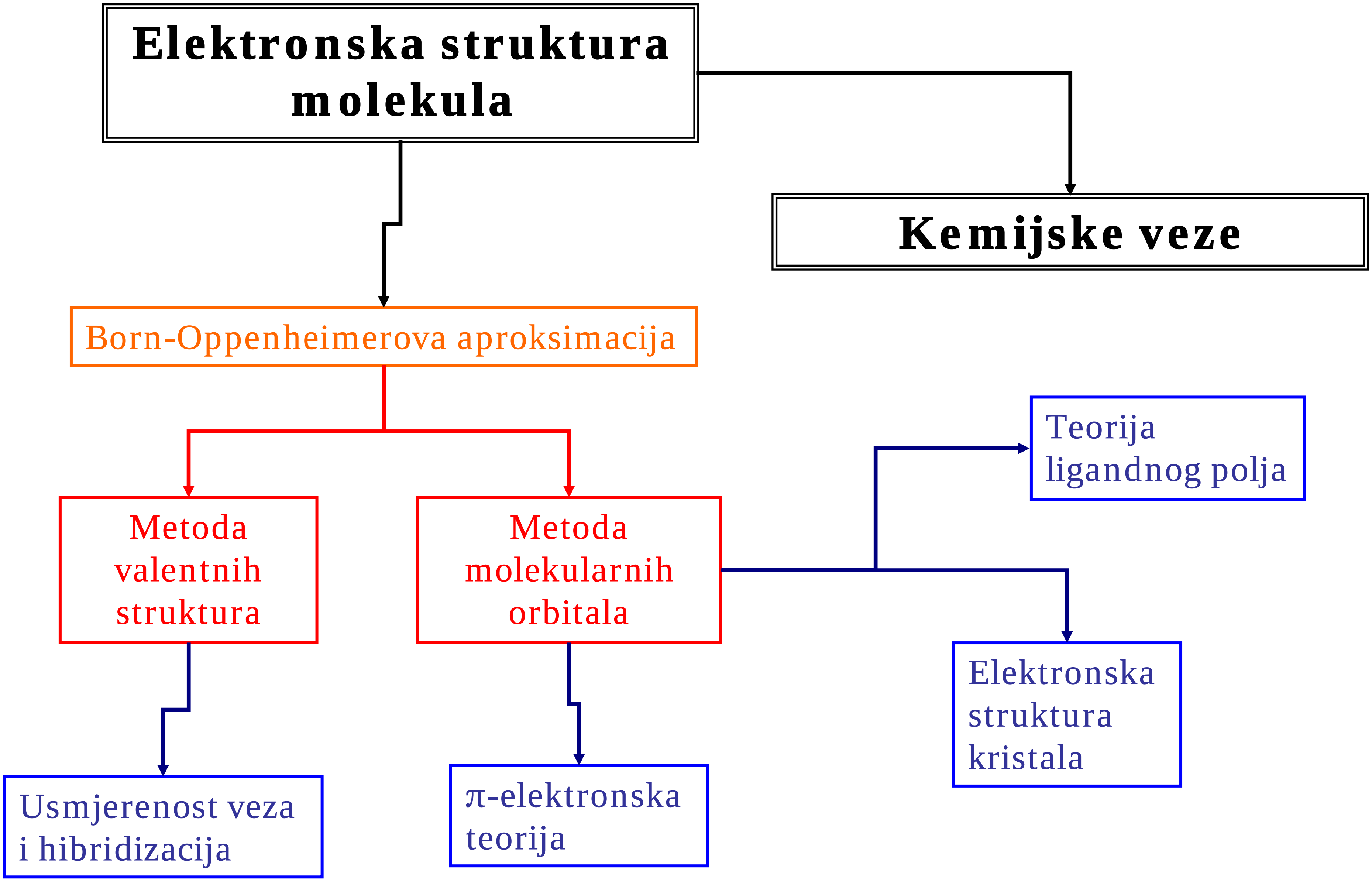

Elektronska struktura molekula
Kemijske veze
Born-Oppenheimerova aproksimacija
Metoda valentnih struktura
Metoda molekularnih orbitala
Teorija ligandnog polja
Elektronska struktura kristala
Usmjerenost veza i hibridizacija
π-elektronska teorija

Born-Opperheimerova aproksimacija

Jezgre se gibaju sporo u odnosu na elektrone

$$\Psi_{\mathrm{uk}} = \Psi_{\mathrm{N}} \cdot \Psi_{\mathrm{e}}$$

Ukupna valna funkcija

$$H = T_{\mathrm{N}} + T_{\mathrm{e}} + V$$

$$\left(\hat{T}_N + \hat{T}_e + V\right)\Psi_{\mathrm{uk}} = E\Psi_{\mathrm{uk}}$$

$$\left(\hat{T}_e + V\right)\Psi_{\mathrm{e}} = E_{\mathrm{e}} \cdot \Psi_{\mathrm{e}}$$

GIBANJE ELEKTRONA UZ STALNI POLOŽAJ JEZGARA

$$\left(\hat{T}_N + E_{\mathrm{e}}\right)\Psi_{\mathrm{N}} = E \cdot \Psi_{\mathrm{N}}$$

GIBANJE JEZGRA POD UTJECAJEM POTENCIJALA E_{e}

Metoda varijacije

1.

$$\Psi = c_1\Psi_1 + c_2\Psi_2$$

2.

$$E = \frac{\int (c_1^{*}\Psi_1^{*} + c_2^{*}\Psi_2^{*})\hat{H}(c_1\Psi_1 + c_2\Psi_2)\mathrm{d}\tau}{\int (c_1^{*}\Psi_1^{*} + c_2^{*}\Psi_2^{*})(c_1\Psi_1 + c_2\Psi_2)\mathrm{d}\tau}$$

3.

$$\frac{\partial E}{\partial c_1} = 0 \qquad \frac{\partial E}{\partial c_2} = 0$$

4.

$$c_1(H_{11} - ES_{11}) + c_2(H_{12} - ES_{12}) = 0$$

$$c_2(H_{21} - ES_{21}) + c_2(H_{22} - ES_{22}) = 0$$

5.

$$E_1 < E_2$$

$$E_1 = \frac{H_{11} + H_{12}}{1 + S_{12}}$$

$$H_{ij} = \int \Psi_i^{*}\hat{H}\Psi_j \mathrm{d}\tau$$

$$E_2 = \frac{H_{11} - H_{12}}{1 - S_{12}}$$

$$S_{ij} = \int \Psi_i^{*}\Psi_j \mathrm{d}\tau$$

Elektronska struktura molekula

Born-Oppenheimerova aproksimacija

Metoda valentnih struktura

Molekula se izgrađuje od atoma koji zbližavanjem međusobno počinju djelovati

$$= \left(\hat{T}_1 - \frac{e^2}{4\pi\varepsilon_0 r_{A1}} \right) + \left(\hat{T}_2 - \frac{e^2}{4\pi\varepsilon_0 r_{B2}} \right) + \frac{e^2}{4\pi\varepsilon_0} \left(-\frac{1}{r_{B1}} - \frac{1}{r_{A2}} + \frac{1}{r_{12}} + \frac{1}{r_{AB}} \right)$$

