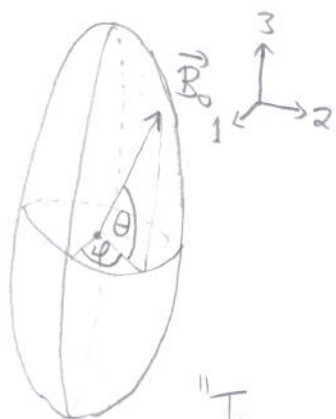


EPR an Festkörpern

Anisotropie von Zeeman- und Hyperfein-WW



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

$$\tilde{A} = \begin{pmatrix} A_{xx} & A_{xy} & A_{xz} \\ A_{yx} & A_{yy} & A_{yz} \\ A_{zx} & A_{zy} & A_{zz} \end{pmatrix}$$

g-Faktor \rightarrow g-Tensor

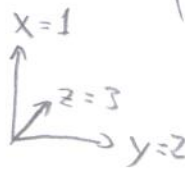
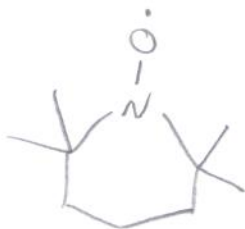
"Tensor-Ellipsoid"

A- und g-Tensoren sind je symmetrisch, dh. $A_{xy} = A_{yx}$, u. sw.

\rightarrow Es existiert ein "Hauptachsensystem" (principle axis system, PAS), in dem der Tensor diagonal ist.

$$\begin{pmatrix} g_{xx} & g_{xy} & g_{xz} \\ g_{yx} & g_{yy} & g_{yz} \\ g_{zx} & g_{zy} & g_{zz} \end{pmatrix} \xrightarrow{\text{Rotation}} \begin{pmatrix} g_{11} & 0 & 0 \\ 0 & g_{22} & 0 \\ 0 & 0 & g_{33} \end{pmatrix}$$

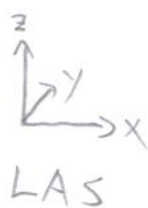
Bsp.: Nitroxid



Molekülachsensystem

MAS \approx PAS

$B_0 \parallel x_{MAS}$



Rotation α um y

MAS



Drehmatrix

$$\tilde{D} = \begin{pmatrix} \cos \alpha & 0 & \sin \alpha \\ 0 & 1 & 0 \\ -\sin \alpha & 0 & \cos \alpha \end{pmatrix} = \begin{pmatrix} 0 & 0 & 1 \\ 0 & 1 & 0 \\ -1 & 0 & 0 \end{pmatrix} \text{ für } \alpha = 90^\circ$$

Rotation: unitäre Transformation $\tilde{D}^{-1} = \tilde{D}^*$
adjungierte Matrix

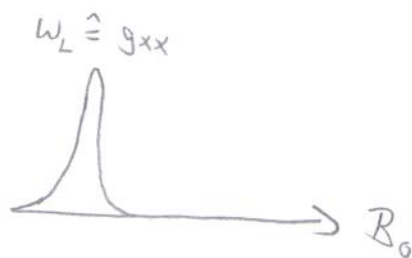
$$\tilde{g}_{LAS} = \tilde{D} \cdot g_{MAS} \cdot \tilde{D}^* \quad \tilde{D}^* = \begin{pmatrix} 0 & 0 & -1 \\ 0 & 1 & 0 \\ 1 & 0 & 0 \end{pmatrix}$$

$$\tilde{g}_{LAS} = \begin{pmatrix} 0 & 0 & 1 \\ 0 & 1 & 0 \\ -1 & 0 & 0 \end{pmatrix} \begin{pmatrix} g_{xx} & 0 & 0 \\ 0 & g_{yy} & 0 \\ 0 & 0 & g_{zz} \end{pmatrix} \begin{pmatrix} 0 & 0 & -1 \\ 0 & 1 & 0 \\ 1 & 0 & 0 \end{pmatrix}$$

$$= \begin{pmatrix} 0 & 0 & 1 \\ 0 & 1 & 0 \\ -1 & 0 & 0 \end{pmatrix} \begin{pmatrix} 0 & 0 & -g_{xx} \\ 0 & g_{yy} & 0 \\ g_{zz} & 0 & 0 \end{pmatrix} = \begin{pmatrix} g_{zz} & 0 & 0 \\ 0 & g_{yy} & 0 \\ 0 & 0 & g_{xx} \end{pmatrix}$$

