

Dualismus částice - vlna

LIGHT IS A
WAVE!

.....a elektron taky

Born-Oppenheimerova aproximace

Oddělení elektronického a jaderného pohybu

Jádra jsou $2000 \times$ těžší než elektrony

Elektrony – **kvantová** chemie, popis systému do 100 atomů na základě vlastností elektronů
jádra nepohyblivá, *Ab initio* výpočty

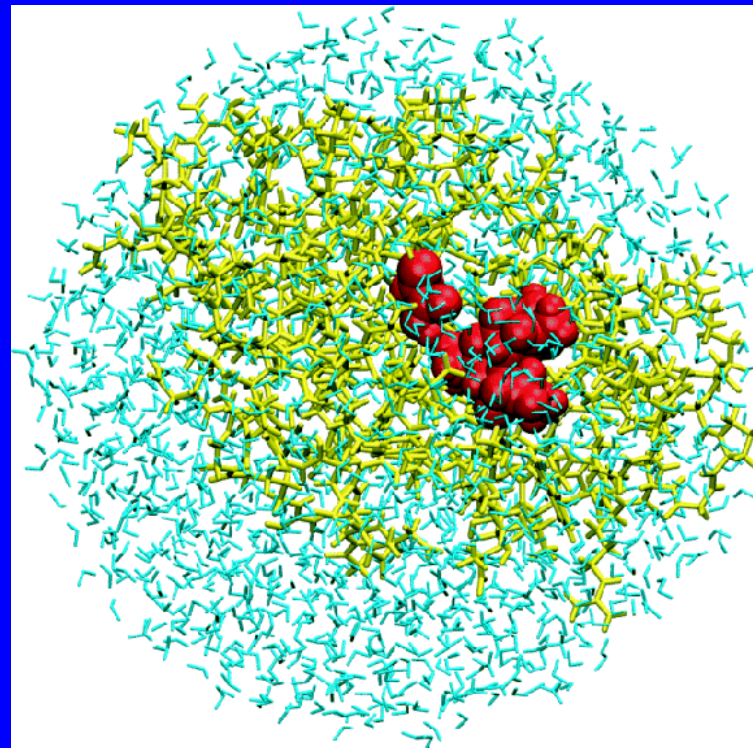
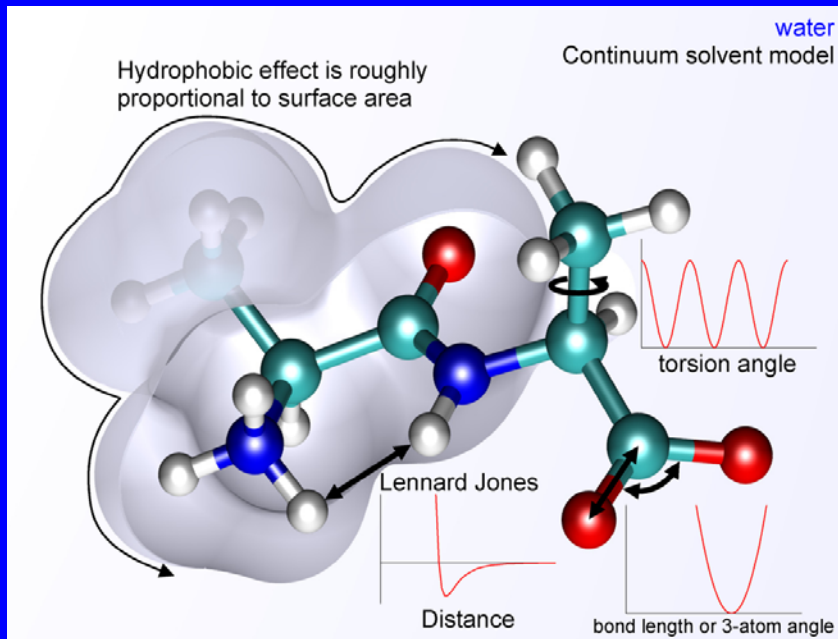
Jádra – **klasická** Newtonova mechanika, popis celkové energie systému (10 000 atomů) jen na základě polohy jader, chování elektronů nepopisuje (chemická vazba = pružina), Molekulová mechanika – silové pole, Molekulová dynamika

$$E = T_n + T_e + V_{ee} + V_{nn} + V_{en}$$

T = kinetická energie

V = potenciální energie

Molekulová mechanika

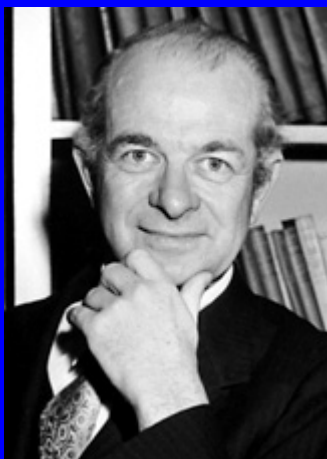


$$\begin{aligned}
 U = & \sum_{i < j} \sum 4\epsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right] \\
 & + \sum_{i < j} \sum \frac{q_i q_j}{4\pi\epsilon_0 r_{ij}} \\
 & + \sum_{\text{bonds}} \frac{1}{2} k_b (r - r_0)^2 \\
 & + \sum_{\text{angles}} \frac{1}{2} k_a (\theta - \theta_0)^2 \\
 & + \sum_{\text{torsions}} k_\phi [1 + \cos(n\phi - \delta)]
 \end{aligned}$$

VB versus MO

Teorie valenčních vazeb (VB)

Teorie molekulových orbitalů (MO)



Linus Pauling

(1901 - 1994)

NP za chemii 1954, za mír 1963

Lokalizované vazby



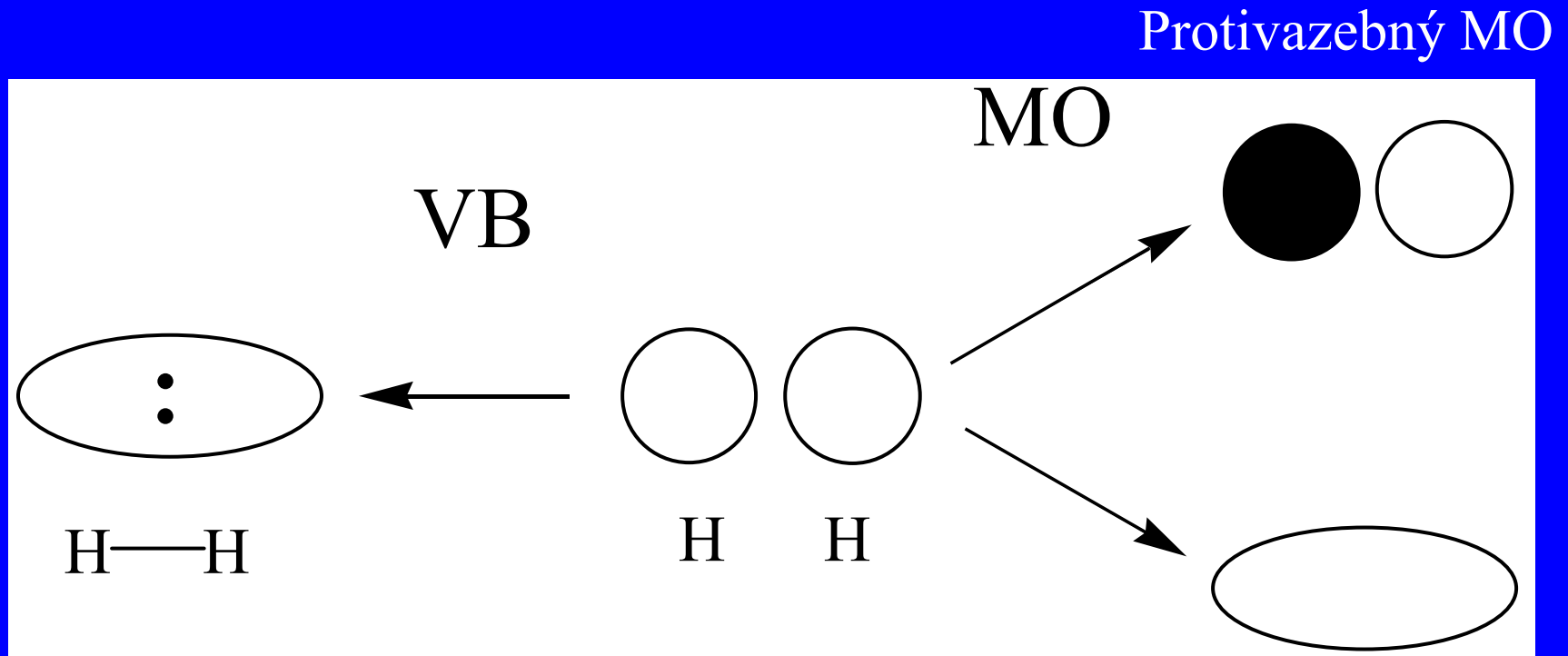
Robert S. Mulliken

(1896 - 1986)

NP za chemii 1966

Delokalizované vazby

Rozdíl mezi VB a MO



Teorie Molekulových Orbitalů (MO)

Kombinace **atomových** orbitalů na **všech atomech** v molekule

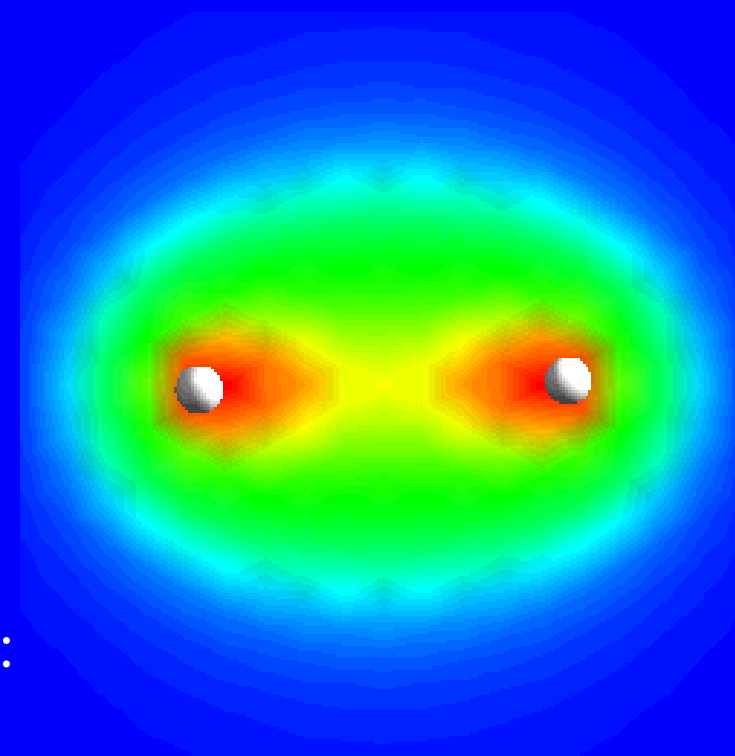
- Vhodná symetrie
- Vhodná (podobná) energie

Z n AO vytvoříme n MO

Pro začátek dvouatomové molekuly:

H_2 , F_2 , CO ,....

Stejně i pro víceatomové: BF_3 , CH_4 ,....

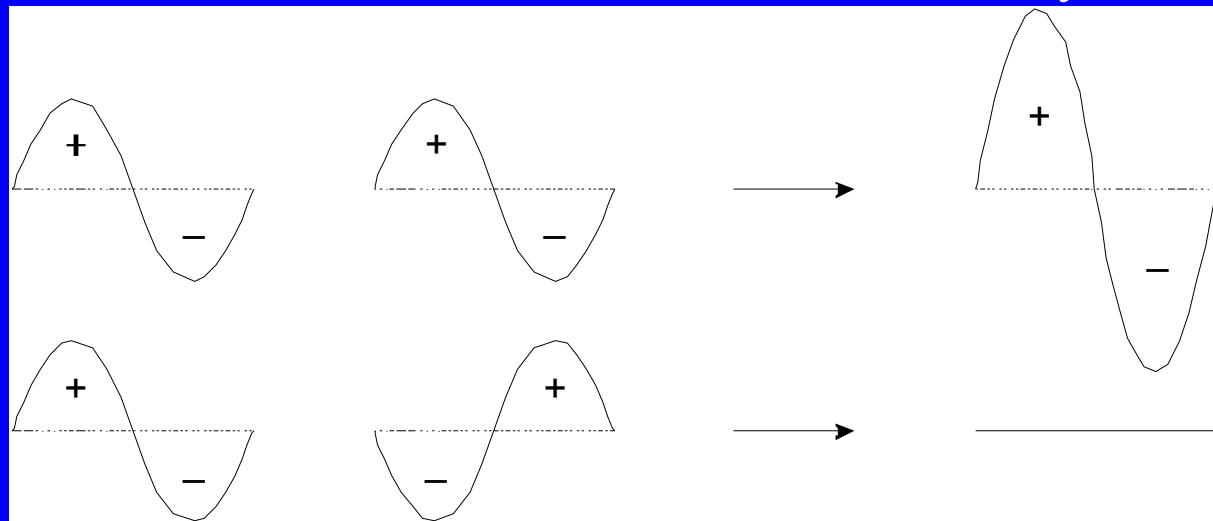


Vazebný MO v molekule H_2

Interference vlnových funkcí

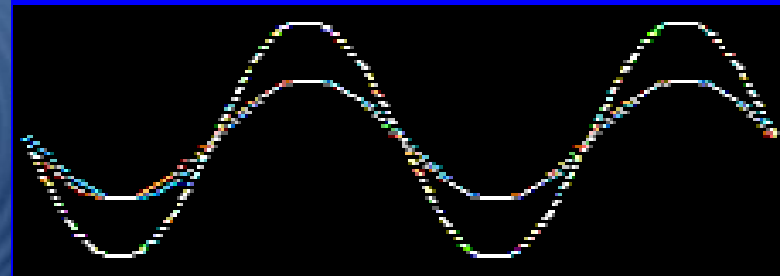
Vazebný MO

Konstruktivní

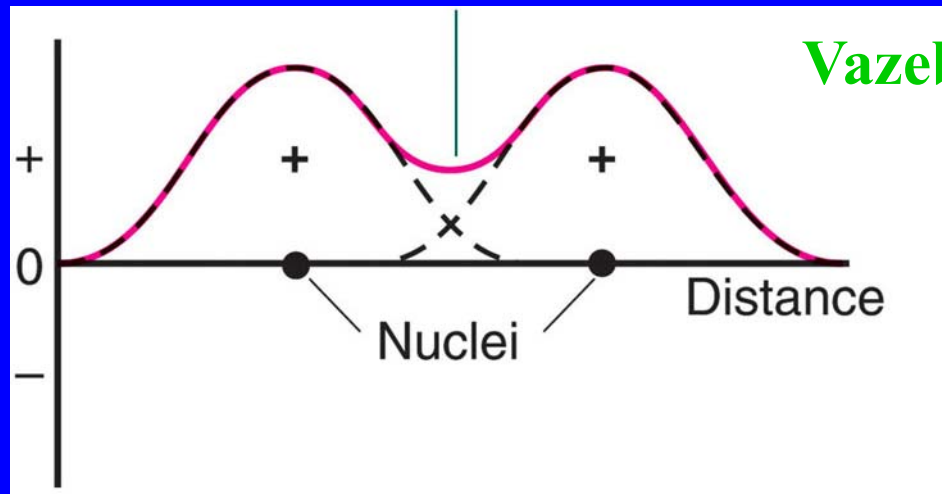


Destruktivní

Protivazebný MO



LCAO = Lineární kombinace atomových orbitalů

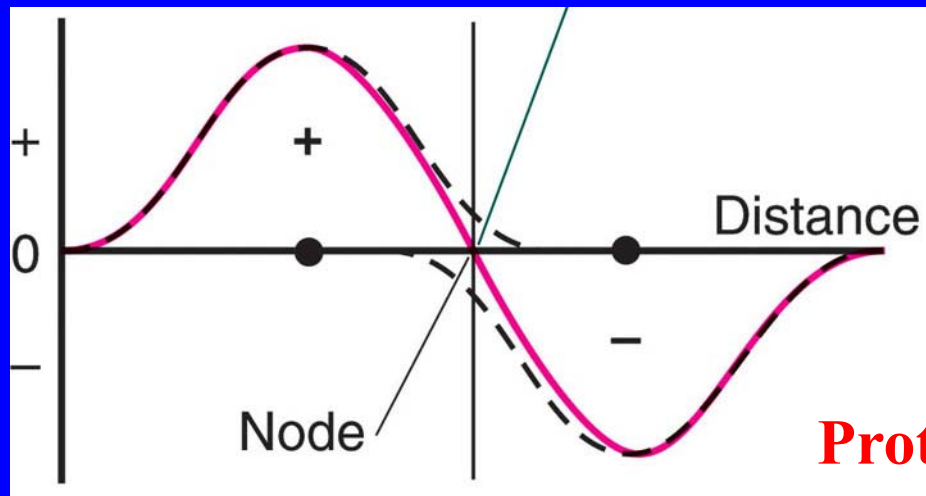


Vazebný MO

Kombinace dvou vlnových funkcí (orbitalů) se stejným znaménkem

$$\Psi = c_1 \Psi_A + c_2 \Psi_B$$

$$\Psi^* = c_3 \Psi_A - c_4 \Psi_B$$



Protivazebný MO

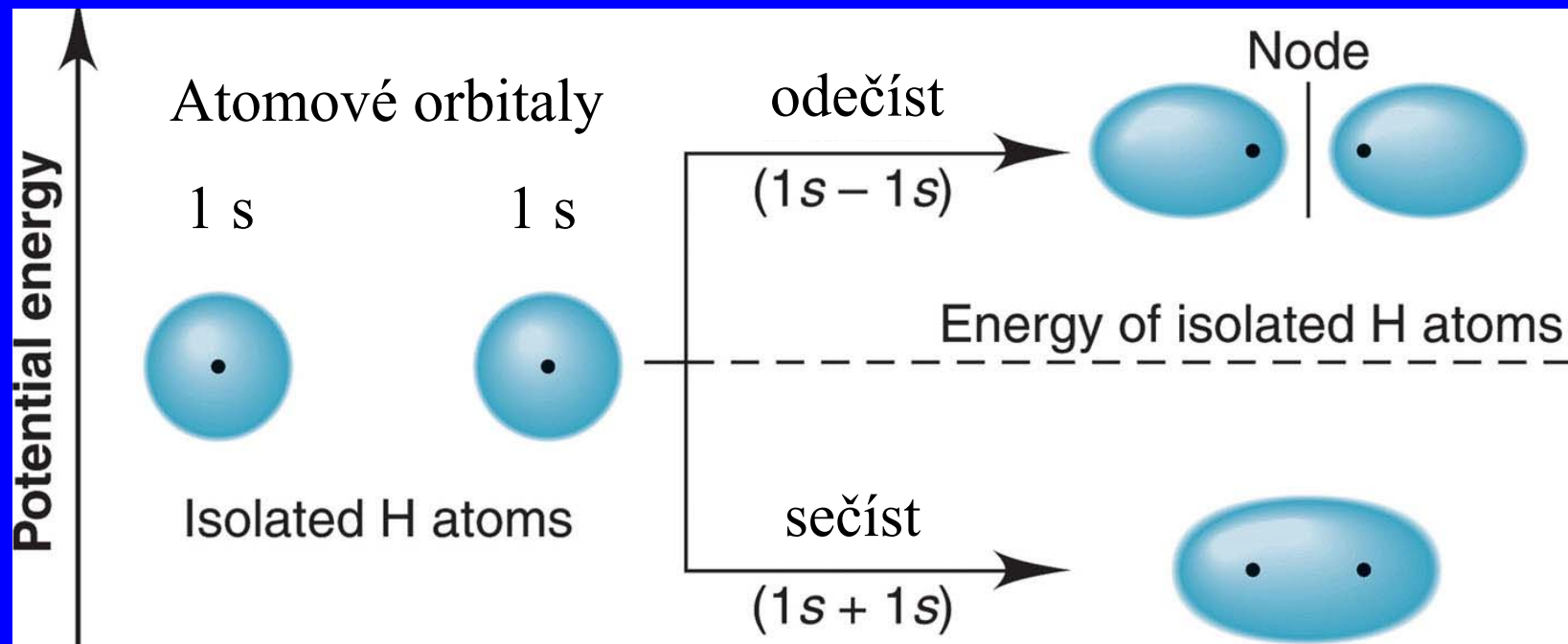
Kombinace dvou vlnových funkcí (orbitalů) s opačným znaménkem

