

# Störungstheorie

Tuesday, November 6, 2018 11:04 AM

→ zeitunabhängig  
→ 2-Zustandssystem

$$\hat{A} = \hat{A}_0 + \lambda \hat{V}$$

ungestörtes Hamiltonian    Störung

$$\hat{A}_0 = \begin{pmatrix} \epsilon_\alpha & 0 \\ 0 & \epsilon_\beta \end{pmatrix} \quad \lambda \hat{V} = \begin{pmatrix} 0 & \lambda V \\ \lambda V & 0 \end{pmatrix} \quad " \lambda \rightarrow 0 "$$

$$\hookrightarrow \left. \begin{aligned} \hat{A}_0 |\alpha\rangle &= \epsilon_\alpha |\alpha\rangle \\ \hat{A}_0 |\beta\rangle &= \epsilon_\beta |\beta\rangle \end{aligned} \right\} \epsilon_\alpha - \epsilon_\beta = \Delta E_0$$

$$\Rightarrow \underline{(\hat{A}_0 + \lambda \hat{V}) |\chi_k\rangle = E_k |\chi_k\rangle} \quad \rightsquigarrow \boxed{E_k = ? \quad \chi_k = ?}$$

$$\text{Basis: } \{|\alpha\rangle, |\beta\rangle\} \xrightarrow{\text{Störung}} \left\{ \underbrace{|\alpha\rangle + q_1 |\beta\rangle}_{|1\rangle}; \underbrace{|\beta\rangle + q_2 |\alpha\rangle}_{|2\rangle} \right\}$$

mit  $p_k^2 + q_k^2 = 1$

$$\text{Für } \lambda V \ll |\epsilon_\alpha - \epsilon_\beta|: \quad E_1 = \epsilon_\alpha + \lambda E_1^{(1)} + \lambda^2 E_1^{(2)} + \dots$$

$$E_2 = \epsilon_\beta + \lambda E_2^{(1)} + \lambda^2 E_2^{(2)} + \dots$$

$$q_1 = 0 + \lambda q_1^{(1)} + \lambda^2 q_1^{(2)} + \dots$$

$$q_2 = 0 + \lambda q_2^{(1)} + \lambda^2 q_2^{(2)} + \dots$$

ST 1. Ordnung → alle Terme mit  $\lambda^n, n \geq 1 \rightarrow 0$

$$\Rightarrow \lambda E_1^{(1)} = \langle \alpha | \lambda \hat{V} | \alpha \rangle = 0; \quad \lambda E_2^{(1)} = \langle \beta | \lambda \hat{V} | \beta \rangle = 0$$

$$\lambda q_1^{(1)} = \frac{\langle \alpha | \lambda \hat{V} | \beta \rangle}{\epsilon_\beta - \epsilon_\alpha} = -\frac{\lambda V}{\Delta E_0}; \quad \lambda q_2^{(1)} = \frac{\langle \beta | \lambda \hat{V} | \alpha \rangle}{\epsilon_\alpha - \epsilon_\beta} = +\frac{\lambda V}{\Delta E_0}$$

ST 2. Ordnung → inkl.  $\lambda^2$ -Terme

$$\Rightarrow E_1^{(2)} = -E_2^{(2)} = \frac{\langle \alpha | \lambda \hat{V} | \beta \rangle \langle \beta | \lambda \hat{V} | \alpha \rangle}{\epsilon_\beta - \epsilon_\alpha} = -\frac{(\lambda V)^2}{\Delta E_0}$$

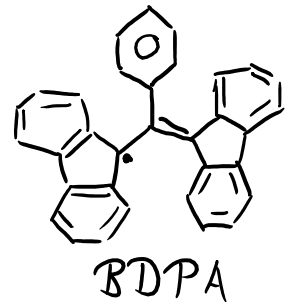
# Anwendungen der EPR

Monday, October 29, 2018 3:08 PM

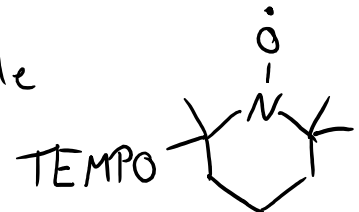
- chemische Analyse, z.B. Identifikation von Radikal-  
Intermediaten  
g-Faktor, HFI-Multiplizität (isotrop)
- Strukturklärung, z.B. Komplexgeometrie  
g-Tensor, Punkt-dipolare HFI (anisotrop)
- Redox-Prozesse in Materialien  
g-Tensor, A-Tensor (→ Fingerprinting)
- chemische Umgebung von Spin-Sonden  
g-Faktor, HFI-Aufspaltung
- Abstandsmessung in (Bio-)Polymeren (→ Faltung)  
dipolare e-e-WW
- sonstiges (z.B. Lebensmittel-Kontrolle)