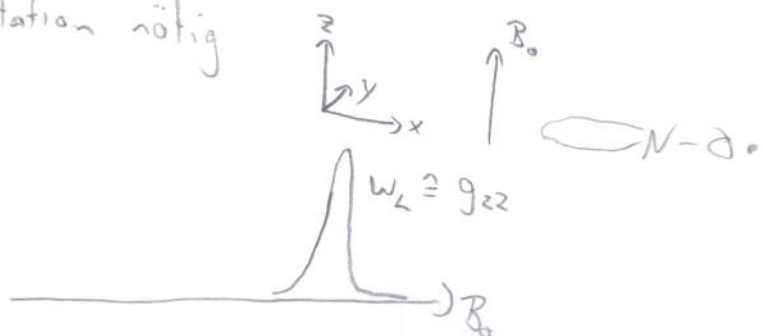
$$\hat{H}_{sz} = \beta_e \vec{B}_0 \tilde{g} \vec{S} = \beta_e (0, 0, B_0) \begin{pmatrix} g_{zz} & 0 & 0 \\ 0 & g_{yy} & 0 \\ 0 & 0 & g_{xx} \end{pmatrix} \begin{pmatrix} \hat{S}_x \\ \hat{S}_y \\ \hat{S}_z \end{pmatrix}$$

$$= \beta_e B_0 g_{xx} \hat{S}_z$$



$B_0 \parallel z_{MAS} \rightarrow$ keine Rotation nötig

$$\hat{H}_{sz} = \beta_e B_0 g_{zz} \hat{S}_z$$



(3)

Drehung um nur 45° um y -Achse (MAS)

$$\tilde{D} = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 & 0 & 1 \\ 0 & \sqrt{2} & 0 \\ -1 & 0 & 1 \end{pmatrix}$$

$$\tilde{g}_{LAS} = \tilde{D} \tilde{g}_{MAS} \tilde{D}^* = \frac{1}{2} \begin{pmatrix} g_{xx} + g_{zz} & 0 & -g_{xx} + g_{zz} \\ 0 & 2g_{yy} & 0 \\ -g_{xx} + g_{zz} & 0 & g_{xx} + g_{zz} \end{pmatrix}$$

nicht diagonal für $g_{xx} \neq g_{zz}$

$$\left. \begin{aligned} \alpha &= \frac{1}{2} (g_{xx} + g_{zz}) \\ \beta &= \frac{1}{2} (g_{zz} - g_{xx}) \end{aligned} \right\} \alpha \gg \beta$$

$$\hat{H}_{sz} = \beta_e B_0 (\beta \hat{S}_x + \alpha \hat{S}_z) = \frac{\beta_e B_0}{2} \begin{pmatrix} \alpha & \beta \\ \beta & -\alpha \end{pmatrix}$$

→ nicht mehr diagonal, $|\frac{1}{2}, -\frac{1}{2}\rangle$ und $|\frac{1}{2}, +\frac{1}{2}\rangle$
keine EF mehr zu \hat{H} !

Störungsrechnung: $\alpha \gg \beta$

1. Ordnung: $E_1 = \frac{\beta_e B_0}{2} \alpha$; $E_2 = \frac{\beta_e B_0}{2} (-\alpha)$

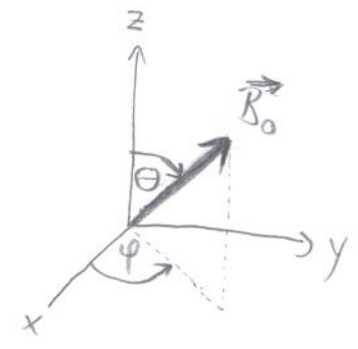
$$\Rightarrow \Delta E = \beta_e B_0 \alpha = \beta_e B_0 \left(\frac{g_{xx} + g_{zz}}{2} \right)$$