Metoda molekularnih orbitala

Molekula se izgrađuje tako da se pretpostave fiksni položaji jezgra te se određuju jednoelektronske energije i valne funkcije molekulskih orbitala.

$$\hat{H} = \left[\hat{T}_1 - \frac{e^2}{4\pi\varepsilon_0} \left(\frac{1}{r_{A1}} + \frac{1}{r_{B1}} \right) \right] + \left[\hat{T}_2 - \frac{e^2}{4\pi\varepsilon_0} \left(\frac{1}{r_{A2}} + \frac{1}{r_{B2}} \right) \right] + \frac{e^2}{4\pi\varepsilon_0} \left(\frac{1}{r_{12}} + \frac{1}{r_{AB}} \right)$$

Metoda molekularnih orbitala

$$H_2^+ \quad \Rightarrow \quad \hat{H}_{\mathrm{MO}} = \hat{T}_1 - \frac{e^2}{4\pi\varepsilon_0}\left(\frac{1}{r_{\mathrm{A1}}} + \frac{1}{r_{\mathrm{B1}}} + \frac{1}{r_{\mathrm{AB}}}\right)$$

$$\Psi_{\mathrm{H_2}^+} = c_{\mathrm{A}}\phi_{\mathrm{A}}(1) + c_{\mathrm{B}}\phi_{\mathrm{B}}(1)$$

$$\phi_{\mathrm{A}}(1) = \phi_{\mathrm{B}}(1) = 1\mathrm{s} = 2\left(\frac{1}{a_0}\right)^{\frac{3}{2}} \exp\left(\frac{-r}{a_0}\right)$$

$$c_{\mathrm{B}} = c_{\mathrm{A}} \qquad \frac{\partial E}{\partial c_{\mathrm{A}}} = 0 \quad \frac{\partial E}{\partial c_{\mathrm{B}}} = 0$$

$$c_{\mathrm{A}} = -c_{\mathrm{B}}$$

H_2^+

$$\psi_{\mathrm{s}} = c_{\mathrm{A}}\left[\phi_{\mathrm{A}}(1) + \phi_{\mathrm{B}}(1)\right] = N_{\mathrm{s}}\left[\phi_{\mathrm{A}}(1) + \phi_{\mathrm{B}}(1)\right]$$

$$\psi_{\mathrm{a}} = c_{\mathrm{A}}\left[\phi_{\mathrm{A}}(1) - \phi_{\mathrm{B}}(1)\right] = N_{\mathrm{a}}\left[\phi_{\mathrm{A}}(1) - \phi_{\mathrm{B}}(1)\right]$$

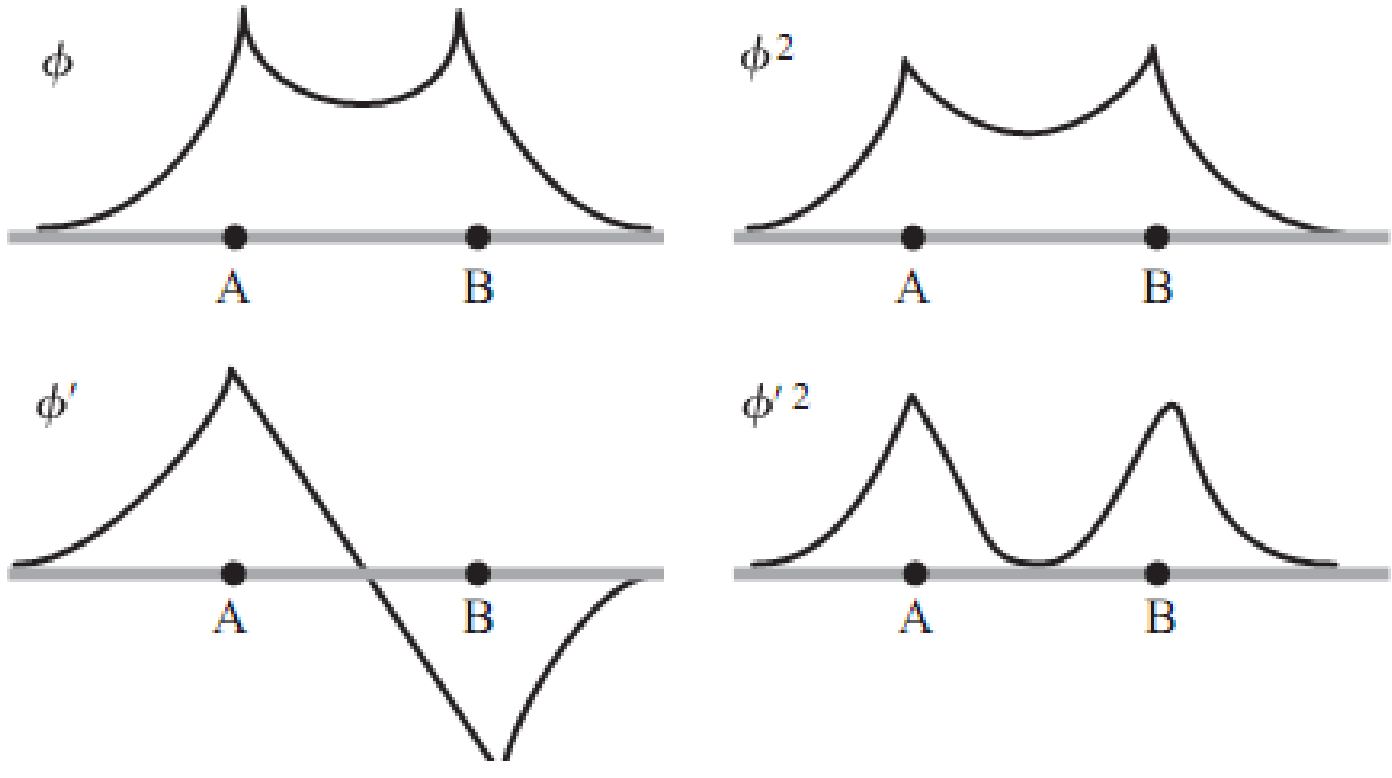
$$\int_t N_{\mathrm{s}}^{\,2}\left[\phi_{\mathrm{A}}(1) + \phi_{\mathrm{B}}(1)\right]^2 = 1 \longrightarrow N_{\mathrm{s}} = (2 + 2S)^{\frac{1}{2}}$$

$$\int_t N_{\mathrm{a}}^{\,2}\left[\phi_{\mathrm{A}}(1) - \phi_{\mathrm{B}}(1)\right]^2 = 1 \longrightarrow N_{\mathrm{a}} = (2 - 2S)^{\frac{1}{2}}$$

