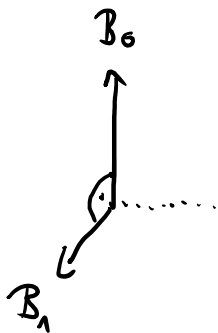
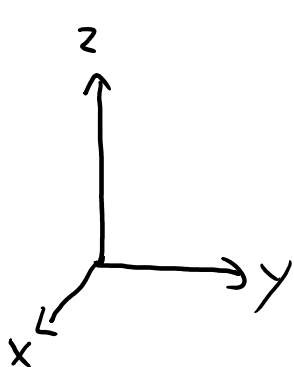


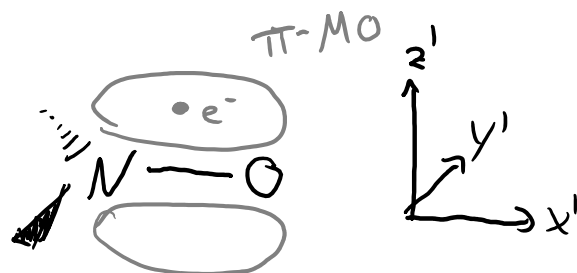
Fast alle WW in MR sind richtungsabhängig!  
(sehr wenige Ausnahmen)  
↳ Anisotropie

Bezugsachse: Laborkoordinatensystem



definiert durch  
äußeres Magnetfeld

anschaulich: Molekül-Koordinatensystem



MO-Struktur

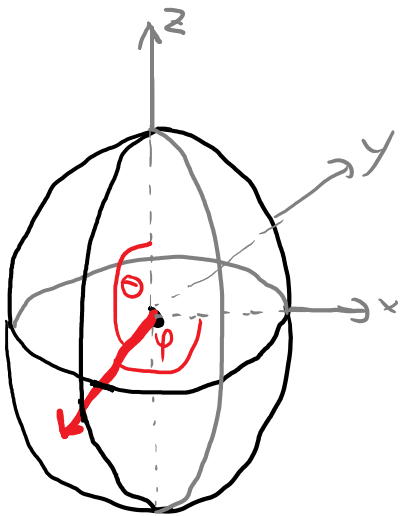
beeinflusst Spin-Moment durch Bahndrehimpuls  
und Spin-Bahn-Kopplung

Weiteres Bsp.: HFI (Dipol-Dipol) zwischen  $e^-$  und  $n$

## Dipol-Dipol-HFI im EPR-Spektrum

$$\hat{A}_{\text{HFI, dip}} = d_{\text{HFI}} (3 \cos^2 \theta - 1) \hat{S}_z \hat{I}_z$$

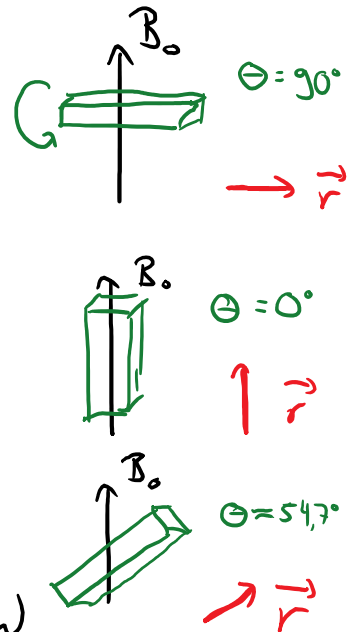
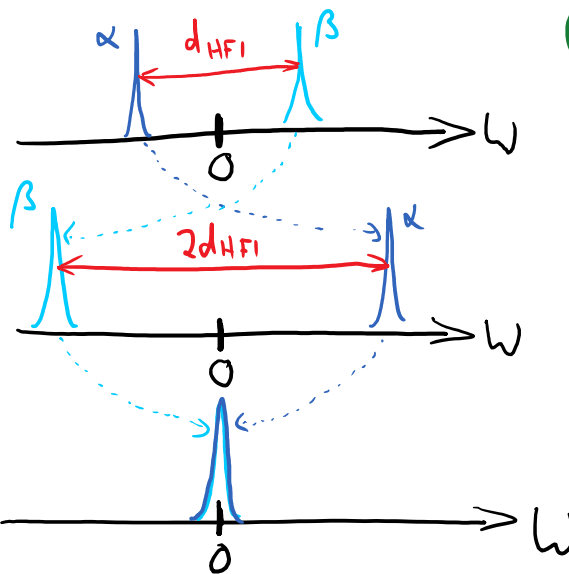
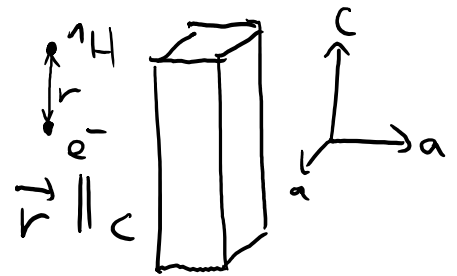
$$d_{\text{HFI}} = \frac{\mu_0 \mu_B g_M g_N}{4 \pi \hbar r^3}$$



