# HYPERJEMNÁ STRUKTURA

hyperjemná struktura = štěpení spektrálních čar
vlivem spin-spinové interx

vodík: $p^+e^-$: $p^+$ $-e$ $1/2$
$e^-$ $e$ $1/2$
⇒ mají vnitřní magn. moment
⇒ magn. interx

proton: vnitřní magn. moment $\vec{\mu} = g_j \frac{-Ze}{m_j} \vec{S}_j$

gyromagnetický poměr jádra
$g_p \simeq 2{,}792$

⇒ budí magn. pole:

$$\vec{A} = \frac{1}{4\pi} \frac{\vec{\mu} \times \vec{r}}{r^3}$$

$$\vec{B} = \frac{1}{4\pi} \frac{3\vec{n}\,\vec{n}\cdot\vec{\mu} - \vec{\mu}}{r^3} + \frac{2}{3}\vec{\mu}\,\delta(\vec{r})$$

$e^-$ se nachází v tomto magn. poli
⇒ Pauliho hamiltonián pro popis částice se spinem ve vnějším EM poli

$$H = \frac{p^2}{2m} - \frac{Z\alpha}{r} \Rightarrow H = \frac{p^2}{2m} - \frac{Z\alpha}{r} - \frac{e}{m}\vec{A}\cdot\vec{p} - \frac{e}{m}\vec{B}\cdot\vec{S}$$

⇒ pro HFS dostaneme:

$$H = \underbrace{\frac{p^2}{2m} - \frac{Z\alpha}{r}}_{H_0} - \frac{e}{m}\frac{\vec{\mu}\cdot\vec{L}}{4\pi r^3} - \frac{e}{4\pi r^3}\Big[\vec{S}\cdot\vec{\mu}\,\frac{8\pi}{3}\delta(r) - \frac{1}{r^3}\left(\vec{S}\cdot\vec{\mu} - 3(\vec{n}\cdot\vec{S})(\vec{n}\cdot\vec{\mu})\right)\Big]$$

⇒ v 1. řádu PT

⇒ v 1. řádu PT (+ přechod z AU)

$$E_n^{(1)} = \frac{Z\alpha g_j}{m_e m_j} (m_r Z\alpha)^3 \langle \psi_n | \Big[ \frac{1}{r^3} \vec{S}_j \cdot \vec{L} + \frac{8\pi}{3} \delta(r)\, \vec{S}_e \cdot \vec{S}_j - \frac{1}{r} \left( \vec{S}_e \cdot \vec{S}_j - 3 \vec{n} \cdot \vec{S}_e \, \vec{n} \cdot \vec{S}_j \right) \Big] | \psi_n \rangle$$

interx spin jádra + orb. m.h. $e^-$ (pro S =0)

spin-spinová interx (nenulové pouze pro S-stavy)

střední hodnota tenzorového působení (pro S-stavy nulové)

## $\boxed{\text{HFS základního stavu vodíku}}$

$|\psi_0\rangle = |1s\rangle$ ⇒ přispěje pouze $\underbrace{\vec{S}_e \cdot \vec{S}_j \frac{8\pi}{3} \delta(r)}_{= H_1}$

možné stavy: |spin e⟩ |spin jádra⟩

$$\{|\uparrow\rangle, |\downarrow\rangle\} \otimes \{|\uparrow\rangle, |\downarrow\rangle\}$$

⇒ 4 možné stavy: $|\uparrow\uparrow\rangle, |\uparrow\downarrow\rangle, |\downarrow\uparrow\rangle, |\downarrow\downarrow\rangle$

⇒ degenerovaná PT

$$\vec{S}_e \cdot \vec{S}_j = \frac{1}{2} \left[ S_+^e S_-^j + S_-^e S_+^j \right] + S_z^e S_z^j$$

$$\Rightarrow \quad \vec{S}_e \cdot \vec{S}_j |\uparrow\uparrow\rangle = \frac{1}{4} |\uparrow\uparrow\rangle$$

$$\vec{S}_e \cdot \vec{S}_j |\uparrow\downarrow\rangle = \frac{1}{2} |\downarrow\uparrow\rangle - \frac{1}{4} |\uparrow\downarrow\rangle$$

$$\vec{S}_e \cdot \vec{S}_j |\downarrow\uparrow\rangle = \frac{1}{2} |\uparrow\downarrow\rangle - \frac{1}{4} |\downarrow\uparrow\rangle$$

$$\vec{S}_e \cdot \vec{S}_j |\downarrow\downarrow\rangle = \frac{1}{4} |\downarrow\downarrow\rangle$$

protože $S_\pm |\pm\rangle = 0$

$$S_\mp |\pm\rangle = |\mp\rangle$$

$$S_z |\pm\rangle = \pm\tfrac{1}{2}|\pm\rangle$$

$\Rightarrow$ matice pro PM
$$\begin{pmatrix} 1/4 & 0 & 0 & 0 \\ 0 & -1/4 & 1/2 & 0 \\ 0 & 1/2 & -1/4 & 0 \\ 0 & 0 & 0 & 1/4 \end{pmatrix}$$