$$S = \int_\tau \phi_{\mathrm{A}}(1)\phi_{\mathrm{B}}(1)\,\mathrm{d}\tau$$

H_2^+

$$\psi_s = N_s\left[\phi_A(1) + \phi_B(1)\right]$$

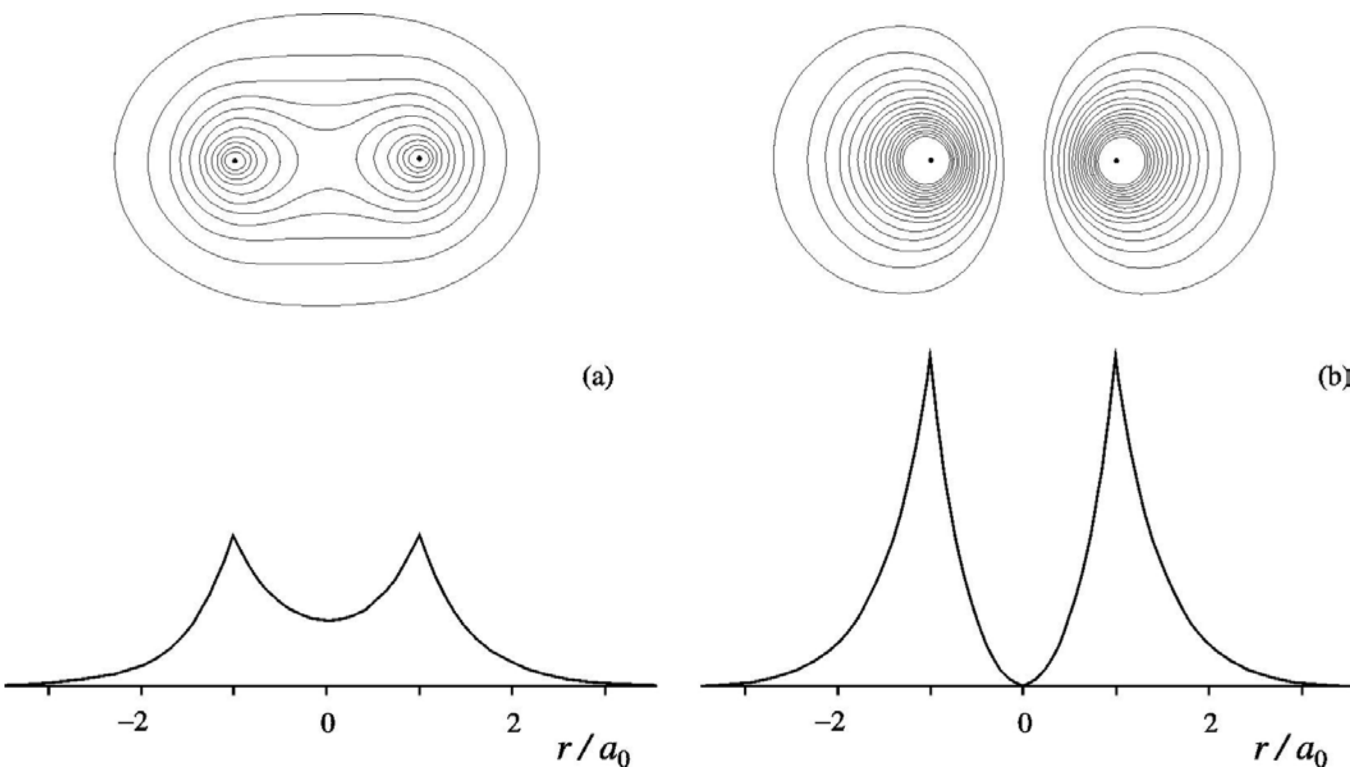


$$\psi_a = N_a\left[\phi_A(1) - \phi_B(1)\right]$$

H_2^+

Krivulje jednake elektronske gustoće i presjek duž internuklearne osi za molekulske orbitale H_2^+

$\psi_s^{\ 2}$ $\psi_a^{\ 2}$

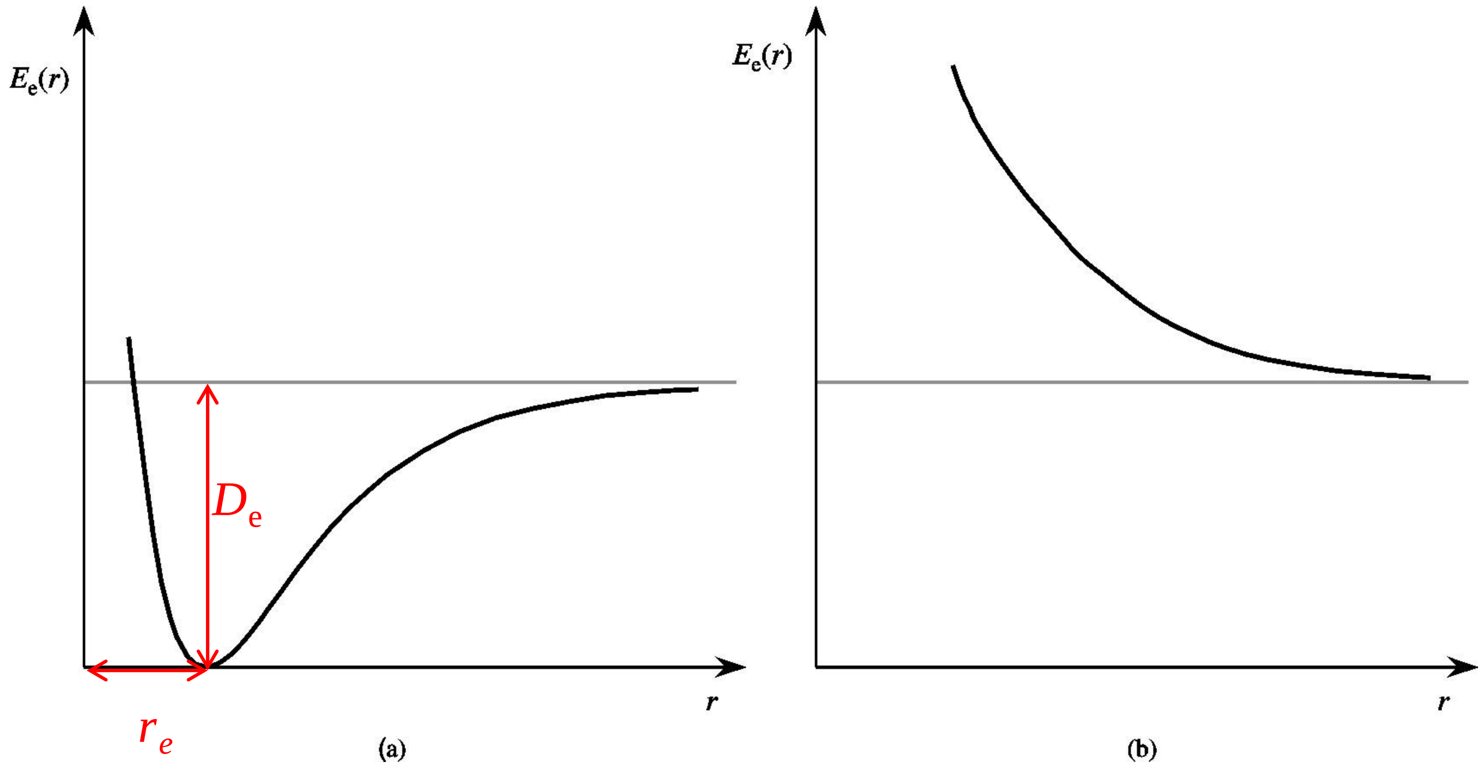


Ovisnost elektronske energije o internuklearnoj udaljenosti

$$\left(\hat{T}e + V\right)\Psi_{\mathrm{e}} = E_{\mathrm{e}} \cdot \Psi_{\mathrm{e}}$$