LCAO = Lineární kombinace atomových orbitalů

$$\Psi = c_1 \Psi_A + c_2 \Psi_B$$

$$\Psi^* = c_3 \Psi_A - c_4 \Psi_B$$

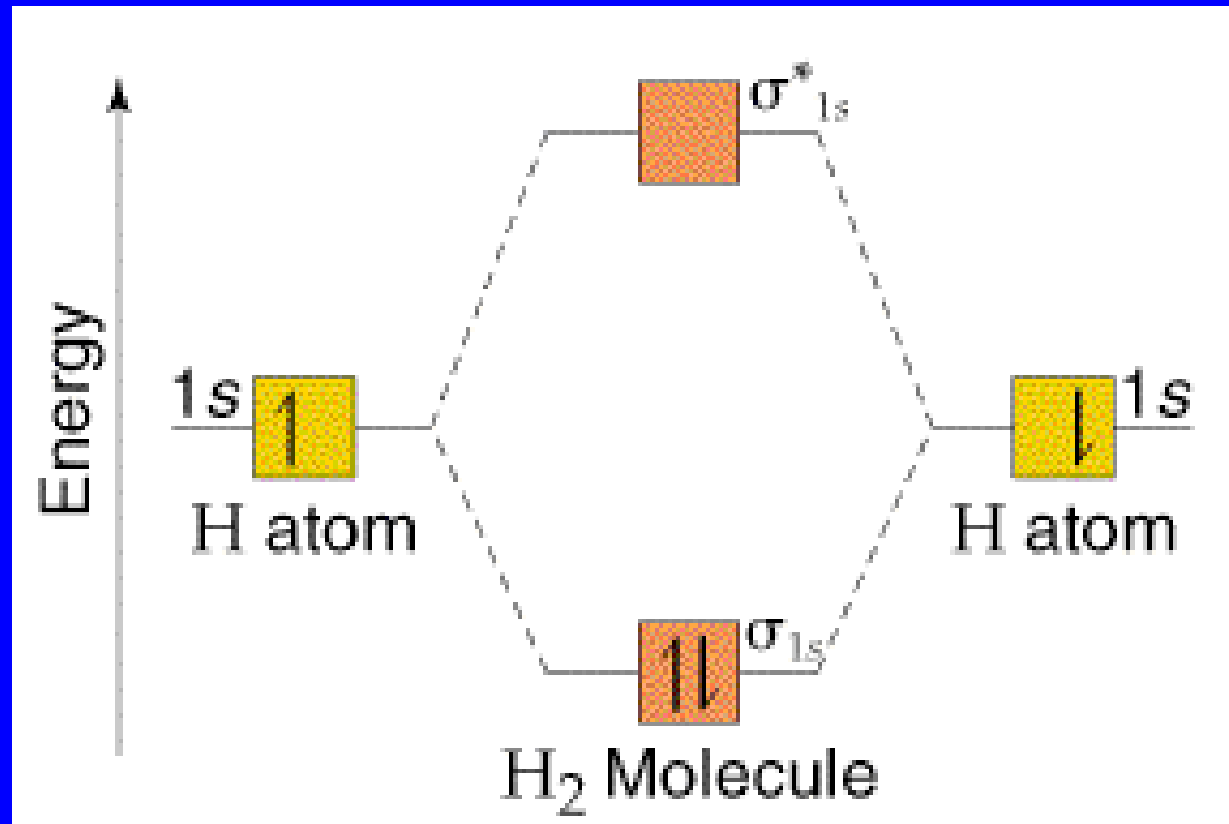
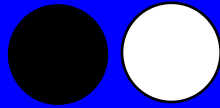
Ψ^* Protivazebný MO



Ψ Vazebný MO

Počet MO = počet AO

Ψ^* Protivazebný MO



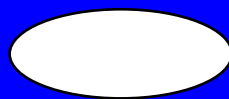
Energetická

destabilizace

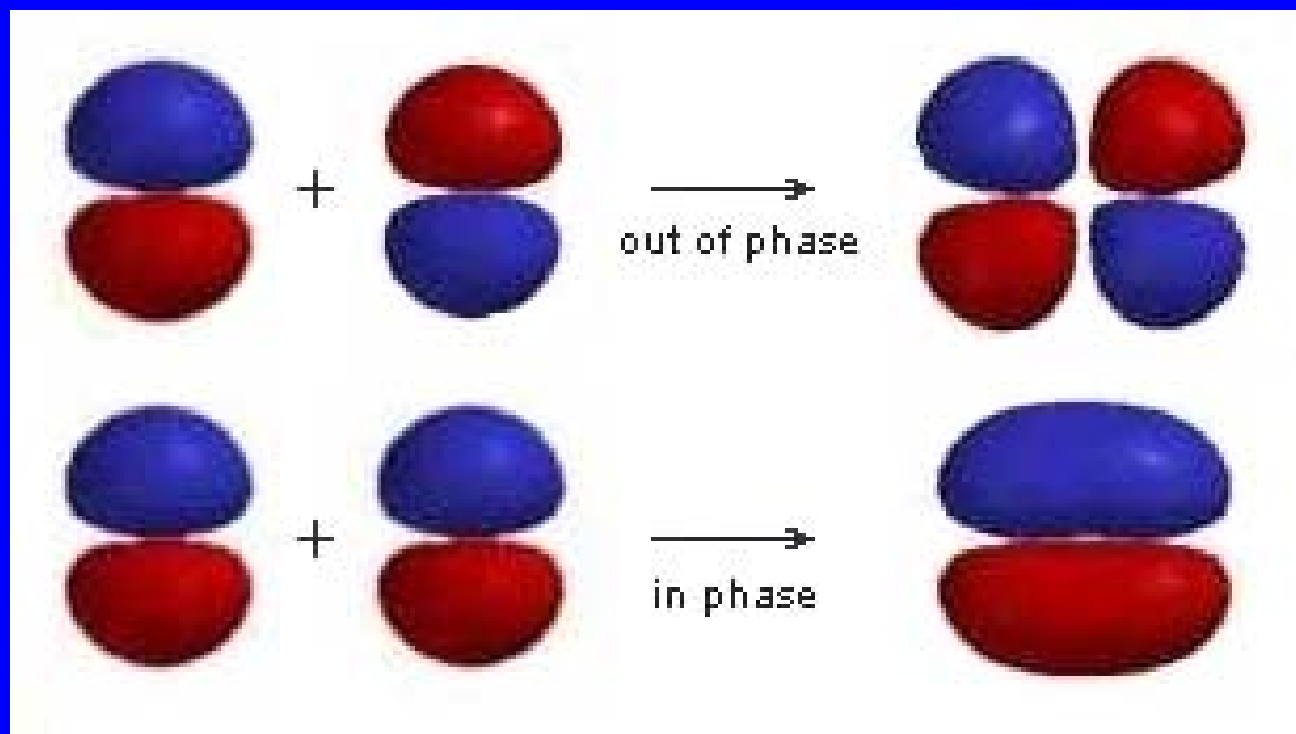
stabilizace

ve srovnání s
volnými atomy

Ψ Vazebný MO



π MO vzniklé kombinací p AO



Protivazebný π MO

Vazebný π MO

p_x

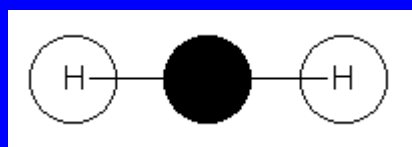
p_x

p_y

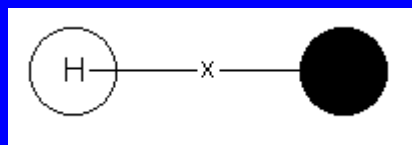
p_y

Lineární tříjaderný kation H_3^+

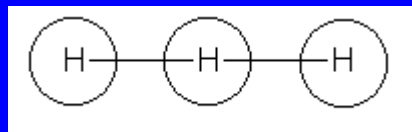
Vzrůstá energie, klesá stabilita



Protivazebný MO

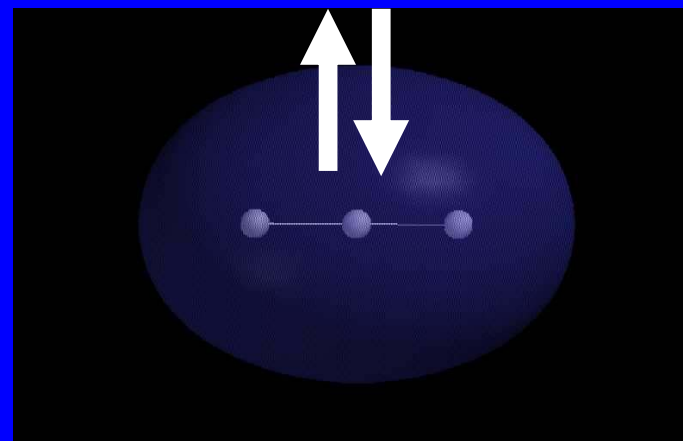
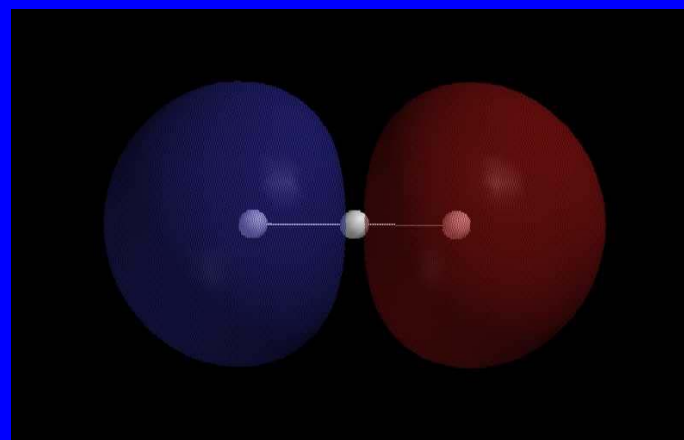
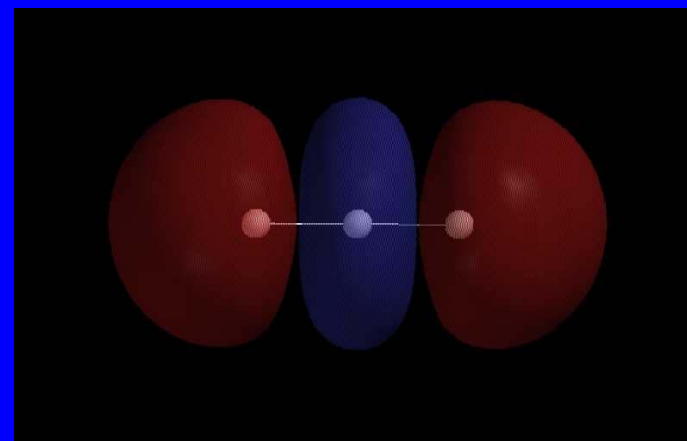


Nevazebný MO



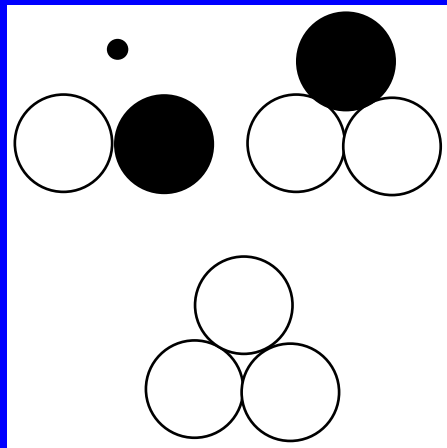
Vazebný MO

Vzrůstá počet uzlových rovin



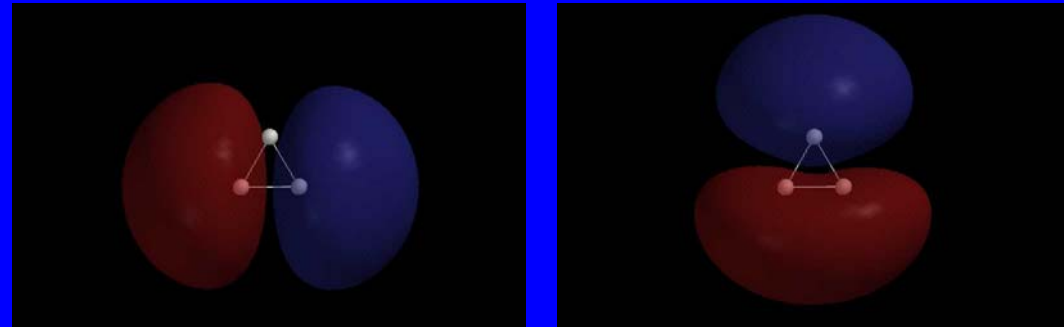
Cyklický tříjaderný kation H_3^+

Vzrůstá energie,
klesá stabilita



Vzrůstá počet uzlových rovin

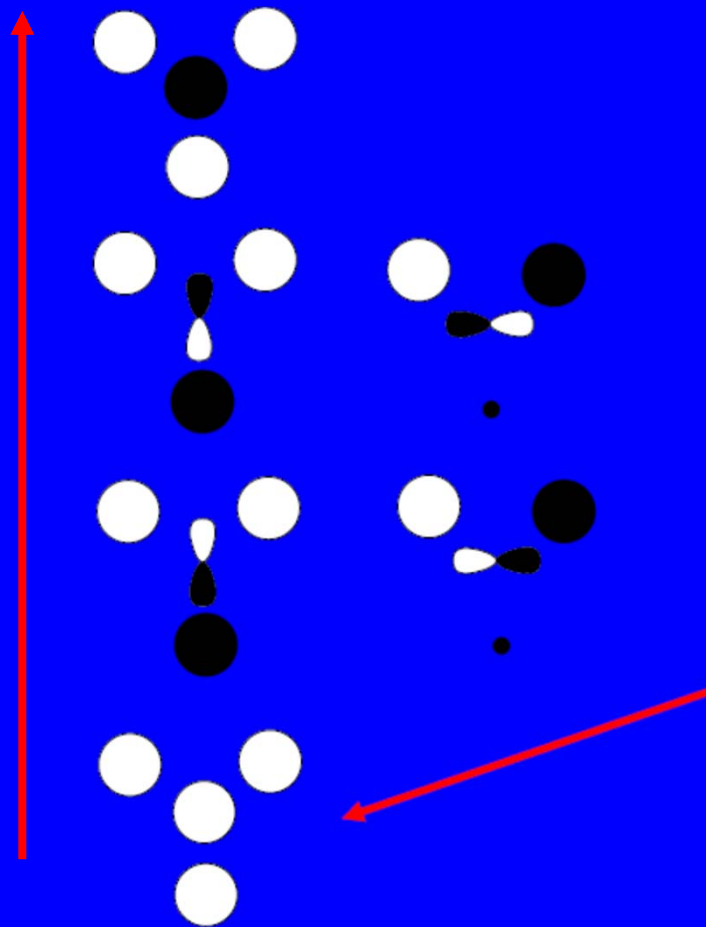
Protivazebné MO



Vazebný MO

LCAO = Lineární kombinace AO

Energie



LCAO

obecně pro n atomů a m orbitalů

$$\Psi_i = c_1 \Psi_1 + c_2 \Psi_2 + c_3 \Psi_3 + \dots + c_n \Psi_n$$

Ze 6 AO vznikne 6 MO

- Centrální atom = $1 \times s + 2 \times p$ (třetí p?)
- Ligandy = $3 \times s$

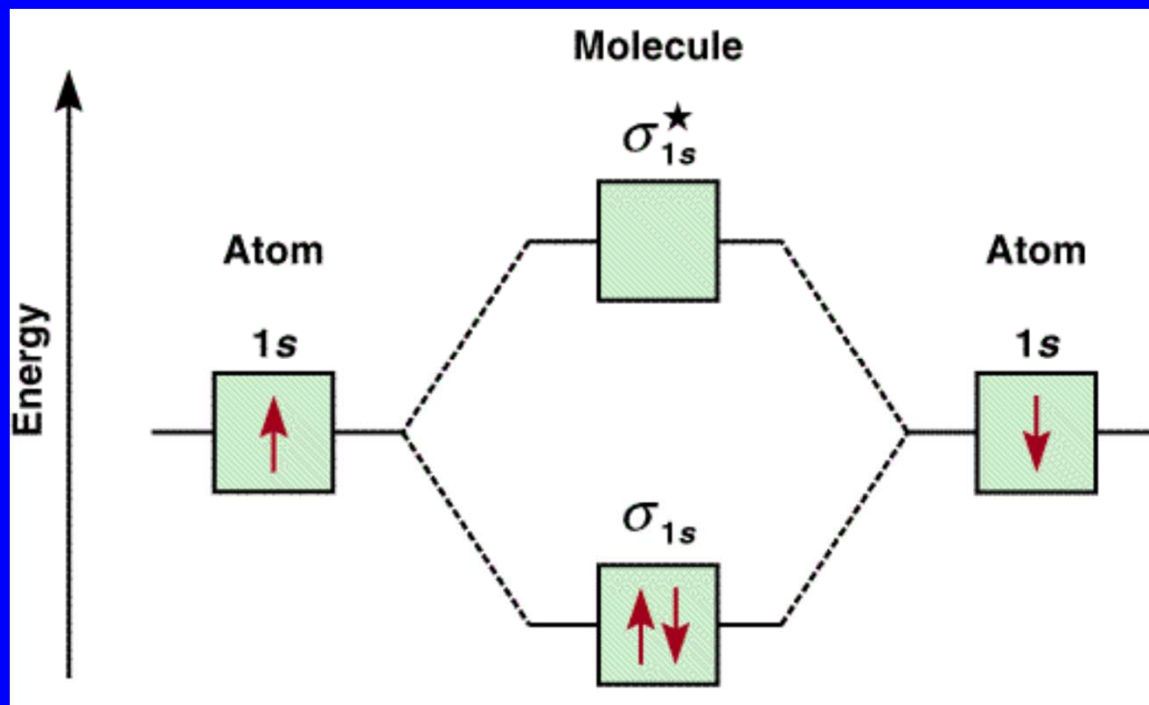
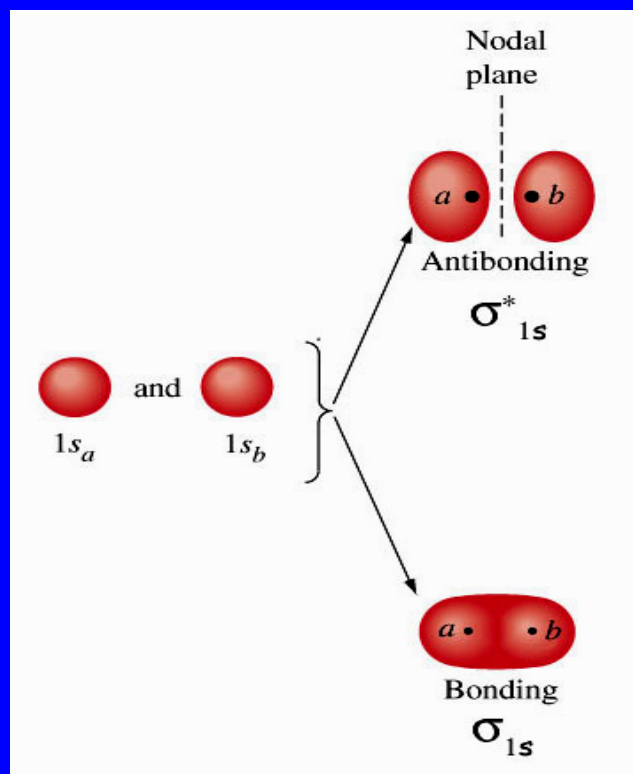
MO s nejnižší energií, nemá žádnou uzlovou rovinu, nejvíce vazebný, kombinace po jednom AO z každého atomu, všechny se stejným znaménkem

