(1)

1. cvičení (2.3.2021) – úlohy z textu

(I) $\underline{\underline{P_2}} = |\langle 2|\psi\rangle|^2 = \langle 2|\psi\rangle\langle\psi|2\rangle = c_2\underbrace{\langle 2|2\rangle}_{=1}\cdot c_2^*\underbrace{\langle 2|2\rangle}_{1} = \underline{\underline{|c_2|^2}}$

(II) hermitovsky sdružené vektory:

$|1\rangle = \begin{pmatrix}1\\0\end{pmatrix} \qquad \langle 1| = (1\ 0)$

$|-1\rangle = \begin{pmatrix}0\\1\end{pmatrix} \qquad \langle -1| = (0\ 1)$

$|\psi\rangle = c_1|1\rangle + c_2|2\rangle - \begin{pmatrix}c_1\\c_2\end{pmatrix} \Rightarrow \langle\psi| = (c_1^*\ c_2^*)$

(III) trojhladinový systém:

bázové vektory: $|1\rangle = \begin{pmatrix}1\\0\\0\end{pmatrix} \quad |2\rangle = \begin{pmatrix}0\\1\\0\end{pmatrix} \quad |3\rangle = \begin{pmatrix}0\\0\\1\end{pmatrix}$

operátor $\hat{S}$ v této bázi: $\hat{S} = \begin{pmatrix}\langle 1|\hat{S}|1\rangle & \langle 1|\hat{S}|2\rangle & \langle 1|\hat{S}|3\rangle\\ \langle 2|\hat{S}|1\rangle & \langle 2|\hat{S}|2\rangle & \langle 2|\hat{S}|3\rangle\\ \langle 3|\hat{S}|1\rangle & \langle 3|\hat{S}|2\rangle & \langle 3|\hat{S}|3\rangle\end{pmatrix}$

(IV) $\langle +z|-z\rangle = (1\ 0)\begin{pmatrix}0\\1\end{pmatrix} = 1\cdot 0 + 0\cdot 1 = 0$

$\langle -z|+z\rangle = (0\ 1)\begin{pmatrix}1\\0\end{pmatrix} = 0$

(V) $\hat{S}_i = \begin{pmatrix}\langle +x|S_i|+x\rangle & \langle +x|S_i|-x\rangle\\ \langle -x|S_i|+x\rangle & \langle -x|S_i|-x\rangle\end{pmatrix}$

(VI) $\hat{S}_z|+z\rangle = \frac{1}{2}\begin{pmatrix}1&0\\0&-1\end{pmatrix}\begin{pmatrix}1\\0\end{pmatrix} = \frac{1}{2}\begin{pmatrix}1\\0\end{pmatrix} = \frac{1}{2}|+z\rangle$

$\hat{S}_z|-z\rangle = \frac{1}{2}\begin{pmatrix}1&0\\0&-1\end{pmatrix}\begin{pmatrix}0\\1\end{pmatrix} = -\frac{1}{2}\begin{pmatrix}0\\1\end{pmatrix} = -\frac{1}{2}|-z\rangle$

(VII) $\hat{S}_\pm|l,m\rangle = \sqrt{l(l+1) - m(m\pm 1)}\,|l,m\pm 1\rangle$

$\underline{\underline{\hat{S}_+|\tfrac{1}{2},+\tfrac{1}{2}\rangle}} = \sqrt{\tfrac{1}{2}(\tfrac{1}{2}+1) - \tfrac{1}{2}(\tfrac{1}{2}+1)}\,|\tfrac{1}{2},+\tfrac{3}{2}\rangle = \underline{\underline{0}}$

