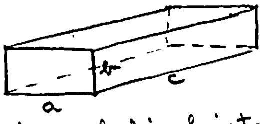
RAZCEP p-ORBITAL (V ORTOROMBSKEM KRISTALU, Z UPOŠTEVANJEM KRISTALNEGA POLJA) V ZUNANJEM MAGNETNEM POLJU



ortorombski kristal

→ obravnavali bomo p-orbitale:

- $p_x = x\, f(r)$
- $p_y = y\, f(r)$
- $p_z = z\, f(r)$

$\xrightarrow{\text{drugačen zapis}}$

$$|p_x\rangle = \frac{|1-1\rangle - |11\rangle}{\sqrt{2}}$$

$$|p_y\rangle = i\,\frac{|11\rangle + |1-1\rangle}{\sqrt{2}}$$

$$|p_z\rangle = |10\rangle$$

TIRNA VRTILNA KOL.:

$\vec{L}^2, L_z$ (velikost)

p orbitala ⇒ $l = 1$

$$l=1 \begin{cases} |11\rangle \\ |10\rangle \\ |1-1\rangle \end{cases} \quad (l\ l_z)$$

→ ker je atom v kristalu čuti dodaten potencial

$$V(\vec{r}) = Ax^2 + By^2 - (A+B)z^2$$

(1.) popravek zaradi kristalnega polja

$$H = H_{at} + V(\vec{r})$$

vemo: → $V(\vec{r})$ je soda funkcija
→ $p_x \propto x,\ p_y \propto y,\ p_z \propto z$
} Neničelni bodo samo prispevki diagonalnih elementov

- $\langle p_x | V(\vec{r}) | p_y\rangle = \underset{\text{po celem prostoru}}{\iiint} dx\,dy\,dz\ (Ax^2 + By^2 - (A+B)z^2 \cdot x \cdot y\, f^2(r) = 0$

- $\langle p_x | V(\vec{r}) | p_x\rangle = \iiint x^2 f^2(r)\,(Ax^2 + By^2 - (A+B)z^2)\,dx\,dy\,dz =$

$$= \iiint (Ax^4 + Bx^2y^2 - Ax^2z^2 - Bx^2z^2)\, f^2(r)\, dx\,dy\,dz = AI_1 + \cancel{BI_2} - AI_2 - \cancel{BI_2} = A(I_1 - I_2)$$

vpeljemo: $I_1 = \iiint f^2(r)\, x^4\, dx\,dy\,dz$ (enako za y^4 ali z^4 ker integriramo po celem prostoru)

(ker $f(r)$ ne poznamo)

in

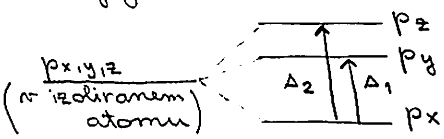
$$I_2 = \iiint f^2(r)\, \underset{(x^2z^2)}{\overset{(y^2z^2)}{x^2y^2}}\, dx\,dy\,dz$$

- Ekvivalentno:

$\langle p_y | V(\vec{r}) | p_y\rangle = B(I_1 - I_2)$ in $\langle p_z | V(\vec{r}) | p_z\rangle = (A+B)(I_1 - I_2)$

V izoliranem atomu imajo p_x, p_y in p_z enako energijo, v ortorombskem kristalu pa se nivoji razcepijo.

V nadaljevanju bomo predpostavili, da so A, B, I_1 in I_2 taki, da ima p_x najnižjo energijo. (v kristalnem polju)



→ vsaka energija je 2x degenerirana zaradi spina
(v zun. mag. polju bi se razcepila za $\vec{\mu}\vec{B} \to \pm \mu_s B_0$; $\mu_s = g\mu_B s_z \hbar$ če je $\vec{B} = B_0 \hat{e}_z$)

(2.) upoštevati moramo sklopitev tirne in spinske vrtilne količine

Zanimalo nas bo kaj se zgodi z energijo p_x.

$$H = H_{at} + V(\vec{r}) + \lambda \vec{L}\vec{S}$$

Računamo v najnižjem redu perturbacije za $|p_x\uparrow\rangle$ in $|p_x\downarrow\rangle$

$$|n\rangle = |n^\circ\rangle + \sum_{m \neq n} \frac{\langle m^\circ | \lambda \vec{L}\vec{S} | n^\circ\rangle}{E_n^\circ - E_m^\circ}\, |m^\circ\rangle$$