Zaplňování MO elektrony

Aufbau
Hund
Pauli

Pravidla pro zaplňování MO elektrony

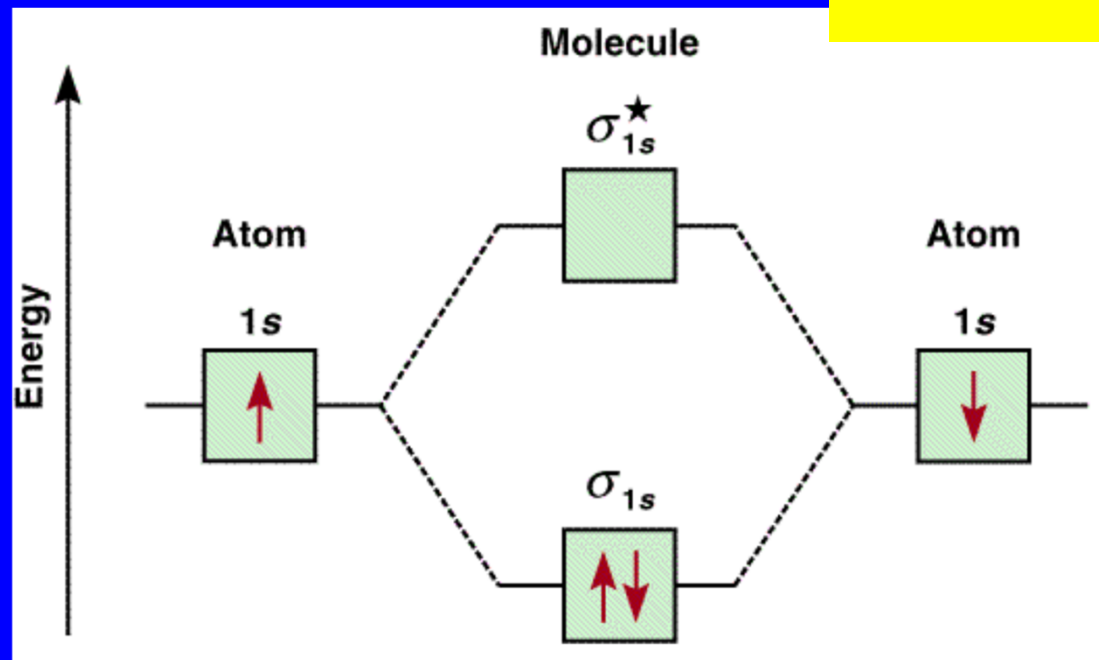
Protivazebný MO



Vazebný MO

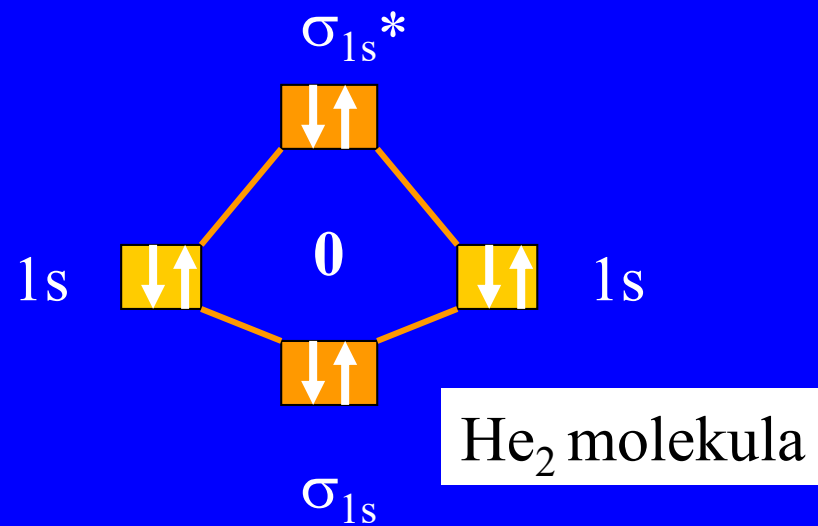
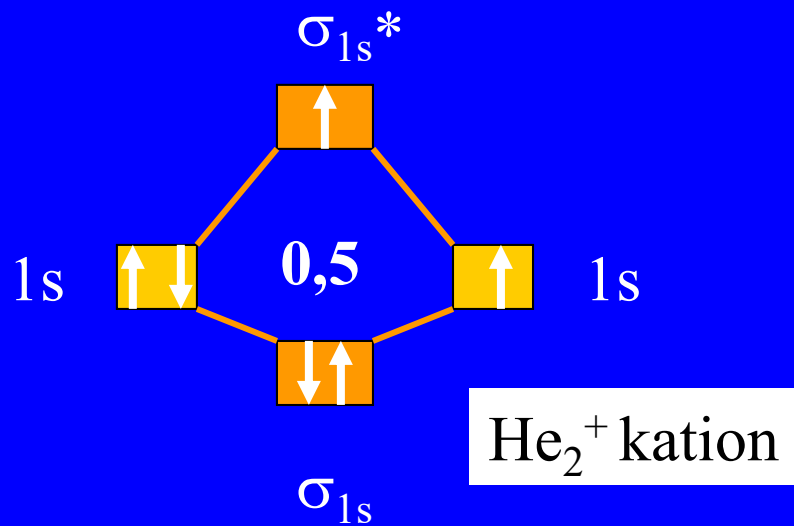
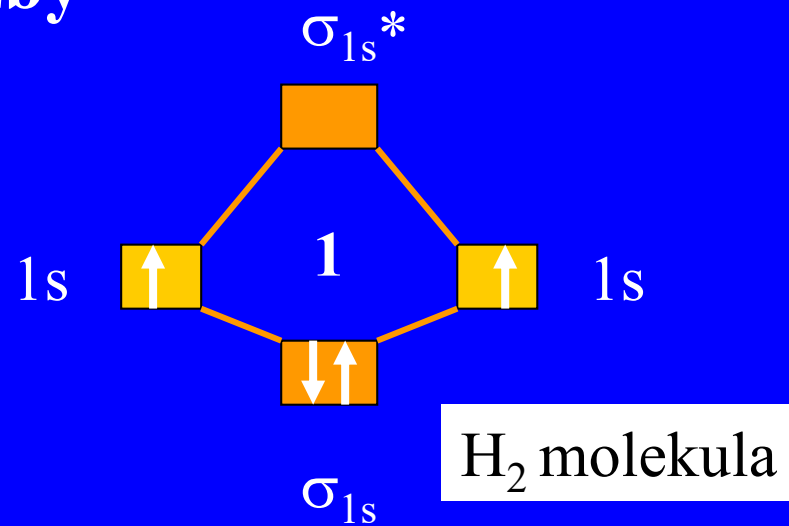
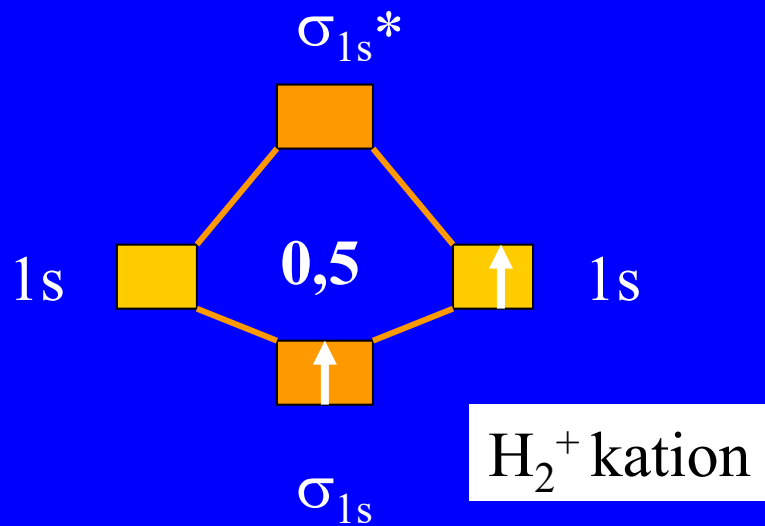
Řád vazby

$$\text{Řád} = \frac{eMO - eMO^*}{2}$$



Řád vazby = $\frac{1}{2}$ (počet vazebných e – počet protivazebných e)

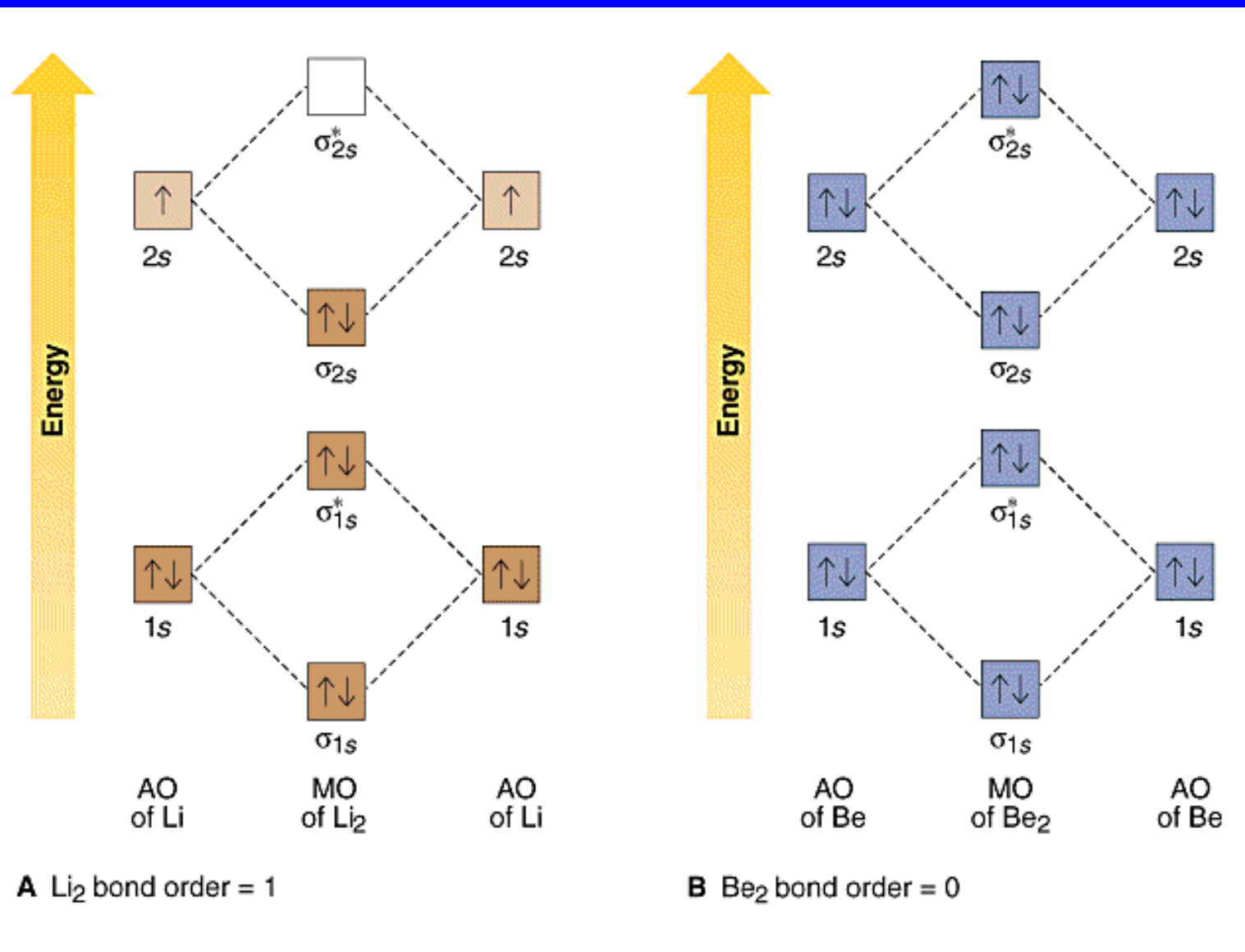
Řád vazby



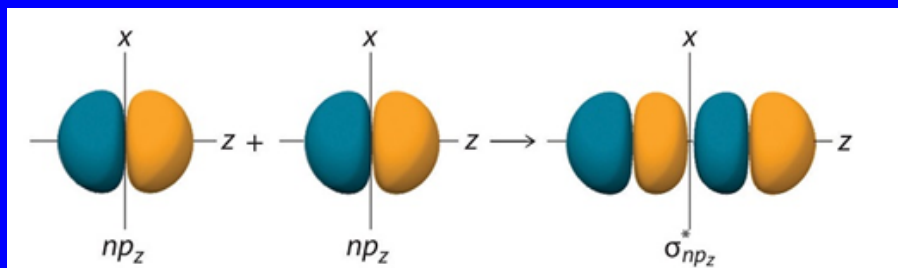
Řád vazby

Molekula	Vazebné elektrony	Protivaz. elektrony	Řád vazby	Délka vazby, Å	Vazebná energie, kJ mol ⁻¹
H₂⁺	1	0	0,5	1,06	255
H₂	2	0	1	0,74	432
H₂⁻	2	1	0,5	-	-
He₂⁺	2	1	0,5	1,08	230
He₂	2	2	0	---	0

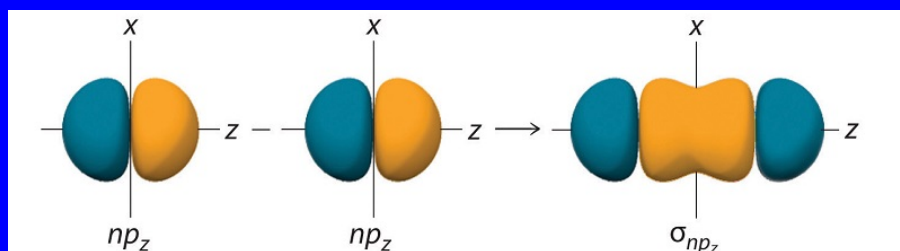
1 elektronová vazba: 1 vazebný e⁻ tvoří silnější vazbu než 2 vazebné a 1 protivazebný e⁻



MO vzniklé kombinací p AO



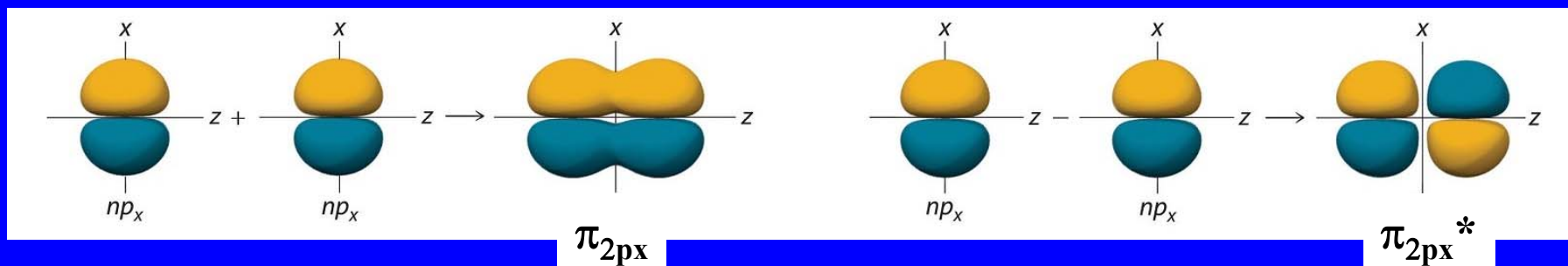
Protivazebný MO σ_{2pz}^*



Vazebný MO σ_{2pz}

Vazebný MO π_{2px}

Protivazebný MO π_{2px}^*



MO vzniklé kombinací p AO

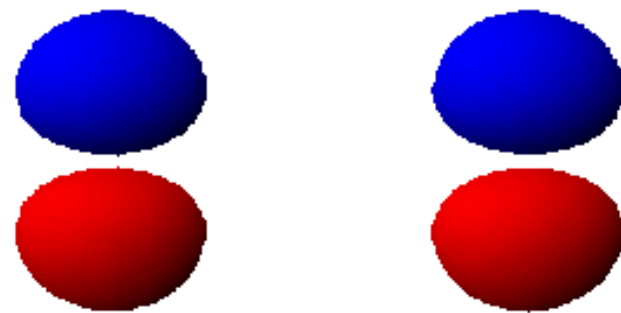
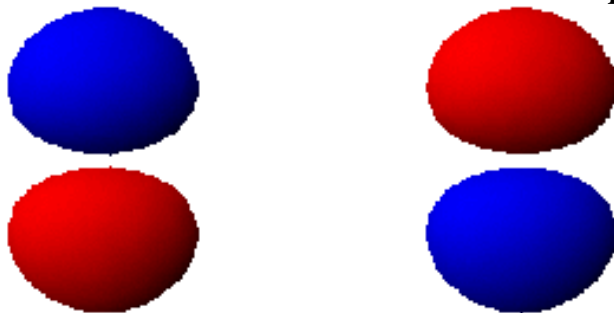
Protivazebný MO σ_{2pz}^*