GIBANJE ELEKTRONA
UZ STALNI POLOŽAJ JEZGARA

- pretpostavi se geometrija i računa E_{e}



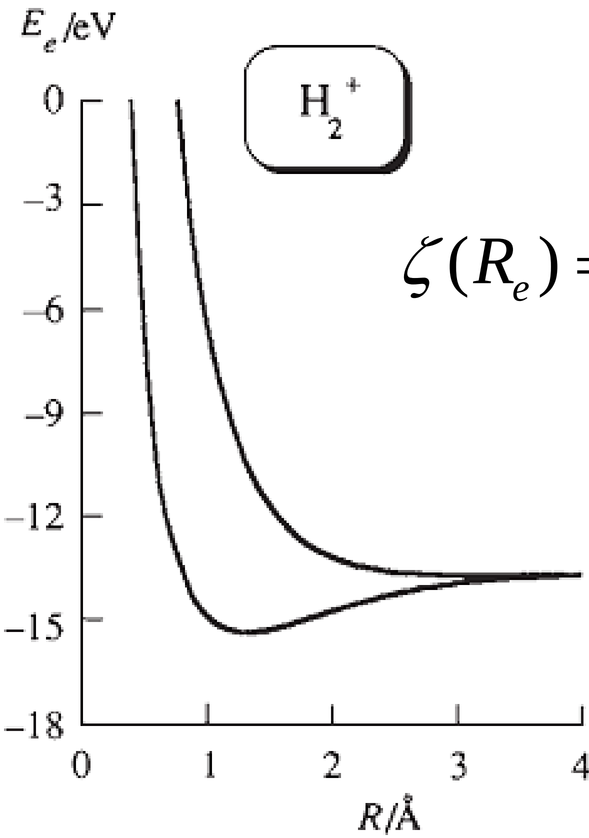
Stabilno elektronsko stanje dvoatomne molekule

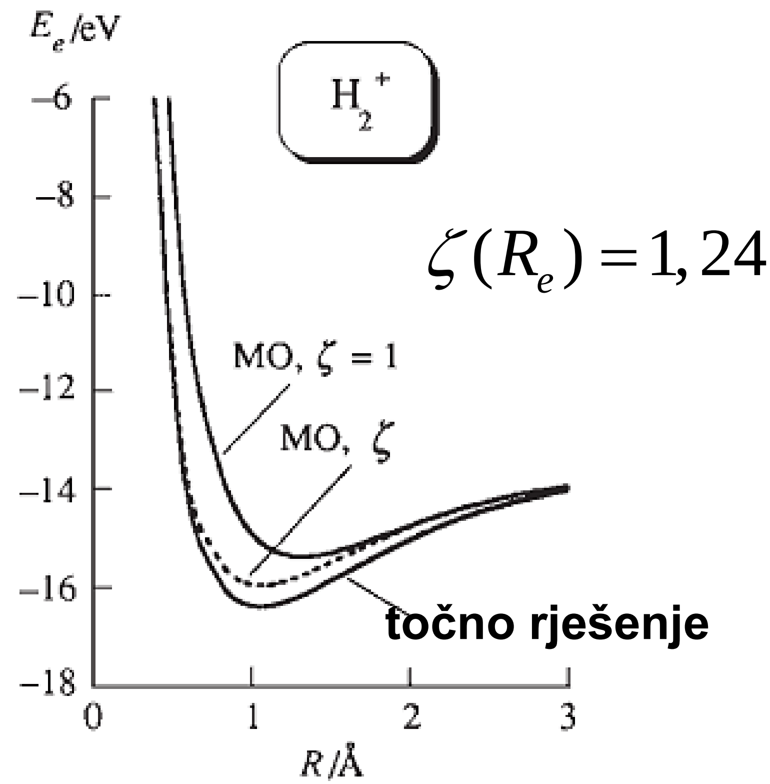
Nestabilno elektronsko stanje dvoatomne molekule

Metoda molekularnih orbitala

H_2^+

$$\phi_A(1) = \phi_B(1) = 1s = 2\left(\frac{1}{a_0}\right)^{\frac{3}{2}} \exp\left(\frac{-\zeta r}{a_0}\right)$$





eksperiment : D_e= 2,8 eV R_e= 1,06 Å

E_s: D_e= 1,8 eV R_e= 1,32 Å

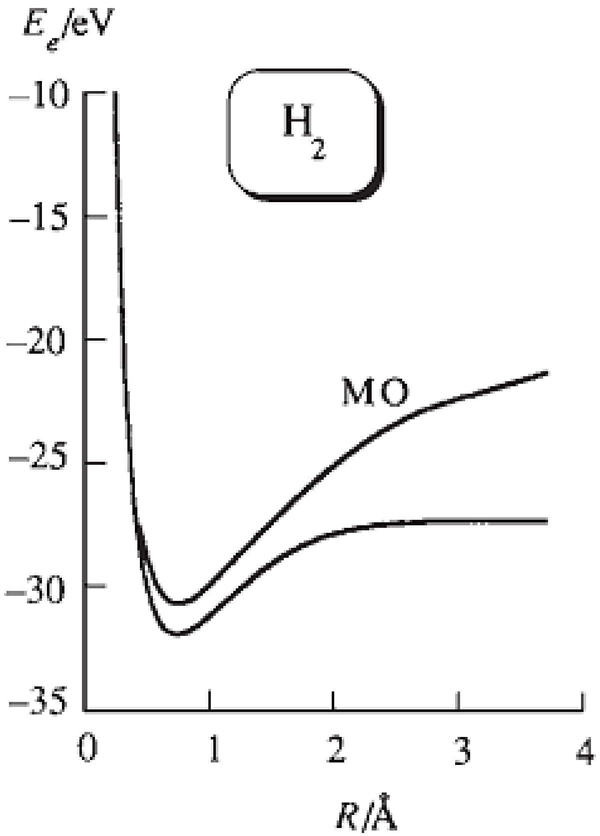
eksperiment : D_e= 2,8 eV R_e= 1,06 Å

$E_{s(\zeta)}$: D_e= 2,35 eV R_e= 1,07 Å

H_2

$$\sigma_g 1s(1) \cdot \sigma_g 1s(2) \cdot = N\left[1s_A(1) + 1s_B(1)\right] \cdot \left[1s_A(2) + 1s_B(2)\right]$$

$$\sigma_g 1s(1) \cdot \sigma_g 1s(2) \cdot 2^{\frac{-1}{2}}\left[\alpha(1)\beta(2) - \alpha(2)\beta(1)\right]$$



Izgradnja molekula **metodom MO**:

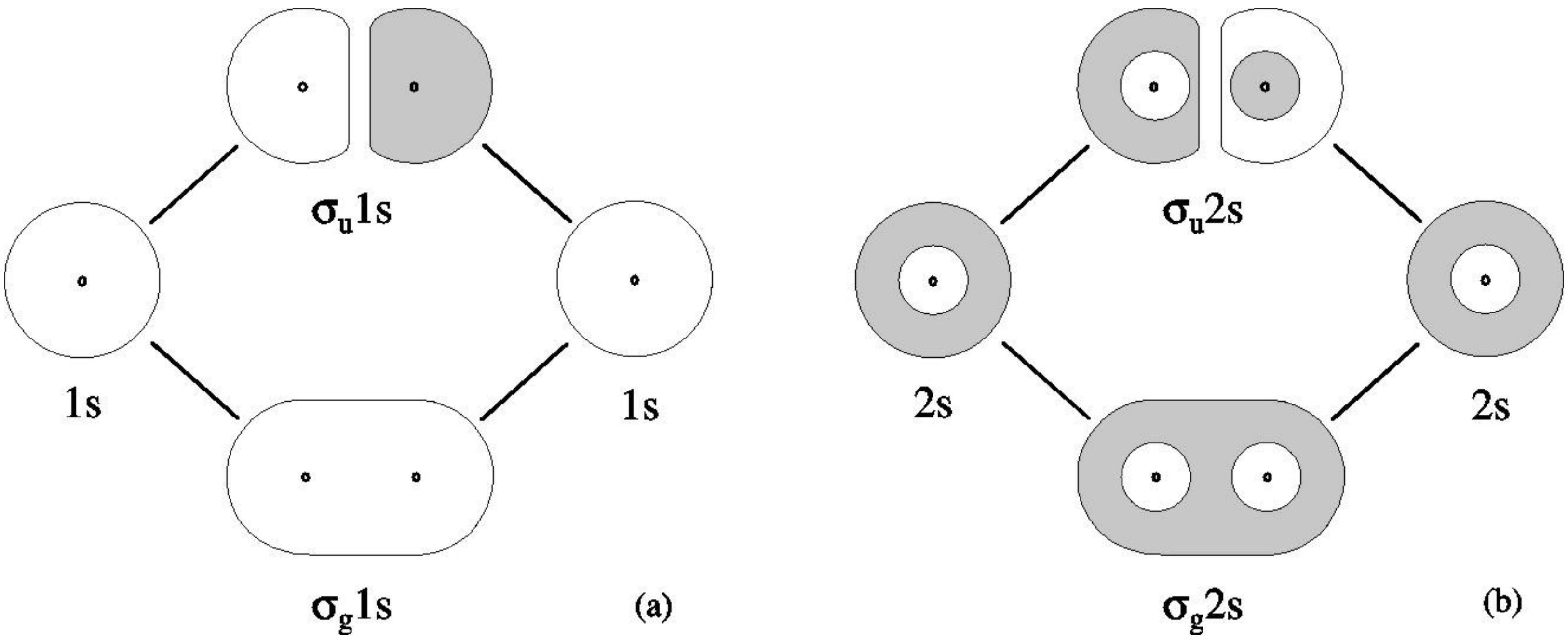
-pretpostave se fiksni položaji atoma
- odrede se jednoelektronske energije i valne funkcije (MO),
-svaka MO opisuje dva elektrona
- popunjavanje MO određenim redoslijedom