Orientierungsvektor  
Einheitskugel  
Laborkoordinatensystem

↳ Winkelabhängigkeit der HFI

↓  
Einkristall:



Achtung: obige Formel nur gültig in Punkt-Dipol-Näherung  
(Abstand zwischen e<sup>-</sup> und Kern ≫ Delokalisation)

typisch: r ≥ 0.25 nm

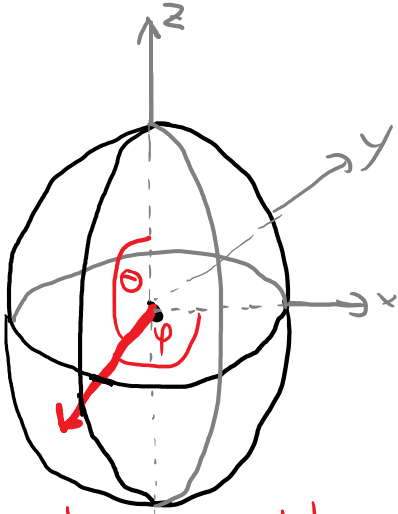
→ andernfalls Integration über Raum nötig!

# Pulver-Spektrum

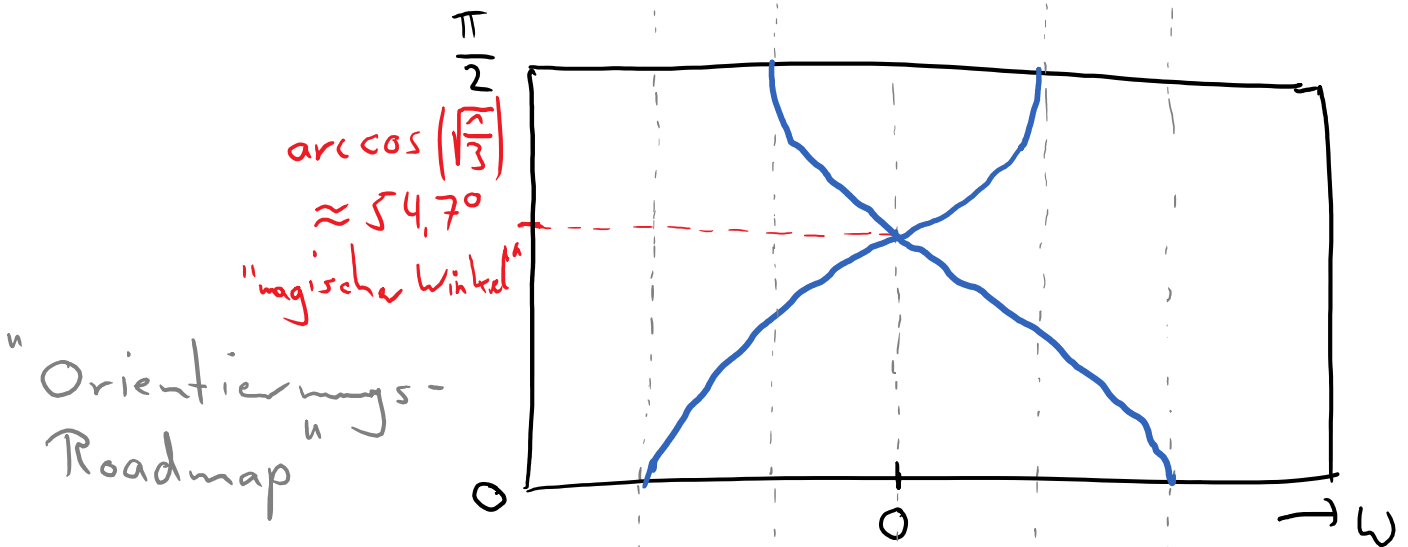
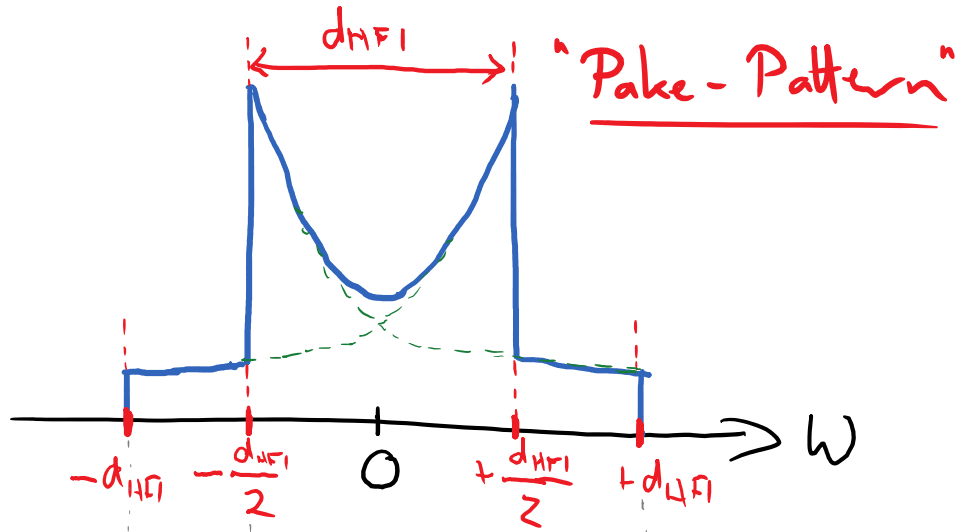
Tuesday, November 21, 2017 1:45 PM