• $\vec{L}\vec{S} = (L_x S_x + L_y S_y + L_z S_z)$

$L_+|lm\rangle = \hbar\sqrt{l(l+1)-m(m+1)}\,|j,m+1\rangle$
$L_-|lm\rangle = \hbar\sqrt{l(l+1)-m(m-1)}\,|j,m-1\rangle$

$L_{x,y}$ in $S_{x,y}$ bi radi zapisali z operatorji: $L_\pm$ in $S_\pm$

Iz kvantne mehanike vemo: $L_x = \frac{1}{2}(L_+ + L_-)$ in $S_+ = \frac{1}{2}(S_+ + S_-)$

$L_y = \frac{1}{2i}(L_+ - L_-)$ $\quad S_- = \frac{1}{2i}(S_+ - S_-)$

$\vec{L}\vec{S} = L_xS_x + L_yS_y + L_zS_z =$

$= \frac{1}{4}(L_+ + L_-)(S_+ + S_-) - \frac{1}{4}(L_+ - L_-)(S_+ - S_-) + L_zS_z =$

$= \frac{1}{4}(\cancel{L_+S_+} + L_-S_+ + L_+S_- + \cancel{L_-S_-} - \cancel{L_+S_+} + L_-S_+ + L_+S_- - \cancel{L_-S_-}) + L_zS_z$

$= \frac{1}{2}(L_-S_+ + L_+S_-) + L_zS_z$

$\vec{L}\vec{S}|p_x\uparrow\rangle = \left(\frac{1}{2}(\overset{S_+|\uparrow\rangle = \emptyset}{\cancel{L_-S_+}} + L_+S_-) + L_zS_z\right)\frac{|1-1\rangle - |11\rangle}{\sqrt{2}}|\uparrow\rangle =$

$= \frac{1}{2}\frac{\sqrt{2}|10\rangle}{\sqrt{2}}\hbar^2|\downarrow\rangle + \frac{i}{i}\frac{-\hbar|1-1\rangle - \hbar|11\rangle}{\sqrt{2}}\frac{\hbar}{2}|\uparrow\rangle = \frac{\hbar^2}{2}|p_z\downarrow\rangle - \frac{1}{2i}\hbar^2|p_y\uparrow\rangle$

$\vec{L}\vec{S}|p_x\downarrow\rangle = \left(\frac{1}{2}(L_-S_+ + \cancel{L_+S_-}) + L_zS_z\right)\frac{|1-1\rangle - |11\rangle}{\sqrt{2}}|\downarrow\rangle =$

$= -\frac{1}{2}\frac{\hbar\sqrt{2}\,|10\rangle}{\sqrt{2}}\hbar|\uparrow\rangle + \frac{+|1-1\rangle + |11\rangle}{\sqrt{2}}\frac{i}{i}\frac{\hbar^2}{2}|\downarrow\rangle = -\frac{\hbar^2}{2}|p_z\uparrow\rangle + \frac{\hbar^2}{2i}|p_y\downarrow\rangle$

Za določitev novih valovnih funkcij $|p_x\uparrow\rangle'$ uporabimo perturbacijo:

$|p_x\uparrow\rangle' = |p_x\uparrow\rangle + \frac{\langle p_y\uparrow|\lambda\vec{L}\vec{S}|p_x\uparrow\rangle}{-\Delta_1}\cdot|p_y\uparrow\rangle + \frac{\langle p_z\downarrow|\lambda\vec{L}\vec{S}|p_x\uparrow\rangle}{-\Delta_2}|p_z\downarrow\rangle$

$= |p_x\uparrow\rangle + \frac{\lambda\hbar^2}{\Delta_1\cdot 2i}|p_y\uparrow\rangle - \frac{\lambda\hbar^2}{2\Delta_2}|p_z\downarrow\rangle$

$|p_x\downarrow\rangle' = |p_x\downarrow\rangle + \frac{\langle p_z\uparrow|\lambda\vec{L}\vec{S}|p_x\downarrow\rangle}{-\Delta_2}|p_z\uparrow\rangle + \frac{\langle p_y\downarrow|\lambda\vec{L}\vec{S}|p_x\uparrow\rangle}{-\Delta_1}|p_y\downarrow\rangle =$

