5.5 $\Psi_{s,p}$ $\Psi_{a,s}$ & Slaterovy determinanty

(5-43 a) ... Sl. det.?

$$\Psi_{a,s}(1,2) = \frac{1}{\sqrt{2}}\left[1s(1)2s(2) - 2s(1)1s(2)\right]\alpha(1)\alpha(2)$$

$$\big(1s(1)\alpha(1)\,2s(2)\alpha(2)\big)$$

AO

se zanedbáním repulze $\left(\frac{1}{r_{12}}\right)$

Aprox. nezáv. e^-

elektron

žádný prvek: spin α

$$\Psi_{a,s}(1,2) = \frac{1}{\sqrt{2}}\begin{vmatrix} 1s(1) & 1s(2) \\ 2s(1) & 2s(2) \end{vmatrix} =$$

Explic. spin

$$= \frac{1}{\sqrt{2}}\big(1s(1)\alpha(1)\cdot 2s(2)\alpha(2) - 2s(1)\alpha(1)\cdot 1s(2)\alpha(2)\big) =$$

$$= \frac{1}{\sqrt{2}}\big(1s(1)2s(2) - 2s(1)1s(2)\big)\alpha(1)\alpha(2)\ \checkmark$$

$$\Psi_{\substack{S,\omega \\ \omega,S}}(1,2) = \frac{1}{\sqrt{2}}\left\{ \frac{1}{\sqrt{2}} \begin{vmatrix} 1s(1) & 1s(2) \\ \overline{2s}(1) & \overline{2s}(2) \end{vmatrix} \mp \frac{1}{\sqrt{2}} \begin{vmatrix} \overline{1s}(1) & \overline{1s}(2) \\ 2s(1) & 2s(2) \end{vmatrix} \right\}$$

$\frac{1}{\sqrt{2}}$ → míchání 2 S.D.

→ 1 S.D.

→ 1. S.D

(obecně $\frac{1}{\sqrt{n!}}$)

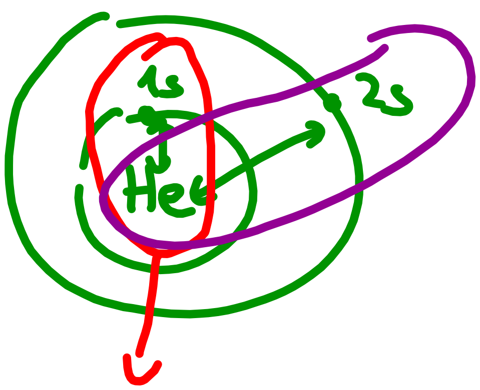
1 Slaterův determinant neodráží vždy celou symetrii správné VF

Výpočet energie pro $\Psi_{s,a}(1,2)$ a $\Psi_{a,s}(1,2)$?

→ bl. fce ← $\hat{H}_{approx}$

aprox. NEINT. e^- aprox. NEINT e^-

(1. krok metody selfkonzistentního pole)



$He^{2+} + 1e^- = He^+$

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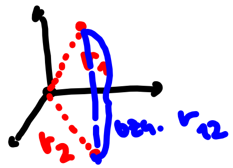
Použijeme pro výp. energie z. $\hat{H}_{(full)}$

jako zkuš. VF

$$\bar{E} = \frac{\int \psi^* \hat{H} \psi \, d\tilde{\tau}}{\underbrace{\int \psi^* \psi \, d\tilde{\tau}}_{1}}$$

$d\tilde{\tau}$ .... integrace přes spin A prostor



$d\tilde{\tau} = dv \, d\omega$

dv → obj. pr.

$d\omega$ → spinová proměnná

$$\bar{E} = \int \psi^* \Big[\underbrace{-\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - \frac{2}{r_1} - \frac{2}{r_2} +}_{} \frac{1}{r_{12}}\Big] \psi \, d\tilde{\tau}$$

působí pouze na prost. proměnné =>

=> průměrné energie budou zcela určeny prost. č.

↳ vyintegrujeme jen prost. č. a dv

$$\bar{E}_{1,3} = \frac{1}{2} \iint \underbrace{\left[1s^*(1)\,2s^*(2) \pm 2s^*(1)\,1s^*(2)\right]}_{2} \underbrace{\left[-\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2\right.}_{2} - \frac{2}{r_1} - \frac{2}{r_2} + \left.\frac{1}{r_{12}}\right] \underbrace{\left[1s(1)\,2s(2) \pm 2s(1)\,1s(2)\right]}_{2} \, dv_1 \, dv_2$$

BREAK 10:04 - 10:24.

Expanze pro ∇_1^2 a ∇_2^2 :

$$(1)\quad \frac{1}{2}\Big\{ \int 1s^*(1)\left[-\frac{1}{2}\nabla_1^2\right]1s(1)\,d\tau(1)\cdot \underbrace{\int 2s^*(2)\,2s(2)\,d\tau(2)}_{1} +$$

$$(2)\quad + \int 2s^*(2)\left[-\frac{1}{2}\nabla_2^2\right]2s(2)\,d\tau(2)\cdot \underbrace{\int 1s^*(1)\,1s(1)\,d\tau(1)}_{1}$$

$$(3)\quad + \int 2s^*(1)\left[-\frac{1}{2}\nabla_1^2\right]2s(1)\,d\tau(1)\cdot \underbrace{\int 1s^*(2)\,1s(2)\,d\tau(2)}_{1}$$

$$(4)\quad + \int 1s^*(2)\left[-\frac{1}{2}\nabla_2^2\right]1s(2)\,d\tau(2)\ \underbrace{\int 2s^*(1)\,2s(1)\,d\tau(1)}_{1}$$

like AOs

$$(5)\quad \pm \int 1s^*(1)\left[-\frac{1}{2}\nabla_1^2\right]2s(1)\,d\tau(1)\ \underbrace{\int 2s^*(2)\,1s(2)\,d\tau(2)}_{0}$$

$$(6)\quad \pm \int 2s^*(2)\left[-\frac{1}{2}\nabla_2^2\right]1s(2)\,d\tau(2)\ \underbrace{\int 1s^*(1)\,2s(1)\,d\tau(1)}_{0}$$