→ Polykristallines Pulver  
oder  
gefrorene Lösung

alle Orientierungen gleichermasse wahrscheinlich  
→ Überlagerung aller möglichen Orientierungen

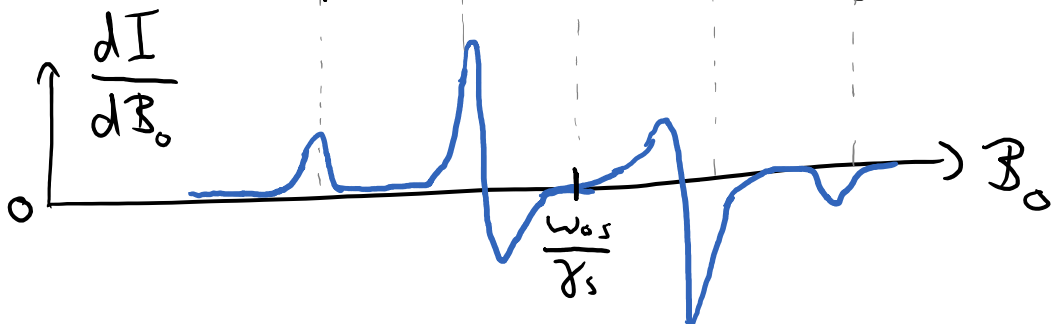


Orientierungsvektor



in EPR oft Absorption in 1. Ableitung zu  $B_0$

→

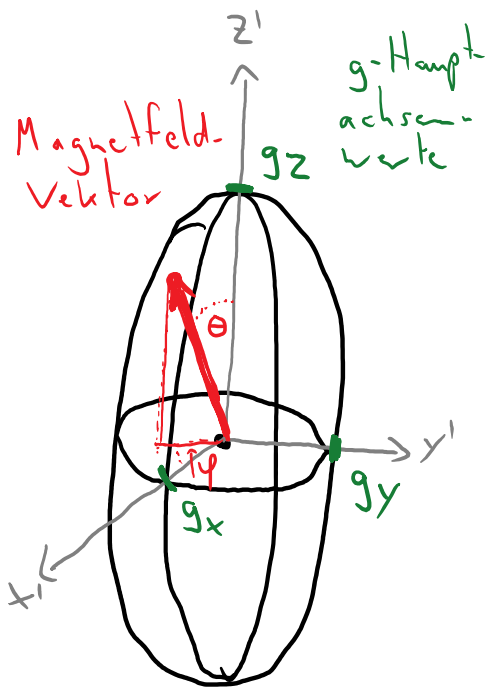


# g-Anisotropie

Tuesday, November 21, 2017 12:16 PM

$$\hat{H}_{EZ} = \frac{\mu_B}{\hbar} \vec{B}_0 \cdot \underline{\underline{g}} \hat{S}$$

Koordinatentransf.  
Rotation von g-Tensor  
ins Laborkoordinatensystem



Tensor-Ellipsoid  
in Diagonal-KS

$$\hat{H}_{EZ} = \frac{\mu_B}{\hbar} B_0 g(\theta, \varphi) \hat{S}_z$$

$$g(\theta, \varphi) = \sqrt{g_x^2 \sin^2 \theta \cos^2 \varphi + g_y^2 \sin^2 \theta \sin^2 \varphi + g_z^2 \cos^2 \theta}$$

