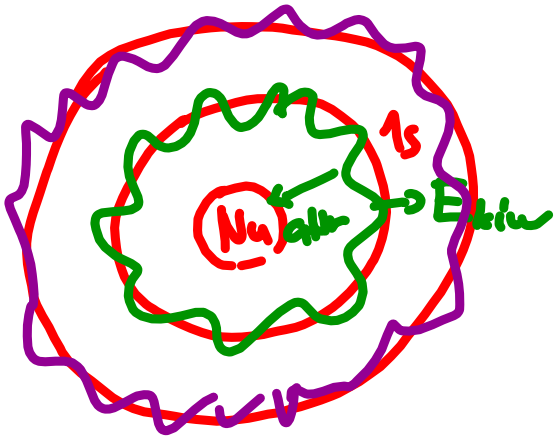
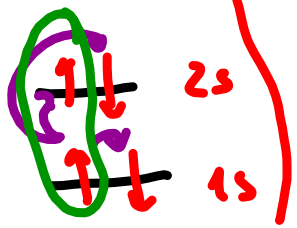
Př. $_4Be$



$H_{11} = E_{kin}(1s) + Nu\,Atr(1s)$

$H_{22} = E_{kin}(2s) + Nu\,Atr(2s)$



$$\varepsilon_1 = \varepsilon(1s) = H_{11} + J_{11} + 2J_{12} - K_{12}$$

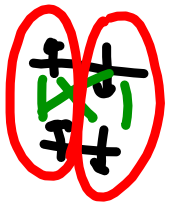
$$\varepsilon_2 = \varepsilon(2s) = H_{22} + J_{22} + 2J_{12} - K_{12}$$

Součet orb. energií pro 4 elektrony:

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

$2H_{11} + 2J_{11} + 4J_{12}$ $2H_{22} + 2J_{22} + 4J_{12}$

$-2K_{12}$ $-2K_{12}$



Celková energie čtveřice e^- na základě F úrovně:

$$E_{TOT} = 2H_{11} + 2H_{22} + J_{11} + J_{22} + 4J_{12} - 2K_{12}$$

$$E_{tot} = 2\varepsilon_1 - (J_{11} + 2J_{12} - K_{12})$$

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

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

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

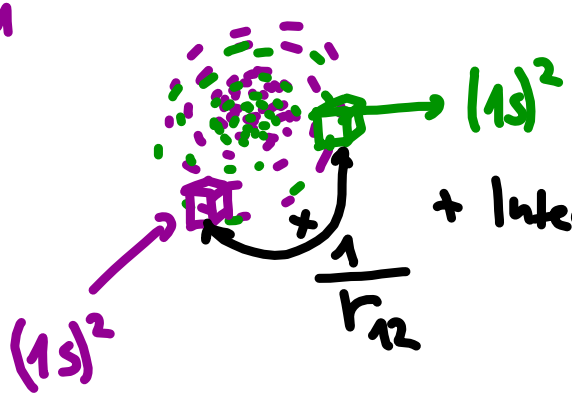
$$= 2\varepsilon_1 - \sum_{i=1}^{2}(2J_{1i} - K_{1i})$$

