HFI in der Pseudo-Hochfeld-Näherung

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$$\hat H = \omega_{0S}\hat S_z + \omega_{0I}\hat I_z + \hat{\vec S}\underline{\underline{A}}\hat{\vec I}$$

$$\hat{\vec S}\underline{\underline{A}}\hat{\vec I} = A_{xx}\hat S_x\hat I_x + A_{xy}\hat S_x\hat I_y + A_{xz}\hat S_x\hat I_z + A_{yx}\hat S_y\hat I_x + A_{yy}\hat S_y\hat I_y + A_{yz}\hat S_y\hat I_z + A_{zx}\hat S_z\hat I_x + A_{zy}\hat S_z\hat I_y + \boxed{A_{zz}\hat S_z\hat I_z}$$

vollständige HFI

Pseudo-Hochfeld

Hochfeld

Näherung

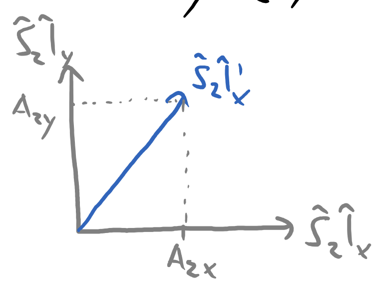
Pseudo-Hochfeld ist relevante Näherung!

$$\hat H = \omega_{0S}\hat S_z - \omega_{0I}\hat I_z + A_{zz}\hat S_z\hat I_z + A_{zx}\hat S_z\hat I_x + A_{zy}\hat S_z\hat I_y$$

Rotation des Kernspin-Raumes um $\hat I_z$

$A = A_{zz}$

$B = \sqrt{A_{zx}^2 + A_{zy}^2}$



$$\hat H = \omega_{0S}\hat S_z - \omega_{0I}\hat I_z + A\hat S_z\hat I_z + B\hat S_z\hat I'_x$$

säkulare HFI / pseudo-säkulare HFI

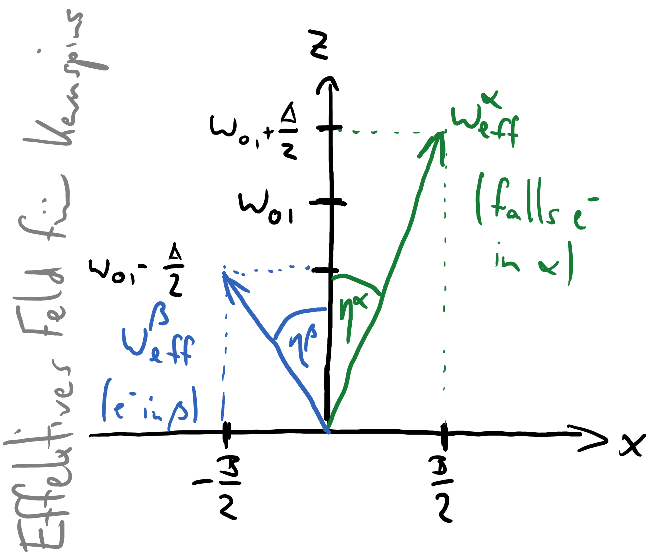
Begründung Pseudo-Hochfeld:

