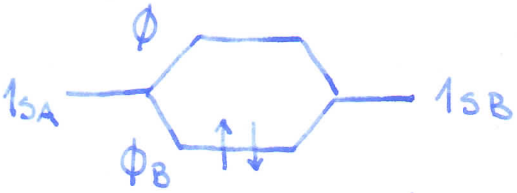
Molekula H_2

TMO : TEORIJA MOLEKULSKIH ORBITAL :



$\phi_B = 1s_A + 1s_B$

$\phi_A = 1s_A - 1s_B$

$$\boxed{\Psi(1,2) = \phi_B(1)\phi_B(2) \cdot \frac{1}{\sqrt{2}}(\alpha(1)\beta(2) - \beta(1)\alpha(2))}$$

f. zapisano na tak način, da je ANTISIMETRIČNA na zamenjavo 2 delcev

$$\Psi(1,2) = \phi_B(1)\,\phi_B(2)\,\frac{1}{\sqrt{2}}(\alpha(1)\beta(2) - \beta(1)\alpha(2))$$

$$\Psi(2,1) = \phi_B(2)\,\phi_B(1)\,\frac{1}{\sqrt{2}}(\alpha(2)\beta(1) - \beta(2)\alpha(1))$$

$$\Psi(1,2) = -\Psi(2,1)$$

TMO :

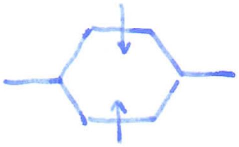
$E_V = -2,69\,eV$

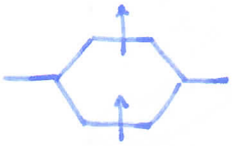
$R = 0,85\,Å$

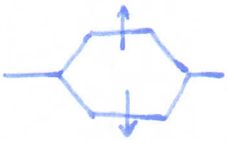
eksperiment :

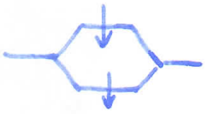
$E_V = -4,75\,eV$

$R = 0,74\,Å$









za 1× vzbujeno stanje imamo 4 možnosti :

$\phi_B(1)\alpha(1)$	$\phi_B(1)\alpha(1)$	$\phi_B(1)\beta(1)$	$\phi_B(1)\beta(1)$
$\phi_A(2)\beta(2)$	$\phi_A(2)\alpha(2)$	$\phi_A(2)\alpha(2)$	$\phi_A(2)\beta(2)$

TVB : TEORIJA VALENČNIH VEZI :

$$\boxed{\begin{aligned} * \int 1s_A^2(1)\,dV_1 &= 1 \\ \int 1s_B^2(2)\,dV_2 &= 1 \end{aligned}}$$

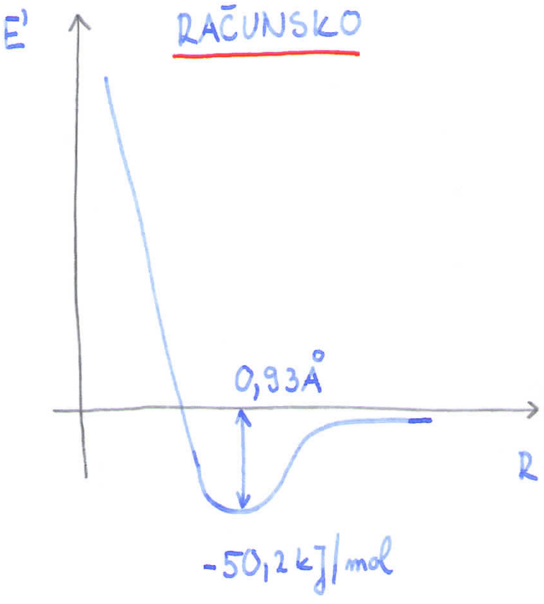
popravek : $E' = \langle \Psi(1,2) | V' | \Psi(1,2) \rangle$

$$E' = \iint 1s_A(1)\,1s_B(2)\left(-\frac{e_0^2}{4\pi\varepsilon_0 r_{B1}} - \frac{e_0^2}{4\pi\varepsilon_0 r_{A2}} + \frac{e_0^2}{4\pi\varepsilon_0 R} + \frac{e_0^2}{4\pi\varepsilon_0 r_{12}}\right) 1s_A(1)\,1s_B(2)\,dV_1\,dV_2 =$$

