

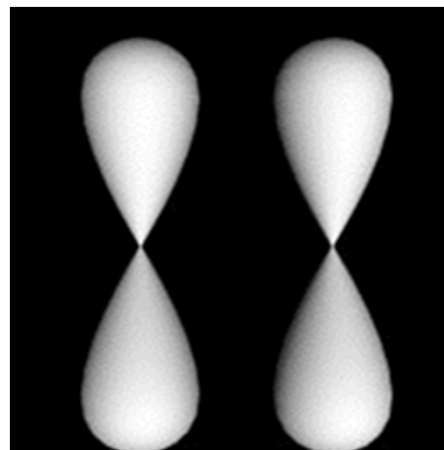
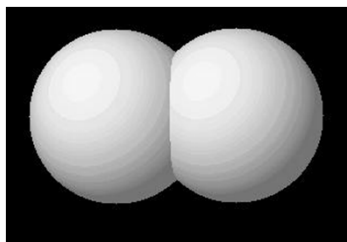
Překryv orbitalů

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

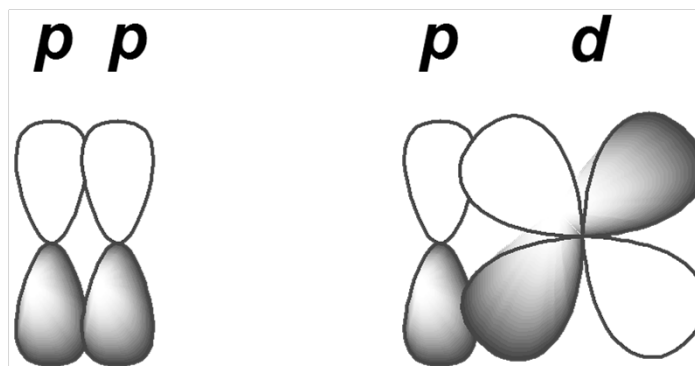
Spojnicí jader obvykle značíme jako **osu z**



Pi vazba, π

Elektronová hustota lokalizována mimo spojnici jader

Jedna uzlová rovina

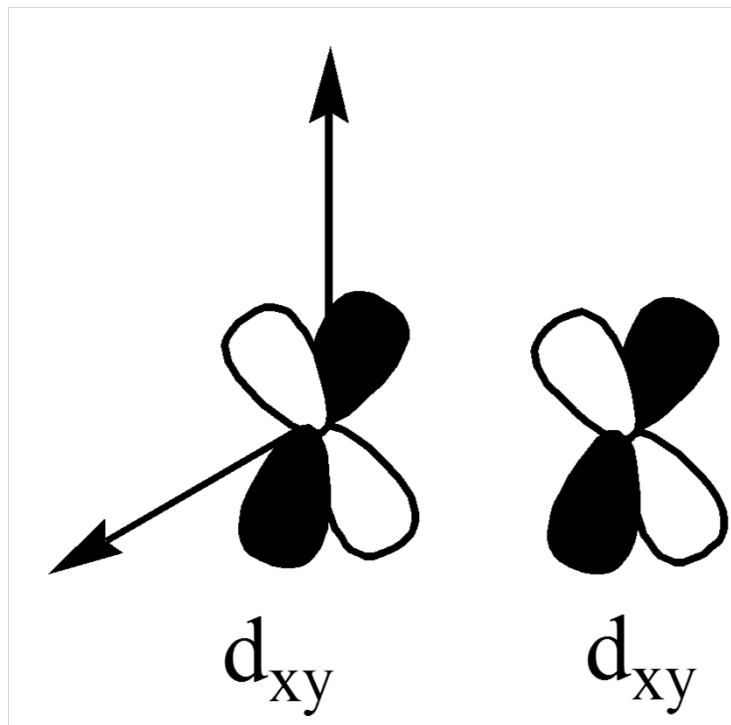


Typy překryvu orbitalů

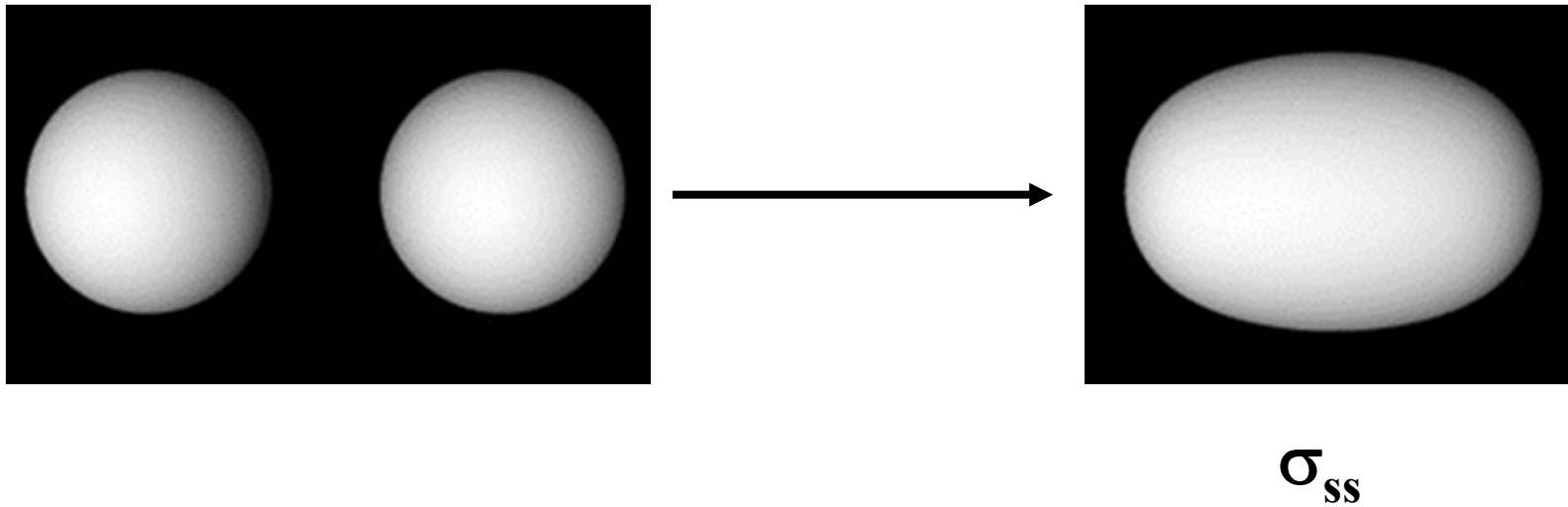
Delta vazba, δ

Elektronová hustota lokalizována mimo spojnici jader

Dvě uzlové roviny

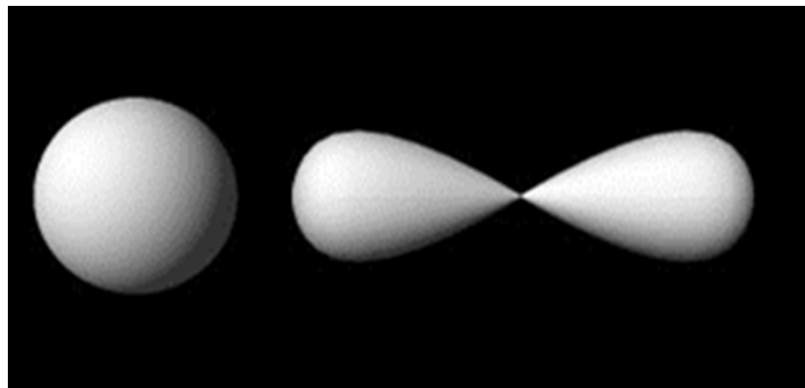


Sigma vazba, σ_{ss}

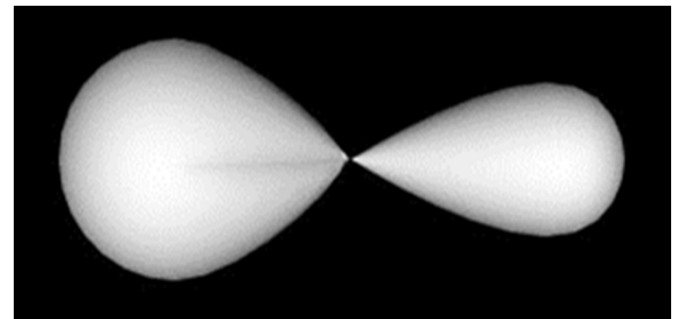


Elektronová hustota lokalizována na spojnici jader

Sigma vazba, σ_{sp}

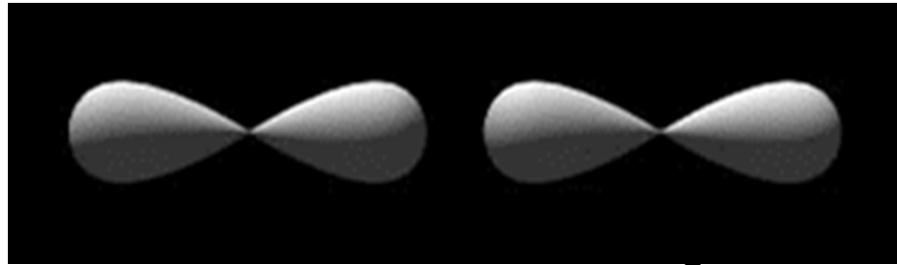


Z

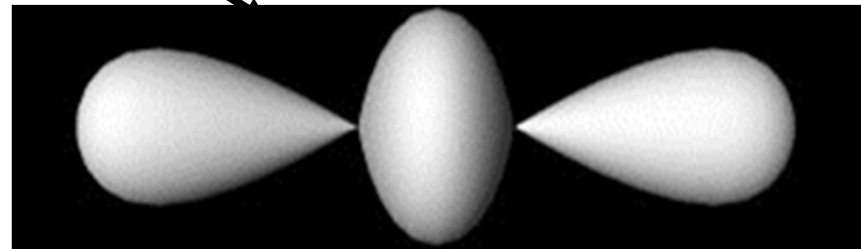


σ_{sp}

Sigma vazba, σ_{pp}



Z

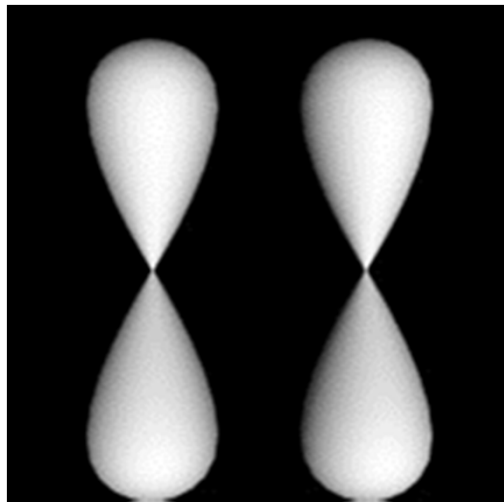


σ_{pp}

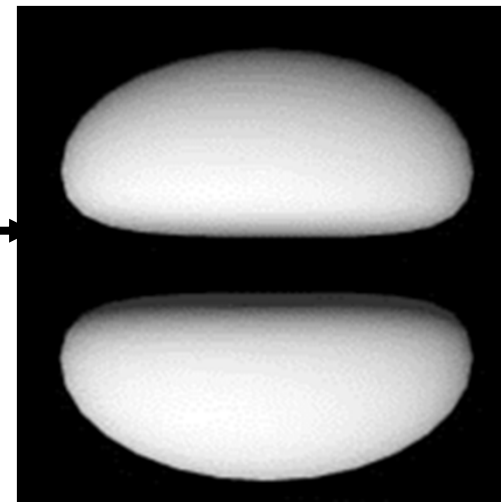
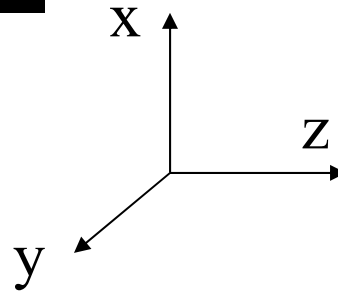
Pi vazba, π

Elektronová hustota lokalizována mimo spojnici jader

Jedna uzlová rovina



Stejně pro p_x a p_y



$2 \times \pi_{pp}$

Účinnost překryvu orbitalů

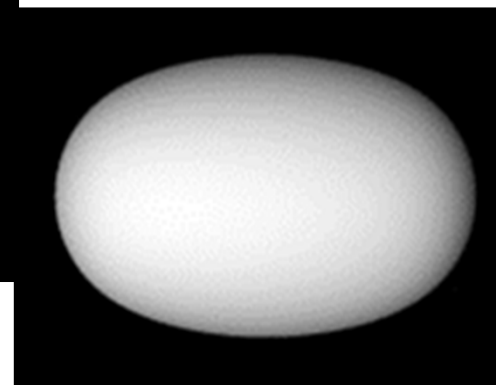
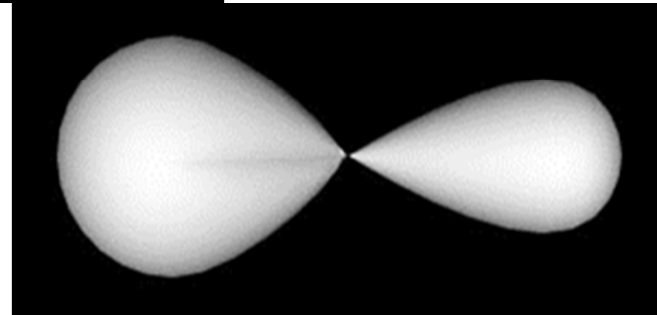
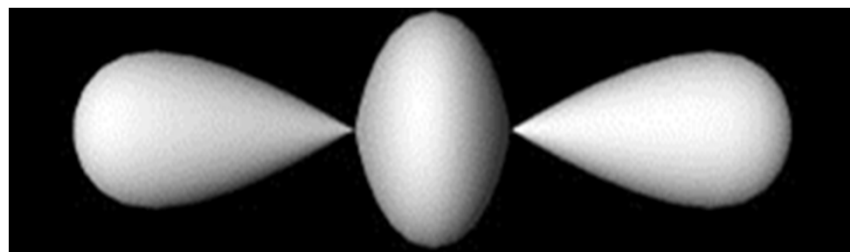
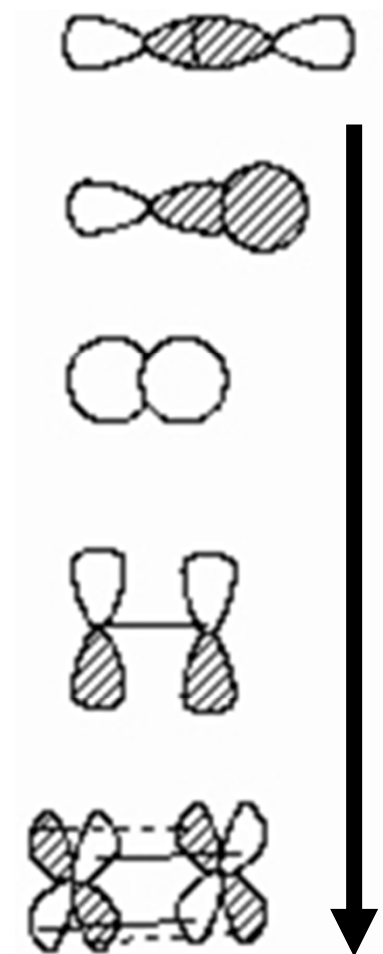
Kratší vzdálenost = lepší překryv

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

Pro σ : $p_z-p_z > p_z-s > s-s$

Překryv
klesá

Slabší
vazba



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 [\AA]	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

Vazebné parametry

Vazba	E, kJ mol ⁻¹	Polarita vazby
H–H	431	Nepolární
F–F	155	Nepolární
H–F	565	Polární

Vazba		Teplota tání, °C
Ge–Ge	188	937
Si–Si	226	1412
C–C	347	3827

Vazebné parametry

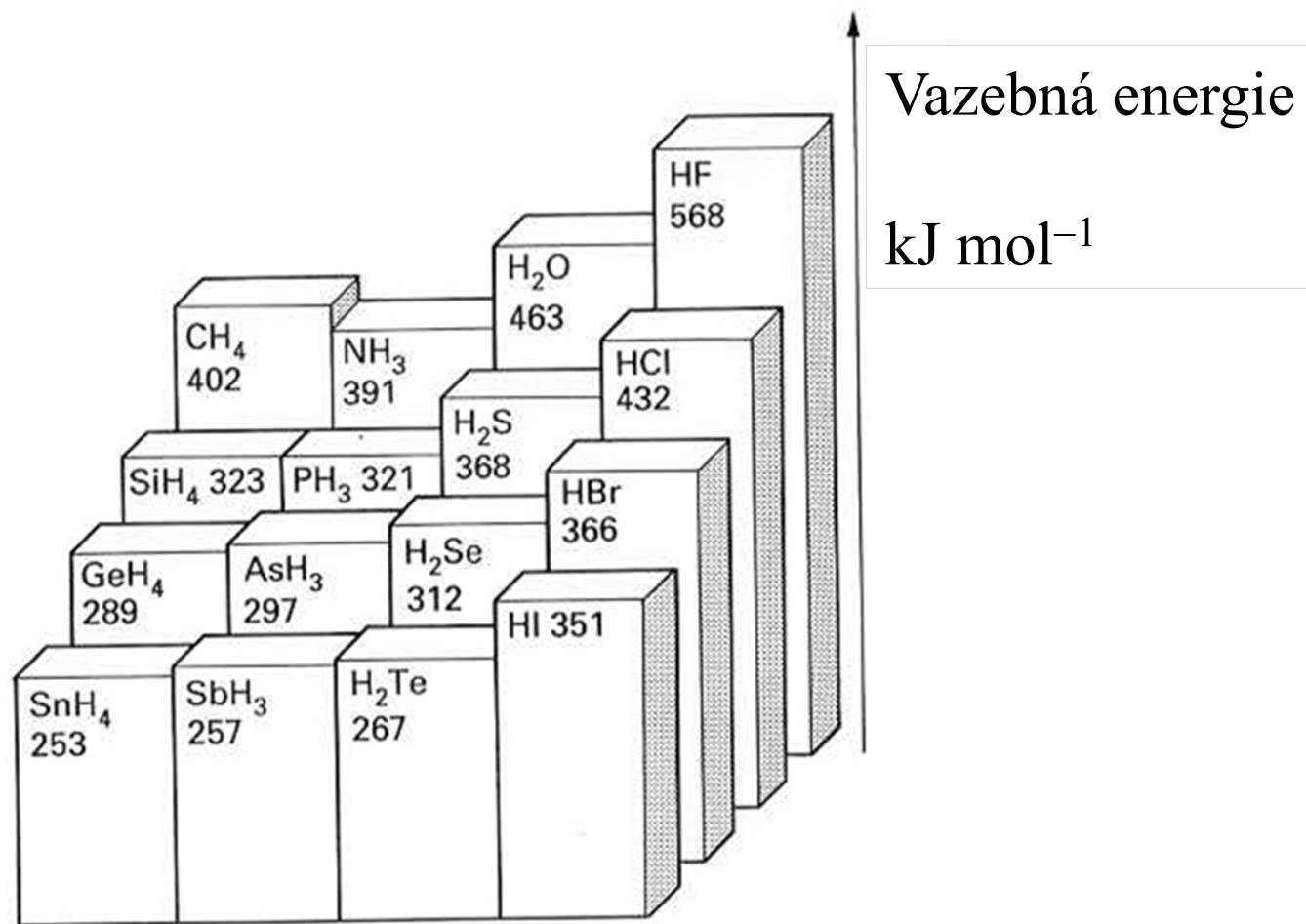
Vazba	E, kJ mol ⁻¹	délka, Å	
C–I	240	2.16	 <p>Polarita vazby roste</p>
C–Br	276	1.91	
C–Cl	339	1.79	
C–F	485	1.40	

