STARKŮV JEV

= štěpení spektrálních čar vlivem vnějšího el. pole

atom vodíku $H_0 = \frac{p^2}{2m} - \frac{e^2}{4\pi\varepsilon_0}\frac{1}{r}$

$\Rightarrow \quad H_0|\psi_n\rangle = E_n|\psi_n\rangle$

$E_n = -\frac{1}{n^2}R$ R = Rydbergova konst.

$R = \frac{m}{2\hbar^2}\left(\frac{e^2}{4\pi\varepsilon_0}\right)^2$

$1\,Ry = 0{,}5\,Ha = 13{,}6\,eV$

(I) degenerace $E_n = -R\frac{1}{n^2}$:

↳ E_n nezávisí na $l = 0, \dots, n-1$

$m = -l, \dots, +l$

$\Rightarrow$ $(2l+1)$ hodnot m pro dané l

$\Rightarrow \sum_{l=0}^{n-1}(2l+1) = 1+3+5+\dots+(2(n-1)+1)$

$= a_1 + a_2 + \dots + a_n$

$(a_0 + a_1 + \dots + a_{n-1})$

$s_k = \frac{k}{2}(x_1 + x_k) \Rightarrow$

$\Rightarrow s_n = \frac{n}{2}\{1 + [2(n-1)+1]\} =$

$= \frac{n}{2}(2n) = \underline{\underline{n^2}}$

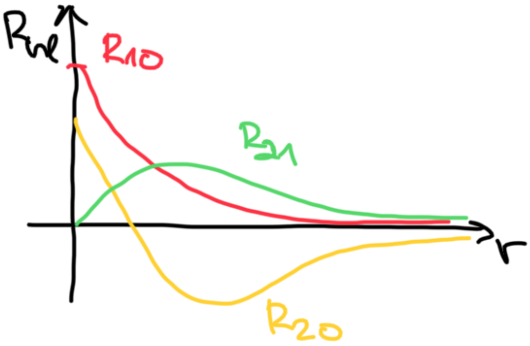
$\Rightarrow$ E_n je n^2-krát deg.

(+ uvážením spinu $2n^2$-krát deg.)

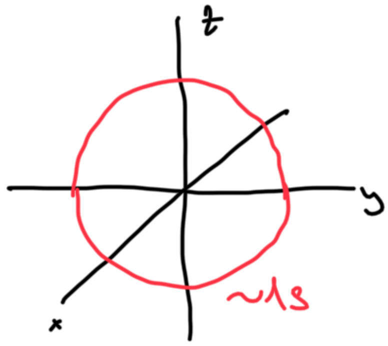
(II) $R_{10}, R_{20}, R_{21} \sim R_{nl}(r) \sim P_n\left(\frac{r}{a}\right) e^{-\frac{r}{na}}$

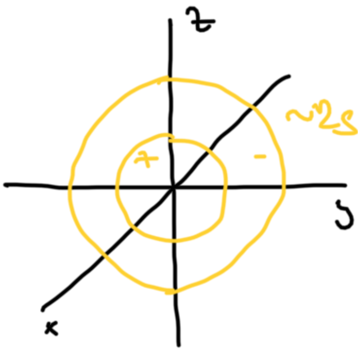
1s 2s 2p

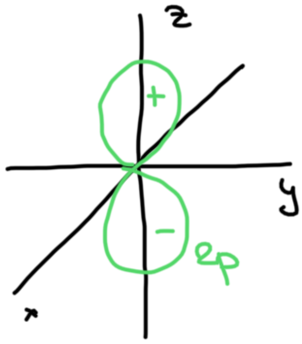
↑ Legendrovy polynomy



$\Psi_{100}, \Psi_{200}, \Psi_{210}$







(III) $\Psi_{100}(-\vec{x}) = \Psi_{100}(\vec{x})$ sudá

$\Psi_{200}(-\vec{x}) = \Psi_{200}(\vec{x})$ sudá

$\Psi_{210}(-\vec{x}) = -\Psi_{210}(\vec{x})$ lichá

$\vec{x} \to -\vec{x}$

$\theta \to \theta + \pi$

parita $\sim (-1)^l$

vnější el. pole: $H_1 = -\vec{D} \cdot \vec{\mathcal{E}} = -e\vec{r} \cdot \vec{\mathcal{E}} = -e\mathcal{E}z$