$\underline{\underline{\hat{S}_+|\tfrac{1}{2},-\tfrac{1}{2}\rangle}} = \sqrt{\tfrac{1}{2}(\tfrac{1}{2}+1) - (-\tfrac{1}{2})(-\tfrac{1}{2}+1)}\,|\tfrac{1}{2},+\tfrac{1}{2}\rangle = \sqrt{\tfrac{3}{4}+\tfrac{1}{4}}\,|\tfrac{1}{2},+\tfrac{1}{2}\rangle = \underline{\underline{|\tfrac{1}{2},+\tfrac{1}{2}\rangle}}$

$\underline{\underline{\hat{S}_-|\tfrac{1}{2},+\tfrac{1}{2}\rangle}} = \sqrt{\tfrac{1}{2}(\tfrac{1}{2}+1) - \tfrac{1}{2}(\tfrac{1}{2}-1)}\,|\tfrac{1}{2},-\tfrac{1}{2}\rangle = \underline{\underline{|\tfrac{1}{2},-\tfrac{1}{2}\rangle}}$

$\underline{\underline{S_-|\tfrac{1}{2},-\tfrac{1}{2}\rangle}} = \sqrt{\tfrac{1}{2}(\tfrac{1}{2}+1) - (-\tfrac{1}{2})(-\tfrac{1}{2}-1)}\,|\tfrac{1}{2},-\tfrac{3}{2}\rangle = \underline{\underline{0}}$

(VIII) $\frac{1}{2}\begin{pmatrix}0&1\\1&0\end{pmatrix}\begin{pmatrix}a\\b\end{pmatrix} = \lambda\begin{pmatrix}a\\b\end{pmatrix}$

$\begin{pmatrix}-\lambda & \frac{1}{2}\\ \frac{1}{2} & -\lambda\end{pmatrix}\begin{pmatrix}a\\b\end{pmatrix} = 0 \Rightarrow \det\begin{pmatrix}-\lambda & \frac{1}{2}\\ \frac{1}{2} & -\lambda\end{pmatrix} = \lambda^2 - \frac{1}{4} \overset{!}{=} 0$

$\underline{\underline{\lambda = \pm\frac{1}{2}}}$

$\lambda_1 = +\frac{1}{2}: \quad \frac{1}{2}b = \frac{1}{2}a \Rightarrow a = b$

$|a|^2 + |b|^2 = 1 \qquad \Rightarrow \underline{\underline{v_1}} = \begin{pmatrix}a\\b\end{pmatrix} = \underline{\underline{\frac{1}{\sqrt{2}}\begin{pmatrix}1\\1\end{pmatrix}}}$

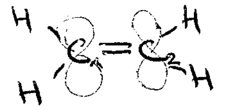
$\lambda_2 = -\frac{1}{2}: \quad \frac{1}{2}b = -\frac{1}{2}a \Rightarrow a = -b$

$|a|^2 + |b|^2 = 1 \qquad \Rightarrow \underline{\underline{v_2}} = \begin{pmatrix}a\\b\end{pmatrix} = \underline{\underline{\frac{1}{\sqrt{2}}\begin{pmatrix}1\\-1\end{pmatrix}}}$

HÜCKELOVA METODA

-> pro výpočet elektronové struktury molekul s π-elektrony

-> ukážeme si na ethylenu (ethene) C_2H_4



-> sp^2 hybridizované C => $\sigma\, e^-$ ⇝ neinteragují (s πe^-), pohybují se volně

nás ale zajímají πe^-

⇓

pouze na C_1, C_2

na přednášce se bude probírat:

-> systém popsán vln. fcí $\Psi(x)$

-> Hamiltonián systému $H \to \hat{H}$ (v QM operátor)

} => Schrödinger: $H\Psi = E\Psi$ ←

bezčasová Schrödingerova rovnice

-> pro výpočet stacionárních stavů

=> pro náš případ:

celková vln. fce $|\Psi\rangle = c_1|1\rangle + c_2|2\rangle$ MO je lineární kombinací 2p orbitalů na C_1, C_2