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

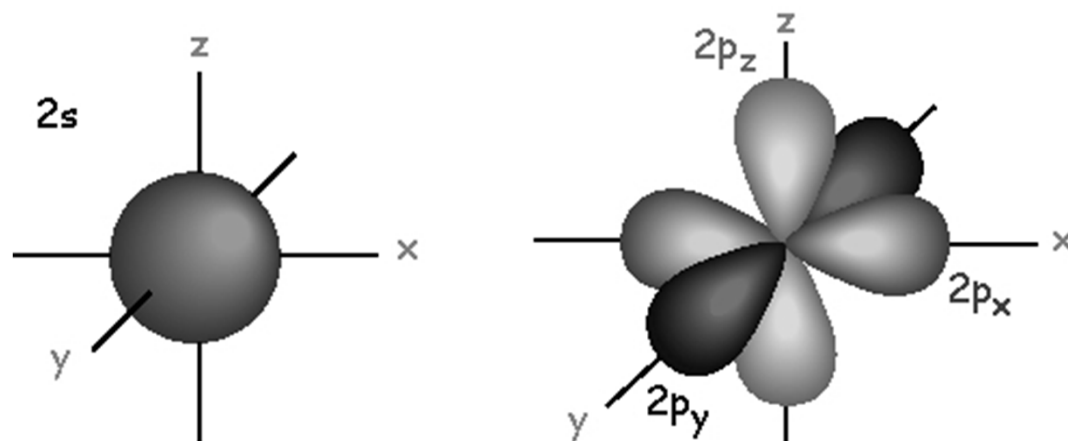
$$r_{\text{AB}} = r_{\text{A}} + r_{\text{B}} - 0.09 |\chi_{\text{A}} - \chi_{\text{B}}|$$





Linus Pauling

Hybridizace

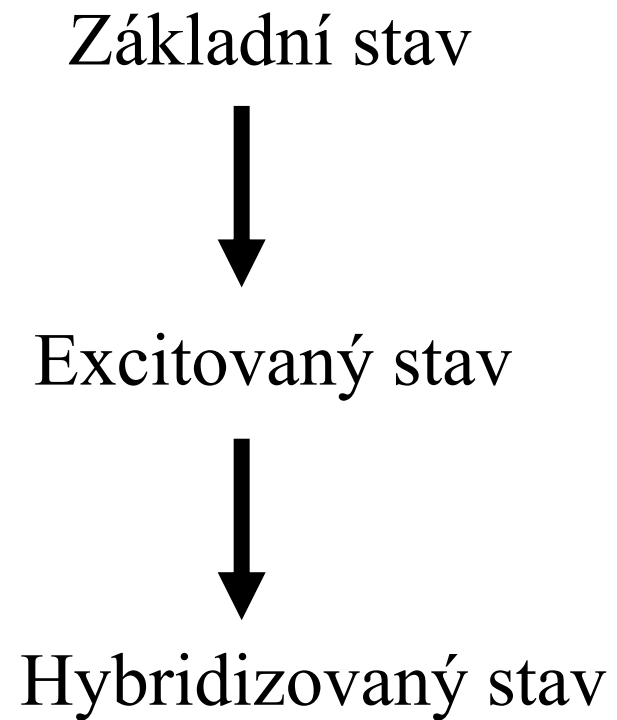


Vazebné úhly 90° jsou vzácné (u prvků hlavních skupin), obvyklé úhly jsou 109 , 120 , 180°

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

Počet hybridních orbitalů = počet smísených atomových orbitalů

Hybridizace sp



$2s$



$2p$



$2s$



$2p$

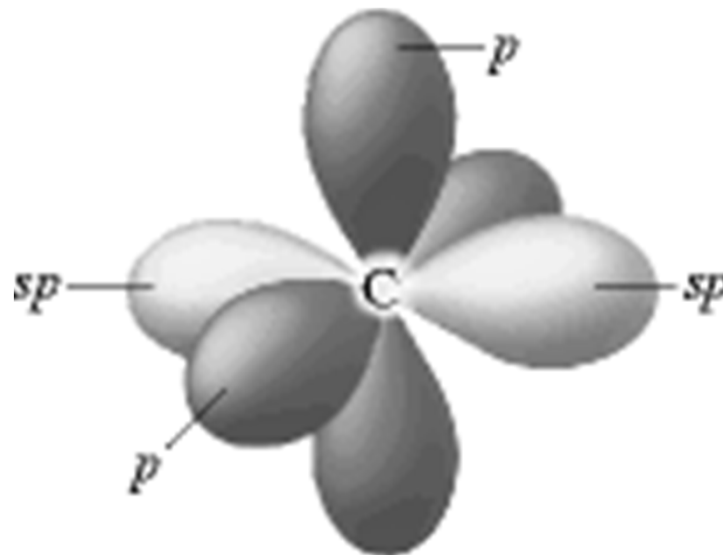


sp orbitals

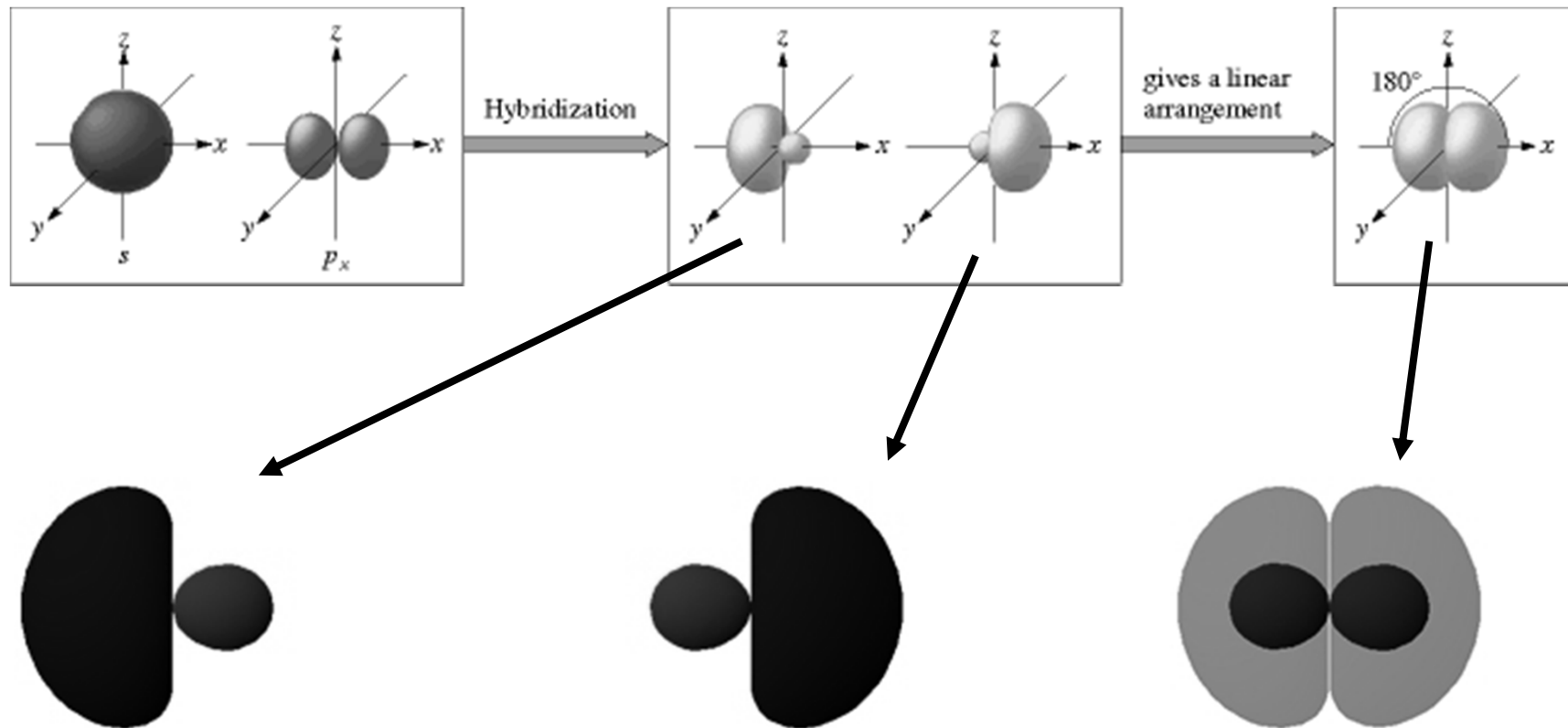


$2p_y$ $2p_z$

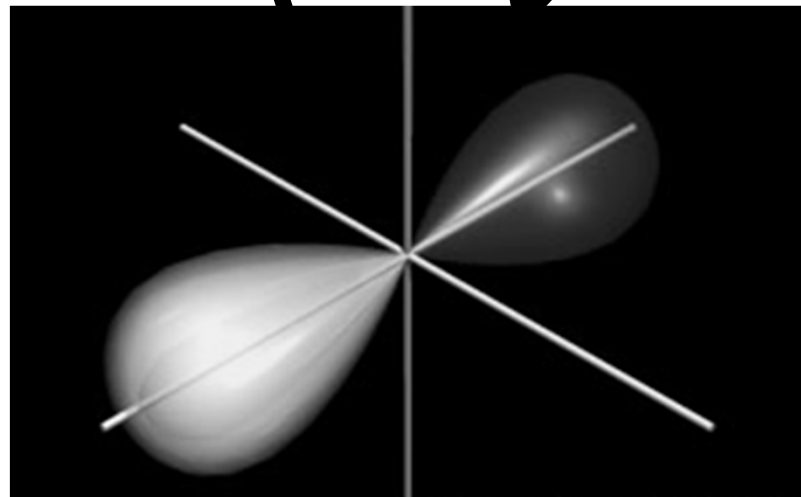
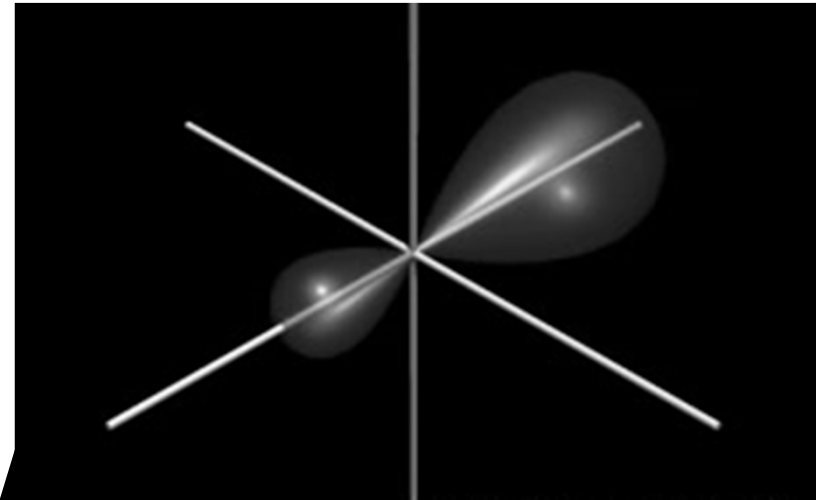
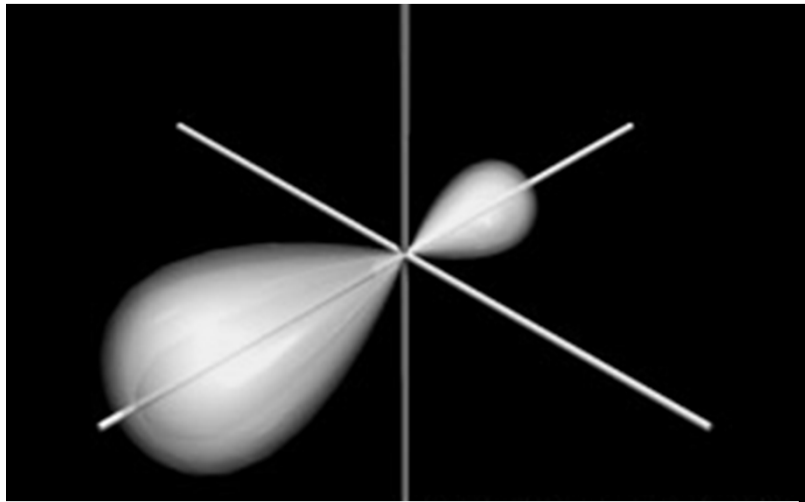
Hybridize sp



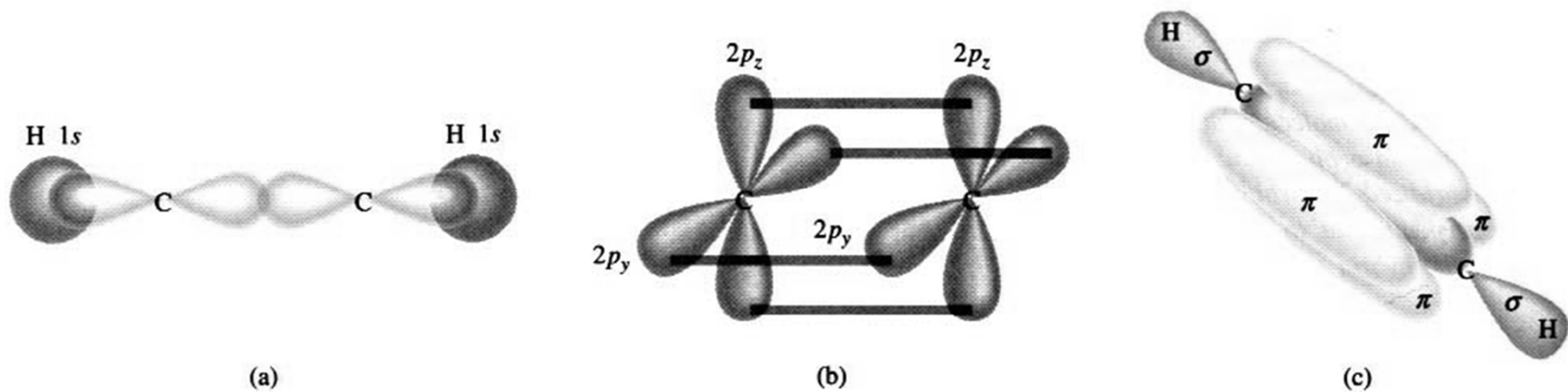
Hybridize sp



Hybridize sp

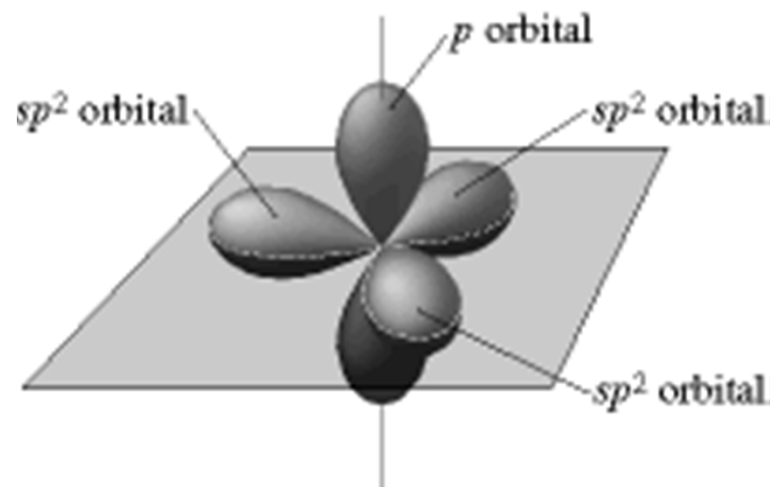


Acetylen

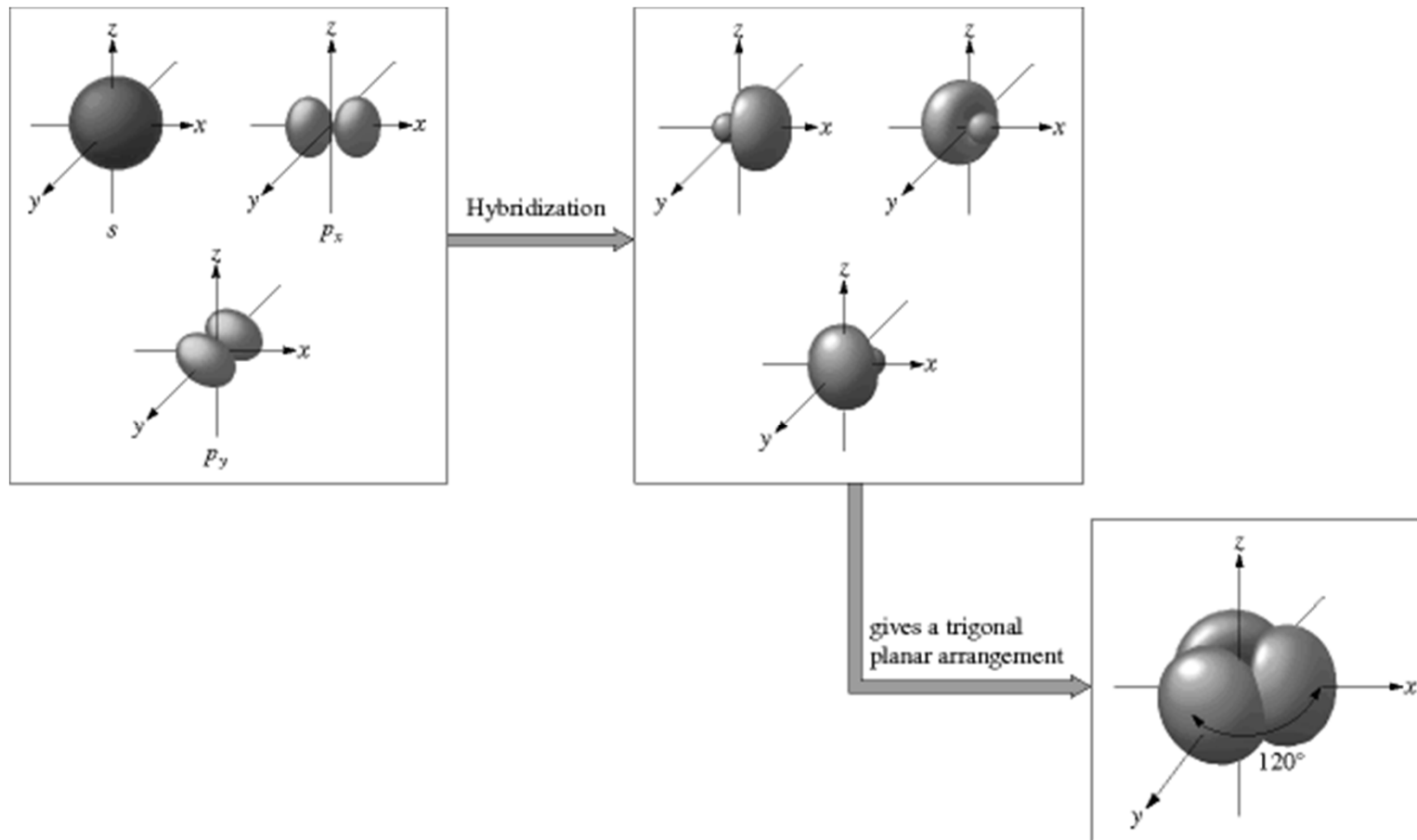


- 2 σ vazby překryvem C(sp)–H(s)
- 1 σ vazba překryvem C(sp)–C(sp)
- 2 navzájem kolmé π -vazby (x, y) překryvem C(p)–C(p)