$\vec{D}$ = dipólový moment

$\vec{\mathcal{E}}$ podél osy z

(IV) zákl. stav $\Psi_{100} = |1,0,0\rangle$

$E_1^{(1)} = \langle 1,0,0| H_1 |1,0,0\rangle =$

$= \int$ sudá · lichá · sudá $= 0$

(V) první excit. stav $n=2$

$$\{|2,0,0\rangle,\ |2,1,-1\rangle,\ |2,1,0\rangle,\ |2,1,+1\rangle\}$$

2s 3x 2p

$\Rightarrow$ 4x degenerovaný $E_2^{(0)} = -\frac{1}{4}R$

(VI) $\Rightarrow$ degenerovaná PT

$$\begin{array}{c|cccc} & |2,0,0\rangle & |2,1,0\rangle & |2,1,-1\rangle & |2,1,+1\rangle \\ \hline \langle 2,0,0| & 0 & 3e\mathcal{E} & 0 & 0 \\ \langle 2,1,0| & 3e\mathcal{E} & 0 & 0 & 0 \\ \langle 2,1,-1| & 0 & 0 & 0 & 0 \\ \langle 2,1,+1| & 0 & 0 & 0 & 0 \end{array}$$

$\langle 2,0,0|H_1|2,0,0\rangle = 0$

$\langle 2,1,0|H_1|2,1,0\rangle = \int$ lichá · lichá · lichá $=0$

$\langle 2,1,-1|H_1|2,1,0\rangle = \int$ lichá · lichá · lichá $=0$

$$\langle 2,0,0|H_1|2,1,0\rangle = \int_0^\infty r^2 dr \int_0^\pi \sin\theta\, d\theta \int_0^{2\pi} d\varphi \;\times$$

$$\times\, 2\left(\frac{1}{2a}\right)^{3/2}\left(1-\frac{r}{2a}\right)e^{-\frac{r}{2a}}\cdot\frac{1}{\sqrt{4\pi}} \times \quad \psi_{200}^*$$

$$\times\, (-e\mathcal{E} r\cos\theta) \times \quad H_1$$

$$\times\, \frac{1}{\sqrt{3}}\left(\frac{1}{2a}\right)^{3/2}\left(\frac{r}{a}\right)e^{-\frac{r}{2a}}\sqrt{\frac{3}{4\pi}}\cos\theta = \psi_{210}$$

$$= 2\left(\frac{1}{2a}\right)^3 \cdot \frac{1}{\sqrt{3}}\cdot\frac{1}{a}\cdot\frac{\sqrt{3}}{4\pi}(-e\mathcal{E})\int_0^\infty dr\, r^4\left(1-\frac{r}{2a}\right)e^{-\frac{r}{a}} \times$$

$$\times \int_0^\pi d\theta \sin\theta\cos^2\theta \underbrace{\int_0^{2\pi} d\varphi}_{2\pi} =$$

∞ π

$$= \frac{1}{a}\left(\frac{1}{2a}\right)^3 (-e\mathcal{E}) \int_0^\infty dr\, r^4 \left(1-\frac{r}{2a}\right) e^{-\frac{r}{a}} \int_0^\pi d\vartheta \sin\vartheta \cos^2\vartheta$$

nápověda I: $\int_0^\infty x^4 \left(1-\frac{x}{2}\right) e^{-x} dx = -36$

$$\Rightarrow \int_0^\infty dr\, r^4 \left(1-\frac{r}{2a}\right) e^{-\frac{r}{a}} = \left| r = r'a \right| =$$

