

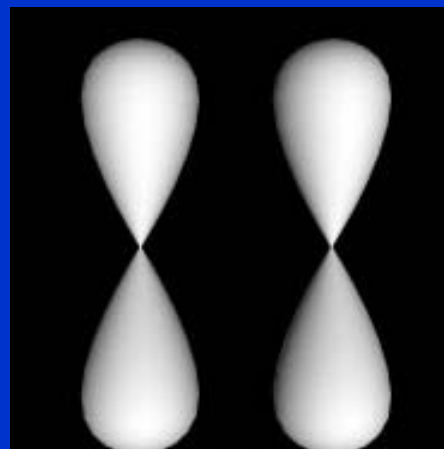
Překryv orbitalů

Vznik vazby překryvem orbitalů na dvou různých atomech A, B
Obsazeno dvojicí elektronů

$$\Psi = \Psi_A \times \Psi_B$$

Podmínky překryvu:

- Vhodná symetrie, znaménko vlnové funkce
- Vhodná energie, srovnatelná, ne velmi rozdílná



Typy překryvu orbitalů

Sigma vazba, σ

Elektronová hustota lokalizována na spojnici jader

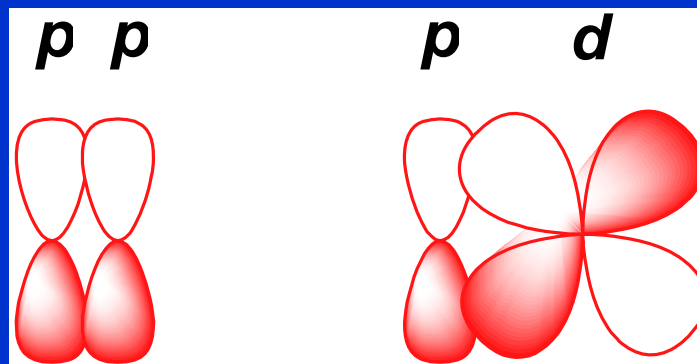
Spojnici jader obvykle značíme jako osu z



Pi vazba, π

Elektronová hustota lokalizována mimo spojnici jader

Jedna uzlová rovina

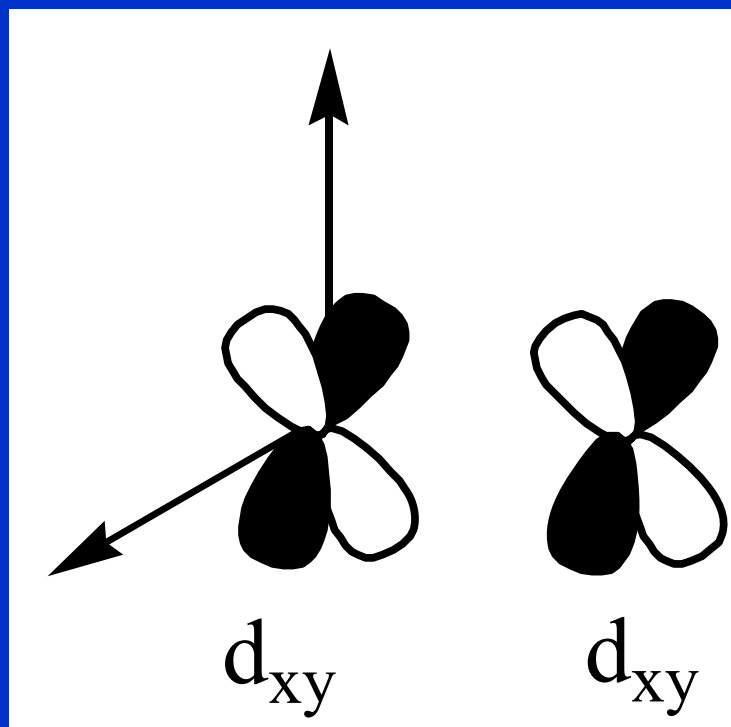


Typy překryvu orbitalů

Delta vazba, δ

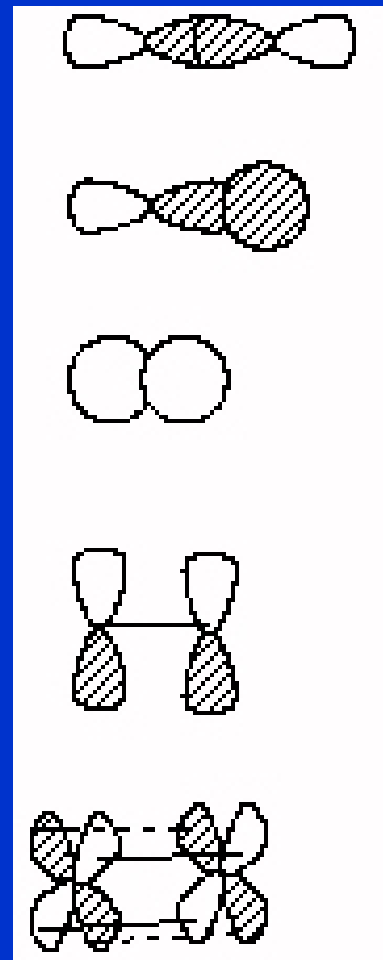
Elektronová hustota lokalizována mimo spojnici jader

Dvě uzlové roviny

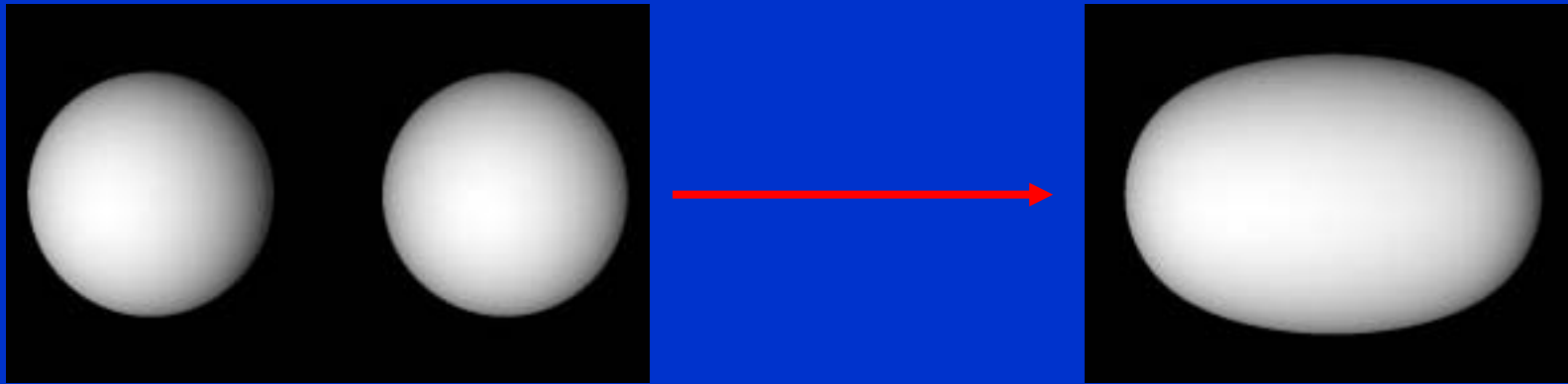


Typy překryvu orbitalů

Překryv klesá
slabší vazba



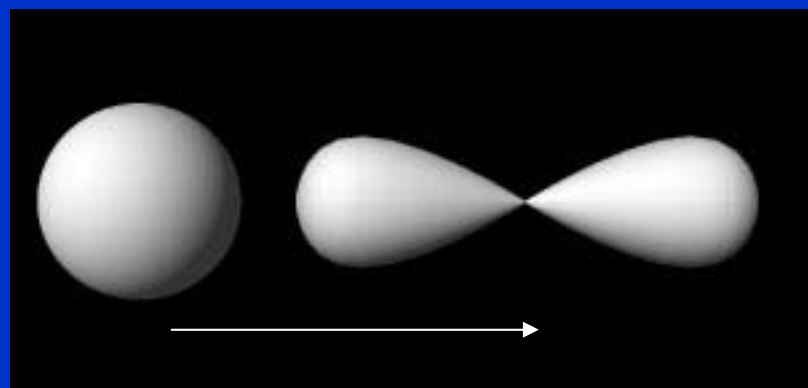
Sigma vazba, σ_{ss}



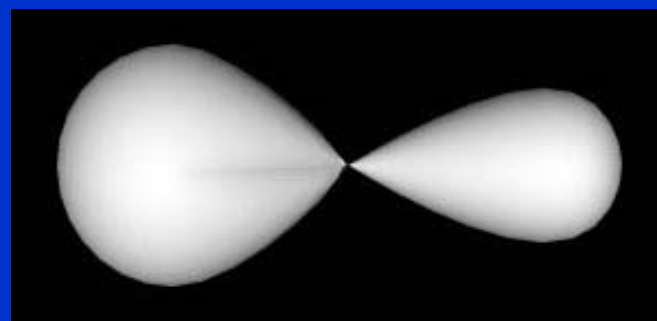
σ_{ss}

Elektronová hustota lokalizována na spojnici jader

Sigma vazba, σ_{sp}

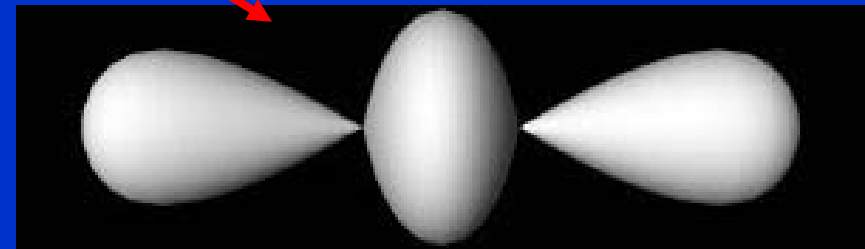
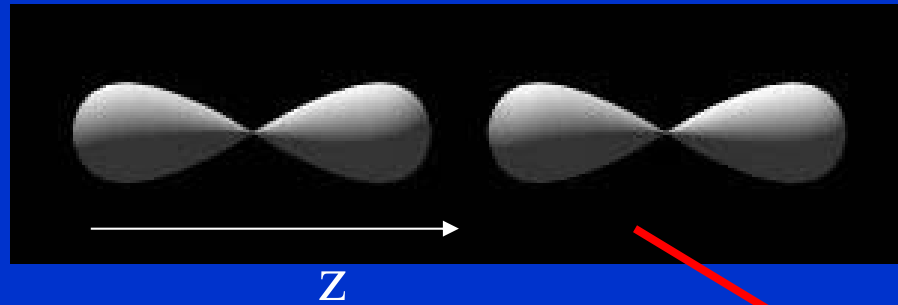


z



σ_{sp}

Sigma vazba, σ_{pp}

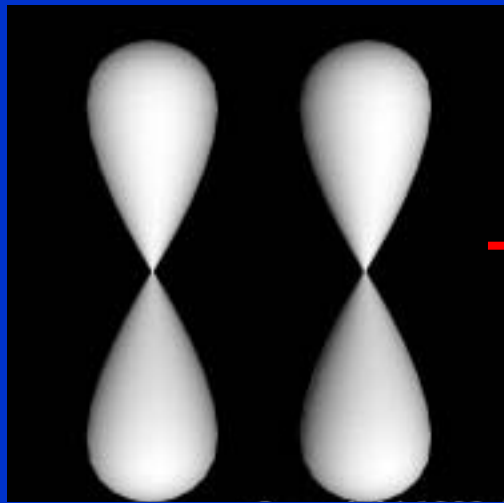


σ_{pp}

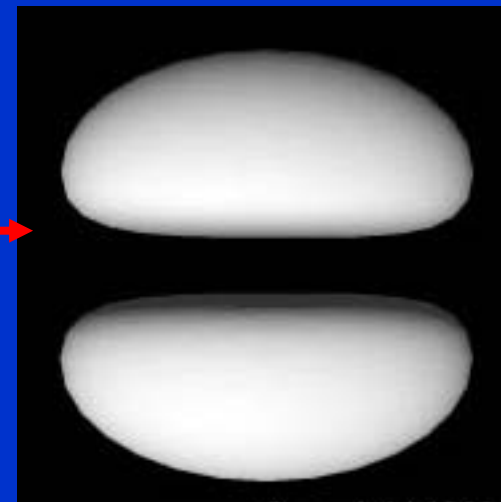
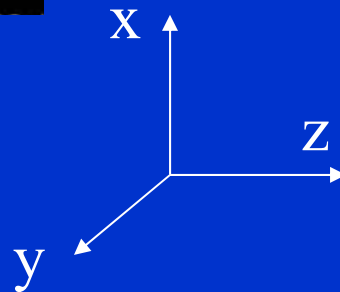
Pi vazba, π

Elektronová hustota lokalizována mimo spojnici jader

Jedna uzlová rovina



Stejně pro p_x a p_y



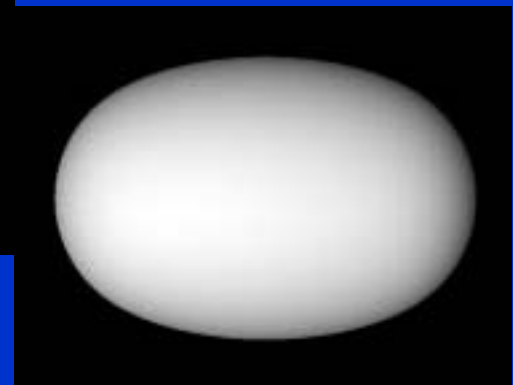
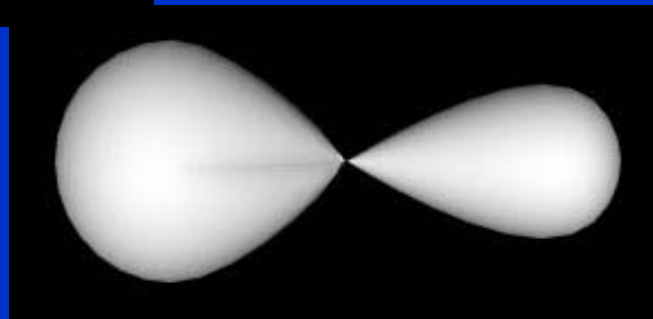
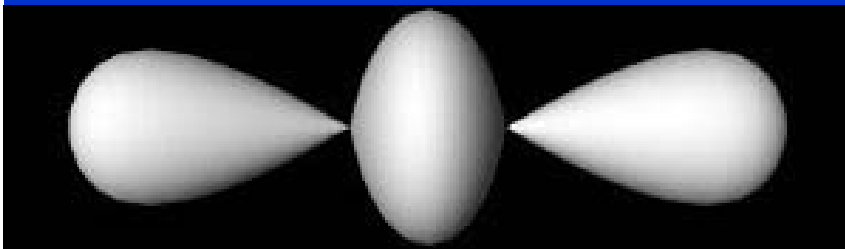
$2 \times \pi_{pp}$

Účinnost překryvu orbitalů

Kratší vzdálenost = lepší překryv

Při stejné vzdálenosti jader: $\sigma > \pi > \delta$

Pro σ : $p_z-p_z > p_z-s > s-s$



Vazebné parametry

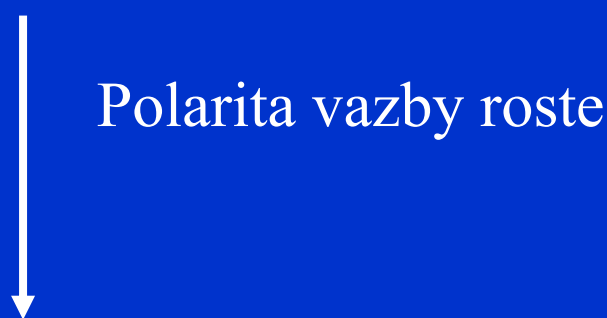
Anion	Řád vazby	Vazebná délka, Å
ClO^-	1.0	1.67
ClO_2^-	1.50	1.58
ClO_3^-	1.67	1.49
ClO_4^-	1.75	1.43
ClO_2^+	2.0	1.39

Řád vazby roste

Vazebná délka klesá

Vazebné parametry

vazba	délka [Å]	energie [kJ mol ⁻¹]
C–C	1.54	348
C=C	1.34	612
C≡C	1.20	837
C–O	1.43	360
C=O	1.23	743
C≡O	1.13	1074
N–N	1.47	163
N=N	1.24	409
N≡N	1.10	944

Vazba	E, kJ mol ⁻¹	Polarita vazby
H-H	431	Nepolární
F-F	155	Nepolární
H-F	565	Polární
C-I	240	
C-Br	276	
C-Cl	339	
C-F	485	
t. tání, °C		
Ge-Ge	188	937
Si-Si	226	1412
C-C	347	3827

Vazebné parametry

Vazba	E, kJ mol ⁻¹	délka, Å
C-I	240	2.16
C-Br	276	1.91
C-Cl	339	1.79
C-F	485	1.40

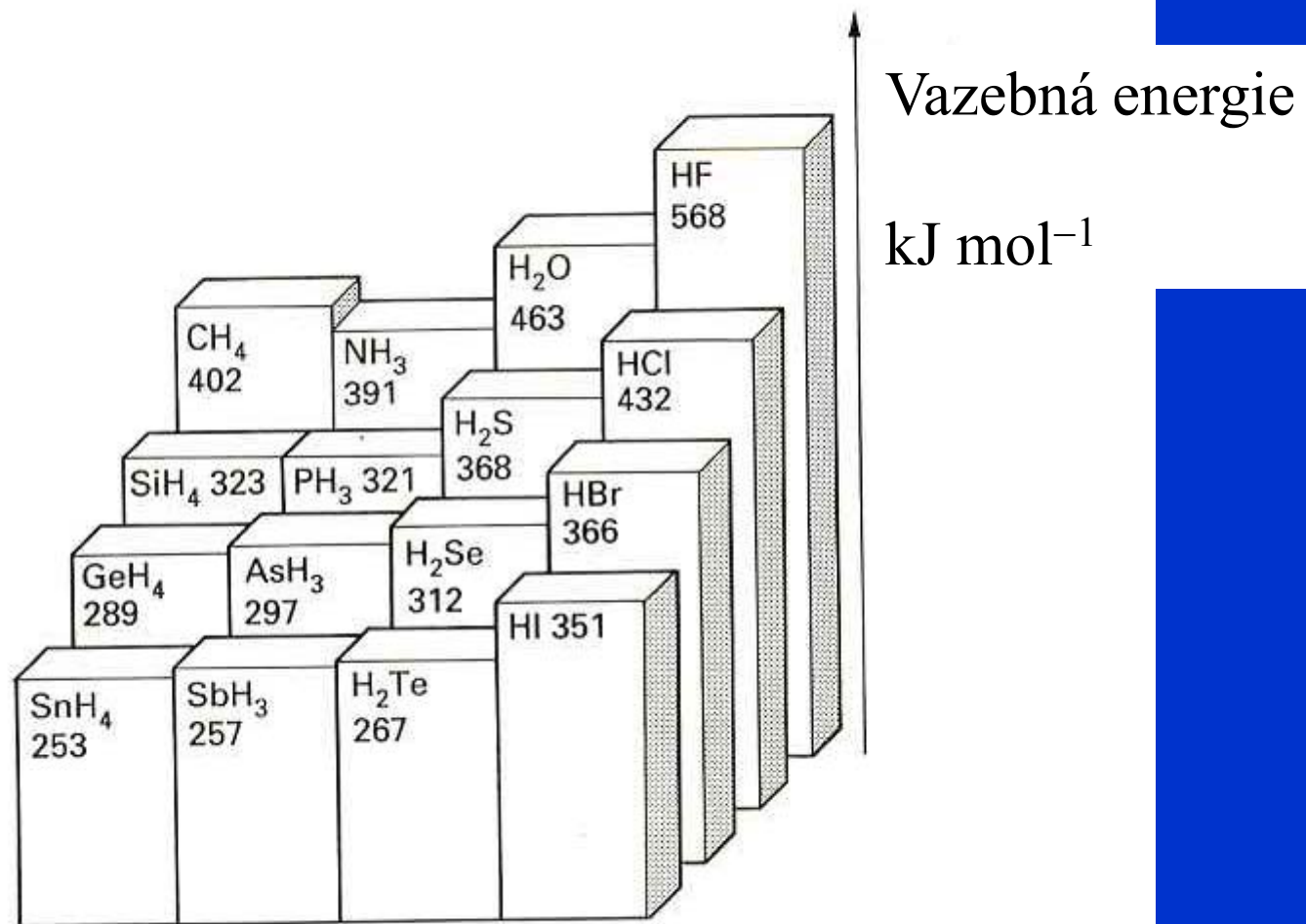
Pauling

$$E_D(\text{AB}) = \{E_D(\text{AA}) \times E_D(\text{BB})\}^{1/2} + \Delta$$

$$\Delta = 96.48 (\chi_A - \chi_B)^2$$

Schomaker-Stevenson

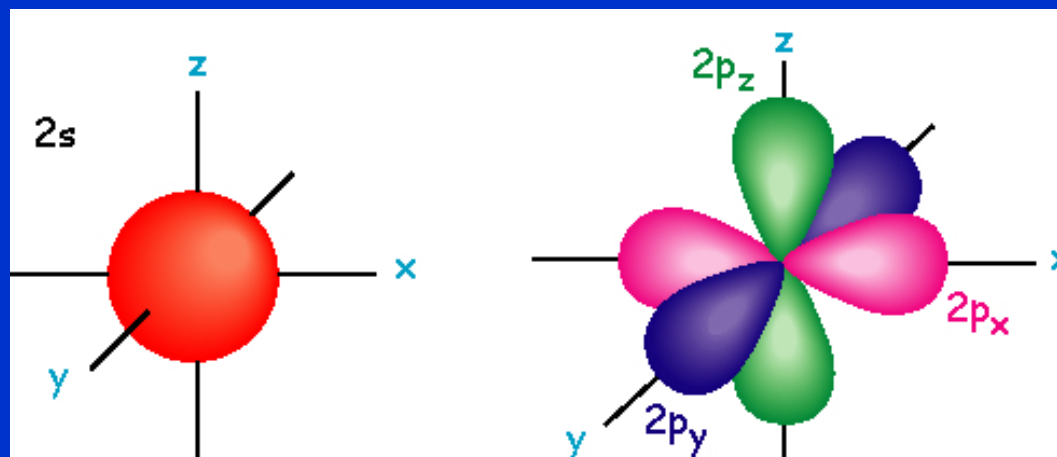
$$r_{\text{AB}} = r_A + r_B - 0.09 |\chi_A - \chi_B|$$





Linus Pauling

Hybridizace



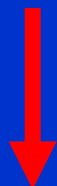
Vazebné úhly 90° jsou vzácné (u prvků hlavních skupin), obvyklé úhly jsou 109 , 120 , 180°

Hybridizace = energetické smíšení a směrové vyrovnání atomových orbitalů na **stejném** atomu

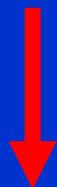
Počet hybridních orbitalů = počet smísených atomových orbitalů

