

EPR of Transition Metal Ions

$3d^n$	Ion	S	ξ (cm ⁻¹)
$3d^1$	Ti ³⁺	1/2	154
$3d^2$	Va ³⁺	1	209
$3d^3$	Cr ³⁺	3/2	273
$3d^4$	Cr ²⁺	2	230
$3d^5$	Mn ²⁺	5/2	347
$3d^6$	Fe ²⁺	2	410
$3d^7$	Co ²⁺	3/2	533
$3d^8$	Ni ²⁺	1	649
$3d^9$	Cu ²⁺	1/2	829

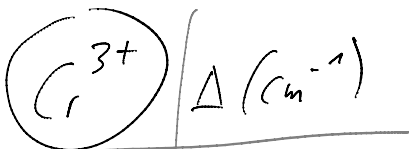
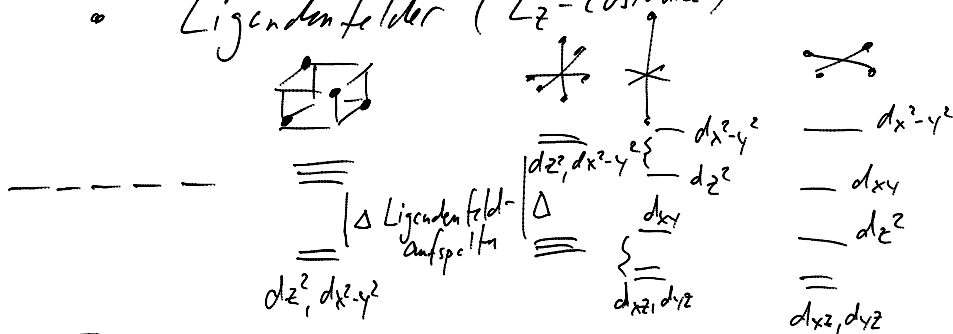
↓ S steigt

↓ S fällt

d-Orbitale $L=2$, $L_z = \pm 2, \pm 1, 0$

Ligandenfeld - Theorie

- Coulomb - Abstößung der e⁻
- Austausch - WW e⁻ denselben Spins } 1000 - 10000 cm⁻¹
- Spin - Bahn WW $\xi \vec{L} \cdot \vec{S}$
- Ligandenfelder (L_z -Zustände)

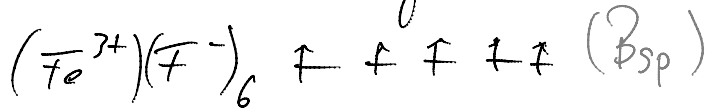


I⁻, Ce⁻, F⁻, H₂O, NH₃, NO₂⁻, OH⁻ als Liganden

$(C_r^{s'})$	$\Delta (cm^{-1})$
CN ⁻	26300
NH ₄	21600
H ₂ O	17400
Cl ⁻	13600

I, Cl, +, H₂O, NH₃, NO₂, CN⁻ als Liganden

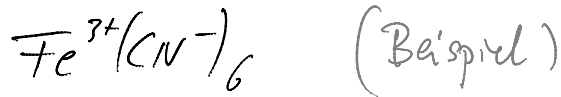
① Δ sehr klein gegenüber Coulomb & Austausch
 ↳ freies Ion als Startmodell
 für e⁻-Besetzung