2. Ordnung: $E_1 = \frac{\beta_e B_0}{2} \left(\alpha - \frac{\beta^2}{2\alpha} \right)$; $E_2 = \frac{\beta_e B_0}{2} \left(-\alpha + \frac{\beta^2}{2\alpha} \right)$

$$\Rightarrow \Delta E = \beta_e B_0 \left| \alpha - \frac{\beta^2}{2\alpha} \right|$$

Vernachlässigung der Störung:

beliebige Drehwinkel Θ, ψ

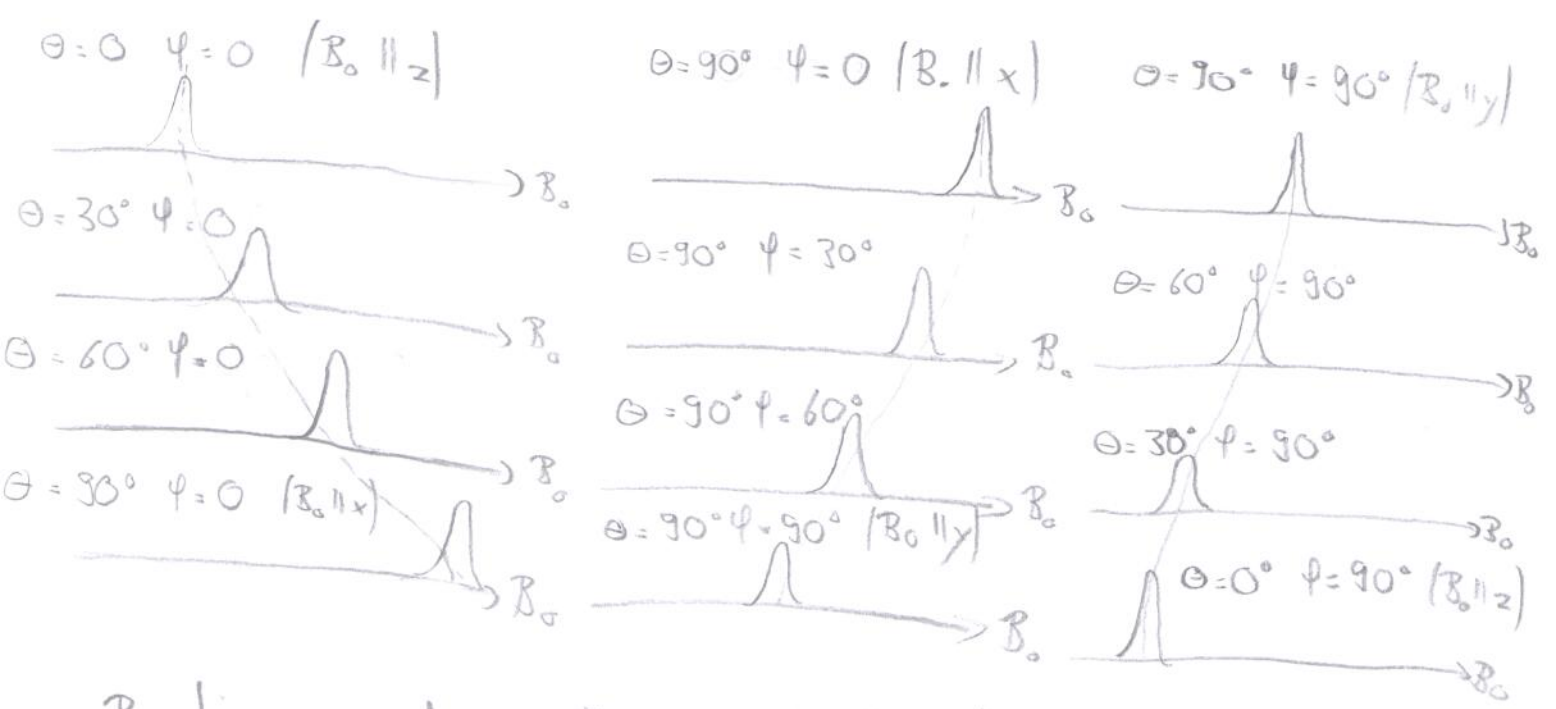


$$g_{eff} = \sqrt{\sin^2 \Theta \cos^2 \Psi g_{xx}^2 + \sin^2 \Theta \sin^2 \Psi g_{yy}^2 + \cos^2 \Theta g_{zz}^2}$$