$$= -\iint 1s_A^2(1)\,\underline{1s_B^2(2)}\,\frac{e_0^2\,dV_1\,\boxed{dV_2}}{4\pi\varepsilon_0 r_{B1}}^{*} - \iint \underline{1s_A^2(1)}\,\underline{1s_B^2(2)}\,\frac{e_0^2\,\boxed{dV_1}\,\boxed{dV_2}}{4\pi\varepsilon_0 r_{A2}}^{*} + \iint 1s_A^2(1)\,1s_B^2(2)\,\frac{e_0^2}{4\pi\varepsilon_0 R}\,dV_1\,dV_2 + \iint 1s_A^2(1)\,1s_B^2(2)\,\frac{e_0^2}{4\pi\varepsilon_0 r_{12}}\,dV_1\,dV_2 =$$

$$E' = -\int \frac{e_0^2}{4\pi\varepsilon_0 r_{B1}}\,1s_A^2(1)\,dV_1 - \int \frac{e_0^2}{4\pi\varepsilon_0 r_{A2}}\,1s_B(2)\,dV_2 + \frac{e_0^2}{4\pi\varepsilon_0 R} + \iint \frac{e_0^2}{4\pi\varepsilon_0 r_{12}}\,1s_A^2(1)\,1s_B^2(2)\,dV_1\,dV_2$$

RAČUNSKO



EKSPERIMENT:

$R = 0,74 Å$

$E_v = -458,5$ kJ/mol

↓

ni najboljša, saj ni ne simetrična ne antisimetrična

$$\boxed{\begin{aligned}\Psi(1,2) &= 1s_A(1)1s_B(2)\\ \Psi(2,1) &= 1s_B(1)1s_A(2)\end{aligned}}$$

Bolje :

$$\Psi_+(1,2) = 1s_A(1)1s_B(2) - 1s_A(2)1s_B(1)$$

$$\Psi_-(1,2) = 1s_A(1)1s_B(2) - 1s_A(2)1s_B(1)$$

$$E'_{\pm} = \int \Psi_{\pm}^{2}(1,2)\, V'\, dV_1\, dV_2$$ - funkcijo NORMIRAMO

$$\Psi_{\pm} = N_{\pm}\left(1s_A(1)\,1s_B(2) \pm 1s_A(2)\,1s_B(1)\right) \Rightarrow \int \Psi_{\pm}^{2}\, dV_1\, dV_2 = 1$$

$$\int N_{\pm}^{2}\left(1s_A(1)\,1s_B(2) \pm 1s_A(2)\,1s_B(1)\right)^{2} dV_1\, dV_2 =$$

$$= N_{\pm}^{2}\int\Big(\overbrace{1s_A^{2}(1)\,1s_B^{2}(2)}^{①} \pm 2\cdot 1s_A(1)\,1s_B(2)\,1s_A(2)\,1s_B(1) \pm \underbrace{1s_A^{2}(2)\,1s_B^{2}(1)}_{①}\Big)\, dV_1\, dV_2 =$$

$$\boxed{\int 1s_A^{2}(1)\,1s_B^{2}(2)\, dV_1\, dV_2 = \int 1s_A^{2}(1)\, dV_1 \int 1s_B^{2}(2)\, dV_2 = 1}$$

$$= N_{\pm}^{2}\left(2 \pm 2S^{2}\right) = 1$$

$$\boxed{\int 1s_A(1)\,1s_B(1)\,1s_A(2)\,1s_B(2)\, dV_1\, dV_2 = \int 1s_A(1)\,1s_B(1)\, dV_1 \int 1s_A(2)\,1s_B(2)\, dV_2 = S^{2}}$$

$$E'_{\pm} = \frac{Q \pm J}{1 \pm S^{2}}$$

$$Q = \iint 1s_A^{2}(1)\,1s_B^{2}(2)\, V'\, dV_1\, dV_2$$ - Coulombski integral

$$J = \iint 1s_A(1)\,1s_B(1)\,1s_A(2)\,1s_B(2)\, V'\, dV_1\, dV_2$$ - zamenjalni integral

$$J \simeq 4\text{-}5 \cdot Q$$

za iste funkcije

Ψ_+

TVB (teorija valenčnih vezi):

$E_v = -3,16\ \text{eV}$

$R = 0,87\ \text{Å}$

TMO (teorija molekulskih orbital):

$E_v = -2,69\ \text{eV}$

$R = 0,85\ \text{Å}$

eksperiment:

$E_v = -4,73\ \text{eV}$

$R = 0,74\ \text{Å}$

TMO :

$$\phi_B(1)\,\phi_B(2) = \left(1s_A(1) + 1s_B(1)\right)\left(1s_A(2) + 1s_B(2)\right) =$$

$$= \underbrace{1s_A(1)\,1s_A(2)}_{\substack{\text{H:}\quad \text{H} \\ \text{oz.} \\ \text{H}^{\ominus}\quad \text{H}^{\oplus}}} + \underbrace{1s_A(1)\,1s_B(2) + 1s_B(1)\,1s_A(2)}_{\Psi_+} + \underbrace{1s_B(1)\;1s_B(2)}_{\substack{\text{H}\quad \text{:H} \\ \text{oz.} \\ \text{H}^{\oplus}\quad {}^{\ominus}\text{H}}} =$$

Pri TMO se upoštevajo vse KANONSKE STRUKTURE.

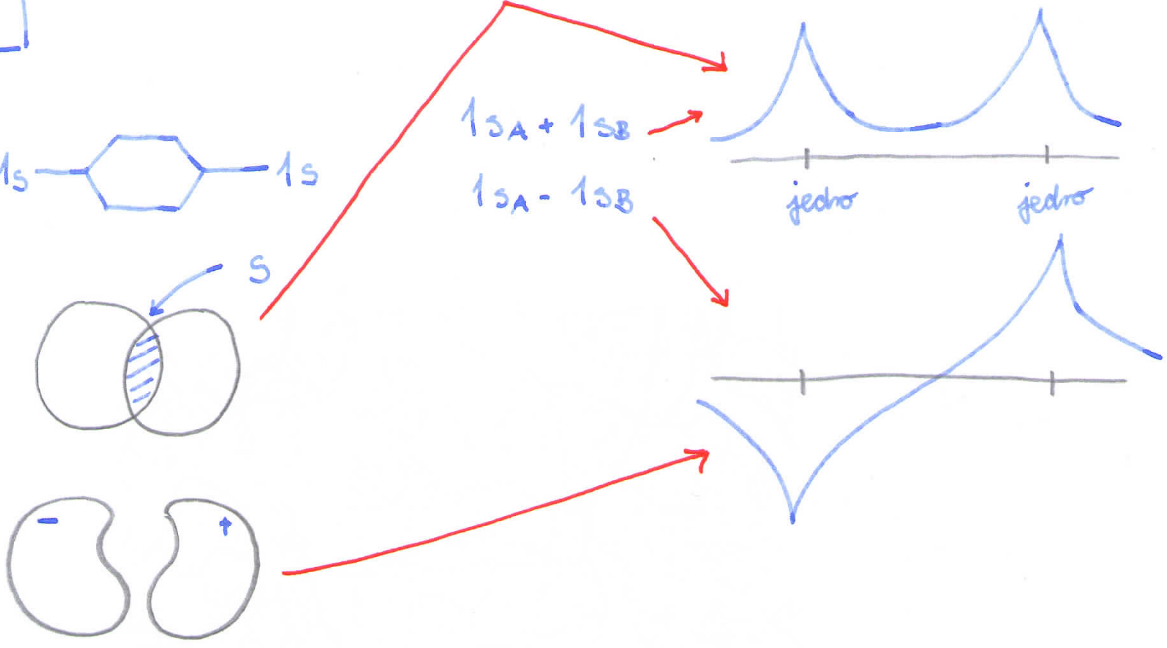
$$\boxed{\Psi_i} = 1s_A(1)\,1s_A(2) + 1s_B(1)\,1s_B(2) \quad \sim \quad \underline{\text{IONSKO STANJE}}$$

Pri TMO dobimo valovno funkcijo Ψ_+ (TVB) in še funkciji za ionsk. stanje.

