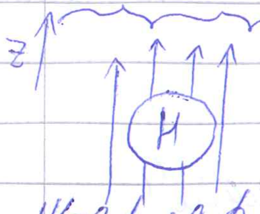
MQCh

20/IV MMXIV

1

Př: Polarizovatelnost atomu H

vnější

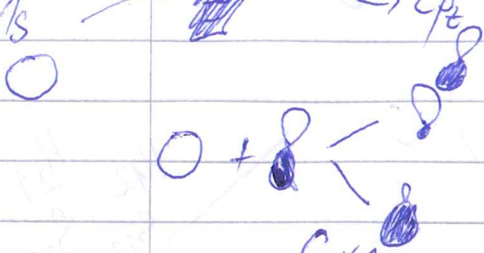


bez pole:
VF zákl. stav: 1s(1)
Energie: −13,6 eV

s polem: (intenzita F)
VF = ?
Energie = ?

$\Psi = c_1\phi_1 + c_2\phi_2$
zkus.

1s $\qquad \rightarrow 2p_z$



zajímá nás: c_2 a E = ?

$$\bar{E} = \frac{\int \Psi^*_{zk}\hat{H}\Psi_{zk}\,d\tau}{\int \Psi^*_{zk}\Psi_{zk}\,d\tau} \geq E_{\substack{\text{přesná}\\ \text{z. stavu}}}$$

... hledáme minimum vzhledem ke koef. c_i (derivace)

$i = 1,2$

$$\frac{\partial}{\partial c_i}\frac{\int\Psi^*\hat{H}\Psi\,d\tau}{\int\Psi^*\Psi\,d\tau} = \frac{\partial}{\partial c_i}\left[\int\Psi^*\hat{H}\Psi\,d\tau\cdot\frac{1}{\int\Psi^*\Psi\,d\tau}\right] = \int\Psi^*\hat{H}\Psi\,d\tau\left(\frac{1}{\int\Psi^*\Psi\,d\tau}\right)' +$$

$$+\left(\int\Psi^*\hat{H}\Psi\,d\tau\right)'\left(\frac{1}{\int\Psi^*\Psi\,d\tau}\right) = \int\Psi^*\hat{H}\Psi\,d\tau\cdot\left[\left(\int\Psi^*\Psi\,d\tau\right)^{-1}\right]' + \frac{1}{\int\Psi^*\Psi\,d\tau}\cdot\left(\int\Psi^*\hat{H}\Psi\,d\tau\right)' =$$

$$= \int\Psi^*\hat{H}\Psi\,d\tau\cdot(-1)\left(\int\Psi^*\Psi\,d\tau\right)^{-2}\cdot\left(\int\Psi^*\Psi\,d\tau\right)' + \frac{1}{\int\Psi^*\Psi\,d\tau}\cdot\left(\int\Psi^*\hat{H}\Psi\,d\tau\right)' = -\frac{\int\Psi^*\hat{H}\Psi\,d\tau}{\int\Psi^*\Psi\,d\tau}\cdot$$

$$\cdot\left(\int(c_1\phi_1 + c_2\phi_2)^*(c_1\phi_1 + c_2\phi_2)\,d\tau\right)' + \frac{1}{\int\Psi^*\Psi\,d\tau}\cdot\left[\int(c_1\phi_1 + c_2\phi_2)^*\hat{H}(c_1\phi_1 + c_2\phi_2)\,d\tau\right]'$$

$$= -\frac{\int\Psi^*\hat{H}\Psi\,d\tau}{\int\Psi^*\Psi\,d\tau}\cdot\left[c_1^*c_1\underbrace{\int\phi_1^*\phi_1\,d\tau}_{S_{11}} + c_1^*c_2\int\phi_1^*\phi_2\,d\tau + c_2^*c_1\int\phi_2^*\phi_1\,d\tau +\right.$$

$$\left. c_2^*c_2\int\phi_2^*\phi_2\,d\tau\right]' + \frac{1}{\int\Psi^*\Psi\,d\tau}\cdot\left[c_1^*c_1\underbrace{\int\phi_1^*\hat{H}\phi_1\,d\tau}_{H_{11}} + c_1^*c_2\int\phi_1^*\hat{H}\phi_2\,d\tau + c_2^*c_1\int\phi_2^*\hat{H}\phi_1\,d\tau\right.$$