Vazebný MO σ_{2pz}

MO vzniklé kombinací p AO

Protivazebný MO π_{2px}^*

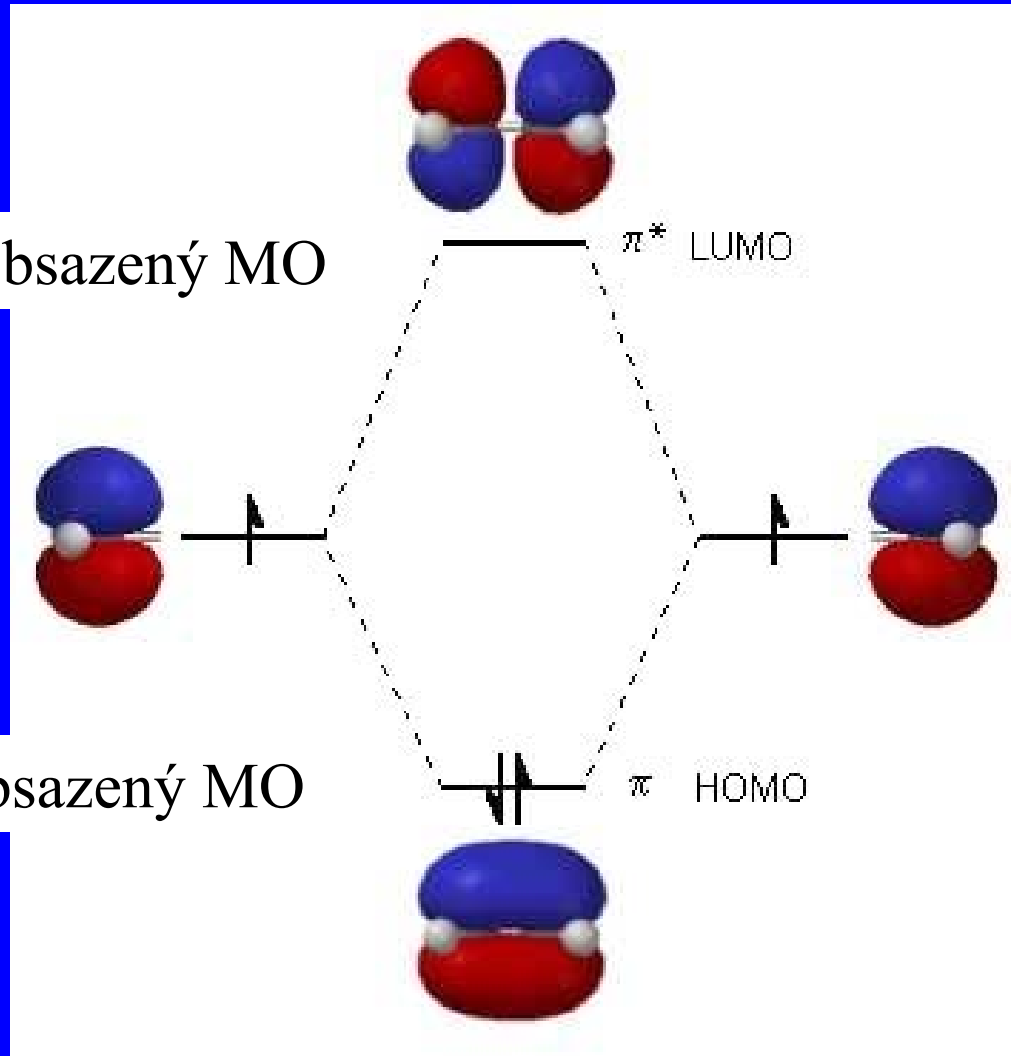


Vazebný MO π_{2px}

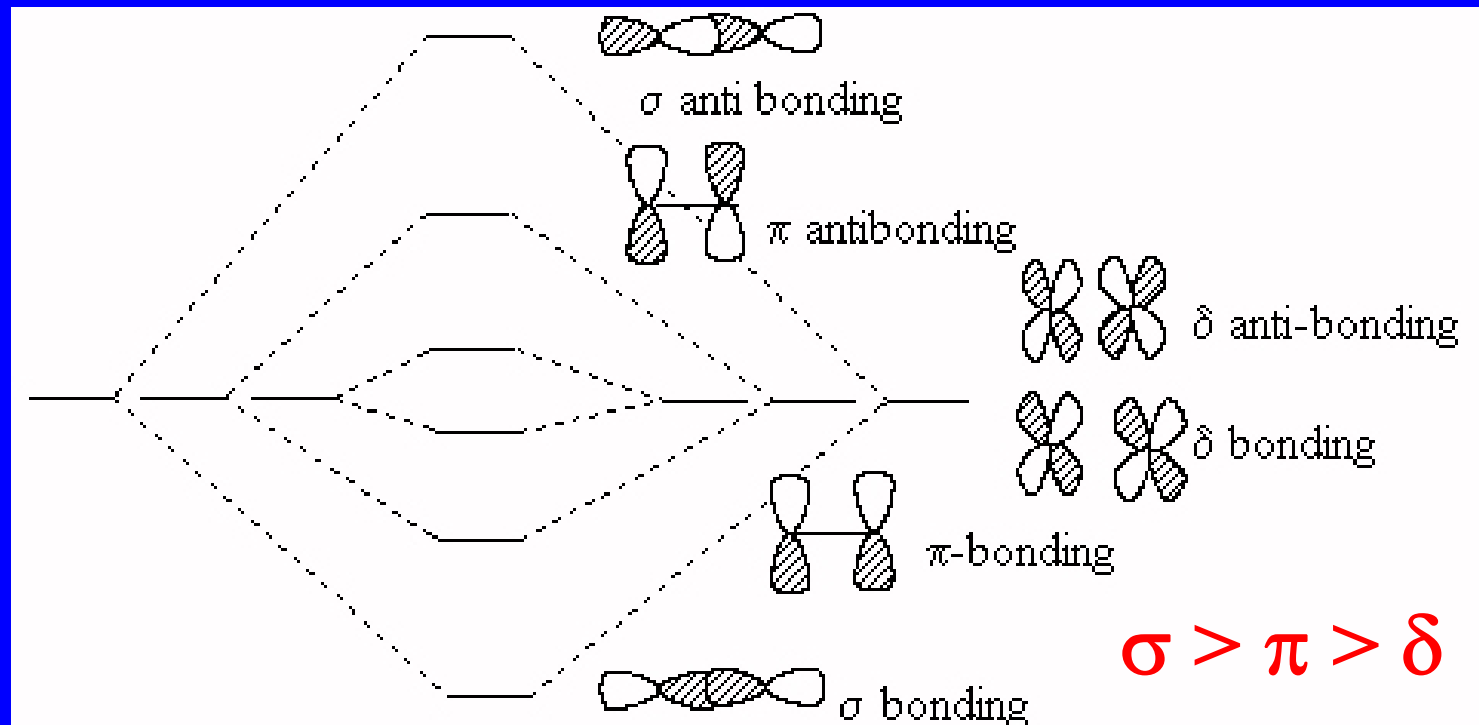
Pi vazba v ethenu pomocí MO

LUMO = nejnižší neobsazený MO

HOMO = nejvyšší obsazený MO



Typy molekulových orbitalů

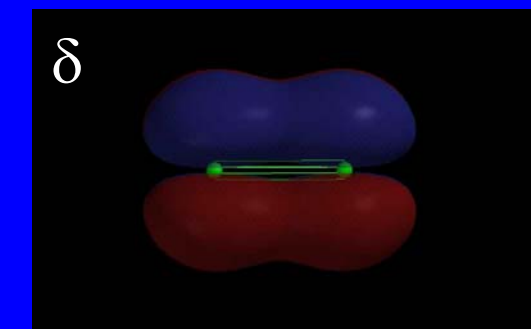
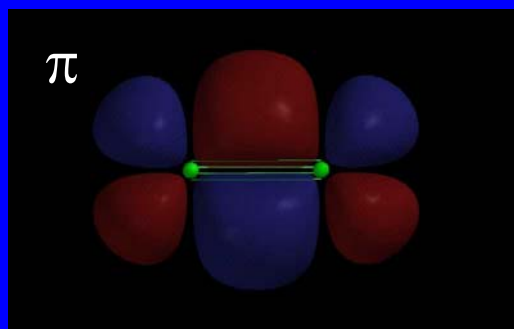
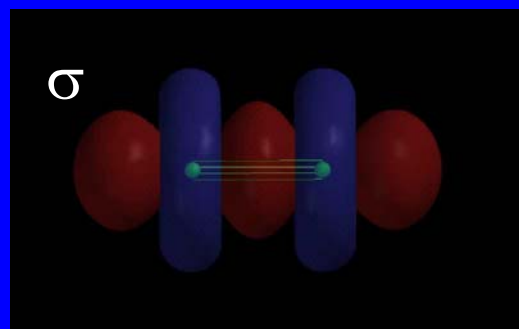
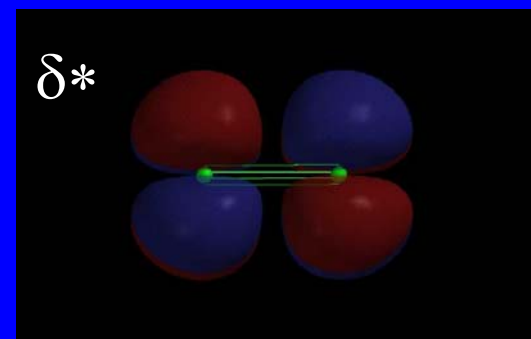
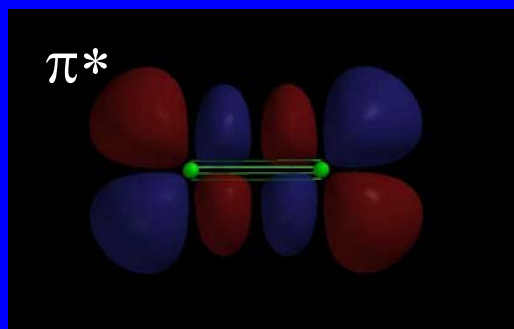
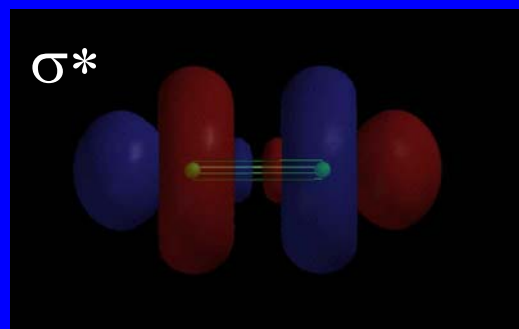
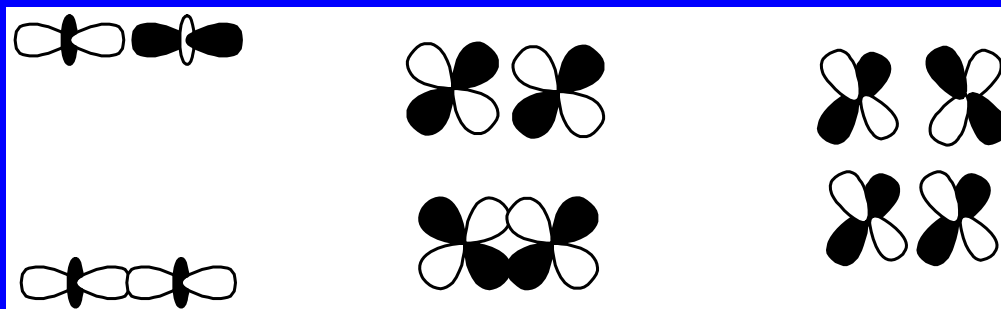


Lepší překryv

snižuje energii **vazebného** MO

zvyšuje energii **protivazebného** MO

Tvorba MO z d orbitalů



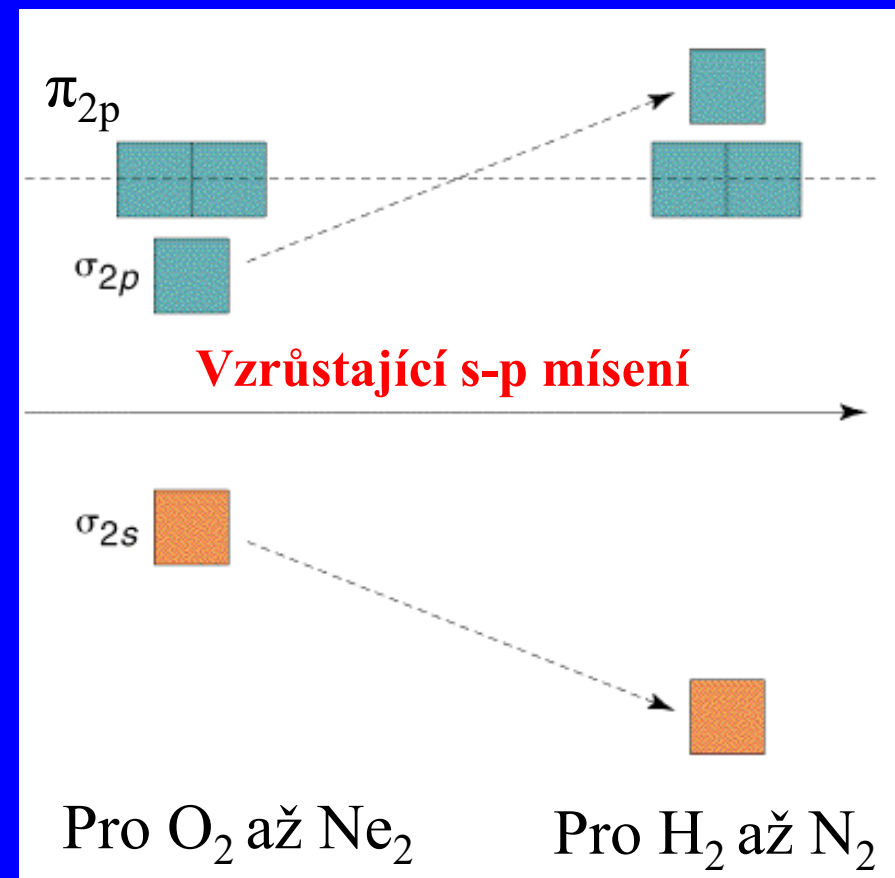
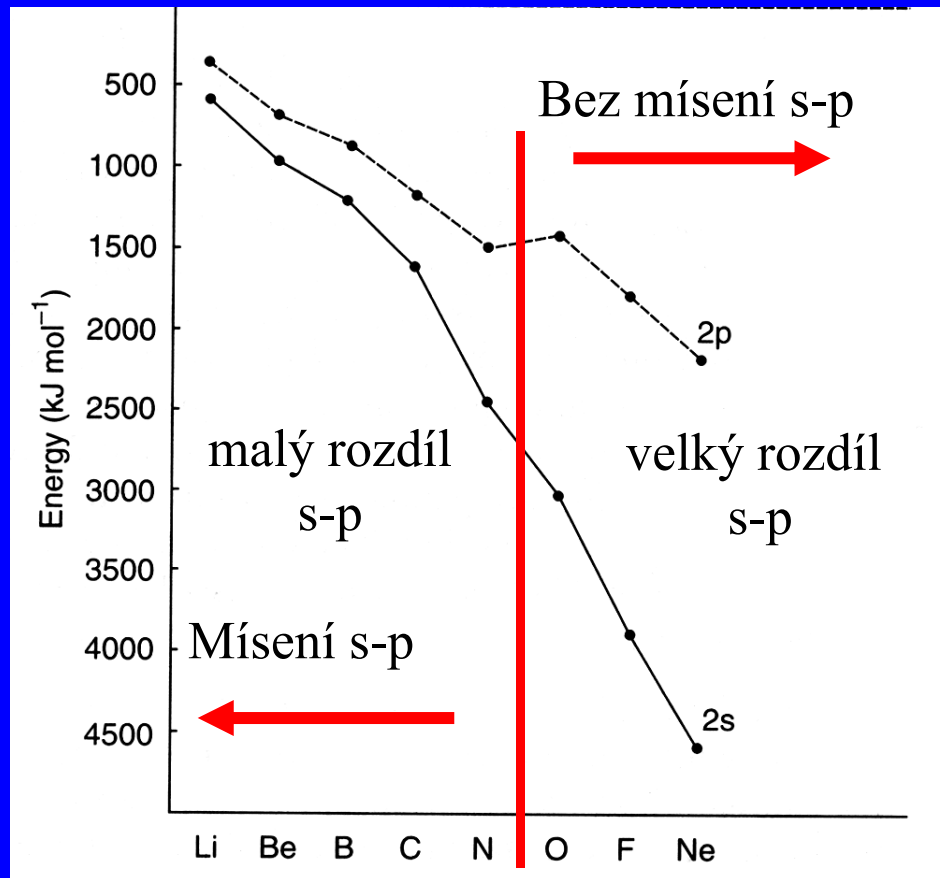
$d(z^2) d(z^2)$

$d(xz) d(xz)$
 $d(yz) d(yz)$

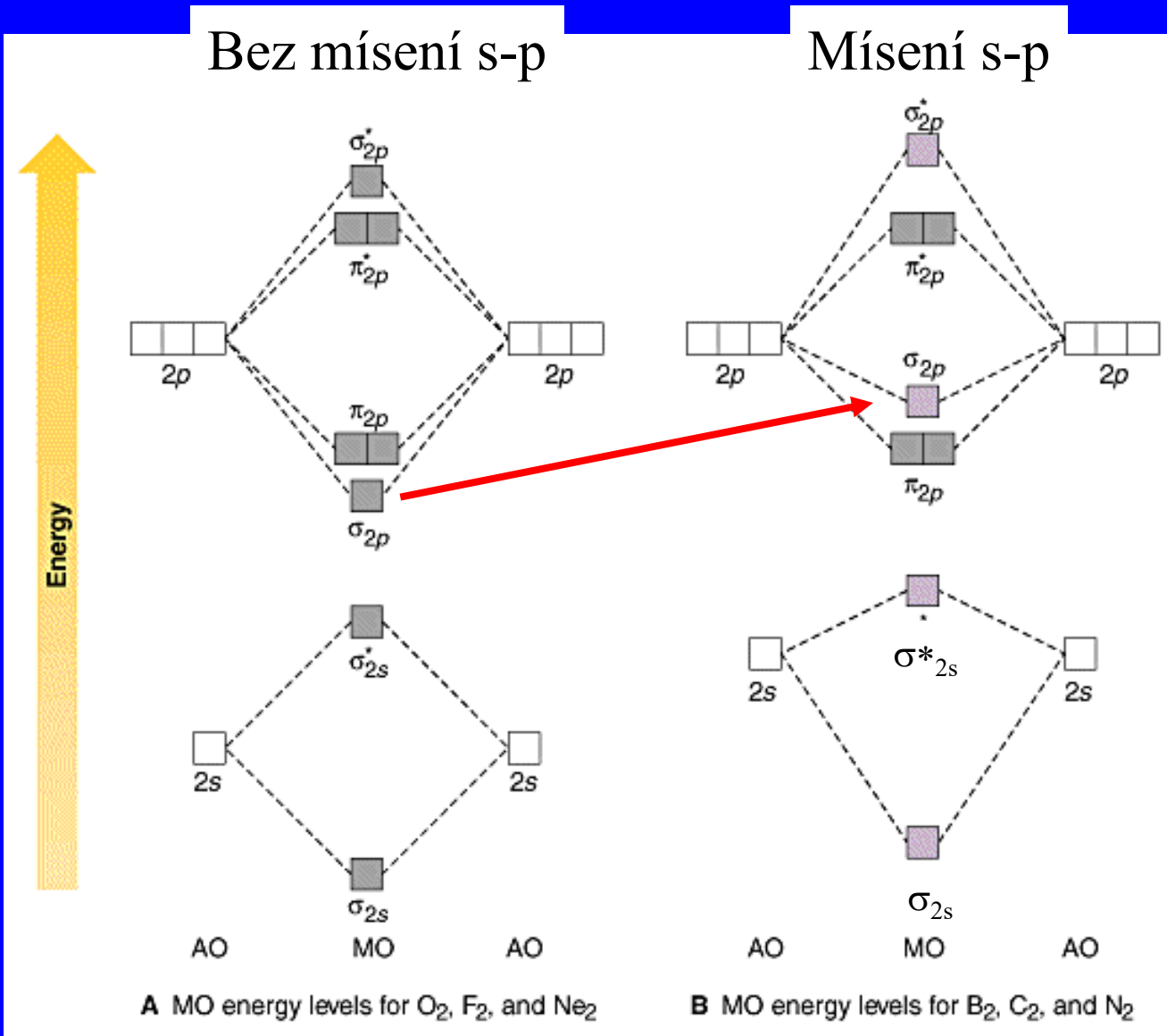
$d(x^2-y^2) d(x^2-y^2)$
 $d(xy) d(xy)$ ²⁵