Homonuklearni diatomiki

$\boxed{H_2 , N_2 , O_2 \ldots}$

H_2 : $2e^-$

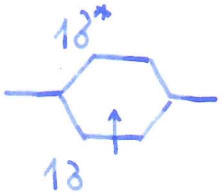


iz tega sledi:

$$\left.\begin{aligned} 1\sigma &= 1s_A + 1s_B \\ 1\sigma^* &= 1s_A - 1s_B \end{aligned}\right\}$$

čelno prekrivanje, nastanek σ vezi

H_2^+

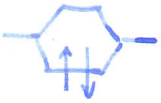


$$b = \frac{\text{št. } e^- \text{ na veznih} - \text{št. } e^- \text{ na razveznih orbitalah}}{2}$$

NETO VEZAVNOST

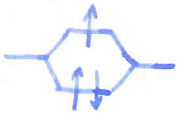
$$b(H_2^+) = \frac{1-0}{2} = \underline{\underline{\frac{1}{2}}}$$

H_2



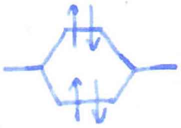
$$b(H_2) = \frac{2-0}{2} = \underline{\underline{1}}$$

He_2^+



$$b(He_2^+) = \frac{2-1}{2} = \underline{\underline{\frac{1}{2}}}$$

He_2



$$b(He_2) = \frac{2-2}{2} = \underline{\underline{0}}$$

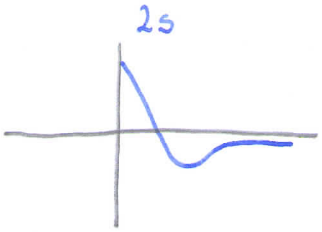
molekula ne obstaja

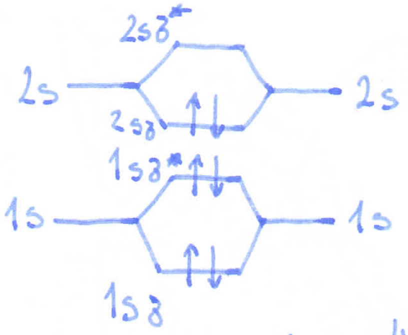
mol. ion	b	R
H_2^+	$\frac{1}{2}$	1,06 Å
H_2	1	0,74 Å
He_2^+	$\frac{1}{2}$	1,08 Å
He_2	0	

Li_2 6e⁻ :

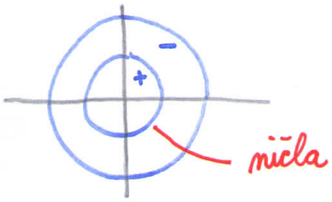
$$2s\sigma = 2s_A + 2s_B$$

$$2s\sigma^* = 2s_A - 2s_B$$



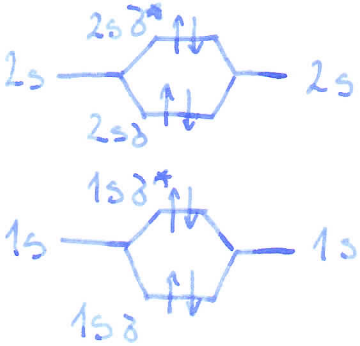


NOT TO SCALE



$$b = \frac{4-2}{2} = \underline{\underline{1}}$$ tvori mol. pri nizki T v plinastem stanju

Be_2 8e⁻ :