$g_i$ : Hauptachsenelemente (Diagonalelemente)  
 $\theta, \varphi$ : Kugelwinkel zwischen g-Diagonal-KS  
und Labor-KS

Parameter zur Beschreibung der g-Matrix:

$g_x, g_y, g_z \rightarrow$  Hauptachsenelemente

$g_{iso}, \Delta g, \eta \rightarrow$  Anisotropie / Asymmetrie

$$g_{iso} = \frac{g_x + g_y + g_z}{3}$$

$$= \frac{1}{3} \text{Tr}(\underline{\underline{g}})$$

↑  
Spur (trace)

$$\Delta g = g_z - g_{iso}$$

Anisotropie

$$\eta = g_y - g_x$$

Asymmetrie

# Symmetriegruppen

Tuesday, November 21, 2017 2:32 PM

kubisch:  $g_x = g_y = g_z$   
 $g_{iso}$

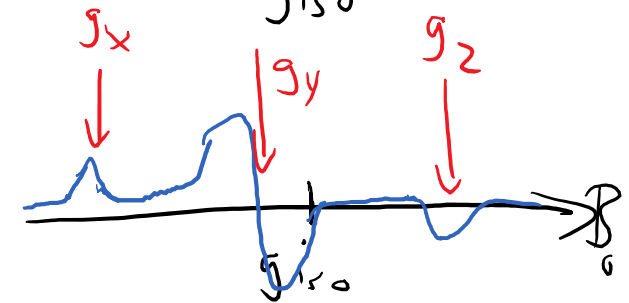
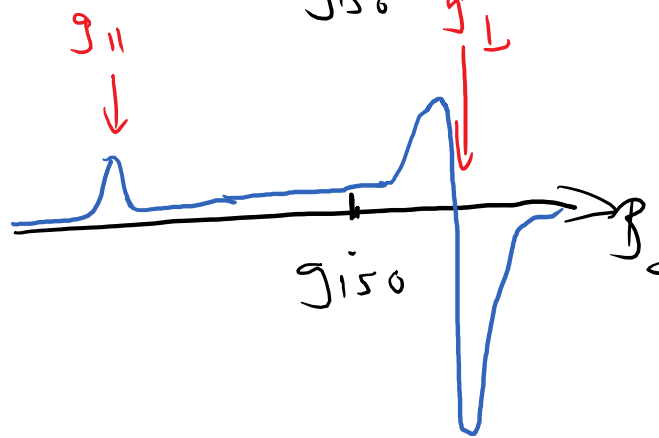
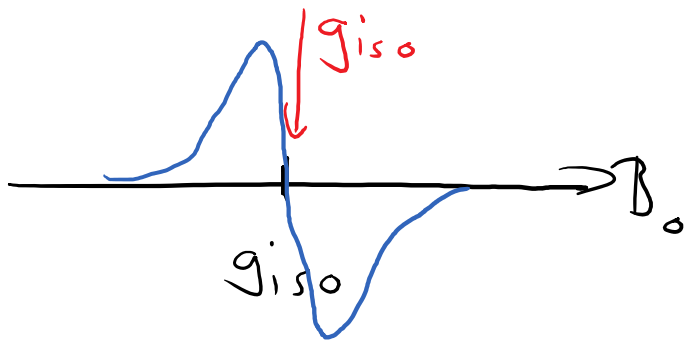
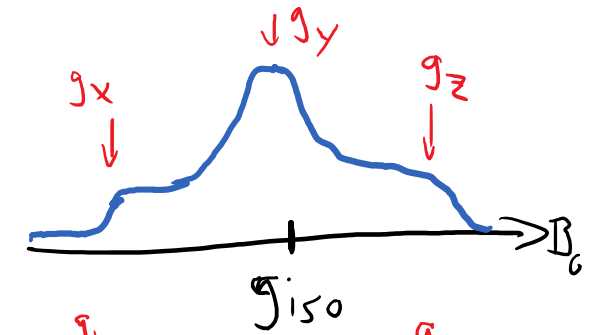
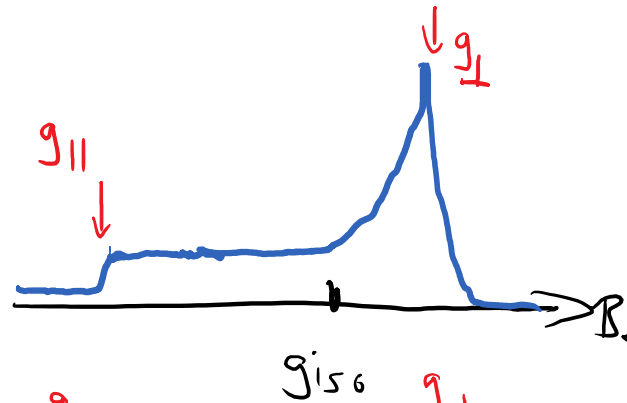
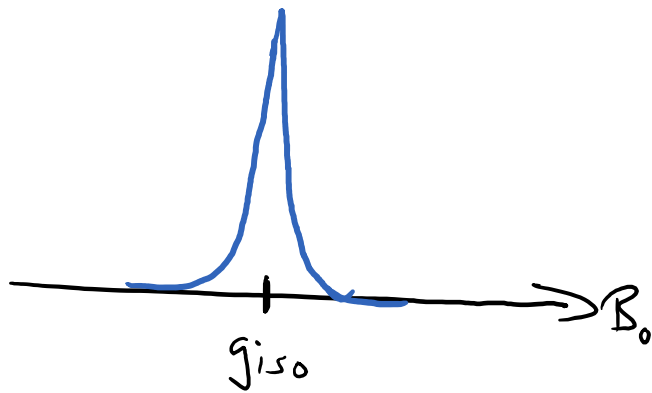
$$\Delta g = 0, \eta = 0$$