Hybridizace sp

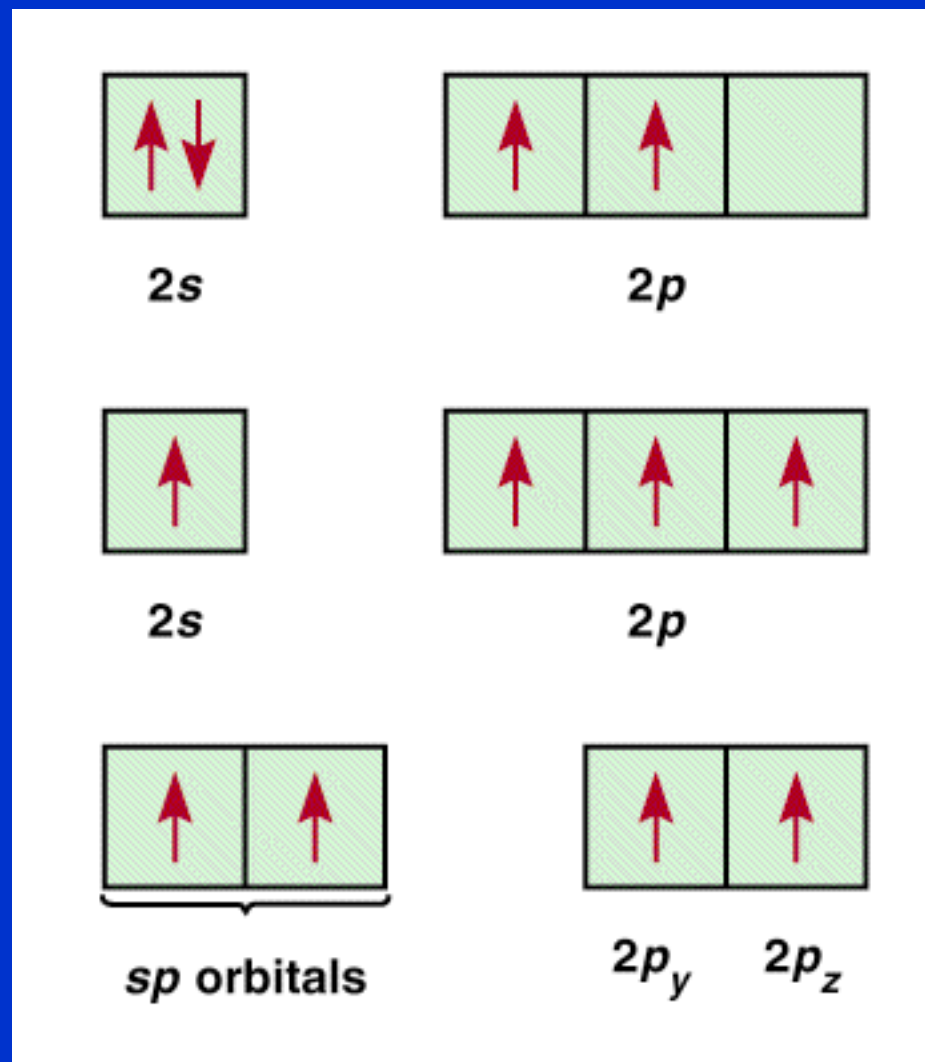
Základní stav



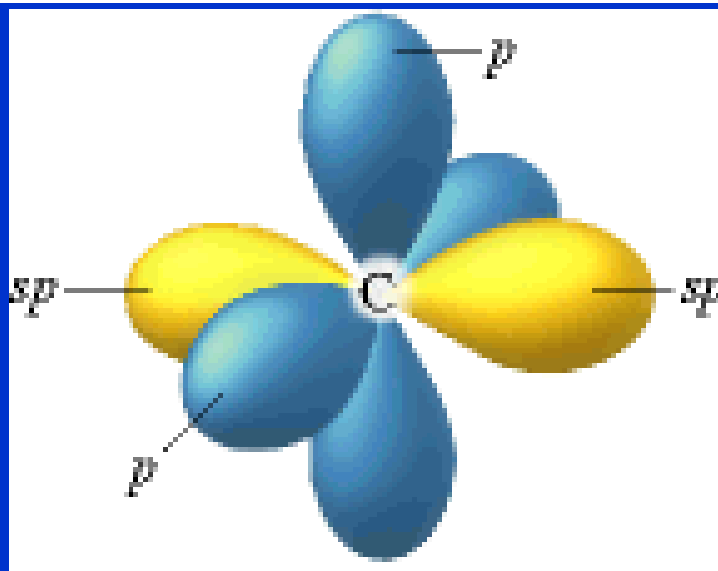
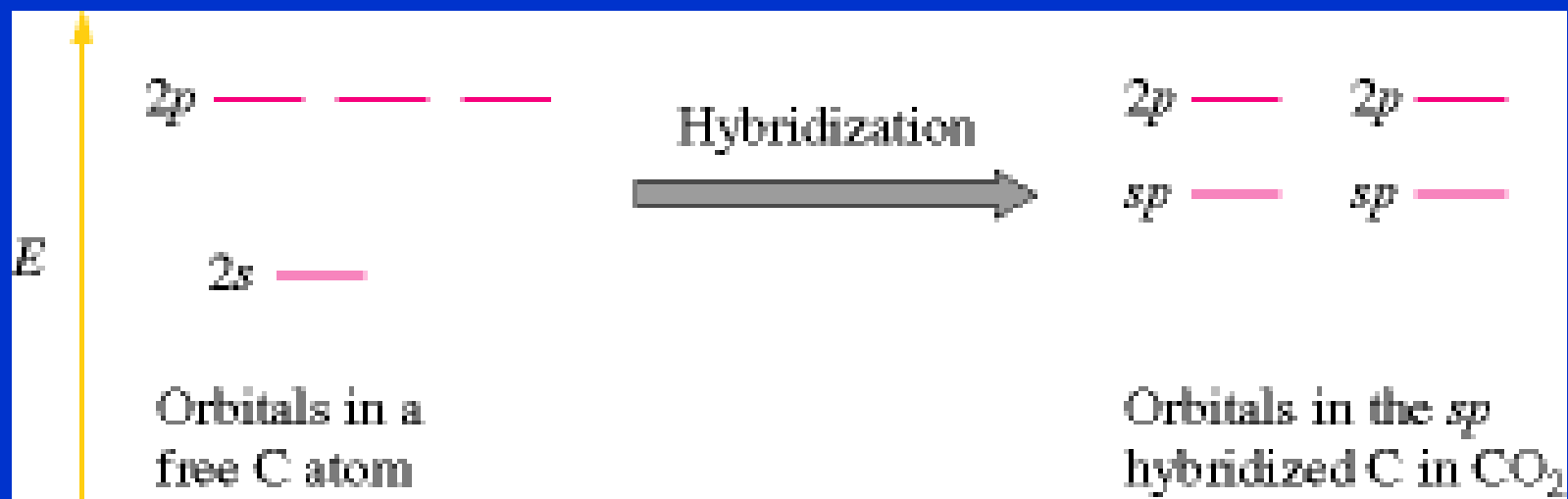
Excitovaný stav



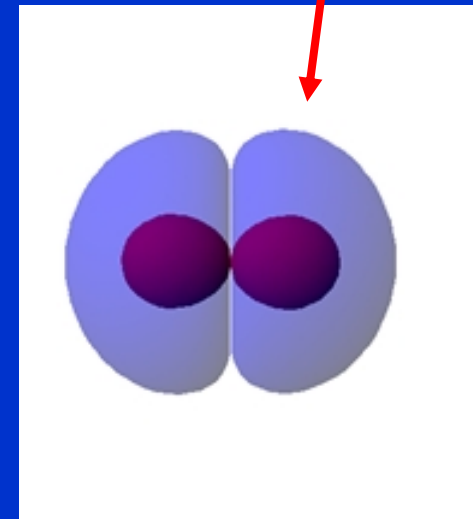
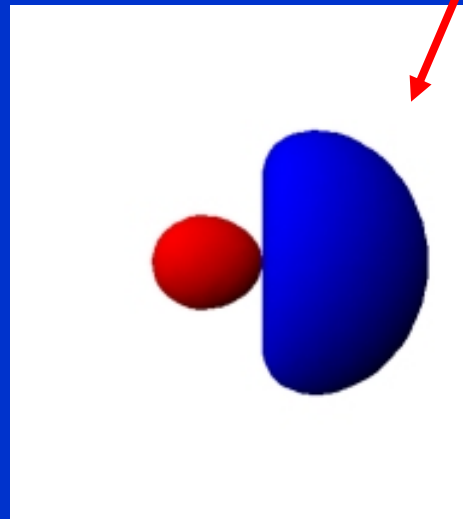
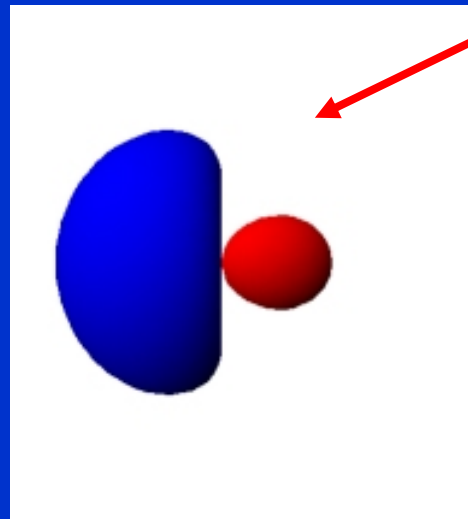
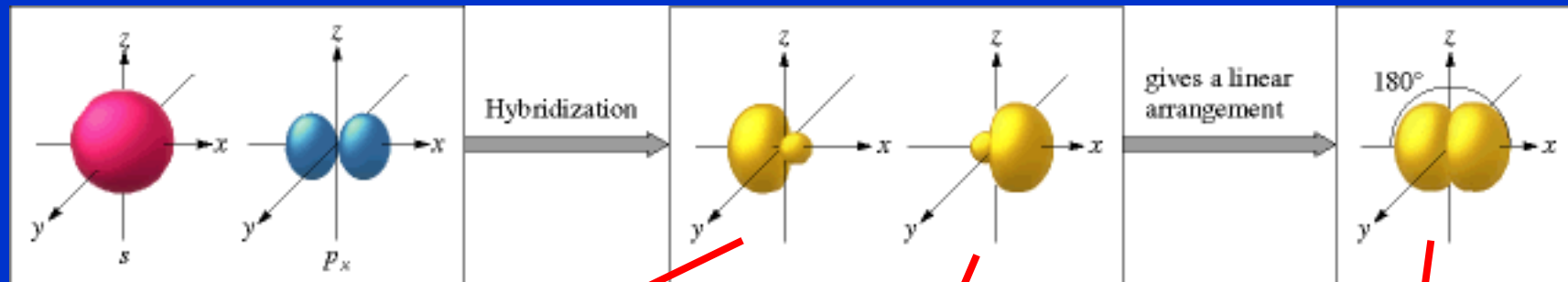
Hybridizovaný stav



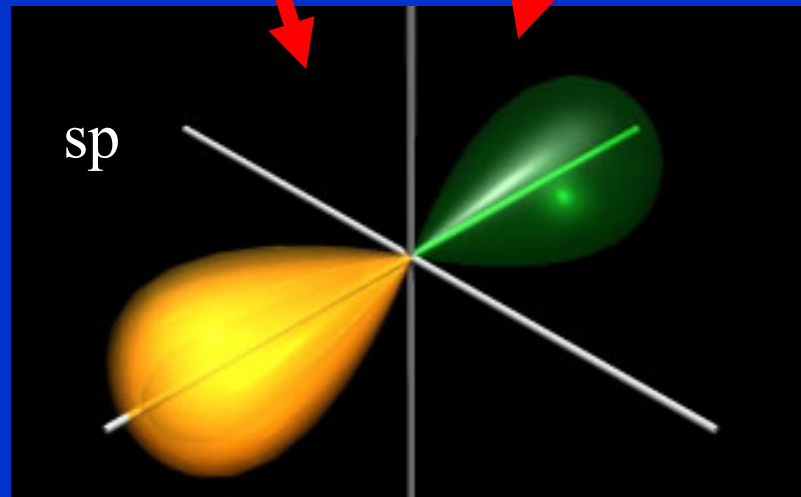
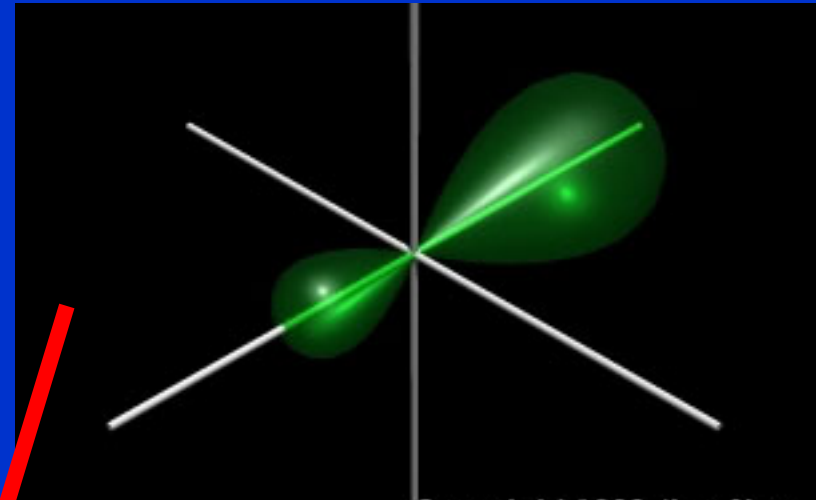
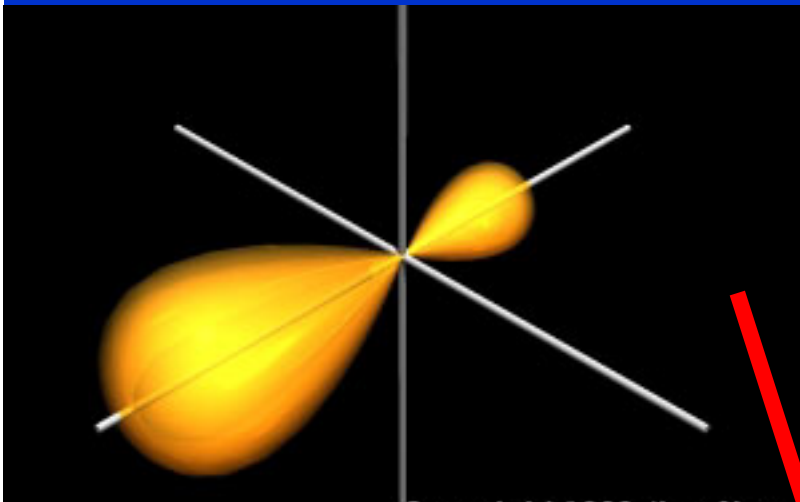
Hybridize sp



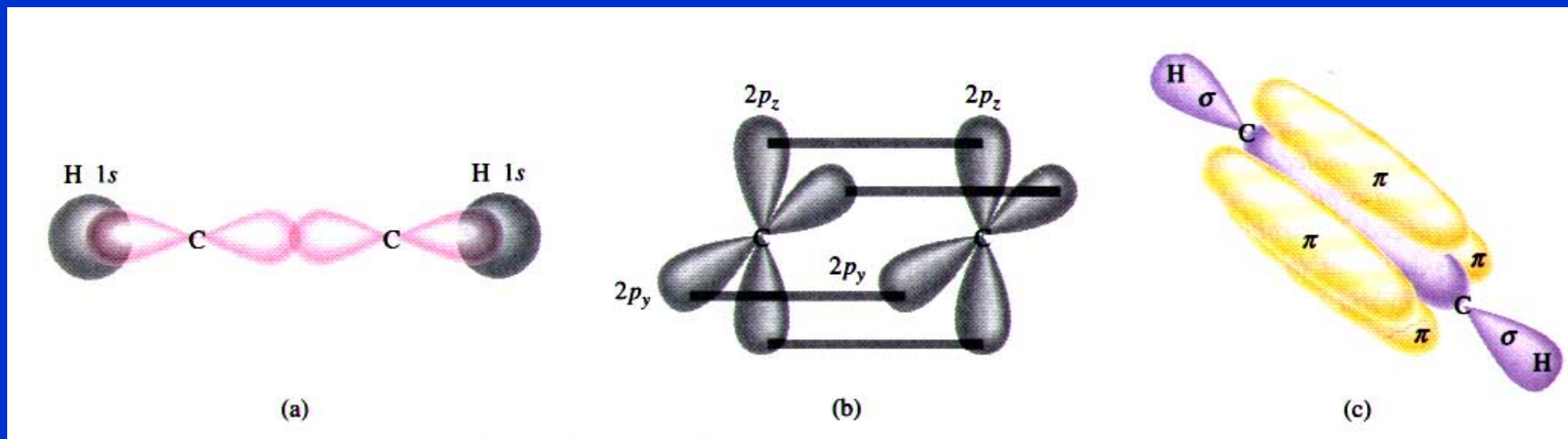
Hybridize sp



Hybridizace sp

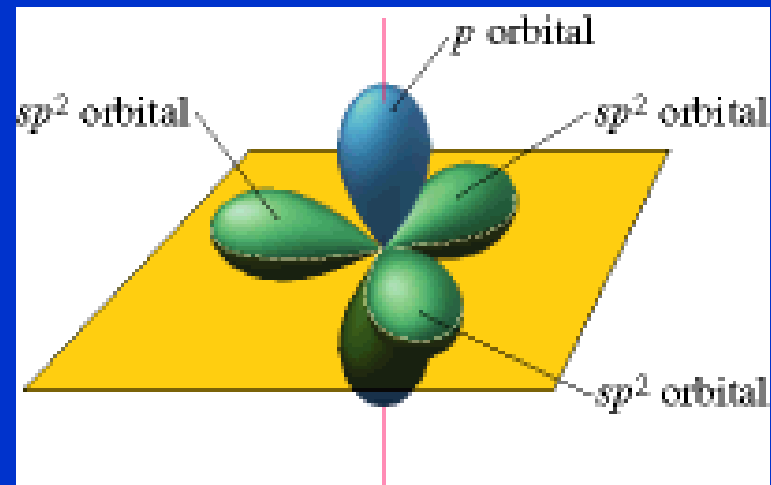
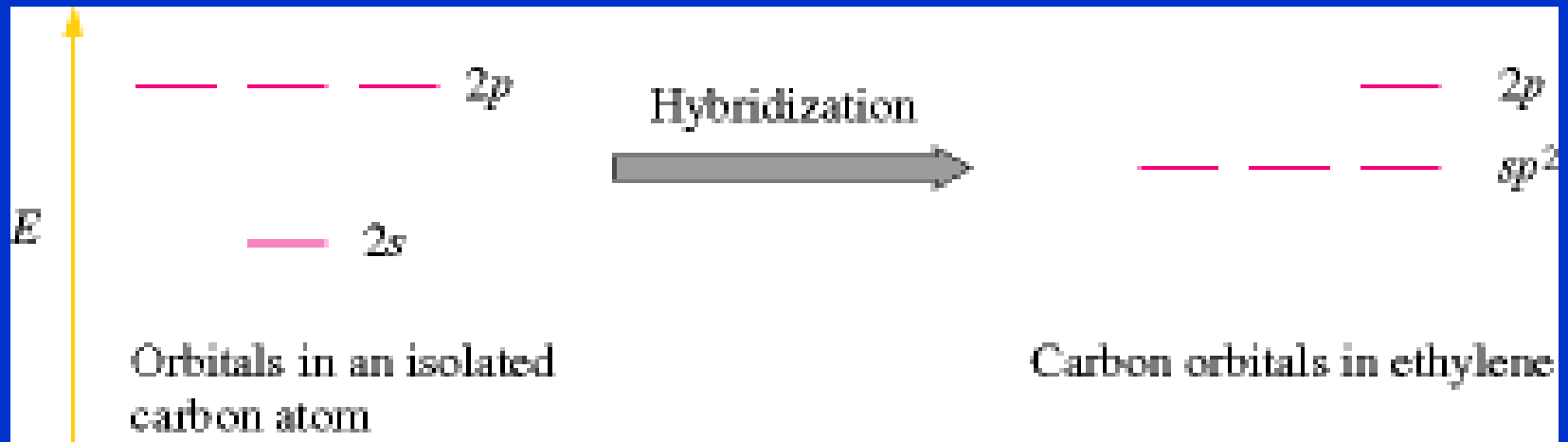


Acetylen

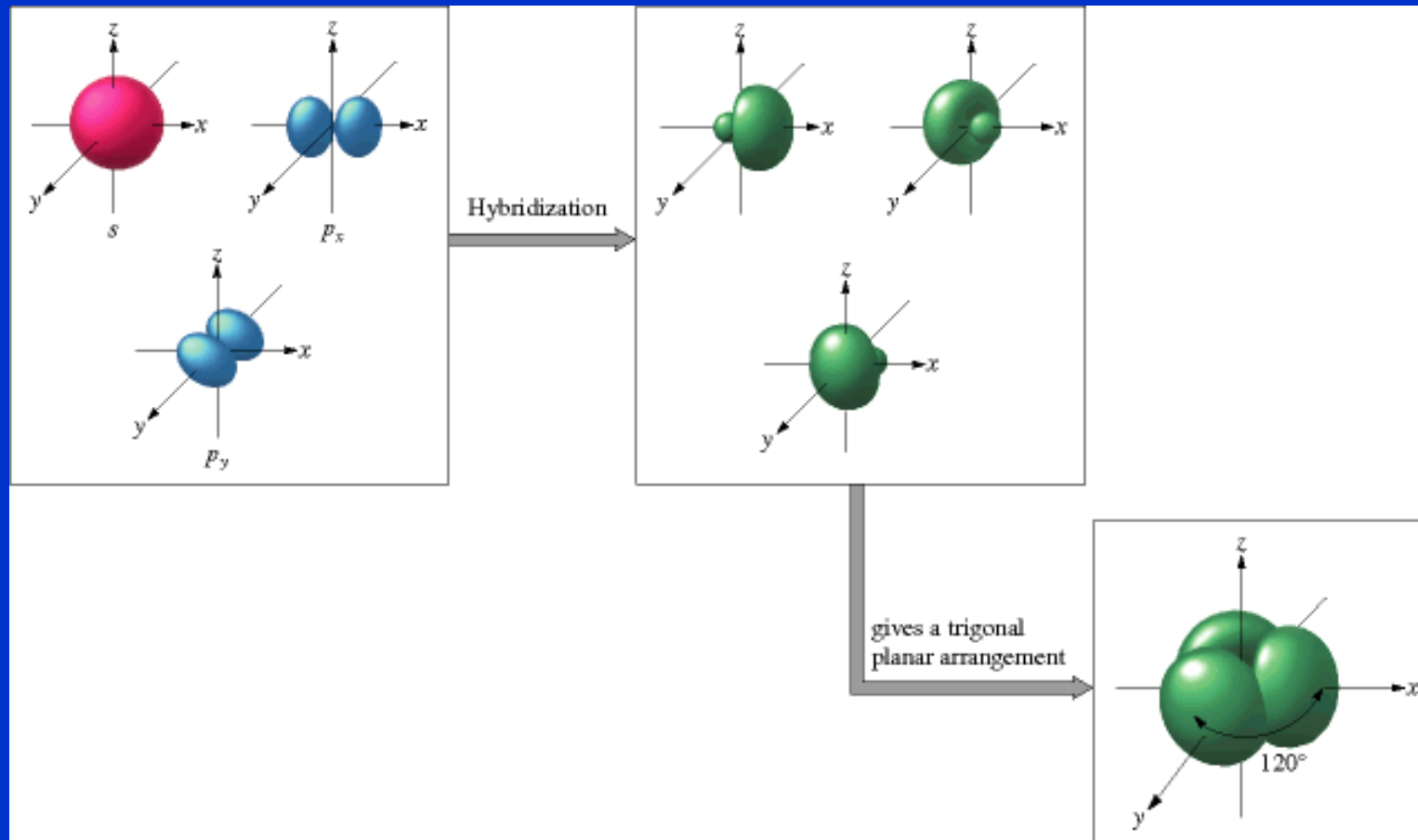


- 2 σ vazby překryvem C(sp)–H(s)
- 1 σ vazba překryvem C(sp)–C(sp)
- 2 navzájem kolmé π -vazby (x, y) překryvem C(p)–C(p)