$\Rightarrow$ musíme diagonalizovat jen $\begin{pmatrix} -1/4 & 1/2 \\ 1/2 & -1/4 \end{pmatrix}$

dva krajní stavy zůstanou

$$\Rightarrow \begin{pmatrix} -1/4 & 1/2 \\ 1/2 & -1/4 \end{pmatrix}\begin{pmatrix} a \\ b \end{pmatrix} = \lambda \begin{pmatrix} a \\ b \end{pmatrix}$$

$$\left(\lambda + \frac{1}{4}\right)^2 - \frac{1}{4} = 0$$

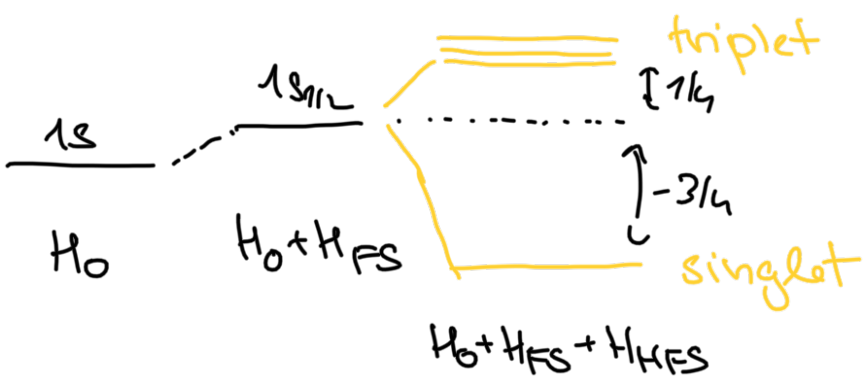
$$\lambda_1 = \frac{1}{4} \qquad \lambda_2 = -\frac{3}{4}$$

$$a_1 = \frac{1}{\sqrt{2}} \quad b_1 = \frac{1}{\sqrt{2}} \qquad a_2 = \frac{1}{\sqrt{2}} \quad b_2 = -\frac{1}{\sqrt{2}}$$

$\Rightarrow$ dostaneme: $\lambda = 1/4 \quad |\uparrow\uparrow\rangle, |\downarrow\downarrow\rangle, (|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle)\frac{1}{\sqrt{2}}$

$\lambda = -3/4 \quad \frac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle)$

$\Rightarrow$ hladiny:



# SODÍKOVÝ DUBLET

atom sodíku $= 11e^-$

$\Rightarrow$ el. konfig. $\rightarrow$ zákl. stav: $\underbrace{1s^2 2s^2 2p^6}\ \underbrace{3s^1}$

zaplněné slupky

$\Rightarrow$ efektivně $1e^-$ atom

$\Rightarrow$ vodíku-podobný systém

$\rightarrow$ 1. excitovaný stav $\underbrace{1s^2 2s^2 2p^6}\ 3p^1$

## ① jemná struktura Na

$\rightarrow$ spin-orbitální interakce:

$$3s: \left.\begin{matrix} l=0 \\ s=1/2 \end{matrix}\right\} \Rightarrow j = 1/2 \quad \Rightarrow 3^2S_{1/2}$$

$$3p: \left.\begin{matrix} l=1 \\ s=1/2 \end{matrix}\right\} \Rightarrow j = 1/2, 3/2 \quad \Rightarrow 3^2P_{1/2}, 3^2P_{3/2}$$

spektroskopická notace $\boxed{n^{2S+1}L_J}$




$n=3\ l=1\ s=1/2\ j=3/2$

$n=3\ l=1\ s=1/2\ j=1/2$

$n=3\ l=0\ s=1/2\ j=1/2$

pro atom s 1 val. $e^-$

$$H_{SO} = \xi(r)\,\vec{L}\cdot\vec{S}$$

$$A := \int_0^\infty dr\, r^2\, |R_{3p}|^2\, \xi(r)$$ ← radiální 3p orbital

$$\langle H_{SO}\rangle_{3p} = \langle 3p|\,\xi(r)\,\vec{L}\cdot\vec{S}\,|3p\rangle$$
$$= A\,\langle 3p|\vec{L}\cdot\vec{S}|3p\rangle$$