$= |p_x\downarrow\rangle + \frac{\lambda\hbar^2}{\Delta_2\cdot 2}|p_z\uparrow\rangle - \frac{\lambda\cdot\hbar^2}{\Delta_1\cdot 2i}|p_y\downarrow\rangle$

3.) Damo v zunanje magnetno polje v z smeri: $\vec{B} = B_0\hat{e}_z$

$-\vec{\mu}\vec{B} = \frac{\mu_B}{\hbar}(\vec{L} + 2\vec{S})\vec{B} = \frac{\mu_B}{\hbar}(L_z + 2S_z)B_0$

${}'\langle p_x\uparrow|\frac{\mu_B}{\hbar}(L_z + 2S_z)|p_x\uparrow\rangle' = \frac{\mu_B B_0}{\hbar}\left[{}'\langle p_x\uparrow|L_z|p_x\uparrow\rangle' + 2\,{}'\langle p_x\uparrow|S_z|p_x\uparrow\rangle'\right] = \star$

$L_z|p_x\rangle = L_z\frac{|1-1\rangle - |11\rangle}{\sqrt{2}} = \frac{-\hbar|1-1\rangle - \hbar|11\rangle}{\sqrt{2}}\frac{i}{i} = \hbar i|p_y\rangle \qquad L_z|p_z\rangle = L_z|10\rangle = 0$

$L_z|p_y\rangle = L_z\, i\frac{|11\rangle + |1-1\rangle}{\sqrt{2}} = i\frac{\hbar|11\rangle - \hbar|1-1\rangle}{\sqrt{2}} = -i\hbar|p_x\rangle$

$\langle\uparrow|S_z|\uparrow\rangle = \langle\uparrow|\frac{\hbar}{2}|\uparrow\rangle = \frac{\hbar}{2} \qquad \langle\downarrow|S_z|\downarrow\rangle = -\frac{\hbar}{2}$

$\langle\uparrow|S_z|\downarrow\rangle = -\frac{\hbar}{2}\langle\uparrow|\downarrow\rangle = \emptyset$

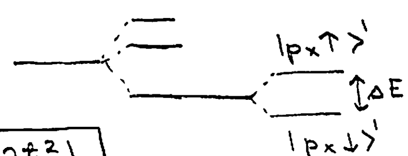
$\propto\lambda^2 \to$ zanemarimo

$(\underbrace{\langle p_x\uparrow|\tfrac{\hbar}{2}|p_x\uparrow\rangle}_{=\frac{\hbar}{2}1} + \cancel{\langle p_y\uparrow|\tfrac{\hbar}{2}\left(\tfrac{\lambda\hbar^2}{2i\Delta_1}\right)^2|p_y\uparrow\rangle} + \cancel{\langle p_z\downarrow|\tfrac{\hbar}{2}\left(\tfrac{\lambda\hbar^2}{2\Delta_2}\right)|p_z\downarrow\rangle})$

$\star = \frac{\mu_B B_0}{\cancel{\hbar}}\left[{}'\langle p_x\uparrow|\left(\cancel{\hbar}i|p_y\rangle + \frac{\lambda\hbar^2}{\Delta_1\cdot 2i}(-i\cancel{\hbar}|p_x\rangle) - \emptyset\right) + \cancel{2}\frac{\cancel{\hbar}}{\cancel{2}}1\,{}'\langle p_x\uparrow|p_x\uparrow\rangle'\right] =$

$= \mu_B B_0\left[-\frac{\cancel{i}\lambda\hbar^2}{2\cancel{i}\Delta_1} + \frac{\lambda\hbar^2}{\Delta_1 2\cancel{i}}(-\cancel{i}) + 1\right] = \mu_B B_0\left[1 - \frac{\lambda\hbar^2}{2\Delta_1} - \frac{\lambda\hbar^2}{2\Delta_1}\right] = \mu_B B_0\left[1 - \frac{\lambda\hbar^2}{\Delta_1}\right]$

${}'\langle p_x\downarrow|\frac{\mu_B B_0}{\hbar}(L_z + 2S_z)|p_x\downarrow\rangle' = \mu_B B_0\left(\frac{\lambda\hbar^2}{\Delta_1} - 1\right)$



$\Delta E = 2\mu_B B_0\left(1 - \frac{\lambda\hbar^2}{\Delta_1}\right) = g\mu_B B_0$ kjer je $\boxed{g = 2\left(1 - \frac{\lambda\hbar^2}{\Delta_1}\right)}$

↑ spektroskopski faktor