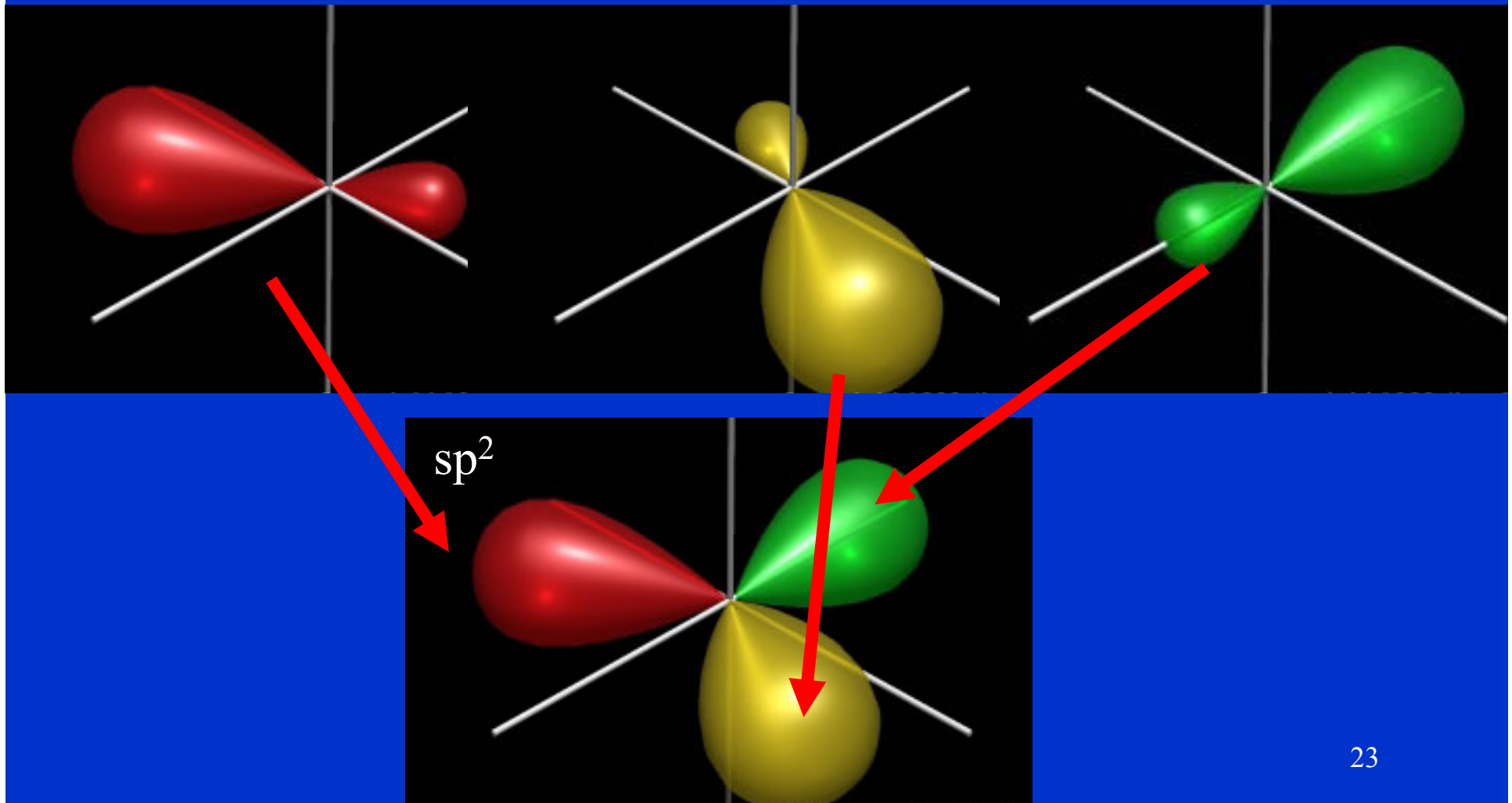
Hybridizace sp^2



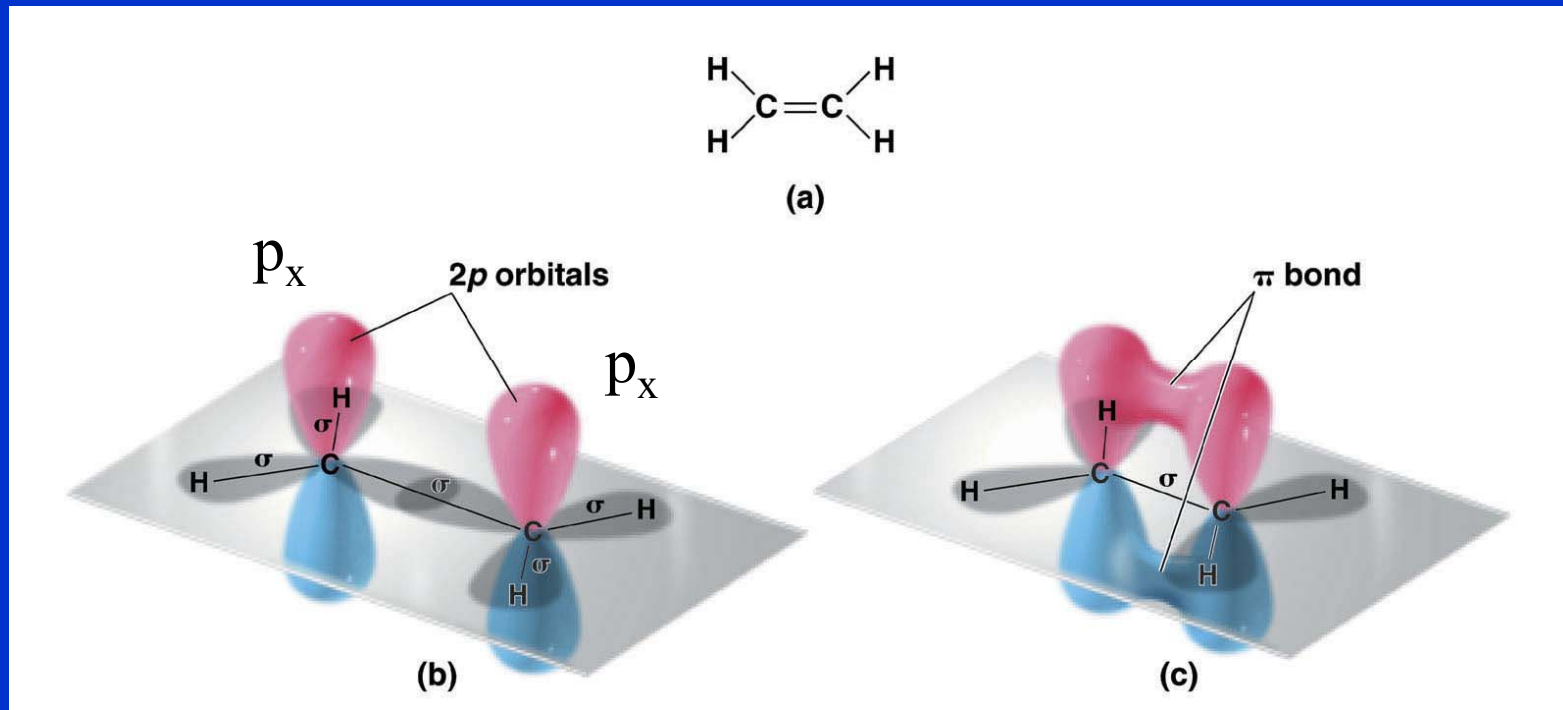
Hybridizace sp^2



Hybridizace sp^2

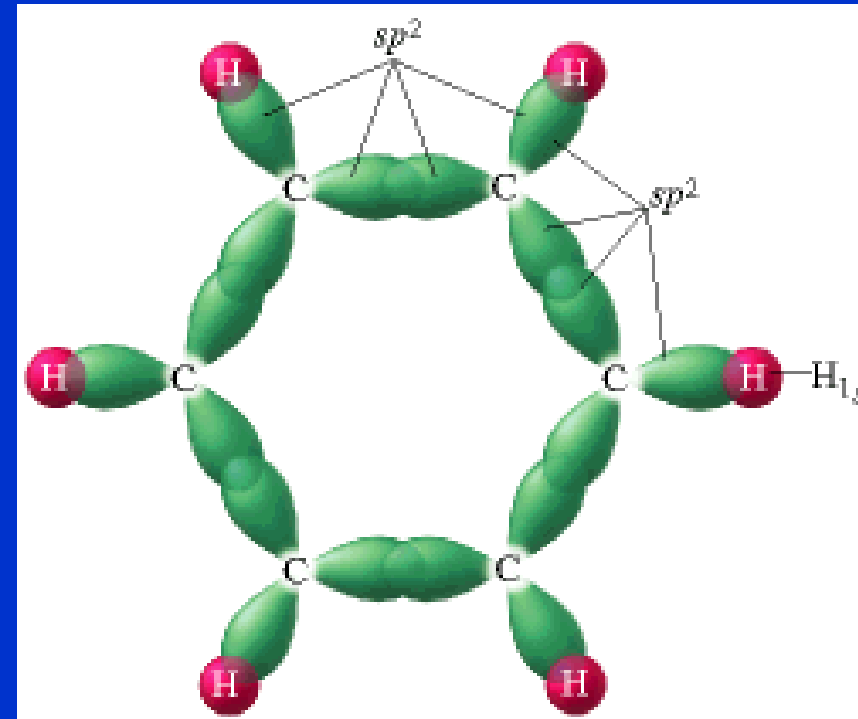
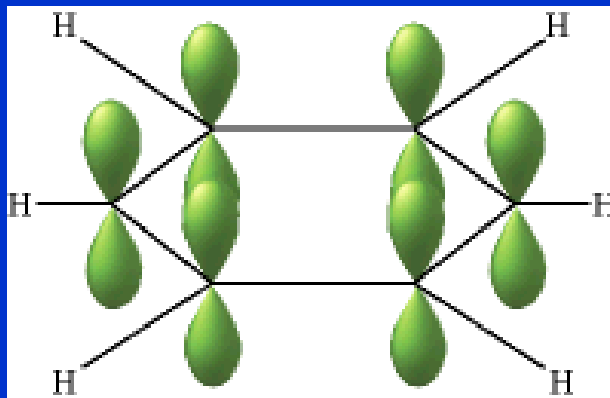
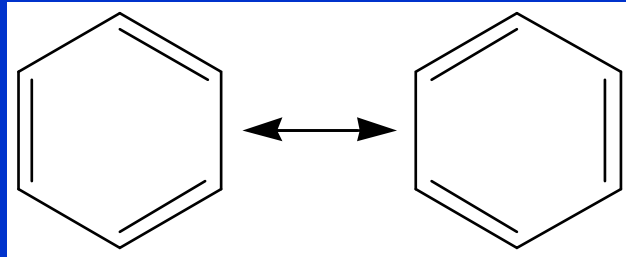


Ethylen



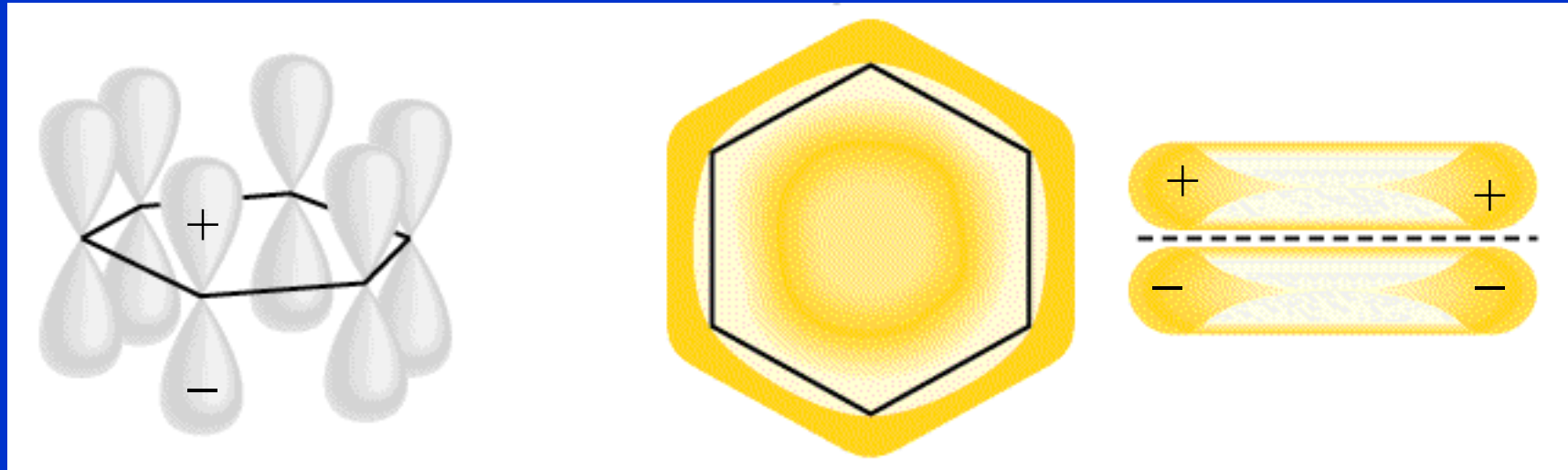
- 4 σ vazby překryvem $C(sp^2)-H(s)$
- 1 σ vazba překryvem $C(sp^2)-C(sp^2)$
- 1 π -vazba překryvem $C(p_x)-C(p_x)$

Benzen

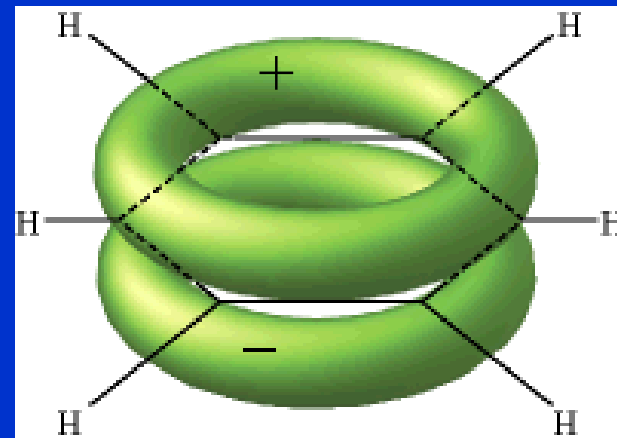


- Každý C použije 3 sp^2 orbitaly pro 3 σ -vazby
2 C – C vazby a 1 C – H vazba
- 1 $2p_x$ orbital na každém C zůstane nepoužitý (pro σ -vazby)

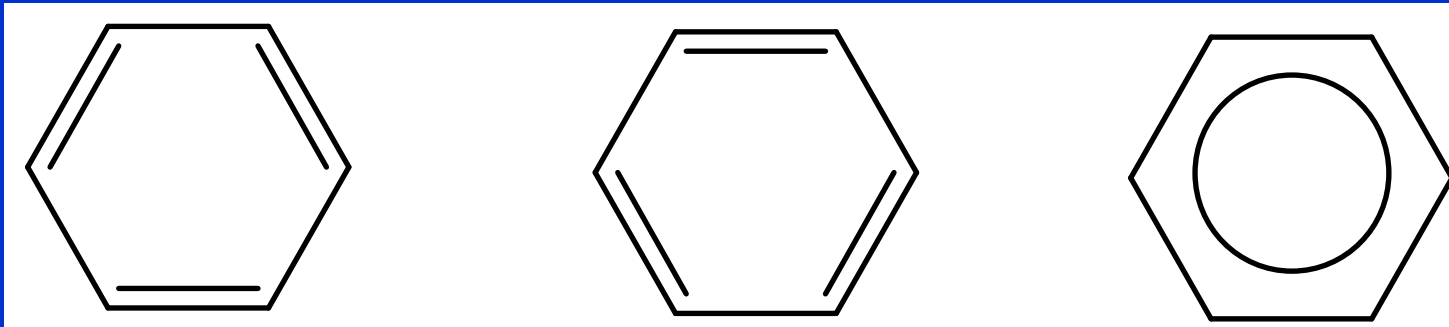
Benzen



6 C $2p_x$ orbitalů použito pro 3 π -vazby



Benzen



(a) Localized π bonds

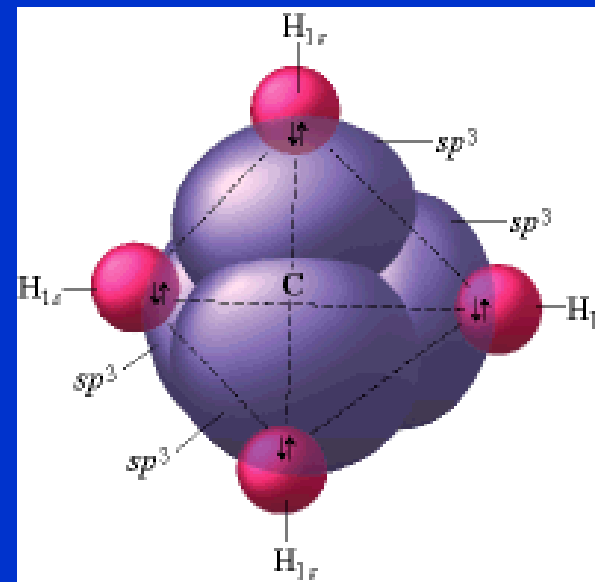
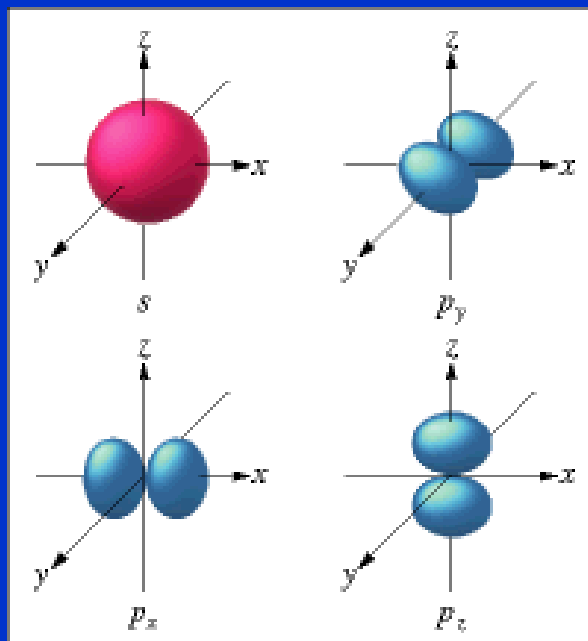
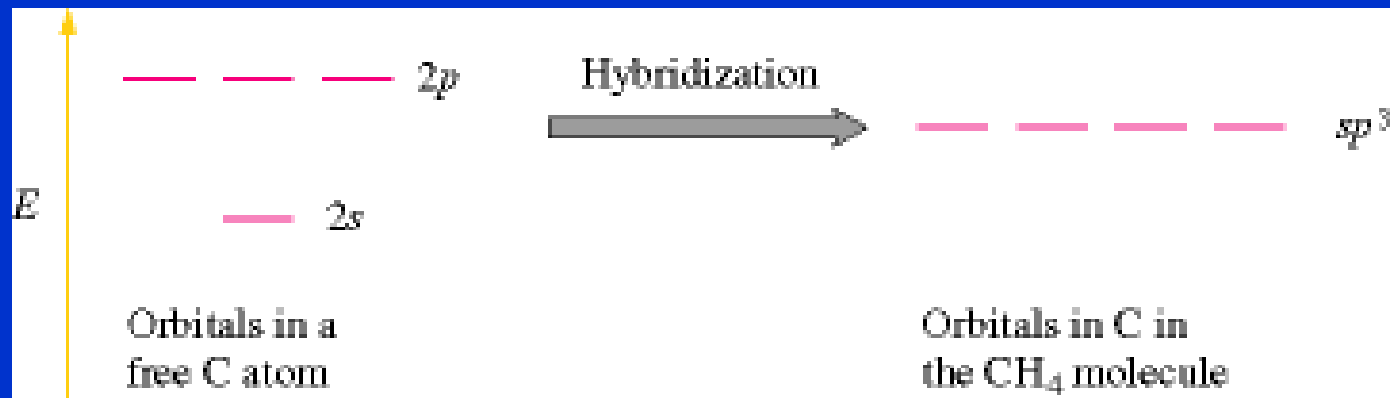


(b) Localized π bonds

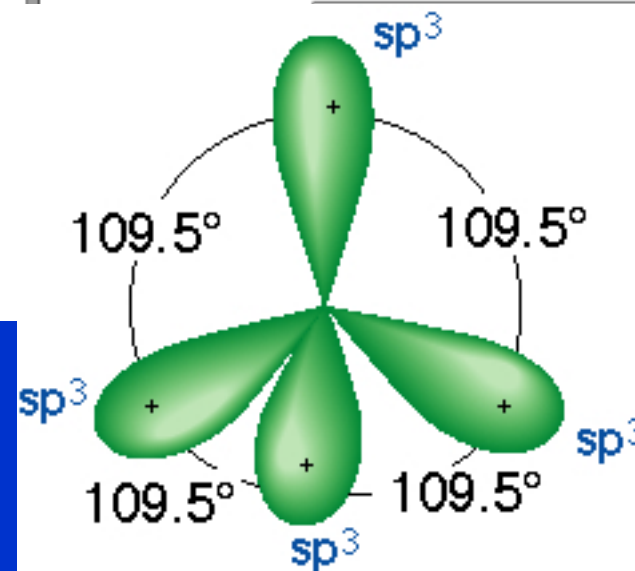
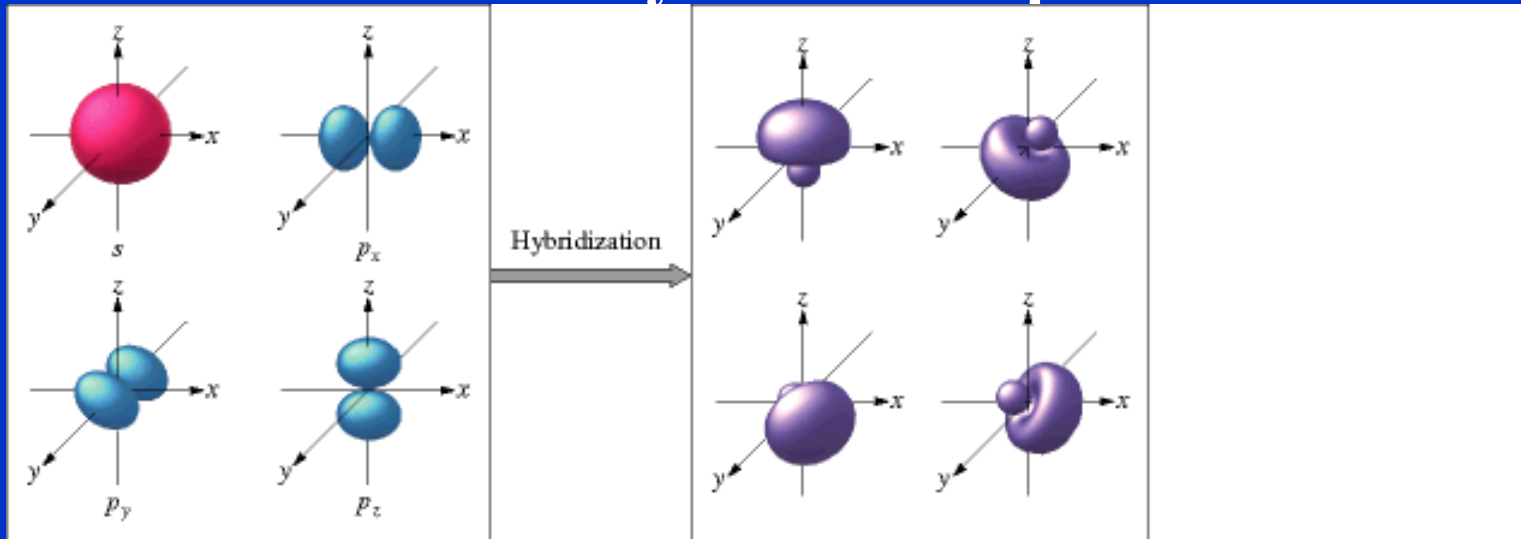