↖ pozn: bra-ket-notace

$$\Psi(x) = c_1\varphi_1(x) + c_2\varphi_2(x)$$

, φ_1 a φ_2 orthonormální: $\int \varphi_1(x)\varphi_2(x)\,dV = 0$

$\int \varphi_1(x)\varphi_1(x)\,dV = \int \varphi_2(x)\varphi_2(x) = 1$

$$H\Psi = E\Psi$$

$$H(c_1\varphi_1 + c_2\varphi_2) = E(c_1\varphi_1 + c_2\varphi_2)$$

$$\begin{pmatrix} \int\varphi_1 H\varphi_1 & \int\varphi_1 H\varphi_2 \\ \int\varphi_2 H\varphi_1 & \int\varphi_2 H\varphi_2 \end{pmatrix}\begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = E\begin{pmatrix} c_1 \\ c_2 \end{pmatrix}$$

⇝ vlastní problém

-> vlastní čísla

-> vlastní vektory

$$(\mathbb{A} - \mathbb{1}\lambda)\cdot\vec{v} = 0$$

=> fyzikální význam:

$$\begin{pmatrix} \alpha & 0 \\ 0 & \alpha \end{pmatrix}\begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = E\begin{pmatrix} c_1 \\ c_2 \end{pmatrix}$$ ⇝ $1e^-$ sedí na C_1, $1e^-$ sedí na C_2

$$\begin{pmatrix} \alpha & -\beta \\ -\beta & \alpha \end{pmatrix}\begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = E\begin{pmatrix} c_1 \\ c_2 \end{pmatrix}$$ ⇝ zahrnuje pst, že e^- může „přeskočit" $C_1 \leftrightarrow C_2$

(β = tzv. rezonanční integrál)

tohle je náš problém, co budeme řešit

= hledáme energii E

a koeficienty c_1, c_2 => pst. výskytu e^- na jednotlivých uhlících

$$\begin{pmatrix} \alpha - E & -\beta \\ -\beta & \alpha - E \end{pmatrix}\begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = 0$$ ~~$\lambda = \frac{\alpha - E}{\beta}$~~

$$\begin{pmatrix} \frac{\alpha - E}{\beta} & -1 \\ -1 & \frac{\alpha - E}{\beta} \end{pmatrix}\begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = 0$$ substit.: $\lambda = \frac{\alpha - E}{\beta}$

$$\begin{pmatrix} \lambda & -1 \\ -1 & \lambda \end{pmatrix}\begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = 0$$ => hledáme vl. čísla: $\det\begin{vmatrix} \lambda & -1 \\ -1 & \lambda \end{vmatrix} \overset{!}{=} 0$

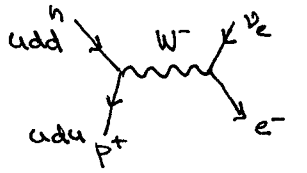
$$\lambda^2 - (-1)^2 = 0$$

$$\lambda^2 - 1 = 0$$

$$\lambda = \pm 1$$

β-ROZPAD TRITIA

$${}^{3}_{1}H \longrightarrow {}^{3}_{1}He^{+} + e^{-} + \tilde{\nu}_e \qquad \beta\text{-rozpad: } n \to p^{+} + e^{-} + \tilde{\nu}_e$$



hamiltonián pro vodík a vodíku-podobné systémy

$$\hat{H} = \frac{\hat{p}^2}{2\mu} - \frac{Ze^2}{4\pi\varepsilon_0 r} \approx \frac{\hat{p}^2}{2m_e} - \frac{Ze^2}{4\pi\varepsilon_0 r}$$