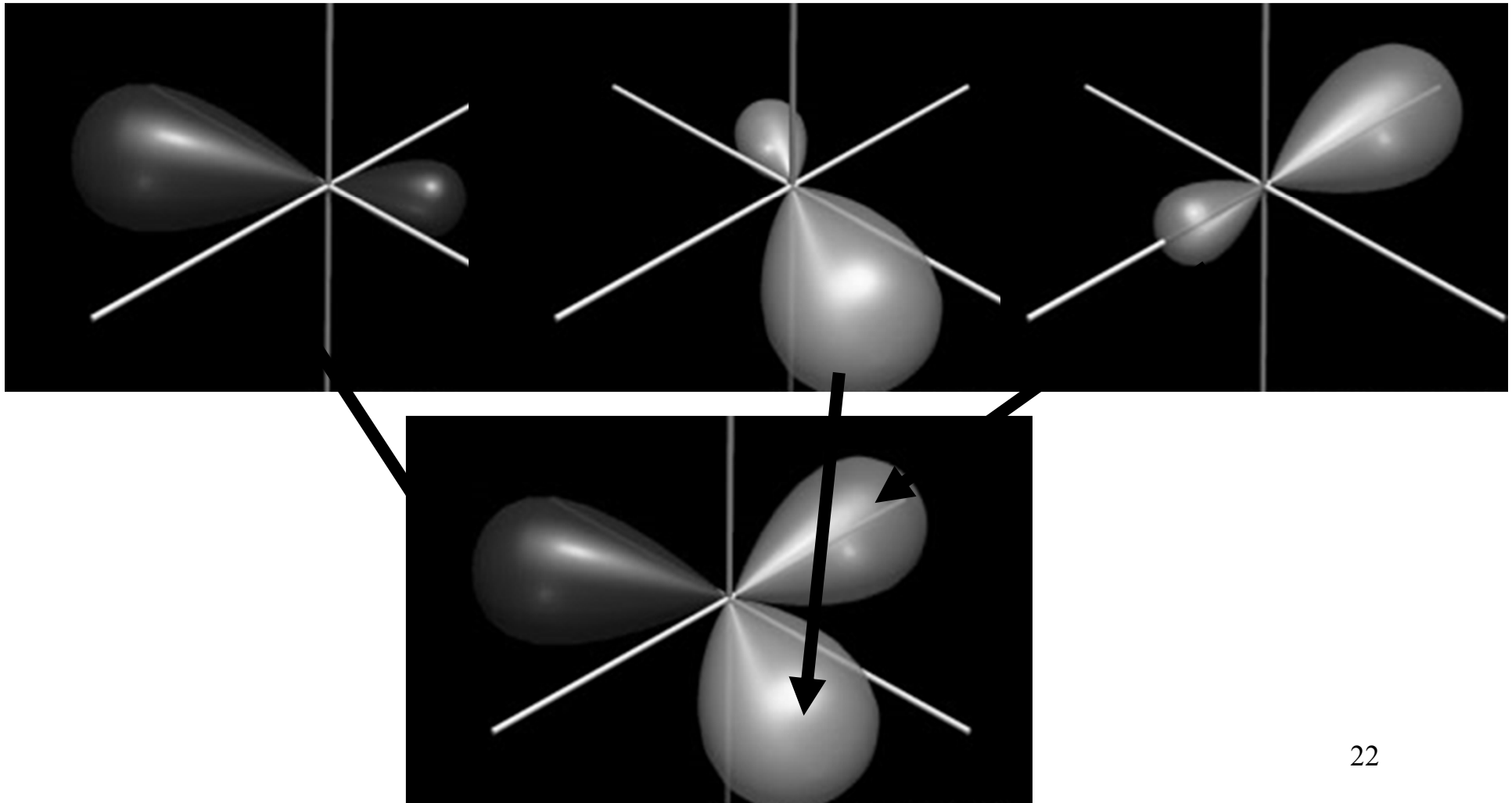
Hybridization sp^2



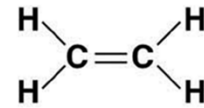
Hybridizace sp^2



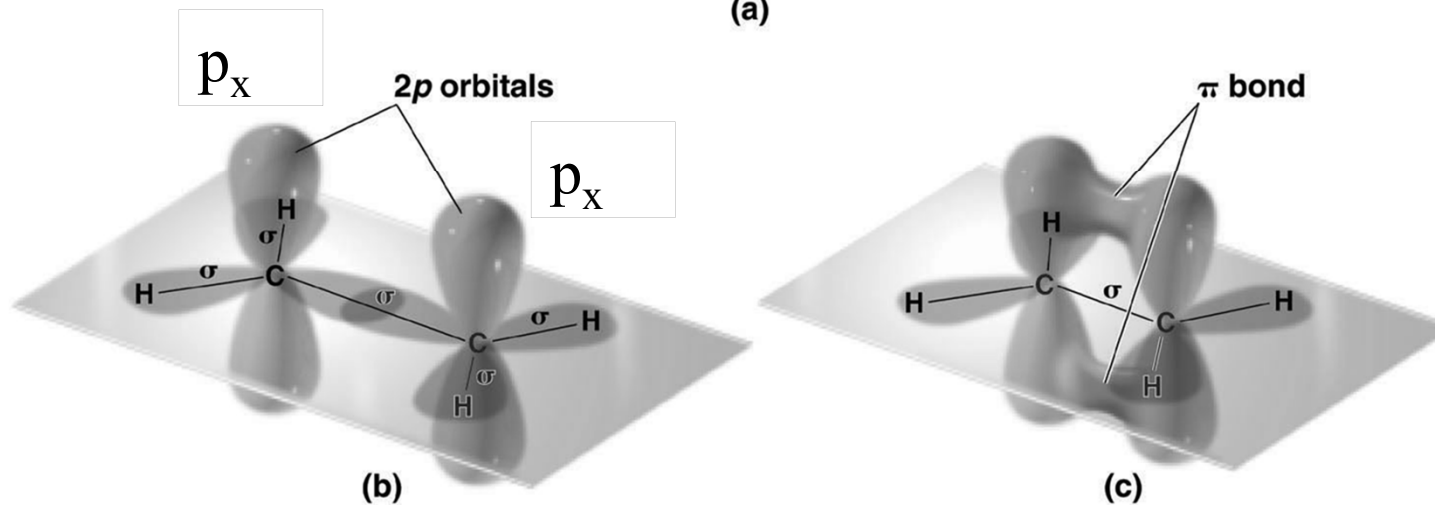
Hybridizace sp^2



Ethylen

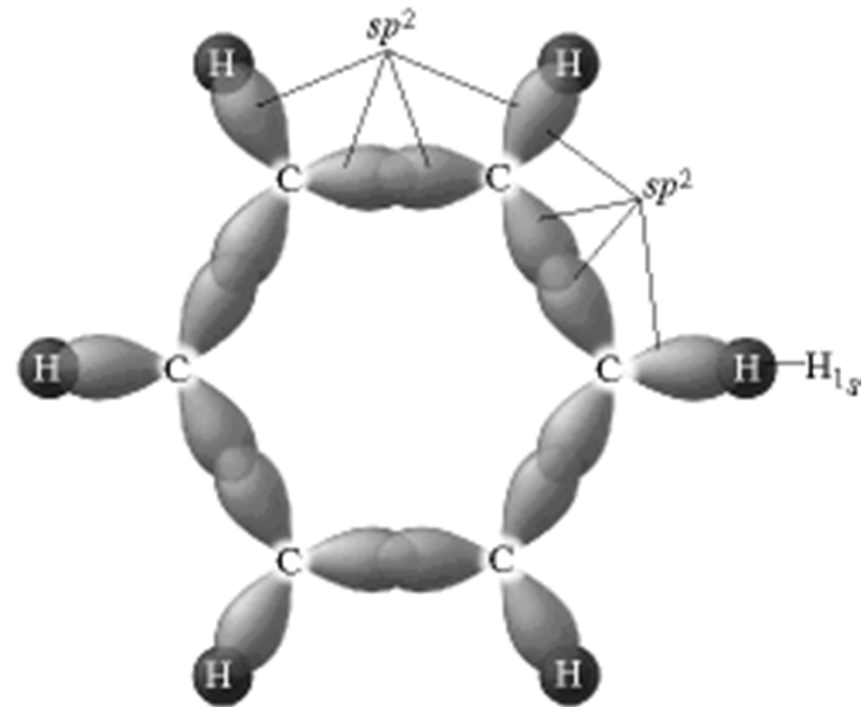
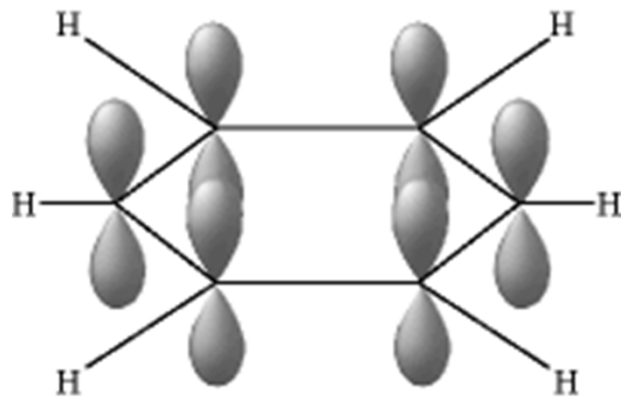
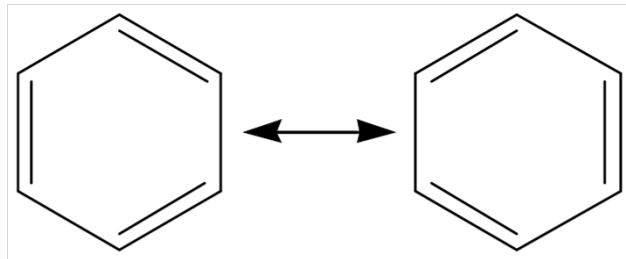


(a)



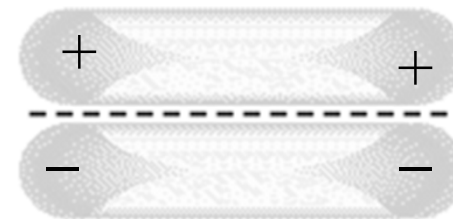
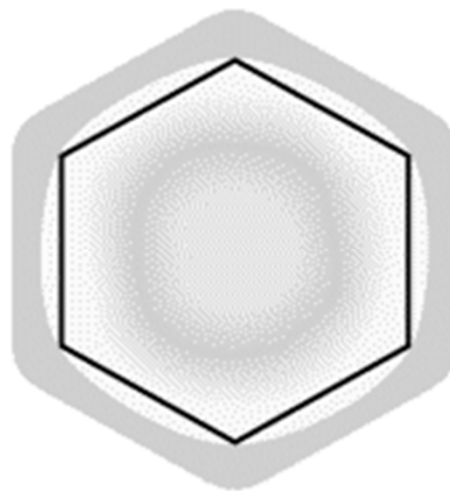
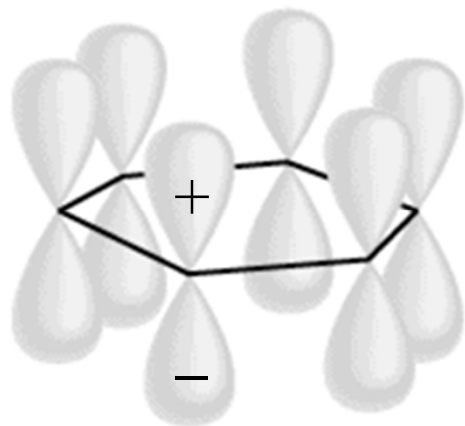
- 4 σ vazby překryvem $C(sp^2)-H(s)$
- 1 σ vazba překryvem $C(sp^2)-C(sp^2)$
- 1 π -vazba překryvem $C(p_x)-C(p_x)$

Benzen

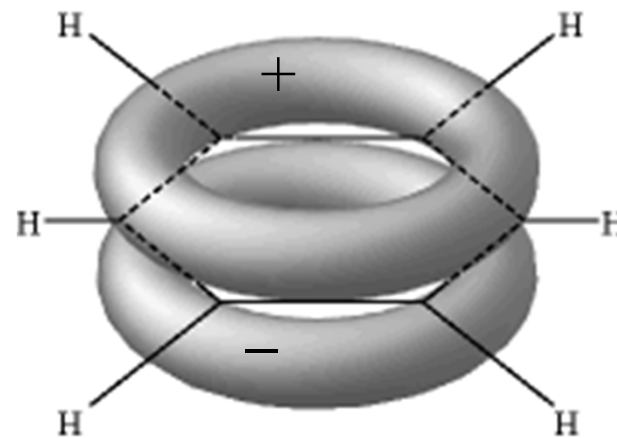


- Každý C použije 3 sp^2 orbitaly pro 3 σ -vazby
2 C – C vazby a 1 C – H vazba
- 1 $2p_x$ orbital na každém C zůstane nepoužitý (pro σ -vazby)

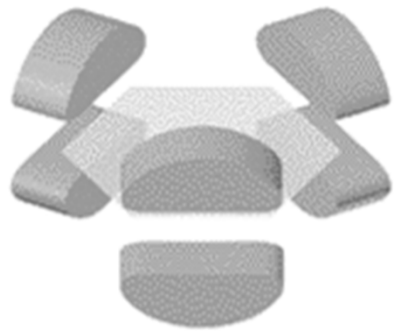
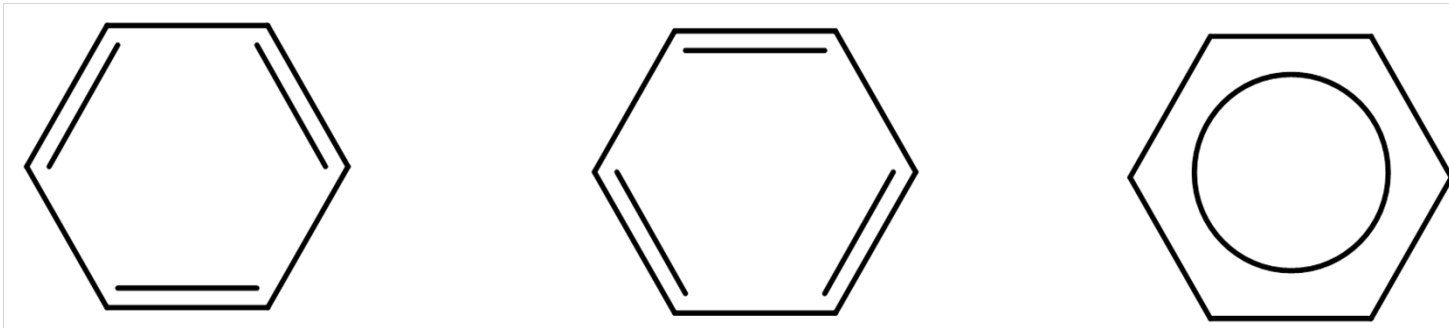
Benzen



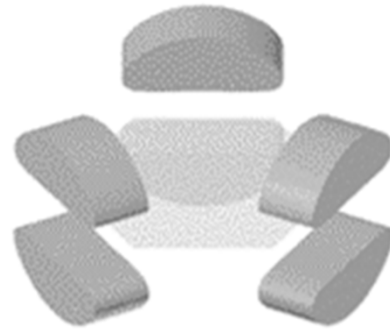
6 C $2p_x$ orbitalů použito pro 3 π -vazby



Benzen



(a) Localized π bonds

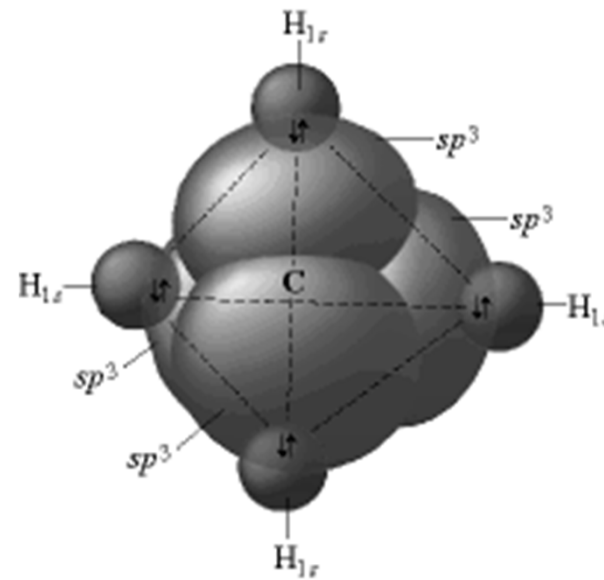
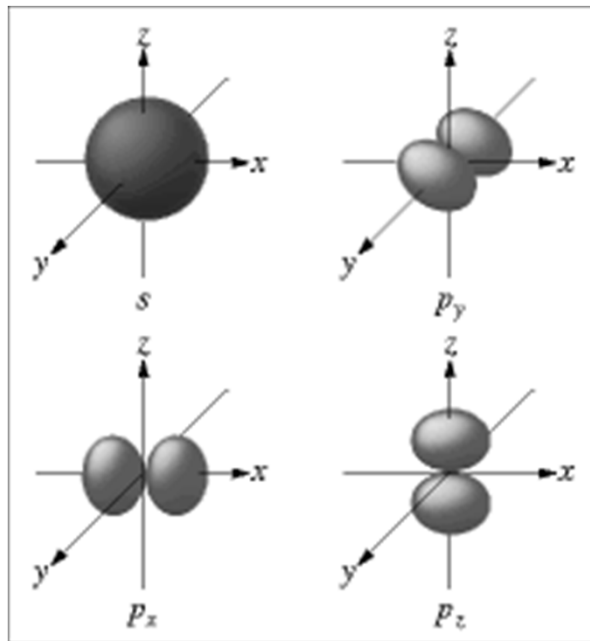