Mísení s-p orbitalů

Energeticky blízké orbitály na stejném atomu se mohou smíchat



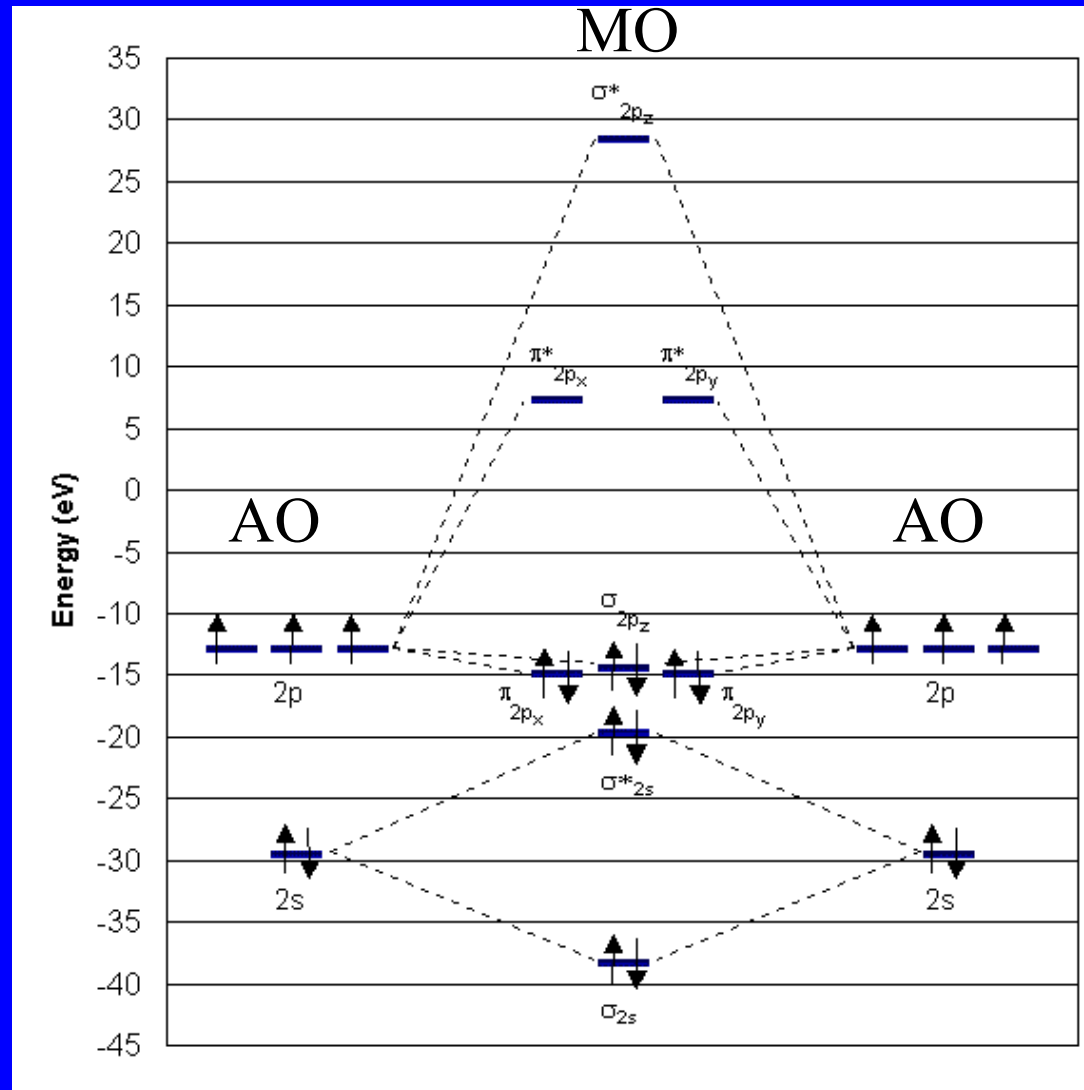
Energie

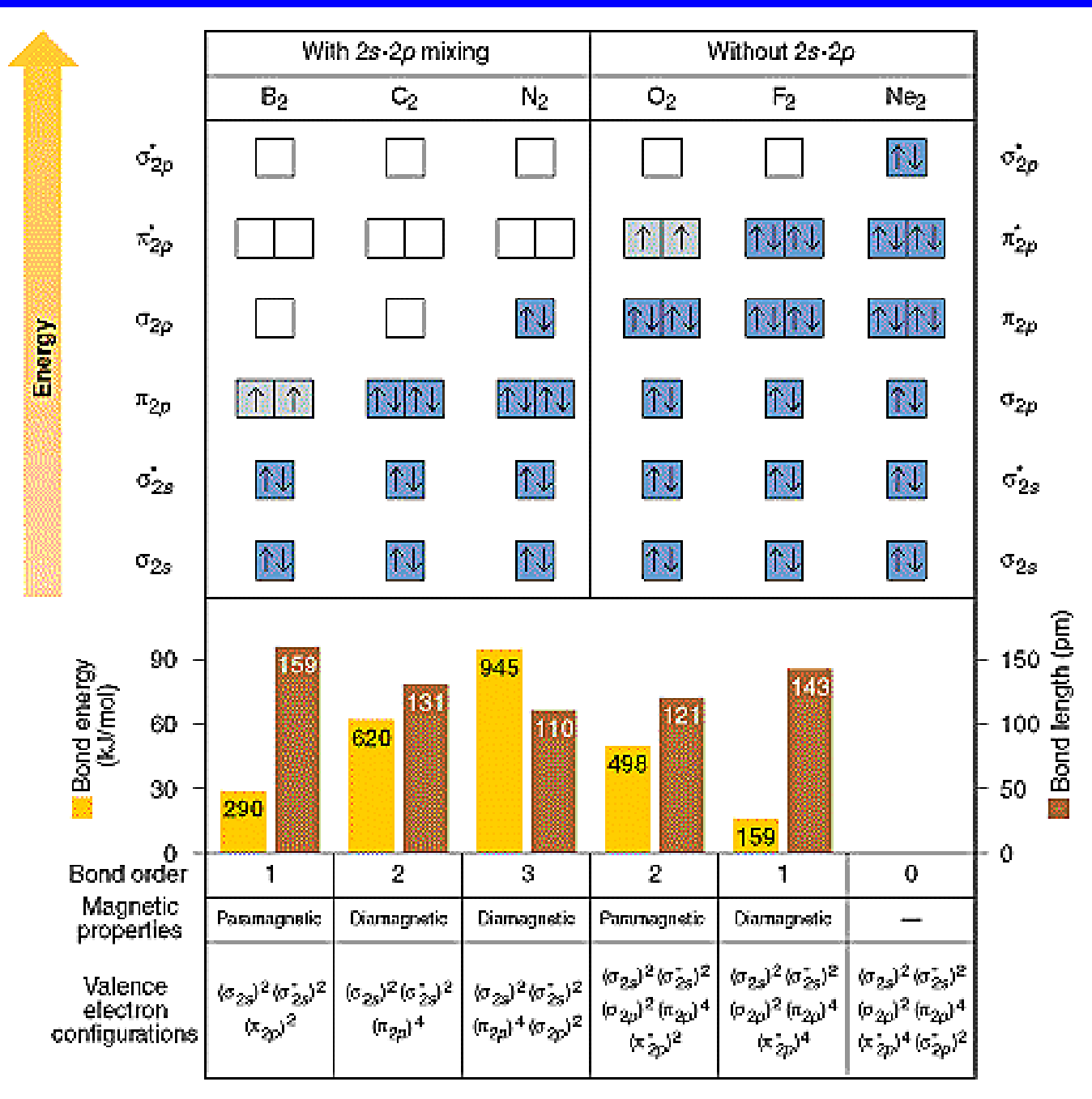


Pro O_2 až Ne_2

Pro H_2 až N_2

Energetický diagram molekuly N₂



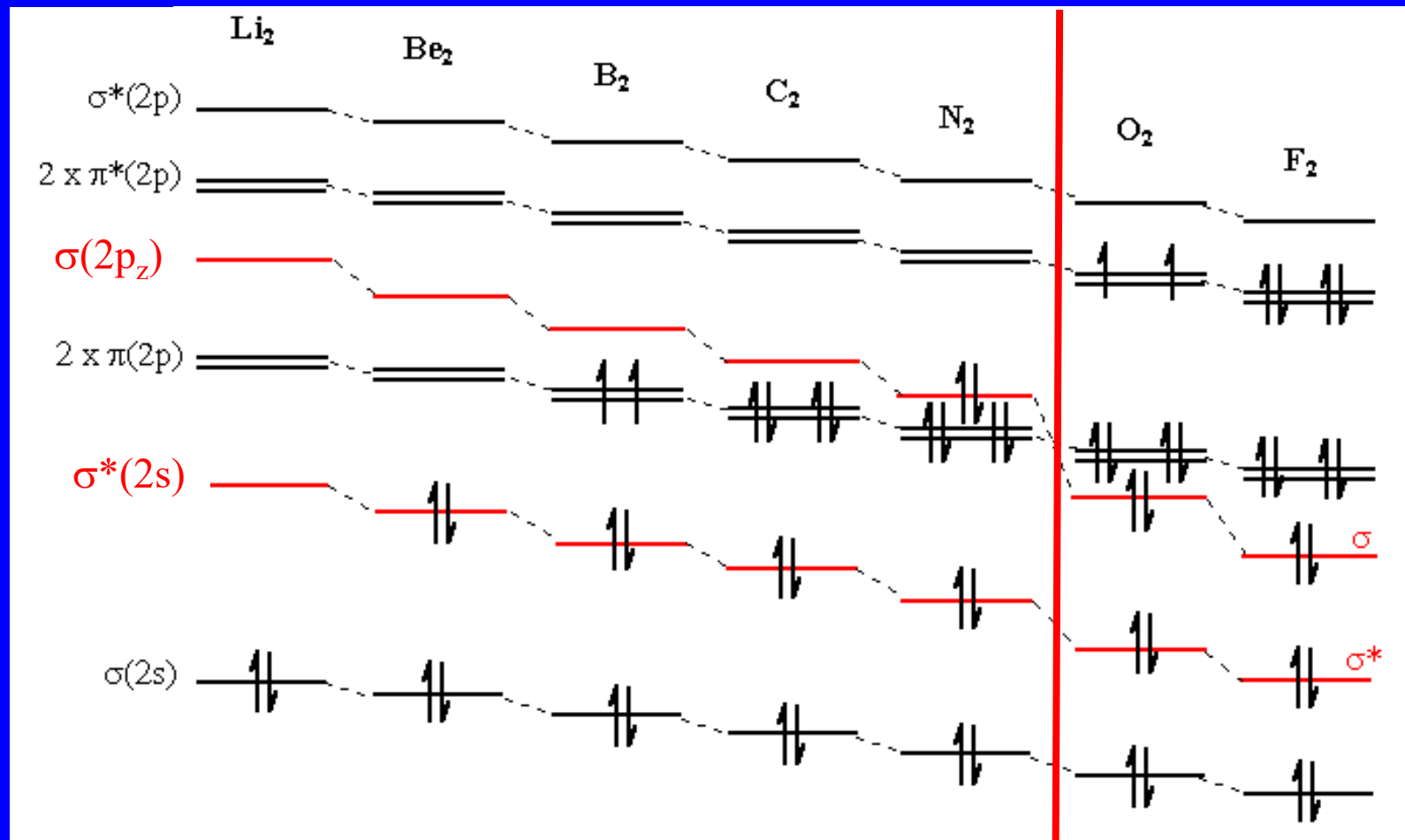


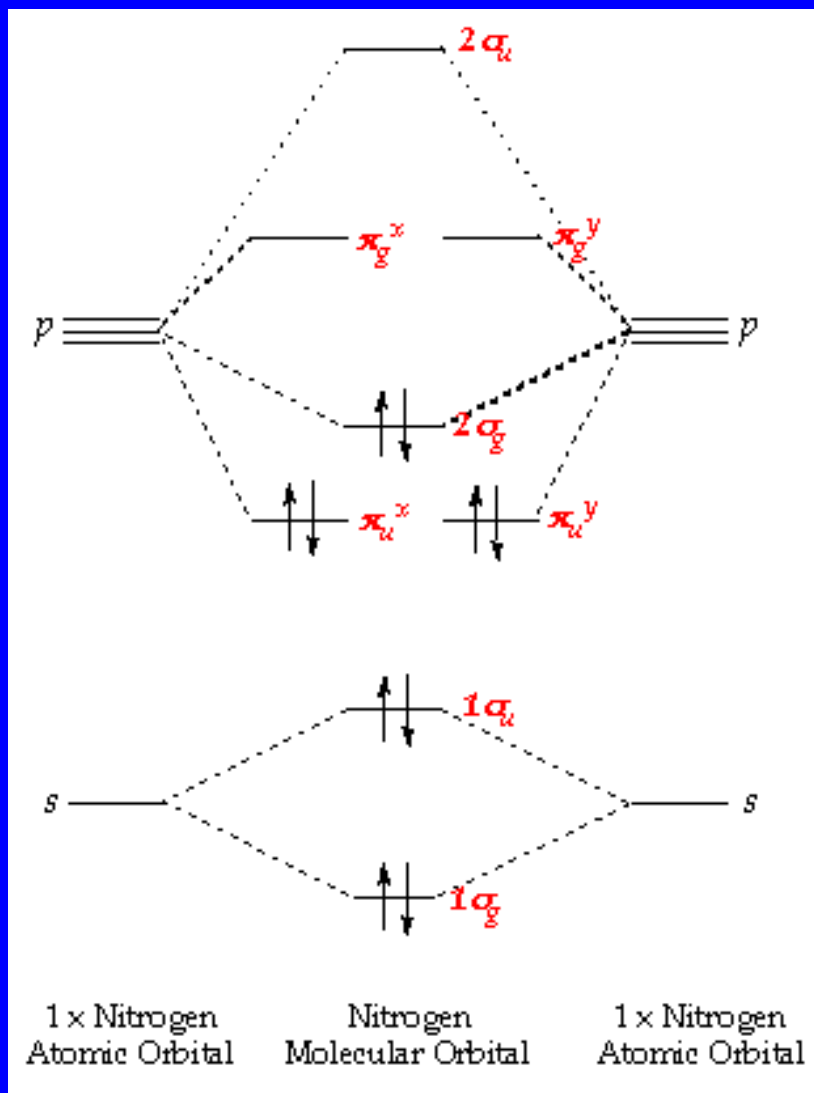
Diatomické molekuly v plynné fázi

		Délka (pm)	E_{vaz} (kJ mol ⁻¹)
Li-Li	σ_{2s}^2	267	110
Be...Be	$\sigma_{2s}^2 \sigma_{2s}^{*2}$?	?
B-B	$\sigma_{2s}^2 \sigma_{2s}^{*2} \pi_{2p}^2$	159	290
C=C	$\sigma_{2s}^2 \sigma_{2s}^{*2} \pi_{2p}^4$	124	602
N≡N	$\sigma_{2s}^2 \sigma_{2s}^{*2} \pi_{2p}^4 \sigma_{2p}^2$	110	942
O=O	$\sigma_{2s}^2 \sigma_{2s}^{*2} \sigma_{2p}^2 \pi_{2p}^4 \pi_{2p}^{*2}$	121	494
F-F	$\sigma_{2s}^2 \sigma_{2s}^{*2} \sigma_{2p}^2 \pi_{2p}^4 \pi_{2p}^{*4}$	142	155

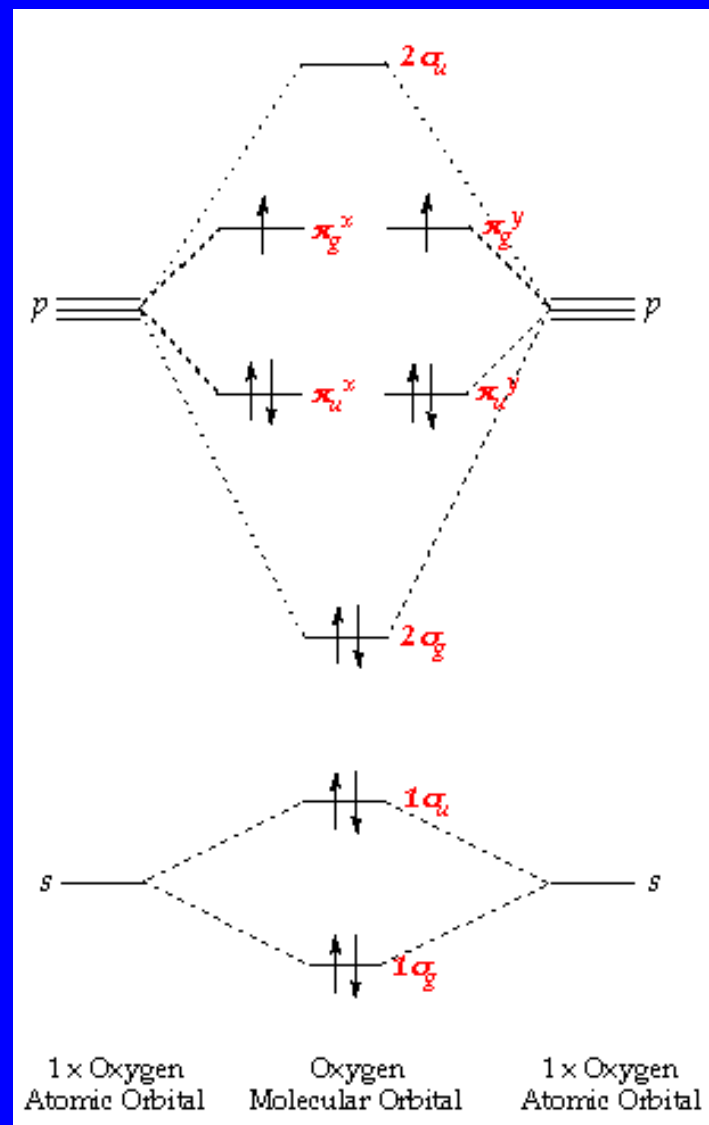
**Aufbau
Hund
Pauli**

Diatomické molekuly



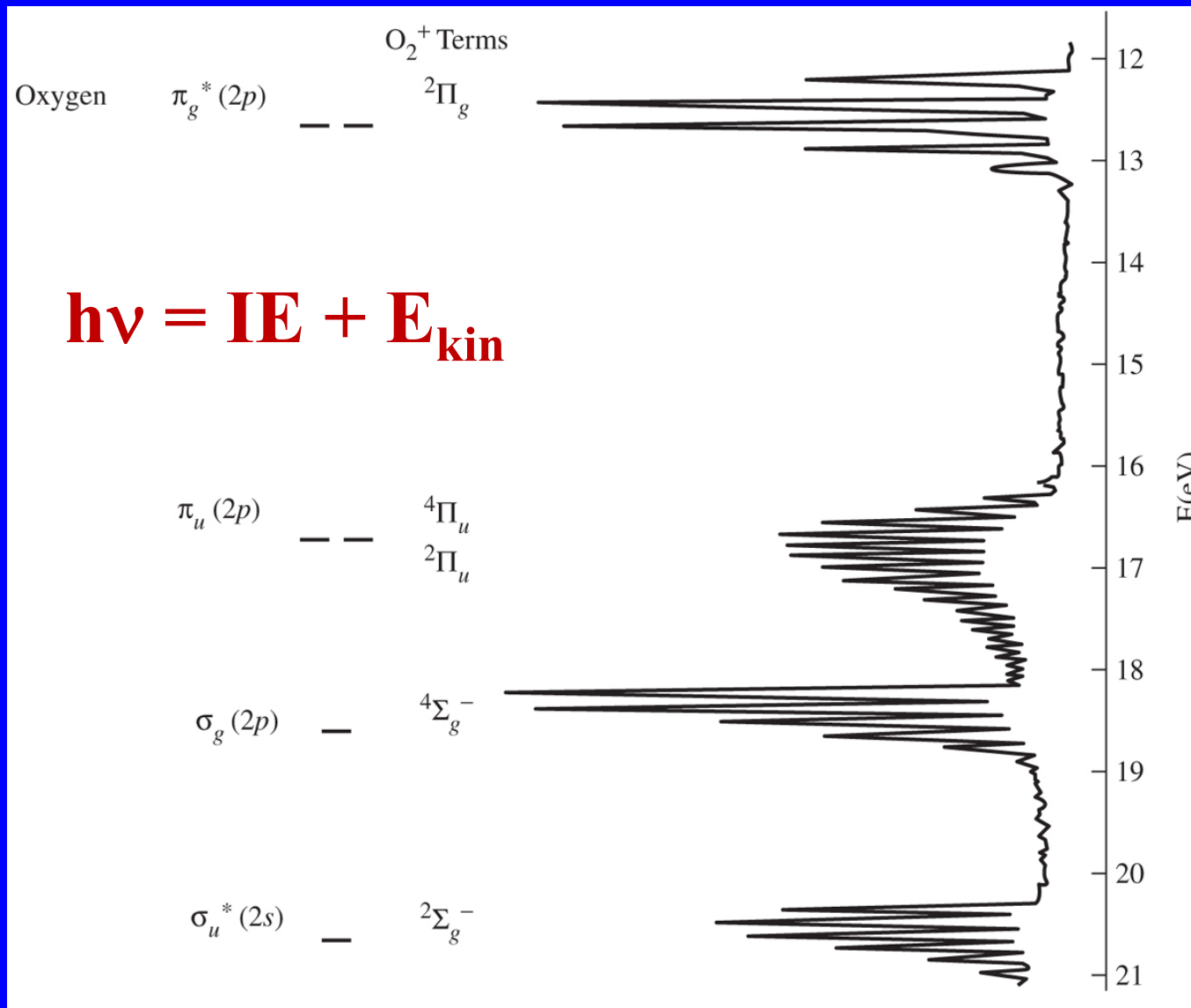


N_2 trojná vazba



O_2 paramagnetická molekula

PES spektrum molekuly O₂



Kyslík a jeho molekulové ionty

	O_2^+	O_2	O_2^-	O_2^{2-}
Počet valenčních elektronů	11	12	13	14
Obsazení HOMO π_x^* a π_y^*	↑	↑ ↑	↑↓ ↑	↑↓ ↑↓
Řád vazby	2,5	2,0	1,5	1,0
Délka vazby, pm	112	121	126	149
Vazebná energie, kJ/mol	643	494	395	126
Magnet. vlastnosti	param	param	param	diam