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

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

(11-17) Löwe pro 2 → N

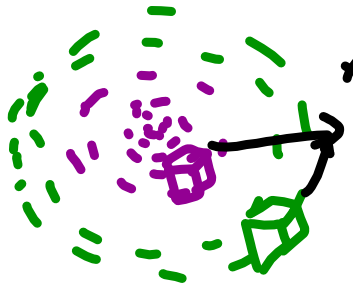
J_{11}



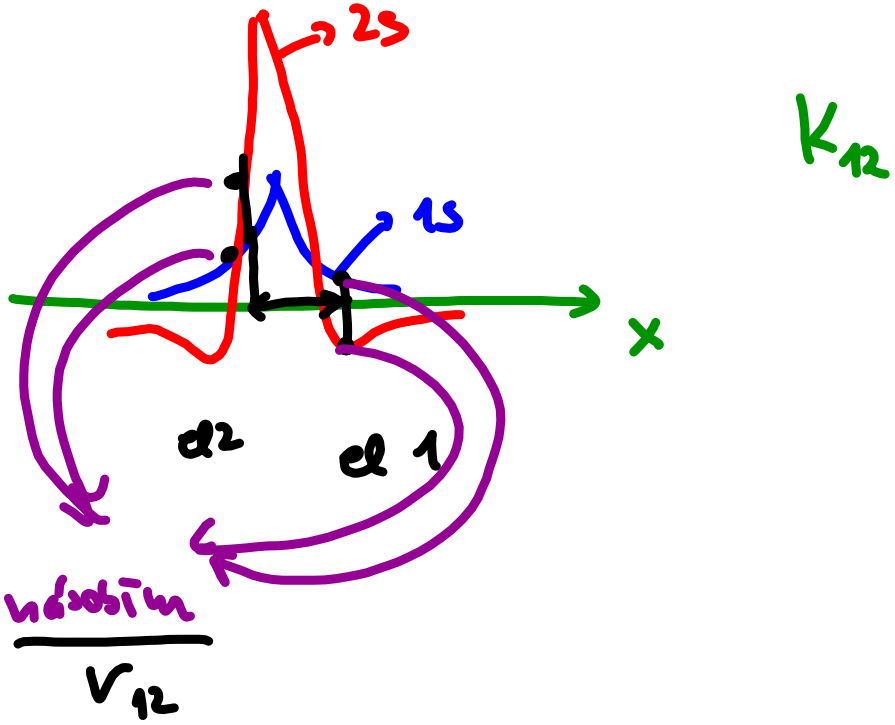
+ integrace přes celý prostor pro oba e^-

J_{22} ... totéž s orb. 2s

J_{12}



+ integrace



K_{12}

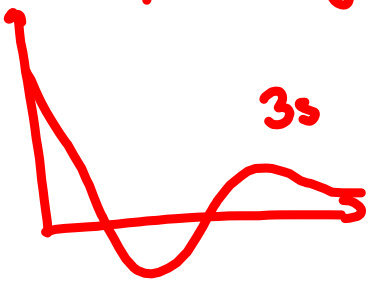
C9920 : MO = LCAO Báze AO = Výchozí množina AO

C9930 MO, AO = LC Bázová funkce

pro systémy s více elektrony

↓

AO pro ionty typu H^{2}



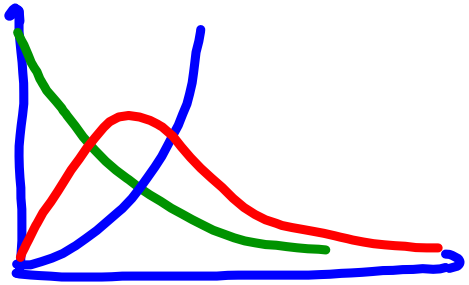
Zjednodušení: Slaterovy orbitaly

(STO)

$$R(n, Z, \zeta) = r^{(n-1)} \cdot e^{-\frac{\overbrace{(Z-\zeta)}^{Z^*} r}{n}}$$

3s ... $n = 3$

$$r^{n-1} = r^2 \cdot e^{-\frac{Z^* r}{n}}$$



STO nemají rad. uzly] → kombinace

více STO

na 1 AO → vozumně

pro své vyjádření.

