupling (high spin electron-electron interactions): *D*, *E*, *a*, *F*

Nuclear hyperfine coupling (electron-nucleus interactions): *A tensor*

# Spectrum Simulation with EasySpin®

Mn
Sys1.S = 5/2;
Sys1.g = 2.0007;
Sys1.Nucs = '55Mn';
Sys1.A = -244;
Sys1.AStrain = 0;
Sys1.aF = [60 0];
Sys1.lwpp = 0.1;
Sys1.D = 90;
Sys1.DStrain = 120;
Sys1.weight = 100;

Fe
Sys2.S = 5/2;
Sys2.g = 2.0027; % isotropic g
Sys2.lwpp = [0.5 0.0]; % Gaussian, Lorentzian peak to peak
width, mT
Zero-field splitting in terms of D and E
Sys2.D = [120 0]; %in MHz
Sys2.DStrain = [600 0];
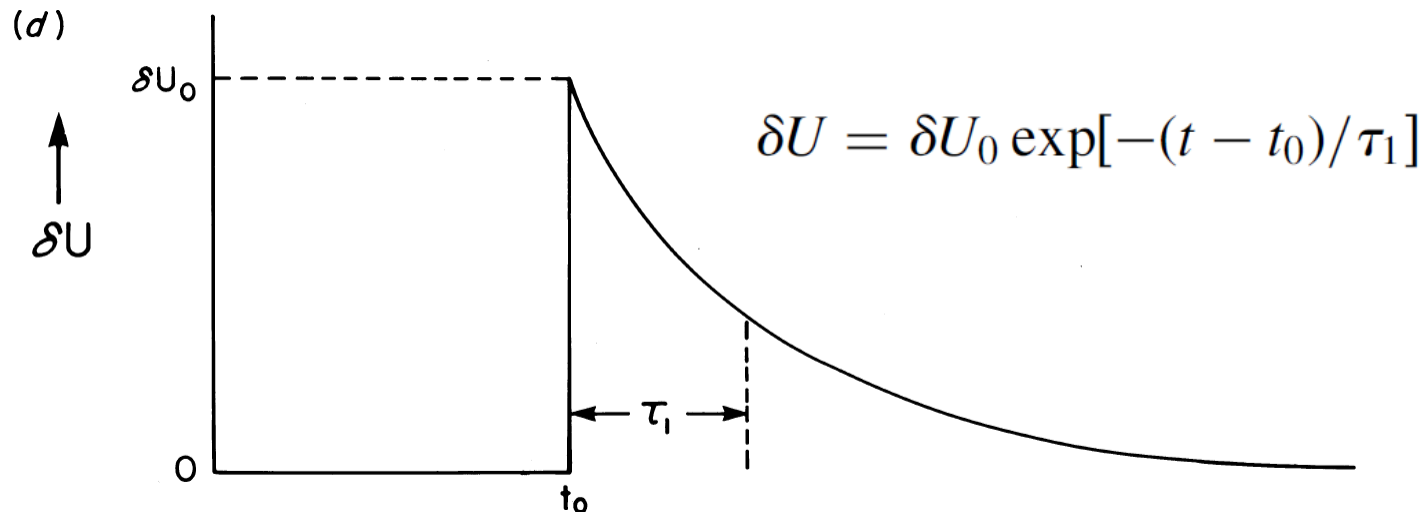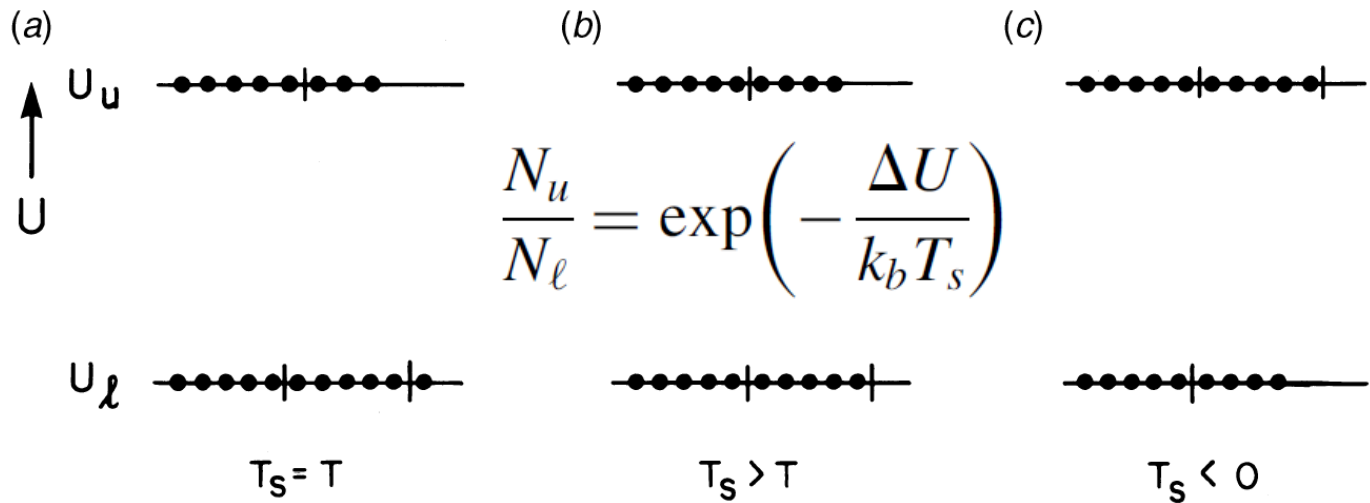Sys2.aF=[650 0];
Sys2.aFStrain = [0 0]
Sys2.weight=16000