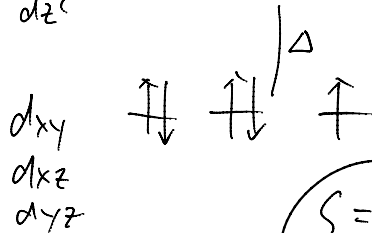
Weak-field approx. / high-spin

$S = 5/2$

② $\Delta \gg$ Austausch & Coulomb



$\frac{dx^2-y^2}{dz^2}$



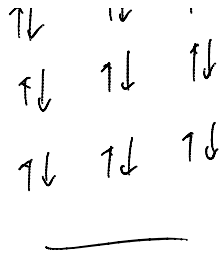
strong-field approx / low-spin

$S = 1/2$

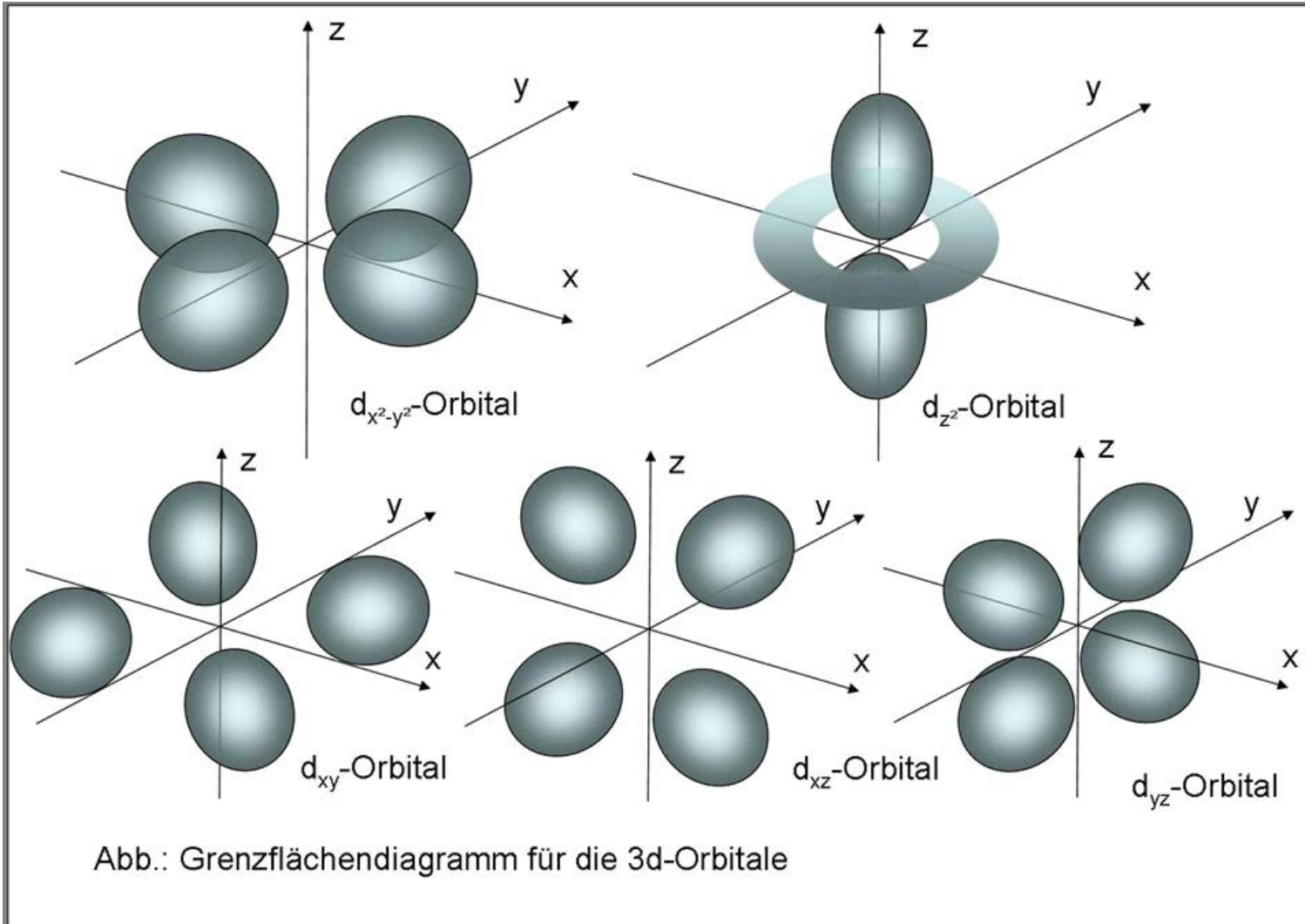
Spinzustände wenn Ligandenfeld dominiert (Oktaedrischer Komplex)

	dxy	dxz	dyz	dz ²	dx ² -y ²	S
d ¹	↑					1/2
d ²	↑	↑				1
d ³	↑	↑	↑			3/2
d ⁴	↑↓	↑	↑			1
d ⁵	↑↓	↑↓	↑			1/2
d ⁶	↑↓	↑↓	↑↓			0

d^5
 d^6
 d^7
 d^8
 d^9



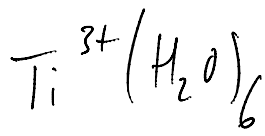
d-Orbitale



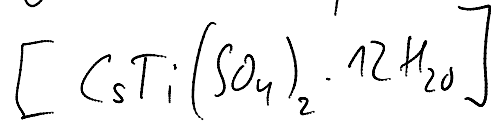
Beispiele

$S = 1/2 \quad d^1$

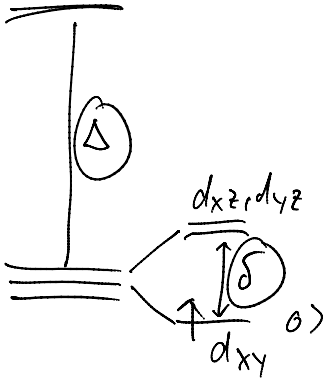
d1-Systeme und d9-Systeme



Oktaedrischer Komplex



$d_{x^2-y^2}$
 d_{z^2}



Anisotroper g-Tensor
(\hookrightarrow Spin-Bahn-WW)

$$\sum_i \frac{\langle \psi_n | LS | \psi_0 \rangle \langle \psi_0 | LS | \psi_n \rangle}{E_n - E_0}$$

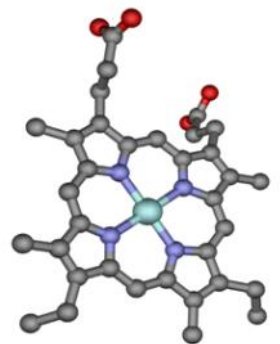
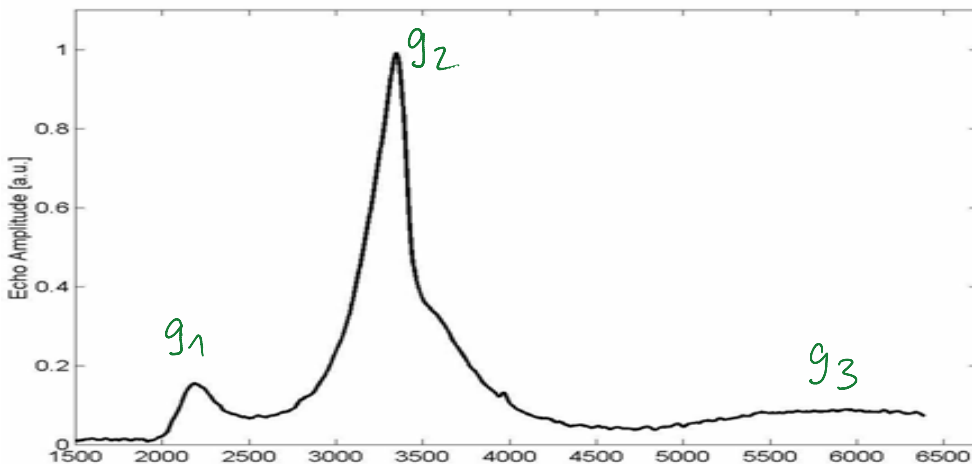
Carrington