$$\left. + c_2^*c_2\int\phi_2^*\hat{H}\phi_2\,d\tau\right]' =$$

$$= -\frac{\int\Psi^*\hat{H}\Psi\,d\tau}{\left(\int\Psi^*\Psi\,d\tau\right)^2}\cdot\overbrace{\left[c_1^*c_1S_{11} + c_1^*c_2S_{12} + c_2^*c_1S_{21} + c_2^*c_2S_{22}\right]'}^{I} + \frac{1}{\int\Psi^*\Psi\,d\tau}\cdot$$

$$\cdot\underbrace{\left[c_1^*c_1H_{11} + c_1^*c_2H_{12} + c_2^*c_1H_{21} + c_2^*c_2H_{22}\right]'}_{II} = 0 \quad \Big/ \int\Psi^*\Psi\,d\tau$$

minimum

$[\text{zátvorka II}] = 0$

(1) " ' " $= \frac{\partial}{\partial c_1}$

$\dots c_j^* H_{ij}] = 0$

$\frac{\partial}{\partial c_1}[\underbrace{c_1^* c_1}_{c_1^2} H_{11} \dots\dots$ reálne!

$- E(\underline{2c_1 S_{11}} + c_2 S_{12} + c_2 S_{21}) = 0$

(2) " ' " $= \frac{\partial}{\partial c_2}$

$- E[c_1 S_{12} + c_1 S_{21} + 2c_2 S_{22}] = 0$

$H_{12} = H_{21}$

$S_{12} = S_{21}$

$(2H_{12} - 2ES_{12}) = 0$

$(2H_{22} - 2ES_{22}) = 0$ / na $\neq 2$

$(\dots - ES_{12}) = 0$

$(\dots - ES_{22}) = 0$

$c_1 = c_2 = 0 \Rightarrow$ nezaujímavé

$c_1\Phi_1 + c_2\Phi_2 = 0$ .. častica nikde nie (je to blbosť)

$c_1 \neq 0$ alebo $c_2 \neq 0$

$\dots ES_{12}$

$\dots ES_{22} \Big| = 0$ ← determinant $= 0$

nad demun (?) pre Ellen (?)

$MOCl_2$

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$$H_{11} = \int 1s^*(\hat{H}_H + (-1)Fr\cos\theta)\,1s\,d\tau = \int 1s^*\hat{H}_H\,1s\,d\tau + \int 1s^*(-1)F\cdot r\cos\theta\,1s\,d\tau =$$

$E = \langle\Psi|\hat{H}|\Psi\rangle$ ...normované!

$E = \dfrac{\langle\Psi|\hat{H}|\Psi\rangle}{\underbrace{\langle\Psi|\Psi\rangle}_{\text{norma}}}$ bez ohledu normy.

$$= E_{1s} + \int \underbrace{1s^* 1s}_{S} \cdot \underbrace{(-F)r\cdot\cos\theta\,d\tau}_{A} = -0{,}5\ a.u. + 0$$

$S\cdot A = \int A = 0$

to samé s H_{22}! symetrie vůči rovině xy

$H_{22} = \int 2p_z \ldots$

$$= E_{2p_z} + \int 2p_z^* 2p_z(-F)r\cos\theta\,d\tau = -\frac{1}{8}\ a.u.$$

$$H_{21} = H_{21} = \int 1s^*(\hat{H}_{hydr} + (-Fr\cos\theta))\,2p_z\,d\tau =$$

$$= \underbrace{\int 1s^*\hat{H}_H 2p_z\,d\tau} + \int 1s^*(-F)r\cos\theta)\,2p_z\,d\tau =$$

$$= \int 1s^*\underbrace{\left(-\frac{1}{8}\right)2p_z\,d\tau}_{\text{orthogonální}} + \int 1s^*(-F)r\cos\theta)\,2p_z\,d\tau =$$

$\Rightarrow\ = 0$

$\sqrt{32} = \sqrt{16}\cdot\sqrt{2} = 4\sqrt{2}$

$$= 0 + \int 1s^*(-Fr\cos\theta)\,2p_z\,d\tau$$

$$\int 1s^{(*)}(-Fr\cos\theta)\,2p_z\,d\tau = -F\iiint \underbrace{\pi^{-\frac{1}{2}}e^{-r}}_{1s}\cdot\underbrace{r\cos\theta}_{\text{el. field}}\cdot\underbrace{(32\pi)^{-\frac{1}{2}}re^{-\frac{r}{2}}\cos\theta}_{2p_z}\,\underbrace{\underbrace{r^2\sin\theta\,dr\,d\theta\,d\varphi}_{\text{Jakobián}}}_{d\tau} =$$