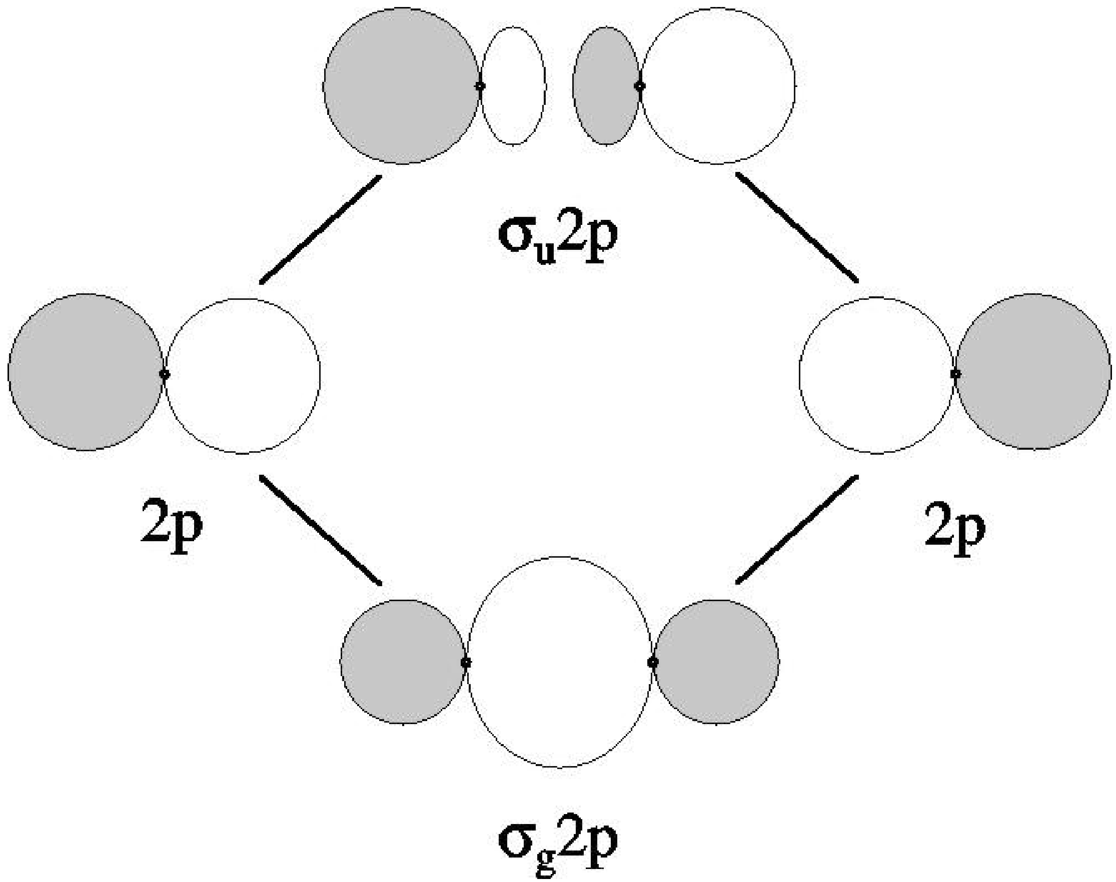
σ - molekulske orbitale

σ – simetrične s obzirom na rotaciju za bilo koji kut oko internuklearne osi

g – simetrične s obzirom na inverziju u centu simetrije

u – antisimetrične s obzirom na inverziju u centu simetrije

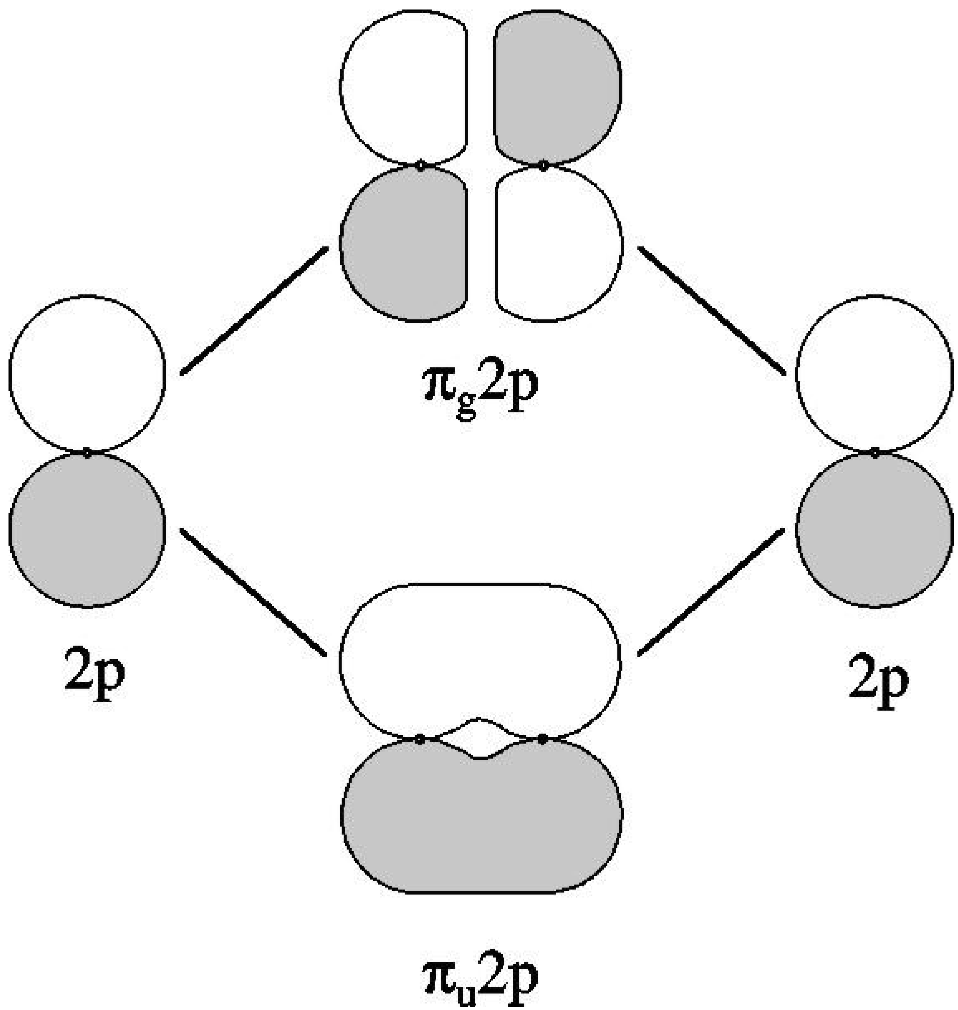


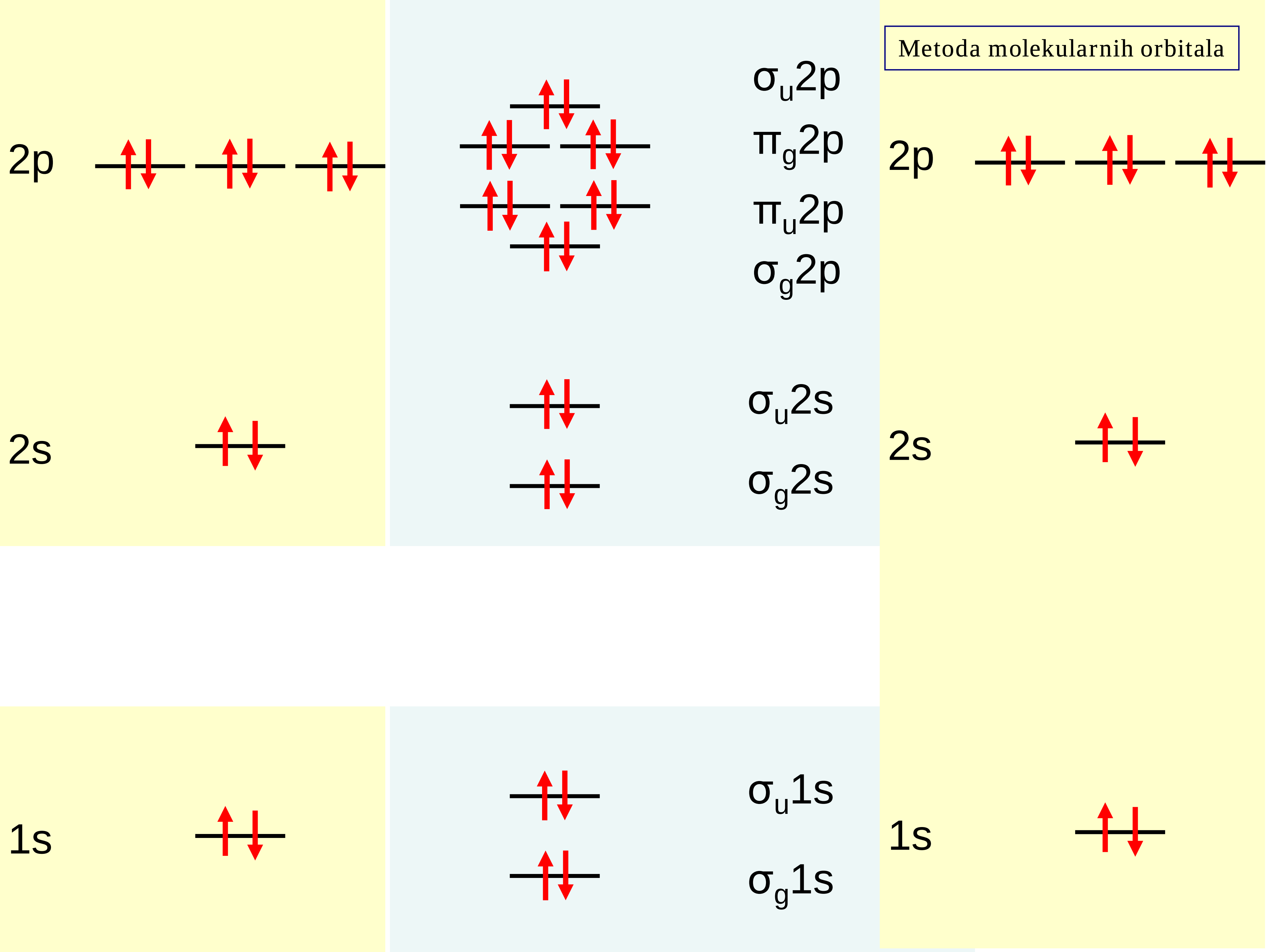


σu2p
2p
2p
σg2p

π molekulske orbitale

π –simetrične s obzirom na rotaciju za 180° oko internuklearne osi




Metoda molekularnih orbitala
2p
2s
1s
σu2p
πg2p
πu2p
σg2p
σu2s
σg2s
σu1s
σg1s
2p
2s
1s