axial:  $g_x = g_y \neq g_z$   
 (tetragonal)  $g_{\perp}$   $g_{\parallel}$

$$\Delta g \neq 0, \eta = 0$$

orthorhombisch  
 $g_x \neq g_y \neq g_z$

$$\Delta g \neq 0, \eta \neq 0$$



# g-Matrix / g-Tensor

$$\underline{\underline{g}} = \begin{pmatrix} g_{xx} & g_{xy} & g_{xz} \\ g_{yx} & g_{yy} & g_{yz} \\ g_{zx} & g_{zy} & g_{zz} \end{pmatrix}$$

$\underline{\underline{g}}$  ist symmetrisch

$$\rightarrow g_{ij} = g_{ji}$$

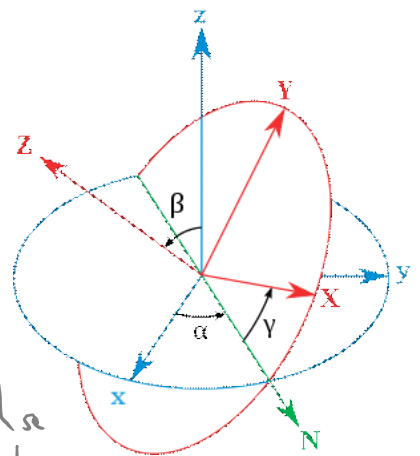
$$\underline{\underline{g}}^T = \underline{\underline{g}}$$

Jede symmetrische Matrix kann diagonalisiert werden:

$$\underline{\underline{g}}' = U \underline{\underline{g}} U^{-1}$$

U: Rotationsmatrix

Rotation um Euler-Winkel

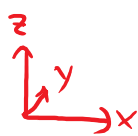
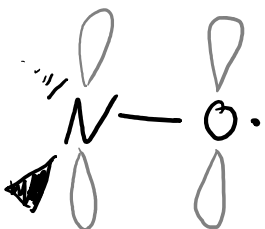


$$\underline{\underline{g}}' = \begin{pmatrix} g_{x'} & & 0 \\ & g_{y'} & \\ 0 & & g_{z'} \end{pmatrix}$$

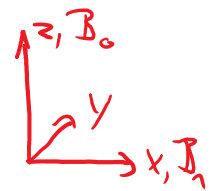
- $\alpha$ : um z-Achse
- $\beta$ : um (neue) x-Achse
- $\gamma$ : um (neue) z-Achse

## Koordinatensysteme (KS)

Molekül-KS  $\longleftrightarrow$  Diagonal-KS "Eigen-KS"  $\longleftrightarrow$  Labor-KS



oft identisch zu Molekül-KS



Auch die WW zwischen  $e^-$  und Kernspin wird durch Tensor 2. Grades (Matrix) beschrieben:

$$\hat{H}_{\text{HFI}} = \sum_{\hat{I}} \underline{\underline{A}} \hat{I} = a_{\text{iso}} \sum_{\hat{I}} \hat{I} + \underline{\underline{T}} \hat{I}$$

$\uparrow$  Vektor      $\uparrow$  Vektor  
 $\uparrow$  Matrix

$$\underline{\underline{A}} = a_{\text{iso}} \underline{\underline{1}} + \underline{\underline{T}}$$

in Hochfeld-Näherung:  $\hat{H}_{\text{HFI}} = A_{zz} \hat{S}_z \hat{I}_z = (a_{\text{iso}} + T_{zz}) \hat{S}_z \hat{I}_z$