Terminologie STO bází

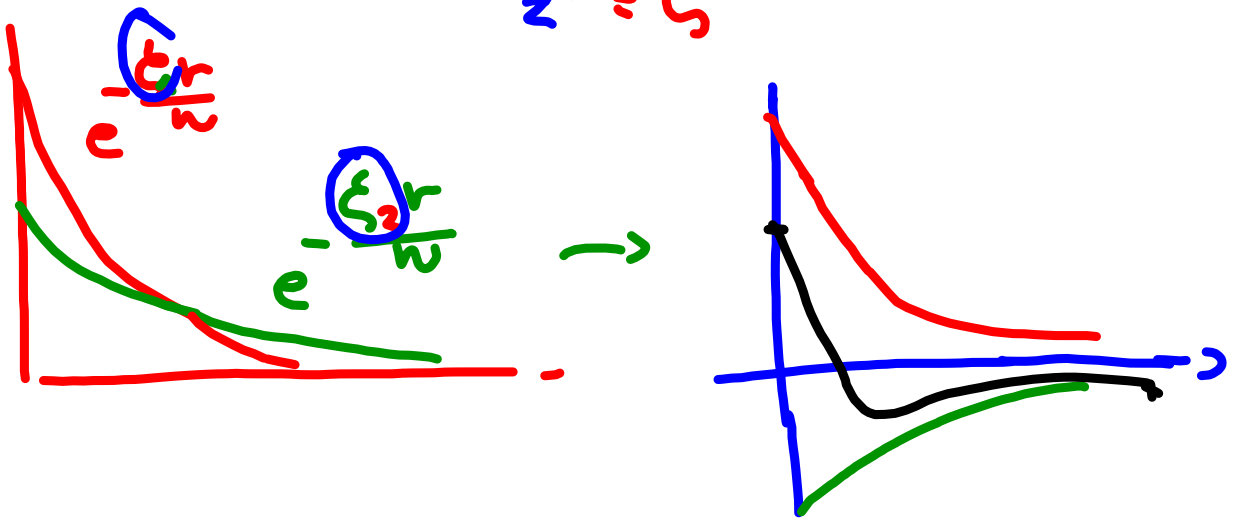
MINIMÁLNÍ BÁZE: 1 STO / 1 vnitřní i valenční AO

DOUBLE-ZETA (DZ) BÁZE: 2 STO / —"—

ob. exp $\underbrace{\zeta}$ (viz EHT)

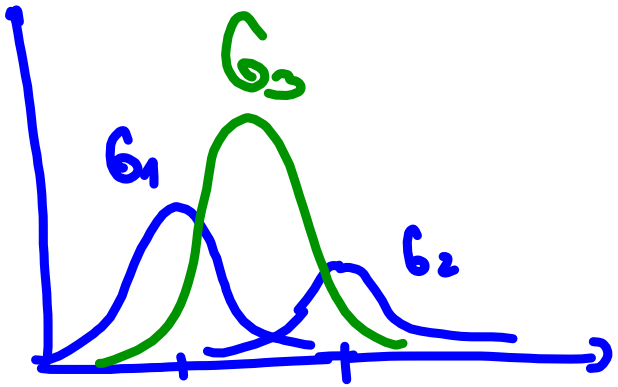
určuje, jak je AO kontr. nebo difúzní

$z^* = \zeta$



STO → Gaussian Type Orbital (GTO)