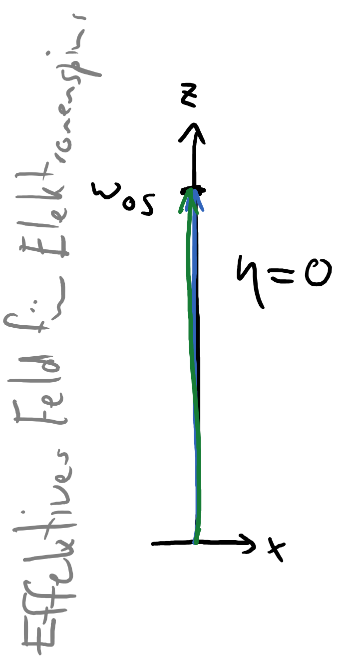
$\omega_{0S}/2\pi = 9$ GHz

$\omega_{0I}/2\pi \approx 15$ MHz

$A, B/2\pi \approx 10$ MHz

$\Rightarrow A, B \approx \omega_{0I} \ll \omega_{0S}$





Block-diagonaler Hamiltonian

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$$\hat H = \underbrace{\omega_{0S}\,\hat S_z + \omega_{0I}\,\hat I_z + A\,\hat S_z \hat I_z}_{\text{diagonal}} + \underbrace{B\,\hat S_z \hat I_x}_{\text{nicht-diagonal}}$$

als Matrix:

$$\hat H = \begin{array}{c} \\ \langle\alpha\alpha| \\ \langle\alpha\beta| \\ \langle\beta\alpha| \\ \langle\beta\beta| \end{array} \begin{array}{c} \begin{array}{cccc} |\alpha\alpha\rangle & |\alpha\beta\rangle & |\beta\alpha\rangle & |\beta\beta\rangle \end{array} \\ \left(\begin{array}{cc|cc} \frac{\omega_{0S}}{2}+\frac{\omega_{0I}}{2}+\frac{A}{4} & \frac{B}{4} & & \\ \frac{B}{4} & \frac{\omega_{0S}}{2}-\frac{\omega_{0I}}{2}-\frac{A}{4} & & \\ \hline & & -\frac{\omega_{0S}}{2}+\frac{\omega_{0I}}{2}-\frac{A}{4} & -\frac{B}{4} \\ & & -\frac{B}{4} & -\frac{\omega_{0S}}{2}-\frac{\omega_{0I}}{2}+\frac{A}{4} \end{array}\right) \end{array}$$

Hamiltonian ist Block-Diagonal in elektronischen α- und β-Subräumen!

$$\text{"}\hat S_z\text{"} = \hat S_z \hat 1 = \frac{1}{2}\begin{pmatrix} 1 & & & 0 \\ & 1 & & \\ & & -1 & \\ 0 & & & -1 \end{pmatrix} \qquad \text{"}\hat I_z\text{"} = \hat 1 \hat I_z = \frac{1}{2}\begin{pmatrix} 1 & & & 0 \\ & -1 & & \\ & & 1 & \\ 0 & & & -1 \end{pmatrix}$$

$$\hat S_z \hat I_z = \frac{1}{4}\begin{pmatrix} 1 & & & 0 \\ & -1 & & \\ & & -1 & \\ 0 & & & 1 \end{pmatrix} \qquad \hat S_z \hat I_x = \frac{1}{4}\begin{pmatrix} 0 & 1 & & \\ 1 & 0 & & \\ & & 0 & -1 \\ & & -1 & 0 \end{pmatrix}$$

Elektronenspin-Subräume

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e^--Spin-Subräume können separat diagonalisiert werden!

$\rightarrow$ Polarisations-Operatoren

$$\boxed{\begin{aligned} \hat{S}_\alpha &= \frac{1}{2}\hat{1} + \hat{S}_z = \begin{pmatrix} 1 & \\ & 0 \end{pmatrix} \\ \hat{S}_\beta &= \frac{1}{2}\hat{1} - \hat{S}_z = \begin{pmatrix} 0 & \\ & 1 \end{pmatrix} \\ \Rightarrow \quad \hat{S}_\alpha + \hat{S}_\beta &= \hat{1} \qquad \frac{1}{2}(S_\alpha - S_\beta) = \hat{S}_z \end{aligned}}$$

$$\hat{S}_\alpha \hat{1} = \begin{pmatrix} 1 & & & \\ & 1 & & \\ & & 0 & \\ & & & 0 \end{pmatrix}$$

$$\hat{S}_\beta \hat{1} = \begin{pmatrix} 0 & & & \\ & 0 & & \\ & & 1 & \\ & & & 1 \end{pmatrix}$$