(b) Localized π bonds

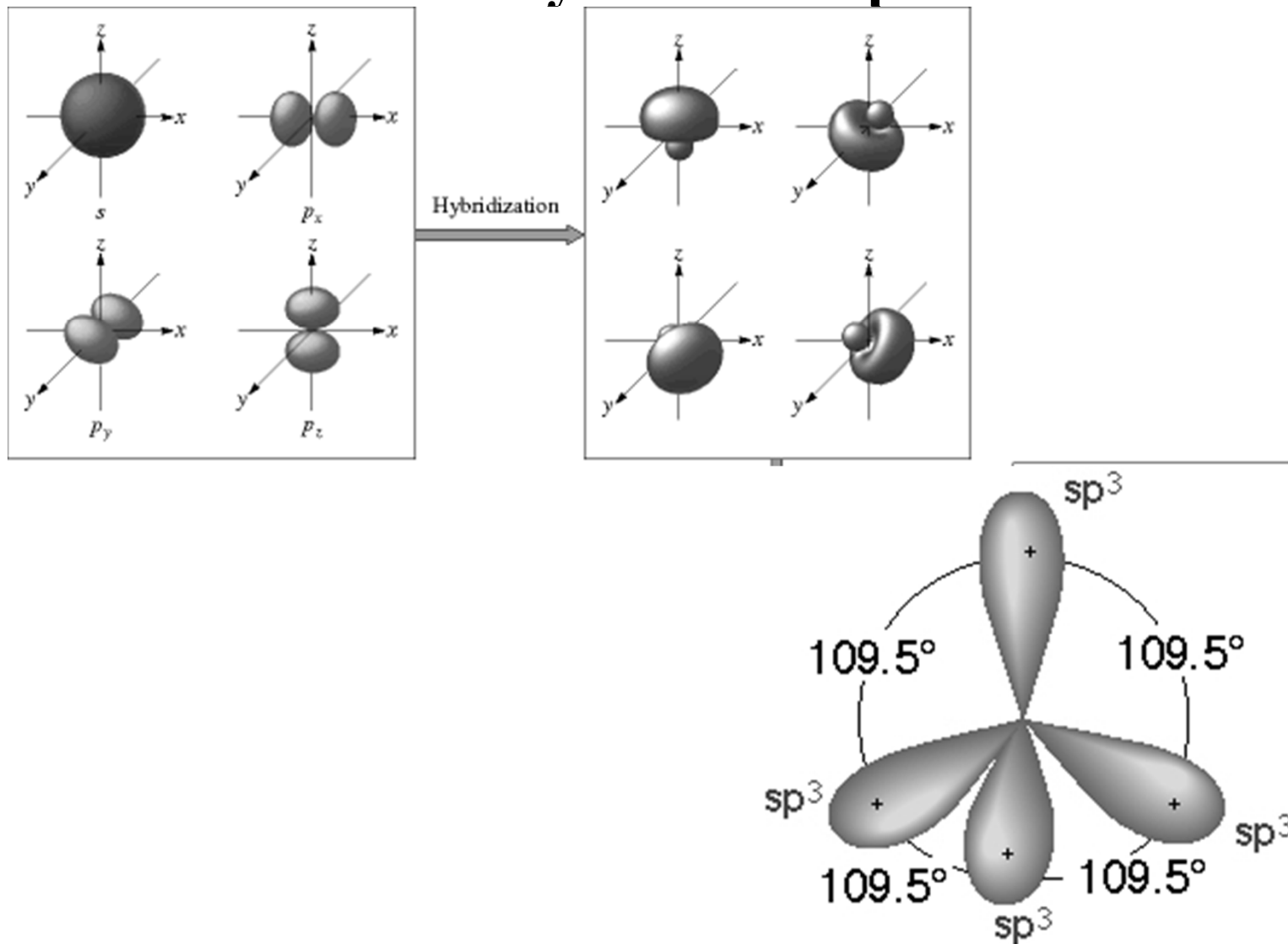


(c) Delocalized π bonds

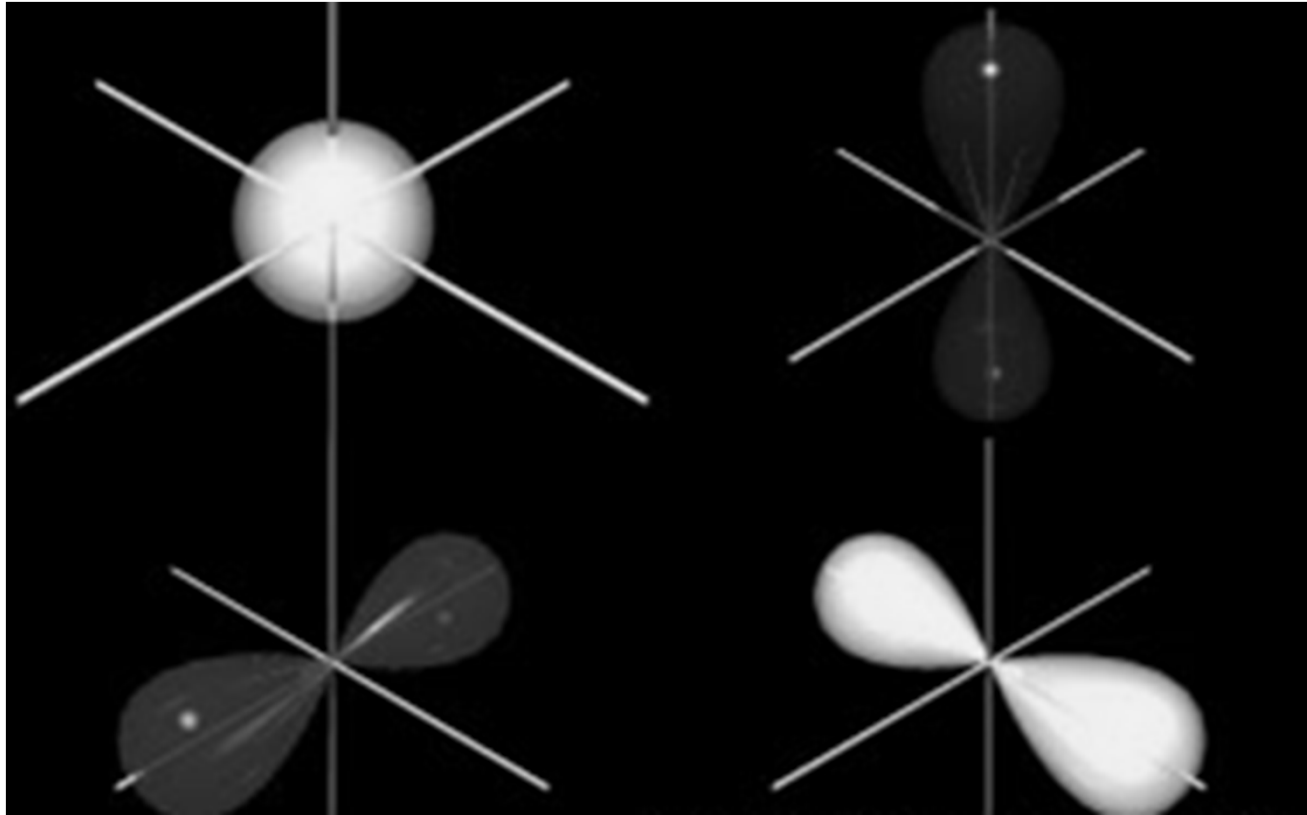
Hybridization sp^3

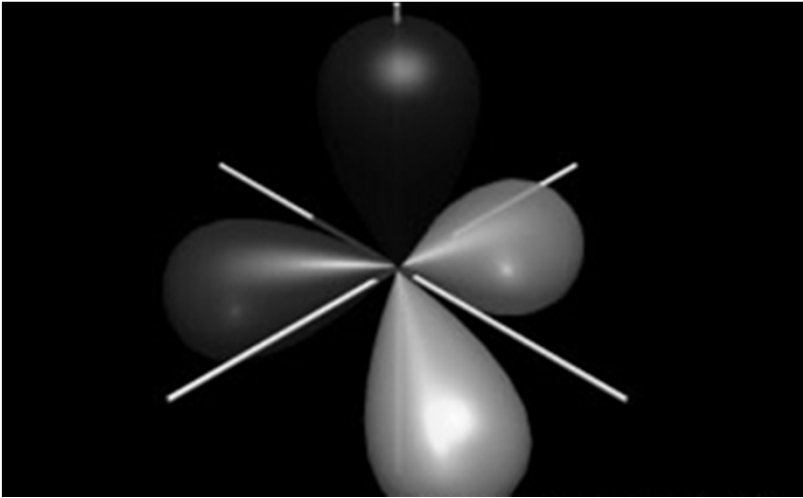
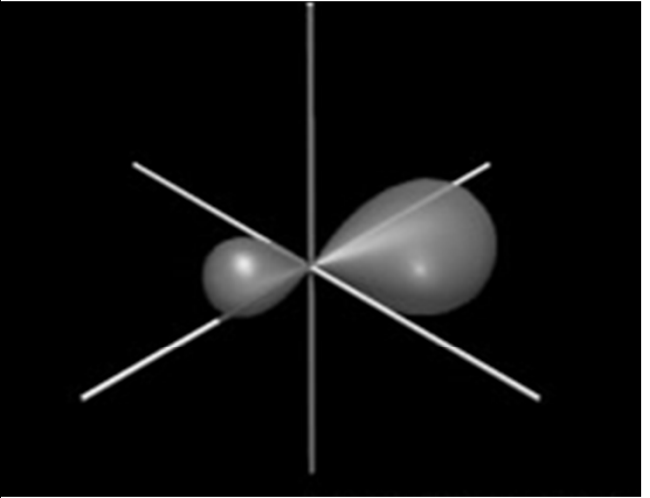
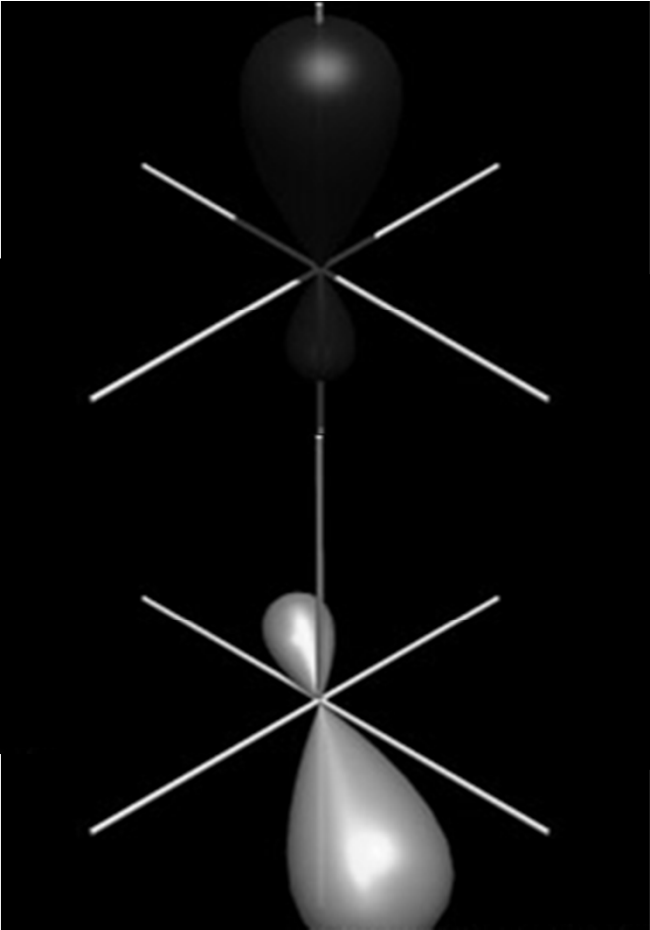
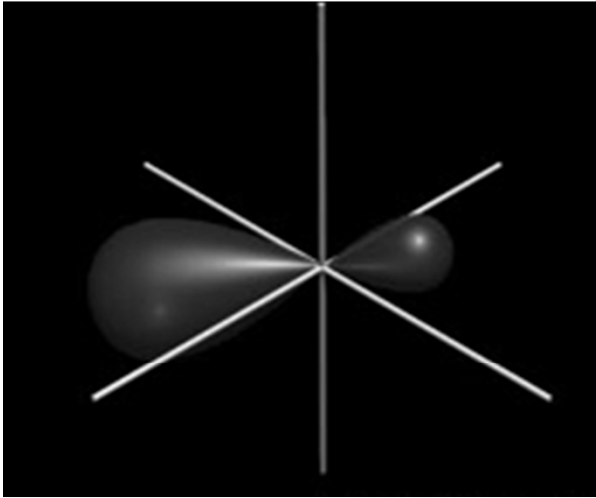


Hybridizace sp^3



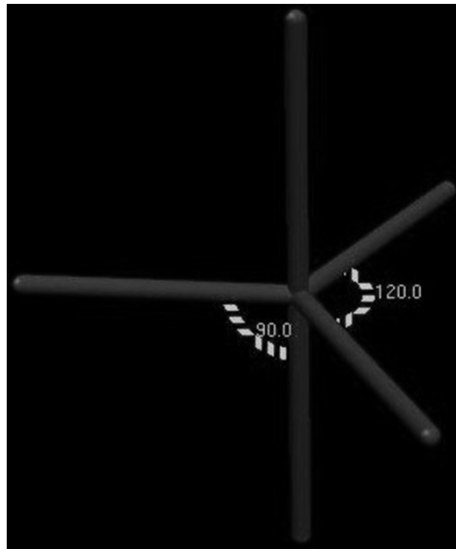
Hybridizace sp^3



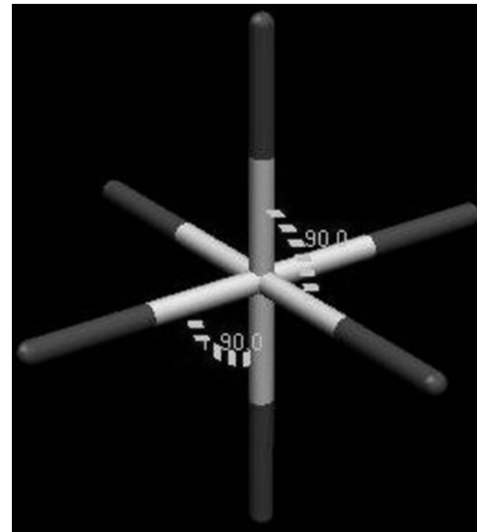


Hybridize

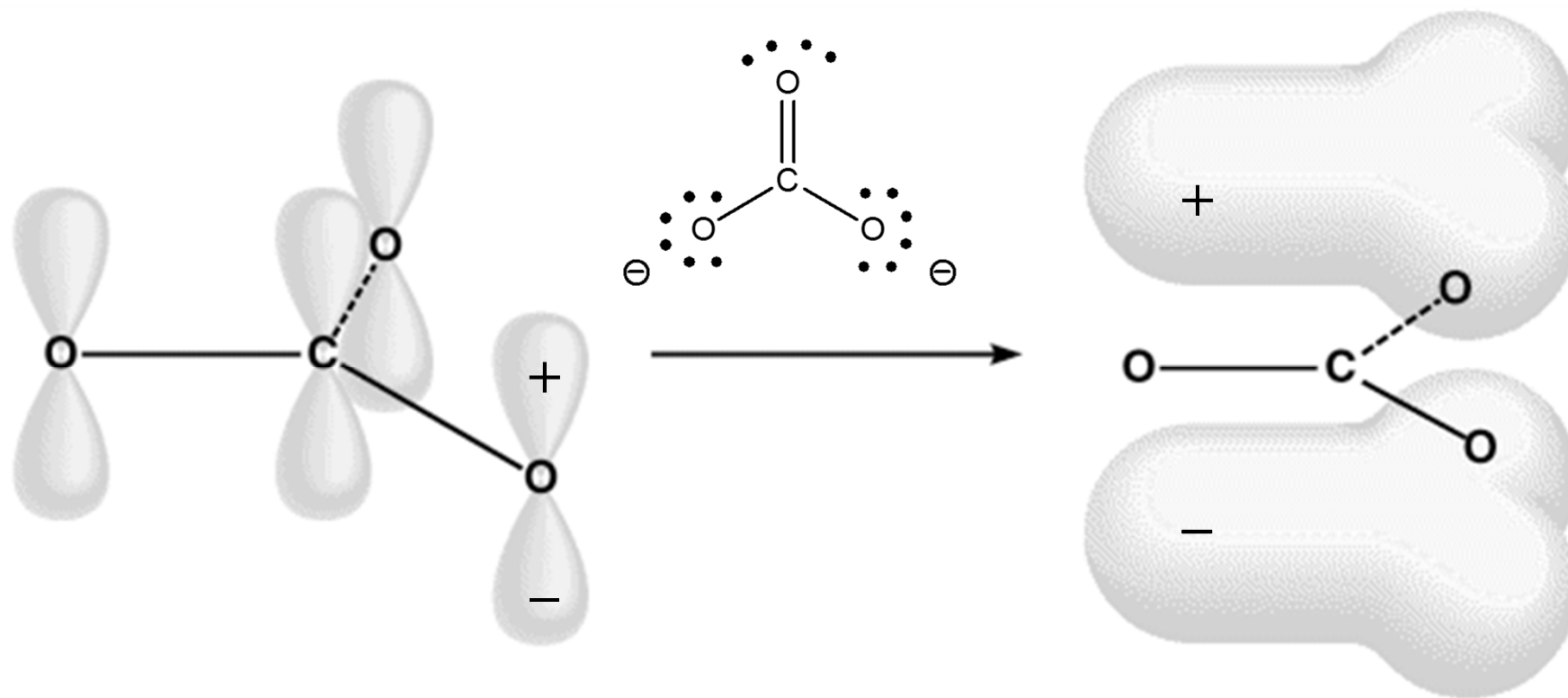
sp^3d



sp^3d^2

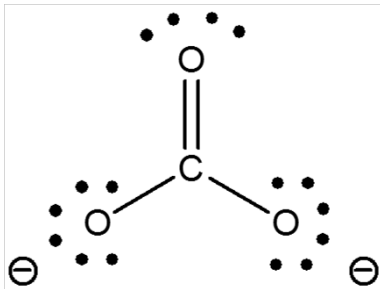


Vazba v CO_3^{2-} a NO_3^-



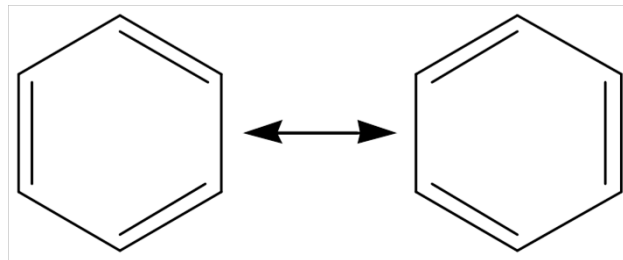
3 σ vazby překryvem $\text{C}(\text{sp}^2)\text{--O}(\text{sp}^2)$
1 π -vazba překryvem $\text{C}(\text{p}_x)\text{--O}(\text{p}_x)$

Řád vazby



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

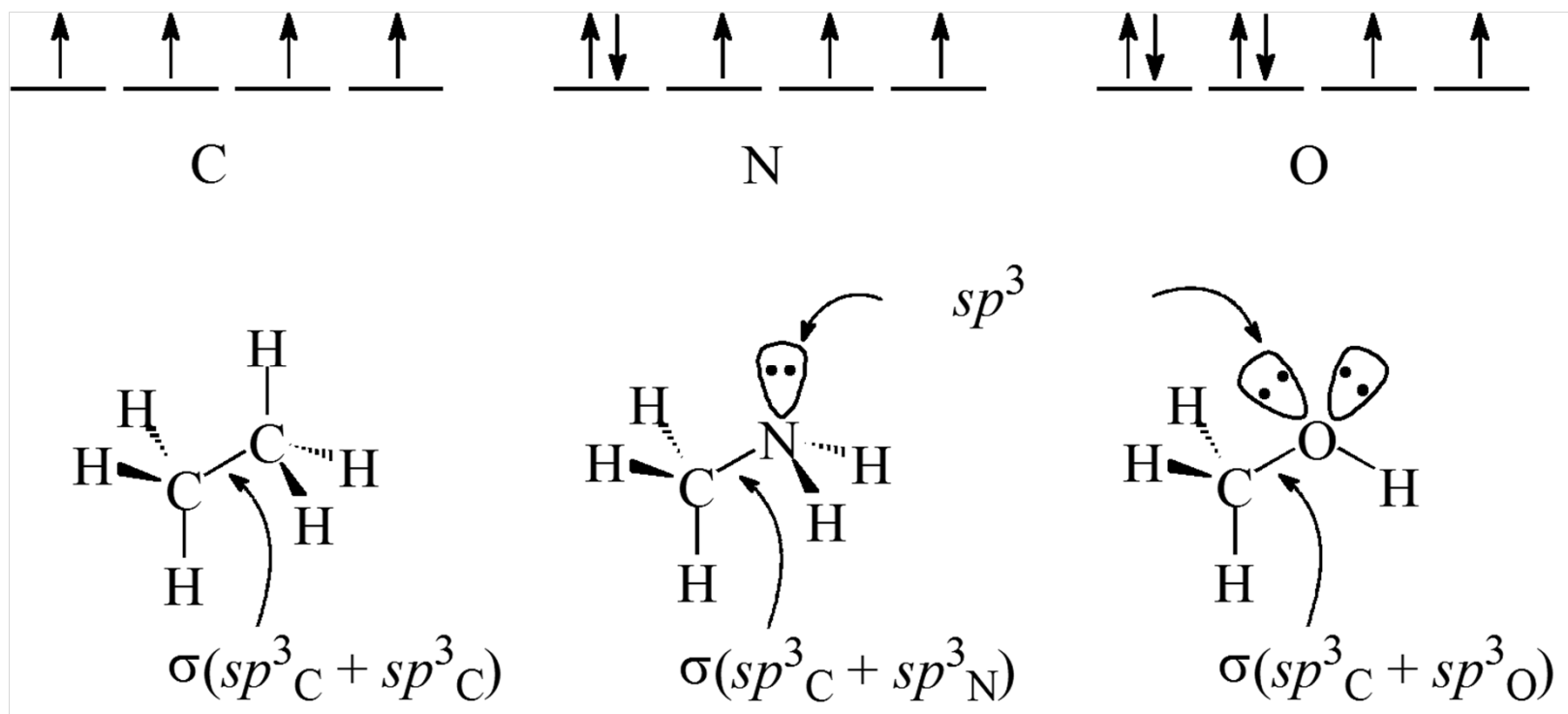
Řád vazby = 1.3333



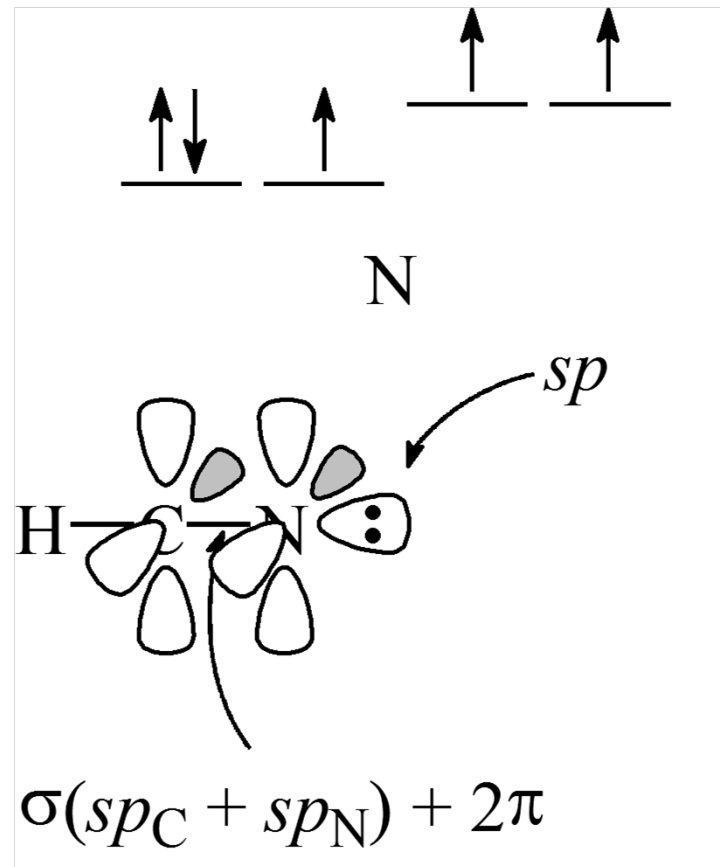
9 (6+3) vazebných elektronových párů / 6 vazeb