(c) Delocalized π bonds

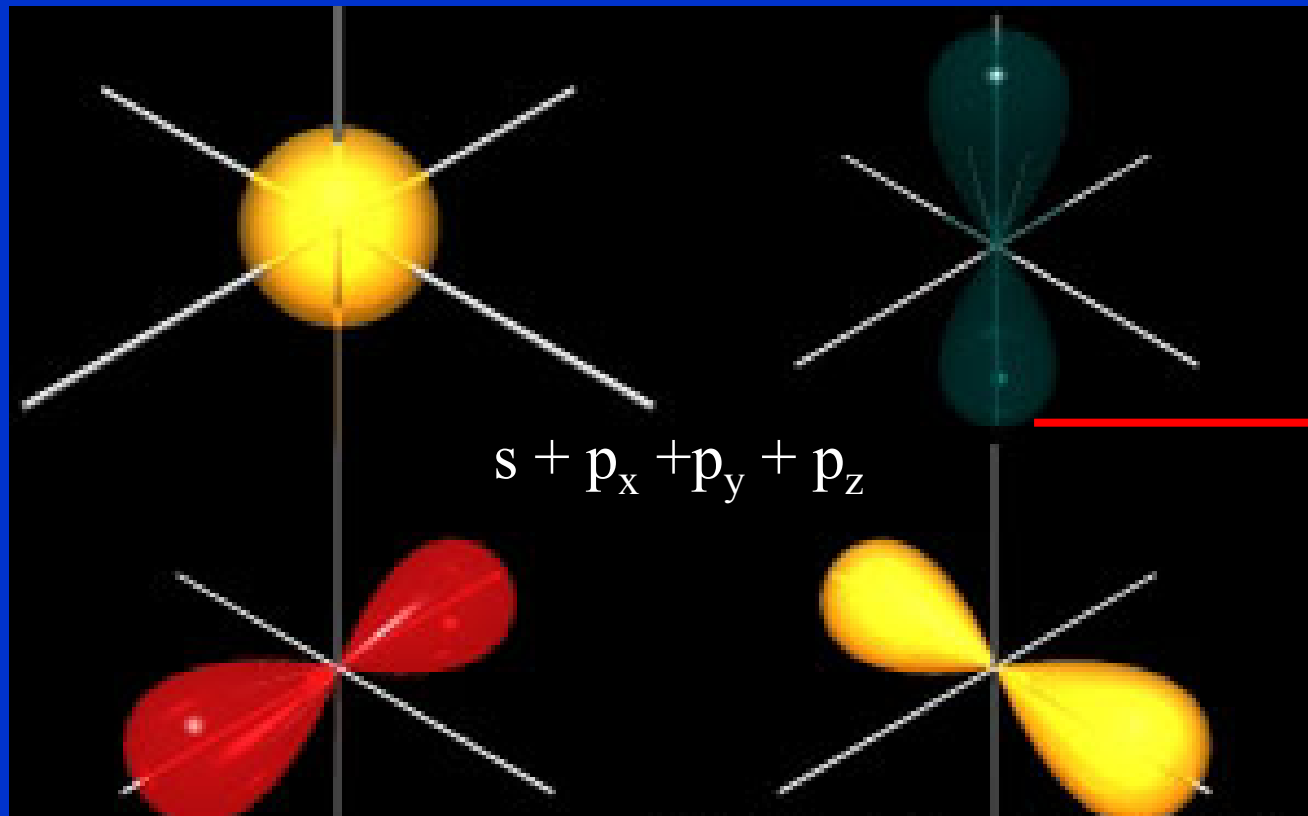
Hybridizace sp^3

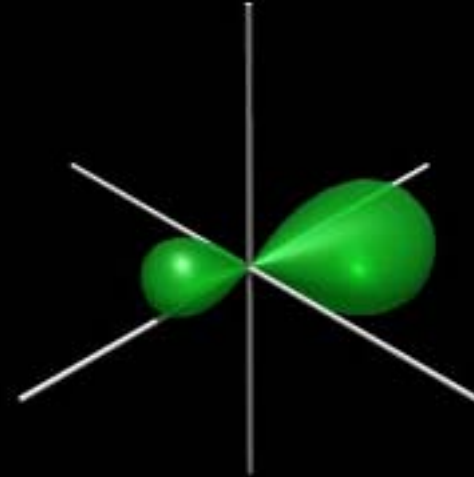
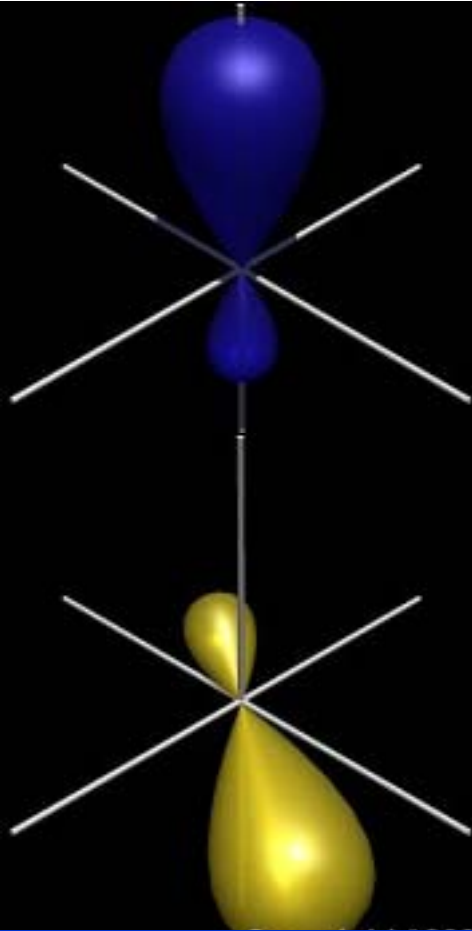
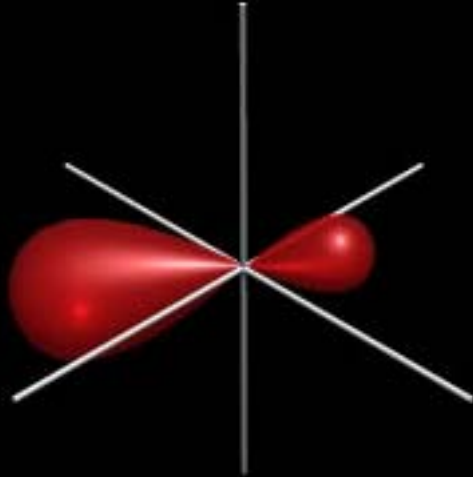


Hybridizace sp^3

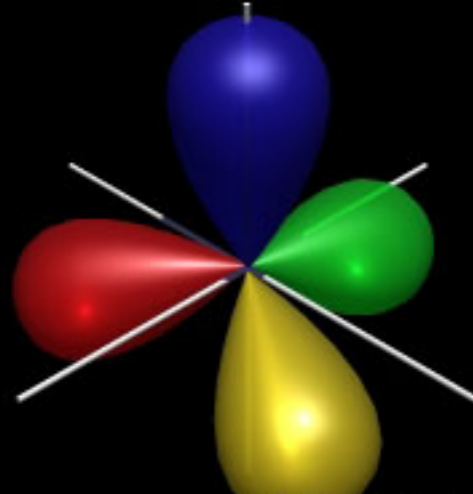


Hybridizace sp^3



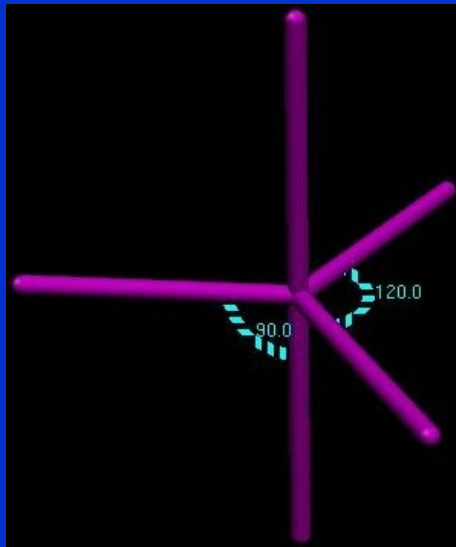


sp^3

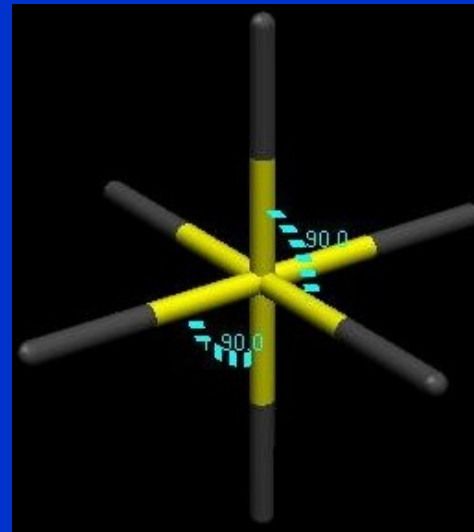


Hybridizace

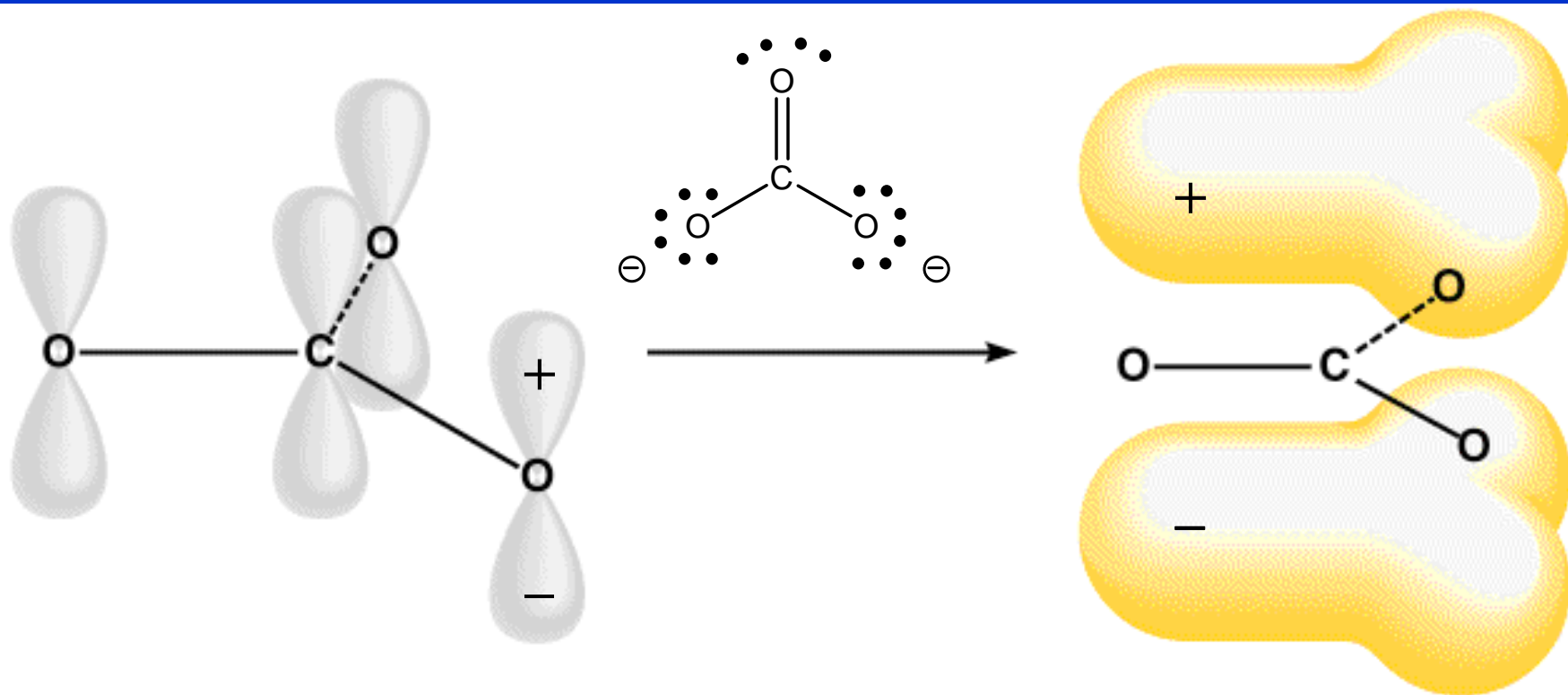
sp^3d



sp^3d^2



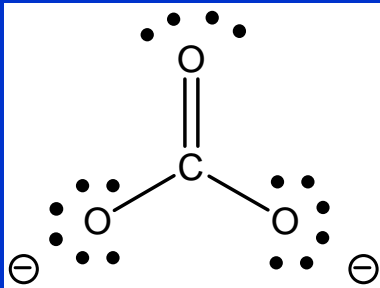
Vazba v CO_3^{2-} a NO_3^-



3 σ vazby překryvem $\text{C}(\text{sp}^2)\text{--O}(\text{sp}^2)$

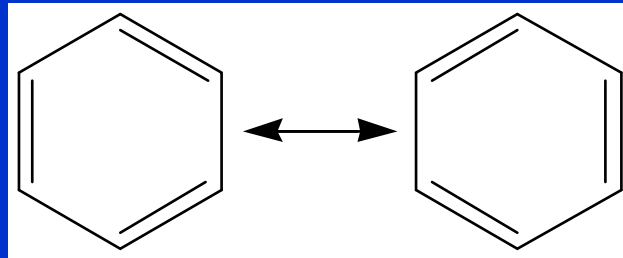
1 π -vazba překryvem $\text{C}(\text{p}_x)\text{--O}(\text{p}_x)$

Řád vazby



4 (3+1) vazebné elektronové páry / 3 vazby

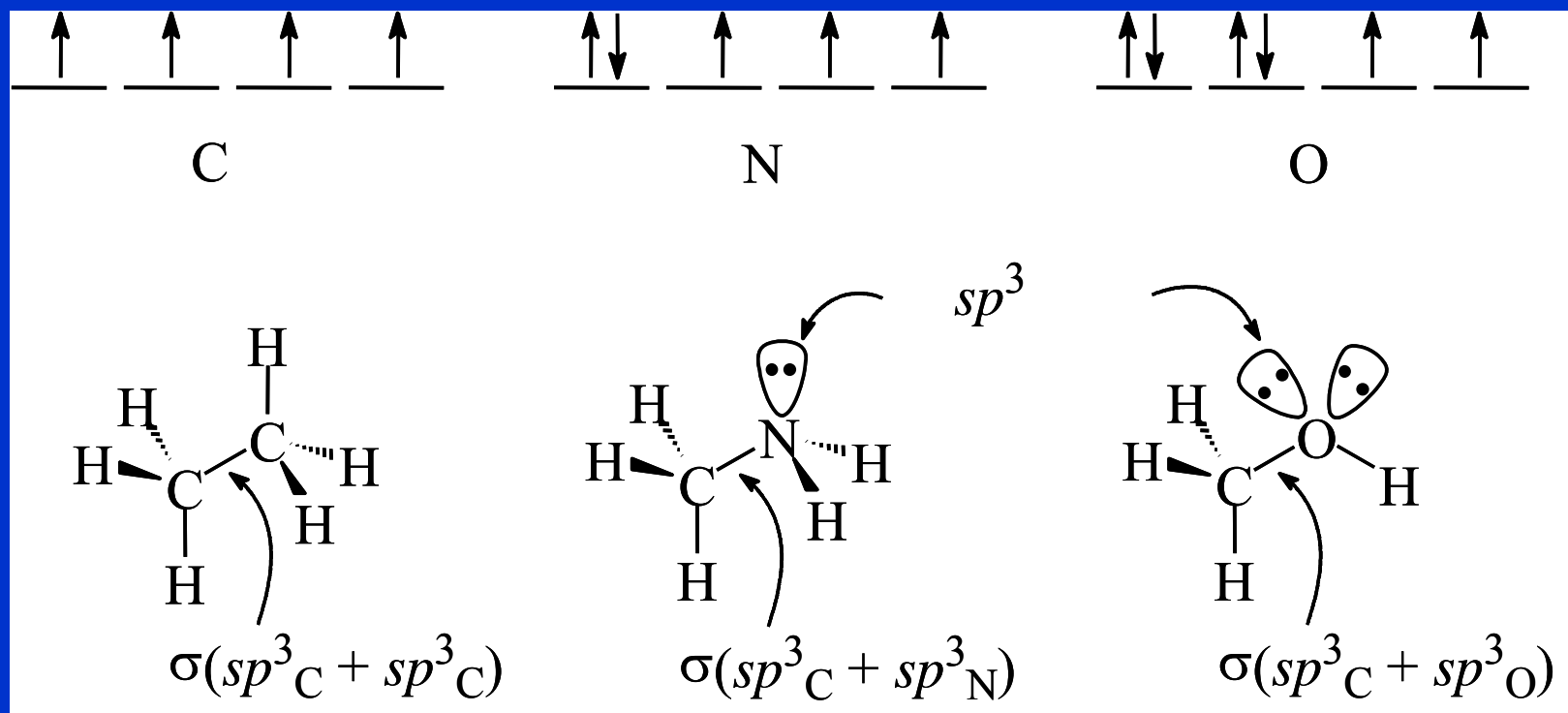
Řád vazby = 1.3333



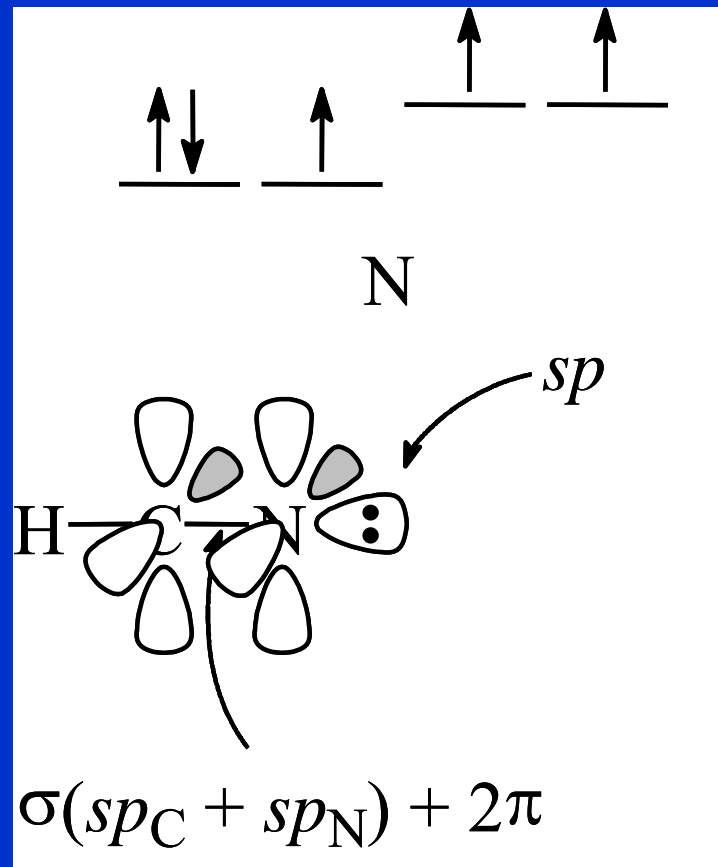
9 (6+3) vazebných elektronových párů / 6 vazeb

Řád vazby = 1.5

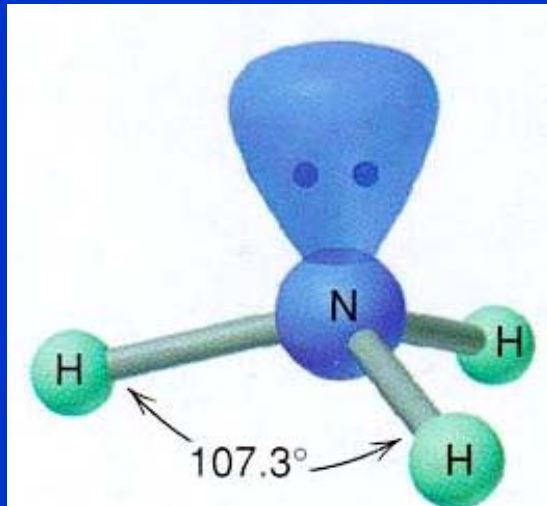
Vazba v C_2H_6 , CH_3NH_2 a CH_3OH



Vazba v HC≡N



Elektronegativita a vazebné úhly



Vazebný úhel Hybridizace

NH ₃	107.3°	sp ³
PH ₃	93.8°	
AsH ₃	91.8°	
SbH ₃	91.3°	s + 3p



NF₃ 102.5°

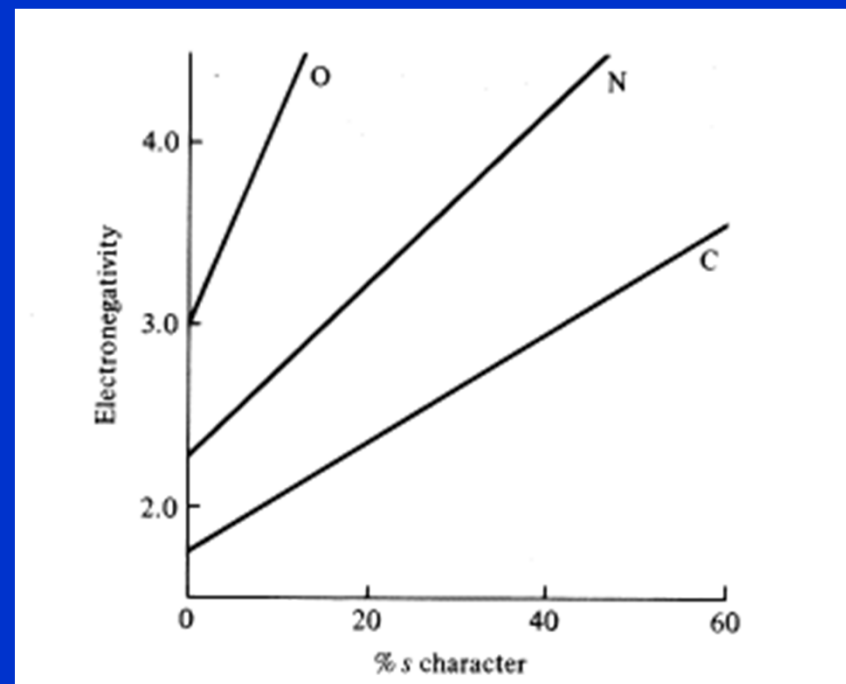
Rostoucí $\Delta\chi$ snižuje
vazebné úhly

OH₂ 104.5°

OF₂ 103.2°

Hybridizace a elektronegativita

Hybridizace	% s	% p
sp	50	50
sp ²	33	66
sp ³	25	75



s-charakter

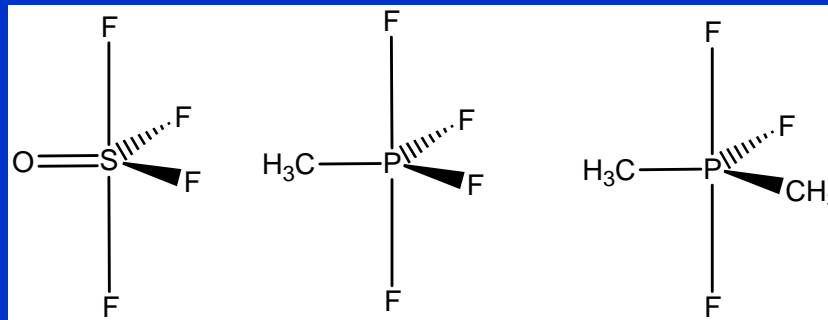
p-charakter

Elektron v s-orbitalu je vázán pevněji než v p-orbitalu

Orbital s vyšším s-charakterem má vyšší elektronegativitu

Bentovo pravidlo

Elektronegativnější substituenty preferují hybridní orbitály s menším s-podílem a naopak elektropozitivní substituenty (lepší donory) preferují hybridní orbitály s větším s-podílem.



