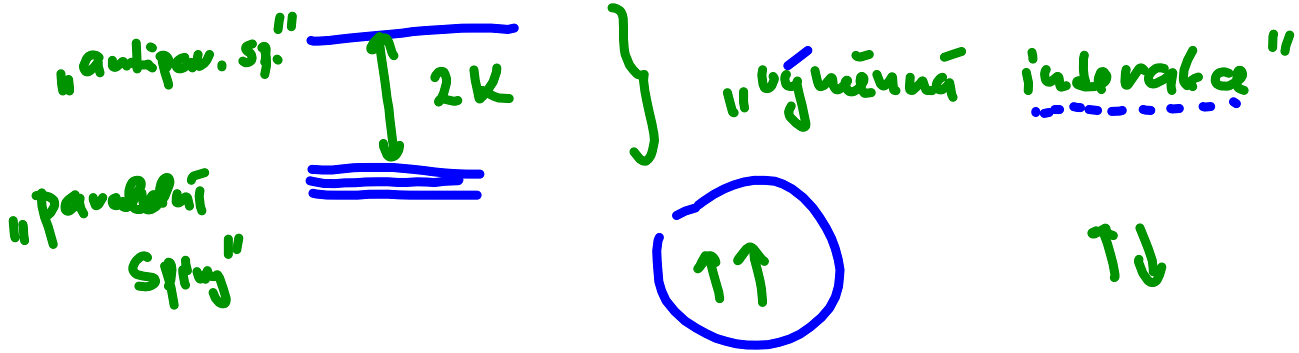
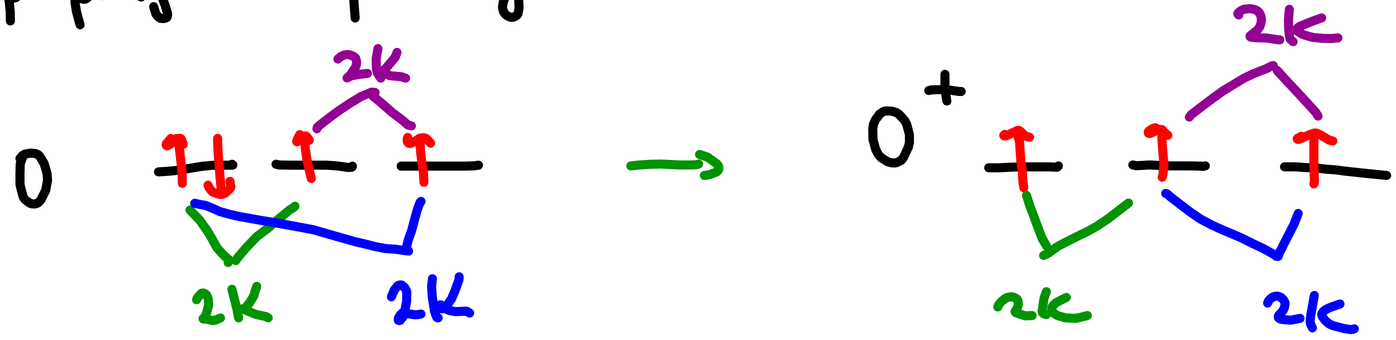
5-5 K je kladný, z rovnice pro

E_1 (3) leží $\equiv$ pod —

a pro vzdálenost $=$ a — platí:



p-prvky 2. periody



$\sum$ vým. en. 6K —||—

	vým. energie		
IP	neutrální →	kationt	Δ
EA	(anion) ←	(neutrální)	
B	0K	0K	0
C (B⁻)	2K	0K	2K
N (C⁻)	6K	2K	4K
O (N⁻)	6K	6K	0
F (O⁻)	8K	6K	2K
Ne (F⁻)	12K	8K	4K

11-5 Rovnice pro metodu Hartreeho vs. Hartree-Fock

Př. Atom Li:

A. TVAR VF

Hartree vs. Hartree-Fock

$$\Psi = 1s(1)\cdot\overline{1s}(2)\cdot 2s(3)$$

$$\Psi = \frac{1}{\sqrt{3!}}\begin{vmatrix} 1s(1) & 1s(2) & 1s(3) \\ \overline{1s}(1) & \overline{1s}(2) & \overline{1s}(3) \\ 2s(1) & 2s(2) & 2s(3) \end{vmatrix}$$

B. OPERÁTOR

Energie

$$\hat{H}\Psi = E\Psi$$

Douglas R. Hartree (1897–1958)

$$\hat{H}\Psi = E\Psi$$

Vladimir A. Fock (1898–1974)

Ψ.... AO (součin)

rovnice pro Ψ

↓

Hartreeho rovnice pro AO

↓

vystupuje v nich tzv. Hartreeho op.

obs. E_{kin}, $E_{přit.j.}$,

Coulombův operátor

↳ J

Hartree

Ψ.... AO (Slater det.)

rovnice pro Ψ

↓ Hartree-Fockovy rovnice pro AO

↓

— " —

tzv. Fockův operátor

F

obs. E_{kin}, $E_{přit.j.}$,

Coulombův operátor → J

a Výměnný operátor → K

Hartree-Fock (HF)

Naleznete: Energie AO (MO) a celková energie

Break 10:19 – 10:40

↓ teď

→ Dotazy

Pokrač.

