Približek povprečnega polja

$$V = \sum_{i \neq j} \frac{e_0^2}{4\pi\varepsilon_0 |\vec{r}_i - \vec{r}_j|}$$ } tega člena za pravilen račun ne smemo zanemariti

Li : $3e^-$ $1s\,\alpha$

$1s\,\beta$

$\rightarrow 2s\,\alpha,\ 2s\,\beta,\ 2p\,\alpha,\ 2p\,\beta$

[redacted]

$4\pi\varepsilon_0 r^2 D(r) = e(r)$ Max. enačba

$$e(r) = 2e_0 \int_0^r \rho_e(r')\, 4\pi r'^2 dr'$$

$$\rho_e(r') = R_{10}^2(r')\, Y_{00}^2$$

Gostota elektronov.

Izračunamo popravka :

$\langle 2s | V_{ef}(r) | 2s \rangle \simeq -4{,}6\,eV$

$\langle 2p | V_{ef}(r) | 2p \rangle \simeq -3{,}4\,eV$

} 3. e^- bo šel na stanje 2s, saj je tu NIŽJA ENERGIJA

Vzamemo še golemu jedru (vodikov atom):

3s — — — — 3p — — — — — 3d

2s — — — — 2p

1s —

Pri več elektronskih sistemih to ne velja več; nivoji se razcepijo zaradi odboja e^-.

— — — — — 3d

He, Li...

3s — — — — — 3p

— — — — 2p

2s —

1s —

I

AUFBAU PRINCIP - določa, v kakšnem vrstnem redu se polnijo orbitale:

~~1s~~
~~2s 2p~~
~~3s 3p 3d~~
~~4s 4p 4d 4f~~
~~5s~~

Najprej se polnijo orbitale $\boxed{n+l}$:

	$n+l$
1s	1
2s	2
2p	3
3s	3
3p	4
4s	4
3d	5
4p	5
5s	5

prej se polnijo tiste orbitale pri enakem $n+l$, kjer je n najmanjše št.

najprej se polni 3d, nato 4p in nazadnje 5s

He:

$\Psi(1,2) = 1s(1)\,\alpha(1)\,1s(2)\,\beta(2)$

α, β - spina e^-

V kv. mehaniki mora veljati: $\boxed{\Psi(1,2) = \Psi(2,1)}$.

$\hat{P}$ - operator zamenjave obeh delcev

$\hat{P}\Psi(1,2) = \Psi(2,1)$
$\hat{P}\Psi(2,1) = \Psi(1,2)$
$\hat{P}^2\Psi(1,2) = \Psi(1,2)$

lastna vrednost $\hat{P}^2$ je $\underline{1}$

$\hat{P}$ je $\underline{\pm 1}$

$\hat{A} f = a f$
$\hat{A}^2 f = \hat{A}\hat{A} f = \hat{A}\, a f = a \hat{A} f = a^2 f$

$\hat{P}\Psi'(1,2) = \pm \Psi'(1,2)$

$\phi_1(1)$
$\phi_2(2)$

$\Psi(1,2) = \phi_1(1)\,\phi_2(2)$

$\hat{P}\,\Psi(1,2) = \phi_1(2)\,\phi_2(1)$

} to ne velja, saj se predznaki ne ujemajo glede na l. vrednost $\hat{P}$

zato:

$\Psi_1(1,2) = \phi_1(1)\,\phi_2(2)$

$\Psi_2(1,2) = \phi_1(2)\,\phi_2(1)$

} $\hat{P}\,\Psi_1(1,2) = \phi_1(2)\,\phi_2(1)$

$\hat{P}\,\Psi_2(1,2) = \phi_1(1)\,\phi_2(2)$

$\Psi_S(1,2) = \phi_1(1)\phi_2(2) + \phi_1(2)\phi_2(1)$

$\hat{P}\,\Psi_S(1,2) = \phi_1(2)\phi_2(1) + \phi_1(1)\phi_2(2)$

$\hat{P}\,\Psi_S(1,2) = 1 \cdot \Psi_S(1,2)$ simetrična funkcija

$\Psi_a(1,2) = \phi_1(1)\phi_2(2) - \phi_1(2)\phi_2(1)$

$\hat{P}\,\Psi_a(1,2) = \phi_1(2)\phi_2(1) - \phi_1(1)\phi_2(2)$

$\hat{P}\,\Psi_a(1,2) = -\Psi_a(1,2)$ antisimetrična funkcija

$\Psi(1,2) = \phi_1(1)\phi_1(2)$ - ta funkcija ne obstaja zaradi Paulijevega izključitvenega principa