## Probensysteme

- organische Radikale z.B. C-basiert
  - ↳ Curie-Weiss-Paramagnetismus



Nitroxide



- Übergangsmetallionen/Lanthanoide  
z.B.  $\text{Cu}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Gd}^{3+}$

- Leitungselektronen → Pauli-Paramagnetismus

HFI zu 1 Kern: Multiplizität  $M = 2I + 1$

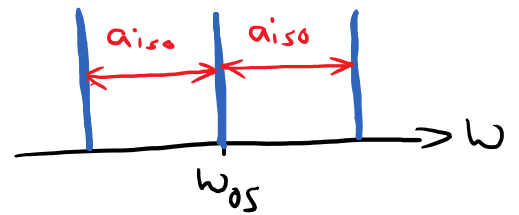
$I = \frac{1}{2}$  ( $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{15}\text{N}$ ,  $^{19}\text{F}$ , ...)

↳ Dublett



$I = 1$  ( $^2\text{H}$ ,  $^{14}\text{N}$ , ...)

↳ Triplett

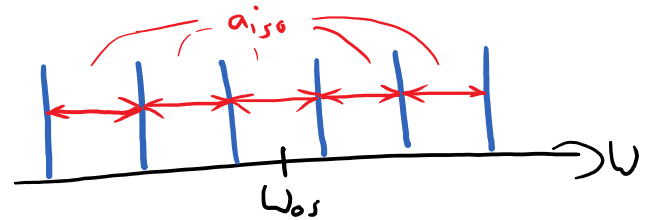


⋮

$I = \frac{5}{2}$  ( $^{55}\text{Mn}$ )

↳ Sextett

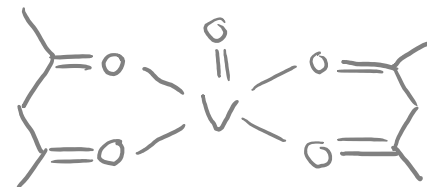
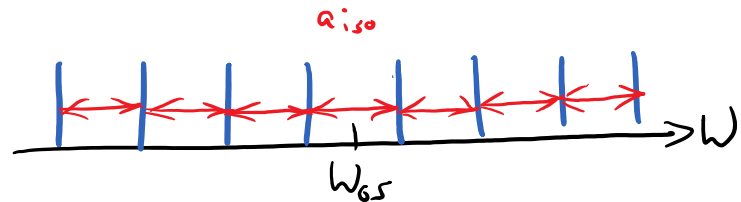
z.B.  $\text{Mn}(\text{OH}_2)_6\text{Cl}_2$



$I = \frac{7}{2}$  ( $^{51}\text{V}$ )