Multiplicita

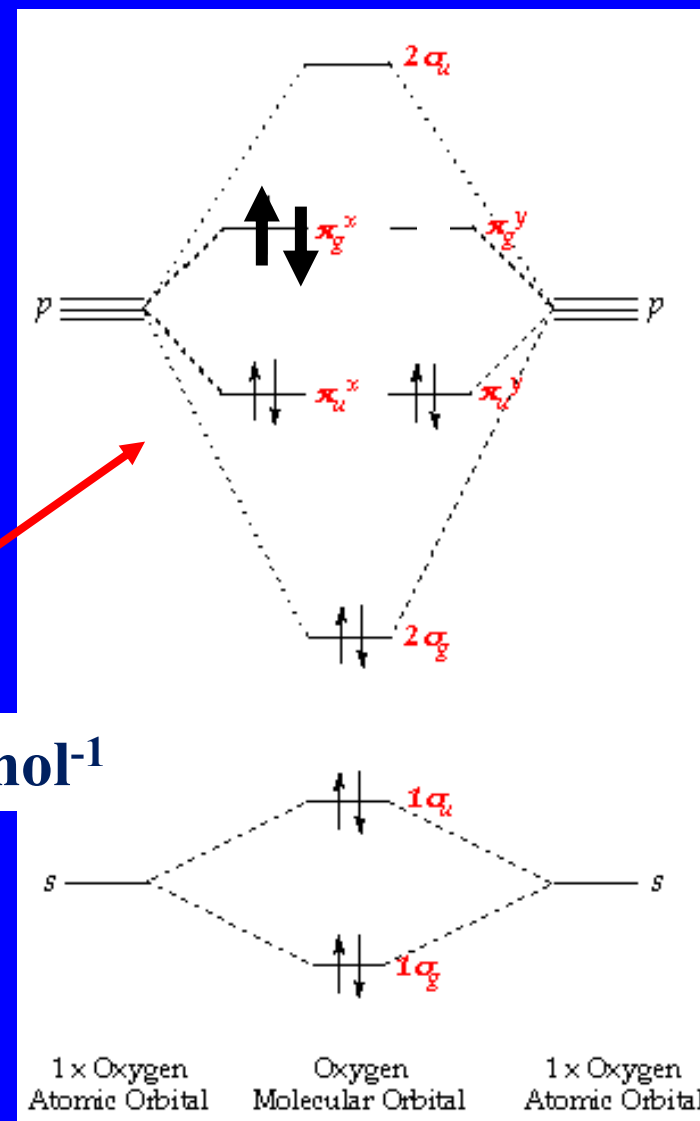
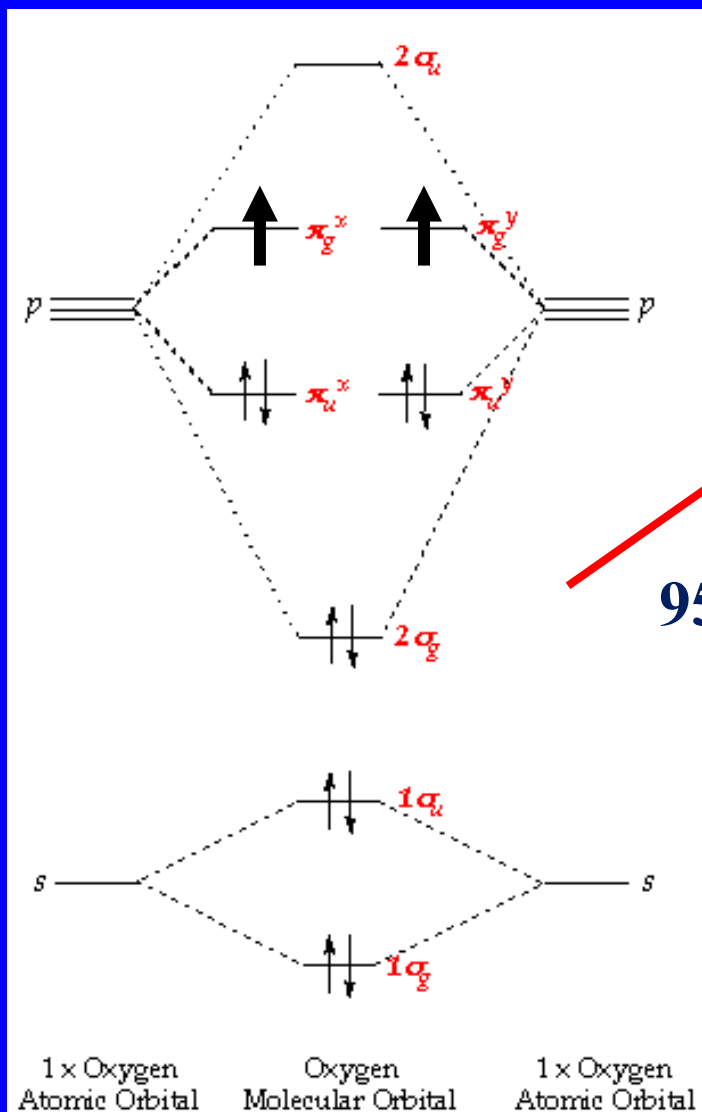
$$M = 2S + 1$$

S = součet nepárových spinů ($\frac{1}{2}$) v atomu nebo molekule

M	název	S	
1	singlet	0	↑↓
2	dublet	$\frac{1}{2}$	↑
3	triplet	1	↑↑
4	kvartet	$1\frac{1}{2}$	↑↑↑
5	kvintet	2	↑↑↑↑
6	sextet	$2\frac{1}{2}$	↑↑↑↑↑

Singletový kyslík $^1\Delta$

Tripletový kyslík $^3\Sigma$



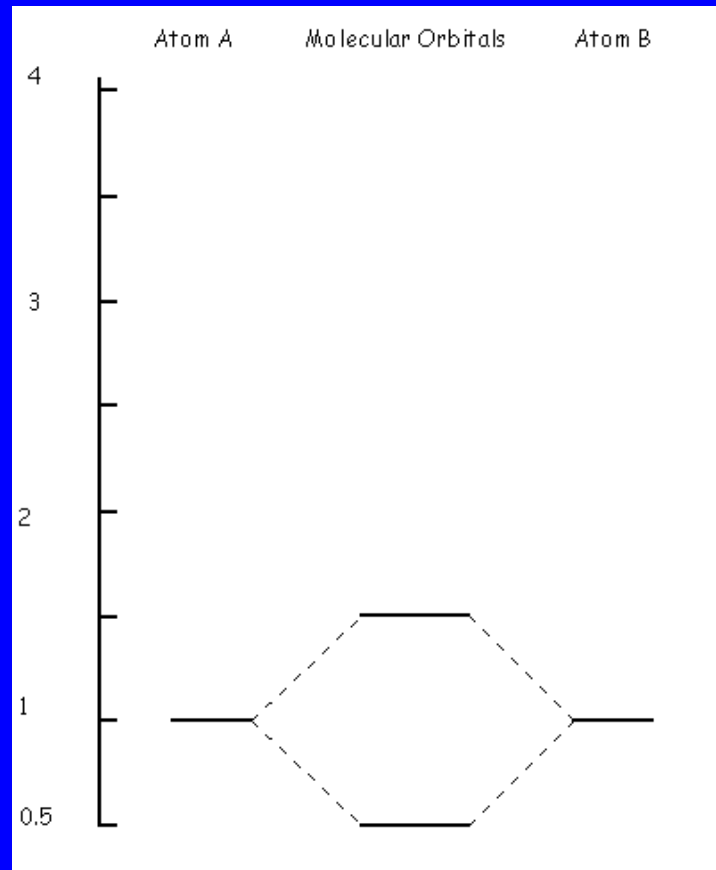
95 kJ mol⁻¹

Izoelektronové molekuly

Počet val. elektr.	Příklady diatomických částic
9	BO, CN, CP, CO ⁺
10	N ₂ , CO, CN ⁻ , BF, NO ⁺ , TiO, SiO
11	O ₂ ⁺ , ·NO, SO ⁺
12	O ₂ , SO
13	O ₂ ⁻ , Cl ₂ ⁺ , ·ClO
14	F ₂ , O ₂ ²⁻ , ClO ⁻

MO v polárních molekulách

$$\Psi^* = c_3 \Psi_A - c_4 \Psi_B$$



$$\Psi = c_1 \Psi_A + c_2 \Psi_B$$

$\chi(A) \ll \chi(B)$ **iontová** vazba

$c_1 \rightarrow 0$ vazebný MO = Ψ_B

$c_4 \rightarrow 0$ protivazebný MO = Ψ_A

$\chi(A) < \chi(B)$ **polární** vazba

$c_1 < c_2$ vazebný MO má větší

příspěvek od B

$c_3 > c_4$ protivazebný MO má větší

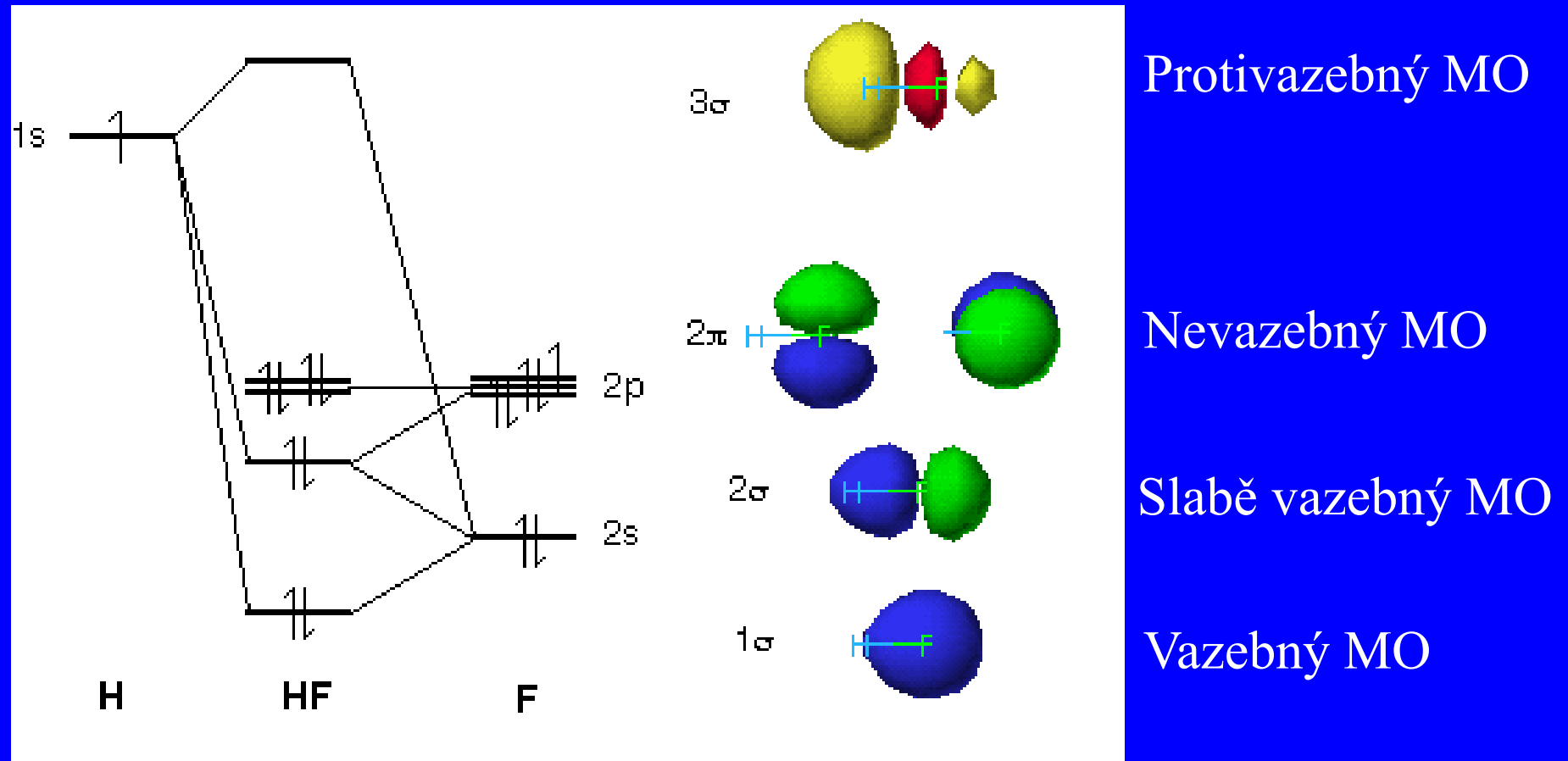
příspěvek od A

$\chi(A) = \chi(B)$ **nepolární** vazba

$c_1 = c_2$ $c_3 = c_4$

stejný příspěvek od obou atomů 38

MO v polárních molekulách, HF

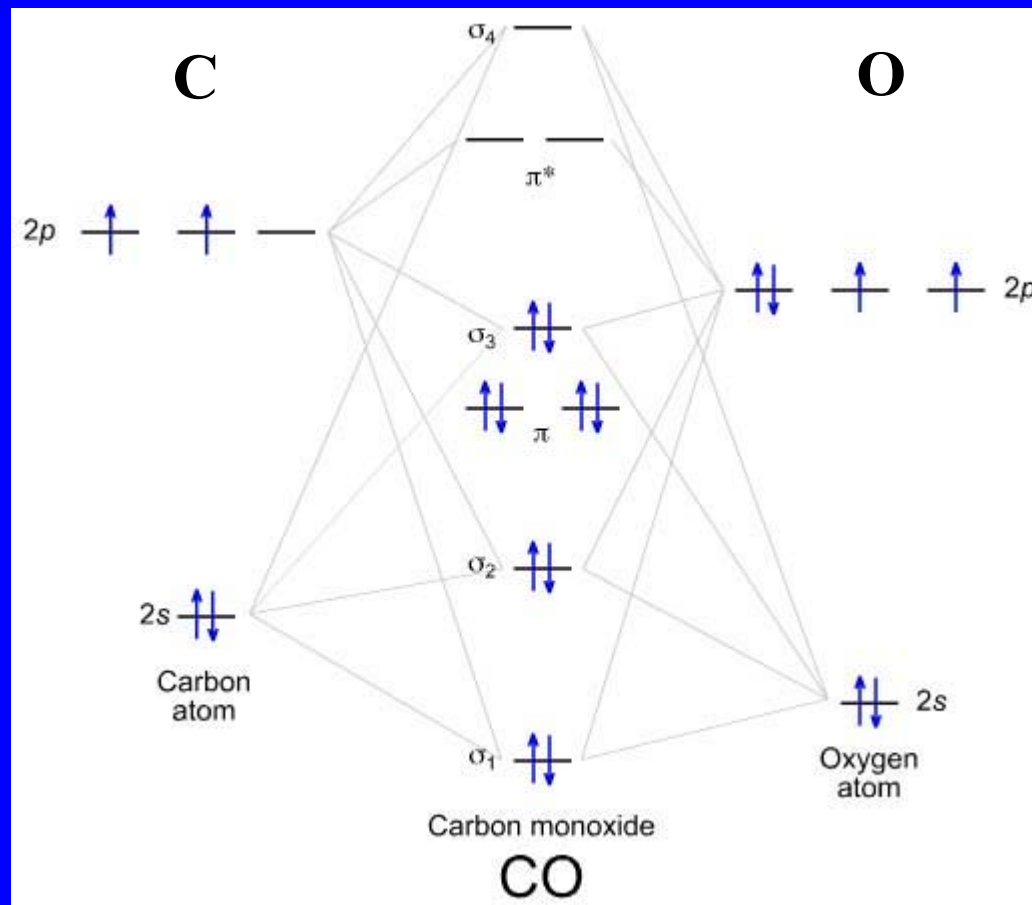


Vazebný MO koncentrován na atomu s vyšší elektronegativitou - F
Protivazebný MO koncentrován na atomu s nižší elektronegativitou - H

MO v C≡O

LUMO

HOMO



σ_{pz}^*
 $\pi_{px, y}^*$

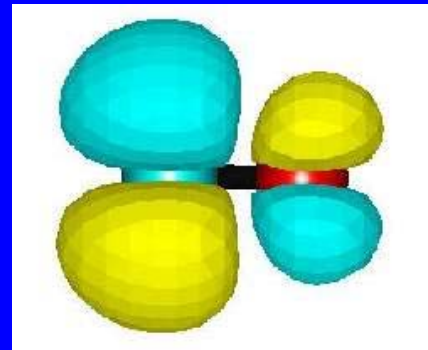
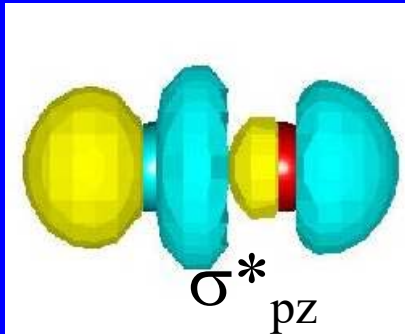
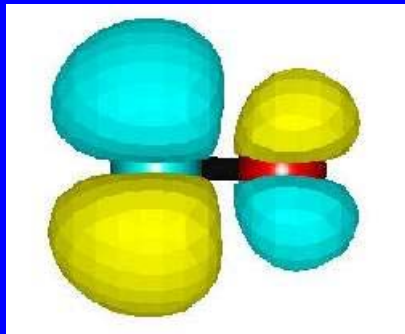
σ_{pz}
 $\pi_{px, y}$

σ_s^*

σ_s

C + O = 10 elektronů

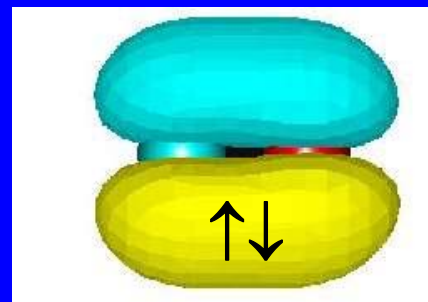
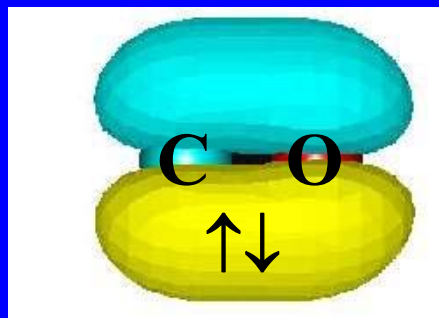
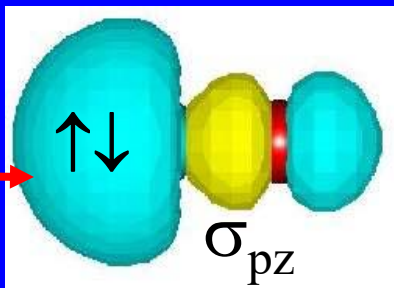
LUMO



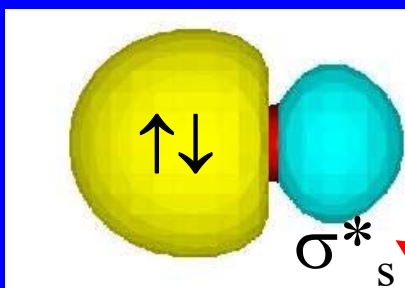
$\pi^*_{px,y}$

HOMO

Volný e pár na C



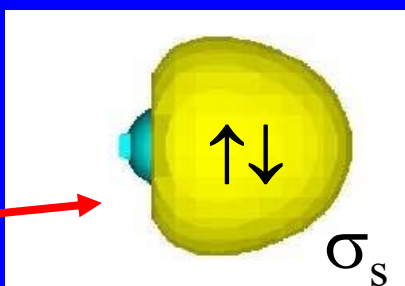
$\pi_{px,y}$



Slabě vazebný (příměs p_z)



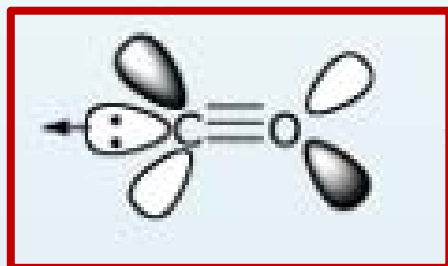
Volný e pár na O



Vazba CO v karbonylech přechodných kovů



Prázdný d_{z^2} orbital
na M (σ)

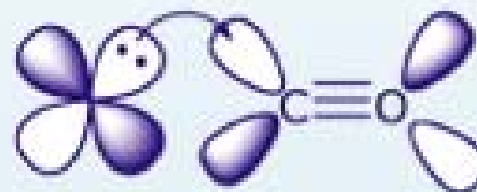


Prázdný d_{xz} , d_{yz}
orbital na M (π)