Projektion des g-Tensors auf B_0 -Vektor

Anisotropie im Einkristall: alle Moleküle gleich geordnet

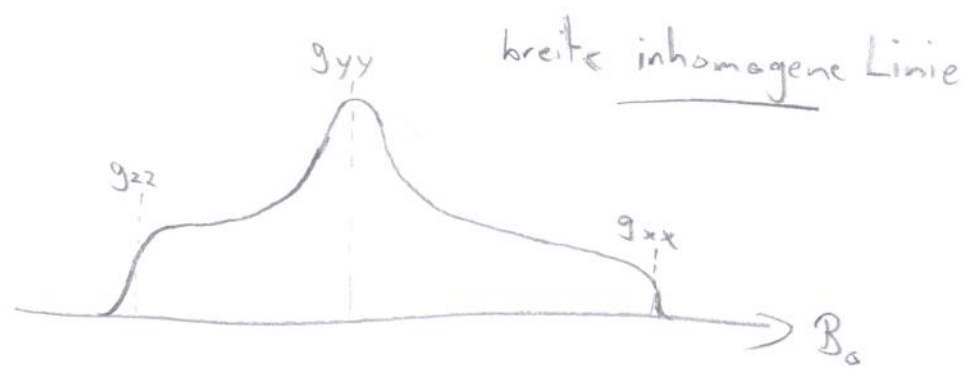
$$g_{xx} < g_{yy} < g_{zz}$$



Bestimmung des g-Tensors durch Rotation des Einkristalls im EPR-Spektrometer \rightarrow Goniometer

Anisotropie im Pulver / gefrorene Lösung:

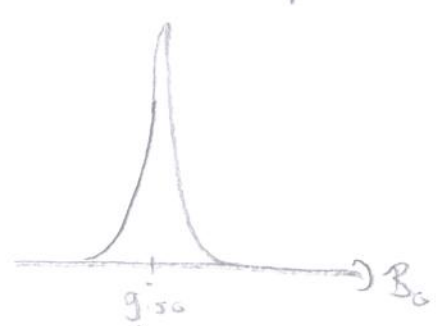
alle Moleküle willkürlich ausgerichtet, homogene Verteilung aller Orientierungen



g-Tensor kann direkt aus Spektrum abgelesen werden / durch spektrale Simulation bestimmt werden

Symmetriekriterien

$g_{xx} = g_{yy} = g_{zz}$
isotrop / kubisch

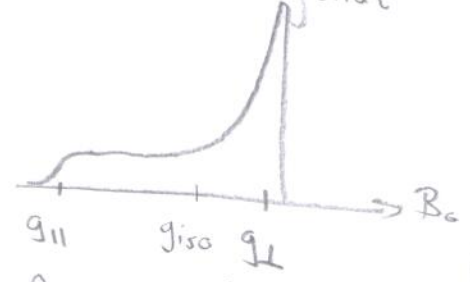


$g_{iso} = g_{xx} = g_{yy} = g_{zz}$

$\Delta g = 0$ (Anisotropie)

$\eta = 0$ (Asymmetrie)

$g_{xx} = g_{yy} \neq g_{zz}$
 g_{\perp} g_{\parallel}
axial / tetragonal

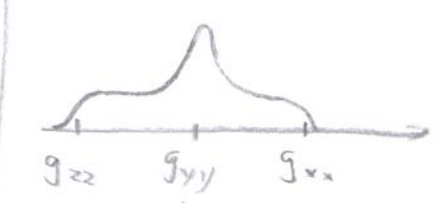


$g_{iso} = \frac{2g_{\perp} + g_{\parallel}}{3}$

$\Delta g = \frac{g_{\parallel} - g_{\perp}}{3}$

$\eta = 0$

$g_{xx} \neq g_{yy} \neq g_{zz}$
orthorhombisch



$g_{iso} = \frac{g_{xx} + g_{yy} + g_{zz}}{3}$

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

$\eta = \frac{g_{yy} - g_{xx}}{\Delta g}$