} v isto val. funkcijo hočemo vstaviti 2 delca: v ϕ_1 delca 1,2

$\Psi_S(1,2) = \phi_1(1)\phi_1(2) + \phi_1(1)\phi_1(2) =$

$= 2\phi_1(1)\phi_1(2)$ - ne obstaja

$\Psi_a(1,2) = \phi_1(1)\phi_1(2) - \phi_1(2)\phi_1(1) = 0$ - antisimetrična funkcija upošteva Paulija, saj ta funkcija ne obstaja - kot smo izračunali.

$$\Psi_{He} = \frac{1}{\sqrt{2}}\left(1s(1)\,\alpha(1)\,1s(2)\,\beta(2) - 1s(2)\,\alpha(2)\,1s(1)\,\beta(1)\right)$$

normirana

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

Slaterjeva determinanta

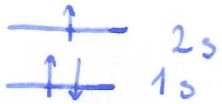
če hočemo 2 delca v isto stanje, dobimo determinanto enako 0

Li: $3e^-$

$1s\alpha$
$1s\beta$
$2s\alpha$

$$\Psi_{Li} = \frac{1}{\sqrt{3!}} \begin{vmatrix} 1s(1)\alpha(1) & 1s(2)\alpha(2) & 1s(3)\alpha(3) \\ 1s(1)\beta(1) & 1s(2)\beta(2) & 1s(3)\beta(3) \\ 2s(1)\alpha(1) & 2s(2)\alpha(2) & 2s(3)\alpha(3) \end{vmatrix}$$

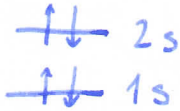
el. konf. - $1s^2 2s^1$



Be: $4e^-$

el. konf. - $1s^2 2s^2$

$1s\alpha$
$1s\beta$
$2s\alpha$
$2s\beta$

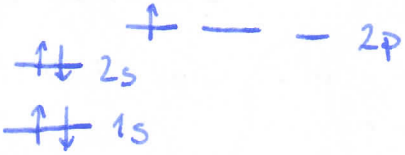


- det $|4 \times 4|$

B: $5e^-$

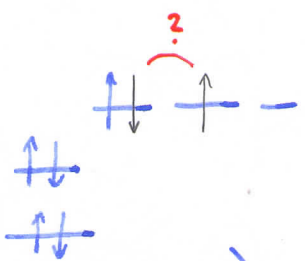
el. konf. - $1s^2 2s^2 2p_x^1$

$1s\alpha$
$1s\beta$
$2s\alpha$
$2s\beta$
$2p_x\alpha$

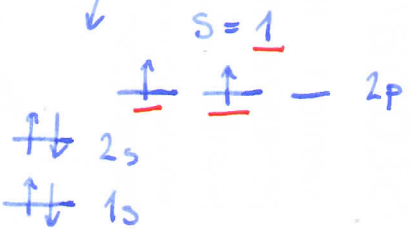


C: $6e^-$

$1s\alpha$
$1s\beta$
$2s\alpha$
$2s\beta$
$2p_x\alpha$
$2p_x\beta$ | $2p_y\alpha$?



Elektron (nadrji) po Hundovem pravilu zasede tisto mesto, da je skupni spin največji.



Razlaga Hundovega pravila:

- če bi 2 e^- bila v isti val. funkciji, bi se medsebojno sencila glede na jedro => med e^- in jedrom bi delovala šibkejša sila => 2 e^- bi bila dlje stran od jedra => sistem bi moral imeti VEČJO SKUPNO ENERGIJO

Sparjeni e^- imajo torej večjo E kot nesparjeni.

Hartree-Fockova metoda

Hartreejeva metoda:

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

$$\hat{H} = \sum_i -\frac{\hbar^2}{2m}\vec{\nabla}_i^2 + \sum_i \frac{-Ze_0^2}{4\pi\varepsilon_0 r_i} + \frac{1}{2}\sum_{i\neq j}\frac{e_0^2}{4\pi\varepsilon_0 r_{ij}}$$

