Schwingungsspektro

25.05.18

Wiederholung: C_{3v}

C_3v	E	$2C_3$	$3\sigma_v$	$h=6$
A_1: Γ_1	1	1	1	
A_2: Γ_2	1	1	-1	
E = Γ_3	2	-1	0	

4.5 Orthogonalitätstheoreme

GoT: großes Orthogonalitätstheorem

$$\text{GoT}: \sum_R \underbrace{[\Gamma_i(R)_{mn}][\Gamma_i(R)_{m'n'}]^*}_{\text{irred. Darstellung}} = \frac{h}{\sqrt{l_i \cdot l_j}} \delta_{ij}\delta_{mm'}\delta_{nn'}$$

h → Ordnung

$\sum_R$ ↓ SO

irred. Darstellung → $[v_{imn}][v_{jm'n'}]^*$

$\sqrt{l_i l_j}$ ↑ $3\times3 \to l=3$ Dimension d Matrix

<u>Anw.</u> C_3V

$$\sum_R \Gamma_3(R)_{11}\,\Gamma_3(R)_{22} = 1\cdot1 + (-\tfrac{1}{2})\cdot(-\tfrac{1}{2}) + \ldots = 0$$

$$\sum_R \Gamma_3(R)_{11}\,\Gamma_3(R)_{11} = \frac{6}{2} = 3 = 1\cdot1 + (-\tfrac{1}{2})\cdot(-\tfrac{1}{2})$$

Anzahl an Vektoren: l_i^2

Gesamtdimension: $\sum_i l_i^2 = h$

GoT → LoT (Ü6)

LoT:

$$\sum_R \chi_i(R)\chi_j^*(R) = \delta_{ij} h \qquad i=j: \sum_R |\chi_i(R)|^2 = h$$

$$R \to C \qquad \sum_C g(C)\,\chi_i(C)\,\chi_j(C)^* = h\,\delta_{ij} \qquad i=j: \sum_R g(C)|\chi_i(C)|^2 = h$$

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Wiederholung: C_{3v}

C_{3v}	E	$2C_3$	$3\sigma_v$	$h = 6$
$A_1 = \Gamma_1$	1	1	1	
$A_2 = \Gamma_2$	1	1	-1	
$E = \Gamma_3$	2	-1	0	

4.5 Orthogonalitätstheoreme

GoT: großes Orthogonalitätstheorem

$$\text{GoT:}\quad \underbrace{\sum_R}_{\text{SO}} \underbrace{[\Gamma_i(R)_{mn}][\Gamma_j(R)_{m'n'}]^*}_{\substack{\text{irred. Darstellung} \\ \downarrow \\ [v_{imn}][v_{jm'n'}]^*}} = \frac{\overset{\nearrow \text{Ordnung}}{h}}{\sqrt{\underbrace{l_i l_j}_{\substack{3\times 3 \to l=3 \\ \text{Dimension d. Matrix}}}}}\,\delta_{ij}\,\delta_{mm'}\,\delta_{nn'}$$

Anw. C_{3v}

$$\sum_R \Gamma_3(R)_{11}\,\Gamma_3(R)_{22} = 1\cdot 1 + (-\tfrac{1}{2})\cdot(-\tfrac{1}{2}) + \ldots = 0$$

$$\sum_R \Gamma_3(R)_{11}\,\Gamma_3(R)_{11} = \frac{6}{2} = 3 = 1\cdot 1 + (-\tfrac{1}{2})\cdot(-\tfrac{1}{2})$$

Anzahl an Vektoren: l_i^2

Gesamtdimension: $\sum_i l_i^2 = \underline{h}$

GoT → LoT (ü6)

LoT:

$$\sum_R \chi_i(R)\,\chi_j(R) = \delta_{ij}\,h \qquad i=j:\ \sum_R |\chi_i(R)|^2 = h$$

$R \to C$ $$\sum_R g(C)\,\chi_i(C)\,\chi_j(C)^* = h\,\delta_{ij} \qquad i=j:\ \sum_R g(C)|\chi_i(C)|^2 = h$$

Anw: C_{3v} GoT: $\sum_i l_i^2 = h \rightarrow 1^2 + 2^2 + l^2 = 6 \rightarrow l = 1 \; (\Gamma_2)$

LoT: $[\chi_{\Gamma_2}(E)]^2 + 2[\chi_{\Gamma_2}(C_3)]^2 + 3[\chi_{\Gamma_2}(\sigma_v)]^2 \overset{\uparrow}{=} 6$ $\quad i = j$

$$\chi_{\Gamma_2}(E)\chi_{\Gamma_1}(E) + 2\chi_{\Gamma_2}(C_3)\chi_{\Gamma_1}(C_3) + \dots \underset{i \neq j}{\overset{!}{=}} 0$$

$$\chi_{\Gamma_2}(E)\chi_{\Gamma_3}(E) + \dots + \dots = 0$$

$\hookrightarrow \chi_{\Gamma_2}(E) = 1$; $\chi_{\Gamma_2}(C_3) = 1$; $\chi_{\Gamma_2}(\sigma_v) = -1$

„Wissen wir hier": $1^2 + 2^2 + l^2 = 6 \rightarrow l = 1 \; (\Gamma_2)$

		C_{3v}	E	$2C_3$	$3\sigma_v$	$h=6$
irred	A_1 =	Γ_1	1	1	1	
	A_2 =	Γ_2	1	1	-1	
	A_2 =	Γ_3	2	-1	0	
red		Γ_a	5	2	-1	

Symbolik:
- 1×1: A, B
- 2×2: E
- 3×3: T (F)

[$C_{\infty v}$, $D_{\infty h}$: 1×1: Σ, ...]