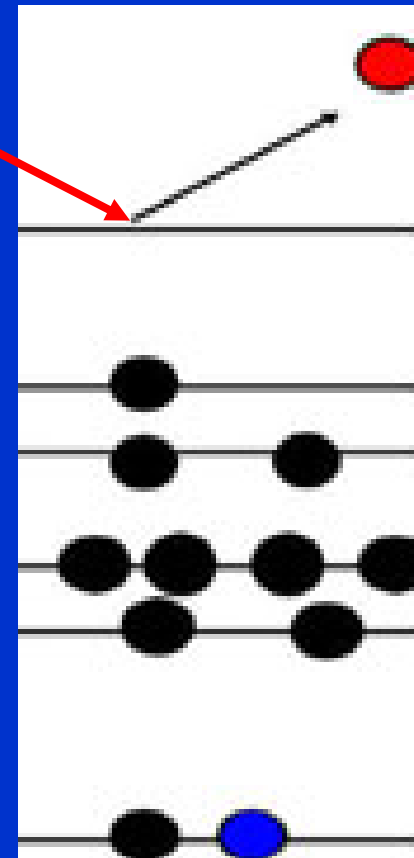
Lepší donory obsazují ekvatoriální rovinu v TBP (sp^2) a akceptory obsazují axiální polohy (pd).

Volný elektronový pár je nejlepší donor = substituent s nulovou elektronegativitou

PES = Fotoelektronová spektroskopie

$$h\nu = IE + E_{kin}$$

$h\nu$



E_{kin}

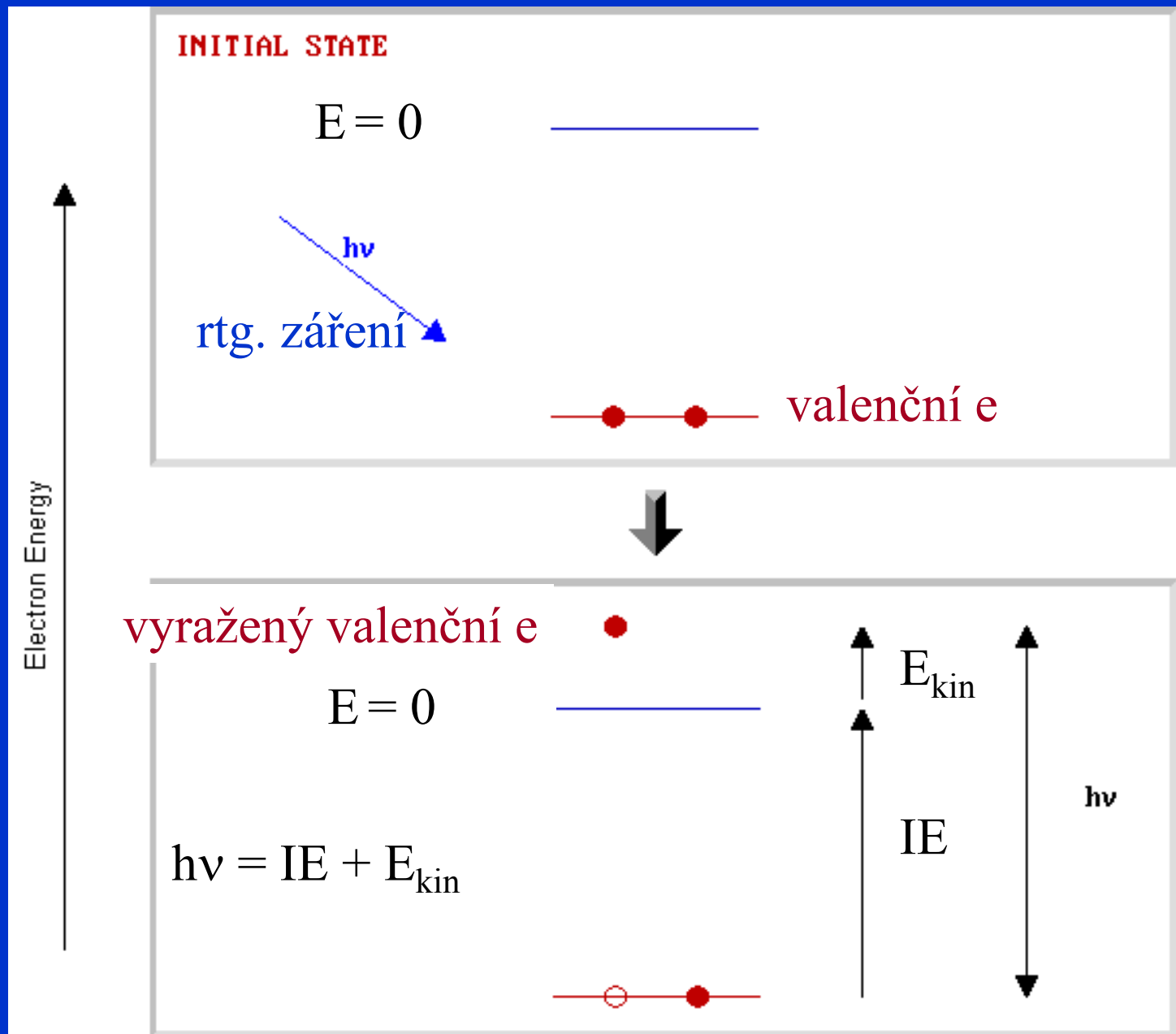
měříme

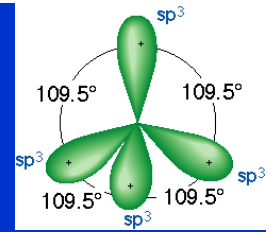
X-ray Fotoelektronová Spektroskopie (XPS)

- měkké rtg. záření (200 - 2000 eV)
vyráží vnitřní e

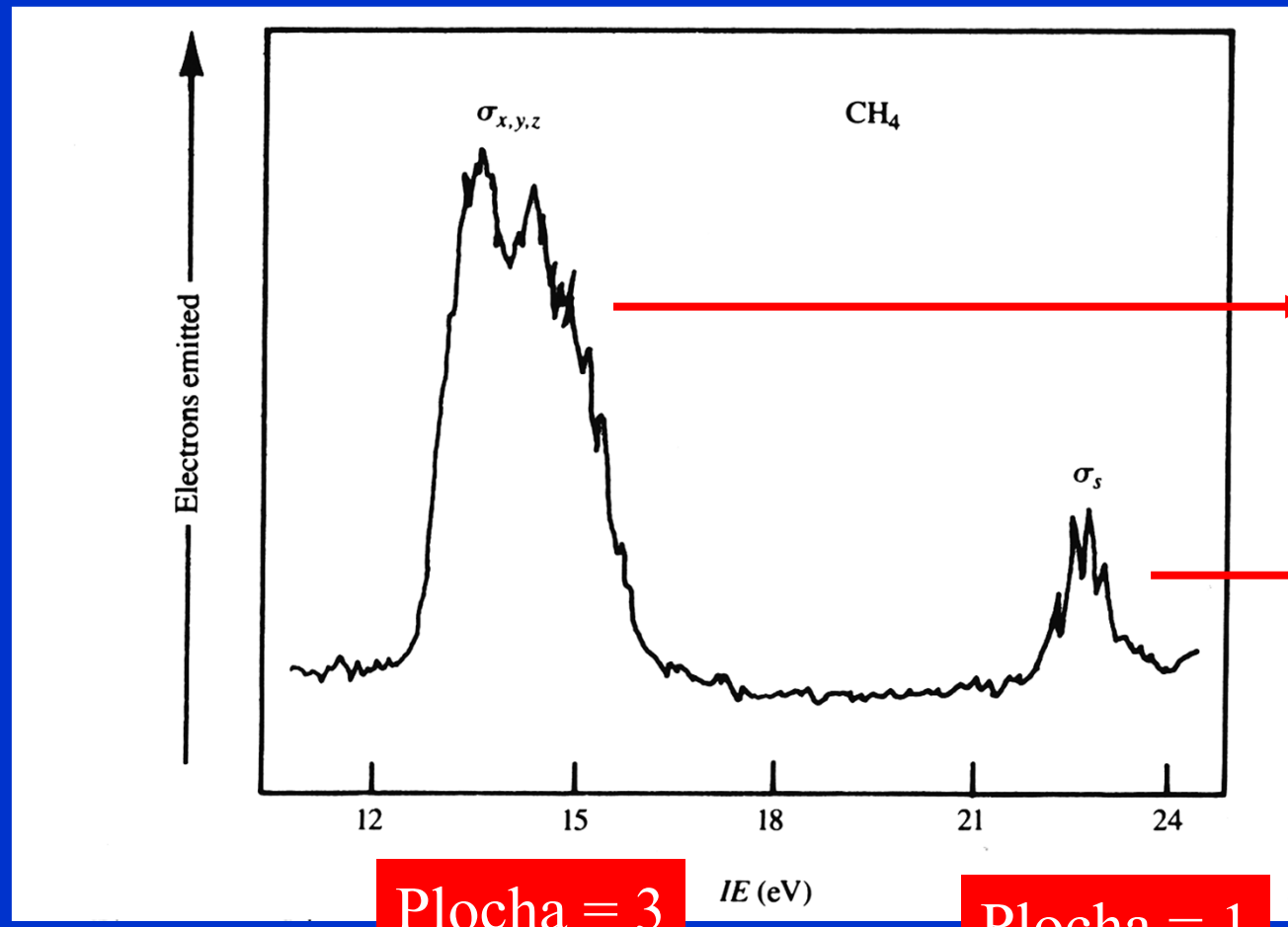
UV Fotoelektronová Spektroskopie (UPS)

- vakuové UV záření (10 - 45 eV)
vyráží valenční e.



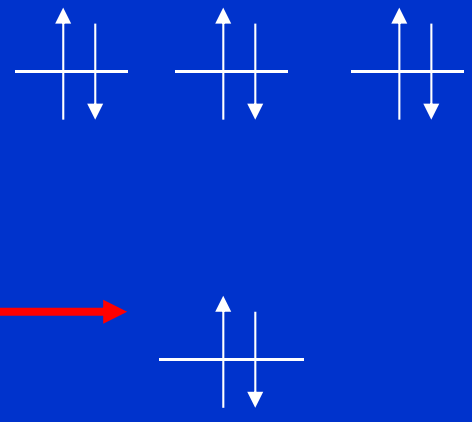


PES methanu nesouhlasí s modelem 4 sp³

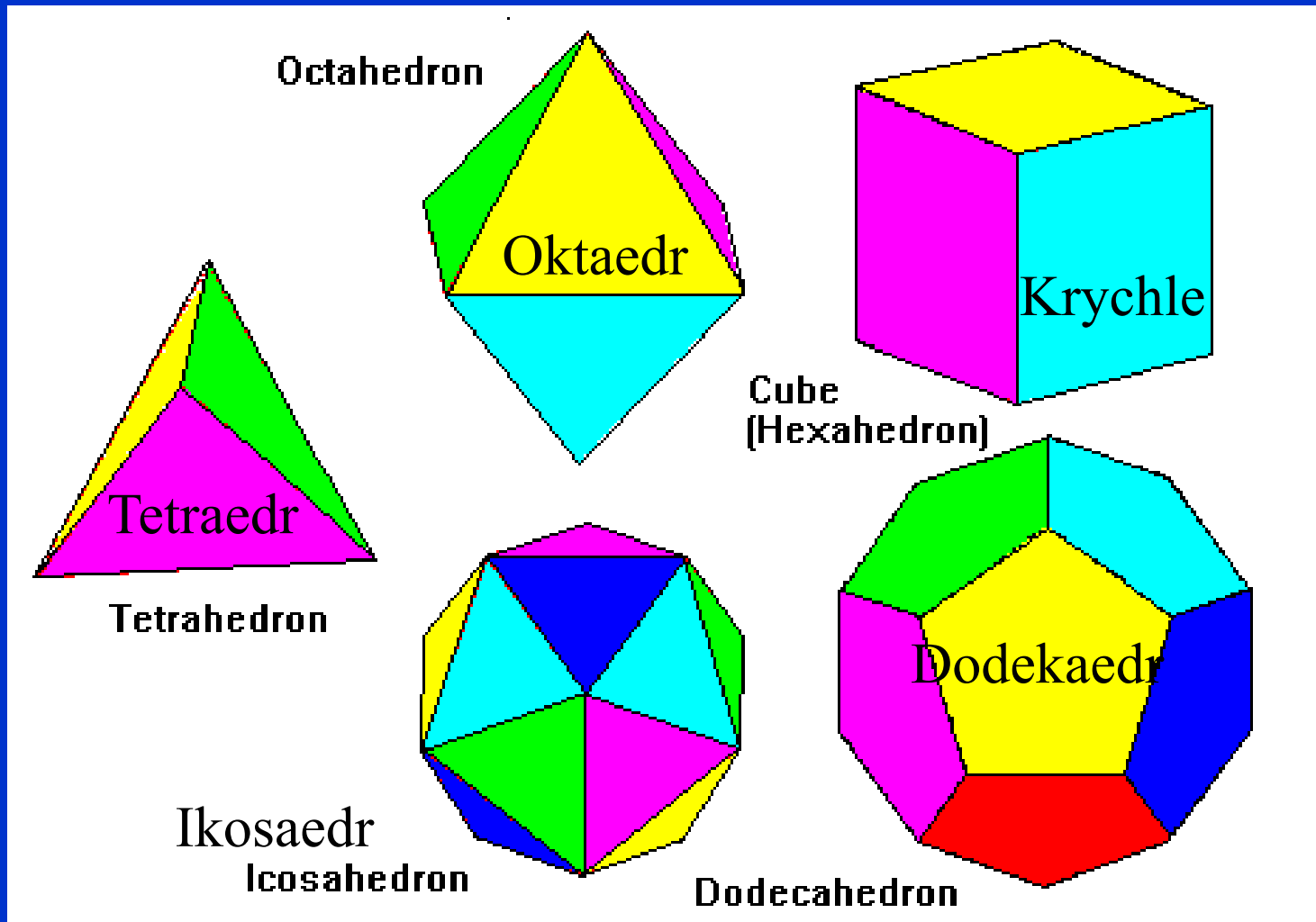


Plocha = 3

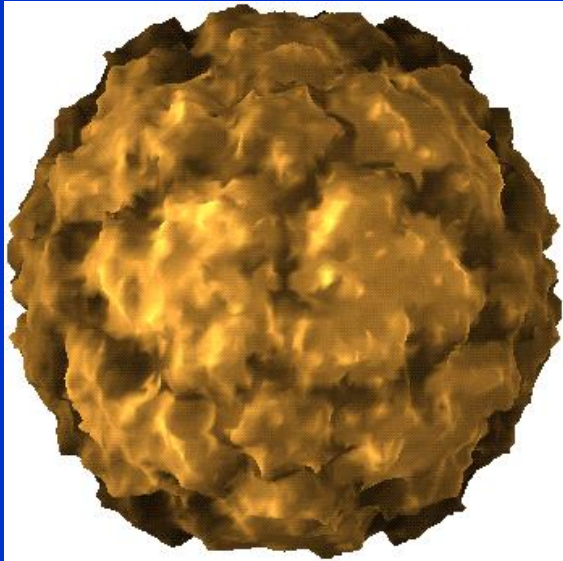
Plocha = 1



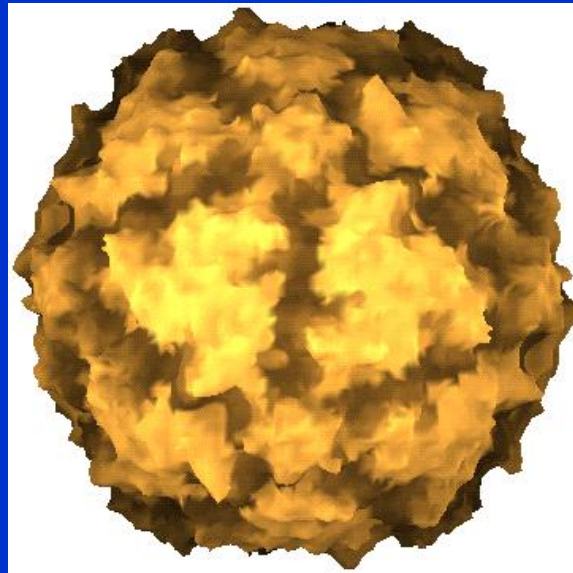
Symetrie – Platonovská tělesa



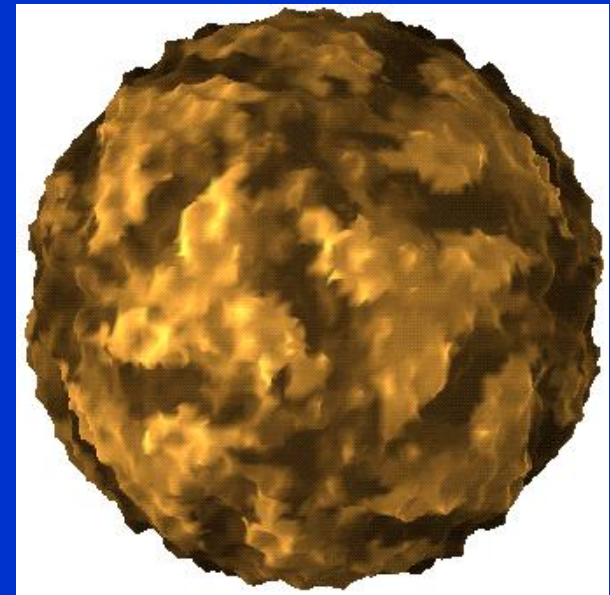
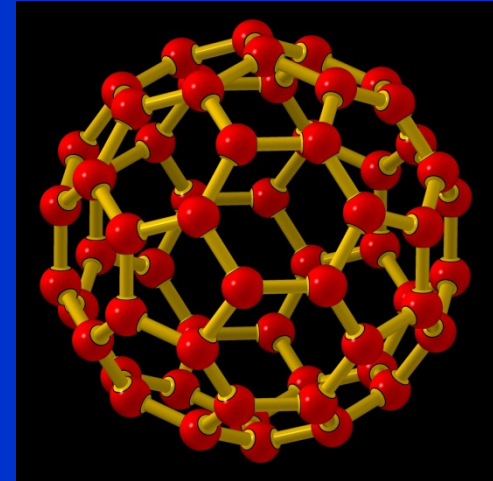
Symetrie



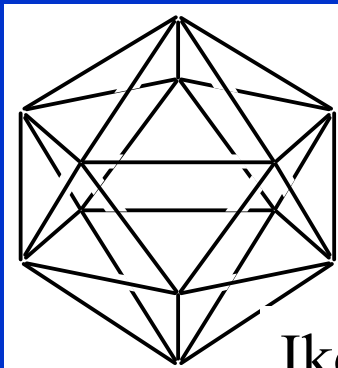
Virus rýmy



Virus obrny



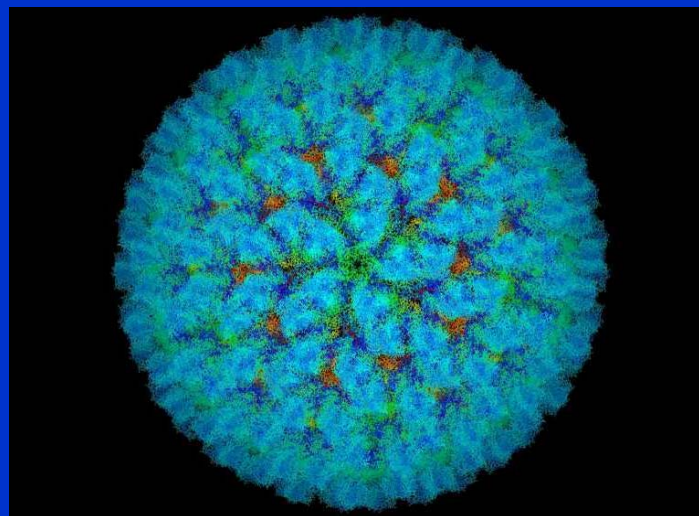
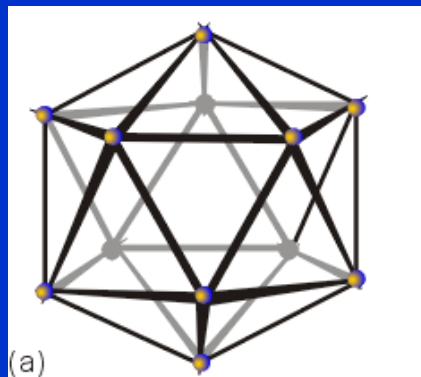
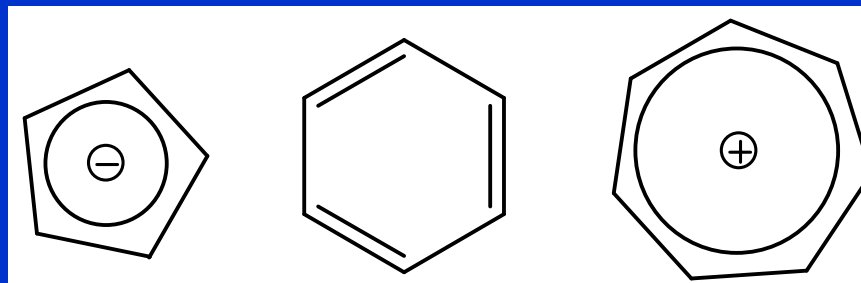
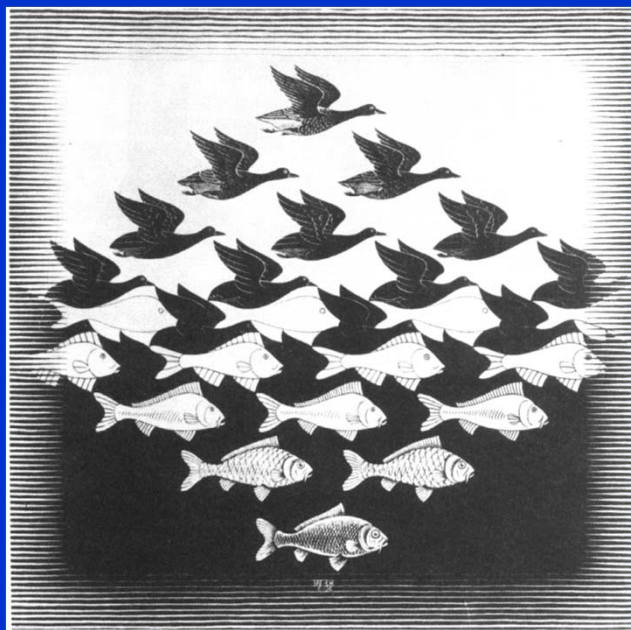
Virus slintavky a kulhavky