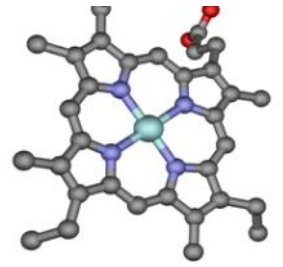
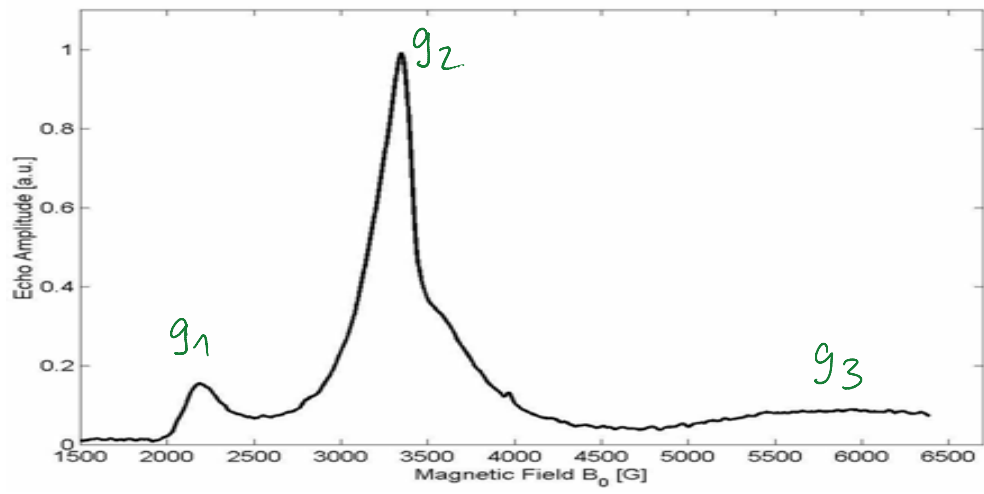
$$g_{||} = \frac{3(\xi + 2\delta)}{\sqrt{(\xi + 2\delta)^2 + 8\xi^2}} - 1 = 1.25$$

$$g_{\perp} = \frac{(2\delta - 3\xi)}{\sqrt{(\xi + 2\delta)^2 + 8\xi^2}} + 1 = 1.14$$

Im allgemeinen haben Übergangsmetalle stark anisotrope g-Werte
 \hookrightarrow breite Spektren !!

Beispiel: Cytochrome c



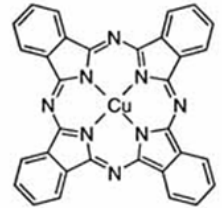
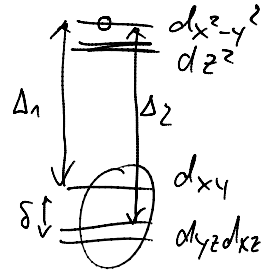


→ d^9 sehr ähnlich → $1e^- \Leftrightarrow 1 \text{ hole}$
 formal sehr ähnlich

$$g_{\parallel} = 2 \left(1 + \frac{4\xi}{\Delta_1} \right)$$

$$g_{\perp} = 2 \left(1 + \frac{\xi}{\Delta_2} \right)$$

Cu^{2+}



Cu-Phthalocyanine

$$\xi = 870 \text{ cm}^{-1}$$

$$g_{\parallel} = 2.165$$

$$g_{\perp} = 2.045$$

$$\Delta_1 = 31700 \text{ cm}^{-1}, \Delta_2 = 29600 \text{ cm}^{-1}$$

d_{xy} unbel. b. v. d_{xz}, d_{yz}

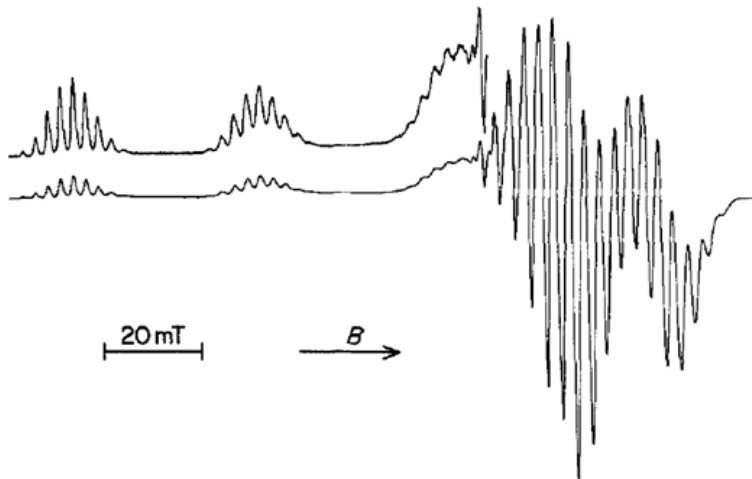
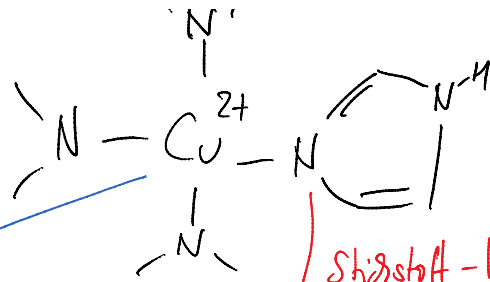


Figure 1. EPR spectrum of $^{63}\text{CuPc-}^{14}\text{N}(\text{pyrr.})_4\text{-}^{14}\text{N}(\text{aza})_4$, 0.01 M in concentrated sulphuric acid. The low-field region of the spectrum was rerecorded with increased gain. $T = 133 \text{ K}$; microwave power, 20 mW; microwave frequency, 9.255 GHz; total width, 93.11 mT. $A^{\text{Cu}} = 19.8 \text{ mT}$; $B^{\text{N}} = 1.36 \text{ mT}$; $g_{\parallel} = 2.203$.