Řád vazby = 1.5

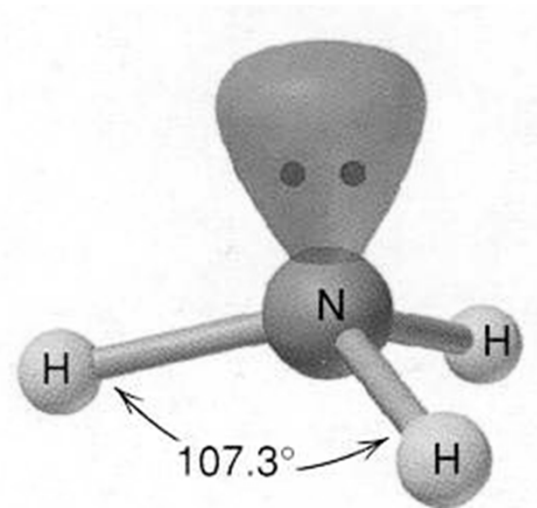
Vazba v C_2H_6 , CH_3NH_2 a CH_3OH



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
NF ₃	102.5°	
OH ₂	104.5°	
OF ₂	103.2°	

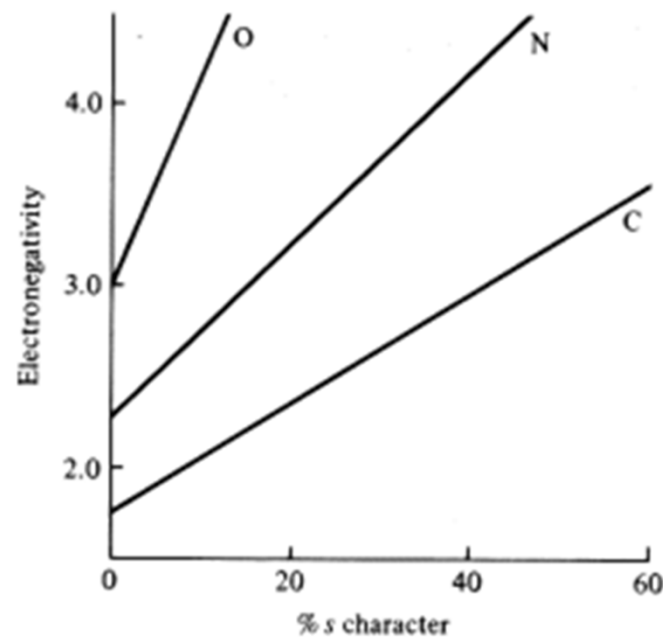
Rostoucí $\Delta\chi$ snižuje
vazebné úhly

Hybridizace a elektronegativita

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

↑
s-charakter

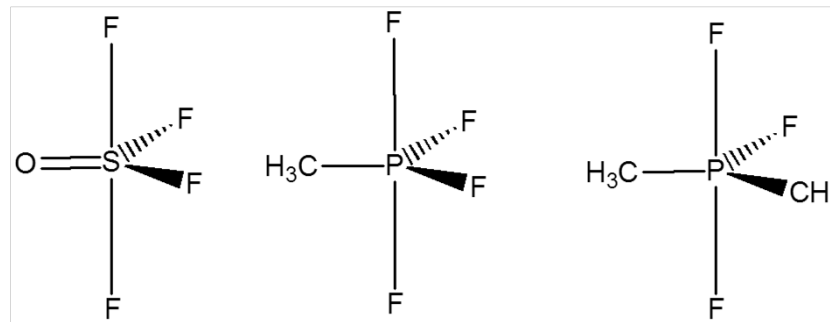
↑
p-charakter



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.

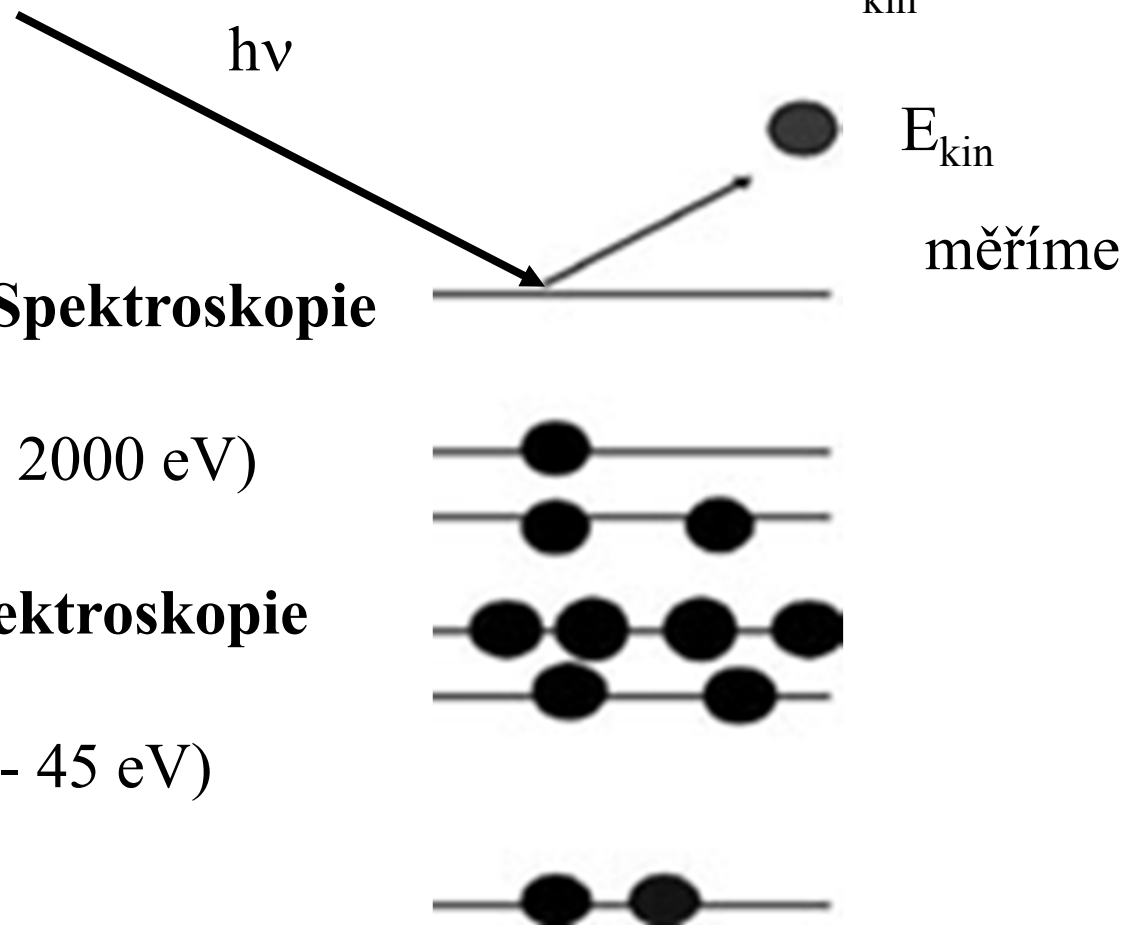


Lepší donory obsazují ekvatoriální rovinu v TBP (sp^2) a akceptory obsazují axiální polohy (pd).

Volný elektronový pár je nejlepší donor = substituent s nulovou elektronegativitou

PES = Fotoelektronová spektroskopie

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

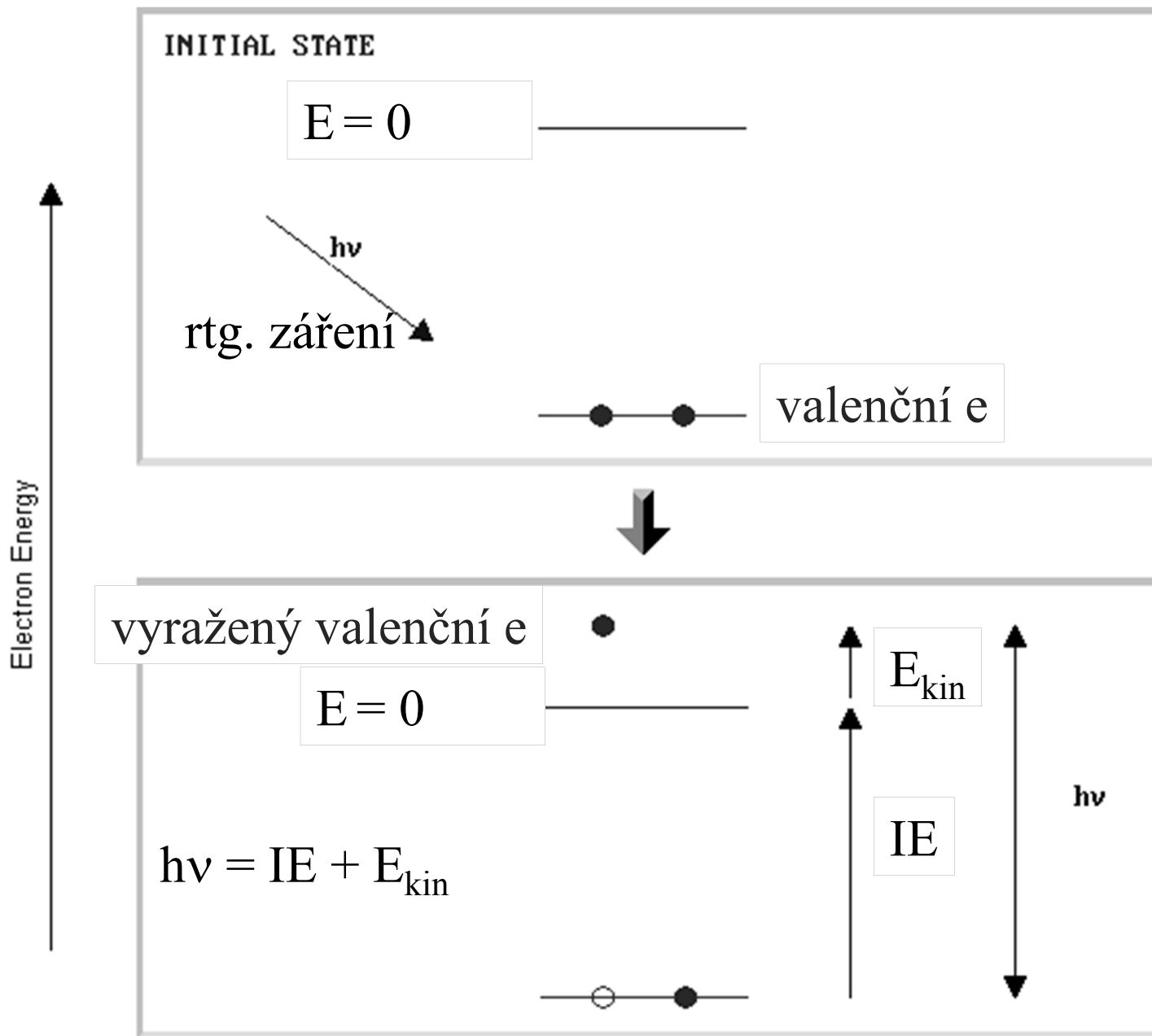


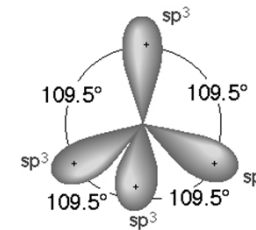
X-ray Fotoelektronová Spektroskopie (XPS)

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

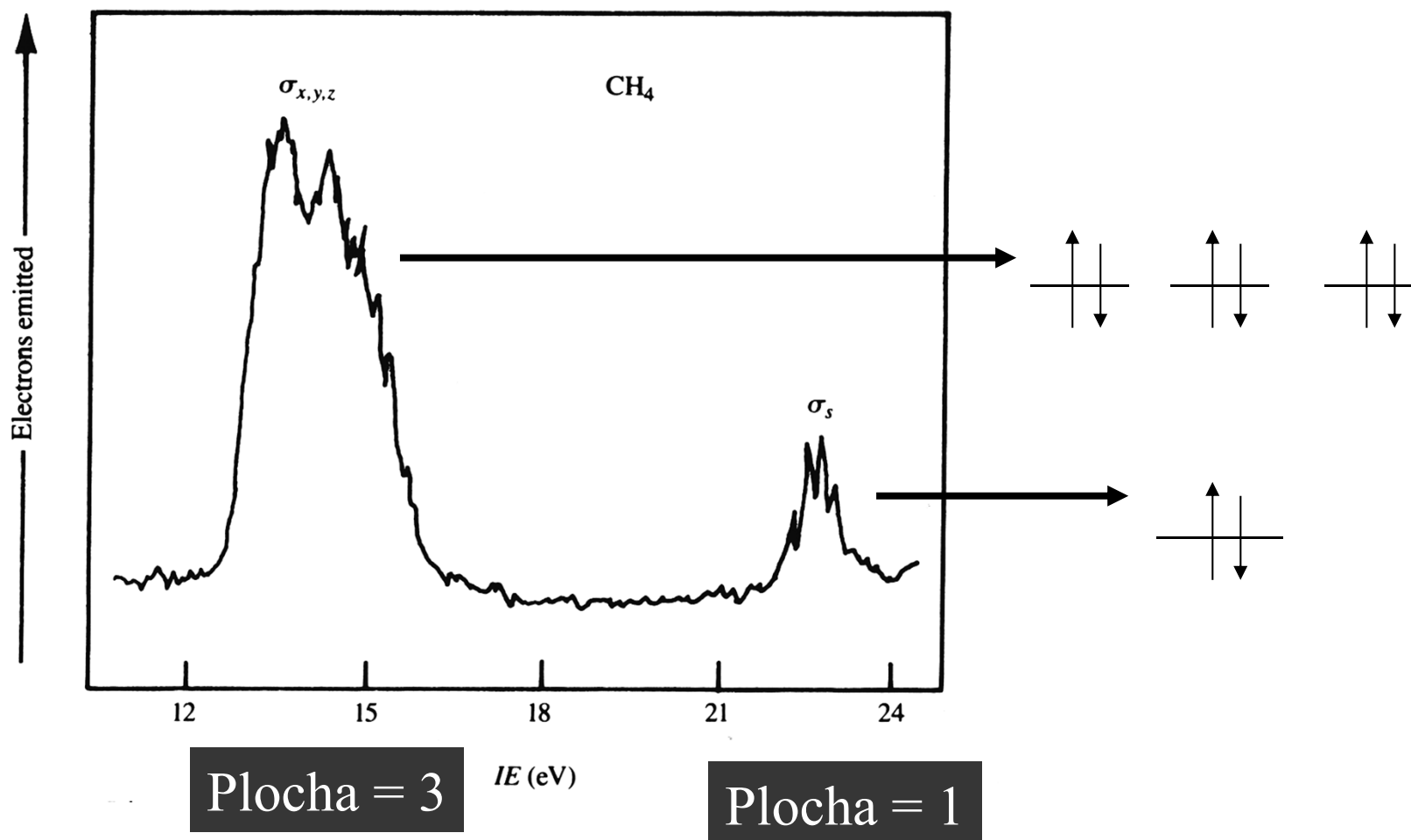
UV Fotoelektronová Spektroskopie (UPS)