Cr
Sys3.S=3/2;
Sys3.g=1.98;
Sys3.Nucs='Cr';
Sys3.A=3;
Sys3.lwpp=0.2;
Sys3.weight=5;

Fe^{3+}, Mn^{2+}, Cr^{3+} in MgO
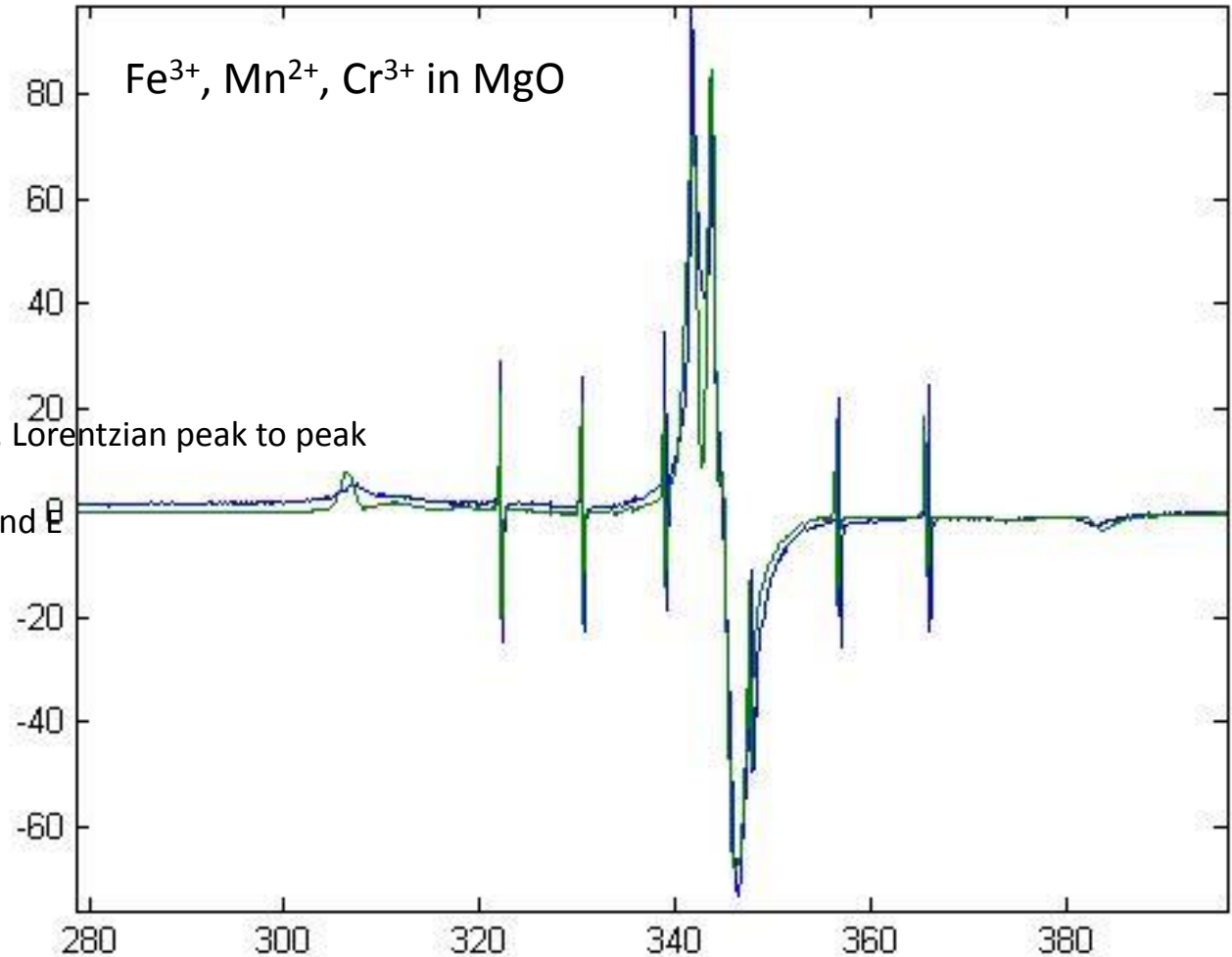
5. Linewidths