$r_{ij} = |\vec{r}_i - \vec{r}_j|$

$$\Psi(1,2,3\ldots,N) = \phi_1(1)\phi_2(2)\ldots\phi_N(N)$$

$$\sum_i V_i^{ef}$$

$$V_i^{ef} = \sum_{i\neq j}\int \frac{e_0\phi_j\phi_j}{4\pi\varepsilon_0|r_i - r_j|}d\vec{r}_j$$

$$\hat{H} = \sum_i \left(-\frac{\hbar^2}{2m}\vec{\nabla}_i^2 - \frac{Ze_0^2}{4\pi\varepsilon_0 r_i} + V_i^{ef}\right)$$

$$\hat{H}\phi_i = E_i\phi_i$$

NUMERIČNO REŠEVANJE

postopek reševanja

Izmislimo si sistem funkcij ϕ_i

↓

izračunamo V_i^{ef}

↓

rešujemo $\hat{H}\phi_i = E_i\phi_i$

↓

NE ← primerjamo nove ϕ_i in E_i

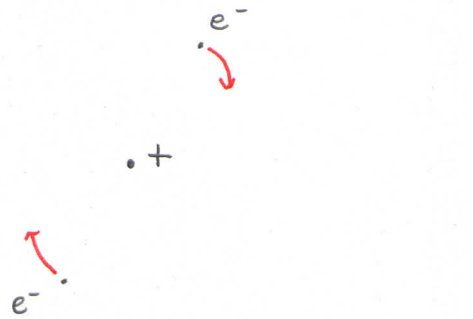
↓ DA

KONEC

Končamo takrat, ko imamo želeno natančne ϕ_i in E_i.

Hartree - Fockova metoda

$$\Psi = \sqrt{\frac{1}{n!}} \begin{vmatrix} \phi_1(1) & \phi_1(2) & \dots \\ \phi_2(1) & \phi_2(2) & \\ \vdots & & \ddots \end{vmatrix}$$



Elektrona se hočeta „skriti" za pozitivnim jedrom - KORELACIJA MED GIBANJI ELEKTRONOV.

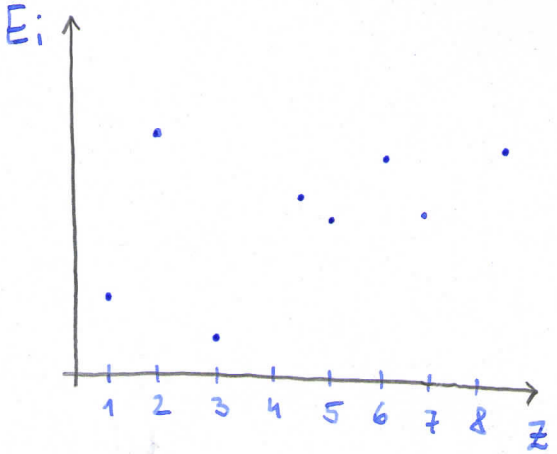
to korelacijo po H.-F. metodi ZANEMARIMO (velika pomanjkljivost)

ION. ENERGIJA :

$$X \rightarrow X^+ + e^-$$

AFINITETA :

$$X + e^- \rightarrow X^-$$



Ion. energija je NAJNIŽJA ENERGIJA, da izbijemo elektron iz delca (atoma, iona).

Afiniteta je energija, ki se sprosti oz. porabi, ko delec (atom, ion) sprejme en elektron.

Molekule

$$\hat{H} = \underbrace{\sum_j -\frac{\hbar^2}{2M}\vec{\nabla}_j^2}_{\text{kin. energija jedra}} + \underbrace{\sum_i -\frac{\hbar^2}{2m_e}\vec{\nabla}_i^2}_{\text{kin. energija } e^-} + \underbrace{\sum_{i,j} \frac{-Z_j e_0^2}{4\pi\varepsilon_0 |\vec{R}_j - \vec{r}_i|}}_{\text{odboj med } e^- \text{ in jedri}} + \underbrace{\frac{1}{2}\sum_{k\neq j} \frac{Z_j Z_k e_0^2}{4\pi\varepsilon_0 |\vec{R}_j - \vec{R}_k|}}_{\text{odboj med jedri}} + \underbrace{\frac{1}{2}\sum_{i\neq l} \frac{e_0^2}{4\pi\varepsilon_0 |\vec{r}_i - \vec{r}_e|}}_{\text{odboj med } e^-}$$

kin. energija jedra: R_j; kin. energija e^-: $\vec{r}_i$; odboj med jedri: $\vec{R}_j$; odboj med e^-: $\vec{r}_i$

molekula z najmanj delci je H_2^+

$m_e = 9{,}1 \cdot 10^{-31}\,kg$

$m_p = 1{,}67 \cdot 10^{-27}\,kg$

Gledamo: $\sum_j \frac{-\hbar^2}{2M}\vec{\nabla}_j^2$ in $\sum_i -\frac{\hbar^2}{2m_e}\vec{\nabla}_i^2$