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

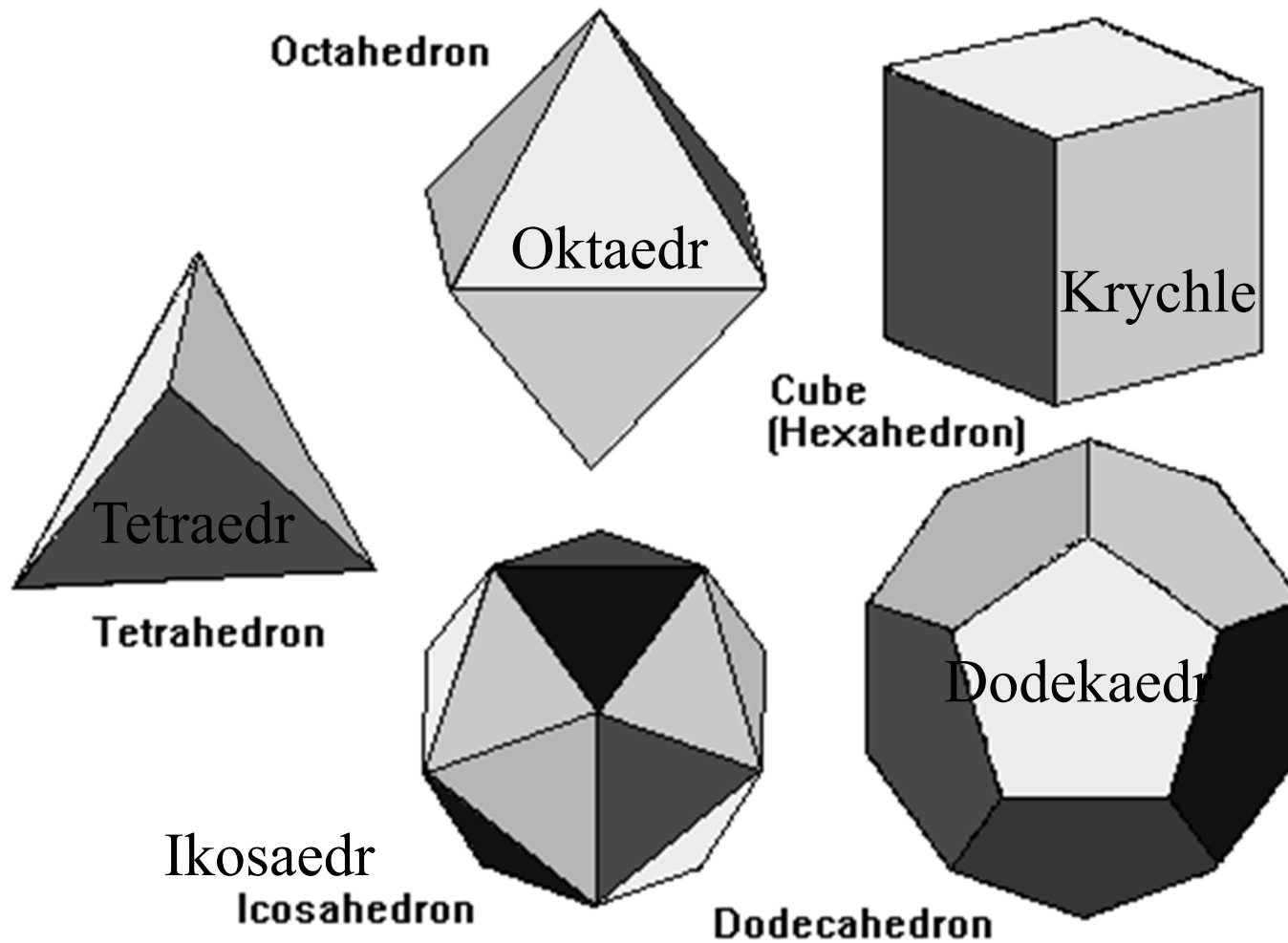




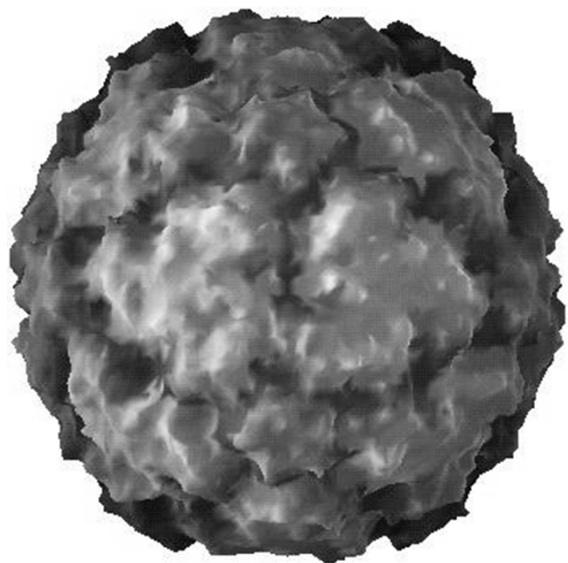
PES methanu nesouhlasí s modelem 4 sp^3



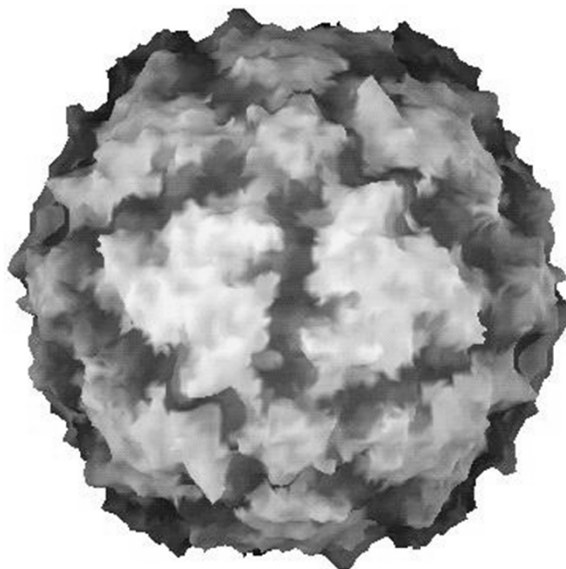
Symetrie – Platonovská tělesa



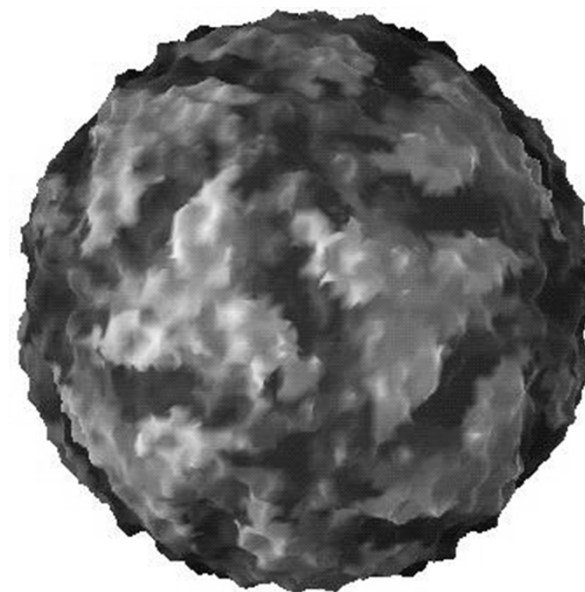
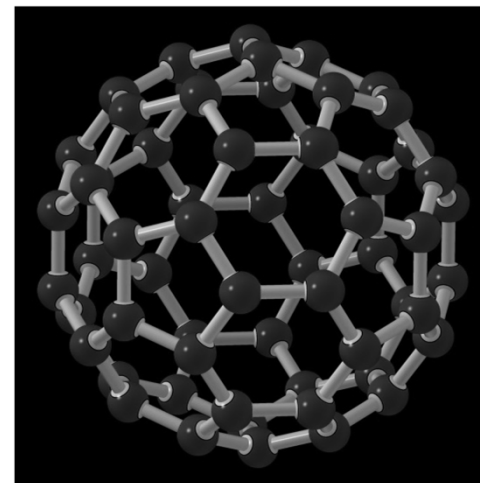
Symetrie



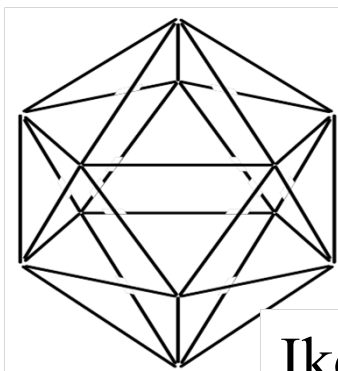
Virus rýmy



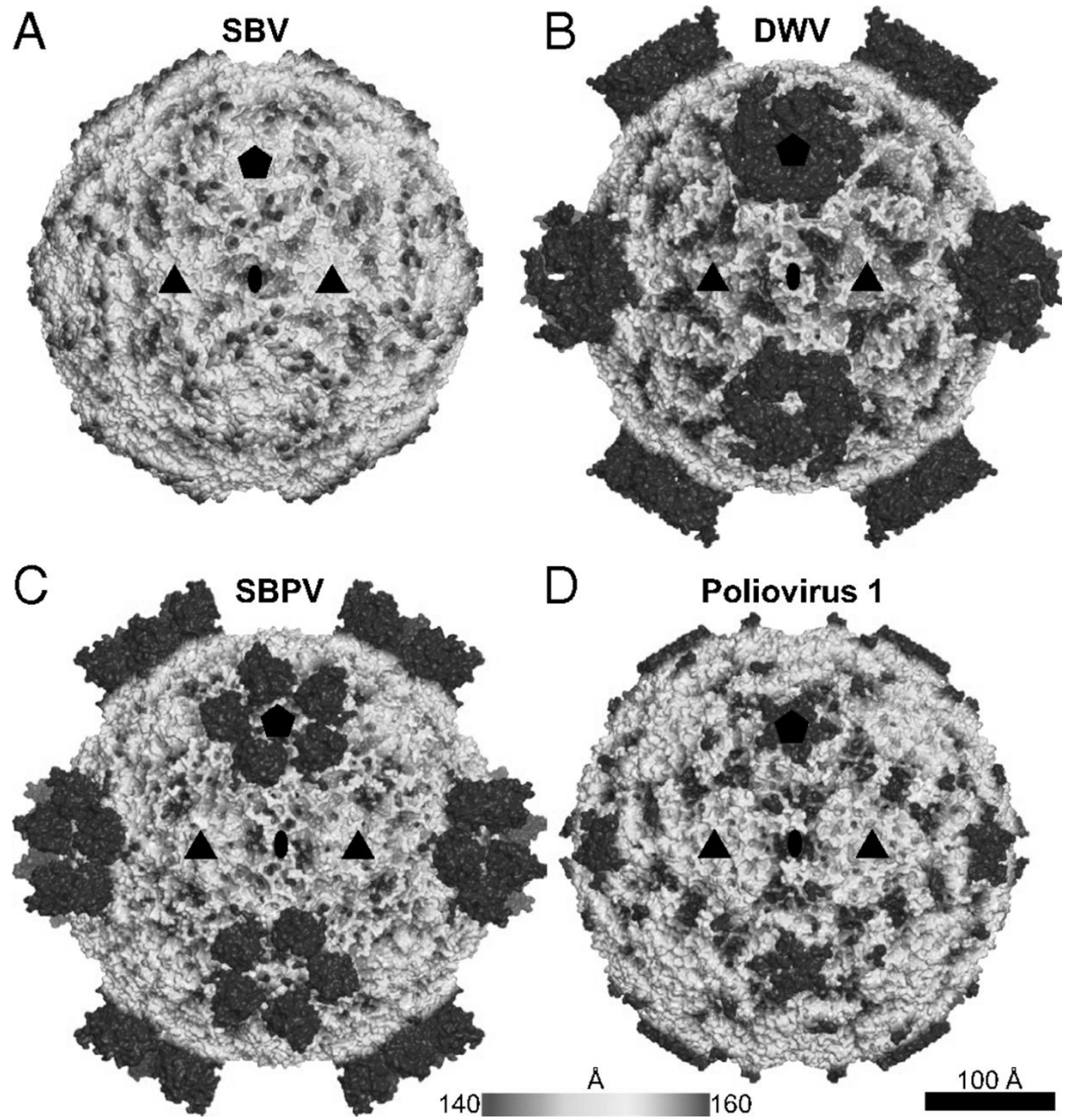
Virus obrny



Virus slintavky a kulhavky

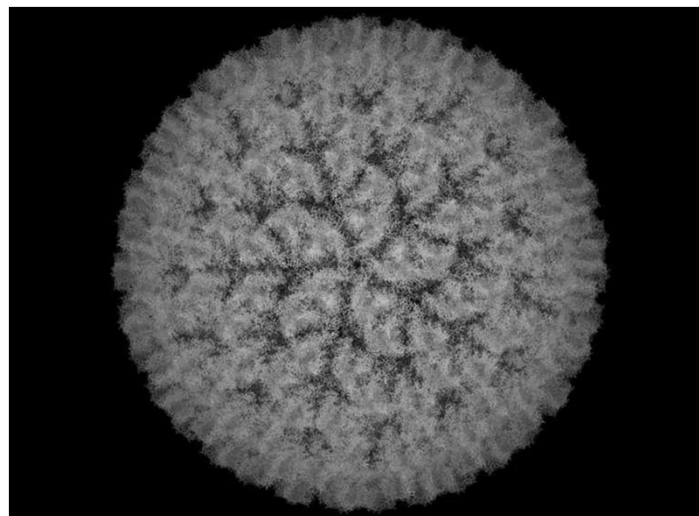
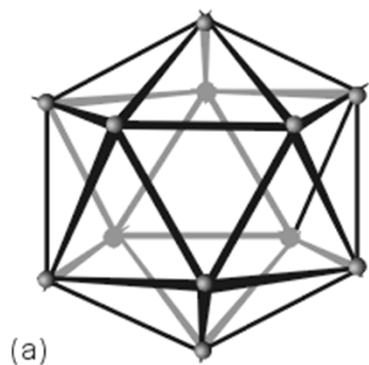
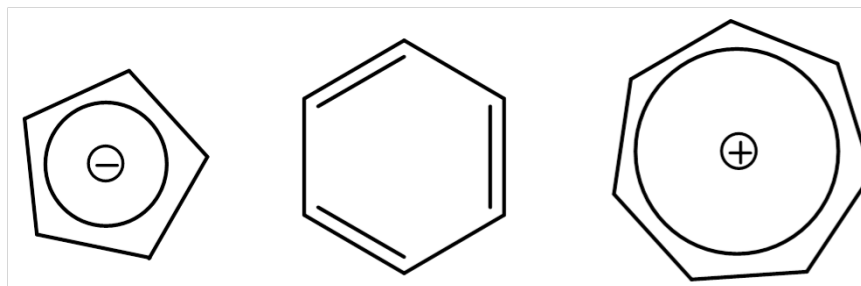
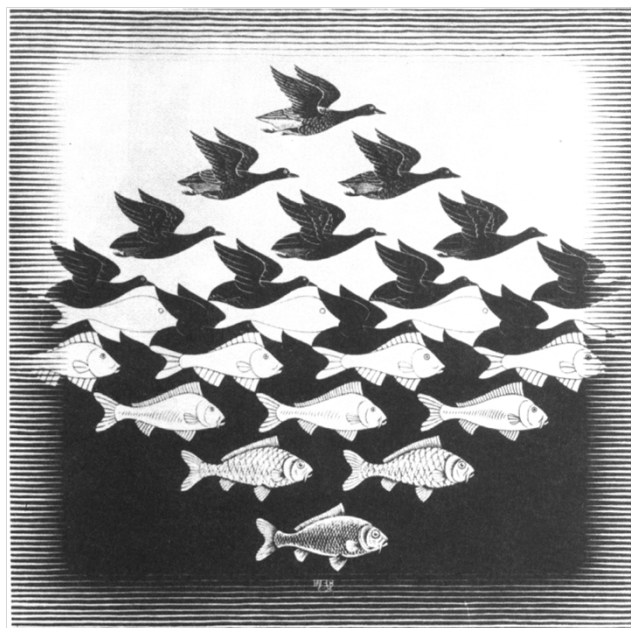


Ikosaedr



Symetrie molekul

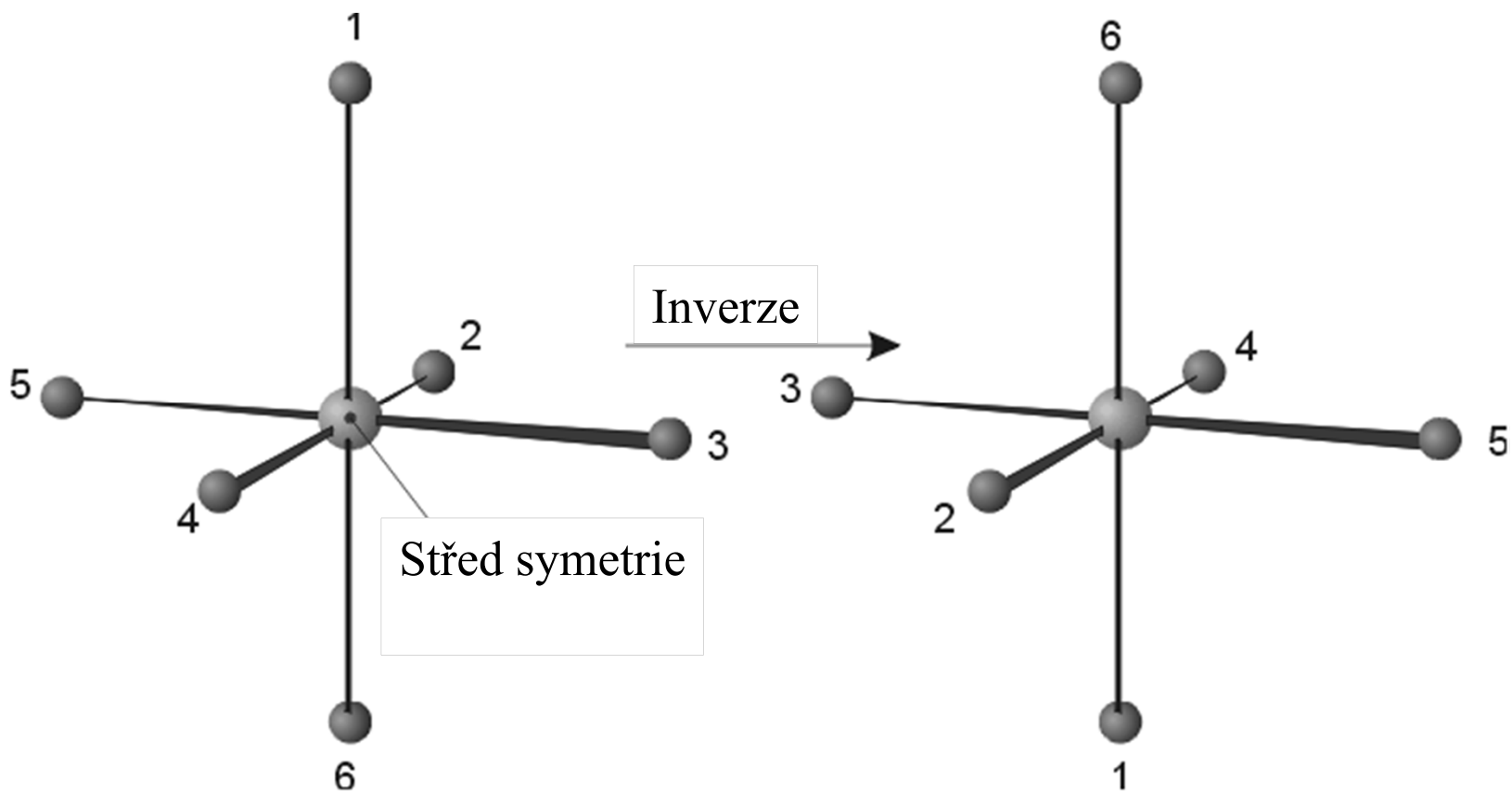
Jak jsou atomy v molekule uspořádány = ekvivalentní atomy



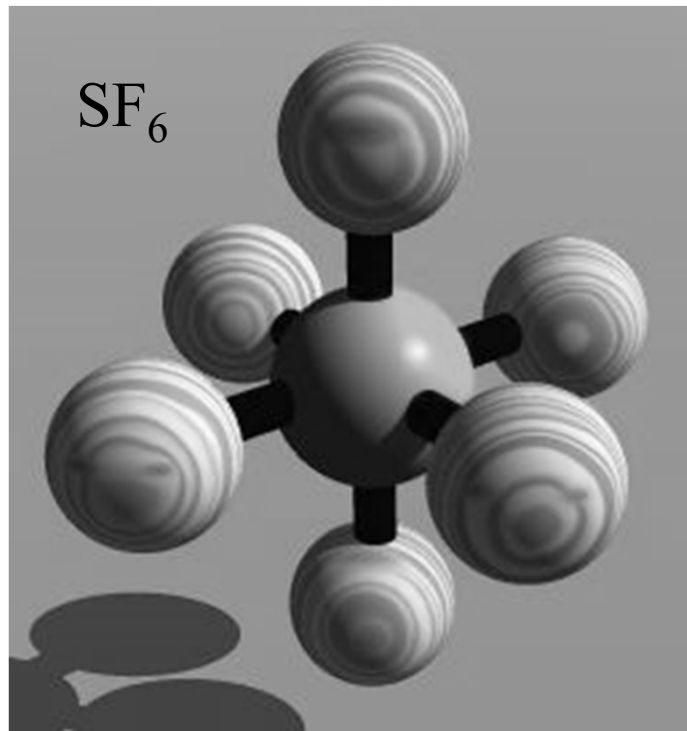
Prvky a operace symetrie

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

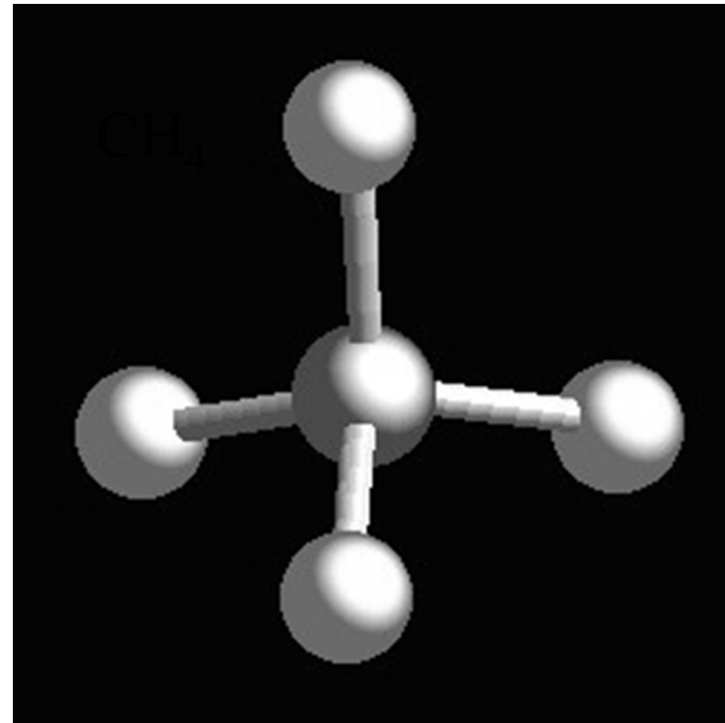
Střed symetrie



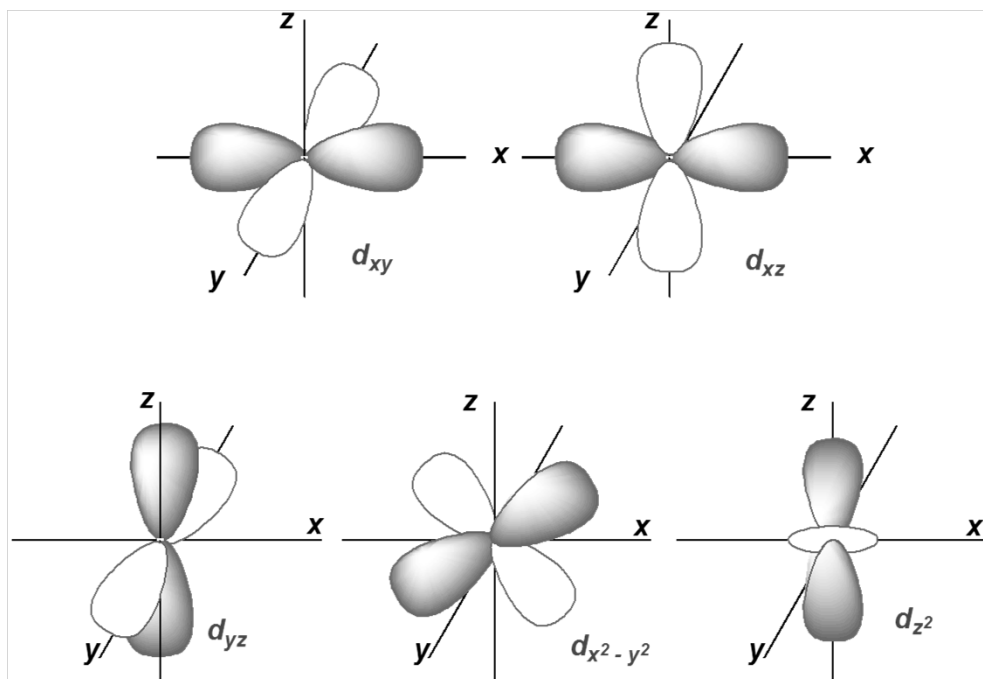
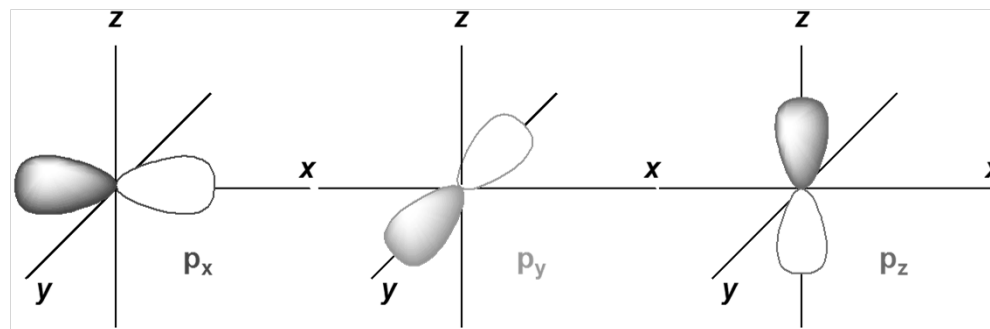
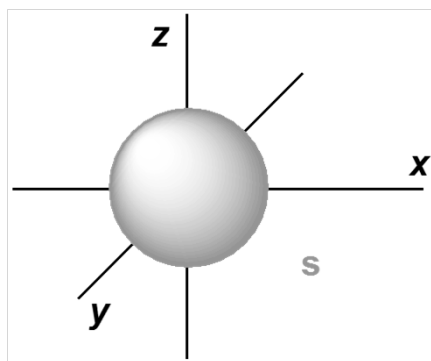
Střed symetrie