5. Linewidths

➢ **Spin relaxation: spin-lattice relaxation time τ_1** (spin interaction with surroundings, longitudinal relaxation time)

(a)

U_u

U

U_ℓ

$T_S = T$

(b)

$$\frac{N_u}{N_\ell} = \exp\left(-\frac{\Delta U}{k_b T_s}\right)$$

$T_S > T$

(c)

$T_S < 0$

(d)

δU_0

δU

$$\delta U = \delta U_0 \exp[-(t - t_0)/\tau_1]$$

τ_1

0

t_0

5. Linewidths

➤ **Spin relaxation: spin-spin relaxation time τ_2** (spin spin interaction, transversal relaxation time)
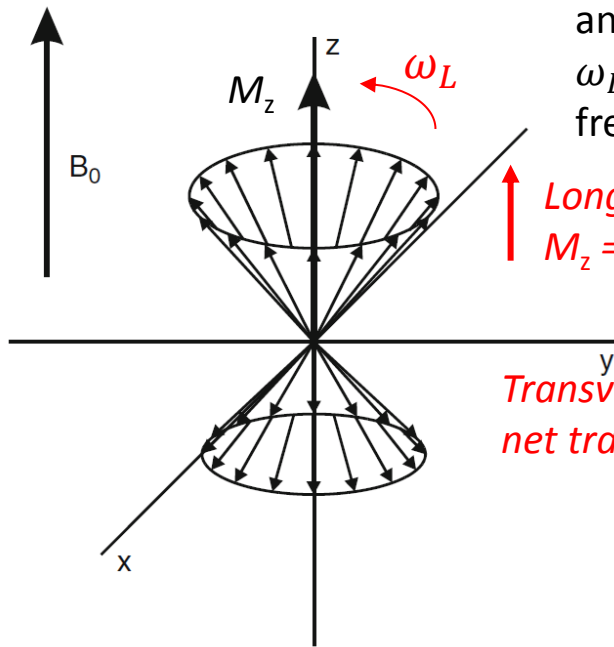
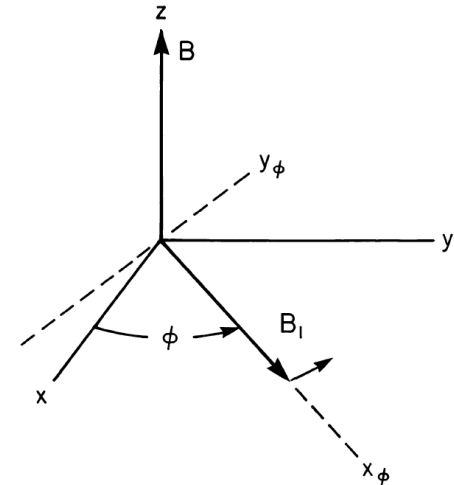**M** precesses about **B**$_0$ with angular frequency
$\omega_L = -\gamma_e \mathbf{B}_0$ (Larmor frequency)

Frame rotates with the angular frequency ω

Longitudinal magnetization M_z = const.