$$= a^5 \int_0^\infty dr\, r^4 \left(1-\frac{r}{2}\right) e^{-r} = -36a^5$$

nápověda II: $\int_0^\pi \cos^2\vartheta \sin\vartheta\, d\vartheta = \frac{2}{3}$

$$\Rightarrow \langle 2,0,0|H_1|2,1,0\rangle = \frac{1}{8a^4} \cdot (-e\mathcal{E}) \cdot (-36a^5) \cdot \frac{2}{3} =$$

$$= \underline{\underline{3ae\mathcal{E}}}$$

$$\langle 2,0,0|H_1|2,1,\pm1\rangle \sim \int \dots dr \underbrace{\int Y_{00}^* \overset{\sim \cos\vartheta}{Y_{10}} Y_{1,\pm1}\, d\Omega}$$

$$= Y_{00}^* \underbrace{\int Y_{10} Y_{1,\pm1}}_{=0} = 0$$

$\Rightarrow$ chceme najít vl. čísla a vl. vektory

$$\begin{pmatrix} -E_2^{(1)} & 3ae\mathcal{E} & 0 & 0 \\ 3ae\mathcal{E} & -E_2^{(1)} & 0 & 0 \\ 0 & 0 & -E_2^{(1)} & 0 \\ 0 & 0 & 0 & -E_2^{(1)} \end{pmatrix}$$

$\Rightarrow E_2^{(1)} = 0 \quad 2\times$

$$\det\begin{pmatrix} -\lambda & 3ae\mathcal{E} \\ \dots & \dots \end{pmatrix} \overset{!}{=} 0$$

$\det(3ae\mathcal{E} - \lambda \quad)$

$$\lambda = \pm 3ae\mathcal{E}$$

$\Rightarrow \quad \lambda_1 = 0 \quad |2,1,+1\rangle$ } s těmito stavy se
$\quad\ \ \lambda_2 = 0 \quad |2,1,-1\rangle$ } nic nestane

$\lambda_3 = -3ae\mathcal{E}$ a vl. stav $\frac{1}{\sqrt{2}}\begin{pmatrix}1\\-1\end{pmatrix}$

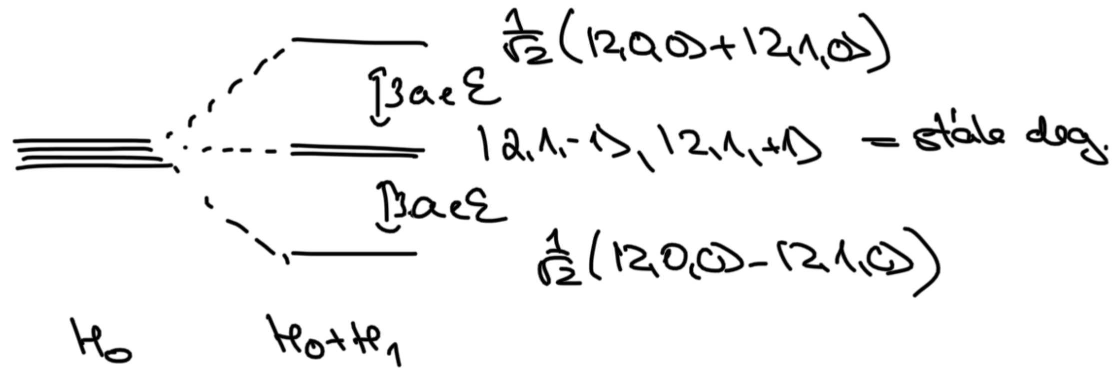
tj. $|\varphi\rangle = \frac{1}{\sqrt{2}}\left(|2,0,0\rangle - |2,1,0\rangle\right)$

$\lambda_4 = -3ae\mathcal{E}$ a vl. stav $\frac{1}{\sqrt{2}}\begin{pmatrix}1\\1\end{pmatrix}$

tj. $|\varphi\rangle = \frac{1}{\sqrt{2}}\left(|2,0,0\rangle + |2,1,0\rangle\right)$