S = střed symetrie



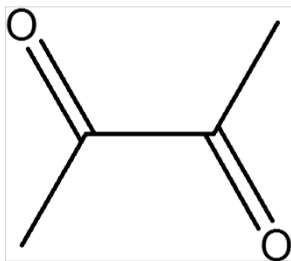
Nemá střed symetrie



Orbitaly

s a d **mají** *i* (střed symetrie)

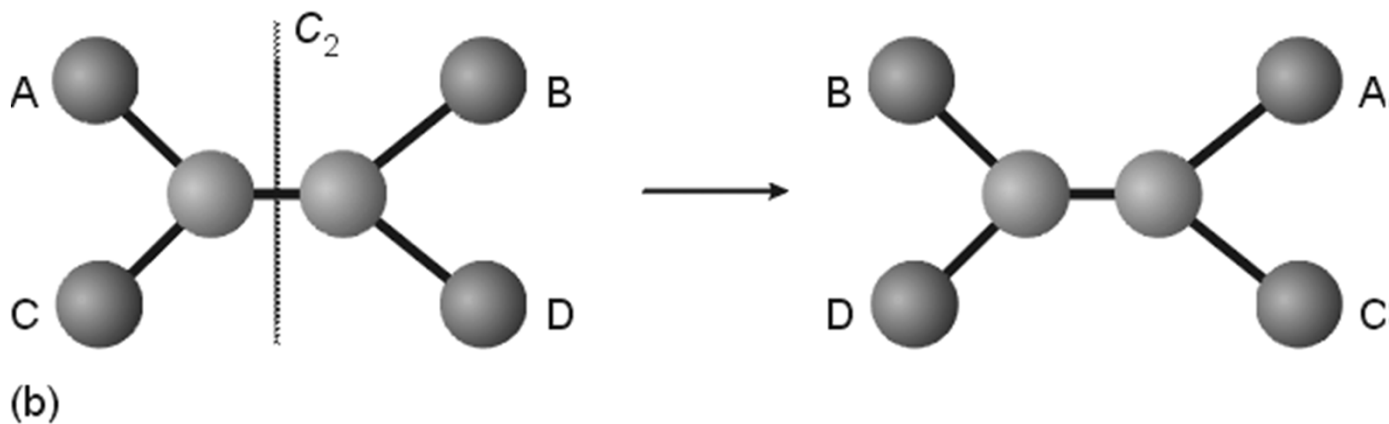
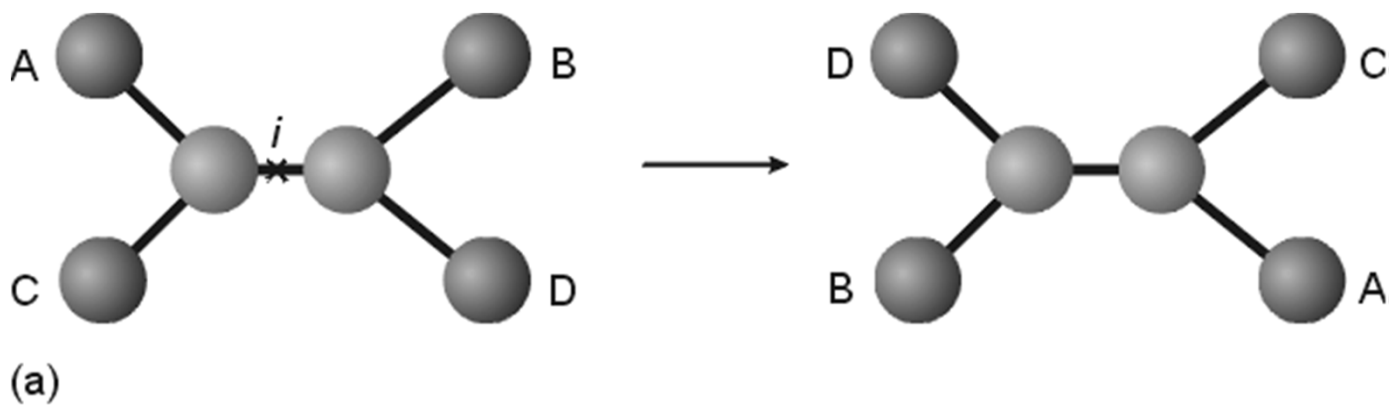
p a f **nemají** *i* (střed symetrie)



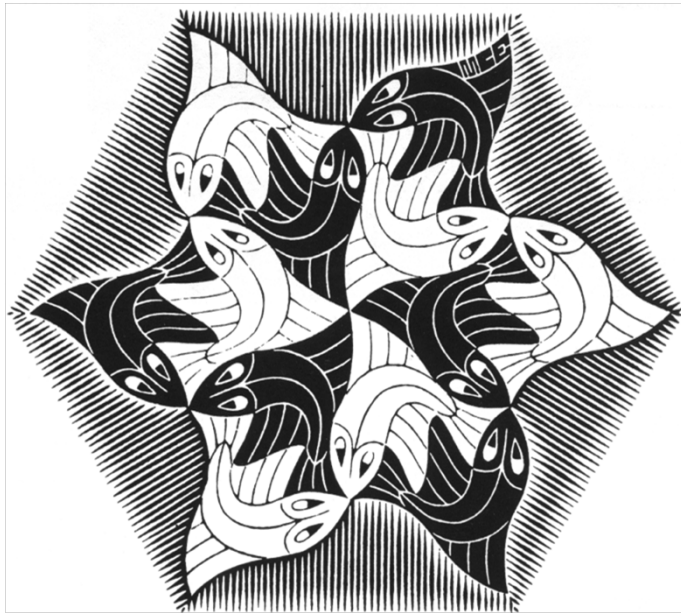
Rotační osa C_2



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

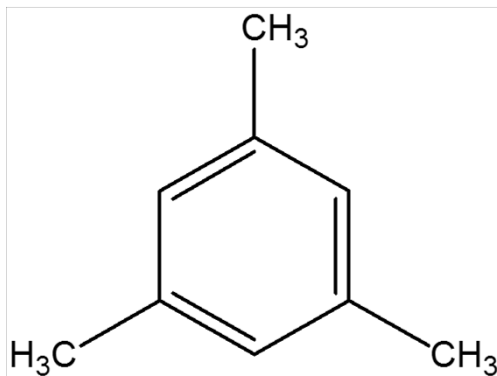
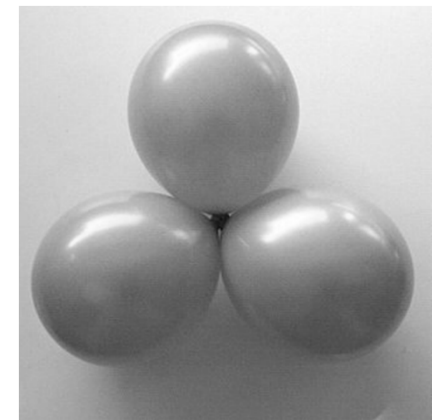
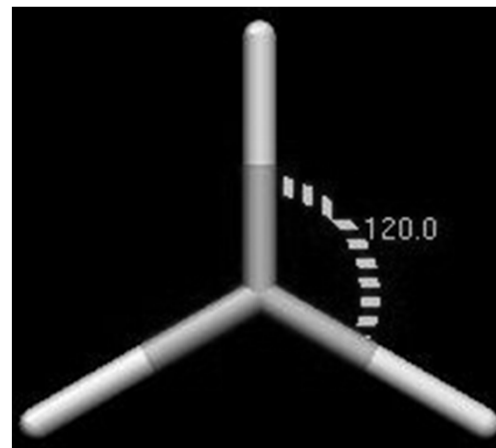


Rotační osa C_3



Rotace o úhel $360/n$

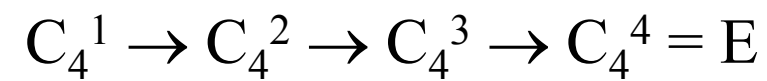
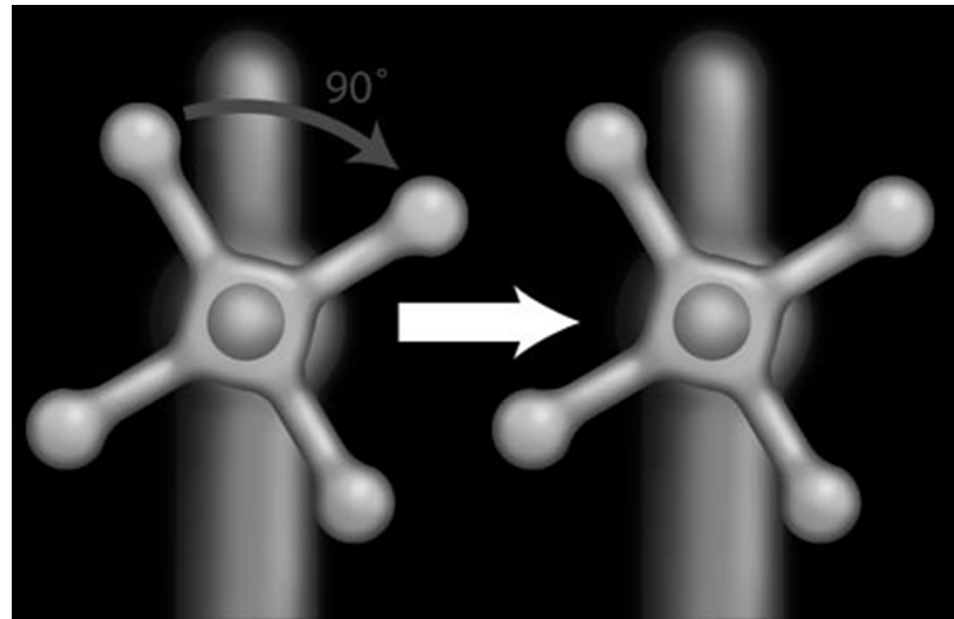
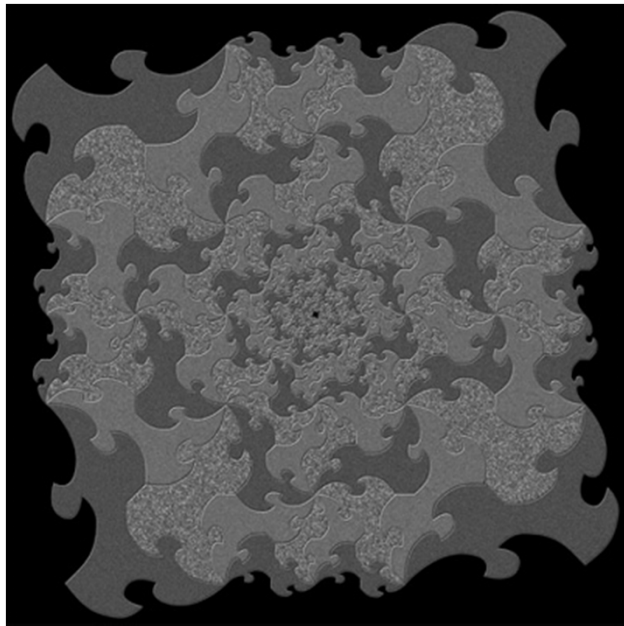
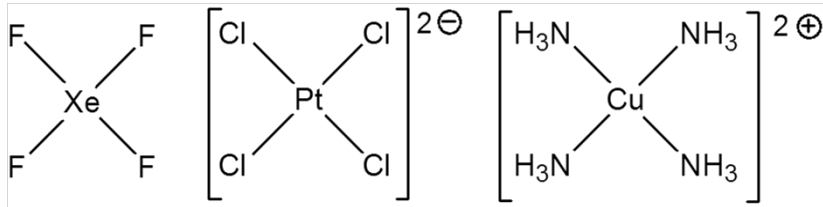
Vzniklá situace je nerozlišitelná od výchozí



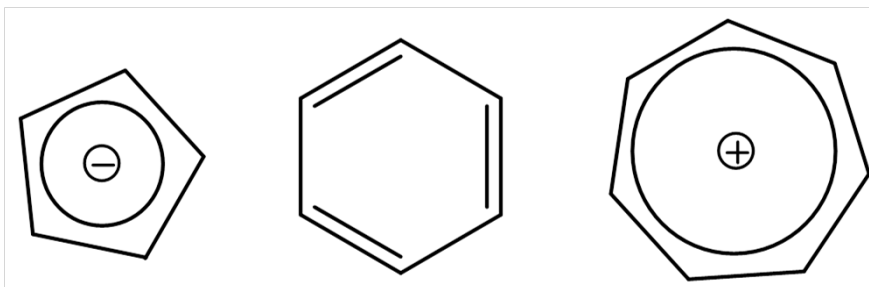
Rotační osa C_4

Rotace o úhel $360/4$.

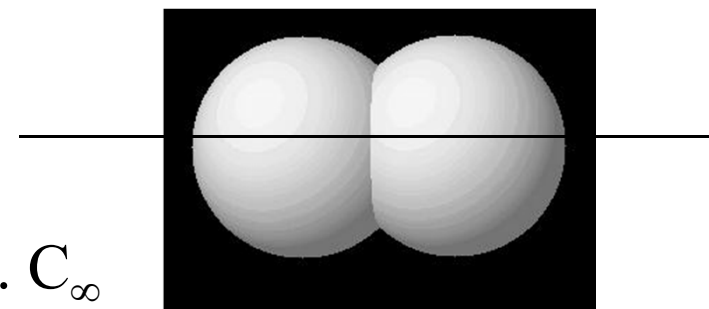
Vzniklá situace je nerozlišitelná od výchozí.



Rotační osa C_n



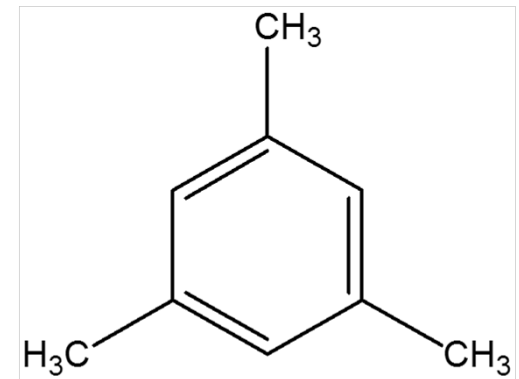
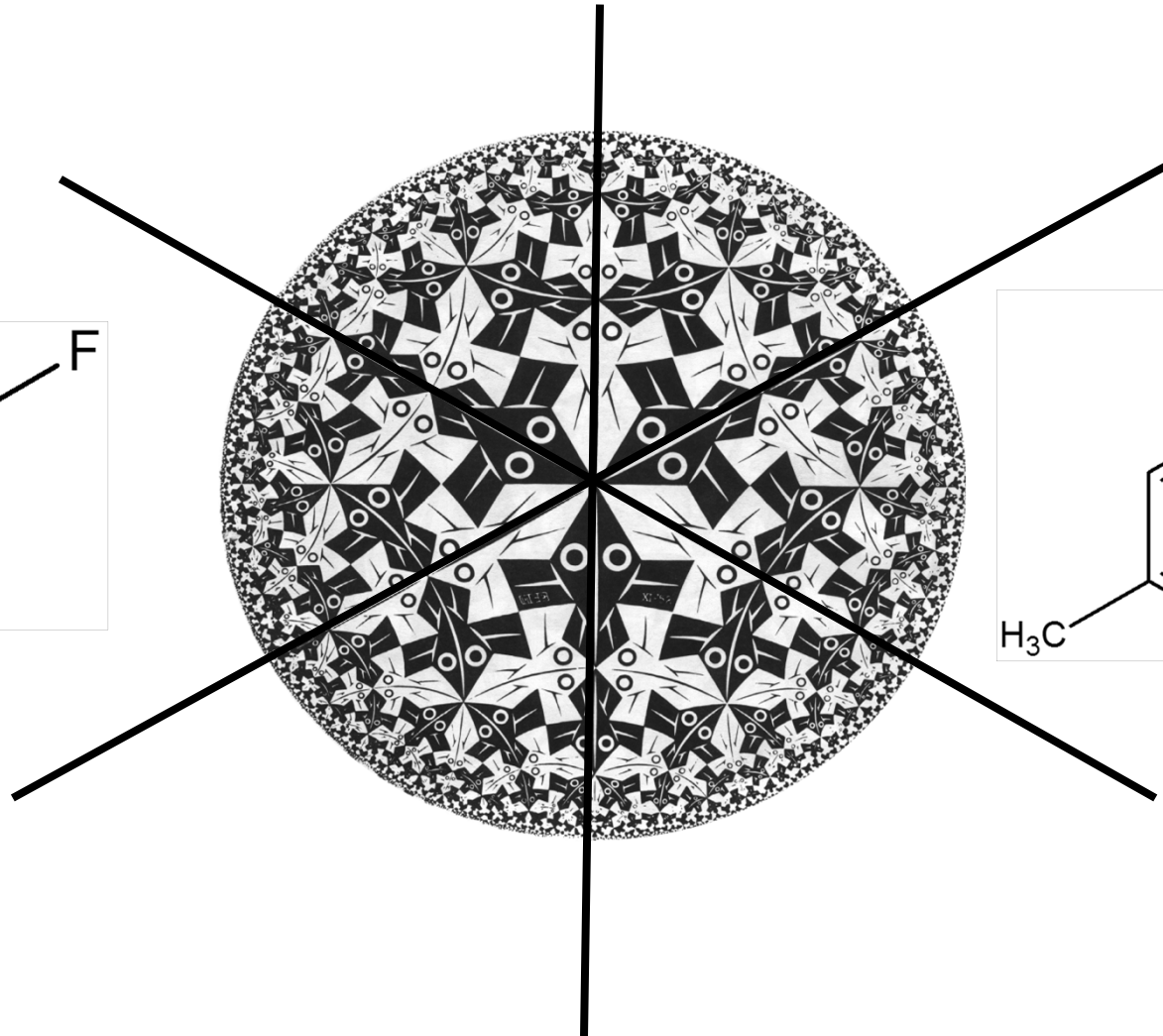
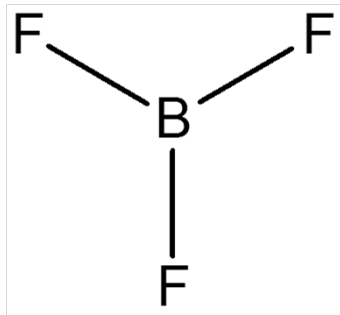
$C_5, C_6, C_7, \dots, C_\infty$



