

Blatt 7

Aufgabe 22:

Titon: $[Ar] 3d^2 4s^2$

a) $4s^2$: abgeschlossene Schale $\Rightarrow L=0$; $S=0$
 $\Rightarrow$ kein Beitrag

$3d^2$: 2 äquivalente Elektronen

nach Pauli-Prinzip müssen mindestens eine

Quantenzahl n, l, m_l, m_s unterschiedlich sein.

$$l_1 = 2 \quad ; \quad s_1 = \frac{1}{2}$$

$$l_2 = 2 \quad ; \quad s_2 = \frac{1}{2}$$

Russel-Saunders: $L = 4, 3, 2, 1, 0$; $S = 1, 0$

! Bemerkung: Die folgende Lösung ist keine zwingende
Ordnung, sondern eine Art kombinatorische
„Abzählspiel“. J

m_{l1}	m_{l2}	m_{s1}	m_{s2}	M_L	M_S				
+2	+2	Pauli: $+\frac{1}{2}$	$-\frac{1}{2}$	4	0				
	+1	$\pm\frac{1}{2}$	$\pm\frac{1}{2}$	3	0	$0, \pm 1$			
	0	$\pm\frac{1}{2}$	$\pm\frac{1}{2}$	2	0	$0, \pm 1$			
	-1	$\pm\frac{1}{2}$	$\pm\frac{1}{2}$	1	0	$0, \pm 1$			
	-2	$\pm\frac{1}{2}$	$\pm\frac{1}{2}$	0	0	$0, \pm 1$			
+1	+1	Pauli: $+\frac{1}{2}$	$-\frac{1}{2}$	2			0		
	0	$\pm\frac{1}{2}$	$\pm\frac{1}{2}$	1			0	$0, \pm 1$	
	-1	$\pm\frac{1}{2}$	$\pm\frac{1}{2}$	0			0	$0, \pm 1$	
	-2	$\pm\frac{1}{2}$	$\pm\frac{1}{2}$	-1	0		0	$0, \pm 1$	
0	0	Pauli: $+\frac{1}{2}$	$-\frac{1}{2}$	0					0
	-1	$\pm\frac{1}{2}$	$\pm\frac{1}{2}$	-1		$0, \pm 1$	0		
	-2	$\pm\frac{1}{2}$	$\pm\frac{1}{2}$	-2	0	$0, \pm 1$			
-1	-1	Pauli: $+\frac{1}{2}$	$-\frac{1}{2}$	-2					0
	-2	$\pm\frac{1}{2}$	$\pm\frac{1}{2}$	-3	0	$0, \pm 1$			
-2	-2	Pauli: $+\frac{1}{2}$	$-\frac{1}{2}$	-4	0				

	1G_4	${}^3F_{4,3,2}$	1D_2	${}^3P_{2,1,0}$	1S_0
Komponenten	9	21	5	9	1

b) Grundzustand finden mit Hilfe der Hund'sche Regeln

I.) $4s^2$ fällt weg (volle Schale $L=0; S=0$)

II.) Gesamtspin S maximieren: $S=1$

III.) Gesamtdrehimpuls L maximieren (Pauli beachten!): $L=3$

IV.) d^2 : weniger als halb gefüllte Schale $\rightarrow J = L - S = 2$

$\Rightarrow$ Grundzustand 3F_2 (Multiplizität: $3 = 2S + 1$)

c) $3d^1 4s^1 d^1 5s^1$: alle Elektronen inequivalent

$$l_1 = 2, l_2 = 0, l_3 = 2, l_4 = 0$$

$$L = l_1 + l_3, \dots, l_1 - l_3$$

$$L = 4, 3, 2, 1, 0$$

$$G \quad F \quad D \quad P \quad S$$

4 Elektronen mit $s = \frac{1}{2}$

$$S = 2, 1, 0 \leadsto \text{Multiplizität } (2S+1): 5, 3, 1$$

mögliche Terme:

$$L = 0: \quad {}^1S_0$$

$3S_1$

$5S_2$

$$L = 1: \quad {}^1P_1$$

$${}^3P_{2,1,0}$$

$${}^5P_{3,2,1}$$

Multiplizität nicht voll entwickelt

$$L = 2: \quad {}^1D_2$$

$${}^3D_{3,2,1}$$

$${}^5D_{4,3,2,1,0}$$

$$L = 3: \quad {}^1F_3$$

$${}^3F_{4,3,2}$$

$${}^5F_{5,4,3,2,1}$$

$$L = 4: \quad {}^1G_4$$

$${}^3G_{5,4,3}$$

$${}^5G_{6,5,4,3,2}$$

Aufgabe 23:

a) orthogonal:

$$\text{Es gilt für } \iint Y_{l,m}^*(u, \varphi) Y_{l',m'}(u, \varphi) du d\varphi = \delta_{l,l'} \delta_{m,m'}$$