Ikosaedr

Symetrie molekul

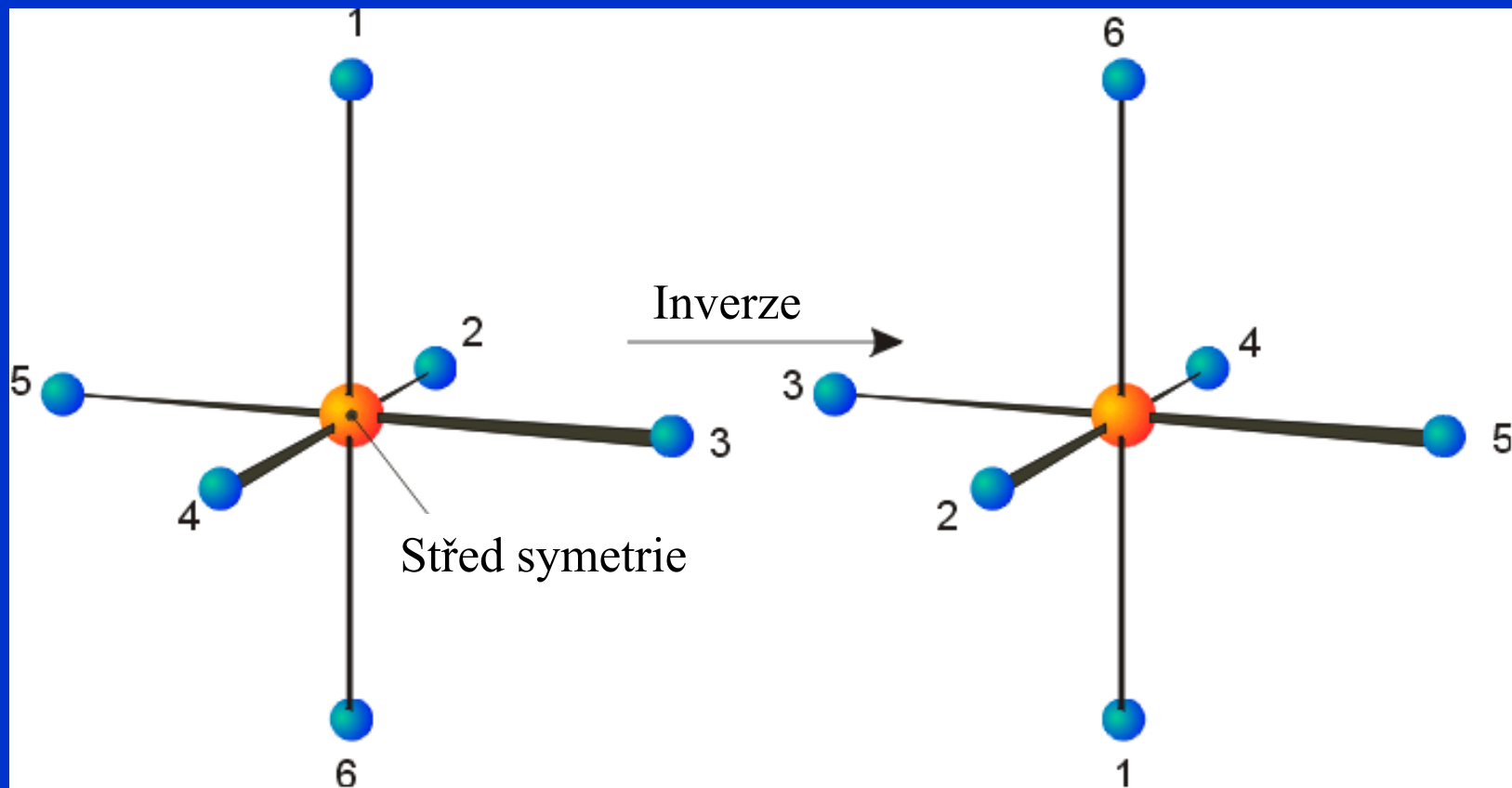
Jak jsou atomy v molekule uspořádány = ekvivalentní atomy



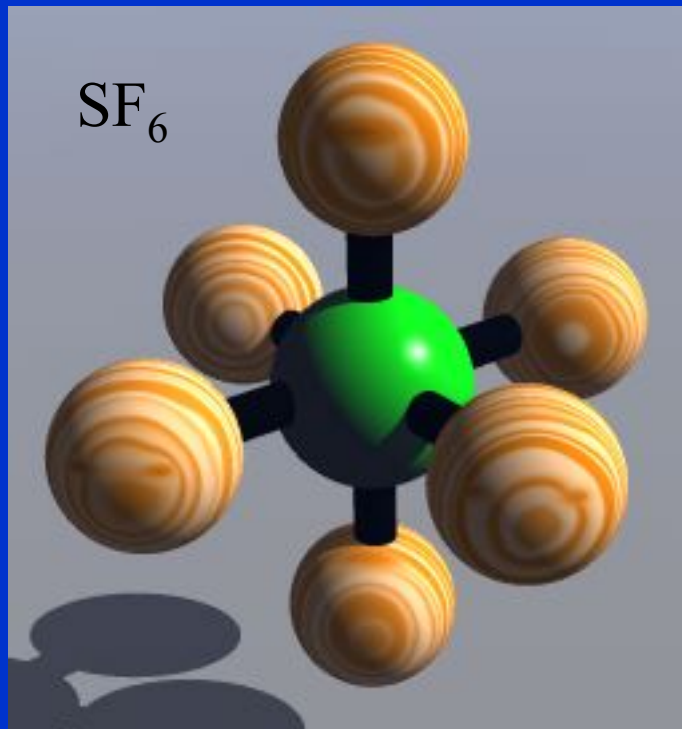
Prvky a operace symetrie

Značka	Prvek	Operace	Pozn.
E	Identita	Identita	Bezezměny, (= 1)
i	Střed symetrie (inverze) BOD	Inverze	Převrácení přes střed
C_n	Rotační osa PŘÍMKA	Pravá (vlastní) rotace	Otočení o úhel 360/n
σ	Rovina symetrie, zrcadlová ROVINA	Zrcadlení, reflexe	Zrcadlení přes rovinu
S_n	Zrcadlově-rotační osa PŘÍMKA	Nepravá (nevlastní) rotace	Otočení o úhel 360/n následované zrcadlením

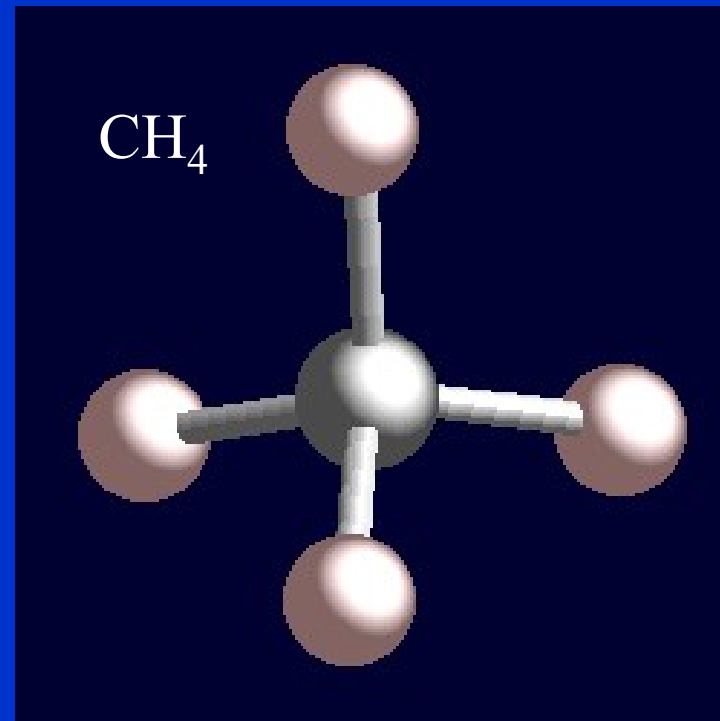
Střed symetrie



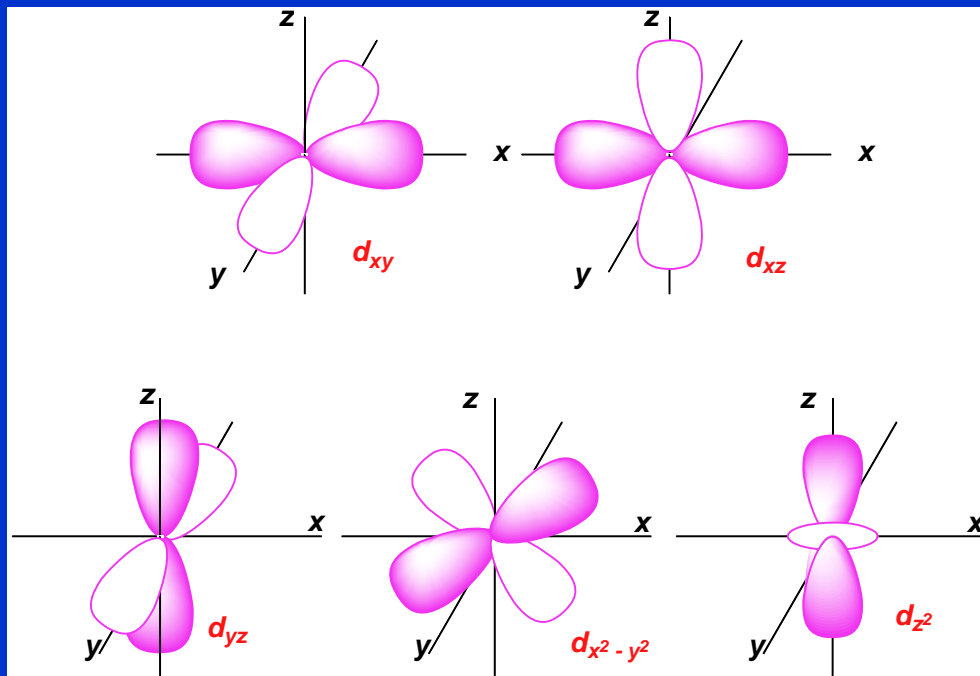
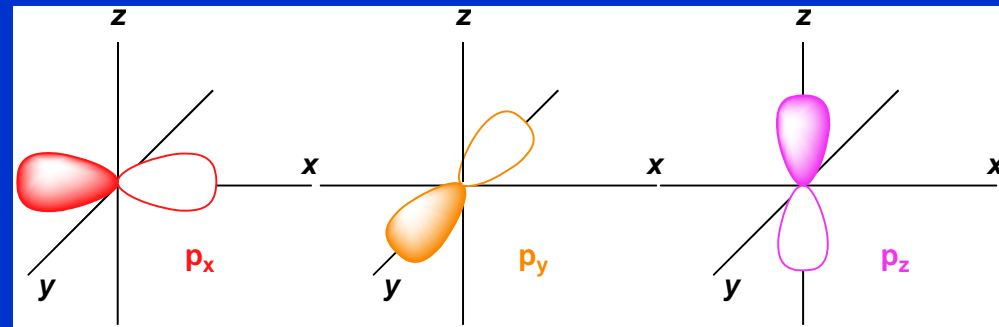
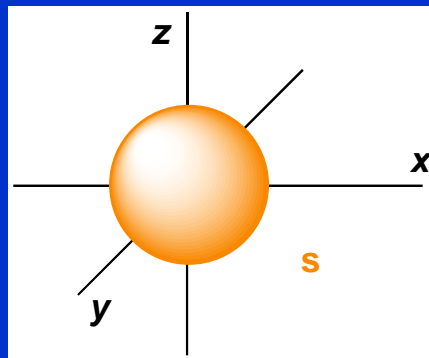
Střed symetrie



S = střed symetrie



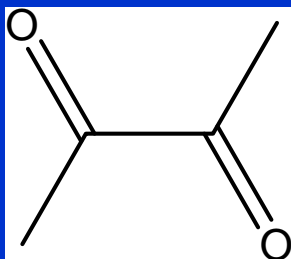
Nemá střed symetrie



Orbitaly

s a d mají *i* (střed symetrie)

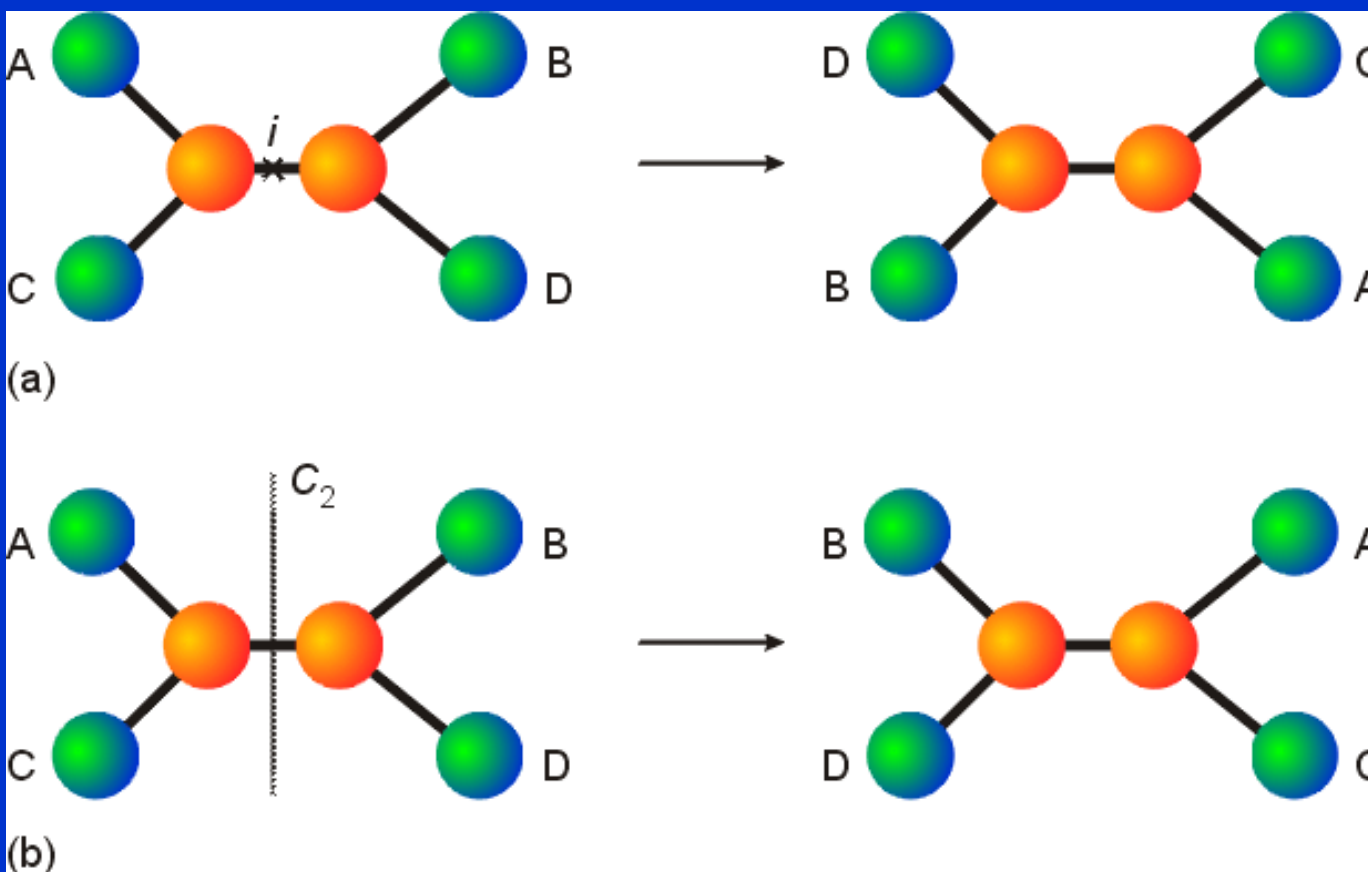
p a f nemají *i* (střed symetrie)



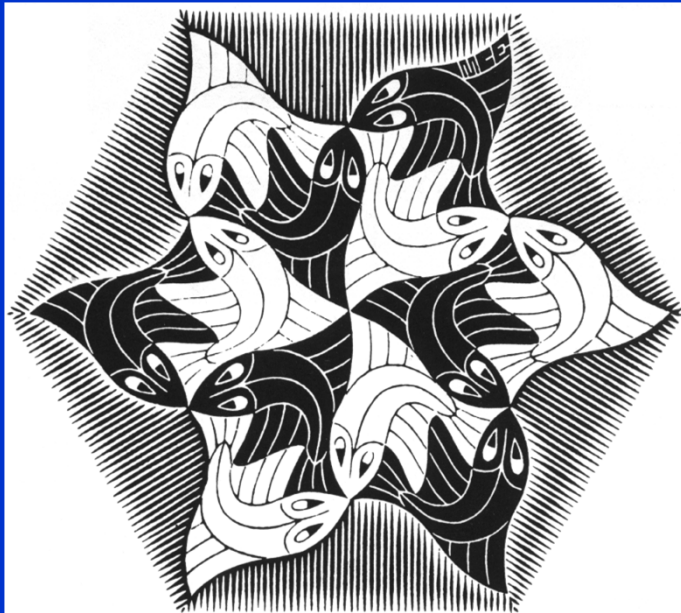
Rotační osa C_2



Rotace o úhel $360/n$. Vzniklá situace je nerozlišitelná od výchozí.

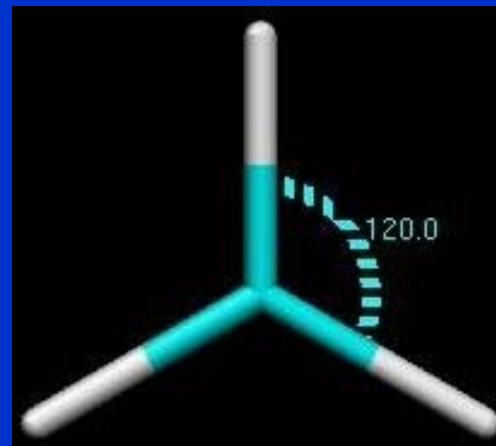
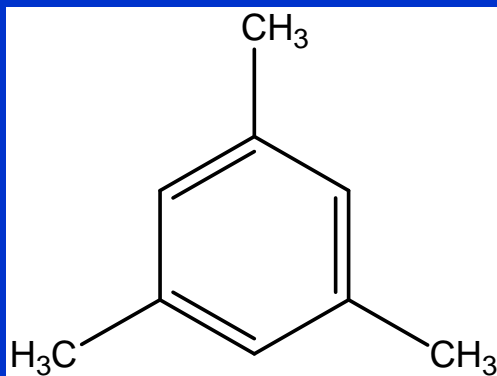


Rotační osa C_3



Rotace o úhel $360/n$

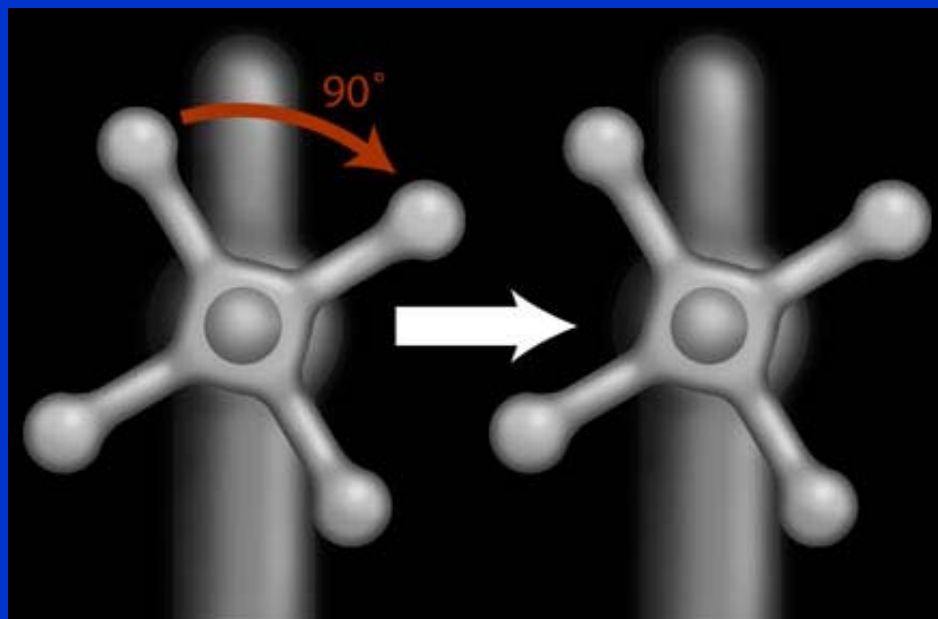
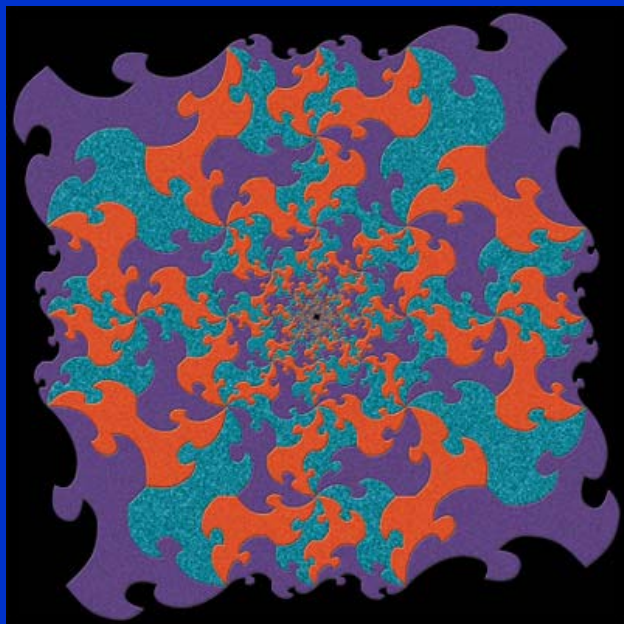
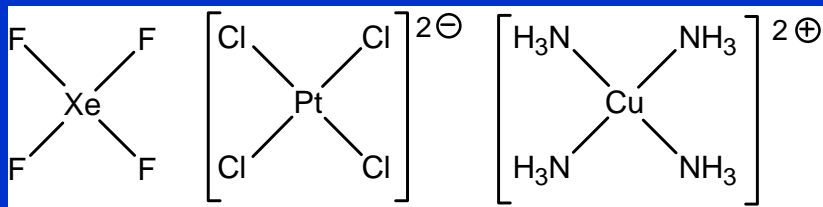
Vzniklá situace je nerozlišitelná od výchozí



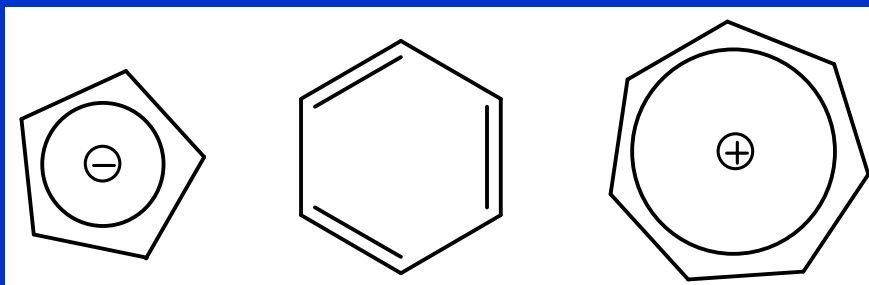
Rotační osa C_4

Rotace o úhel $360/4$.