Transversal M_x, M_z oscillate, no net transversal magnetization

Net transversal magnetization (all spins rotate in phase with ω)

Transversal magnetization decays with τ_2

Superposition of a rotating perpendicular field B$_1$

$$M_{xy} = M_{xy}(0)e^{-t/\tau_2}$$

At resonance: $\omega = \omega_L$

37/43
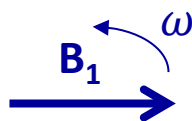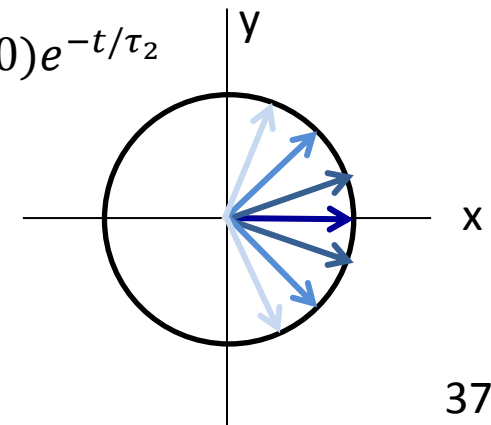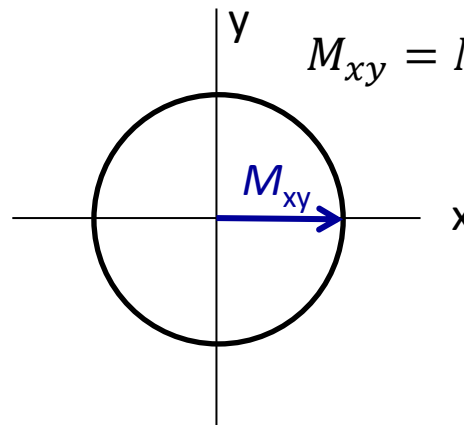
5. Linewidths

➢ **Linewidths: homogeneous broadening by τ_1 and τ_2**

Lorentzian line shape

Half width at half height:

$$\Gamma = \frac{1}{|\gamma_e|\tau_2}(1 + \gamma_e{}^2 B_1{}^2 \tau_1 \tau_2)^{1/2} \approx \frac{1}{|\gamma_e|\tau_2}$$