Integrace přes $d\varphi$ rychle dopředu:

$$\int_{\pi}^{2\pi} 1\,d\varphi = [\varphi]_0^{2\pi} = 2\pi$$

$$= -\frac{2\pi F}{4\sqrt{2}\pi}$$

$$= -\frac{2\pi F}{4\sqrt{2}\pi}\int_0^{\infty}\underbrace{r^4 e^{-r} e^{-\frac{r}{2}}\,dr}_{\int_0^{\infty} r^4 e^{-\frac{3r}{2}}dr}\int_0^{\pi}\cos^2\theta\sin\theta\,d\theta = -\frac{F}{2\sqrt{2}}$$

④

$$x^n e^{-qx} dx = \frac{n!}{q^{n+1}} \; ; n > -1$$
$$q > 0$$

$$\Rightarrow \frac{4!}{\left(\frac{3}{2}\right)^{4+1}}$$

$\cos^3\theta = 3\cos^2\theta(-\sin\theta)$

$\left[-\frac{1}{3}\cos^3\theta\right]_0^{\pi}$

$$\frac{F}{2\sqrt{2}} \cdot \frac{4!}{\left(\frac{3}{2}\right)^5} \left[-\frac{1}{3}\cos^3\theta\right]_0^{\pi} = \frac{-F}{2\sqrt{2}} \cdot \frac{4!}{\left(\frac{3}{2}\right)^5} \cdot \left(-\frac{1}{3}\right) \left[\underbrace{(-1)^3 - (+1)}_{-2}\right] =$$

$$\frac{4!\,2^5}{3^5} \left(-\frac{1}{3}\right) = \frac{-F \cdot 2^{-\frac{1}{2}} \cdot 2^3 \cdot 3 \cdot 2^5}{3^5 \cdot 3} = \underline{3^{-5}(-F) \cdot 2^{15/2}}$$

$$\begin{vmatrix} \ldots S_{11} & H_{12} - ES_{12} \\ \ldots_1 & H_{22} - ES_{22} \end{vmatrix} = 0$$

$$\begin{vmatrix} \ldots 1 & \frac{-2^{15/2}F}{3^5} \\ \ldots & -\frac{1}{8} - E \cdot 1 \end{vmatrix} = 0$$

$$D = \left(-\frac{1}{2} - E\right)\left(-\frac{1}{8} - E\right) - \left(-\frac{2^{15/2}F}{3^5}\right)^2 = 0 \;/(-1)$$

$$D = \left(\frac{1}{2} + E\right)\left(-\frac{1}{8} - E\right) + \left(\frac{+2^{15/2}F}{3^5}\right)^2 = 0$$

$$D = -\frac{1}{16} - \frac{E}{2} - \frac{E}{8} - E^2 + \frac{2^{15}F^2}{3^{10}} = 0 \;/(-1)$$

$$D = E^2 + \frac{E}{2} + \frac{E}{8} + \frac{1}{16} - \frac{2^{15}F^2}{3^{10}} = 0$$

$$\ldots \frac{5}{8}E + \left(\frac{1}{16} - \frac{2^{15}F^2}{3^{10}}\right) = 0$$

$$E_{1/2} = -\frac{5}{16} \pm \left(\frac{9}{64} + \frac{2^{17}F^2}{3^{10}}\right)^{1/2}$$

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$$E^2 + \frac{5}{8} + \left(\frac{1}{16} - \frac{2^{15} F^2}{3^{10}}\right) = 0$$

řešení pro $F = 0$

$E_1 = -1/2 \ldots 1s$

$E_2 = -\frac{1}{8} \ldots 2p_z$

$c_1(H_{11} - E) + c_2 H_{12} = 0$

$c_1 H_{12} + c_2(H_{22} - E) = 0$

Pro $F = 0{,}1\,\text{au} \longrightarrow E_1 \longrightarrow$ $0{,}01428\,c_1 - 0{,}07449\,c_2 = 0$

$c_1 \doteq 5{,}23\,c_2$

$c_1^2 + c_2^2 = 1$