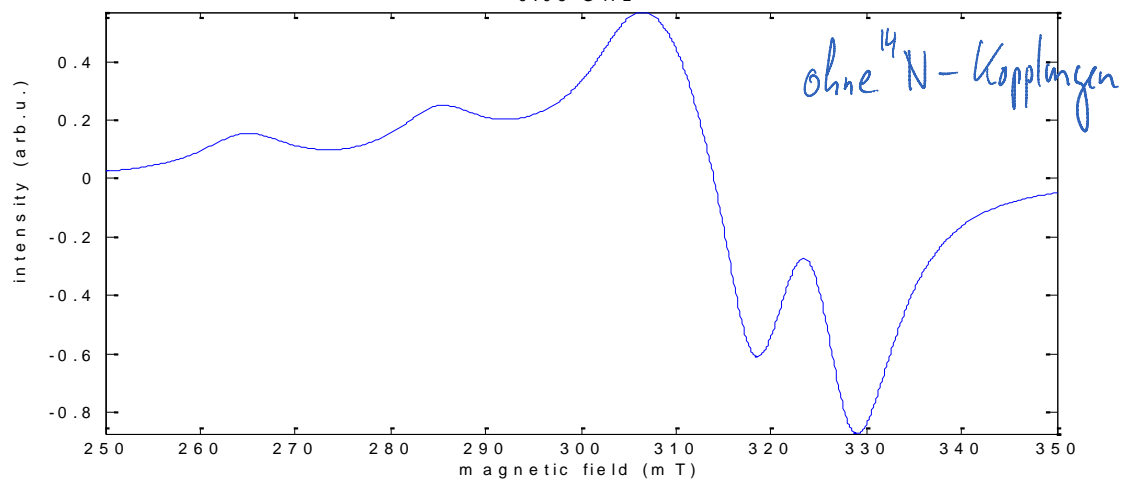
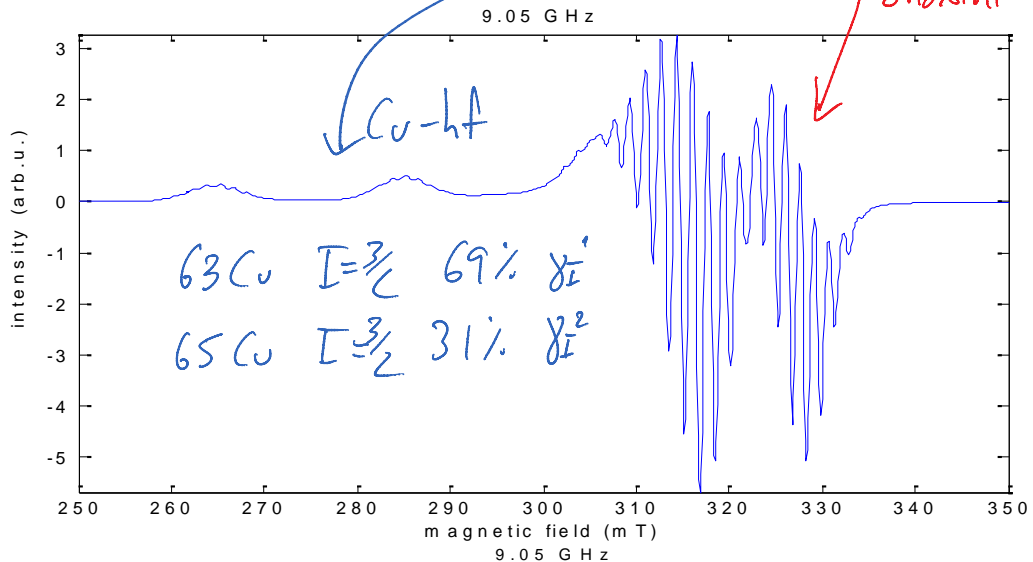
Döscher et al. Org. Mag. Res. (1984) 22, 658



Cu^{2+} - Imidazole Complex



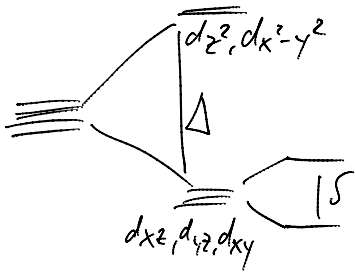
Stickstoff-hf von Liganden



$$S = 1$$

d2-Systeme

V^{3+} Oktaedrischer Komplex



$$-(d_{xz} d_{xy}) (d_{xy} d_{xz}) \quad m_z$$

$$-(d_{xz}, d_{yz}) \rightarrow S = 1 \quad \begin{matrix} \uparrow \\ \downarrow \\ 0 \end{matrix}$$

Nullfeld-Aufspaltung

$$\sim \sum_n \frac{\langle 0 | \vec{L} \vec{S} | n \rangle \langle n | \vec{L} \vec{S} | 0 \rangle}{(E_n - E_0)} \leftarrow \begin{matrix} \text{Spin-Spin Wkr} \\ \text{Spin-Orbit-Kopplg} \end{matrix}$$

$$\text{Wellenfunktion } |n\rangle = \underbrace{\psi_n}_{\text{orb-Wellenfkt}} \cdot \underbrace{\chi}_{\text{Spinwellenfkt}}$$

$$\vec{L} \text{ nur auf } \psi_n$$

$$\vec{S} \text{ nur auf } \chi$$

$$\hat{\mathcal{H}} = \underbrace{\vec{S} \cdot \vec{D} \vec{S}}_{\text{Nullfeldaufspaltung}}$$