Usually: $\tau_1 \gg \tau_2$
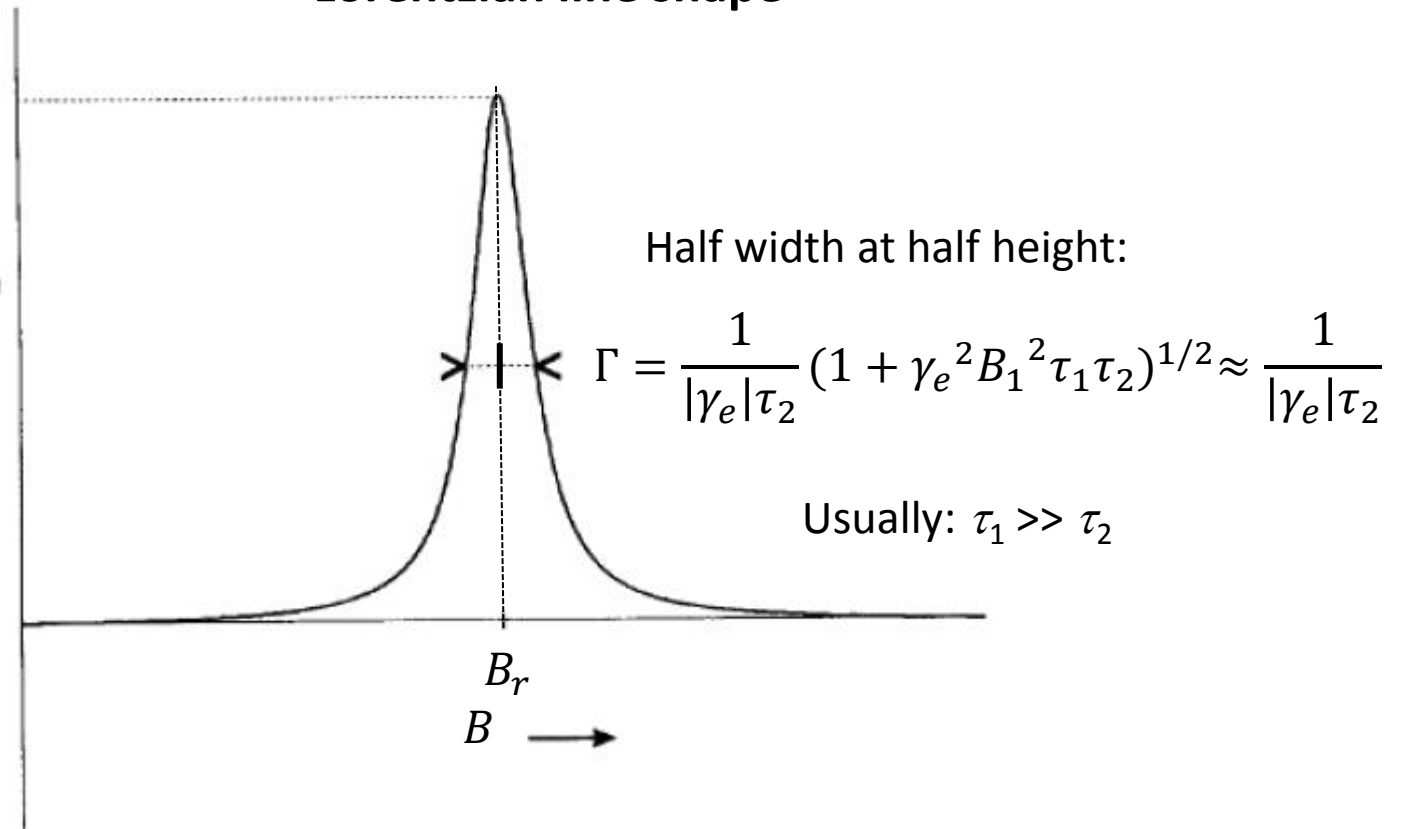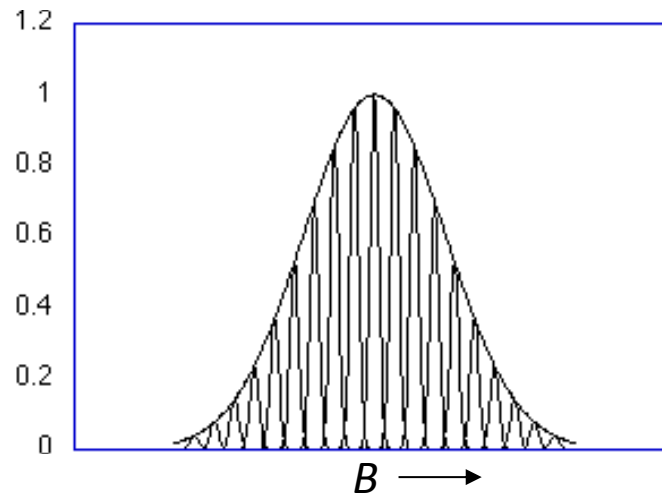
5. Linewidths

➢ **Linewidths: inhomogeneous broadening by superposition of spectra from individual equivalent spins**

Gaussian(-Lorentzian) line shape

$B \longrightarrow$

Caused by
- An inhomogenous external magnetic field
- Unresolved hyperfine structure
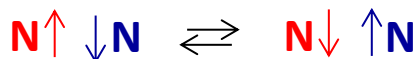- Anisotropic interactions
- Dipolar interactions

5. Linewidths

➢ **Example for line broadening: electron-spin exchange**

(*t*-Bu)$_2$ṄO

^{14}N: $I = 1$ → $M = 2I+1 = 3$ (Triplet)

in EtOH

N↑ **↓N** ⇌ **N**↓ **↑N**

Exchange of spin orientations
between two nuclei
→ Decreases interaction time τ
between (same) nuclear and
electron spin state