d_{z^2} und $d_{x^2-y^2}$:

$$\begin{aligned} \iint Y_{2,0}^* \frac{1}{\sqrt{2}} (Y_{2,-2} + Y_{2,2}) du d\varphi &= \frac{1}{\sqrt{2}} \iint [Y_{2,0}^* Y_{2,-2} + Y_{2,0}^* Y_{2,2}] du d\varphi \\ &= \frac{1}{\sqrt{2}} [\delta_{2,2} \cdot \underbrace{\delta_{0,-2}}_{=0} + \delta_{2,2} \cdot \underbrace{\delta_{0,2}}_{=0}] = 0 \end{aligned}$$

$$\begin{aligned} d_{x^2-y^2} \text{ und } d_{xy}: \iint \frac{1}{\sqrt{2}} (Y_{2,-2}^* + Y_{2,2}^*) \frac{i}{\sqrt{2}} (Y_{2,-2} - Y_{2,2}) du d\varphi \\ = \iint \frac{i}{2} (Y_{2,-2}^* Y_{2,-2} - Y_{2,2}^* Y_{2,2}) du d\varphi \\ = \frac{i}{2} [\delta_{2,2} \cdot \delta_{-2,-2} - \delta_{2,2} \cdot \delta_{2,2}] = 0 \end{aligned}$$

u.s.w.

normiert:

$$\begin{aligned} \iint Y_{2,0}^* Y_{2,0} du d\varphi &= 1 \\ \iint \frac{1}{\sqrt{2}} (Y_{2,-2}^* + Y_{2,2}^*) \frac{1}{\sqrt{2}} (Y_{2,-2} + Y_{2,2}) du d\varphi \\ &= \frac{1}{2} \iint [Y_{2,-2}^* Y_{2,-2} + Y_{2,-2}^* Y_{2,2} + Y_{2,2}^* Y_{2,-2} + Y_{2,2}^* Y_{2,2}] du d\varphi \\ &= \frac{1}{2} [1 + 0 + 0 + 1] = 1 \end{aligned}$$

$$\begin{aligned} \iint -\frac{i}{\sqrt{2}} (Y_{2,-2}^* - Y_{2,2}^*) \frac{i}{\sqrt{2}} (Y_{2,-2} - Y_{2,2}) du d\varphi \\ = \frac{1}{2} \iint (Y_{2,-2}^* Y_{2,-2} - Y_{2,-2}^* Y_{2,2} - Y_{2,2}^* + Y_{2,2}^* Y_{2,2}) du d\varphi \\ = \frac{1}{2} [1 - 0 - 0 + 1] = 1 \end{aligned}$$

u.s.w.

$$b) \quad \vec{L}^2 Y_{\ell, m} = \ell(\ell+1) \hbar^2 Y_{\ell, m}$$

$$\begin{aligned} \underline{d_{z^2}}: \quad \langle \vec{L}^2 \rangle &= \iint Y_{2,0}^* \vec{L}^2 Y_{2,0} \, du \, d\varphi = 2 \cdot 3 \, \hbar^2 \underbrace{\iint Y_{2,0}^* Y_{2,0} \, du \, d\varphi}_{=1} \\ &= 2 \cdot 3 \, \hbar^2 \end{aligned}$$

$$\begin{aligned} \underline{d_{x^2-y^2}}: \quad \langle \vec{L}^2 \rangle &= \iint \frac{1}{\sqrt{2}} (Y_{2,-2}^* + Y_{2,2}^*) \vec{L}^2 \frac{1}{\sqrt{2}} (Y_{2,-2} + Y_{2,2}) \, du \, d\varphi \\ &= \frac{1}{2} \cdot 2 \cdot 3 \cdot \hbar^2 [1 + 0 + 0 + 1] = 2 \cdot 3 \cdot \hbar^2 \end{aligned}$$

$$\begin{aligned} \underline{d_{zy}}: \quad \langle \vec{L}^2 \rangle &= \iint -\frac{i}{\sqrt{2}} (Y_{2,-1}^* - Y_{2,1}^*) \frac{i}{\sqrt{2}} \vec{L}^2 (Y_{2,-1} - Y_{2,1}) \, du \, d\varphi \\ &= \frac{1}{2} \cdot 2 \cdot 3 \, \hbar^2 (1 + 1) = 2 \cdot 3 \cdot \hbar^2 \end{aligned}$$

u.s.w. . . .