$\Rightarrow a_{\text{iso}}$  entspricht Spur von  $\underline{\underline{A}}$ :  $a_{\text{iso}} = \frac{1}{3} \text{Tr}(\underline{\underline{A}})$   
 $\uparrow$  trace

$\underline{\underline{T}}$  ist spurlose Matrix:  $T_{xx} + T_{yy} + T_{zz} = 0$

in Diagonal-KS von  $\underline{\underline{A}}$ :  $\underline{\underline{T}} = \begin{pmatrix} -T & & 0 \\ & -T & \\ 0 & & +2T \end{pmatrix}$

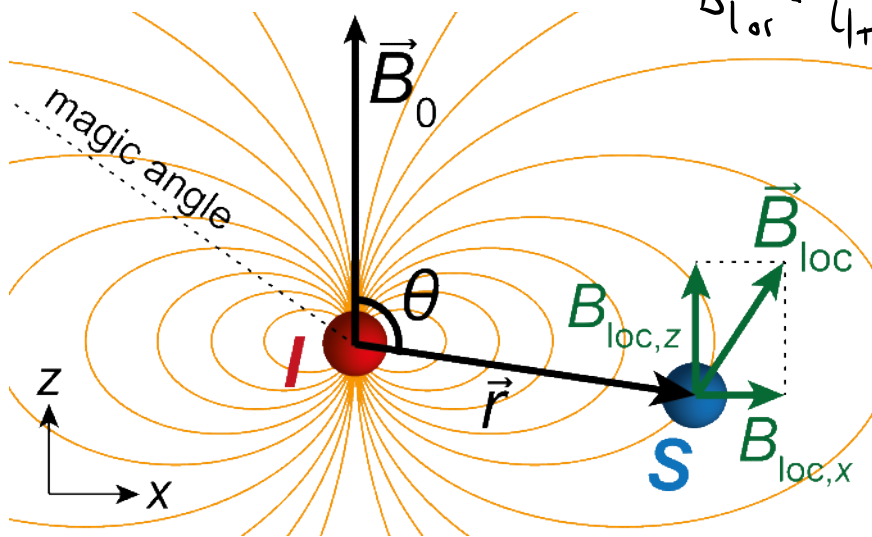
Rotation ins Labor-KS

$\Rightarrow T = d_{\text{HFI}} \leadsto T_z(\theta) = d_{\text{HFI}} (3 \cos^2 \theta - 1)$

in Punkt-Dipol-Näherung ist  $\underline{\underline{A}}$  immer axial!

Lokales Feld:

$$\vec{B}_{loc} = \frac{\mu_0}{4\pi} \left[ \frac{3\vec{r}(\vec{M}_I \cdot \vec{r})}{|\vec{r}|^5} - \frac{\vec{M}_I}{|\vec{r}|^3} \right]$$



$$\frac{\vec{r}}{|\vec{r}|} = \vec{e}_r$$

Einheitsvektor auf  
e-n-Verbindungs-  
Achse

$$\vec{B}_{loc} = \frac{\mu_0}{4\pi|\vec{r}|^3} \left[ 3\vec{e}_r(\vec{M}_I \cdot \vec{e}_r) - \vec{M}_I \right]$$

$$\vec{e}_r = \begin{pmatrix} \sin \Theta \cos \varphi \\ \sin \Theta \sin \varphi \\ \cos \Theta \end{pmatrix}$$

HF-Näherung: nur z-Komponente:

$$B_{loc,z} = \frac{\mu_0}{4\pi|\vec{r}|^3} (3 \cos^2 \Theta - 1) M_{I,z}$$

schnelle Rotation in Lösung:

Integration über alle  $\Theta$

$$\int_0^{2\pi} (3 \cos^2 \Theta - 1) d\Theta = 0$$

Dipol-Dipol-WW in Lösung ausgemittelt!