A (symm.), B (antisymm.) bezgl. Rot um Hauptrotationsachse

g (symm.), u (antisymm.) bezgl. Inversionszentrum

' (symm.), " (antisymm.) bezgl σ_h

4.6 Reduktionsformel

Ähnlichkeitstransformation → Charaktere bleiben erhalten

$$\underset{\text{red.}}{\chi(R)} = \sum_j a_j \underset{\text{irred.}}{\chi_j(R)}$$

$$\sum_R \chi(R)\chi_i(R) = \sum_j a_j \underbrace{\sum_R \chi_j(R)\chi_i(R)}_{h\delta_{ij}}$$

→ für jedes j:

$$\sum_R \chi(R)\chi_i(R) = a_j h \delta_{ij}$$

$i = j$: $\sum_R \chi(R)\chi_i(R) = a_i h \Leftrightarrow \boxed{a_i = \frac{1}{h}\sum_R \chi(R)\chi_i(R)}$

Anw: C_{3v}

$$a(\Gamma_1) = \frac{1}{6}\left[5\cdot1\cdot1 + 2\cdot1\cdot2 + 1\cdot(-1)\cdot3\right] = \underline{\underline{1}}$$

<=> Ergebnis muss ganze Zahl sein!

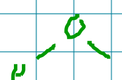
$$a(\Gamma_2) = \frac{1}{6}\left[5\cdot1\cdot1 + 2\cdot1\cdot2 - (-1)\cdot(-1)\cdot3\right] = \underline{\underline{2}}$$

$$a(\Gamma_3) = \quad .. \quad = 1$$

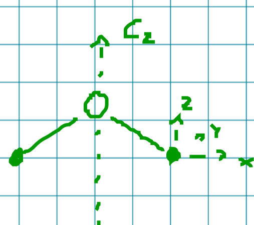
$$\Rightarrow \Gamma_a = \Gamma_1 \oplus 2\Gamma_2 \oplus \Gamma_3$$

4.7 Anwendungen

z.B. H_2O
- Symmetrie d. Normalschwingungen?
- welche Normalschwingungen sind IR aktiv?



Punktgruppe: C_{2v}



C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v'(yz)$	
A_1	1	1	1	1	z
A_2	1	1	-1	-1	R_z
B_1	1	-1	1	-1	x, R_y
B_2	1	-1	-1	1	y, R_x
Γ^{3N}	9	-1	3	1	

$$a(\Gamma_{A_1}) = \frac{1}{4}\left[9\cdot1\cdot1 + (-1)\cdot1\cdot1 + 3\cdot1\cdot1 + 1\cdot1\cdot1\right] = 3$$

$$a(\Gamma_{A_2}) = \quad ... \quad = 1$$

$$a(\Gamma_{B_1}) = \quad .. \quad = 3$$

$$a(\Gamma_{B_2}) = \quad .. \quad = 2$$

<=> $\Gamma^{3N} = 3\,\Gamma_{A_1} \oplus \Gamma_{A_2} \oplus 3\,\Gamma_{B_1} \oplus 2\,\Gamma_{B_2}$

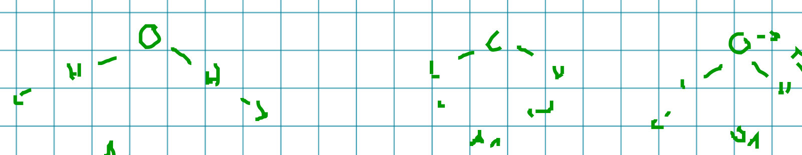
$\Gamma^{trans} = \Gamma_{A_1} \oplus \Gamma_{B_1} \oplus \Gamma_{B_2}$

$\Gamma^{rot} = \Gamma_{A_2} \oplus \Gamma_{B_1} \oplus \Gamma_{B_2}$

$\Gamma^{vib} = \Gamma^{3N} - \Gamma^{trans} - \Gamma^{rot} = 2\,\Gamma_{A_1} \oplus \Gamma_{B_1}$

↳ 3 Normalschwingungen

<=> $3N - 6 = 3$ ✓



IR-Aktivität ~ |R|², $R = \int \psi_{v'}^{*} \vec{\mu} \psi_{v''} \, d\tau \neq 0$

$$R = \int \psi_{v'}^{*} \vec{\mu} \psi_{v''} \, d\tau$$

$$R_x = -e \int \underbrace{\underbrace{\psi_{v'}^{*} \, x}_{B_1 \cdot B_1} \, \psi_{v''}}_{A_1 \cdot A_1 = A_1} \, dx \neq 0 \qquad R_z = -e \int \underbrace{\psi_{v'}^{*} \, z \, \psi_{v''}}_{A_1 \, A_1 \, A_1 = A_1} \, dz \neq 0$$

↳ B_1: IR-aktiv