(VIII)

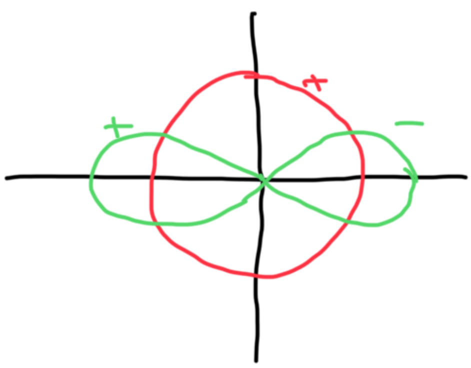
$\Rightarrow$ hladiny:



(IX) vlnové funkce:

$\psi_{2,1,\pm1}$ zůstanou

$\psi_{2,0,0}$ a $\psi_{2,1,0}$ se míchají $\Rightarrow$ polarizace



dále $n=1$ $H = H_0 + H_1$ $H|\Phi_1\rangle = E_1|\Phi_1\rangle$ $E_1 = E_1(\mathcal{E})$

(X) $\langle \Phi_1 | D_z | \Phi_1 \rangle = -\frac{dE_1}{d\mathcal{E}}$

změna el. pole $\to \mathcal{E} + d\mathcal{E}$

$$H(\mathcal{E}) = H_0 - D_z \mathcal{E}$$

$$\begin{aligned} H(\mathcal{E}+d\mathcal{E}) &= H_0 - D_z(\mathcal{E}+d\mathcal{E}) = \\ &= H_0 - D_z\mathcal{E} - D_z d\mathcal{E} = \\ &= H(\mathcal{E}) - D_z d\mathcal{E} \end{aligned}$$

a podobně pro střední hodnotu:

$$\underbrace{\langle \Phi_1 | H(\mathcal{E}+d\mathcal{E}) | \Phi_1 \rangle}_{= E_1(\mathcal{E}+d\mathcal{E})} = \underbrace{\langle \Phi_1 | H(\mathcal{E}) | \Phi_1 \rangle}_{E_1(\mathcal{E})} - \underbrace{\langle \Phi_1 | D_z d\mathcal{E} | \Phi_1 \rangle}_{-\langle \psi_1 | D_z | \psi_1 \rangle d\mathcal{E}}$$

$$E_1(\mathcal{E}+d\mathcal{E}) = E_1(\mathcal{E}) - \langle \psi_1 | D_z | \psi_1 \rangle d\mathcal{E}$$

$$\Rightarrow \underline{\underline{\langle \Phi_1 | D_z | \Phi_1 \rangle}} = \frac{E_1(\mathcal{E}) - E_1(\mathcal{E}+d\mathcal{E})}{d\mathcal{E}} = \underline{\underline{-\frac{dE_1(\mathcal{E})}{d\mathcal{E}}}}$$

(XI) rozvineme v řadu:

$$|\Phi_1\rangle = |\psi_{100}\rangle + \mathcal{E} \sum_{nlm} \frac{\langle \psi_{100} | D_z | \psi_{nlm} \rangle}{E_1^{(0)} - E_n^{(0)}}$$

$$\sum_{\substack{nlm \\ n\neq 1}} \quad E_1^{(0)} - E_n^{(0)}$$

$$\Rightarrow \langle \Psi_1 | D_z | \Psi_1 \rangle = \langle \psi_{100} | D_z | \psi_{100} \rangle^{=0} +$$

$$- \mathcal{E} \sum_{\substack{nlm \\ n\neq 1}}' \frac{\langle \psi_{100} | D_z | \psi_{nlm} \rangle}{E_1^{(0)} - E_n^{(0)}} - \text{opačný člen}$$

$$+ O(\mathcal{E}^2)$$

$$\Rightarrow -\frac{dE_1(\mathcal{E})}{d\mathcal{E}} = \langle \psi_1 | D_z | \psi_1 \rangle = -2\mathcal{E} \sum_{\substack{nlm \\ n\neq 1}}' \frac{|\langle \psi_{100} | D_z | \psi_{nlm} \rangle|^2}{E_1^{(0)} - E_n^{(0)}} + O(\mathcal{E}^2)$$