RED VEZE

	Elektronska konfiguracija	stanje	p_{12}	E_d / eV
H_2	$(\sigma_g 1s)^2$	$^1\Sigma_g^+$	1	4,476
He_2	$(\sigma_g 1s)^2(\sigma_u 1s)^2$	$^1\Sigma_g^+$	0	nestab
Li_2	$KK(\sigma_g 2s)^2$	$^1\Sigma_g^+$	1	1,03
Be_2	$KK(\sigma_g 2s)^2(\sigma_u 2s)^2$	$^1\Sigma_g^+$	0	nestab
B_2	$KK(\sigma_g 2s)^2(\sigma_u 2s)^2(\sigma_g 2p)^2$	$^1\Sigma_g^+$	1	3,6
C_2	$KK(\sigma_g 2s)^2(\sigma_u 2s)^2(\pi_u 2p)^4$	$^1\Sigma_g^+$	2	3,6
N_2	$KK(\sigma_g 2s)^2(\sigma_u 2s)^2(\sigma_g 2p)^2(\pi_u 2p)^4$	$^1\Sigma_g^+$	3	7,37
O_2	$KK(\sigma_g 2s)^2(\sigma_u 2s)^2(\sigma_g 2p)^2(\pi_u 2p)^4(\pi_g 2p)^2$	$^3\Sigma_g^-$	2	5,080
F_2	$KK(\sigma_g 2s)^2(\sigma_u 2s)^2(\sigma_g 2p)^2(\pi_u 2p)^4(\pi_g 2p)^4$	$^1\Sigma_g^+$	1	2,75
Ne_2	$KK(\sigma_g 2s)^2(\sigma_u 2s)^2(\sigma_g 2p)^2(\pi_u 2p)^4(\pi_g 2p)^4(\sigma_u 2p)^2$	$^1\Sigma_g^+$	0	nestab

$$p_{12} = \frac{1}{2}\left(N - N^*\right)$$

Homonuklearne molekule:

C_2

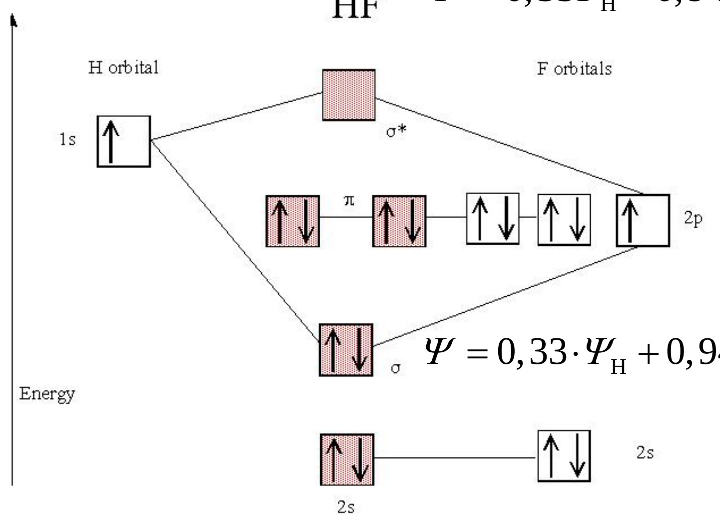
O_2

Heteronuklearne molekule:

CO, HF

izoelektronske molekule: CO i N_2

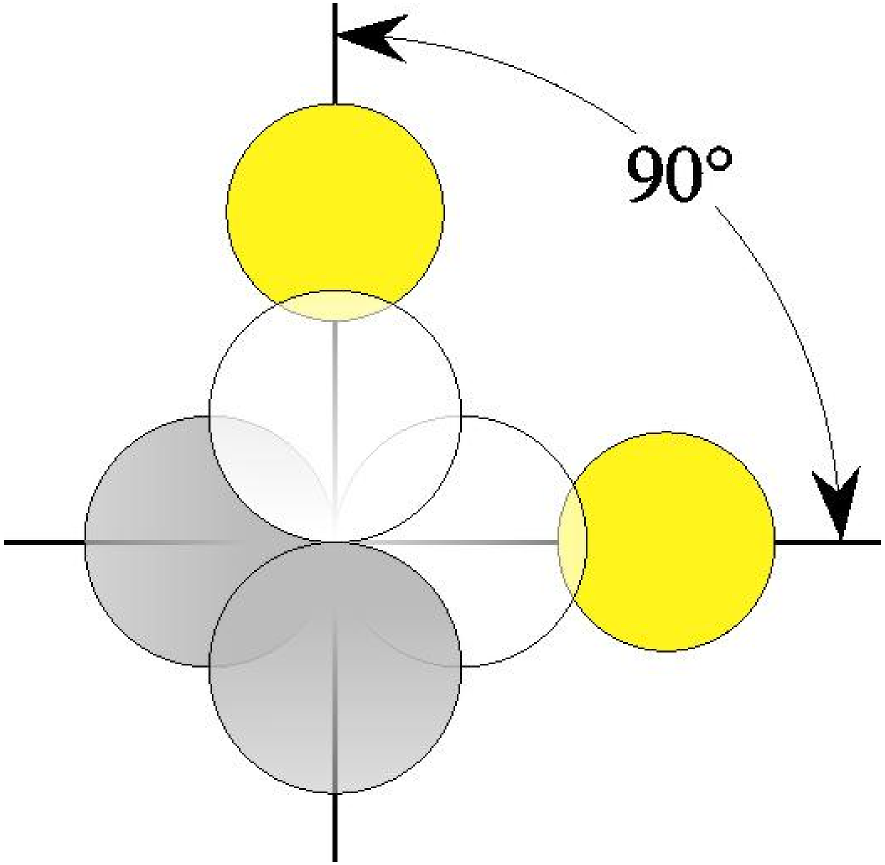
HF $\Psi = 0,33\Psi_{H} - 0,94\cdot\Psi_{F}$



$\Psi = 0,33\cdot\Psi_{H} + 0,94\cdot\Psi_{F}$

$$\Psi = c_{H}\Psi_{H} + c_{F}\Psi_{F}$$

Hibridizacija



H_2O

Eksperiment: 104,5 ° ???

NH_3, CH_4 ???

Eksperiment (NH_3): 107 °
Eksperiment (CH_4): 109,5 °

Hibridizacija

Pauling & Slater

-funkcije se miješaju i nastaju nove funkcije – hibridne funkcije - hibridne orbitale

-s i p hibridne orbitale su ekvivalentne, imaju maksimume u različitim smjerovima

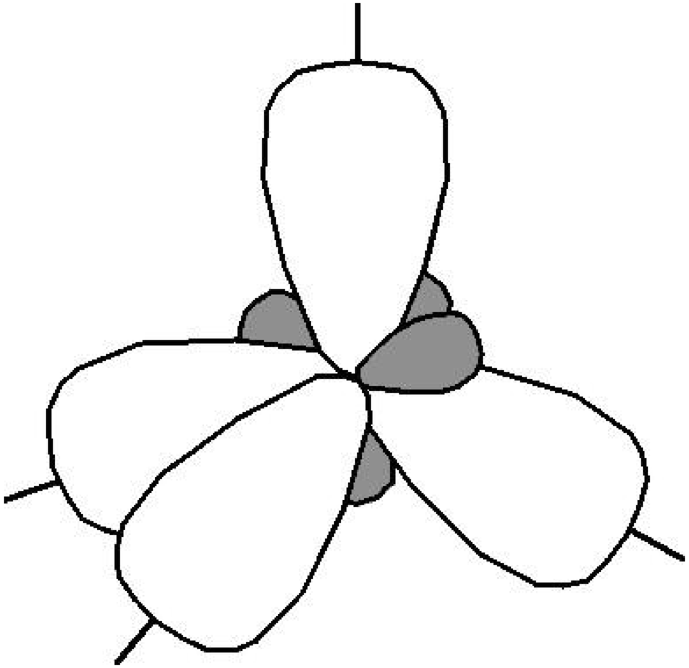
$$\Psi_i = \sum_{j=1}^{n} c_{ij}\phi_j = c_{i1}\phi_1 + c_{i2}\phi_2 + \ldots + c_{in}\phi_n$$