$e^{-\frac{\zeta r}{n}}$



$e^{-\frac{\zeta r^2}{n}}$

Gaussovský součinový teorém

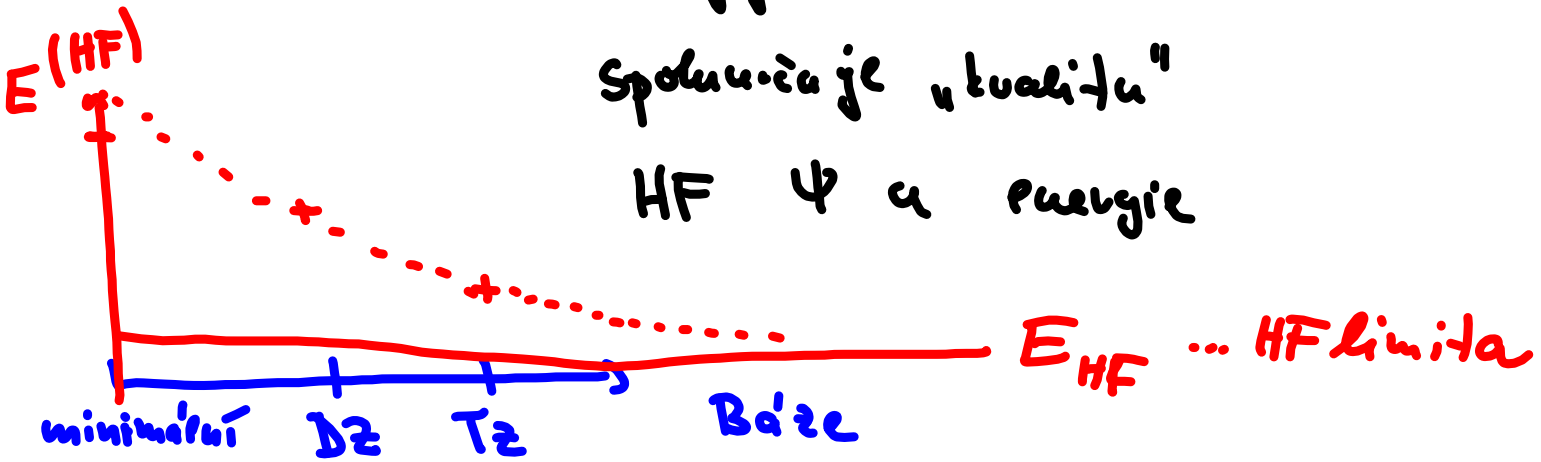
HF → vyžaduje zavedení báze

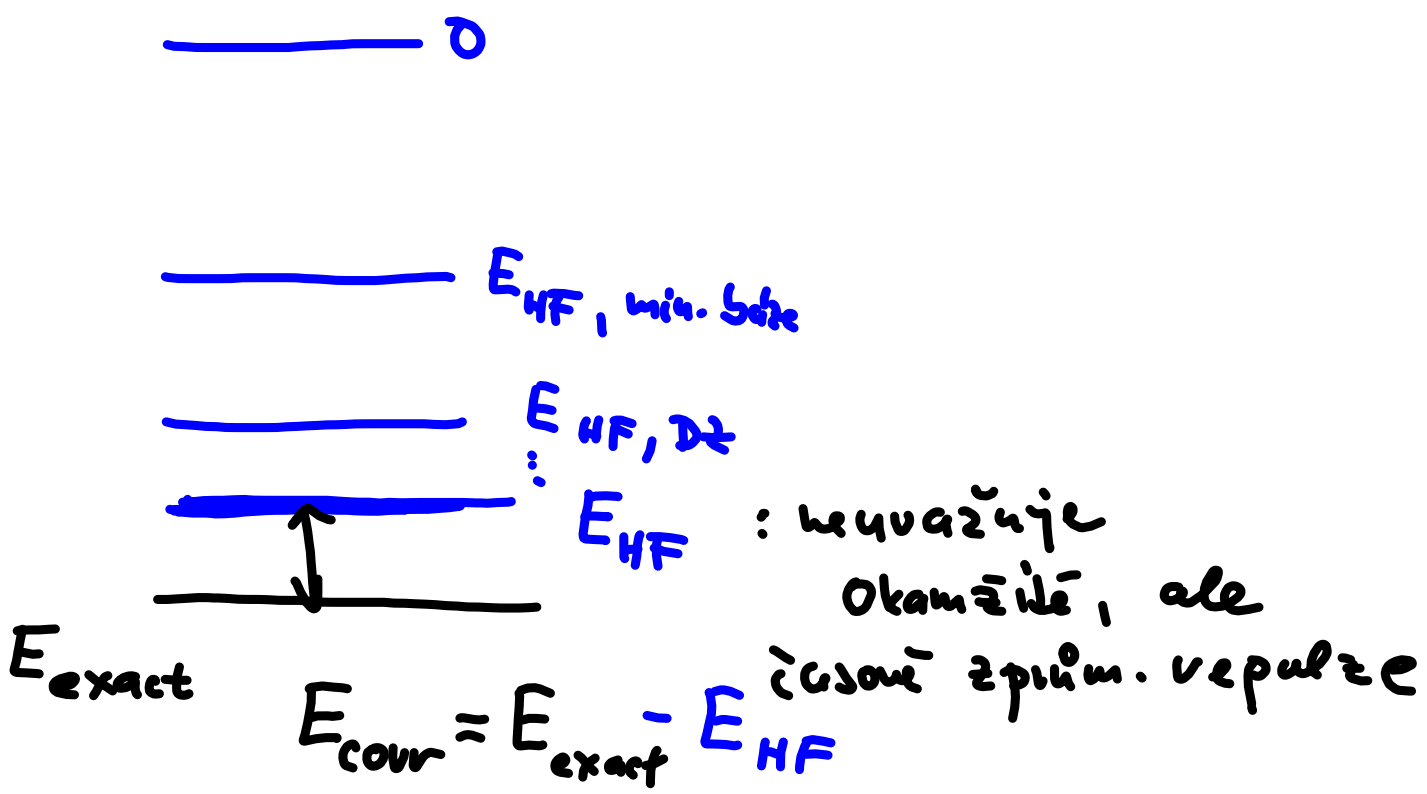
↓

její velikost a složení

spolurozhoduje „kvalitu"