$M \gg m_e$

$\vec{\nabla}_j \ll \vec{\nabla}_i$

⇓

uporabimo Born-Oppenheimerjev približek - v tem približku jedra mirujejo (prim. slon in muha)

$\Psi(\vec{R}_j, \vec{r}_i) = \alpha(\vec{R}_j)\,\beta(\vec{r}_i)$ - teh dveh ne moremo ločiti

$\Psi(\vec{R}_j, \vec{r}_i) = \phi(\vec{R}_j)\,\Psi_e(\vec{R}_j, \vec{r}_i)$

jedro $\hat{H}_n = -\sum_j \frac{\hbar^2}{2M_j}\vec{\nabla}_j^2 + \frac{1}{2}\sum_{j\neq k} \frac{Z_j Z_k e_0^2}{4\pi\varepsilon_0 |\vec{R}_j - \vec{R}_k|}$

e^- $\hat{H}_e = -\sum_i \frac{\hbar^2}{2m_e}\vec{\nabla}_i^2 + \frac{1}{2}\sum_{e\neq i} \frac{e_0^2}{4\pi\varepsilon_0 |\vec{r}_i - \vec{r}_e|}$

jedro in e^- $\hat{H}_{ne} = -\sum_{i,j} \frac{Z_j e_0^2}{4\pi\varepsilon_0 |\vec{R}_j - \vec{r}_i|}$

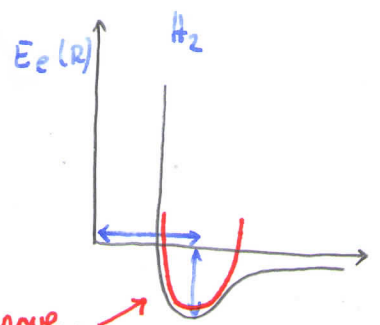
$\hat{H}\Psi = (\hat{H}_{ne} + \hat{H}_n + \hat{H}_e)\Psi =$

$= \hat{H}_n\Psi + (\hat{H}_{ne} + \hat{H}_e)\Psi = E\Psi$

$(\hat{H}_{ne} + \hat{H}_e)\,\phi(\vec{R}_j)\,\Psi_e(\vec{R}_j, \vec{r}_i) =$

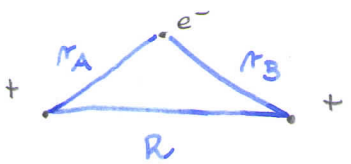
$\phi(\vec{R}_j)\underbrace{(\hat{H}_{ne} + \hat{H}_e)\,\Psi_e(\vec{R}_j, \vec{r}_i)}_{\text{to rešimo}} \Rightarrow \Psi_e(\vec{R}_j, \vec{r}_i)\;;\; E(\vec{R}_j)$

$\hat{H}_n\Psi + E(\vec{R}_j)\,\phi(\vec{R}_j)\,\Psi_e(\vec{R}_j, \vec{r}_i) = E\Psi$



ta parabola pove, kako se gibata jedra

H_2^+



uporabimo B.-O. približek:

$$\hat{H} = -\frac{\hbar^2}{2m}\vec{\nabla}^2 - \frac{e_0^2}{4\pi\varepsilon_0 r_A} - \frac{e_0^2}{4\pi\varepsilon_0 r_B} + \frac{e_0^2}{4\pi\varepsilon_0 R}$$

R = konst.; sistem lahko analitično rešimo le eliptičnima koordinatama ⇒ ne rešujemo

$R \to \infty$

$$\Psi_+ = N_+(1s_A + 1s_B)$$
$$\Psi_- = N_-(1s_A - 1s_B)$$

$$\boxed{\langle \Psi_\pm | \Psi_\pm \rangle = 1}$$

Potrebna je normirizacija.