$$\sum_{j=1}^{n} c_{ij}^{\ 2} = 1$$

$$n = \frac{c_x^2 + c_y^2 + c_z^2}{c_s^2}$$

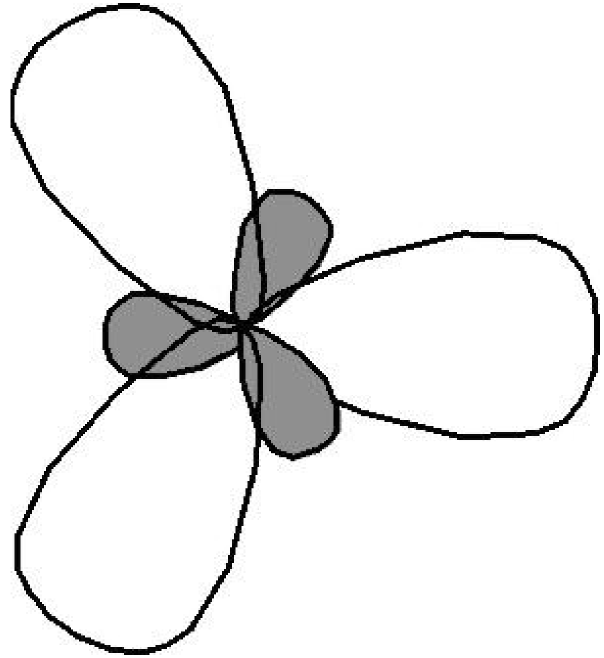
$$\sum_{i=1}^{n} c_{ij}^{\ 2} = 1$$

sp^3



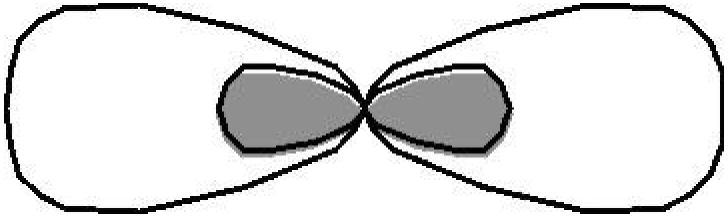
CH_4

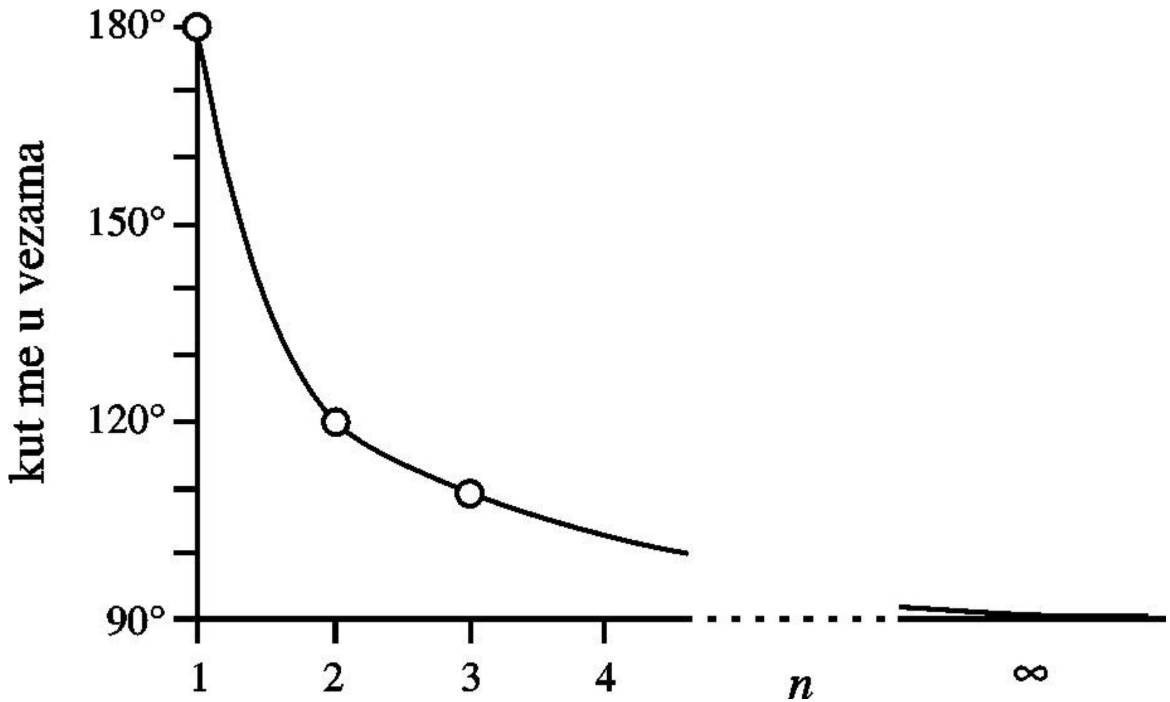
sp^2



$CH_2 = CH_2$

sp $CH \equiv CH$

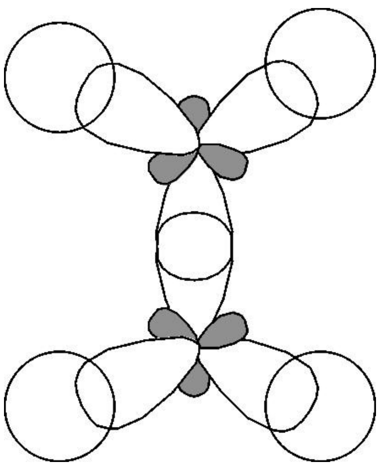


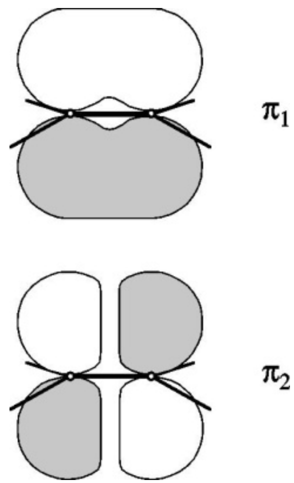


-LCAO (*linear combinations of atomic orbitals*)

$$\Psi = c_1\Psi_1 + c_2\Psi_2 + c_3\Psi_3 + c_4\Psi_4 + c_5\Psi_5 + \ldots$$

Eten





Born-Oppeheimerova aproksimacija

1. U čemu se sastoji Born-Oppeheimerova aproksimacija?
2. Kakvu ulogu ima elektronska energija u Schrödingerovoj jednadžbi za nuklearna gibanja?
3. Kako ovisi elektronska energija o internuklearnoj udaljenosti za stabilno, a kako za nestabilno stanje?

Molekulske orbitale

1. Kako glasi MO-hamiltonijan za dvoatomnu molekulu?
2. Kakve MO dobivamo iz 1s orbitala?
3. Kakve MO dobivamo kombinacijom p-orbitala?
4. Kakve energije očekujete za MO koje su izvedene iz 2p-orbitala?
8. Kako glasi elektronska konfiguracija za O_2?