$$b = \frac{4-4}{2} = \underline{\underline{0}}$$ mol. Be_2 ne obstaja

B_2 10e⁻ : $2p_x$, $2p_y$, $\underline{2p_z}$ – DOGOVOR ⇓ σ vez

$$2p_z\sigma = 2p_z A + 2p_z B$$

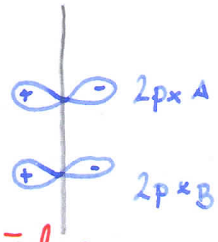
$$2p_z\sigma^* = 2p_z A - 2p_z B$$

$$2p_x\pi = 2p_x A + 2p_x B$$

$$2p_x\pi^* = 2p_x A - 2p_x B$$

isto velja za Py

bočno prekrivanje: σ vez

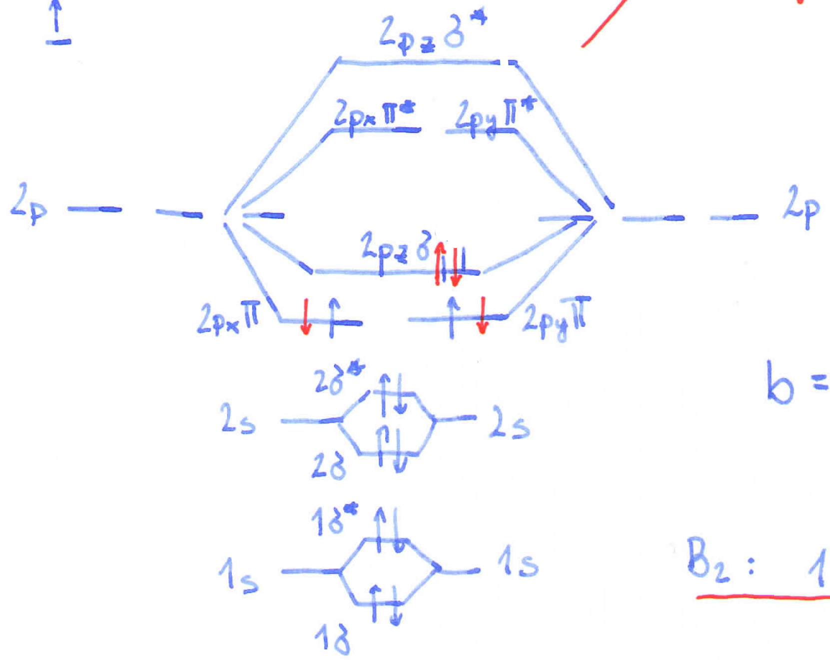


čelno prekrivanje: π vez

B_2 $10e^-$:

↑

ta diagram velja za B, C, N in Ne



$$b = \frac{6-4}{2} = \underline{\underline{1}}$$

B_2 : $1s\sigma^2\, 1s\sigma^{*2}\, 2s\sigma^2\, 2\sigma^{*2}\, 2p_x\pi\, 2p_y\pi$

C_2 $12e^-$:

↑ ↑

$$b = \frac{8-4}{2} = \underline{\underline{2}}$$

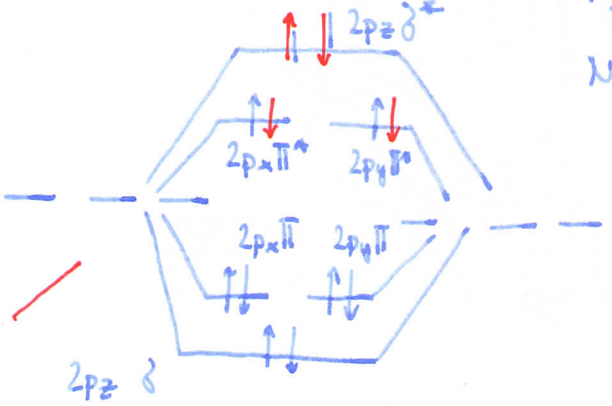
mol.	b	R	Ev
Li_2	1	2,67 Å	- 1,04eV
Be_2	0	/	/
B_2	1	1,59 Å	- 3,0eV
C_2	2	1,24 Å	-6,5eV
N_2	3	1,10 Å	- 9,8eV
O_2	2	1,21 Å	- 5,1eV
F_2	1	1,44 Å	-1,6eV
Ne_2	0	/	/

N_2 $14e^-$:

↑ ↑ ↑

$$b = \frac{10-4}{2} = \underline{\underline{3}}$$

O_2 $16e^-$:



ta diagram velja za O in F

O_2 : $1s\sigma^2\, 1s\sigma^{*2}\, 2s\sigma^2 2s\sigma^{*2}\, 2p_z\sigma^2$
$2p_x\pi^2\, 2p_y\pi^2\, 2p_x\pi^*\, 2p_y\pi^*$

$$b = \frac{10-6}{2} = \underline{\underline{2}}$$

F_2 $18e^-$:

↑ ↑

$$b = \frac{10-8}{2} = \underline{\underline{1}}$$

Ne_2 $20e^-$:

↑ ↑ ↑

$$b = \frac{10-10}{2} = \underline{\underline{0}}$$

$$\boxed{B = \mu \mu_0 \frac{I}{2\pi r}}$$

$\mu > 1$ - paramagnetna snov nesparjeni e^- (O_2, B_2 ...)

$\mu < 1$ - diamagnetna snov sparjeni e^- (C_2, N_2 ...)

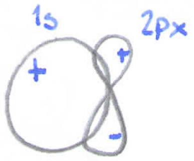
$\mu >> 1$ - feromagnetna snov (Fe ...)