Spin exchange rate:

$$k_{\text{exchange}} = \frac{1}{2\tau[\text{conc.}]}$$

At high concentrations τ can
become so small, that the
time-averaged hyperfine
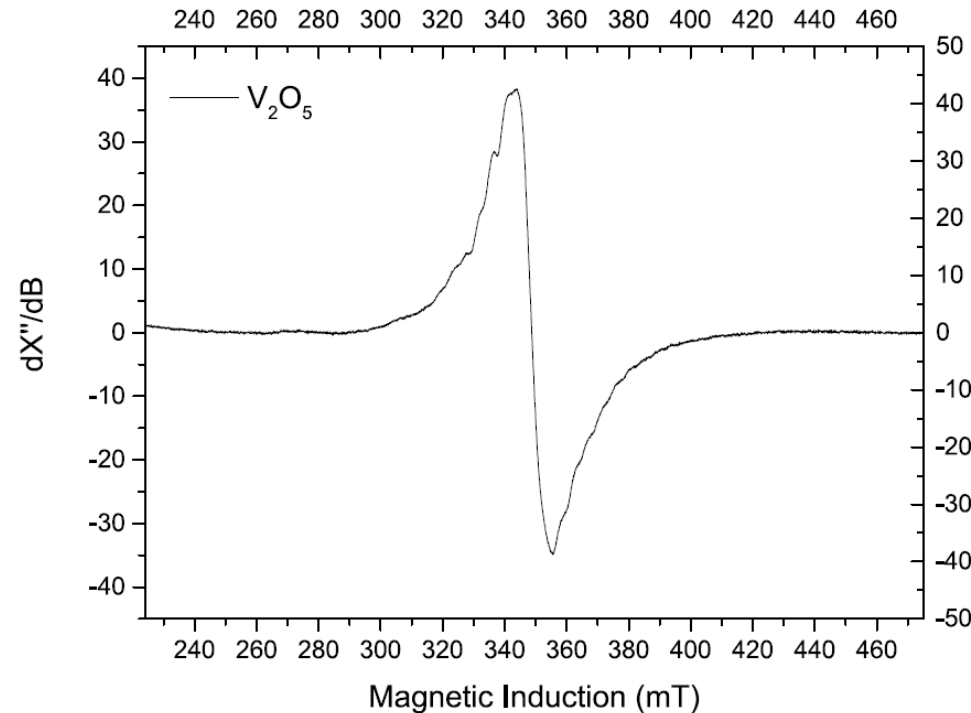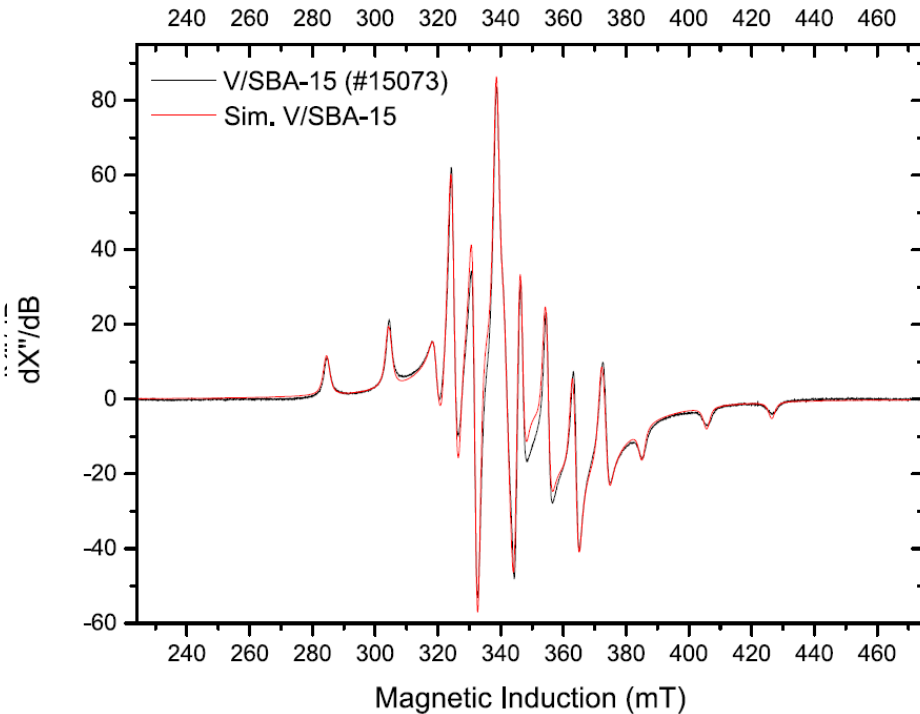field is close to zero and hfs
coalesces to a single,
narrowed line