$$\underline{d_{z^2}}: \quad \langle L_z \rangle = \iint Y_{2,0}^* \underbrace{L_z Y_{2,0}}_{=0} \, du \, d\varphi = 0$$

$$\begin{aligned} \underline{d_{x^2-y^2}}: \quad \langle L_z \rangle &= \iint \frac{1}{\sqrt{2}} (Y_{2,-2}^* + Y_{2,2}^*) L_z \frac{1}{\sqrt{2}} (Y_{2,-2} + Y_{2,2}) \, du \, d\varphi \\ &= \frac{1}{2} \iint (Y_{2,-2}^* + Y_{2,2}^*) (-2\hbar Y_{2,-2} + 2\hbar Y_{2,2}) \, du \, d\varphi \\ &= \frac{1}{2} (-2\hbar + 2\hbar) = 0 \end{aligned}$$

$$\begin{aligned} \underline{d_{zy}}: \quad \langle L_z \rangle &= \iint \frac{i}{\sqrt{2}} (Y_{2,1}^* - Y_{2,-1}^*) \frac{i}{\sqrt{2}} (-\hbar Y_{2,-1} - \hbar Y_{2,1}) \, du \, d\varphi \\ &= -\frac{1}{2} \hbar (1 - 1) = 0 \end{aligned}$$

u.s.w. . . .

c) mit $Y_{\ell,m}(\theta, \varphi) = A_{\ell,m} P_{\ell}^{m}(\cos \theta) e^{im\varphi}$

$$\Rightarrow Y_{\ell,m}(\theta, \varphi + \alpha) = A_{\ell,m} P_{\ell}^{m}(\cos \theta) e^{im(\varphi + \alpha)}$$

$$= Y_{\ell,m}(\theta, \varphi) e^{im\alpha}$$

$$d_{x^2-y^2} : \frac{1}{\sqrt{2}} (Y_{2,-2}(\theta, \varphi) + Y_{2,2}(\theta, \varphi))$$

$$= \frac{1}{\sqrt{2}} (Y_{2,-2}(\theta, \varphi' - \frac{\pi}{4}) + Y_{2,2}(\theta, \varphi' - \frac{\pi}{4}))$$

$$= \frac{1}{\sqrt{2}} (Y_{2,-2}(\theta, \varphi) \underbrace{e^{i\frac{\pi}{2}}}_{=i} + Y_{2,2}(\theta, \varphi) \underbrace{e^{-i\frac{\pi}{2}}}_{=-i})$$

$$= \frac{i}{\sqrt{2}} (Y_{2,-2} - Y_{2,2}) \hat{=} d_{xy}$$

d) Bezeichnung nach Winkelabhängigkeit:

$$\frac{x}{r} = \sin \theta \cos \varphi \quad ; \quad \frac{y}{r} = \sin \theta \sin \varphi \quad ; \quad \frac{z}{r} = \cos \theta$$

$$\Rightarrow P_z \sim \cos \theta \quad ; \quad P_y \sim \sin \theta \sin \varphi \quad ; \quad P_x \sim \sin \theta \cos \varphi$$

mit

$$Y_{1,0} \sim \cos \theta$$

$$Y_{1,1} \sim \sin \theta e^{i\varphi} \quad \text{und} \quad \frac{1}{2i} (e^{i\varphi} - e^{-i\varphi}) = \sin \varphi$$

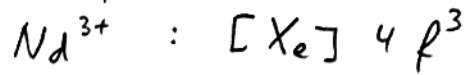
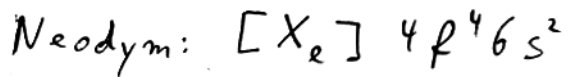
$$Y_{1,-1} \sim \sin \theta e^{-i\varphi} \quad \frac{1}{2} (e^{i\varphi} + e^{-i\varphi}) = \cos \varphi$$

folgt: $P_z = Y_{1,0}$

$$P_y = \frac{i}{\sqrt{2}} (Y_{1,1} - Y_{1,-1}) \sim \frac{i}{\sqrt{2}} \sin \theta (e^{i\varphi} - e^{-i\varphi}) \sim \sin \theta \sin \varphi$$

$$P_x = \frac{1}{\sqrt{2}} (Y_{1,1} + Y_{1,-1}) \sim \frac{1}{\sqrt{2}} \sin \theta (e^{i\varphi} + e^{-i\varphi}) \sim \sin \theta \cos \varphi$$

Aufgabe 24:



$l = l = 3$, maximal $14e^-$

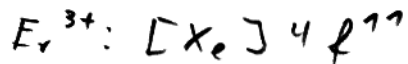
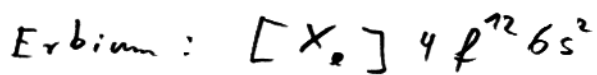
S maximieren $S = \frac{3}{2}$

L maximieren $L = 3+2+1 = 6$

$$J = L - S = \frac{9}{2}$$

↑
da weniger als halb gefüllt

$$g = 1 + \frac{J(J+1) - L(L+1) + S(S+1)}{2J(J+1)} = 0,7273$$



$$S = \frac{3}{2}$$

$$L = 6$$

$$J = L + S = \frac{15}{2}$$

↑
mehr als halbgefüllt

$$\Rightarrow g = 1,20$$