↳ Oktett

z.B.  $\text{VO}(\text{acac})_2$

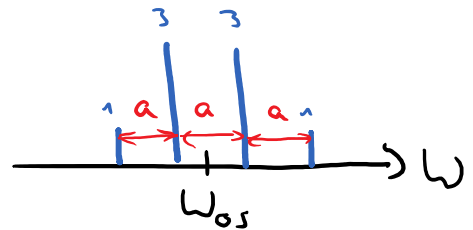


# HFI zu $>1$ äquivalenten Kernen

$M = 2N \cdot I + 1$   
 N: äquivalente Kerne

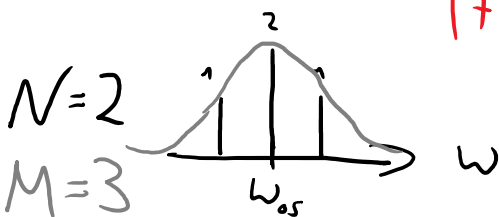
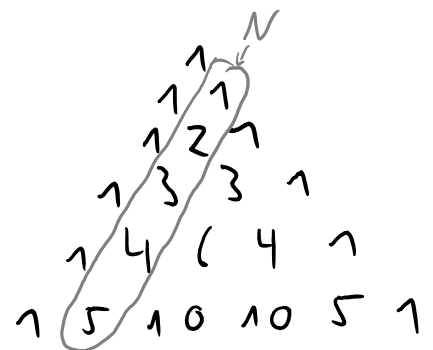
Bsp.:  $\bullet \text{CH}_3$      $N=3$      $I=\frac{1}{2}$      $\leadsto M=4$

Erklärung:  
 mögliche Kombinationen:

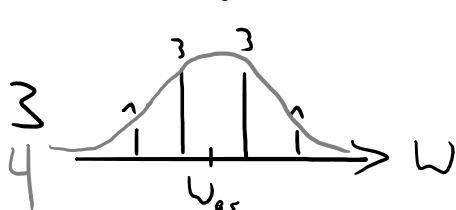


Kern 1	Kern 2	Kern 3	$\epsilon_{\text{HFI}}/h$
$\alpha$	$\alpha$	$\alpha$	$(-a-a-a)/2 = -\frac{3}{2}a$
$\alpha$	$\alpha$	$\beta$	$(-a-a+a)/2$
$\alpha$	$\beta$	$\alpha$	$(-a+a-a)/2$
$\beta$	$\alpha$	$\alpha$	$(+a-a-a)/2$
$\alpha$	$\beta$	$\beta$	$(-a+a+a)/2$
$\beta$	$\alpha$	$\beta$	$(+a-a+a)/2$
$\beta$	$\beta$	$\alpha$	$(+a+a-a)/2$
$\beta$	$\beta$	$\beta$	$(+a+a+a)/2 = +\frac{3}{2}a$

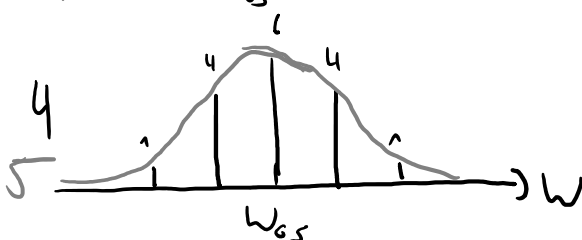
allgemein: Pascalsches Dreieck  
 (für  $I = \frac{1}{2}$ )



Poisson-  
 Verteilung

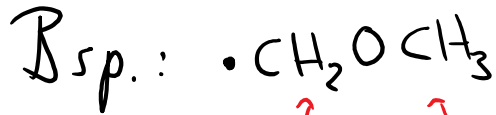


(Gauß-  
 Einhüllende)



HFI zu  $> 1$  nicht-äquivalenten Kernen

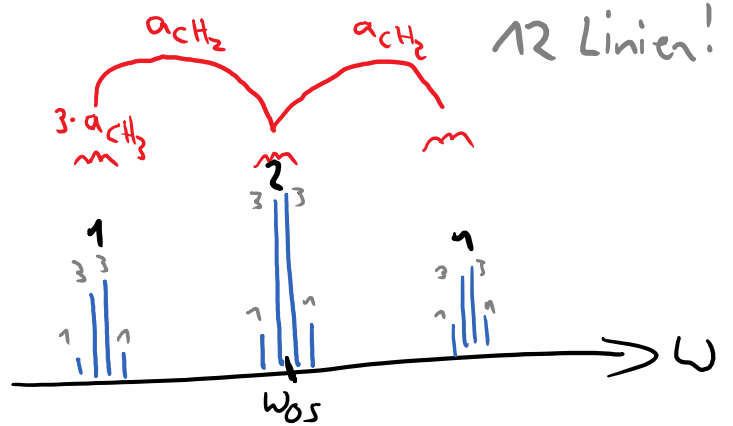
Individuelle Multiplizitäten sind multiplikativ!