$$\vec{J} = \vec{L} + \vec{S}$$

$$J^2 = L^2 + S^2 + 2\vec{L}\cdot\vec{S} \Rightarrow \vec{L}\cdot\vec{S} = \frac{1}{2}(J^2 - L^2 - S^2)$$

$$\Rightarrow \langle \vec{L}\cdot\vec{S}\rangle = \frac{1}{2}\big(j(j+1) - l(l+1) - s(s+1)\big)$$

$$\Rightarrow \text{pro } 3p: \quad 3^2P_{1/2} = -1$$
$$3^2P_{3/2} = +\frac{1}{2}$$

$$\Rightarrow 3^2P_{1/2} \quad \langle H_{SO}\rangle = -A$$
$$3^2P_{3/2} \quad \langle H_{SO}\rangle = \frac{1}{2}A$$

$$E(3^2P_{3/2}) - E(3^2P_{1/2}) = \frac{3}{2}A$$

$$\hookrightarrow 16973{,}4\,\text{cm}^{-1} - 16956{,}2\,\text{cm}^{-1} = \frac{3}{2}A'$$

$$\Rightarrow \underline{\underline{A' \approx 11\,\text{cm}^{-1}}}$$

## ② hyperjemná struktura $^{23}$Na $\quad (I_{23} = 3/2)$

$$H_0 \gg H_{FS} \gg H_{HFS}$$

$$H_{HFS} = K\,\vec{I}\cdot\vec{J} \qquad (K = \text{konstanta spec.}$$

pro daný systém)

$\Rightarrow$ komutátory: $J^2, J_z, I^2, I_z, F^2, F_z$

$$F = J + I$$

složíme MH jádra + + spin-orbitalní

(spin jádra + spin elektronu + + orbitální MH elek.)

$$[H_{HFS}, J^2] = K[\vec{I}\cdot\vec{J}, J^2] =$$
$$= K[I_x J_x + I_y J_y + I_z J_z, J^2] =$$
$$= K(I_x \underbrace{[J_x, J^2]}_{=0} + \dots) =$$
$$\underline{\underline{= 0}}$$

$[H_{HFS}, I^2] = \dots \underline{\underline{= 0}}$ analogicky

$$[H_{HFS}, J_z] = \dots = K(I_x \underbrace{[J_x, J_z]}_{\neq 0} + \dots) \underline{\underline{\neq 0}}$$

$[H_{HFS}, F_z] = \dots \underline{\underline{\neq 0}}$ analogicky

$[H_{HFS}, F^2] =$

$$F = J + I$$
$$F^2 = J^2 + I^2 + 2\vec{J}\cdot\vec{I}$$
$$\Rightarrow \vec{J}\cdot\vec{I} = \frac{1}{2}(F^2 - J^2 - I^2)$$

$$\longrightarrow = K\tfrac{1}{2}[F^2 - J^2 - I^2, F^2] =$$

$$= \tfrac{1}{2}K\left(\underbrace{[F^2, F^2]}_{=0} - \underbrace{[J^2, F^2]}_{=0} - \underbrace{[I^2, F^2]}_{=0}\right) =$$

$$\underline{\underline{= 0}}$$

$$\underline{\underline{[H_{HFS}, F_z]}} = \tfrac{1}{2}K[F^2 - J^2 - I^2, F_z] =$$

$$= \tfrac{1}{2}K\underbrace{[F^2, F_z]}_{=0} = \underline{\underline{0}}$$

$\Rightarrow$ ÚMKO $\{F^2, F_z, J^2, I^2\}$

$\Rightarrow$ budeme pracovat v bázi $\underline{\underline{|J, I, F, M_F\rangle}}$

$\Rightarrow$ posuny hladin: $\langle H_{HFS}\rangle = \Delta E$

$$\langle H_{HFS}\rangle = \langle J, I, F, M_F | H_{HFS} | J, I, F, M_F\rangle =$$

$$= \langle J, I, F, M_F | K\,\vec{J}\cdot\vec{I}\, | J, I, F, M_F\rangle =$$

$$= \langle J, I, F, M_F | K\tfrac{1}{2}(F^2 - J^2 - I^2) | J, I, F, M_F\rangle =$$

$$\underline{\underline{= \tfrac{1}{2}K\left[f(f+1) - j(j+1) - i(i+1)\right] = \Delta E}}$$

$\rightarrow 3\,{}^2S_{1/2}$: $F=1$ $\quad \Delta E = -\frac{5}{4}K({}^2S_{1/2})$

$F=2$ $\quad \Delta E = +\frac{3}{4}K({}^2S_{1/2})$

$\rightarrow 3\,{}^2P_{1/2}$: $F=1$ $\quad \Delta E = -\frac{5}{4}K({}^2P_{1/2})$