Hartree-Fock

$$\hat{F}\phi_i = \varepsilon_i \phi_i$$

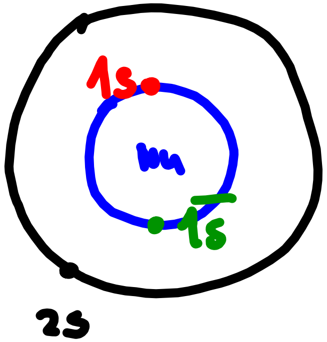
$$(11\text{-}7)\quad \hat{F}(1) = -\frac{1}{2}\nabla^2 - \sum_\mu \frac{Z_\mu}{r_{\mu 1}} + \sum_{j=1}^{n}(2\hat{J}_j - \hat{K}_j)$$

(1) → elektronu

Coulombův operátor: $\hat{J}_j = \int \phi_j^*(2)\frac{1}{r_{12}}\phi_j(2)\,d\tau(2)$

Výměnný –"– $\hat{K}_j\phi_i(1) = \int \phi_j^*(2)\frac{1}{r_{1}}\phi_i(2)\,d\tau(2)\,\phi_j(1)$

Př. Atom Li (2s) $1s^2\, 2s^1$



(1s) $\overline{1s}$, 2s ... aprox. neinterag. e^-
(AO pro ion Li^{2+})

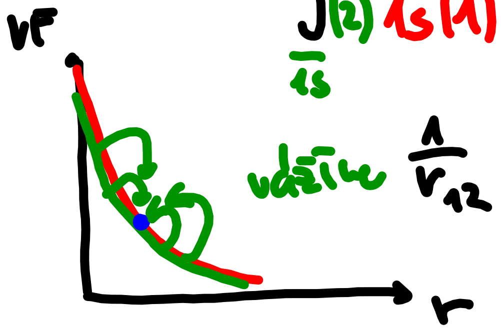
↓

Chceme opravit na repulze

Hartree ✓
HF ✓

$$\hat{J}_{\overline{1s}}(2)\, 1s(1) = \left[\int \overline{1s}^*(2) \frac{1}{r_{12}} \overline{1s}(2)\, d\tilde{\tau}_2 \right] 1s(1)$$

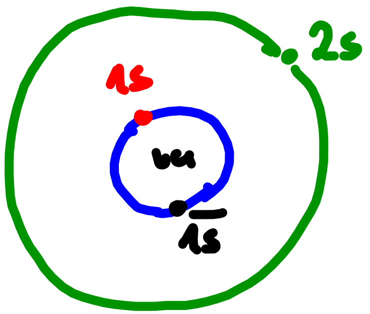
$\tilde{\rho}(2)$ =



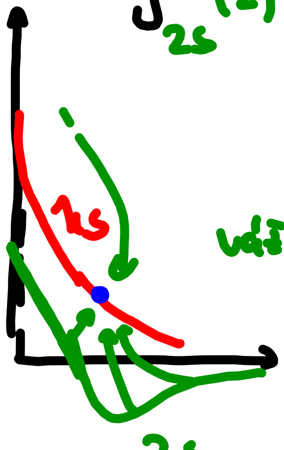
vážíme $\frac{1}{r_{12}}$

ke znalosti $\hat{J}_{\overline{1s}}$ potřebuji zatím $\overline{1s}$

Podobně započteme vliv obsazení AO 2s ($\overline{2s}$) na AO 1s



$$\hat{J}_{2s}(2)\,1s(1) = \left[\int 2s^*(2)\,\frac{1}{r_{12}}\,2s(2)\,d\tau_2\right] 1s(1)$$