$$\langle \Psi_\pm | \Psi_\pm \rangle = \int N_\pm^2 (1s_A \pm 1s_B)^2 dV =$$

$$= N_\pm^2 \int (1s_A^2 \pm 2\, 1s_A 1s_B + 1s_B^2)\, dV =$$

$$= N^2 \pm \Big(\underbrace{\int 1s_A\, dV}_{1} \pm 2 \underbrace{\int 1s_A 1s_B\, dV}_{\text{prekrivalni integral} = S} + \underbrace{\int 1s_B^2 dV}_{1} \Big) =$$

$$1 = N_\pm^2 (2 \pm 2S)$$

$$\boxed{N_\pm = \frac{1}{\sqrt{2(1 \pm S)}}}$$

$$E = \langle \psi_\pm | \hat{H} | \psi_\pm \rangle$$

$$E = N_\pm^2 \int (1s_A \pm 1s_B)\, \hat{H}\, (1s_A \pm 1s_B)\, dV =$$

$$= N_\pm^2 \int (1s_A \hat{H} 1s_A \pm 2\, 1s_A \hat{H} 1s_B + 1s_B \hat{H} 1s_B) =$$

$$1s_A \hat{H} 1s_A = 1s_B \hat{H} 1s_B$$

simetričnost val. funkcij

$$= \frac{1}{2(1 \pm S)} \int (1s_A \hat{H} 1s_A \pm 1s_A \hat{H} 1s_B)\, dV = \frac{\alpha \pm \beta}{1 \pm S}$$

$$\Rightarrow \int \left(1s_A \left(-\frac{\hbar^2}{2m}\vec{\nabla}^2 - \frac{e_0^2}{4\pi\varepsilon_0 r_A} - \frac{e_0^2}{4\pi\varepsilon_0 r_B} + \frac{e_0^2}{4\pi\varepsilon_0 R}\right) 1s_B\, dV\right)$$

!!!

ko gre $R \to \infty$ $\Rightarrow$ ta integral je enak 0

$$1s_A \left(-\frac{\hbar^2}{2m}\vec{\nabla}^2 - \frac{e_0^2}{4\pi\varepsilon_0 r_A} - \frac{e_0^2}{4\pi\varepsilon_0 r_B} + \frac{e_0^2}{4\pi\varepsilon_0 R}\right) 1s_A$$

$= \alpha$ negativen

0, ko $R \to \infty$

oz.

$$\lim_{R \to \infty} \int 1s_A \hat{H} 1s_A\, dV = E_H$$

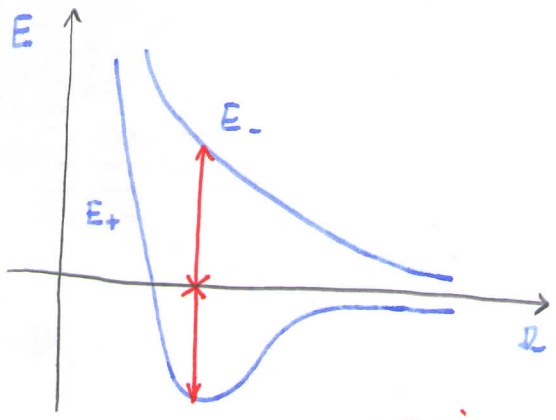
vezna m. orbitala

$$\psi_+ \quad E_+ = \frac{\alpha + \beta}{1 + S} \qquad E_+ = E_H$$

$$\psi_- \quad E_- = \frac{\alpha - \beta}{1 - S} \qquad E_- = E_H$$

razvezna m. orbitala

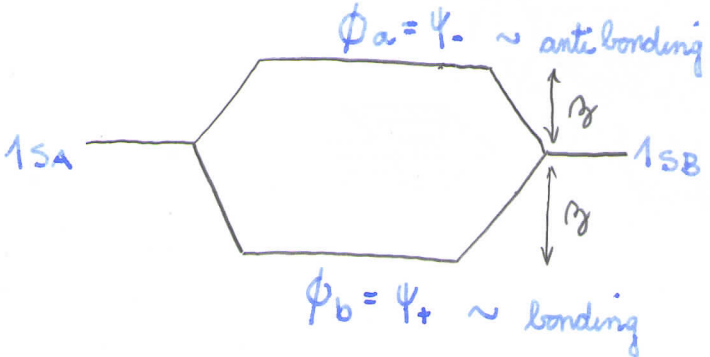
- do upoštevanja linearne kombinacije val. funkcij



smo v min.

$$E(R) = E_0 + (R - R_0)\frac{\partial E}{\partial R} + (R - R_0)^2 \frac{\partial^2 E}{\partial R^2}$$

$$\phi_b = 1s_A + 1s_B$$



Molekula se vrti kot TOGI ROTATOR.