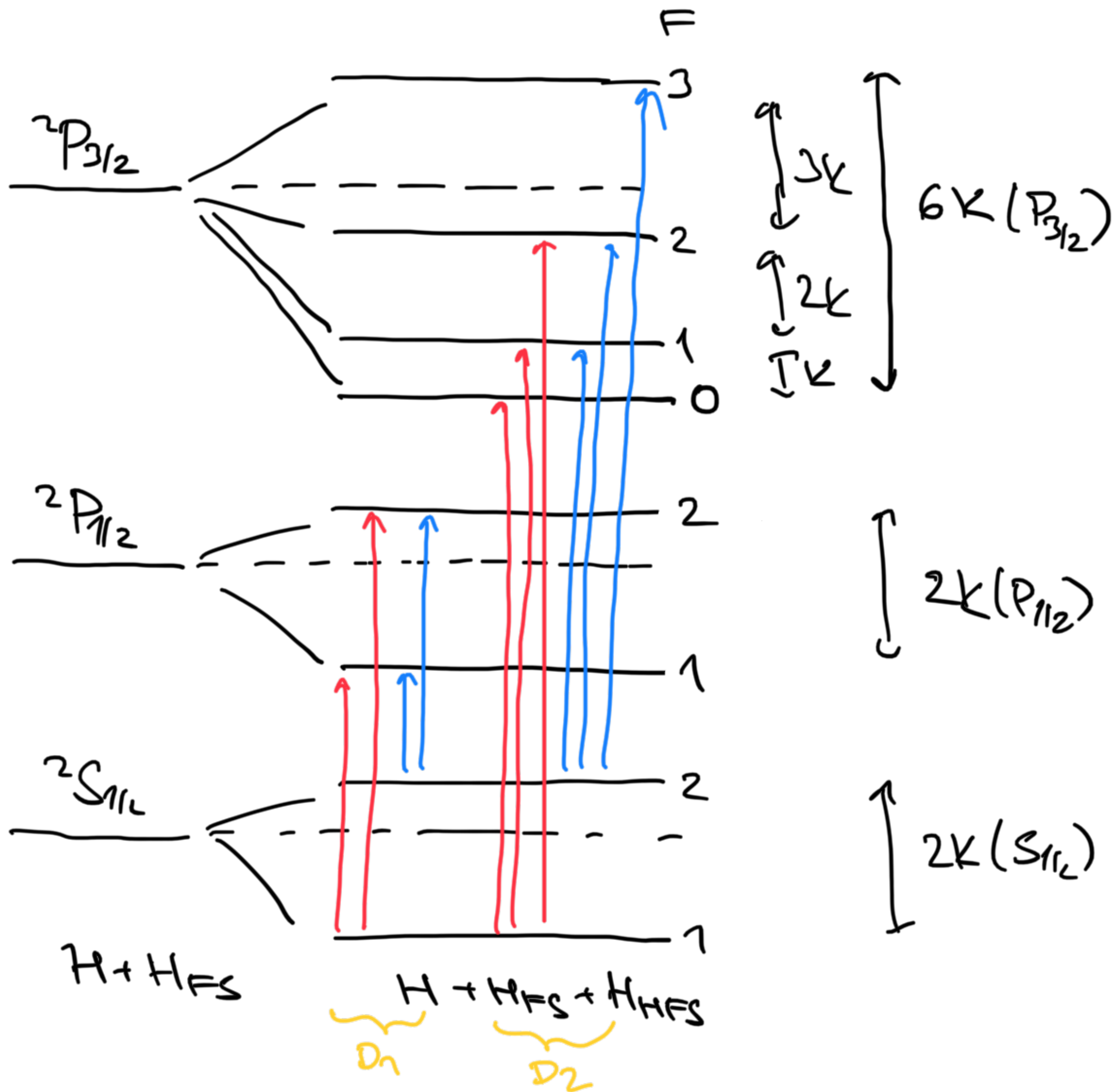
$F=2$ $\quad \Delta E = +\frac{3}{4}K({}^2P_{1/2})$

$\rightarrow 3\,{}^2P_{3/2}$: $F=0$ $\quad \Delta E = -\frac{15}{4}K({}^2P_{3/2})$

$F=1 \qquad \Delta E = -\frac{11}{4} K(^2P_{3/2})$

$F=2 \qquad \Delta E = -\frac{3}{4} K(^2P_{3/2})$

$F=3 \qquad \Delta E = +\frac{9}{4} K(^2P_{3/2})$




$\Rightarrow$ povolené dipólové přechody

$\downarrow$

výběrová pravidla: $\Delta L = \pm 1$

$\Delta J = 0, \pm 1$

$\Delta F = 0, \pm 1$