σ -donation

Volný e pár na C
HOMO



and

π -accepting



Prázdný orbital
na C - LUMO

Molekulové orbitály v NO

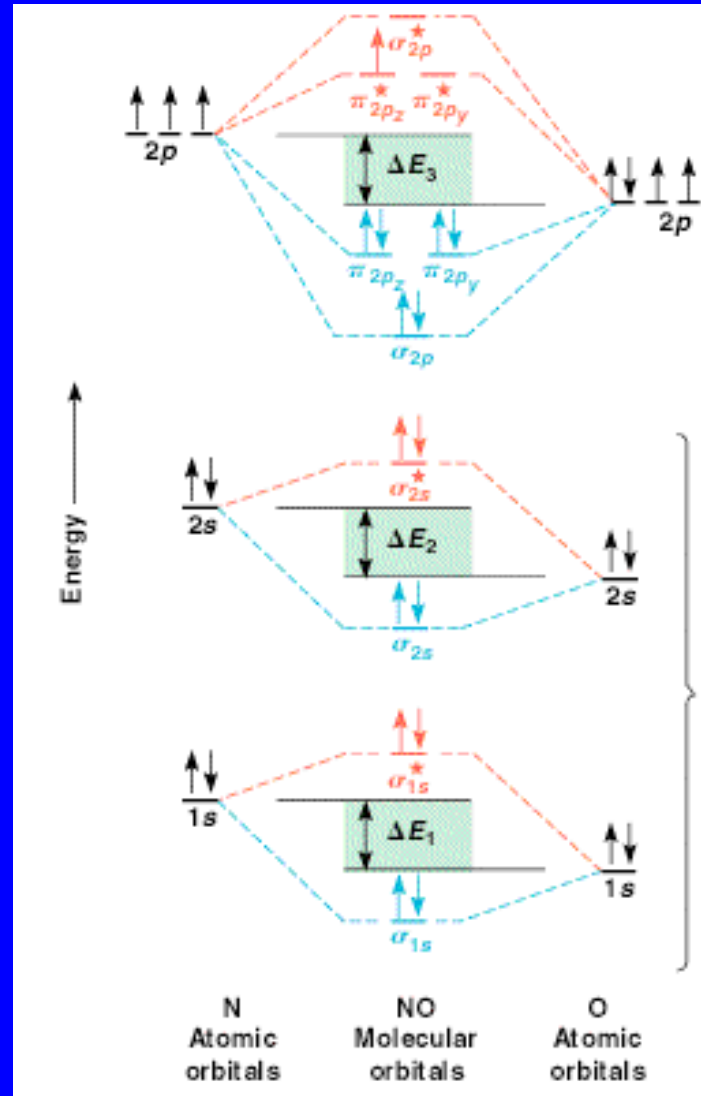
Atomové orbitály N

Multiplicita = 2

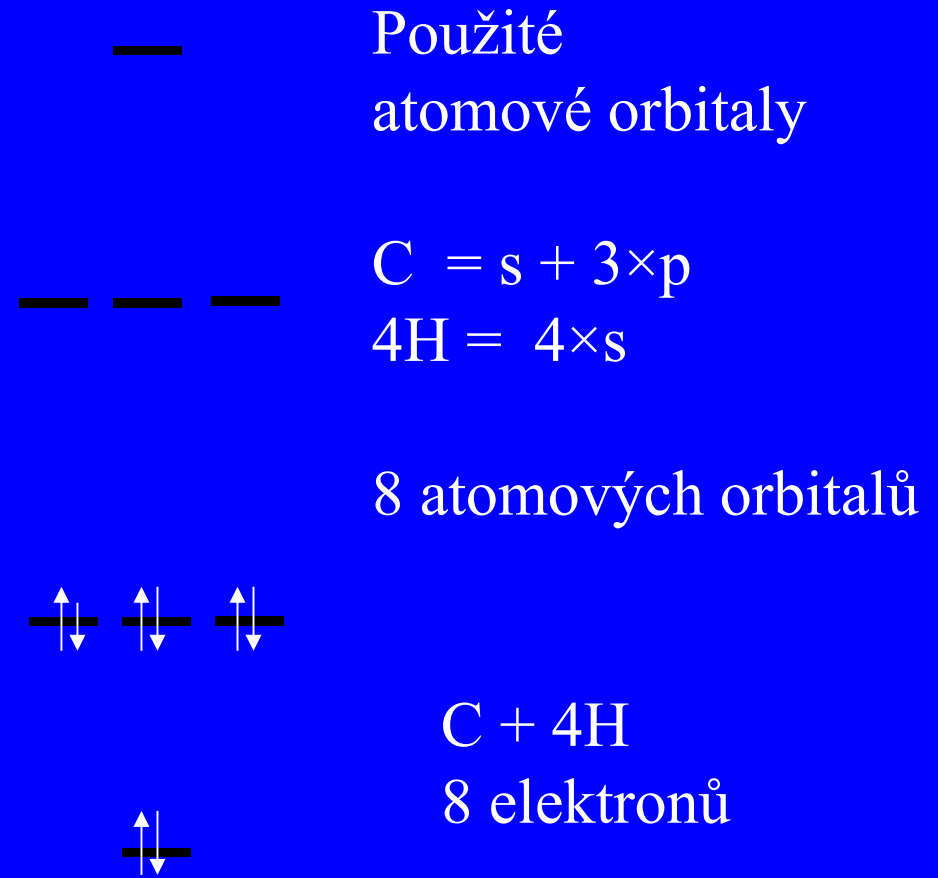
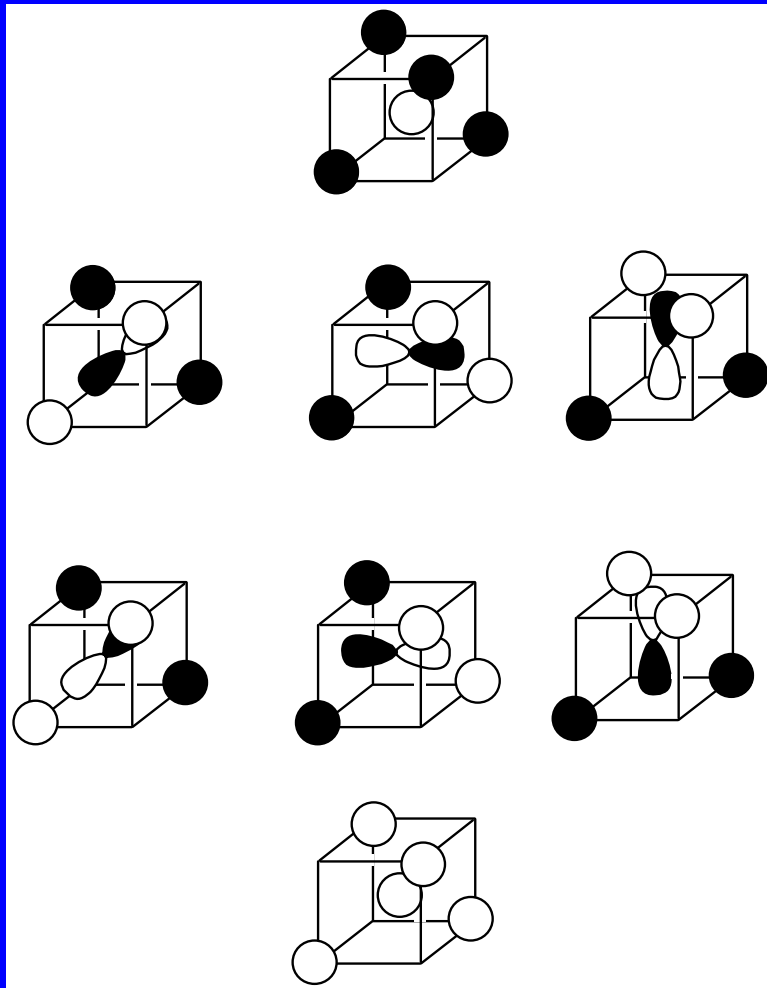
Řád vazby = 2,5

A co NO⁺?

Atomové orbitály O

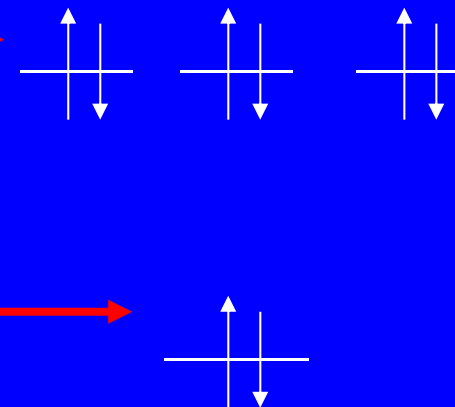
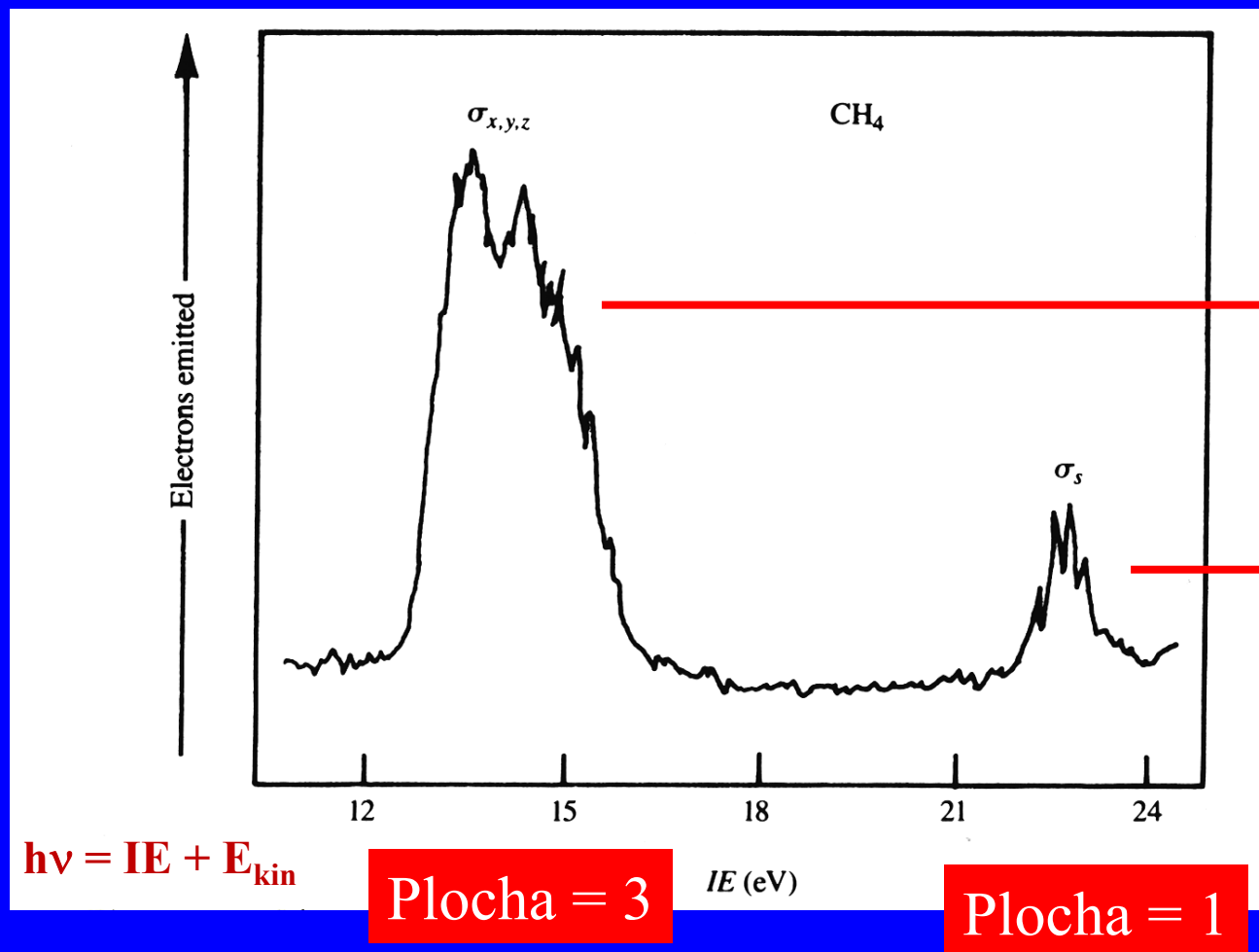


Molekulové orbitály CH₄

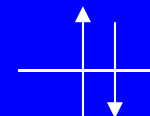
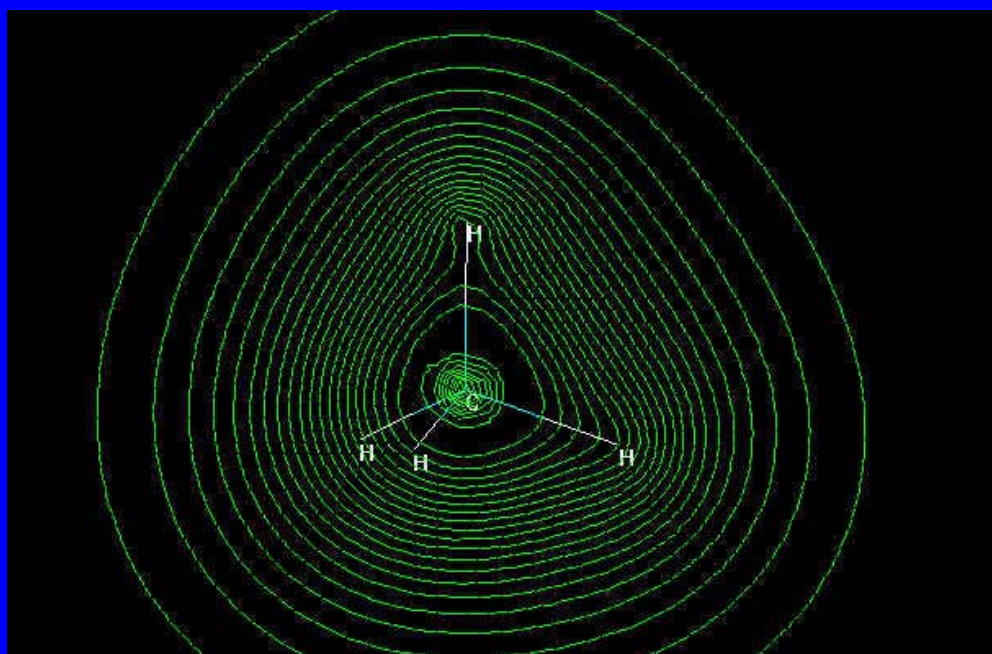
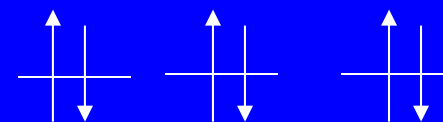
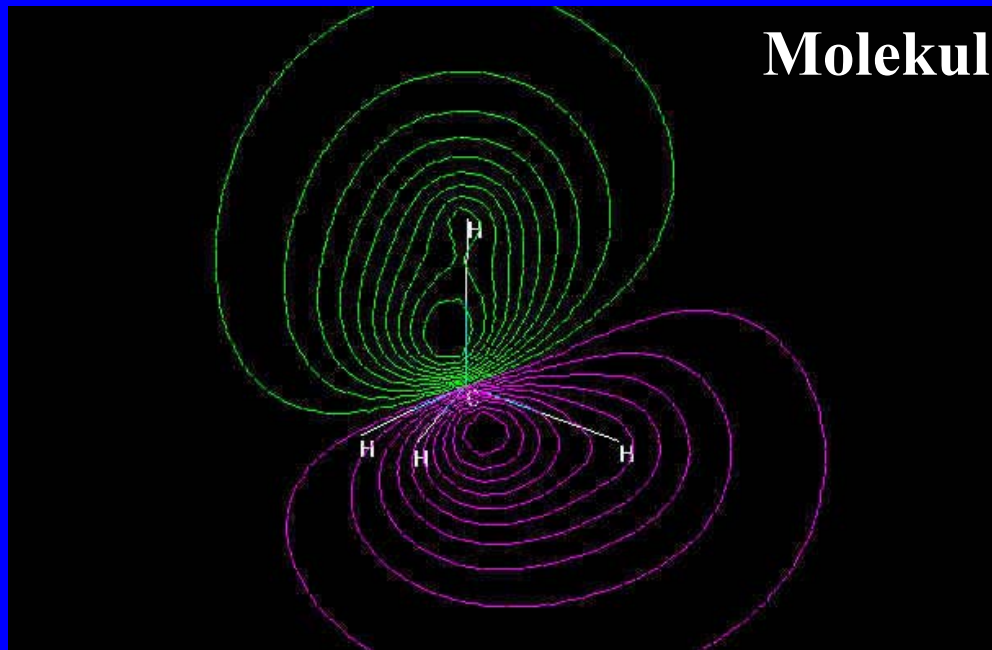


Vzrůstá počet uzlových rovin

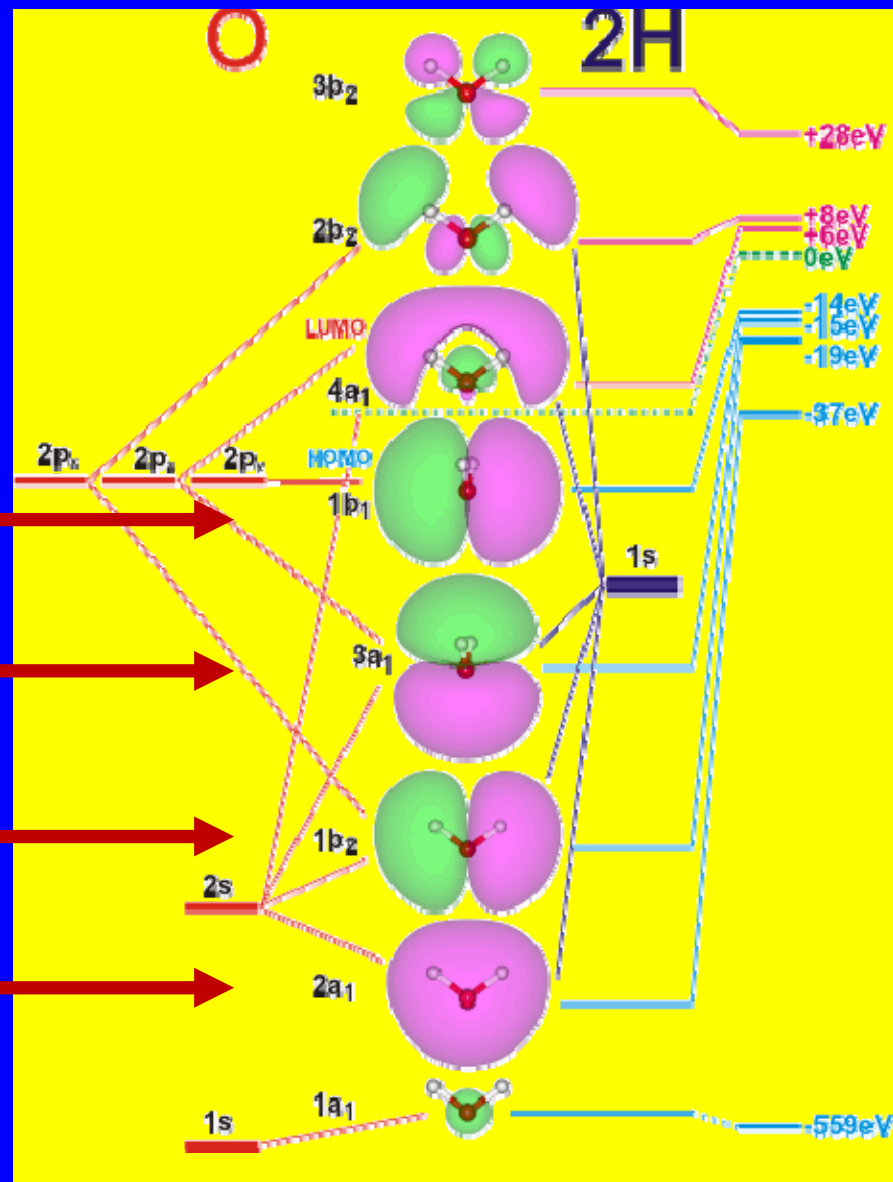
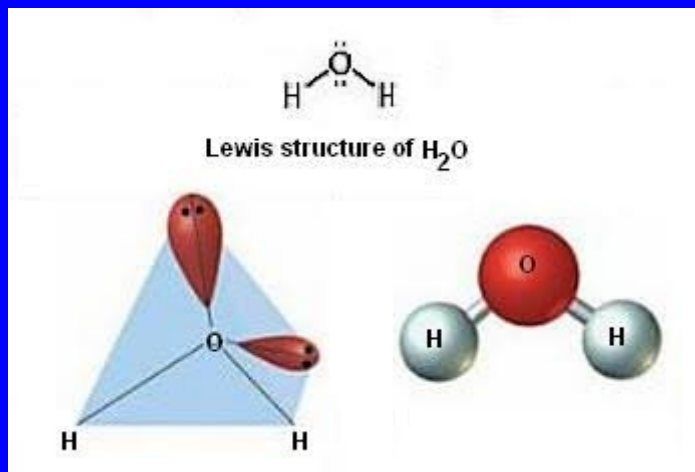
PES methanu souhlasí s modelem MO