Heteronuklearni diatomiki

$\boxed{LiH,\ HF,\ CO\ \ldots}$

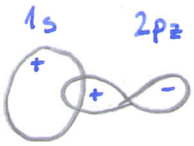
$$\boxed{E_n = \frac{-13{,}6\ eV\ z^2}{n^2}}$$

ϕ_A



$S = 0$

ϕ_B



$S \neq 0$

$\boxed{s,\ p,\ d}$

ϕ_A	ϕ_B OK	ni OK
s, p_z, d_{z^2}	s, p_z, d_{z^2}	$p_x, p_y, d_{x^2-y^2}, d_{xy}, d_{yz}, d_{xz}$
p_x, d_{xz}	p_x, d_{xz}	$s, p_y, p_z, d_{x^2-y^2}, d_{xy}, d_{yz}, d_{z^2}$
p_y, d_{yz}	p_y, d_{yz}	$s, p_x, p_z, d_{x^2-y^2}, d_{z^2}, d_{xy}, d_{xz}$
$d_{x^2-y^2}$	$d_{x^2-y^2}$	$s, p_x, p_y, d_{z^2}, d_{xy}, d_{yz}, d_{xz}$

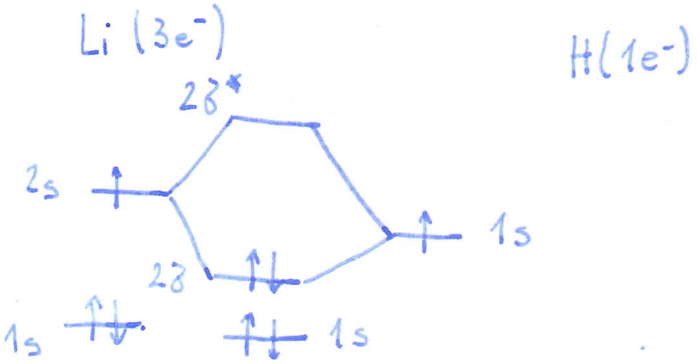
KOMBINIRAMO

NE MOREMO KOMBINIRATI

Skombiniramo energijsko bolj podobne orbitale.

Primer:

LiH



$$\boxed{\begin{aligned} \sigma &= 1s_H + 2s_{Li} \\ \sigma^* &= 1s_H - 2s_{Li} \end{aligned}}$$

$LiH = 1\sigma^2 2\sigma^2$

CO

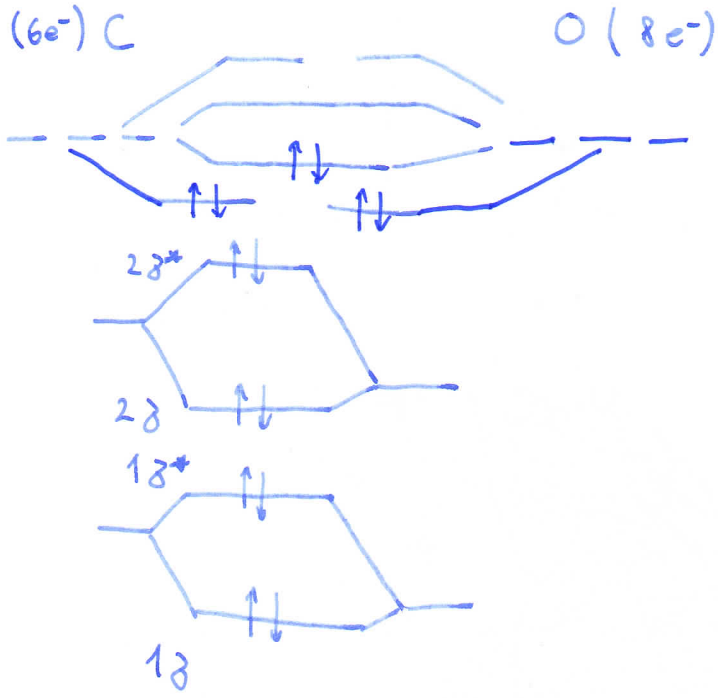


diagram ni več SIMETRIČEN

$CO = 1\sigma^2 1\sigma^{*2} 2\sigma^2 2\sigma^{*2} 2p_x\pi^2 2p_y\pi^2$
$2p_z\sigma^2$

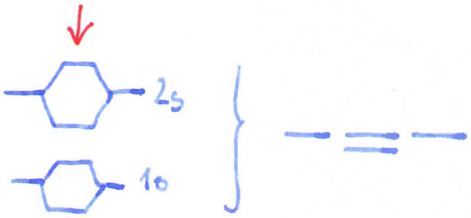
$\phi_b = 1s_A + 1s_B$

$S = \langle 1s_A | 1s_B \rangle$

$J = \int \phi_A(1)\phi_B(2)V'\phi_A(2)\phi_B(1)\,dV_1 dV_2$ ~ 80% prispevek pri interakciji vezi