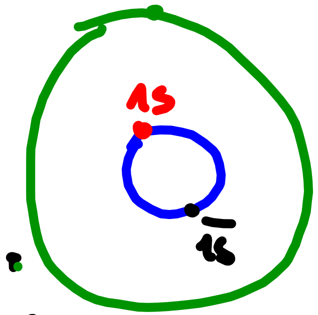


vážím $\frac{1}{r_{12}}$

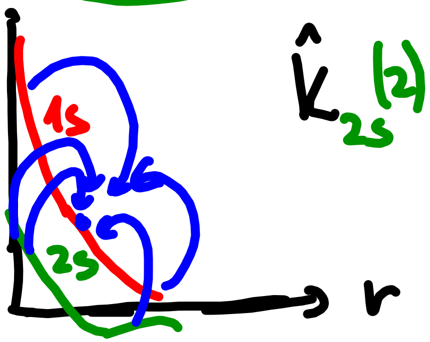
Hartree ✓

HF ✓

Potřebuji znát 2s, chci-li „opravit" 1s



výměnný operátor „působí" (efektivně) pouze v případě el. se stejným spinem

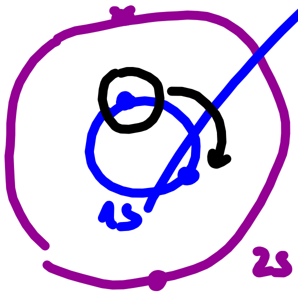


$$\hat{K}_{2s}(2)\,1s(1) = \left[\int 2s^*(2)\,\frac{1}{r_{12}}\,1s(2)\,d\tau_2\right] 2s(1)$$

Chci-li opr. 1s

11.7 Celková energie v HF – SCF

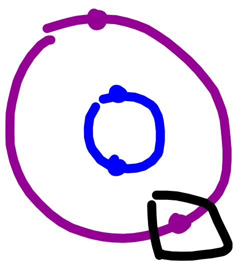
$_4$Be



$$\varepsilon_{1s} = H_{11} + J_{11} + 2J_{12} - K_{12}$$

H_{11} ↙ E_{kin}, $E_{Attr.}$

J_{11} ↙ energetický přísp. do ε_{1s} díky repulzi 2 el. v 1s



$$\varepsilon_{2s} = H_{22} + J_{22} + 2J_{12} - K_{12}$$

2s ↑↓

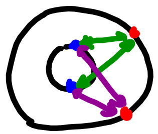
1s ↑↓

$$2\varepsilon_{1s} + 2\varepsilon_{2s} = 2H_{11} + 2J_{11} + 4J_{12} - 2K_{12}$$
$$+ 2H_{22} + 2J_{22} + 4J_{12} - 2K_{12}$$

Energie: suma $2\varepsilon_1 + 2\varepsilon_2$ vs. E_{celk} fyzik.

$$2\varepsilon_1 + 2\varepsilon_2 = 2H_{11} + 2H_{22} + 2J_{11} + 2J_{22} + 8J_{12} - 4K_{12}$$

$$E_{celk,F} = 2H_{11} + 2H_{22} + J_{11} + J_{22} + 4J_{12} - 2K_{12}$$



$J_{11} = K_{11}$

$J_{22} = K_{22}$

$$E_{celk,F} = 2\varepsilon_1 - (J_{11} + 2J_{12} - K_{12}) + 2\varepsilon_2 - (J_{22} + 2J_{12} - K_{12}) =$$

$$= 2\varepsilon_1 - (2J_{11} - K_{11} + 2J_{12} - K_{12}) + 2\varepsilon_2 - (2J_{22} - K_{22} + 2J_{12} - K_{12}) =$$

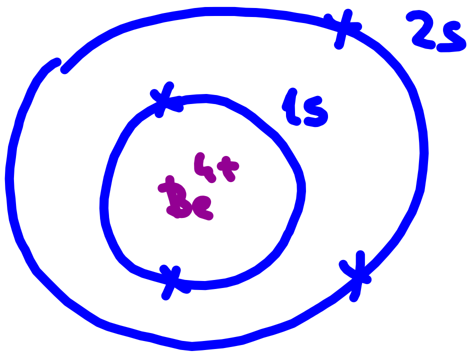
$$= 2\varepsilon_1 - \sum_{j=1}^{2} (2J_{1j} - K_{1j}) + 2\varepsilon_2 - \sum_{j=1}^{2} (2J_{2j} - K_{2j}) =$$

$$= \sum_{i=1}^{2} \left[2\varepsilon_i - \sum_{j=1}^{2} (2J_{ij} - K_{ij}) \right] \qquad (11\text{-}17)$$

suma orb. energií

celková energie v HF

Orbitaly a Elektrony



Orbital = VF pro 1 e^-

Orbital vs. Spin-Orbital

Spin-orbital: VF pro prostorové i spinové proměnné

prostor. č. × spin. část

1s(1) α(1)

1s(2) β(2)

↓

1s(1) ....

$\overline{1s}$(2) ....