μ = redukovaná hmotnost systému

$$\mu = \frac{m_j m_e}{m_j + m_e} \approx m_e \quad (m_j \gg m_e)$$

→ vlastní funkce pro tři nejnižší hladiny:

$$\psi_{100}(r,\theta,\varphi) = \frac{1}{\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2} e^{-Z\frac{r}{a_0}}$$

$$\psi_{200}(r,\theta,\varphi) = \frac{1}{\sqrt{\pi}}\left(\frac{Z}{2a_0}\right)^{3/2}\left(1 - \frac{Zr}{2a_0}\right) e^{-\frac{Zr}{2a_0}}$$

$$\psi_{21m}(r,\theta,\varphi) = \frac{1}{\sqrt{3}}\left(\frac{Z}{2a_0}\right)^{3/2}\left(\frac{Zr}{a_0}\right) e^{-\frac{Zr}{2a_0}} Y_{1m}(\theta,\varphi)$$

$$Y_{1,+1}(\theta,\varphi) = -\sqrt{\frac{3}{8\pi}}\sin\theta\, e^{+i\varphi}$$

$$Y_{1,0}(\theta,\varphi) = \sqrt{\frac{3}{4\pi}}\cos\theta$$

$$Y_{1,-1}(\theta,\varphi) = +\sqrt{\frac{3}{8\pi}}\sin\theta\, e^{-i\varphi}$$

⇒ pro tritium ${}^{3}_{1}H$ $Z=1$

⇒ pro hélium ${}^{3}_{2}He^{+}$ $Z=2$

pst. nalezení systému ve stavu $|F\rangle$, byl-li na počátku ve stavu $|I\rangle$: $P = |\mathcal{U}|^2 = |\langle F|I\rangle|^2$

→ zde $|I\rangle = |\psi^{H}_{100}\rangle$ = zákl. stav tritia $1s$ ${}^{3}H$

$$|F\rangle = \begin{cases} |\psi^{He}_{100}\rangle & 1s\ {}^{3}He^{+} \\ |\psi^{He}_{200}\rangle & 2s\ {}^{3}He^{+} \\ |\psi^{He}_{21m}\rangle & 2p\ {}^{3}He^{+} \end{cases}$$

⇒ pst. nalezení elektronu v zákl. stavu:

$$P_{1s} = |\langle\psi^{He}_{100}|\psi^{H}_{100}\rangle|^2$$

$$\Rightarrow \langle\psi^{He}_{100}|\psi^{H}_{100}\rangle = \int d^3\vec{r}\, \psi^{He*}_{100}\psi^{H}_{100} = \int_0^\infty\int_0^\pi\int_0^{2\pi} \frac{1}{\sqrt{\pi}}\left(\frac{2}{a_0}\right)^{3/2} e^{-\frac{2r}{a_0}} \frac{1}{\sqrt{\pi}}\left(\frac{1}{a_0}\right)^{3/2} e^{-\frac{r}{a_0}} r^2 \sin\theta\, dr\, d\theta\, d\varphi =$$

$$= \frac{1}{\pi}\left(\frac{\sqrt{2}}{a_0}\right)^3 \cdot 4\pi \cdot \int_0^\infty dr\, r^2 e^{-\frac{3r}{a_0}} =$$

$$= \left| u = \frac{3r}{a_0} \quad du = \frac{3}{a_0}dr \quad \begin{matrix} \infty \to \infty \\ 0 \to 0 \end{matrix} \right| =$$

$$= \frac{8\sqrt{2}}{27}\int_0^\infty du\, u^2 e^{-u} = \qquad \int_0^\infty x^{n-1} e^{-x} dx = (n-1)!$$

$$= \frac{8\sqrt{2}}{27}\cdot 2 = \frac{16\sqrt{2}}{27} \qquad \int_0^\infty x^n e^{-ax} dx = \frac{n!}{a^{n+1}}$$

$$P_{1s} = \left|\frac{16\sqrt{2}}{27}\right|^2 = \frac{512}{729} \approx 0{,}70 \quad \text{tj. } \underline{\underline{70\%}}$$