$$\rightarrow \hat{H} = \frac{\omega_{0S}}{2}(\hat{S}_\alpha - \hat{S}_\beta) + \omega_{0I}(\hat{S}_\alpha + \hat{S}_\beta)\hat{I}_z + \frac{A}{2}(\hat{S}_\alpha - \hat{S}_\beta)\hat{I}_z + \frac{B}{2}(\hat{S}_\alpha - \hat{S}_\beta)\hat{I}_x$$

$$= \underbrace{\frac{\omega_{0S}}{2}\hat{S}_\alpha + \left(\omega_{0I} + \frac{A}{2}\right)\hat{S}_\alpha \hat{I}_z + \frac{B}{2}\hat{S}_\alpha \hat{I}_x}_{=\hat{H}^\alpha}$$

$$\underbrace{- \frac{\omega_{0S}}{2}\hat{S}_\beta + \left(\omega_{0I} - \frac{A}{2}\right)\hat{S}_\beta \hat{I}_z - \frac{B}{2}\hat{S}_\beta \hat{I}_x}_{=\hat{H}^\beta}$$

Branching der Kernspin-Quantisierung

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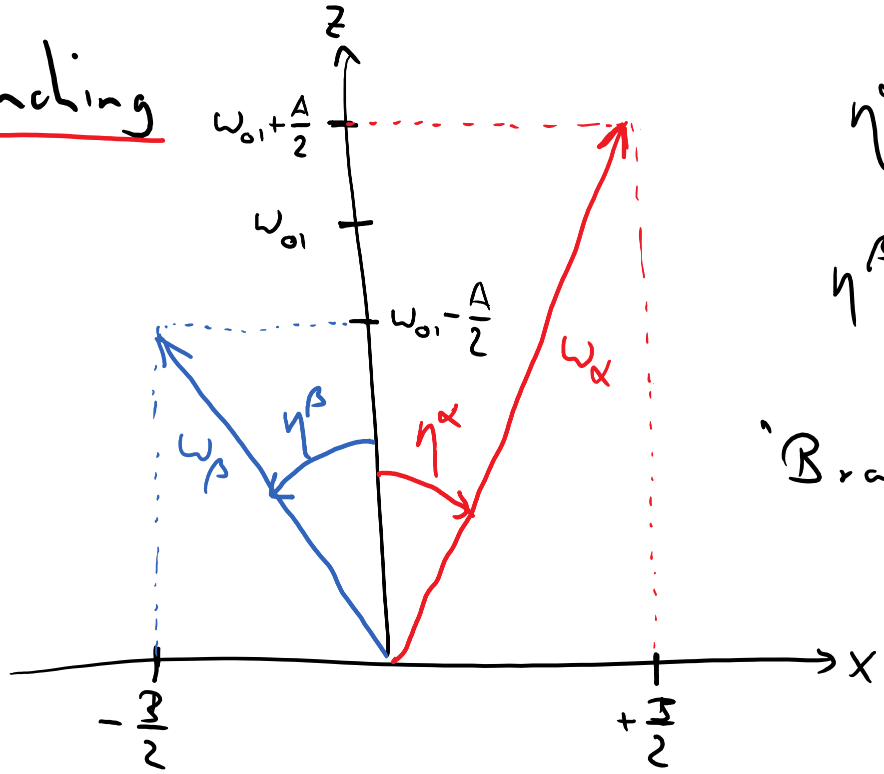
Rotation jedes Subraumes um $\hat{S}_z \hat{I}_y$ mit bestimmtem Winkel η^α bzw. η^β führt zu Diagonalisierung!