$D = 3 \times 3$ Matrix

$i, k = x, y, z$

$$D_{ik} = - \sum_n \frac{\langle \psi_0 | L_i | \psi_n \rangle \langle \psi_n | L_k | \psi_0 \rangle}{E_n - E_0}$$

für $S = 1$ Spinwellenfunktionen

$$\hat{S}_x = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & -i \\ 0 & i & 0 \end{pmatrix}$$

$$\hat{S}_y = \begin{pmatrix} 0 & 0 & i \\ 0 & 0 & 0 \\ -i & 0 & 0 \end{pmatrix}$$

$$\hat{S}_z = \begin{pmatrix} 0 & -i & 0 \\ i & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}$$

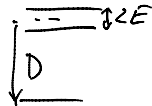
im MAS des Komplexes : $\left\{ G_z = \frac{1}{2} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \text{ für } S = 1/2 \right\}$

$$\tilde{D} = \begin{pmatrix} -X & 0 & 0 \\ 0 & -Y & 0 \\ 0 & 0 & -Z \end{pmatrix} \quad \begin{array}{l} \text{Spur von } D = 0 \\ -X - Y - Z = 0 \end{array}$$

$$\vec{S} \cdot \tilde{D} \cdot \vec{S} = -X \cdot \hat{S}_x^2 - Y \cdot \hat{S}_y^2 - Z \cdot \hat{S}_z^2$$

$$\tilde{D} = \begin{pmatrix} \frac{1}{3}D+E & 0 \\ 0 & \frac{1}{3}D-E \\ 0 & 0 & -\frac{2}{3}D \end{pmatrix} \quad \begin{array}{l} \text{--- } |S_x\rangle |S_y\rangle \\ \text{--- } |D \\ \text{--- } |S_z\rangle \end{array} \quad \begin{array}{l} \text{Oktaedrisch} \\ E=0 \end{array}$$

$z \parallel B_0$



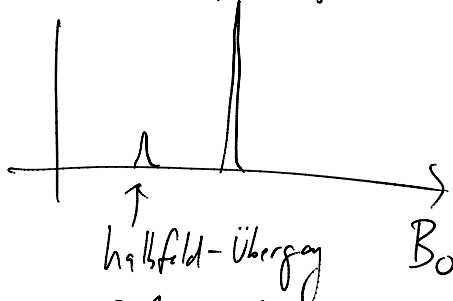
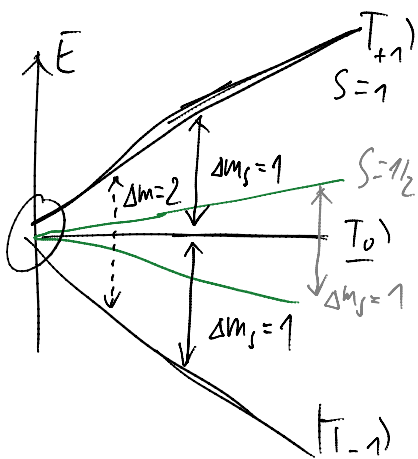
Spin-Eigenzustände ohne Magnetfeld

$(T_x), (T_y), (T_z)$

Spin-Eigenzustände mit großem Magnetfeld

$(T_{+1}), (T_0), (T_{-1})$

$m_s = +1 \quad m_s = 0 \quad m_s = -1$



Nullfeld

T_x, T_y, T_z

Magnetfeld
 $S > 1/2$, große ξ

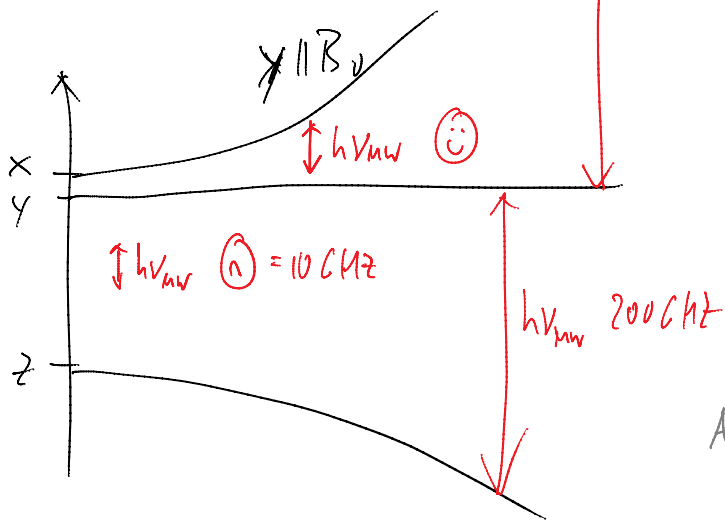
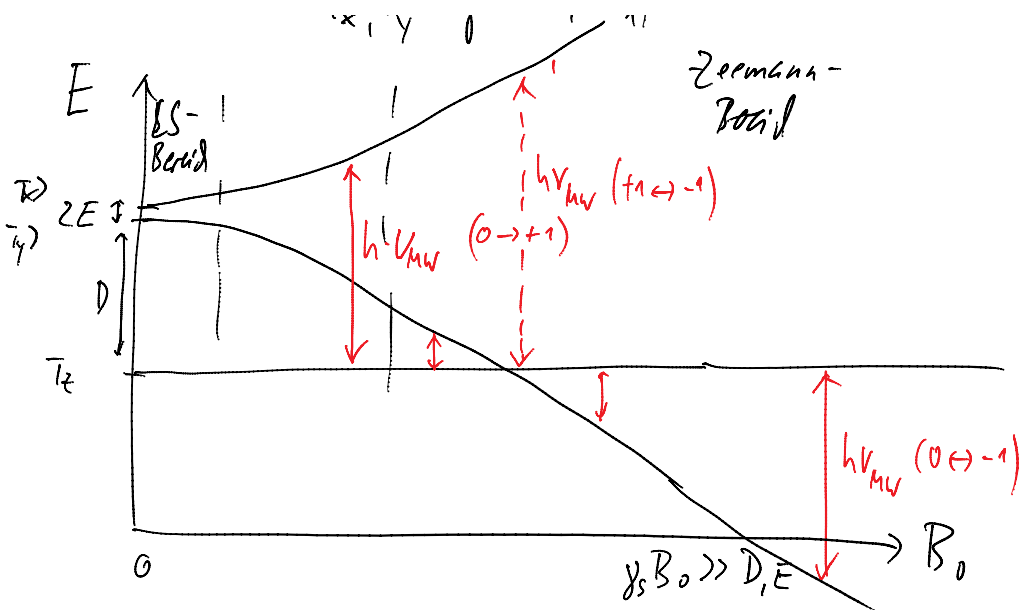
T_{+1}, T_0, T_{-1}