$H_2, Li_2 \ldots O_2$

$S_{H_2} = 0,68$
$S_{Li_2} = 0,01$
$S_{O_2} = 10^{-5}$
} prekrivalni integrali ~ pri tvorjenju vezi sodelujejo samo VALENČNI e⁻

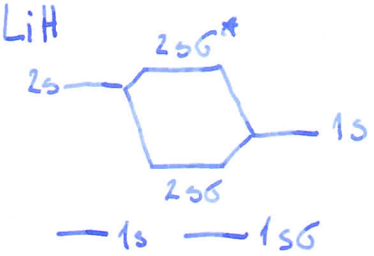


zelo majhne razlike med nivoji

$S = \int \phi_A(1)\phi_B(1)\,dV \Leftarrow \int \phi_A(1)\phi_B(1)V'\phi_B(2)\phi_A(2)\,dV_1 dV_2$

močnejša je vez, čim večji je prekrivalni integral

LiH



$1s\sigma = 1s_{Li}$

$2s\sigma = 0{,}323\ 2s_{Li} + 0{,}231 \cdot 2p_z Li + 0{,}685\ 1s_H$

$2s\sigma = \underline{0{,}397}\,(0{,}813\ 2s_{Li} + 0{,}582\ 2p_z Li) + \underline{0{,}6851}\ 1s_H$

MOLEKULSKA ORBITALA

vez je bližje H-ju kot Li-ju => POLARNA VEZ

$$\boxed{\phi = N(\phi_A + \lambda \phi_B)}$$

, če je $\lambda > 1$, potem je atom B polariziran (vez je bližje atomu B kot atomu A)

$\underline{\lambda = 1}$ e^- porazdeljen enakomerno med A in B

$\underline{\lambda > 1}$ e^- je B

$\underline{\lambda < 1}$ e^- je A

$0{,}813\ 2s_{Li} + 0{,}582\ 2p_z Li$ - ATOMSKA ORBITALA

$2s, 2p_z$ ~ ORTONORMIRANI ORBITALI

$\langle 2s | 2s \rangle = 1$

$\langle 2p_z | 2p_z \rangle = 1$

$\langle 2s | 2p_z \rangle = 0$

$\phi_1 = a_1 2s + b_1 2p_z$

$\phi_2 = a_2 2s + b_2 2p_z$

$\langle \phi_1 | \phi_2 \rangle = 1$ - normirano

$\langle a_1 2s + b_1 2p_z | a_2 2s + b_2 2p_z \rangle = 1$

$$\langle a_1 2s | a_2 2s \rangle + \langle a_1 2s | b_2 2p_z \rangle + \langle b_1 2p_z | a_2 2s \rangle + \langle b_1 2p_z | b_2 2p_z \rangle = 1$$

$$= a_1^2 \underbrace{\langle 2s | 2s \rangle}_{1} + a_1 b_1 \cancel{\langle 2s | 2p_z \rangle} + a_1 b_1 \cancel{\langle 2p_z | 2s \rangle} + b_1^2 \underbrace{\langle 2p_z | 2p_z \rangle}_{1}$$

$$\boxed{\begin{aligned} a_1^2 + b_1^2 &= 1 \\ a_2^2 + b_2^2 &= 1 \end{aligned}}$$