↑  
Triplet  
große HFI

↑  
Quartett  
kleine HFI

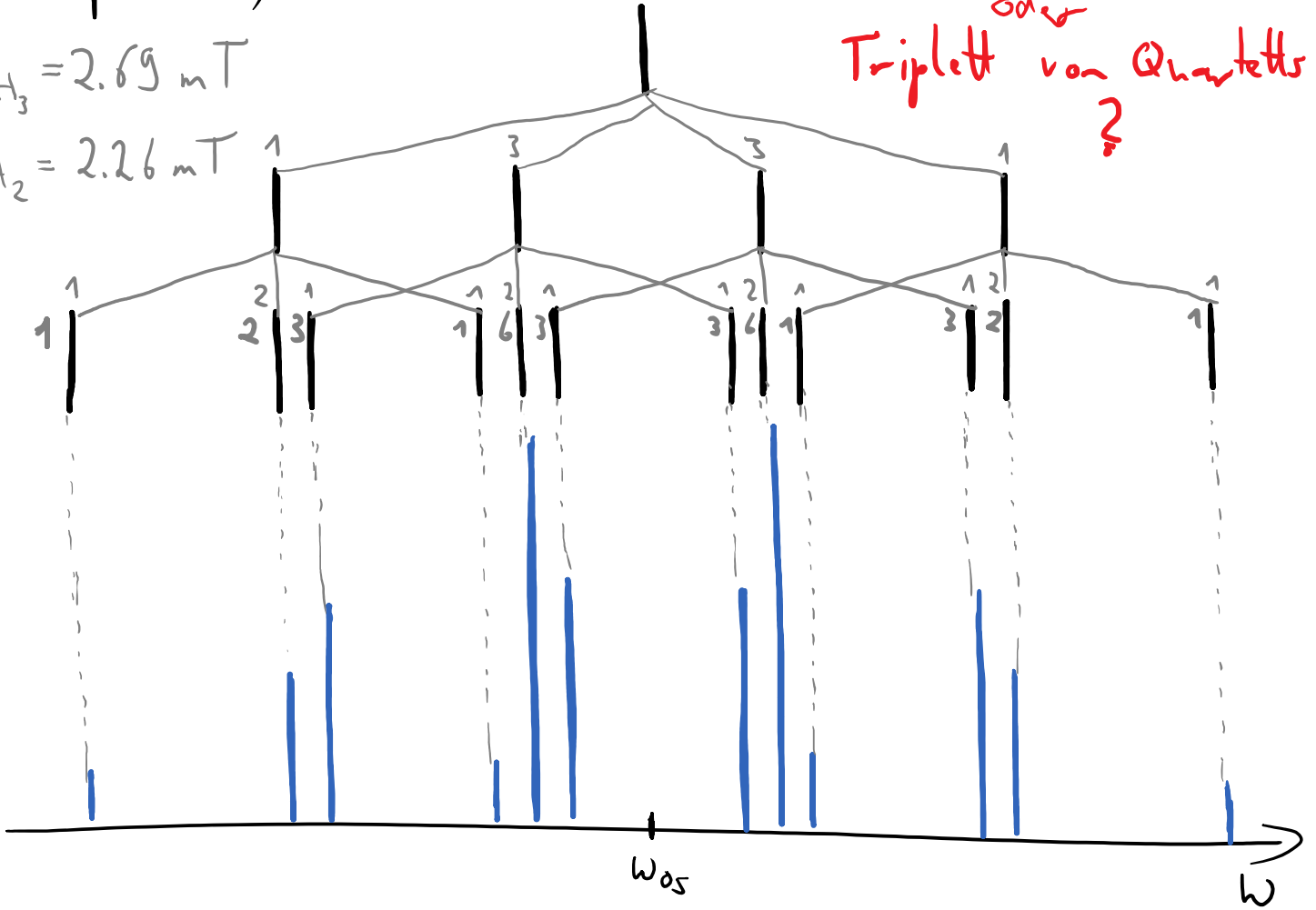
hier:  $a_{\text{CH}_3} \ll a_{\text{CH}_2}$



Quartett von Triplets  
oder  
Triplet von Quartets  
?