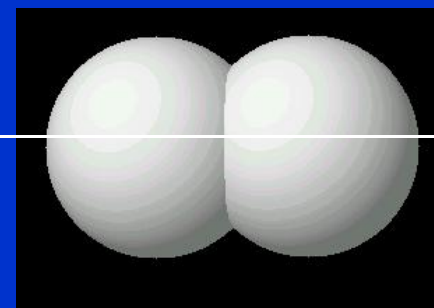
Vzniklá situace je nerozlišitelná od výchozí.



Rotační osa C_n



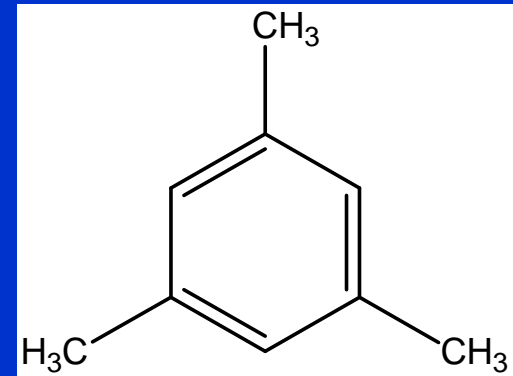
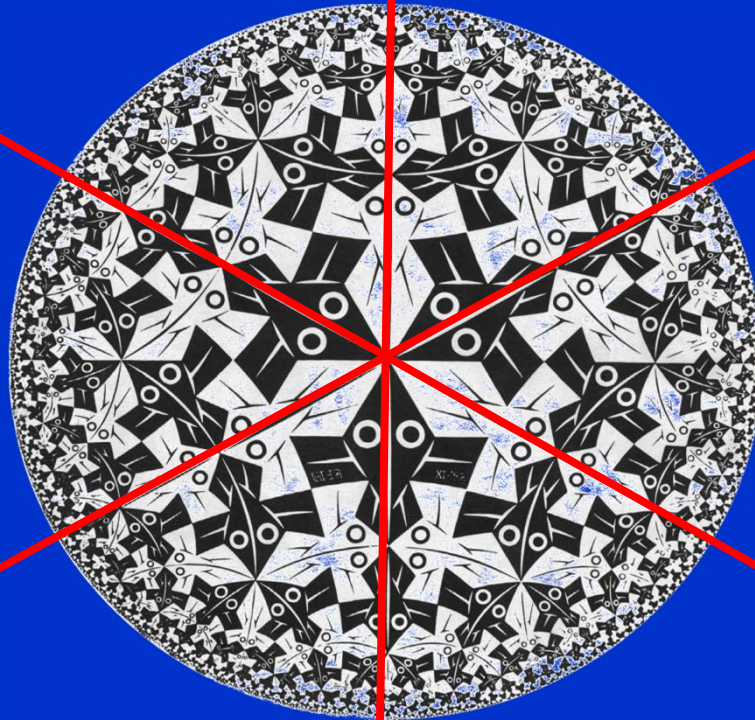
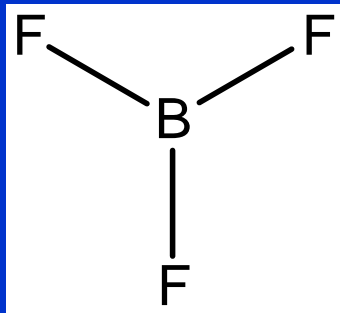
$C_5, C_6, C_7, \dots, C_\infty$



Lineární molekuly



Rovina symetrie σ



Roviny symetrie σ

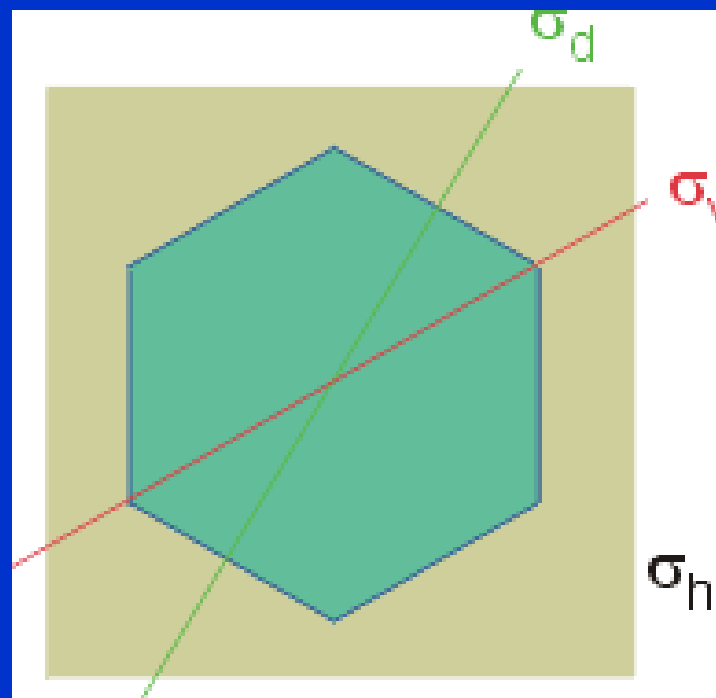
Každá planární molekula má rovinu symetrie ve které leží

σ_h = kolmá k hlavní rotační ose

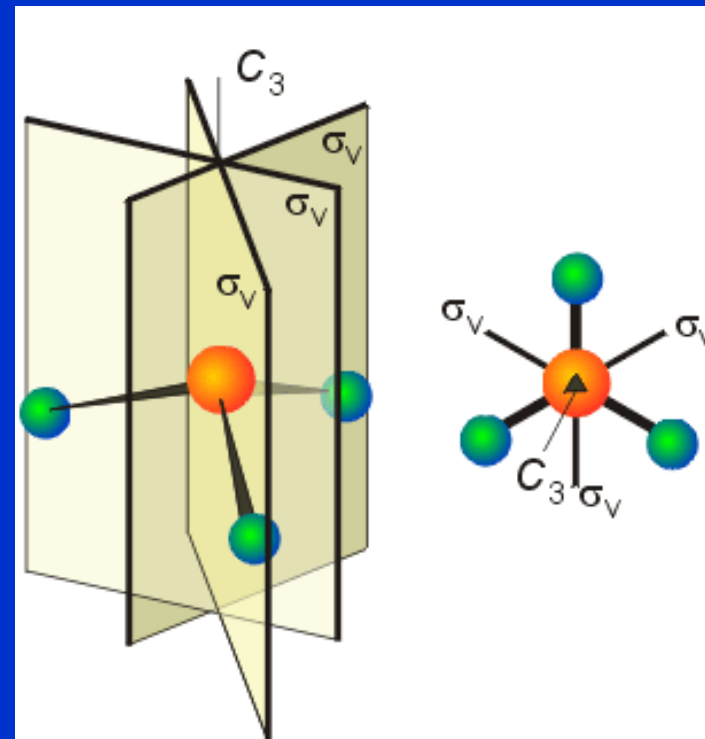
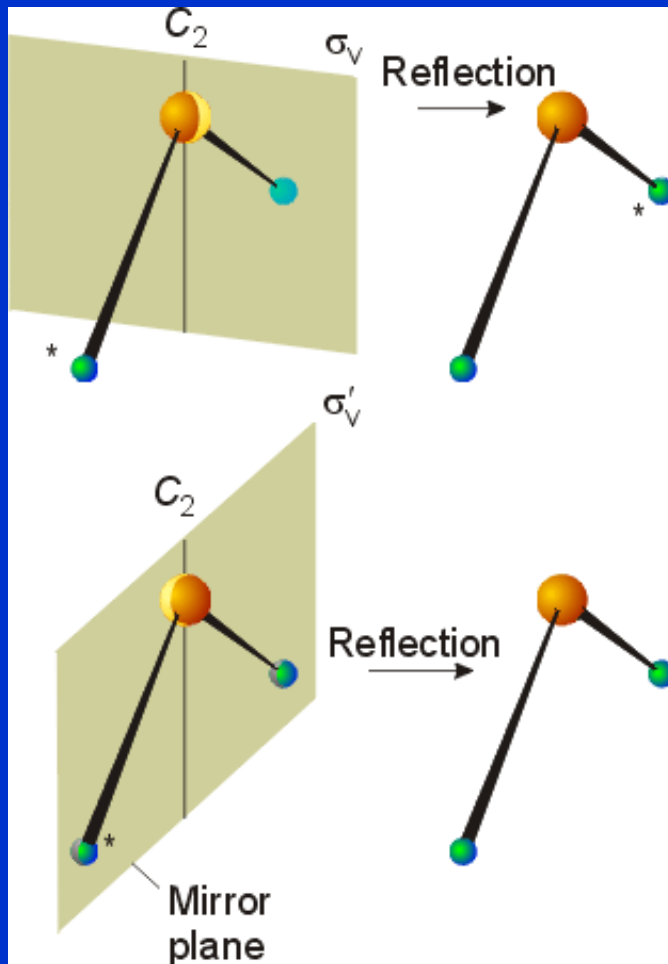
σ_v = obsahuje hlavní rotační osu,
protíná nejvíce atomů

σ_d = obsahuje hlavní rotační osu,
půlí úhly mezi C_2 osami kolnými
na hlavní rotační osu

Všechny σ prochází počátkem



Roviny symetrie σ

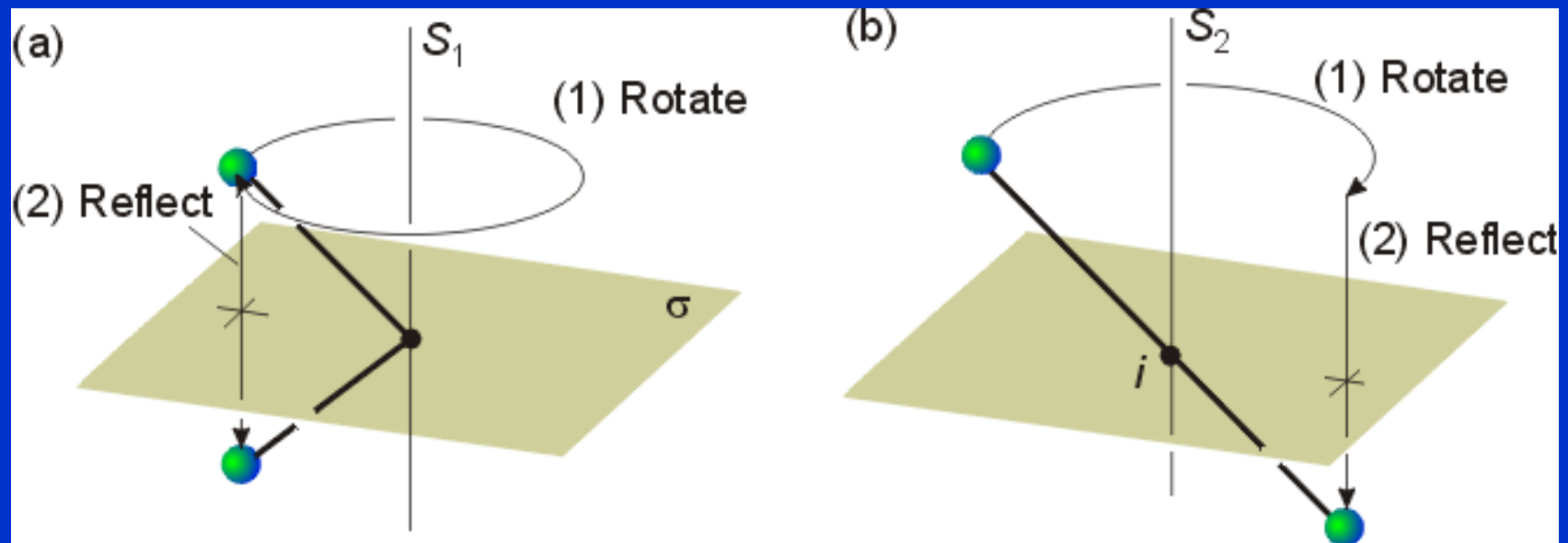


Zrcadlově-rotační osa S_n

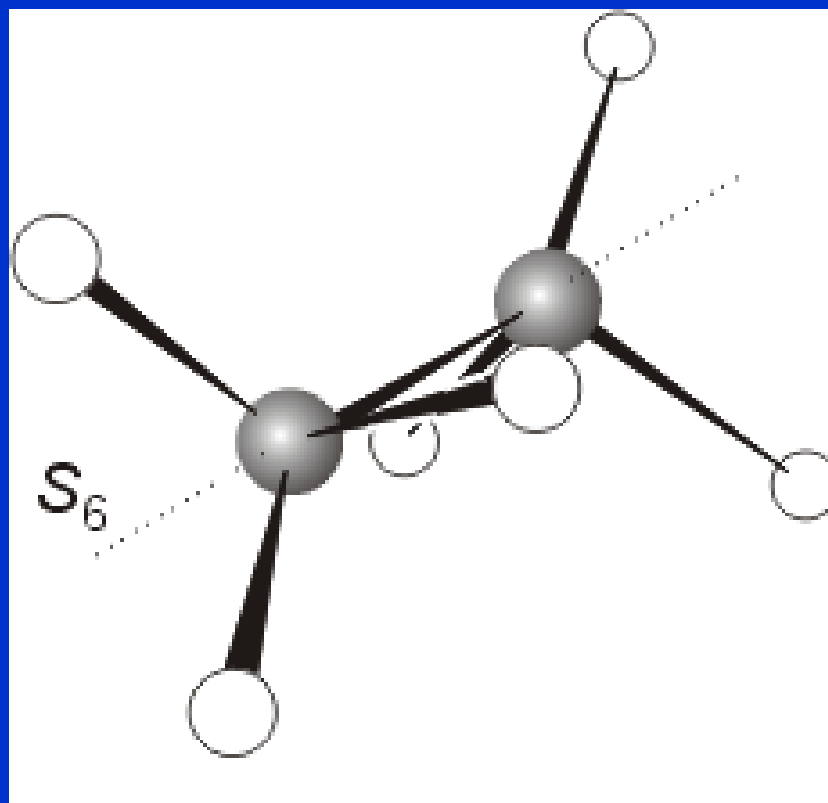
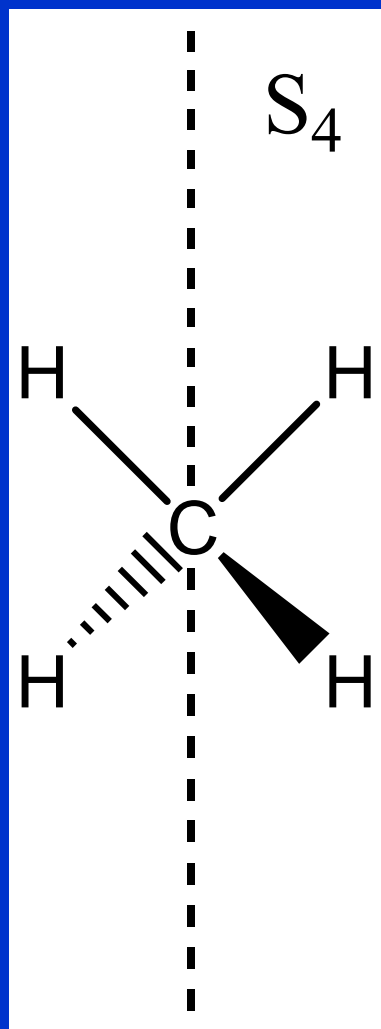
Postupné provedení dvou operací – rotace a zrcadlení

$$S_1 = C_1 \times \sigma = \sigma$$

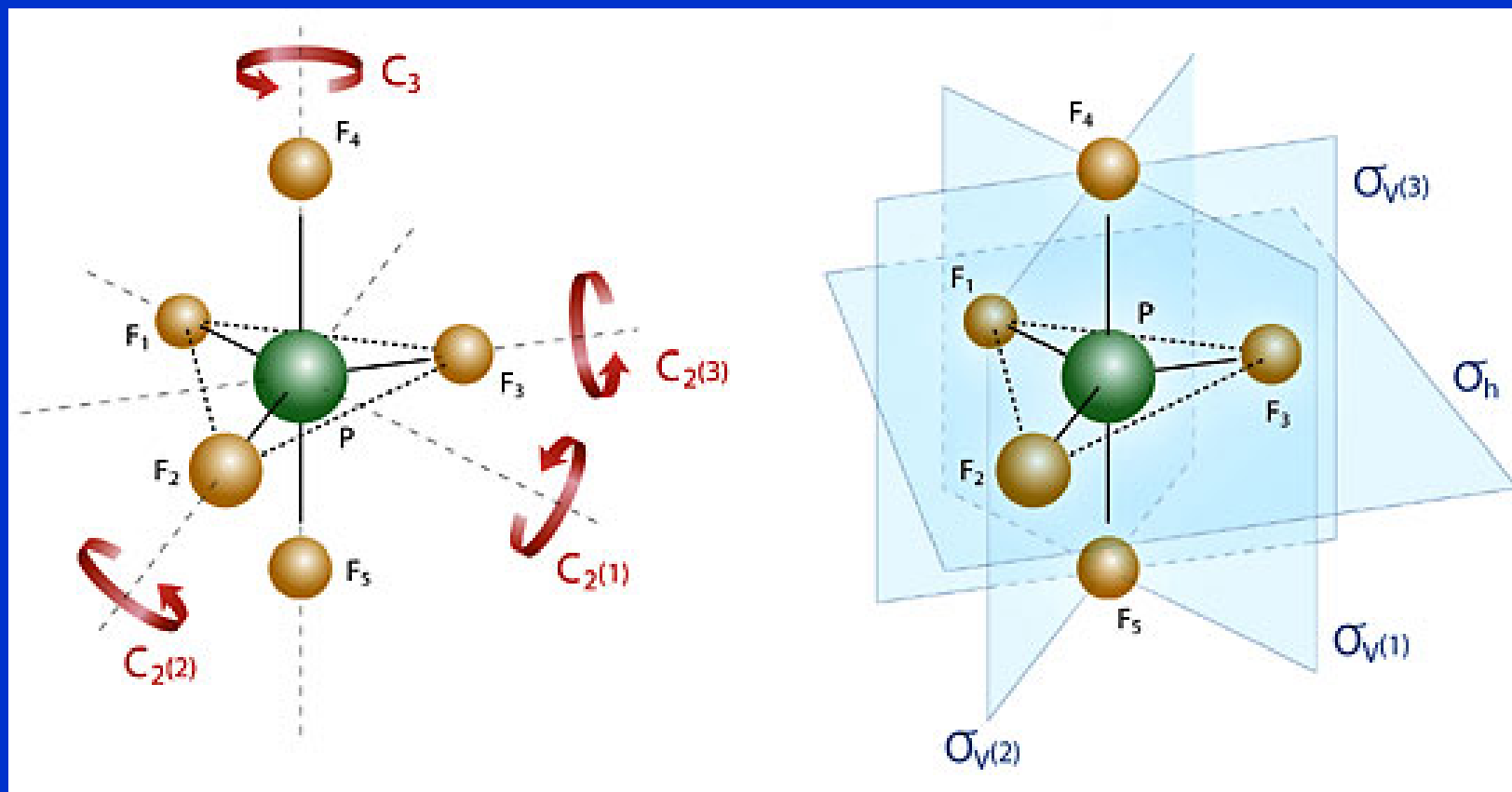
$$S_2 = C_2 \times \sigma = i$$



Zrcadlově-rotační osa S_n



Prvky symetrie v molekule



Ekvivalentní atomy = jsou zaměňovány operacemi symetrie



Chiralita



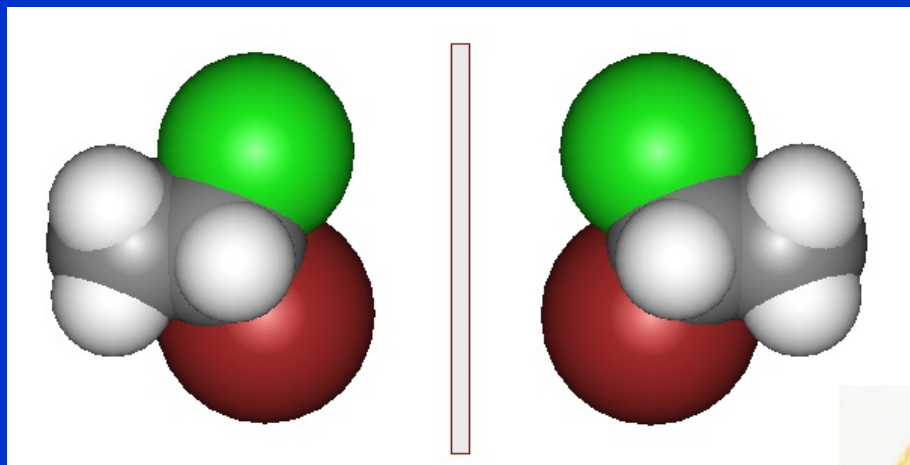
Figure 2. The Founding Fathers. R. M. Barrer (1910–1996) (right) and R. M. Milton (1920–2000) photographed