Branching



$$\eta^\alpha = \arctan\left(\frac{\frac{B}{2}}{\omega_{01}+\frac{A}{2}}\right)$$

$$\eta^\beta = \arctan\left(\frac{-\frac{B}{2}}{\omega_{01}-\frac{A}{2}}\right)$$

"Branching-Winkel"

Diagonalisierung durch

$$\boxed{\hat{U} = \hat{U}_\alpha \cdot \hat{U}_\beta}$$

$$\hat{U}_\alpha = e^{i\eta^\alpha \hat{S}_\alpha \hat{I}_y}$$

$$\hat{U}_\beta = e^{i\eta^\beta \hat{S}_\beta \hat{I}_y}$$

$$\hat{H}_D = \hat{U}\hat{H}U^{-1} = \hat{U}_\alpha \hat{H}_\alpha U_\alpha^{-1} + \hat{U}_\beta \hat{H}_\beta \hat{U}_\beta^{-1}$$

$\hat{U}_\alpha$ wirkt nur auf $\hat{H}_\alpha$, $\hat{U}_\beta$ nur auf $\hat{H}_\beta$,

da $\hat{S}_\alpha \cdot \hat{S}_\beta = 0$

Gemischte Kernspin-Zustandsbasis

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$\Rightarrow$ Basis $\{|\alpha\alpha\rangle, |\alpha\beta\rangle, |\beta\alpha\rangle, |\beta\beta\rangle\}$ ist nicht mehr Eigenbasis

"Neue" Eigenzustände:

$$|1\rangle = \cos\left(\frac{\eta^\alpha}{2}\right)|\alpha\alpha\rangle - \sin\left(\frac{\eta^\alpha}{2}\right)|\alpha\beta\rangle$$

$$|2\rangle = \cos\left(\frac{\eta^\alpha}{2}\right)|\alpha\beta\rangle + \sin\left(\frac{\eta^\alpha}{2}\right)|\alpha\alpha\rangle$$

$$|3\rangle = \cos\left(\frac{\eta^\beta}{2}\right)|\beta\alpha\rangle - \sin\left(\frac{\eta^\beta}{2}\right)|\beta\beta\rangle$$

$$|4\rangle = \cos\left(\frac{\eta^\beta}{2}\right)|\beta\beta\rangle + \sin\left(\frac{\eta^\beta}{2}\right)|\beta\alpha\rangle$$

Vgl.: $\Psi = p|\alpha\rangle + q|\beta\rangle \qquad p^2 + q^2 = 1$

Mischungsparameter $p_{\alpha/\beta} = \cos\left(\frac{\eta^{\alpha/\beta}}{2}\right)$

$q_{\alpha/\beta} = \sin\left(\frac{\eta^{\alpha/\beta}}{2}\right)$

$\Rightarrow$ Kernzustände sind gemischt!

$\rightsquigarrow$ Kernspinübergänge kontinuierlich durch HFI!

$\rightarrow$ ESEEM

aber nur durch dipolare (pseudo-säkulare Terme) HFI!!!

Übergangsfrequenzen im "tilted frame"

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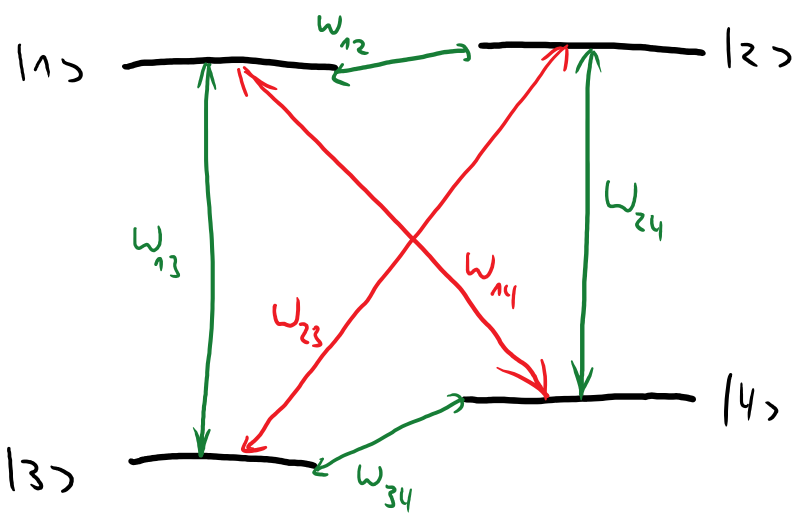
Diagonaler Hamiltonian in "tilted frame":