# Dipolare HFI

Tuesday, November 7, 2017

9:32 AM

$$E_{DD} = -\frac{\mu_0}{4\pi} \left( \frac{3(\vec{\mu}_S \cdot \vec{r})(\vec{\mu}_I \cdot \vec{r})}{|\vec{r}|^5} - \frac{\vec{\mu}_S \cdot \vec{\mu}_I}{|\vec{r}|^3} \right)$$

$$\vec{\mu}_S = -g\mu_B \vec{S}$$

$$\vec{\mu}_I = g\mu_N \vec{I}$$

↓ QM

$$\hat{H}_{DD} = \frac{\mu_0 \mu_B g \mu_N g_N}{4\pi \hbar} \left( \frac{3(\hat{S} \cdot \vec{r})(\hat{I} \cdot \vec{r})}{|\vec{r}|^5} - \frac{\hat{S} \cdot \hat{I}}{|\vec{r}|^3} \right)$$

$$= \frac{\mu_0 \mu_B g \mu_N g_N}{4\pi \hbar |\vec{r}|^3} \left( 3(\hat{S} \cdot \vec{e}_r)(\hat{I} \cdot \vec{e}_r) - \hat{S} \cdot \hat{I} \right)$$

$$\hat{S} = (\hat{S}_x, \hat{S}_y, \hat{S}_z) \quad \hat{I} = (\hat{I}_x, \hat{I}_y, \hat{I}_z) \quad \vec{e}_r = \begin{pmatrix} \sin \Theta \cos \Psi \\ \sin \Theta \sin \Psi \\ \cos \Theta \end{pmatrix}$$

$$\hat{S} \cdot \vec{e}_r = \hat{S}_x \sin \Theta \cos \Psi + \hat{S}_y \sin \Theta \sin \Psi + \hat{S}_z \cos \Theta$$

$$\hat{I} \cdot \vec{e}_r = \hat{I}_x \sin \Theta \cos \Psi + \hat{I}_y \sin \Theta \sin \Psi + \hat{I}_z \cos \Theta$$

$$3(\hat{S} \cdot \vec{e}_r)(\hat{I} \cdot \vec{e}_r) - \hat{S} \cdot \hat{I}$$

$$= 3 \sin^2 \Theta \left[ \cos^2 \Psi \hat{S}_x \hat{I}_x + \sin^2 \Psi \hat{S}_y \hat{I}_y + \cos \Psi \sin \Psi (\hat{S}_x \hat{I}_y + \hat{S}_y \hat{I}_x) \right]$$

$$+ 3 \cos \Theta \sin \Theta \left[ \cos \Psi (\hat{S}_z \hat{I}_x + \hat{S}_x \hat{I}_z) + \sin \Psi (\hat{S}_z \hat{I}_y + \hat{S}_y \hat{I}_z) \right]$$

$$+ 3 \cos^2 \Theta \hat{S}_z \hat{I}_z$$

$$- \hat{S}_x \hat{I}_x - \hat{S}_y \hat{I}_y - \hat{S}_z \hat{I}_z$$

⇒ dipolares Alphabet

$$\hat{S}_+ = \hat{S}_x + i\hat{S}_y \quad \hat{S}_- = \hat{S}_x - i\hat{S}_y$$

$$\hat{I}_+ = \hat{I}_x + i\hat{I}_y \quad \hat{I}_- = \hat{I}_x - i\hat{I}_y$$

$$\cos \Psi \pm i \sin \Psi = e^{\pm i\Psi}$$

# Dipolares Alphabet

Tuesday, November 7, 2017 10:11 AM

$$\hat{H}_{DD} = \frac{M_0 M_B g M_n g_n}{4\pi \hbar |\vec{r}|^3} (A + B + C + D + E + F)$$

$$A = (3 \cos^2 \Theta - 1) \hat{S}_z \hat{I}_z \quad \text{säkulare HFI}$$

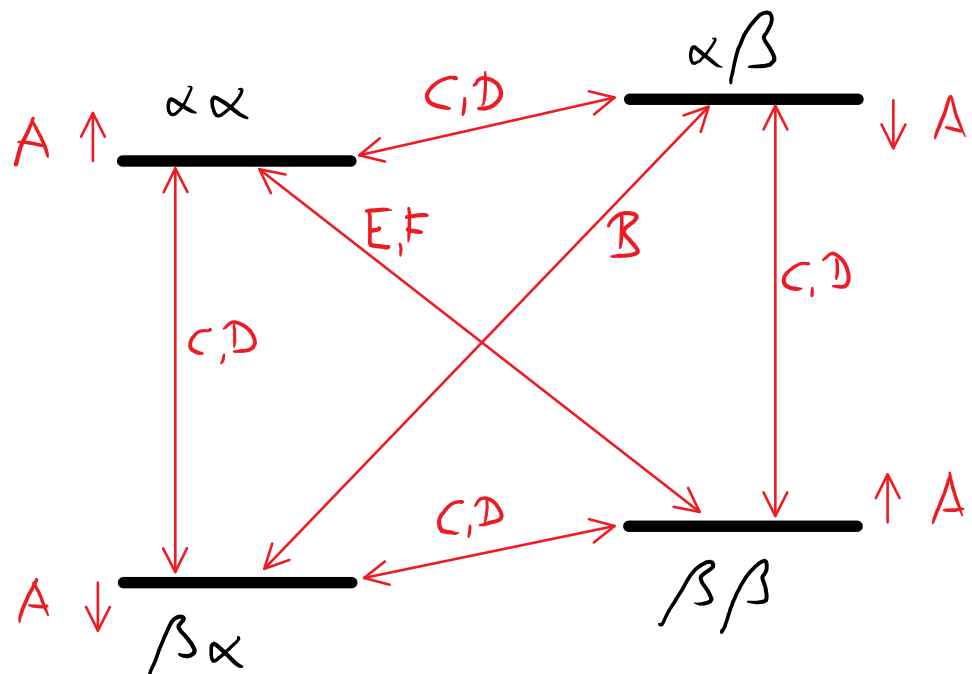
$$B = \frac{1}{4} (3 \cos^2 \Theta - 1) (\hat{S}_+ \hat{I}_- + \hat{S}_- \hat{I}_+) \quad \text{Nullquanten-Kohärenz}$$