$\langle \phi_1 | \phi_2 \rangle = 0$ - pravokotnost

$a_1 a_2 + b_1 b_2 = 0$

$\underline{a_1 = a_2}$

$a_1 = \frac{\sqrt{2}}{2}$ $a_2 = \frac{\sqrt{2}}{2}$

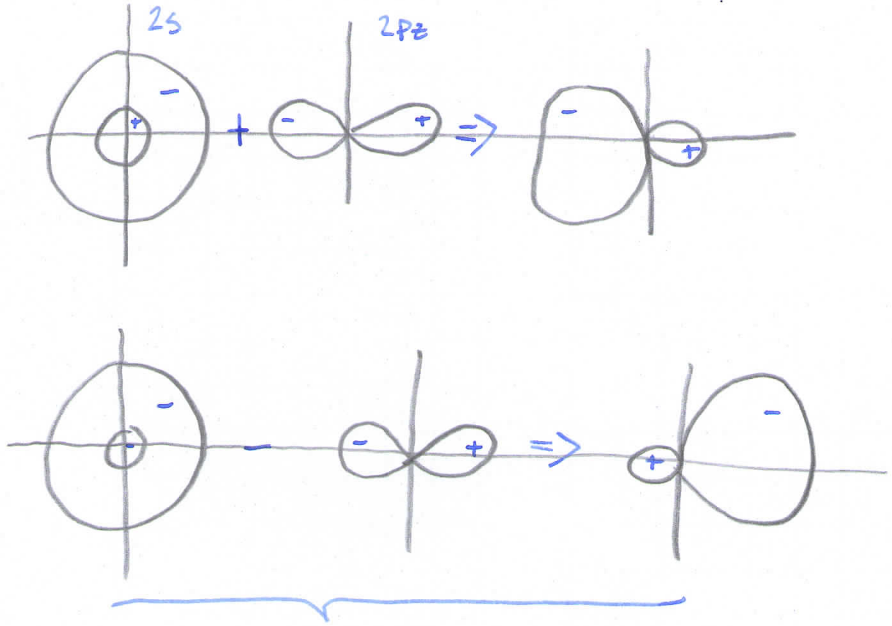
$b_1 = \frac{\sqrt{2}}{2}$ $b_2 = -\frac{\sqrt{2}}{2}$

$$\phi_1 = \frac{\sqrt{2}}{2}(2s + 2p_z)$$

$$\phi_2 = \frac{\sqrt{2}}{2}(2s - 2p_z)$$

$\Rightarrow$

$\Rightarrow$



sp hibridne orbitale

<u>C:</u>

$S(2s, 2s) = 0{,}25$

$S(sp, sp) = 0{,}65$ $\Big\}\begin{matrix} sp_1 \\ sp_2 \end{matrix}$

primeri: C_2H_2, CO_2, BeH_2 ...

$$\left.\begin{aligned} \phi_1 &= a_1 2s + b_1 2p_x + c_1 2p_y \\ \phi_2 &= a_2 2s + b_2 2p_x + c_2 2p_y \\ \phi_3 &= a_3 2s + b_3 2p_x + c_3 2p_y \end{aligned}\right\}$$

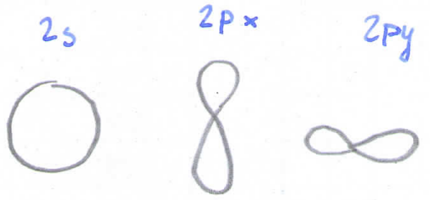
morajo biti normirane,
ortonormirane,
imeti enake deleže s-ja

$\Downarrow$

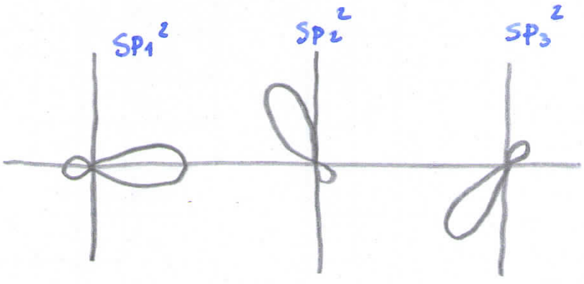
$$\phi_1 = \frac{1}{\sqrt{3}}(2s + \sqrt{2}\, 2p_x)$$

$$\phi_2 = \frac{1}{\sqrt{3}}(2s - \frac{\sqrt{2}}{2} 2p_x + \frac{\sqrt{6}}{2} 2p_y)$$

$$\phi_3 = \frac{1}{\sqrt{3}}(2s - \frac{\sqrt{2}}{2} 2p_x - \frac{\sqrt{6}}{2} 2p_y)$$



primeri: eten,
benzen



sp^2 hibridne orbitale

$2s, 2p_x, 2p_y, 2p_z \Rightarrow$ sp^3 hibridne orbitale

$\phi_1 = \frac{1}{2}(2s + 2p_x + 2p_y + 2p_z)$

$\phi_2 = \frac{1}{2}(2s + 2p_x - 2p_y - 2p_z)$

$\phi_3 = \frac{1}{2}(2s - 2p_x + 2p_y - 2p_z)$

$\phi_4 = \frac{1}{2}(2s - 2p_x - 2p_y - 2p_z)$

primeri: metan, voda