Molekulové orbitály CH₄

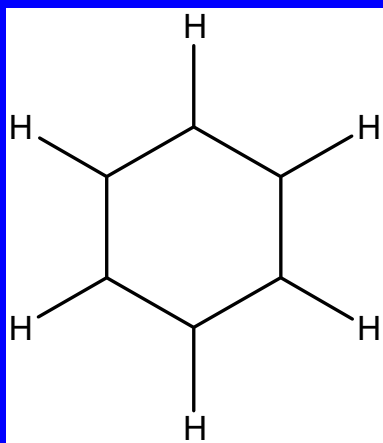


Molekulové orbitály H₂O

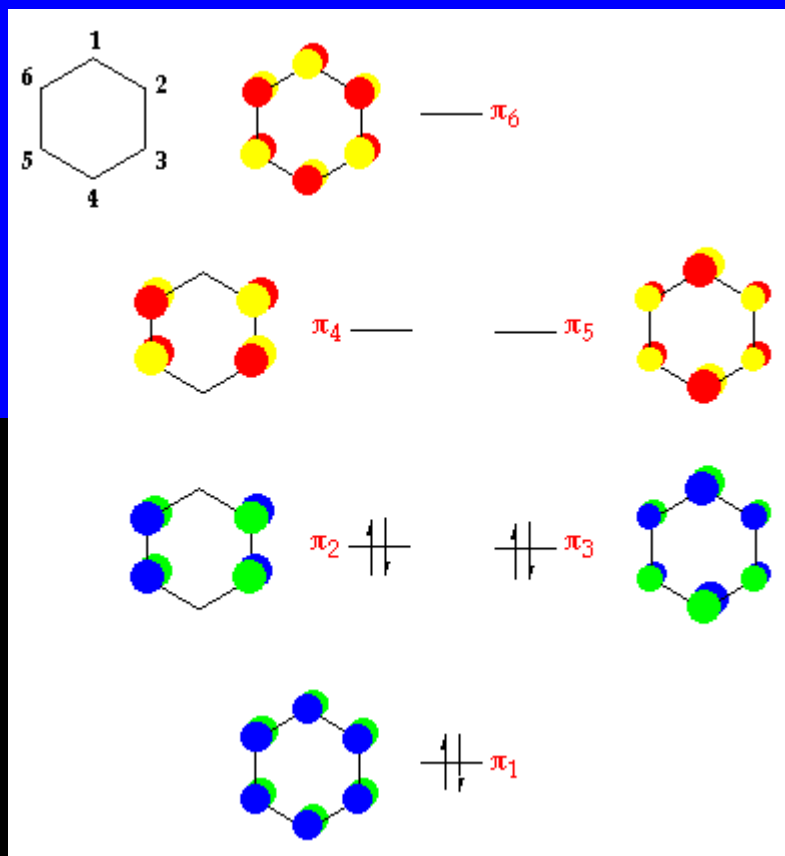


Dvě volné e-páry

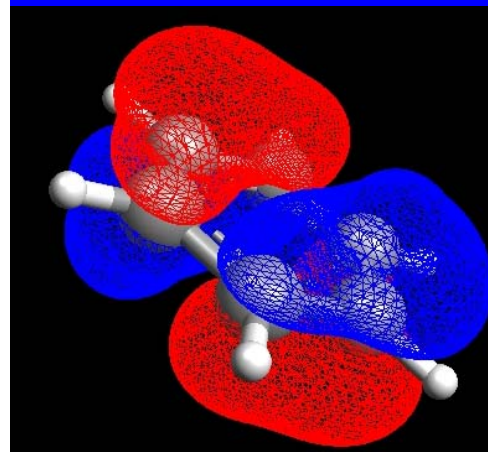
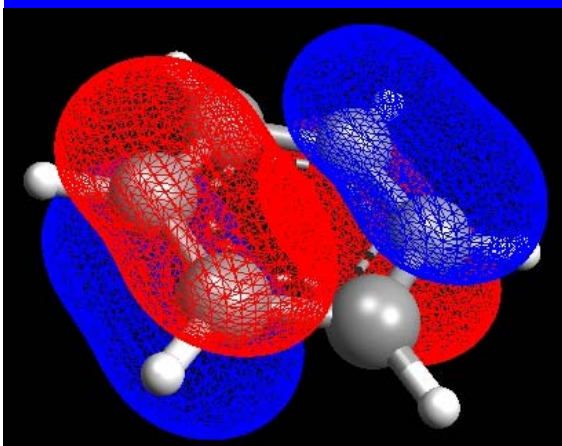
Dvě vazby O-H



Vazebné MO v benzenu



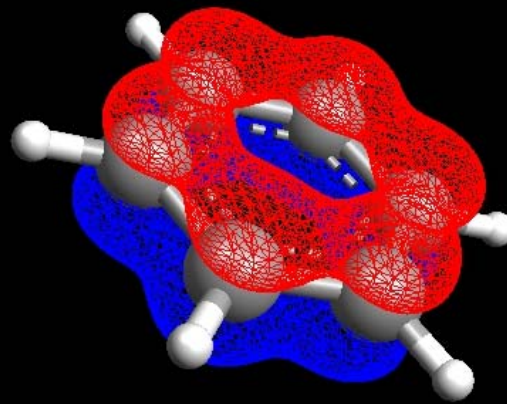
Oddělený pohled
na sigma a pi
systém



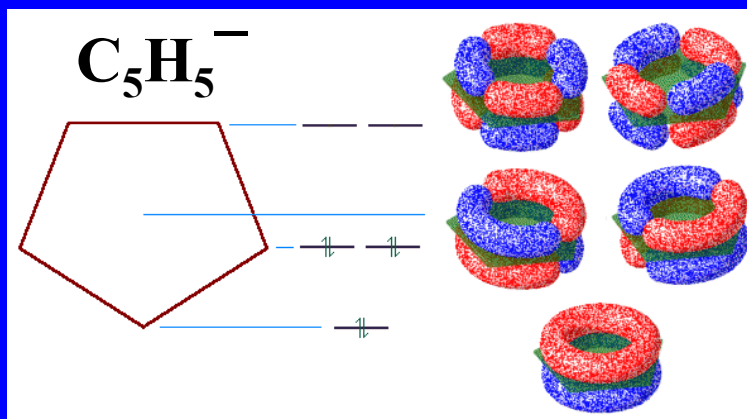
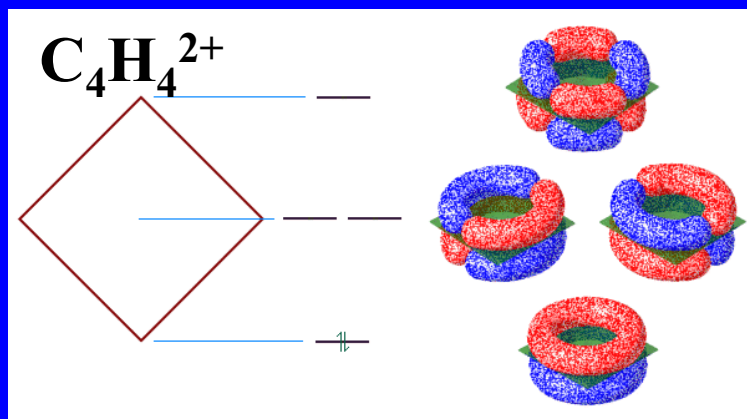
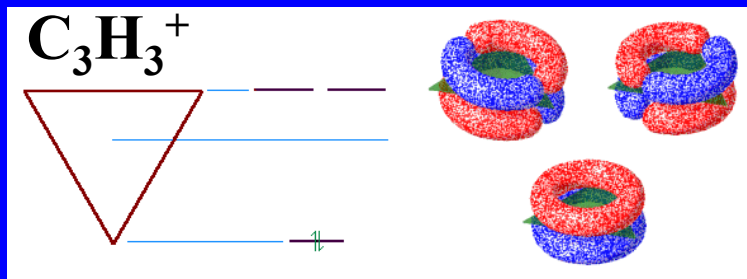
Hückelovo pravidlo

$$\pi = 4n + 2 = 2, 6, 10, 14 \dots$$

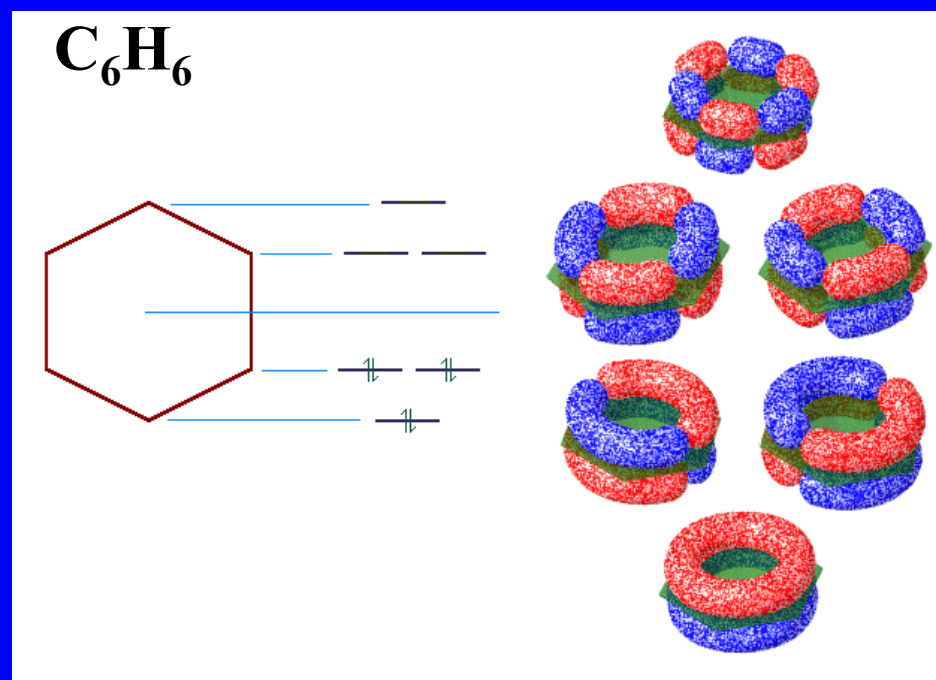
$$n = 0, 1, 2, \dots$$



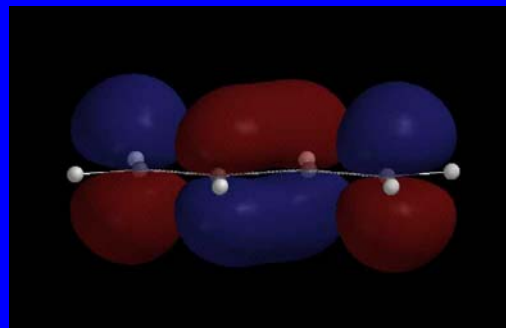
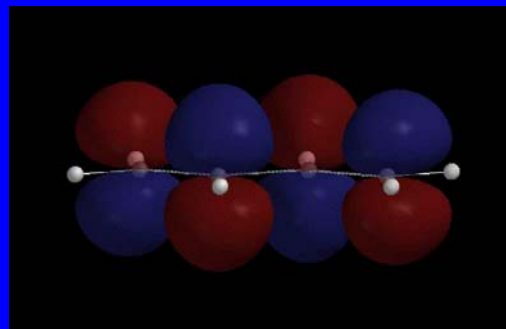
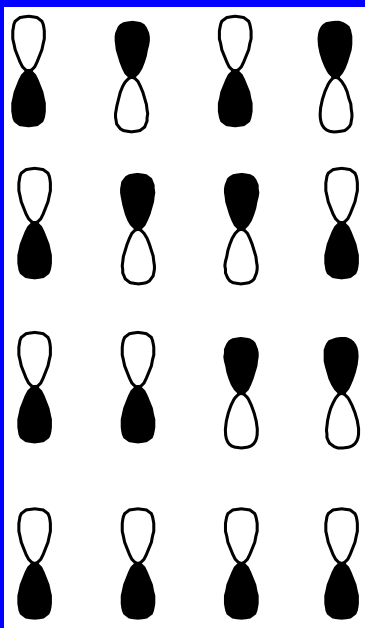
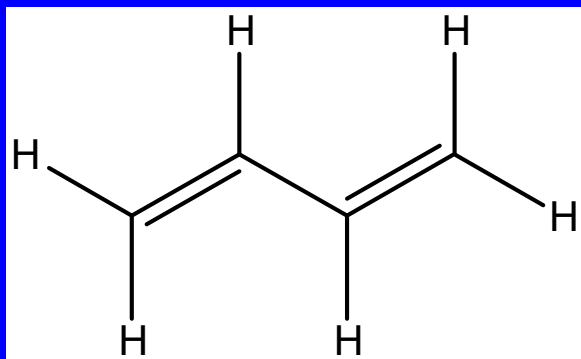
Molekulové orbitály v cyklických π -systémech



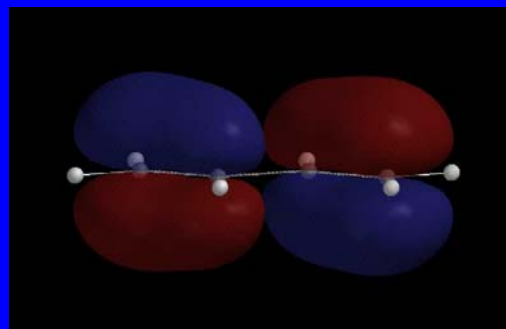
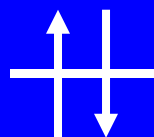
Hückelovo pravidlo $\pi = 4n + 2$



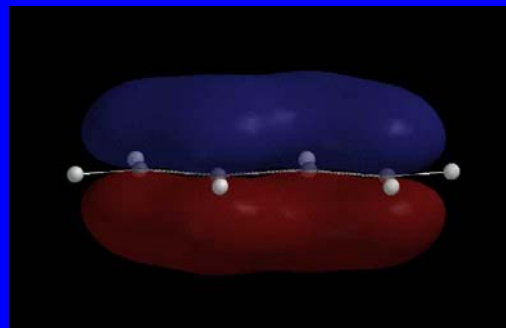
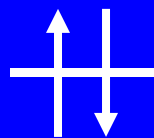
1,3-butadien



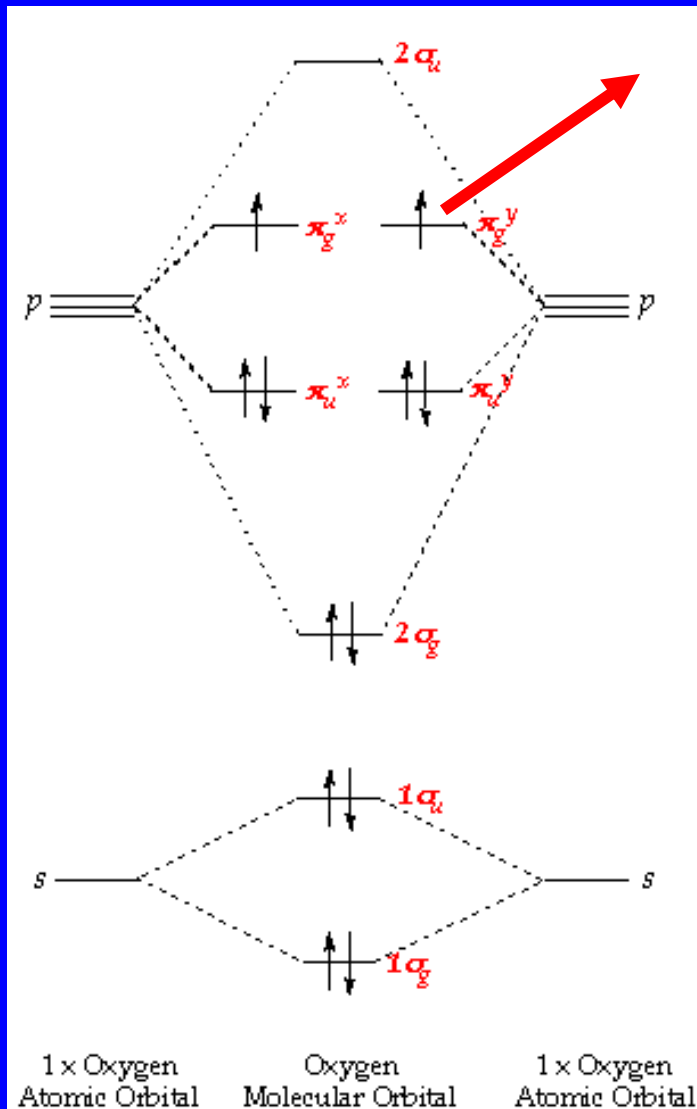
LUMO



HOMO



Molekulové ionty

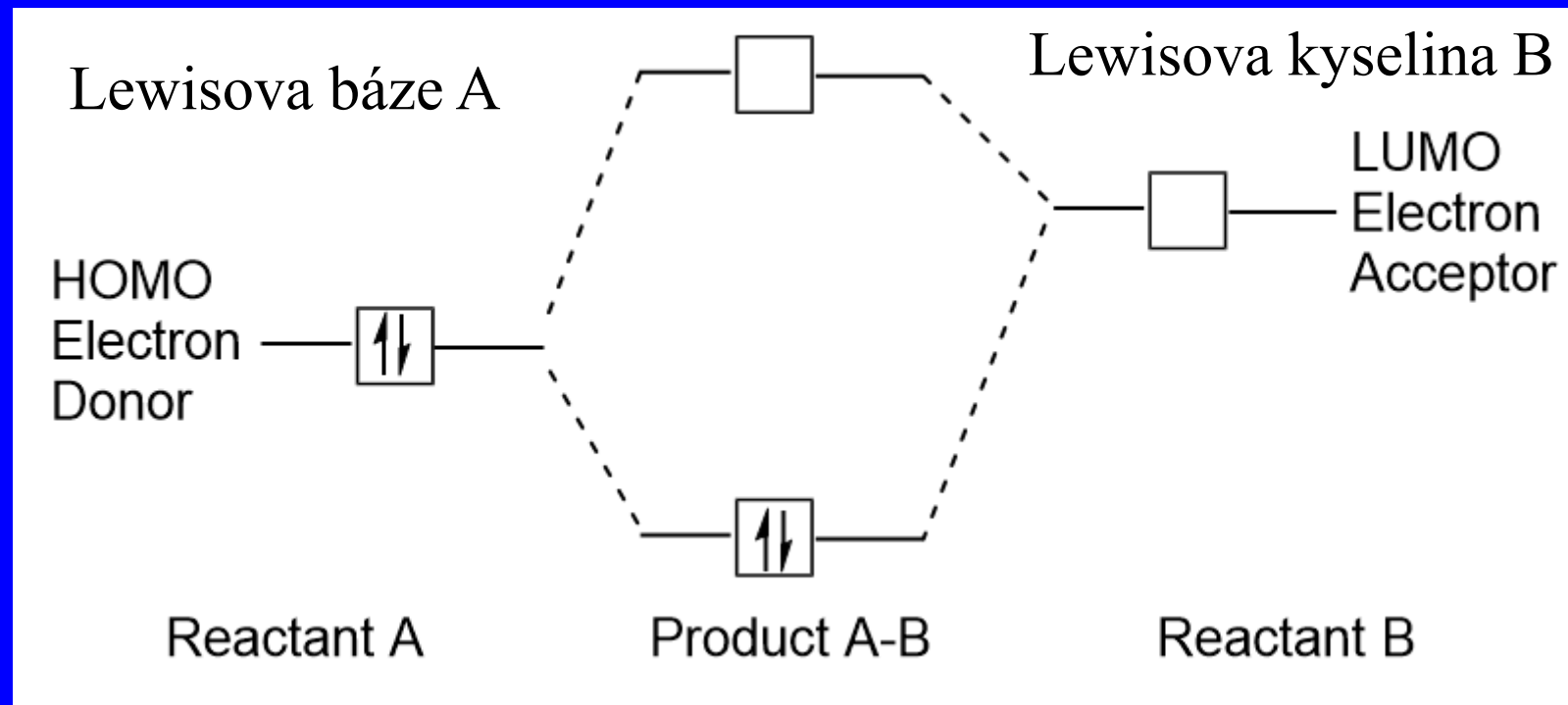


IE



Odtržení nejslaběji vázaného e
v HOMO orbitalu

Hraniční orbitaly



Donor-akceptorová vazba