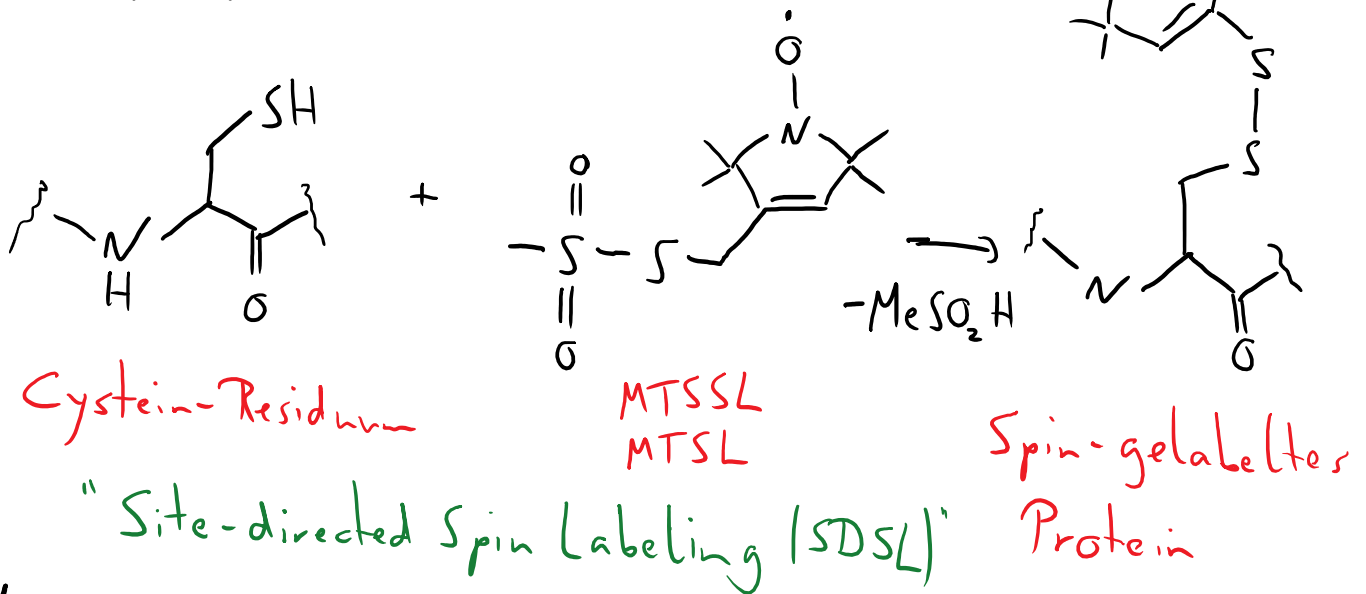
$a_{\text{CH}_3} = 2.69 \text{ mT}$

$a_{\text{CH}_2} = 2.26 \text{ mT}$



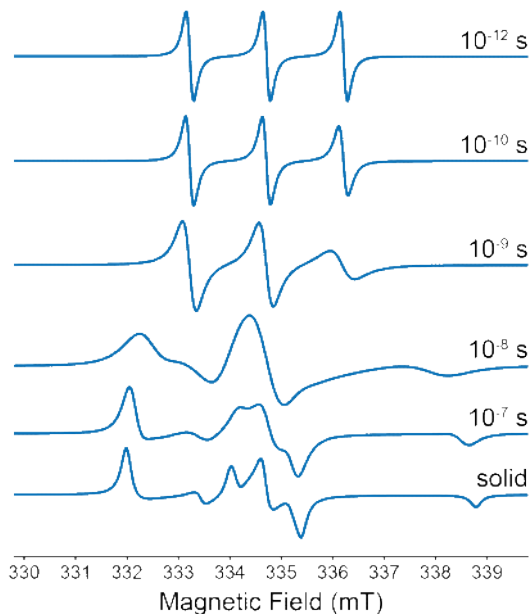
# Site-directed spin labeling (SDSL)

Friday, January 26, 2018 3:56 PM



## Anwendungen

Sonde für chemische Umgebung  
→ Mobilität



Rotationskorrelationszeit  $\tau_c$

$$\text{wenn } \tau_c \approx \frac{1}{\Delta \omega_{\text{aniso}}}$$

↳ Übergang von (isotropem) Lösungsspektrum zu Festkörperspektrum

→ Polarität →  $g_{\text{iso}}$

→ Protizität →  $a_{\text{iso}}$

Anisotropie von  $g$  und  $A$  Tensoren!