(a) 10^{-4} M

(b) 10^{-2} M

B

15 G

(c) 10^{-1} M

exchange-narrowed

(d) pure liquid
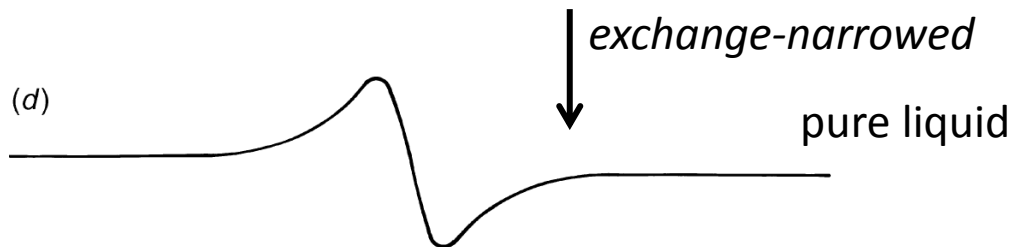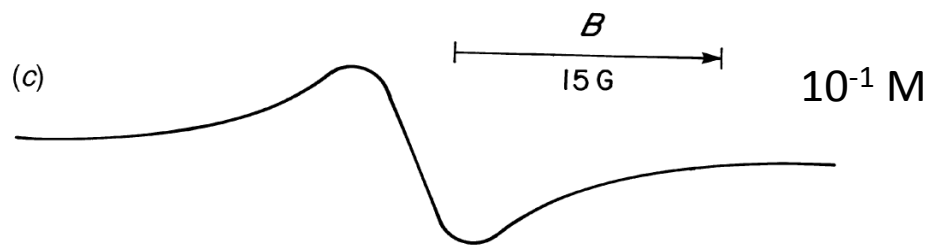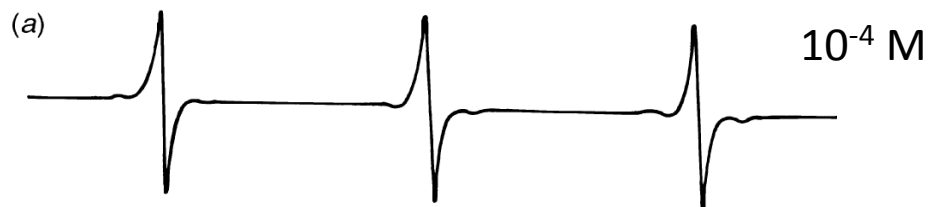
5. Linewidths

> **Example for line broadening: electron-spin exchange**

V/SBA-15 $^{51}V: I = 7/2$

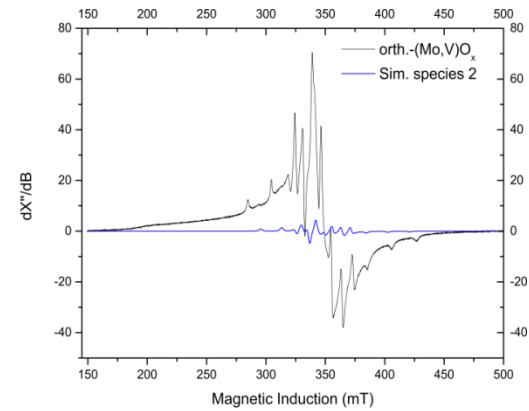| V/SBA-15	Spin S	Nucleus	g Tensor			A Tensor (mT)			ΔB_{pp} (mT)
			g_{xx}	g_{yy}	g_{zz}	A_{xx}	A_{yy}	A_{zz}	
Narrow species	$\frac{1}{2}$	^{51}V	1.979	1.980	1.935	7.22	7.72	20.3	1.0
Broad species	$\frac{1}{2}$			1.969			/		18