Chiralita

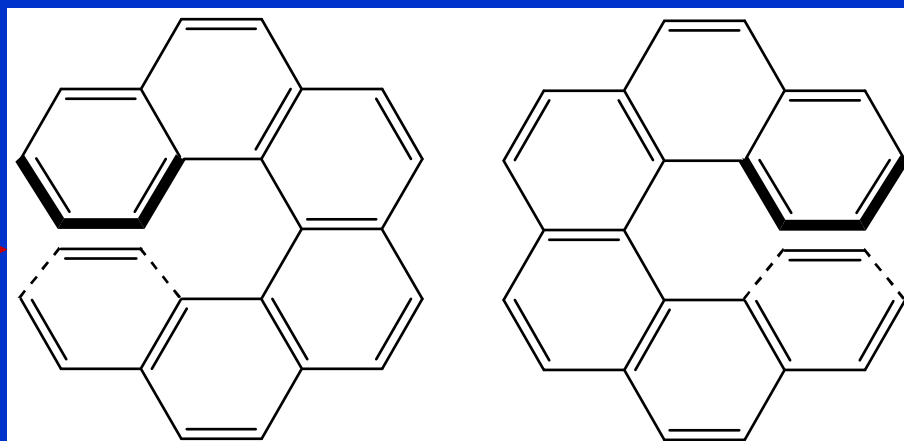
Podmínka chiraloty: v molekule není přítomna S_n

$$S_1 = \sigma$$

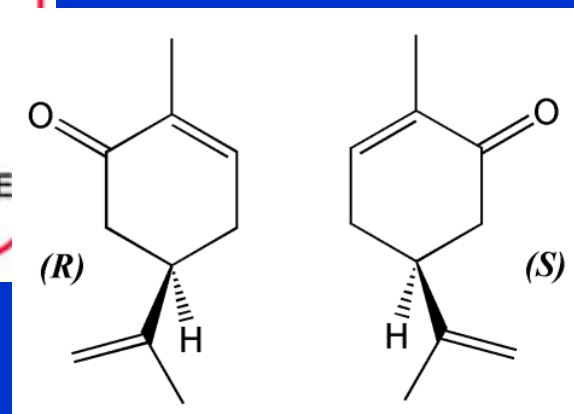
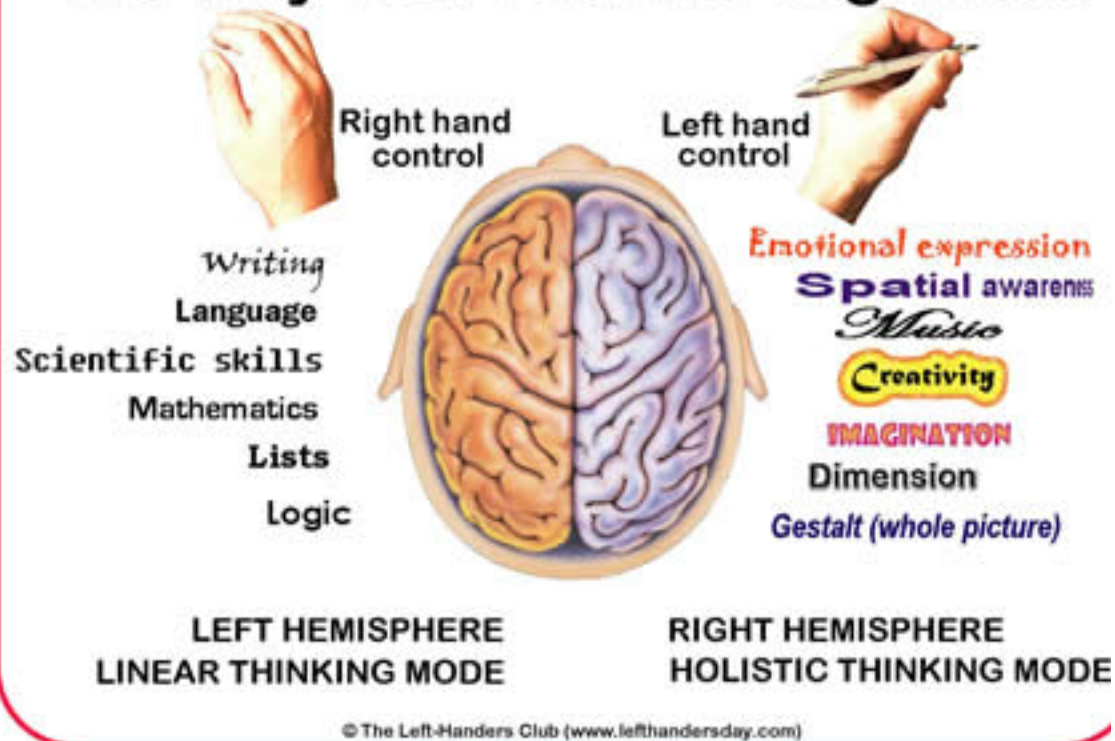
$$S_2 = i$$



C_2



The Way Your Brain Is Organised



(R): Spearmint

(S): Caraway (Kümmel)

Thalidomide

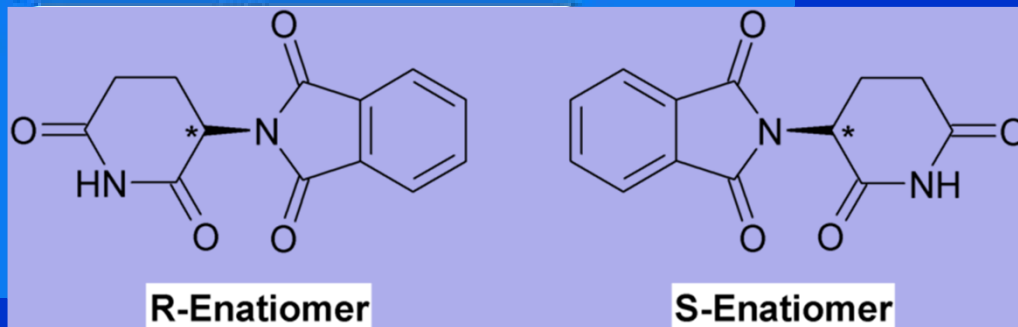


(*R*)-enantiomer

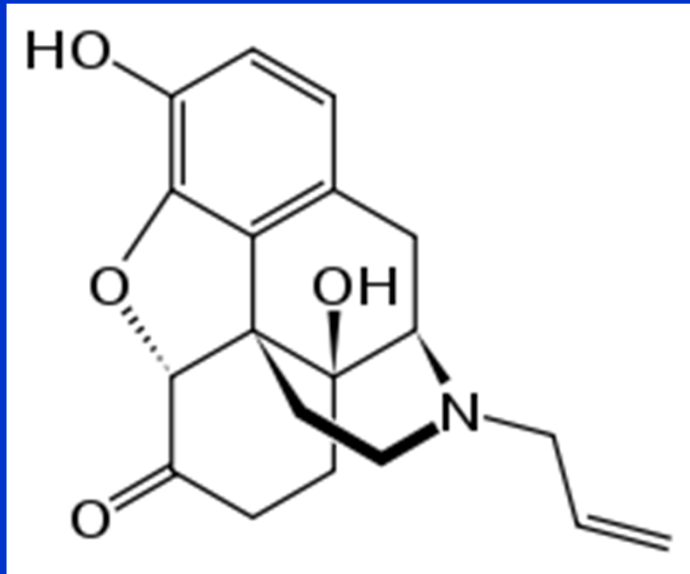
lék na ranní nevolnost

(*S*)-enantiomer

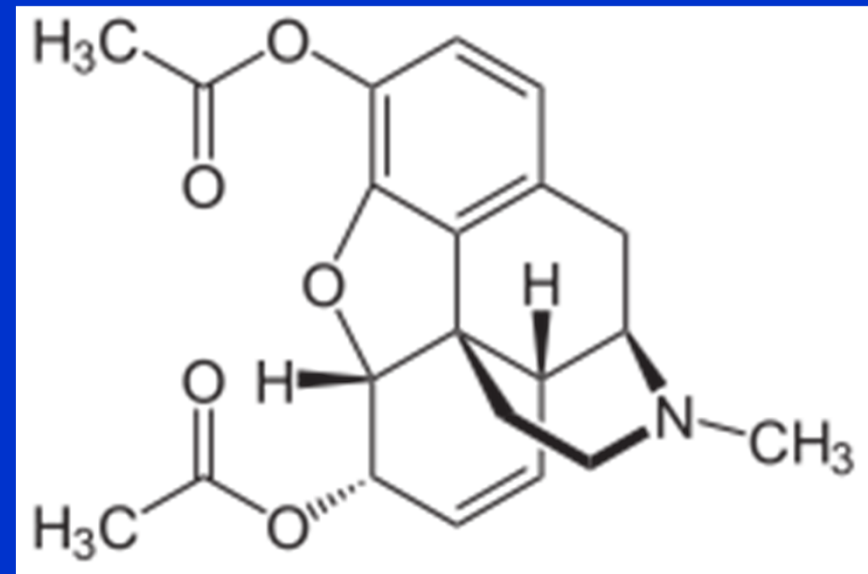
je teratogenní



Chiralita



Naloxone

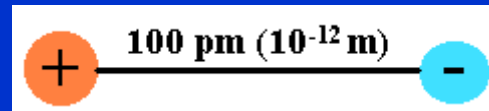


Heroin

Dipolový moment

$$\mu = q L \quad \text{vektor [C m]}$$

$$1 \text{ D debye} = 3.33564 \cdot 10^{-30} \text{ C m}$$

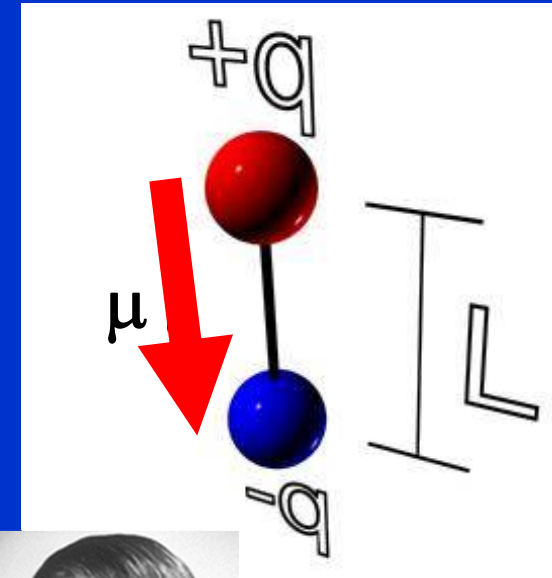


proton a elektron, vzdáleny 1 Å

$$\begin{aligned} \mu &= q L = (1.60 \cdot 10^{-19} \text{ C})(1.00 \cdot 10^{-10} \text{ m}) \\ &= 1.60 \cdot 10^{-29} \text{ C m} = \mathbf{4.80 \text{ D}} \end{aligned}$$

dipolový moment **4.80 D**

je referenční hodnota, čisté +1 a -1
náboje vzdálené 100 pm, vazba mezi nimi
je 100% iontová



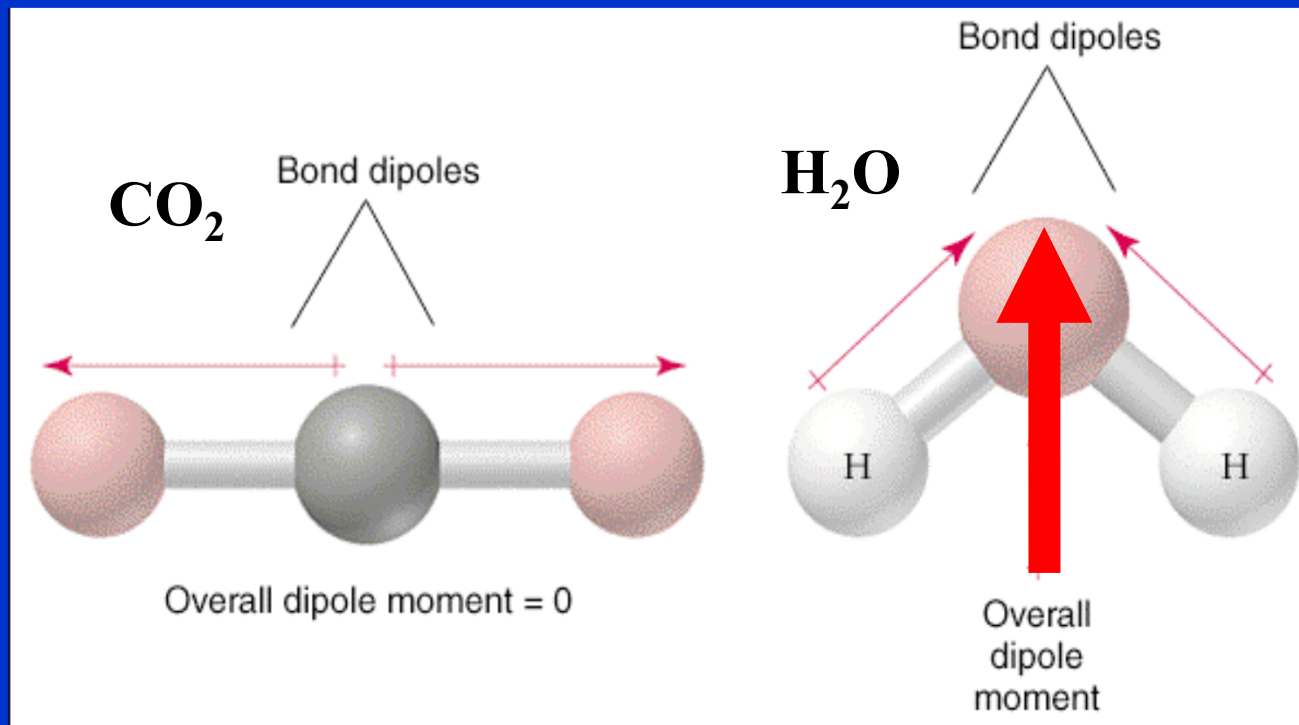
Peter Debye (1884-1966)
1936 NP za chemii

Zahřívání v MW

Dipolový moment molekuly

Dipolový moment molekuly = vektorový součet dipolových momentů vazeb a volných elektronových párů

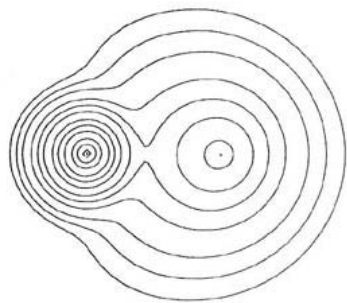
Míra nerovnoměrnosti rozložení náboje v molekule



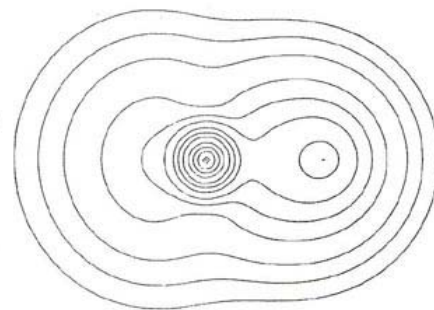
Dipolové momenty diatomických molekul

AH	μ (Debye)	R(Å)
LiH	-6.002	1.595
BeH	-0.282	1.343
BH	1.733	1.236
CH	1.570	1.124
NH	1.627	1.038
OH	1.780	0.9705
FH	1.942	0.9171

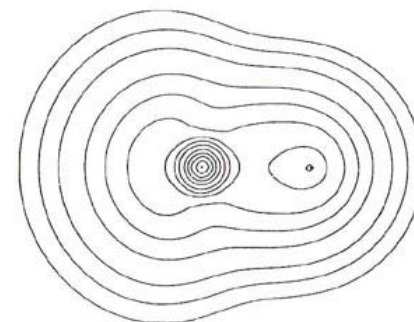
negativní nebo pozitivní znaménko pro $\mu \Rightarrow$ H je negativní nebo pozitivní konec dipolu.



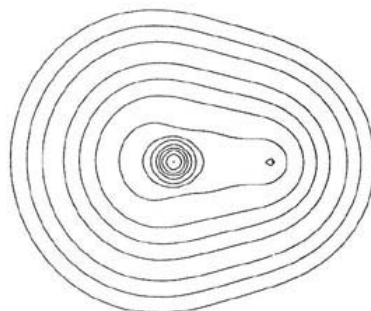
LiH



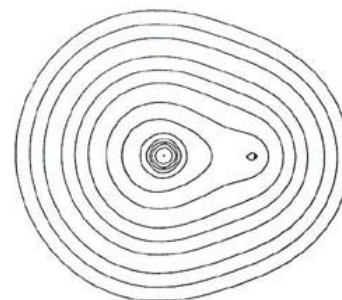
BeH



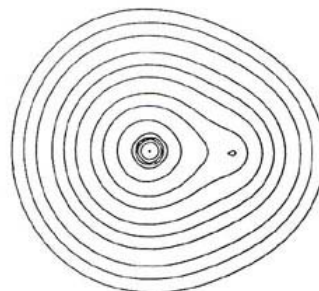
BH



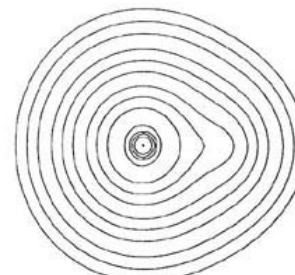
CH



NH



OH



HF

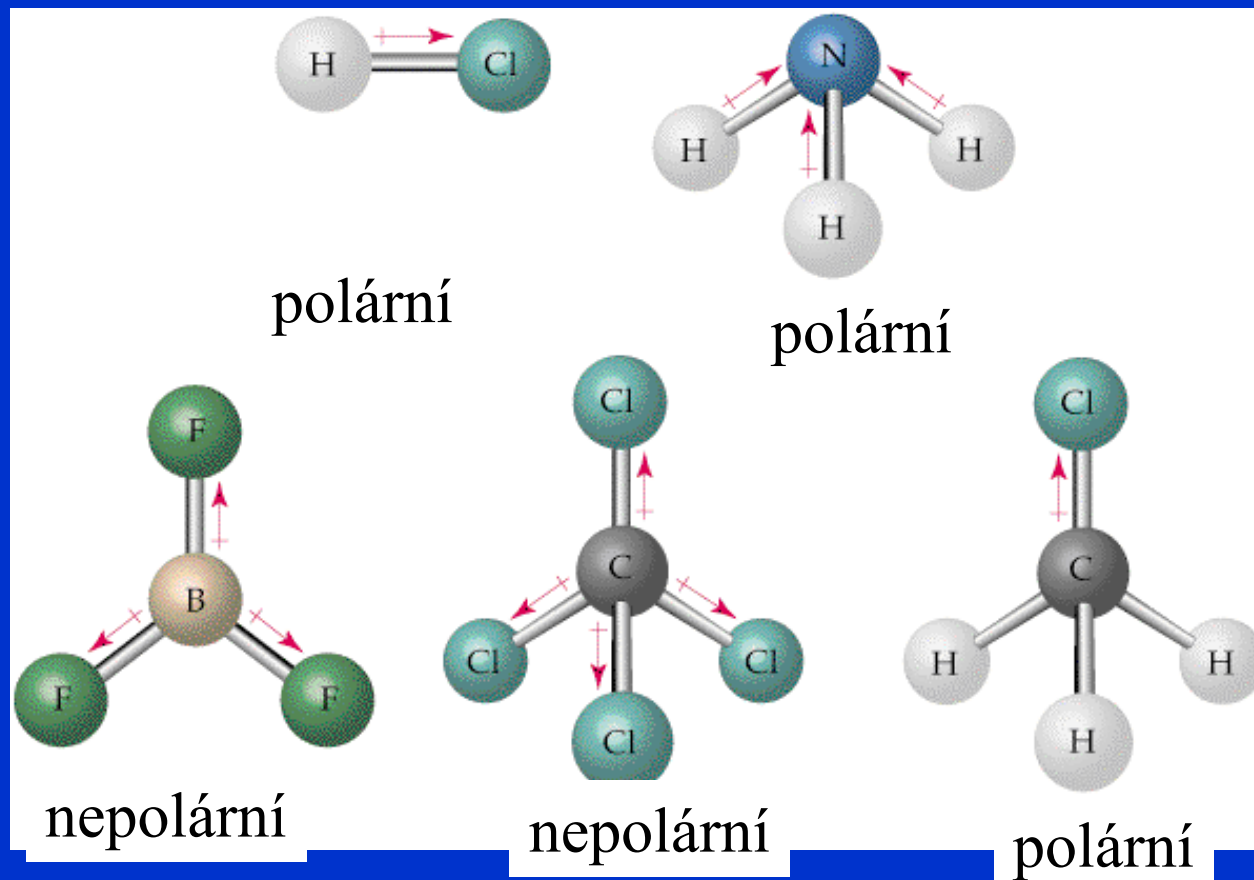
Dipolový moment vazeb

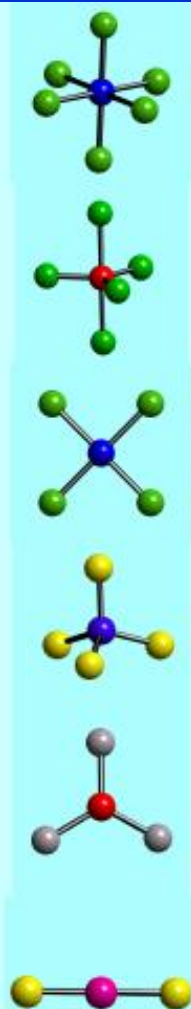
Rozdíl elektronegativit vazebných partnerů

Enlace	$\chi_A - \chi_B$	μ (D)	Enlace	$\chi_A - \chi_B$	μ (D)	Enlace	$\chi_A - \chi_B$	μ (D)
C-H	0.30	0.4	N=C		0.9	Br-P	0.68	0.36
N-H	0.87	1.31	N≡C		3.5	I-P	0.15	0
N-D		1.30	O-C	1.00	0.74	O=As		4.2
H-P	0.14	0.36	O=C		2.3	F-As	1.90	2.03
H-As	0	0.10	C-S	0.06	0.9	Cl-As	0.63	1.64
H-Sb	0.38	0.08	C=S		2.6	Br-As	0.54	1.27
O-H	1.30	1.51	C-Se	0.02	0.8	I-As	0.01	0.78
O-D		1.50	C-Te	0.49	0.6	Cl-Sb	1.01	0.78
S-H	0.24	0.68	F-C	1.60	1.41	Br-Sb	0.92	1.9
F-H	1.90	1.94	Cl-C	0.33	1.46	I-Sb	0.39	0.8
Cl-H	0.63	1.08	Br-C	0.24	1.38	O=S		2.8
Cl-D		1.09	C-I	0.29	1.19	Cl-S	0.39	0.7
Br-H	0.54	0.78	O-N	0.43	0.3	O-Cl	0.67	0.7
I-H	0.01	0.38	O=N		2.0	F-Cl	1.27	0.88
C-C	0	0	F-N	1.03	0.17	F-Br	1.36	1.3
C=C		0	O=P		2.7	Cl-Br	0.09	0.57
C≡C		0	S=P		3.1	Br-I	0.53	1.2
N-C	0.57	0.22	Cl-P	0.77	0.81			

Dipolový moment a polarita molekul

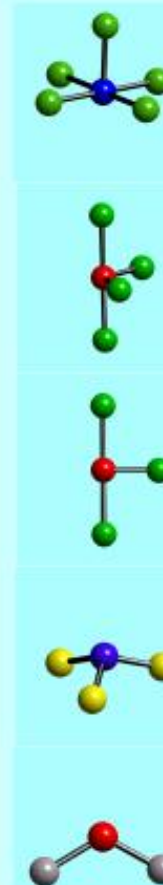
Polární molekula = celkový dipol musí ležet ve všech prvcích symetrie





$\mu = 0$

AB_nE_m	Bodová grupa	μ	Molekula
AB ₂	D _{∞h}	0	CO ₂ , BeCl ₂ (g), ZnX ₂
AB ₃	D _{3h}	0	BX ₃ , GaI ₃ , In(CH ₃) ₃
AB ₂ E	C _{2v}	finito	SnX ₂ , PbX ₂
AB ₄	T _d	0	CX ₄ , SiX ₄ , ThX ₄
AB ₃ E	C _{3v}	finito	NH ₃ , NX ₃ , PX ₃
AB ₂ E ₂	C _{2v}	finito	H ₂ O, SeX ₂ , TeX ₂
AB ₅	D _{3h}	0	PF ₅ , PCl ₅ (g), NbCl ₅ (g)
AB ₄ E	C _{2v}	finito	SF ₄ , SeF ₄
AB ₃ E ₂	C _{2v}	finito	ClF ₃ , BrF ₃
AB ₂ E ₃	D _{∞h}	0	XeF ₂
AB ₆	O _h	0	SF ₆ , SeF ₆ , MoF ₆
AB ₅ E	C _{4v}	finito	ClF ₅ , BrF ₅ , IF ₅
AB ₄ E ₂	D _{4h}	0	XeF ₄
AB ₇	D _{5h}	0	IF ₇



$\mu \neq 0$