$z \parallel B_0 \quad T_z = T_0$
 $T_x, T_y = f(T_{+1}, T_{-1})$ $\mathcal{H} = g \vec{S} \cdot \vec{B}_0$

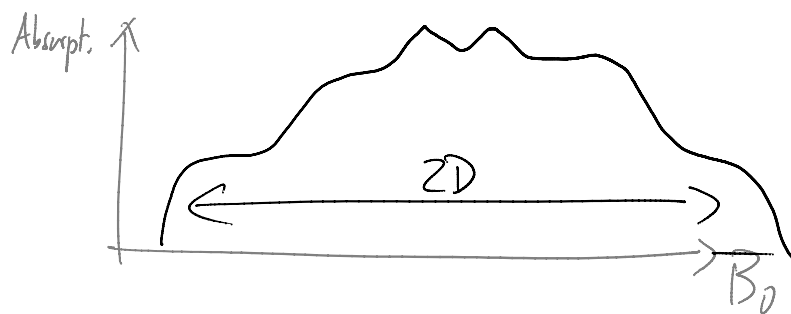
E 1 0 1

1 λ'

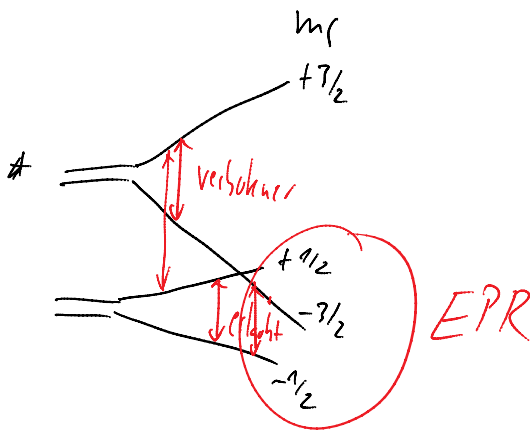
Zerlegung
1 ... 1



Bei ungeordneten Pulverproben
führt dies zu sehr breiten Spektren



$$S = 3/2$$



- { halbzahlige Spin-Systeme $S > 1/2$ sind spektroskopisch einfacher als ganzzahlige, da immer mindestens 1 Übergang beobachtbar ($+1/2 \leftrightarrow -1/2$) }

Übergang $m_s = +1/2 \leftrightarrow -1/2$

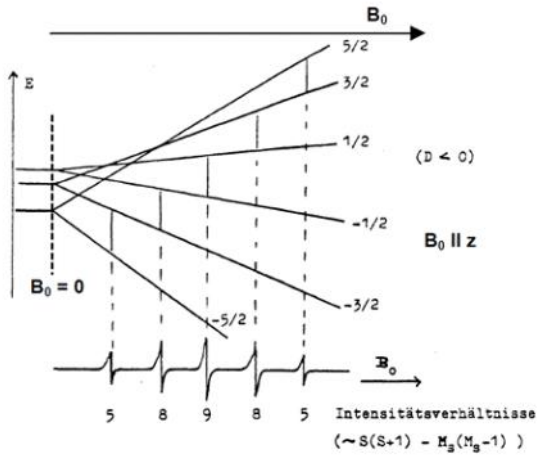
auch im Pulver recht stark;

hängt nur wenig von D, E ab

andere Übergänge $\sim D$ meist sehr breit!

$$S = \frac{5}{2}$$

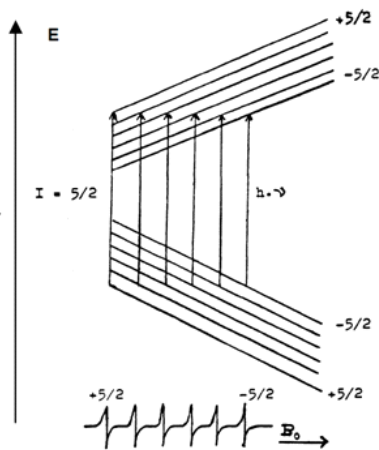
Beispiel Mn^{2+} (kann oft in biologischen Systemen das diamagnetische Mg^{2+} ersetzen)

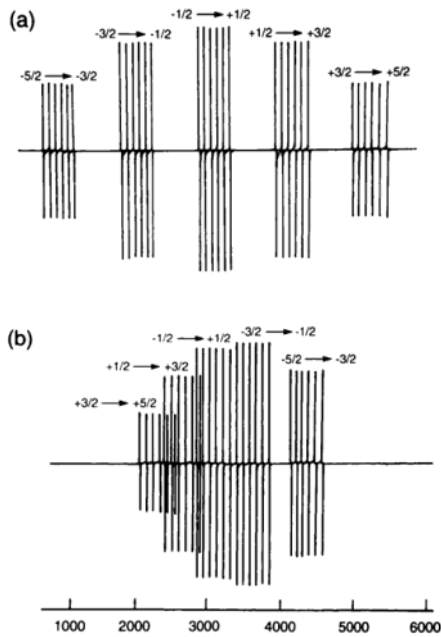


5 unterschiedliche EPR Übergänge

jeweils mit 6 hf-Linien

$Mn (I = \frac{5}{2})$





Eintritt-Spektren

für zwei

Orientierungen vom Magnetfeld B_0

relativ zur Liganden-Symmetrie (D_4h)