Differentiation between isolated and strongly interacting V atoms possible

A. Wernbacher

Orthorhombic MoV oxide
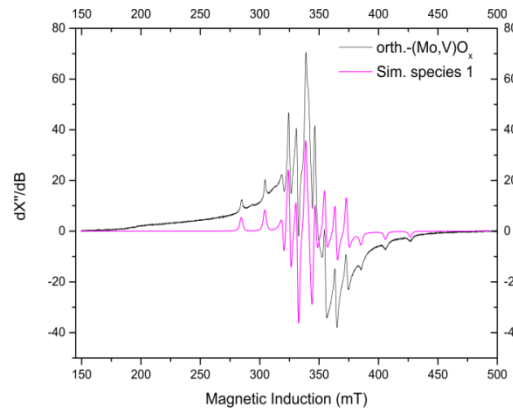
a)

b)
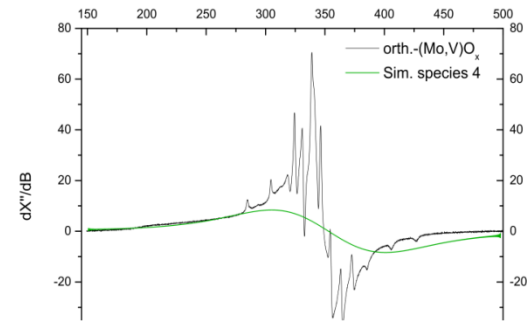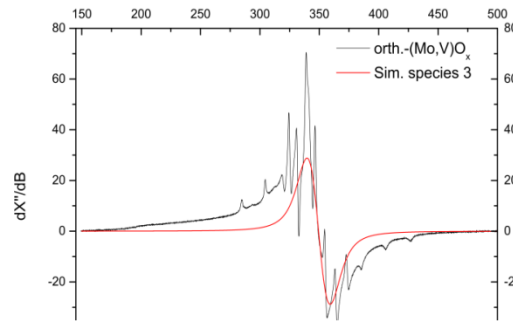
Species	Nucleus	Description and Assignment	Ref
1	^{51}V (V^{4+})	Narrow isolated V^{4+}-species, axially symmetric g and A tensors, "isolated V^{4+} ion in an axial crystal field (tetragonal distortion) … typical for a vanadyl ion VO^{2+} with aqua or comparable ligands" [a], similar to [VO(H$_2$O)$_5$]$^{2+}$ (like heteropoly compound HVOPVMo$_{12}$O$_{40}$ of Lee et al. [3])	Lee et al. [3], Luca et al. [4]
2	^{51}V (V^{4+})	Same as "species 1" but with lower intensity, (like heteropoly compound H$_4$PVMo$_{11}$O$_{40}$ of Lee et al. [3])	Lee et al. [3], Luca et al. [4]
3	V	Broad species centred at g = 1.97 indicating interacting V^{4+}-centres (line broadening caused by spin-spin interactions): bulk species	Luca et al. [4]
4	V (or Mo)	Broad species centred at g = 1.95 indicating strongly interacting paramagnetic species (V^{4+} or Mo^{5+}): bulk species	
5	/	/	/

6. Literature

✘ J. A. Weil, J. R. Bolton, "Electron paramagnetic resonance", John Wiley & Sons **2007** (comprehensive book about cw-EPR theory, also as e-book available)

✘ G. R. Eaton, S. S. Eaton, D. P. Barr, R. T. Weber, "Quantitative EPR"; Springer **2010**

✘ A. Schweiger, "Pulsed Electron Spin Resonance Spectroscopy: Basic principles, Techniques, and Examples of Applications", Angew. Chem. Int. Ed. **1991**, *30*, 265-292

✘ A. Schweiger, G. Jeschke, "Principles of pulse electron paramagnetic resonance", Oxford Univ. Press **2001**

✘ P. Rieger, "Electron Spin Resonance: Analysis and Interpretation", Royal Soc. of Chemistry **2007** (also as e-book available)