$1 \leftrightarrow 2$

$$(7)\quad \pm \int 2s^*(1)\left[-\frac{1}{2}\nabla_1^2\right]1s(1)\,d\tau(1)\ \underbrace{\int 1s^*(2)\,2s(2)\,d\tau(2)}_{0}$$

$1s \leftrightarrow 2s$

$$(8)\quad \pm \int 1s^*(2)\left[-\frac{1}{2}\nabla_2^2\right]2s(2)\,d\tau(2)\ \underbrace{\int 2s^*(1)\,1s(1)\,d\tau(1)}_{0}\Big\}$$

(5-49)

(A) $\Rightarrow E_{kin,1} + E_{kin,2} =$

$$\int 1s^*(1)\left[-\frac{1}{2}\nabla_1^2\right]1s(1)\,d\tau(1) + \int 2s^*(1)\left[-\frac{1}{2}\nabla_1^2\right]2s(1)\,d\tau(1) \qquad (5\text{-}50)$$

(B)

Podobně, pro $\int$ přes $\left(-\frac{2}{r_1} - \frac{2}{r_2}\right)$ ...
přitl. ē jádrem

$$\int 1s^*(1)\left[-\frac{2}{r_1}\right]1s(1)\,d\tau(1) \quad \int 2s^*(1)\left[-\frac{2}{r_1}\right]2s(1)\,d\tau(1) \qquad (5\text{-}51)$$

(C)

$$\frac{1}{2}\Big\{\iint 1s^*(1)\,2s^*(2)\,\frac{1}{r_{12}}\,1s(1)\,2s(2)\,d\tau(1)\,d\tau(2)$$

$1 \leftrightarrow 2$ v obou částech

$1 \leftrightarrow 2$

$$+\iint 2s^*(1)\,1s^*(2)\,\frac{1}{r_{12}}\,2s(1)\,1s(2)\,d\tau(1)\,d\tau(2)$$

$1 \leftrightarrow 2$ ve 2. části

$$\pm \iint 1s^*(1)\,2s^*(2)\,\frac{1}{r_{12}}\,2s(1)\,1s(2)\,d\tau(1)\,d\tau(2)$$

$1 \leftrightarrow 2$ ve 2. části

$1 \leftrightarrow 2$ v 1. č.

$$\pm \iint 2s^*(1)\,1s^*(2)\,\frac{1}{r_{12}}\,1s(1)\,2s(2)\,d\tau(1)\,d\tau(2)\Big\}$$

$$\bar{E}_{1} = \Big\{ \underbrace{\int 1s^{*}(1)\left[-\tfrac{1}{2}\nabla_1^2\right]1s(1)\,d\tau(1)}_{A(He^{+})} + \underbrace{\int 2s^{*}(1)\left[-\tfrac{1}{2}\nabla_1^2\right]2s(1)\,d\tau(1)}_{A'(He^{+})}$$

$$+ \int 1s^{*}(1)\left[-\frac{2}{r_1}\right]1s(1)\,d\tau(1) + \int 2s^{*}(1)\left[-\frac{2}{r_1}\right]2s(1)\,d\tau(1)$$

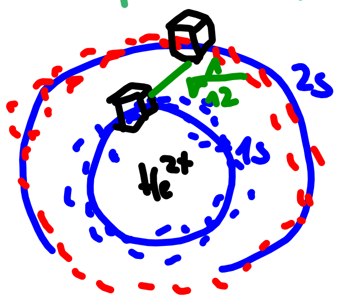
$E_{1s}(He^{+}) =$ first and third integrals; $E_{2s}(He^{+}) =$ second and fourth integrals

$$J:\quad + \iint 1s^{*}(1)\,2s^{*}(2)\left(\frac{1}{r_{12}}\right)1s(1)\,2s(2)\,d\tau(1)\,d\tau(2)$$

$$K:\quad \pm \iint 1s^{*}(1)\,2s^{*}(2)\left(\frac{1}{r_{12}}\right)2s(1)\,1s(2)\,d\tau(1)\,d\tau(2)$$

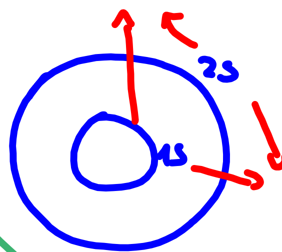
$$E_{1,3} = E_{1s} + E_{2s} + J \pm K$$

Coulombický integrál
odpovídá repulzi oblaků náboje



$J > 0$

el 1 v $1s^* \cdot 2s$



el 2 v $2s^* \, 1s$

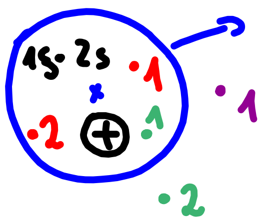
K ... výměnný integrál
který celé mění už J

$$\overbrace{1s(1)2s(1)}^{+}\overbrace{1s(2)2s(2)}^{-}$$

$1s \cdot 2s$ ⊖

nižší [−

vyšší | +
| +



který i započte
příspěvky,
vážené $\frac{1}{r_{12}}$