Simulation of Mn(II) EPR Spectra Using a Full Spin-Hamiltonian Approach

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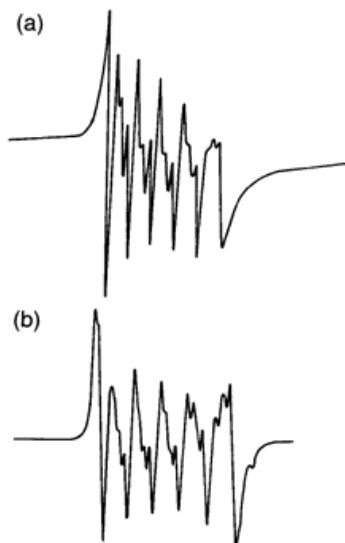


FIG. 9. Experimental and theoretical CW-EPR spectra of Mn(II) aquo. (a) Experimental spectrum of Mn(II) aquo taken at 9 GHz and 77 K. (b) Simulation using our best fit parameters of the ZFS in the full calculation: $D = 155$ G; $E/D = 1/3$. Number of values of $\theta = 70$; number of values of $\phi = 100$. (c) Simulation using Tan, *et al.* (3) parameters for the ZFS in the full calculation: $D = 198$ G; $E/D = 0$. Number of values of $\theta = 200$; number of values of $\phi = 1$. Other parameters used for the calculations are $B_1 = 0.1$ G; $a = -90.0$ G; microwave frequency = 9.1 GHz; temperature = 77 K; resolution = 1.0 G.

Simulation von Hochspinsystemen wie
Mn²⁺ nicht einfach:
Basissatz im Spinhamiltonian ist 36×36

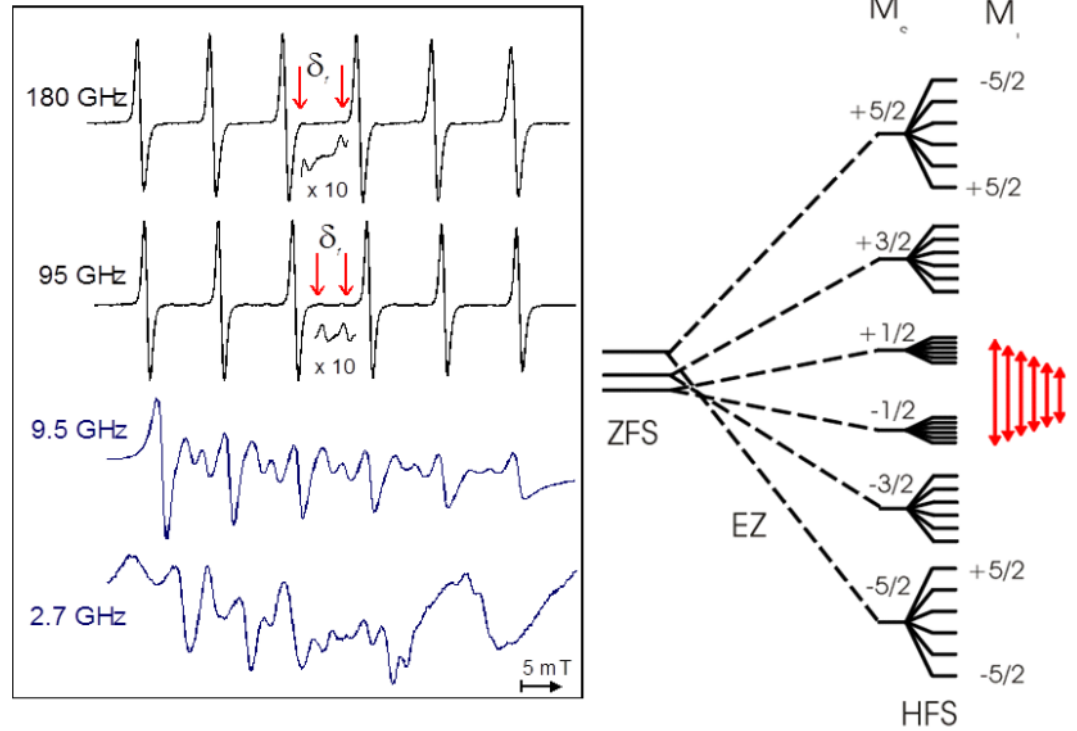
Verbotenen Übergänge $dm_l \neq 0$, $dm_s > 1$

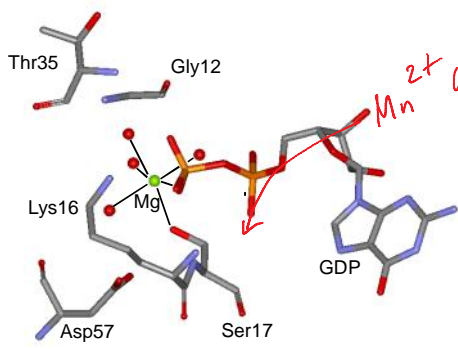
Quantenmechanische Berechnung von
G-Tensoren und hf-Tensoren ebenfalls
nicht einfach:

Spin-Bahn-Kopplung
Relativistische Effekte
d-Orbitale mit mehreren ungepaarten
Spins

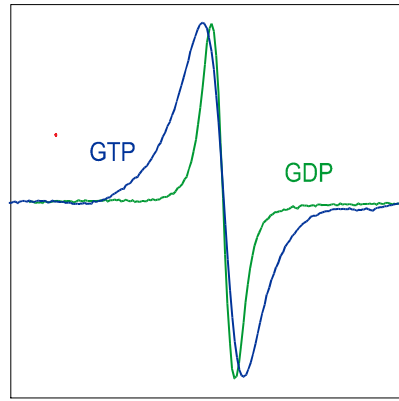
Oft wird nur der zentrale $m_l = \pm 1/2$ Übergang beobachtet