$$\hat{H}' = \omega_{0S}\hat{S}_z + \underbrace{\omega_{12}\hat{S}_\alpha\hat{I}_z + \omega_{34}\hat{S}_\beta\hat{I}_z}_{\text{Kern-Zeeman \& HFI}} = \omega_{0S}\tilde{S}_z + \frac{\omega_+}{2}\hat{I}_z + \frac{\omega_-}{2}\hat{S}_z\hat{I}_z$$

"Neue" Übergangs-frequenzen:

$$\omega_+ = \omega_{12} + \omega_{34}$$
$$\omega_- = \omega_{12} - \omega_{34}$$



$$\omega_{12} = \left(\omega_{0I} + \frac{A}{2}\right)\cos\eta^\alpha - \frac{B}{2}\sin\eta^\alpha$$
$$\omega_{34} = \left(\omega_{0I} - \frac{A}{2}\right)\cos\eta^\beta + \frac{B}{2}\sin\eta^\beta$$

"NMR"
"Δm_I" $= \pm 1$
$\Delta m_S = 0$

$$\omega_{13} = \omega_{0S} + \frac{\omega_-}{2} \approx \omega_{0S} + \frac{A}{2} \qquad \omega_{24} = \omega_{0S} - \frac{\omega_-}{2} \approx \omega_{0S} - \frac{A}{2}$$

(für $A, B \ll \omega_{0I}$)

erlaubte EPR
$\Delta m_S = \pm 1$
"Δm_I" $= 0$

$$\omega_{14} = \omega_{0S} + \frac{\omega_+}{2} \approx \omega_{0S} + \omega_{0I} \qquad \omega_{23} = \omega_{0S} - \frac{\omega_+}{2} \approx \omega_{0S} - \omega_{0I}$$

(für $A, B \ll \omega_{0I}$)

"verbotene" EPR
$\Delta m_S = \pm 1$
"Δm_I" $= \pm 1$

Verbotene Übergänge

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Übergangsmomente:

1-Spin: mw-Hamiltonian: $\hat{H}_1 = \omega_{1S} \hat{S}_x = \frac{\omega_{1S}}{2} (\hat{S}_+ + \hat{S}_-)$

2-Spin inkl. pseudo-säkulare HFI: $\eta = \frac{\eta^\alpha - \eta^\beta}{2}$

$$\hat{H}_1' = \frac{\omega_{1S}}{2} \cos\eta \underbrace{(S_+ + S_-)}_{\substack{\text{Einzelquanten} \\ \Delta m_S = \pm 1 \\ \Delta m_I = 0}} - \frac{\omega_{1S}}{4} \sin\eta \left(\underbrace{\hat{S}_+\hat{I}_+ + \hat{S}_-\hat{I}_-}_{\substack{\text{Doppelquanten} \\ \Delta m_S = \pm 1 \\ \Delta m_I = \pm 1}} + \underbrace{\hat{S}_+\hat{I}_- + \hat{S}_-\hat{I}_+}_{\substack{\text{Nullquanten} \\ \Delta m_S = \pm 1 \\ \Delta m_I = \mp 1}} \right)$$

→ für $A, B \ll \omega_{0I}$: weak coupling
- verbotene Übergänge schwach bzw. hohe mw-Leistung nötig
- ESEEM schwach

$\eta \approx 0$

für $A, B \approx \omega_{0I}$: "cancellation"
- verbotene Übergänge stark "erlaubte" Übergänge schwach
- ESEEM stark, aber schwer interpretierbar

$\eta \approx \frac{\pi}{2}$

für $A, B \gg \omega_{0I}$: strong coupling
- siehe $A, B \ll \omega_{0I}$, aber Kern-Spin-Niveaus nur durch HFI dominiert

$\eta \approx \pi$