HF Ψ a energie



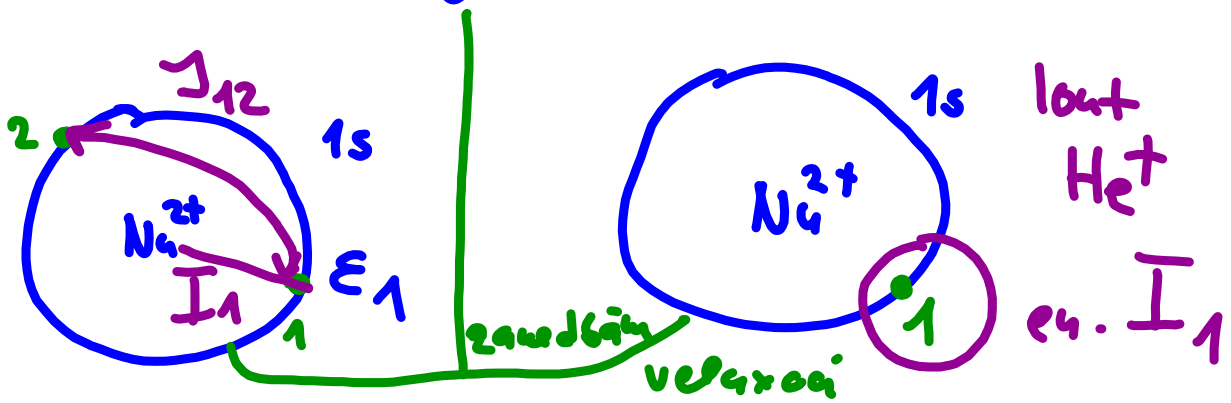

0
$E_{HF,\ min.\ báze}$
$E_{HF,\ DZ}$
E_{HF}
: nevázaný
Okamžité, ale
časově zprům. vepuze
E_{exact}
$E_{corr} = E_{exact} - E_{HF}$

Určení atomových (molekulových) ionizačních energií a elektronových afinit

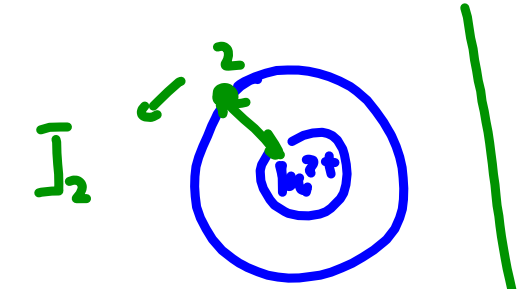
$$IE = \underbrace{E(M^+)}_{<0} - \underbrace{E(M)}_{<0}$$

atom He

$\varepsilon_1 = I_1 + J_{12}$



$$\underline{\varepsilon_1} = I_1 + J_{12} = \underbrace{(I_1 + I_2 + J_{12})}_{E(He)} - I_2$$

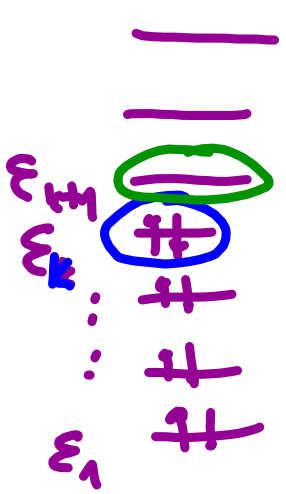


Ion He^+

$$-\varepsilon_1 = I_2 - E(He) = E(He^+) - E(He)$$

IE

"



Velmi dobrá aprox. na úrovni HF

$IE = -\varepsilon_k$

$EA = +\varepsilon_{k+1}$

↳ aproximace méně přesná