$P_{2s} = |\langle \psi^{He}_{200} | \psi^{H}_{100} \rangle|^2$

$\Rightarrow \langle \psi^{He}_{200} | \psi^{H}_{100} \rangle = \int d^3r\, \psi^{He*}_{200}(\vec r)\, \psi^{H}_{100}(\vec r) =$

$$= \int_0^\infty \int_0^\pi \int_0^{2\pi} \frac{1}{\sqrt{\pi}} \left(\frac{2}{2a_0}\right)^{3/2} \left(1 - \frac{2r}{2a_0}\right) e^{-\frac{2r}{2a_0}} \cdot \frac{1}{\sqrt{\pi}} \left(\frac{1}{a_0}\right)^{3/2} e^{-\frac{r}{a_0}}\, r^2 \sin\vartheta\, dr\, d\vartheta\, d\varphi =$$

$$= \frac{1}{\pi}\left(\frac{1}{a_0}\right)^3 \cdot 4\pi \cdot \underbrace{\int_0^\infty \left(1 - \frac{r}{a_0}\right) e^{-\frac{2r}{a_0}} r^2\, dr}_{\frac{2!a^3}{2^3} - \frac{6a^4}{a\, 2^4}} =$$

$$= -\frac{1}{2}$$

$\Rightarrow P_{2s} = |-\tfrac{1}{2}|^2 = \tfrac{1}{4}$ tj. $\underline{\underline{25\%}}$

$P_{2p} = |\langle \psi^{He}_{21m} | \psi^{H}_{100} \rangle|^2$

máme 3x 2p orbitaly: $R_{21}(r) \times Y_{1,-1}(\vartheta,\varphi)$
$\times Y_{1,0}(\vartheta,\varphi)$
$\times Y_{1,+1}(\vartheta,\varphi)$

$\Rightarrow$ obecně musíme uvažovat LK těchto stavů

(resp. přesčítat přes všechny možnosti)

$\Rightarrow \langle \psi^{He}_{21m} | \psi^{H}_{100} \rangle = \int d^3r\, \psi^{He*}_{21m}(\vec r)\, \psi^{H}_{100}(\vec r) =$

$Y_{00} = \frac{1}{\sqrt{4\pi}}$

$$= \int_0^\infty R^*_{21}(r)\, R_{10}(r)\, r^2 dr \underbrace{\int_0^{2\pi}\int_0^{\pi} Y^*_{1m}(\vartheta,\varphi)\, Y_{00}(\vartheta,\varphi) \sin^2\vartheta\, d\vartheta\, d\varphi}$$

- $\int_0^\pi \int_0^{2\pi} Y_{10}(\vartheta,\varphi) \sin\vartheta\, d\vartheta\, d\varphi = \int_0^\pi \int_0^{2\pi} \sqrt{\frac{3}{4\pi}} \cos\vartheta \sin\vartheta\, d\vartheta\, d\varphi =$

$$= \sqrt{\frac{3}{4\pi}} \cdot 2\pi \underbrace{\int_0^\pi \cos\vartheta \sin\vartheta\, d\vartheta}_{\left[\frac{1}{2}\sin^2\vartheta\right]_0^\pi = 0} = \underline{\underline{0}}$$

- $\int_0^\pi \int_0^{2\pi} Y_{1,\pm1}(\vartheta,\varphi) \sin\vartheta\, d\vartheta\, d\varphi = \int_0^\pi \int_0^{2\pi} (\mp) \sqrt{\frac{3}{8\pi}} \sin\vartheta\, e^{\pm i\varphi} \sin\vartheta\, d\vartheta\, d\varphi = \underline{\underline{0}}$

$\int_0^\pi e^{\pm i\varphi}\, d\varphi = 0$

$\Rightarrow \langle \psi^{He}_{21m} | \psi^{H}_{100} \rangle = 0$

$\Rightarrow \boxed{P_{2p} = 0}$

$P_{1s} \approx 70\%$

$P_{2s} = 25\%$

zbývá 5 % $\rightarrow$ další možné exc. stavy (3s, ...)

$\rightarrow$ postupně také přejdou na zákl. stav