$$C = \frac{3}{2} \sin \Theta \cos \Theta e^{i\varphi} (\hat{S}_z \hat{I}_+ + \hat{S}_+ \hat{I}_z) \quad \left. \begin{array}{l} \text{Anti-} \\ \text{Phasen-} \\ \text{Kohärenz} \end{array} \right\}$$

$$D = \frac{3}{2} \sin \Theta \cos \Theta e^{-i\varphi} (\hat{S}_z \hat{I}_- + \hat{S}_- \hat{I}_z) \quad \left. \begin{array}{l} \text{Anti-} \\ \text{Phasen-} \\ \text{Kohärenz} \end{array} \right\}$$

$$E = \frac{3}{4} \sin^2 \Theta e^{2i\varphi} \hat{S}_+ \hat{I}_+ \quad \left. \begin{array}{l} \text{Doppelquanten-} \\ \text{Kohärenz} \end{array} \right\}$$

$$F = \frac{3}{4} \sin^2 \Theta e^{-2i\varphi} \hat{S}_- \hat{I}_- \quad \left. \begin{array}{l} \text{Doppelquanten-} \\ \text{Kohärenz} \end{array} \right\}$$



→ Abweichung  $g$  von  $g_e$

$g_e = 2.0023...$

Erinnerung:  $\hat{H}_{EZ} = \frac{\mu_B}{\hbar} \vec{B}_0 \cdot g \vec{S}$

Obiger Hamiltonian ist effektives Spin-Hamiltonian inkl. bögemischtem Bahnmoment (gemischte Zustandsbasis)

eigentlich:  $\hat{H}_{EZ} = \hat{H}_S + \hat{H}_L + \hat{H}_{LS} = \frac{\mu_B}{\hbar} \vec{B}_0 \cdot (\hat{L} + g_e \hat{S}) + \lambda \hat{L} \hat{S}$

starke LS-Kopplung

↳ Gesamtdrehimpuls

$\vec{J} = \vec{L} + \vec{S}$

Bahndrehimpuls  $\hat{L}$  Spin  $\hat{S}$  Spin-Bahn-Kopplungskonstante  $\lambda$

$\Rightarrow \hat{H}_{EZ} = \frac{\mu_B}{\hbar} B_0 g_J J_z$  (isotrope Näherung)

Landé g-Faktor

$g_J = g_L \frac{J(J+1) + L(L+1) - S(S+1)}{2J(J+1)} + g_S \frac{J(J+1) - L(L+1) + S(S+1)}{2J(J+1)} \approx \frac{3J(J+1) - L(L+1) + S(S+1)}{2J(J+1)}$

"Spin-Only"-Näherung

für nicht-en-artete  $GZ$  ist Bahndrehimpuls "gequentscht" →  $L=0$

$\uparrow$  Zahl der Zellen

Bsp.:  $Cu^{2+} d^9$   $\uparrow\uparrow\uparrow$

aber: Mischung von elektronisch angeregten Zuständen zu Grundzustand: →  $\lambda$  ist sehr klein

$\Rightarrow \hat{H}_{EZ} = \frac{\mu_B}{\hbar} B_0 \cdot g \vec{S}$  mit

$g = g_e \mathbb{1} + 2\lambda \underline{\underline{\Lambda}}$

Störungsansatz:

$\Lambda_{ij} = \sum_{n \neq 0} \frac{\langle \psi_0 | \hat{L}_i | \psi_n \rangle \langle \psi_n | \hat{L}_j | \psi_0 \rangle}{\epsilon_0 - \epsilon_n}$