Wird besser aufgelöst bei hohen Feldern





Einzelne hf-Linie von $m_s = \pm 1/2$



Unterschiedliche
Linienbreite durch
Änderung der Liganden
(Änderung in D, E)

Super-hf WW
mit Kernen der
Liganden
(hier $H_2^{17}O$)

$4^{17}O$
 $3^{17}O$

Fe-S Centre

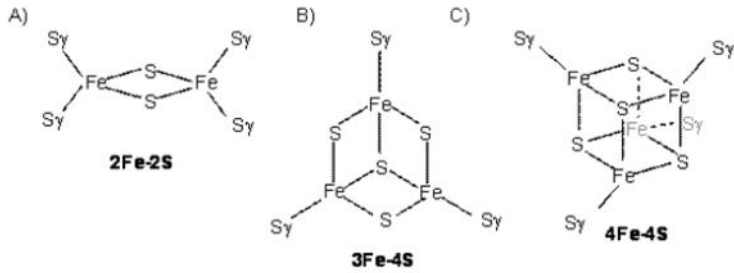


Figure 1: Iron Sulfur Clusters

paramagnetische Fe koppeln
zu einem Gesamtspin S

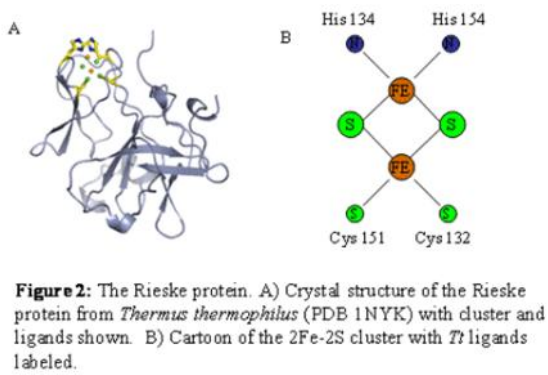
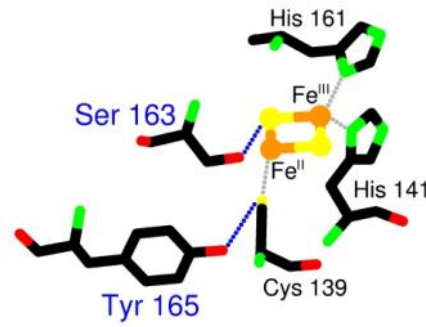


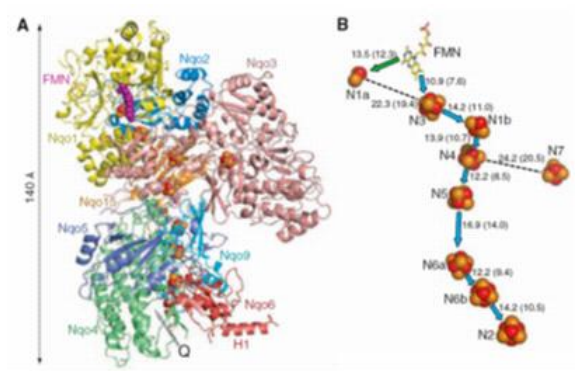
Figure 2: The Rieske protein. A) Crystal structure of the Rieske protein from *Thermus thermophilus* (PDB 1NYK) with cluster and ligands shown. B) Cartoon of the 2Fe-2S cluster with 7 ligands labeled.

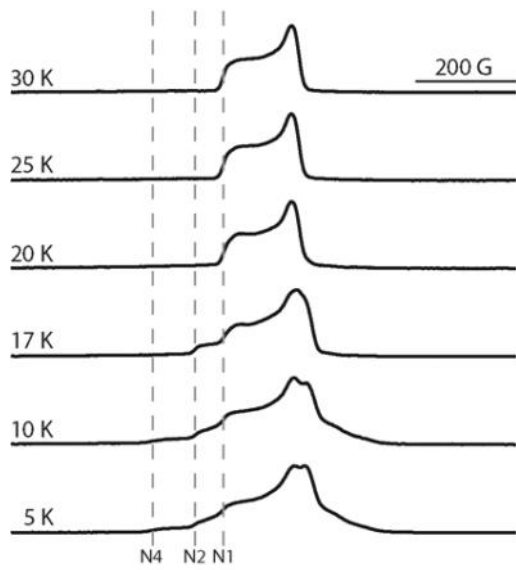


Unterschiedliche
Liganden können
mit
Hyperfine-
Spektroskopie
unterschieden werden

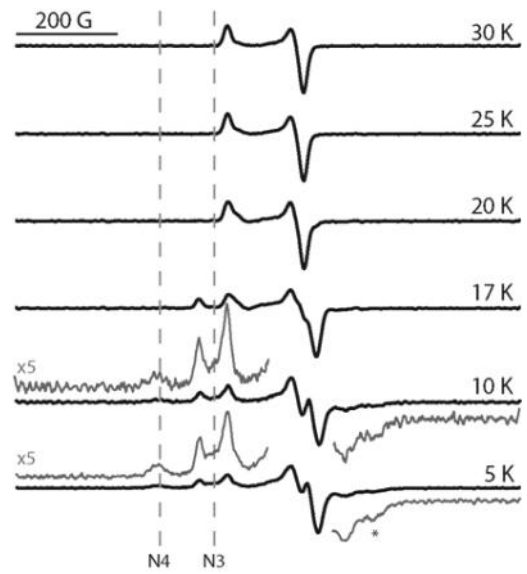
Beispiel: FeS centres of complex I

N_1, N_2, N_3, N_4
observed at different T





absorptionsspectra



derivative EPR spectra