a zintegrujeme:

$$E_1(\mathcal{E}) = E_1^{(0)} + \mathcal{E}^2 \sum_{\substack{nlm \\ n\neq 1}}' \frac{|\langle \psi_{100} | D_z | \psi_{nlm} \rangle|^2}{E_1^{(0)} - E_n^{(0)}}$$

$$\Rightarrow \alpha = -\frac{2}{4\pi\varepsilon_0} \sum' \frac{|\langle \psi_{100} | D_z | \psi_{nlm} \rangle|^2}{E_1^{(0)} - E_n^{(0)}}$$

polarizabilita

(VIII) uvažujme $E_1^{(0)} - E_n^{(0)} \approx 1\,\mathrm{Ry}$

$$\Rightarrow \alpha \approx -\frac{2}{4\pi\varepsilon_0 R} \sum_{\substack{nlm \\ n\neq 1}} \langle \psi_{100} | D_z \underbrace{| \psi_{nlm} \rangle \langle \psi_{nlm} |}_{} D_z | \psi_{100} \rangle$$

$$\sum_{n\neq 1} = \sum_{n \text{ vše}}$$

$$\langle \psi_{100} | D_z | \psi_{100} \rangle = 0$$

$$\alpha \approx -\frac{2}{4\pi\varepsilon_0 R} \sum_{nlm}' \langle \psi_{100} | D_z | \psi_{nlm} \rangle \times$$

$$\times \langle \psi_{nlm} | D_z | \psi_{100} \rangle$$

$$\Rightarrow \alpha \approx -\frac{2}{4\pi\varepsilon_0 R} \langle \psi_{100} | D_z^2 | \psi_{100} \rangle$$

(XIV) izotropni prostredu

$$\langle D_x^2 \rangle = \langle D_y^2 \rangle = \langle D_z^2 \rangle$$

$$\Rightarrow \underline{\underline{\langle D_z^2 \rangle = \frac{1}{3} \langle D^2 \rangle}}$$

(XV) $\alpha \doteq -\frac{2}{4\pi\varepsilon_0 R} \langle 100 | D_z^2 | 100 \rangle =$

$$= -\frac{2}{4\pi\varepsilon_0 R} \int_0^\infty dr\, r^2 \int_0^\pi \sin\vartheta\, d\vartheta \int_0^{2\pi} d\varphi \; \times$$

$$\times \frac{1}{4\pi} \left(2 \left(\frac{1}{a}\right)^{3/2} e^{-\frac{r}{a}} \right)^2 e^2 r^2 \cos^2\vartheta =$$

$$= -\frac{2}{4\pi\varepsilon_0 R} \, 4 \, \frac{1}{a^3} \frac{1}{4\pi} \underbrace{\int_0^\infty e^{-\frac{2r}{a}} r^4 dr}_{} \underbrace{\int_0^\pi \sin\vartheta \cos^2\vartheta\, d\vartheta}_{=\frac{2}{3}} \underbrace{\int_0^{2\pi} d\varphi}_{=2\pi}$$

$$\int_0^\infty r^k e^{-\frac{pr}{a}} dr = k! \left(\frac{a}{p}\right)^{k+1}$$

$$= 4! \left(\frac{a}{2}\right)^5$$

$$= -\frac{2}{4\pi\varepsilon_0 R} \cdot 4 \cdot \frac{1}{a^3} \cdot \frac{1}{4\cancel{\pi}} \cdot 4! \cdot \left(\frac{a}{2}\right)^5 \cdot \frac{2}{3} \cdot 2\cancel{\pi} =$$

$$= -\frac{2}{4\pi\varepsilon_0 R} a^2 \cdot 3 \cdot \frac{1}{3} = -\frac{2a^2}{4\pi\varepsilon_0 R}$$

$R =$