Lineární molekuly



Rovina symetrie σ



Roviny symetrie σ

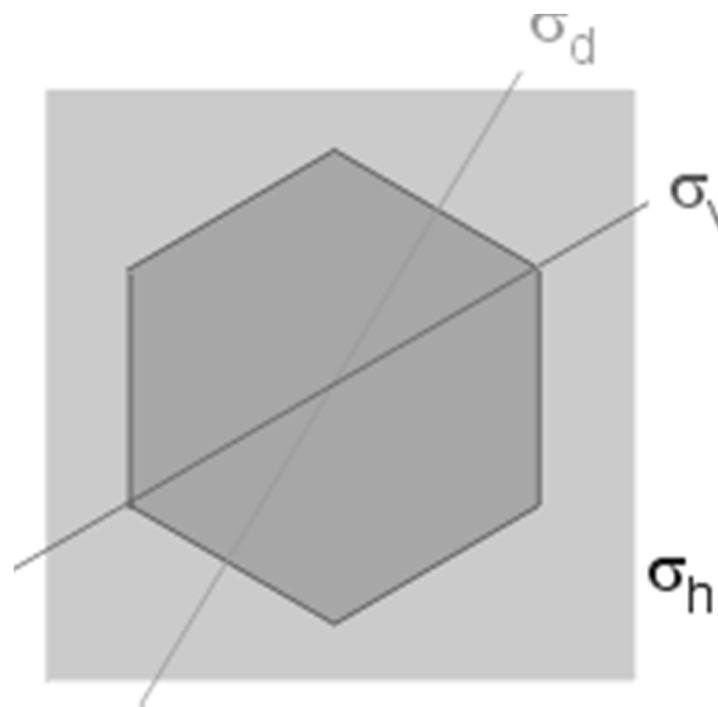
Každá planární molekula má rovinu symetrie ve které leží

σ_h = kolmá k hlavní rotační ose

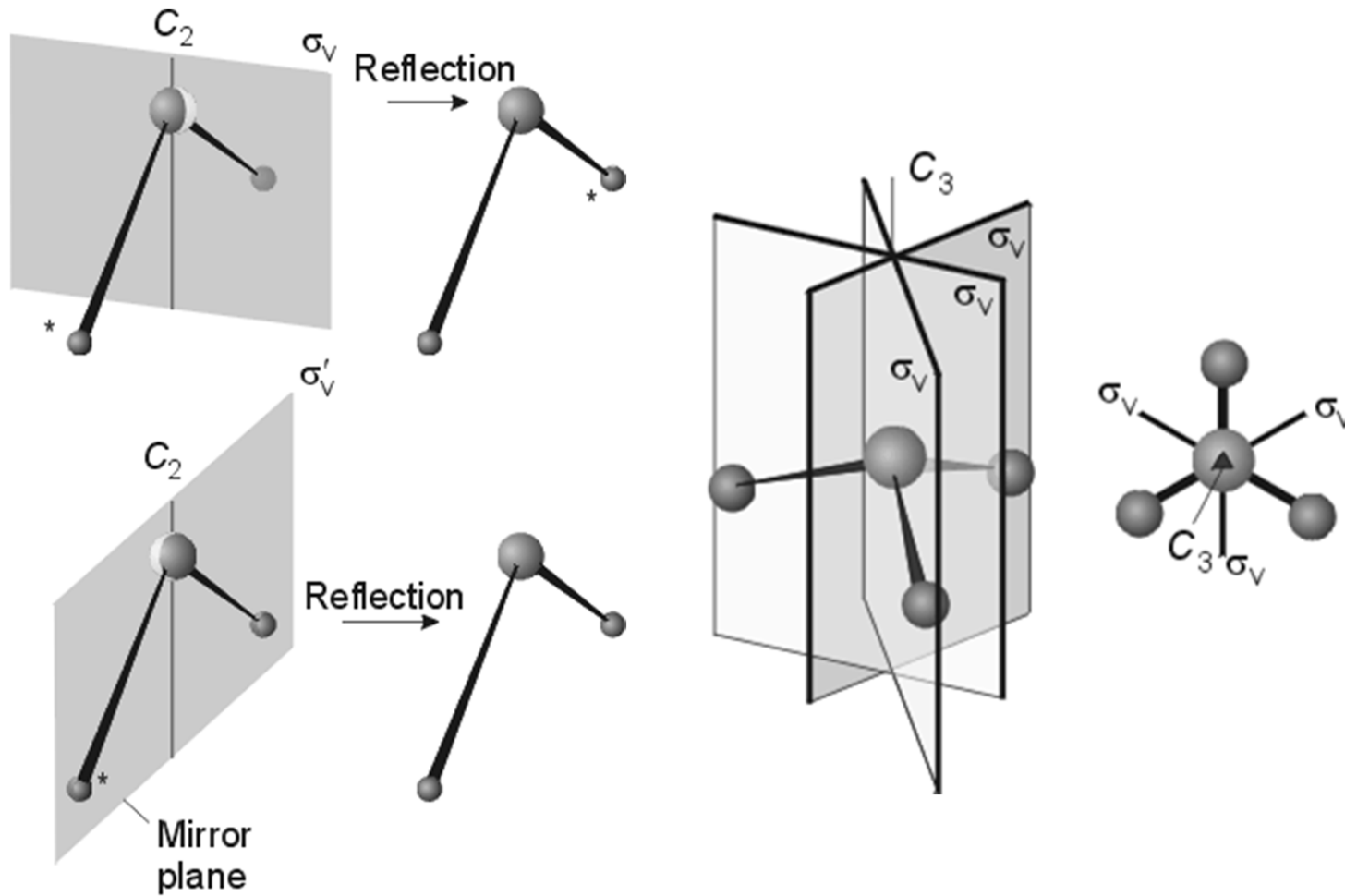
σ_v = obsahuje hlavní rotační osu,
protíná nejvíce atomů

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

Všechny σ prochází počátkem



Roviny symetrie σ

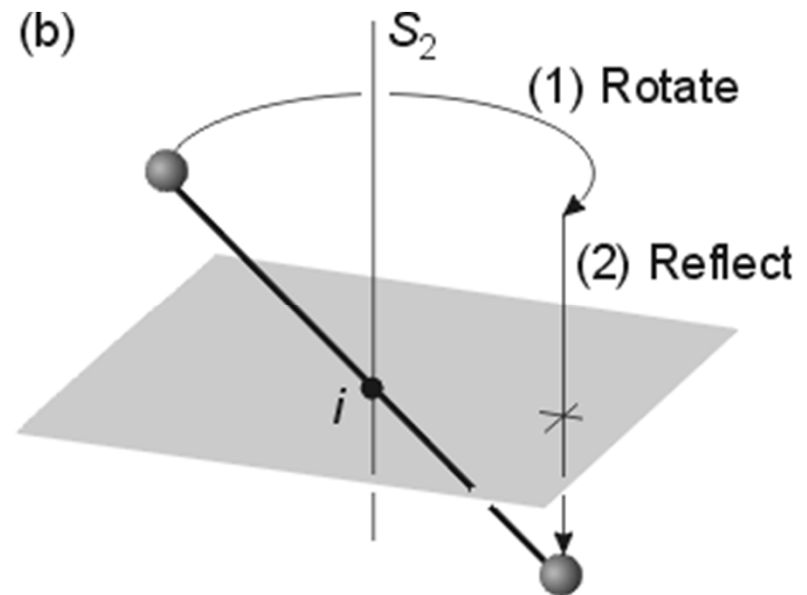
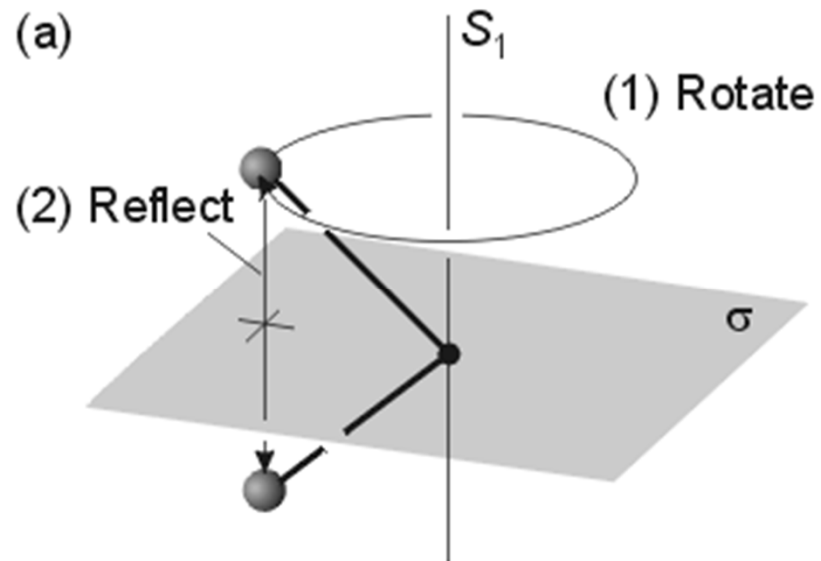


Zrcadlově-rotační osa S_n

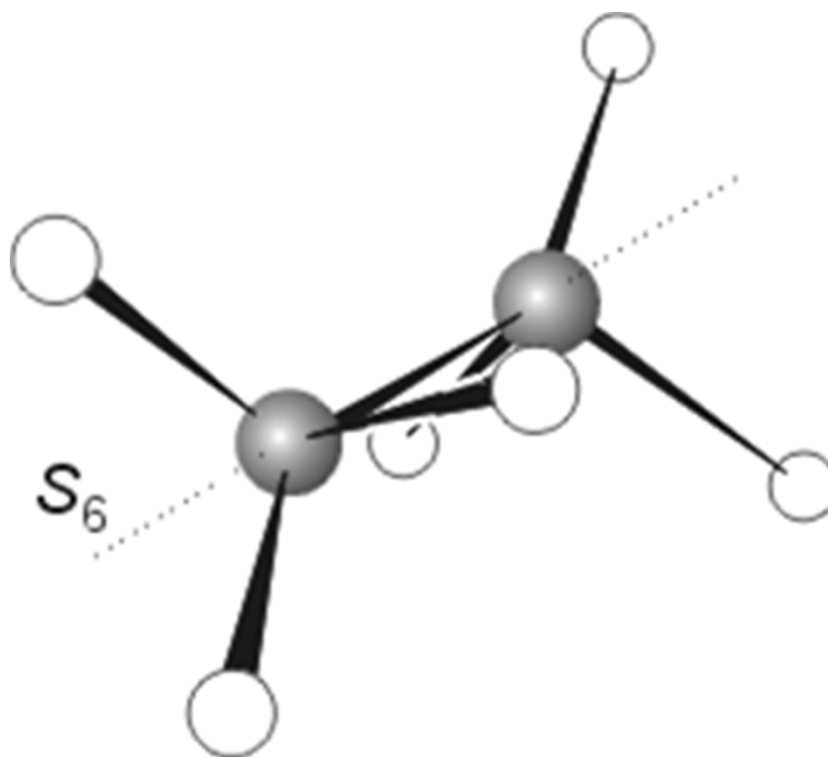
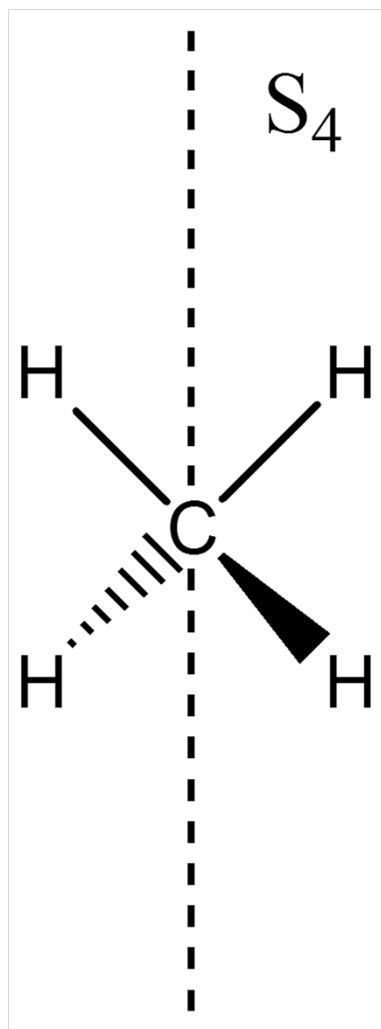
Postupné provedení dvou operací – rotace a zrcadlení

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

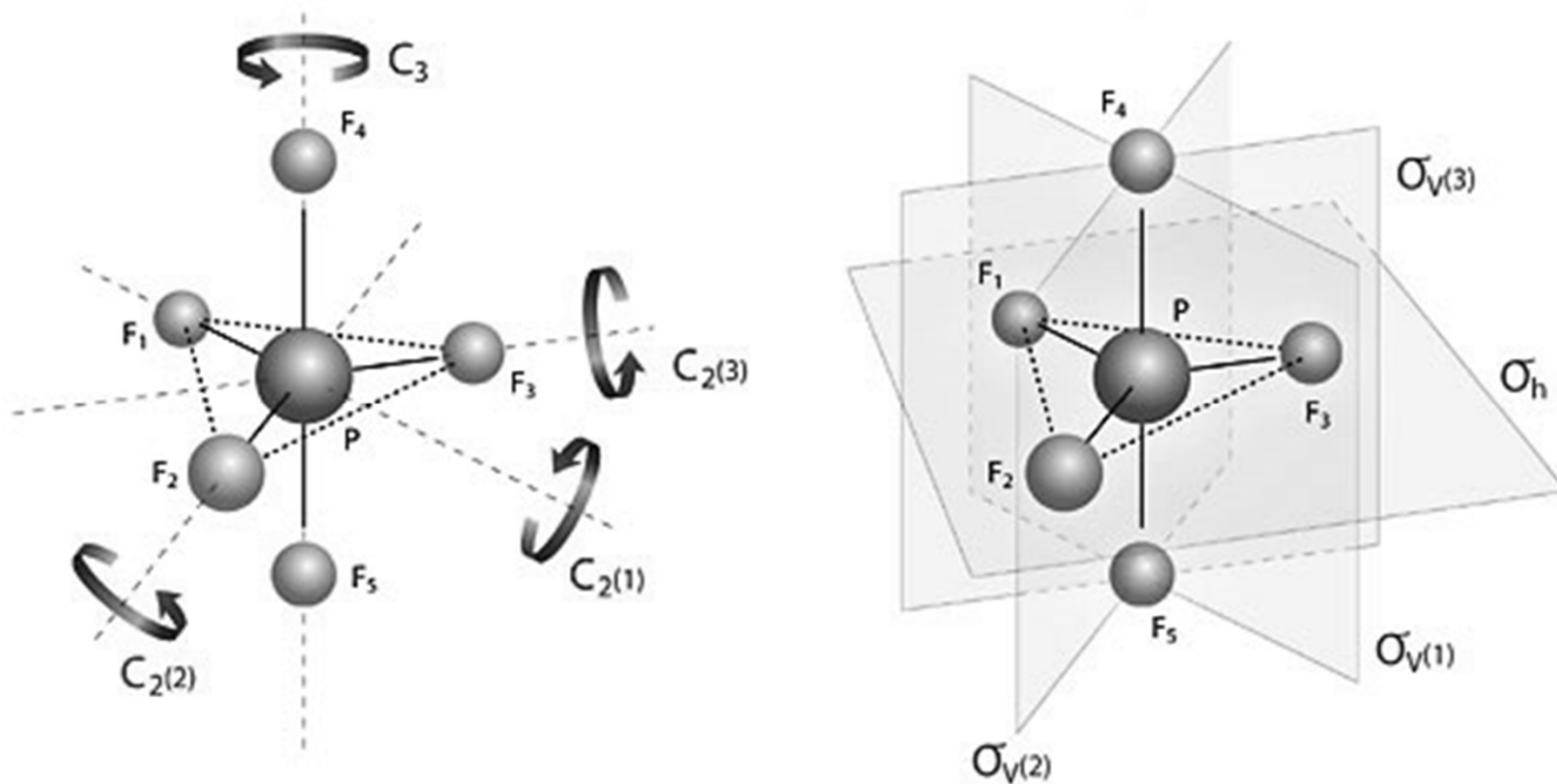
$$S_2 = C_2 \times \sigma = i$$



Zrcadlově-rotační osa S_n



Prvky symetrie v molekule



Ekvivalentní atomy = jsou zaměňovány operacemi symetrie



Chiralita



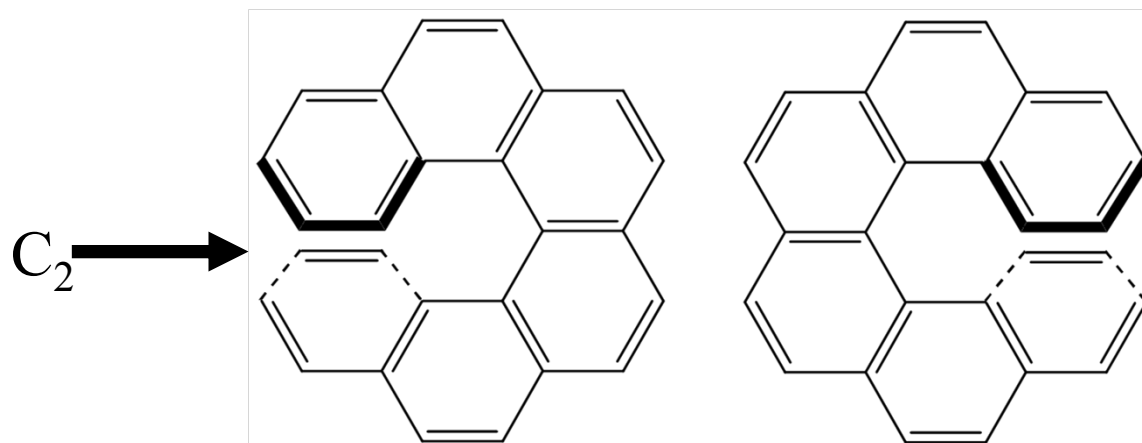
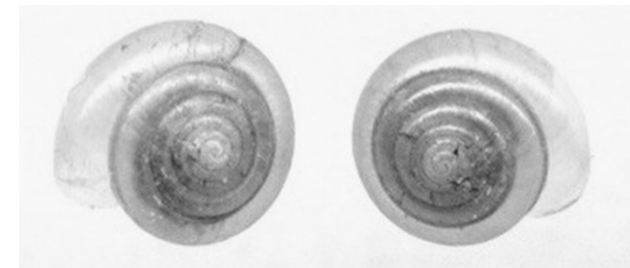
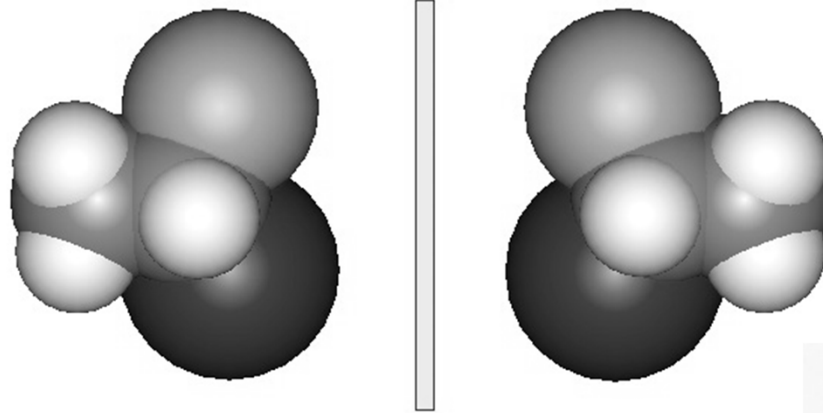
Figure 2. The Founding Fathers. R. M. Barrer (1910–1996) (right) and R. M. Milton (1920–2000) photographed

Chiralita

Podmínka chiraloty: v molekule není přítomna S_n

$$S_1 = \sigma$$

$$S_2 = i$$



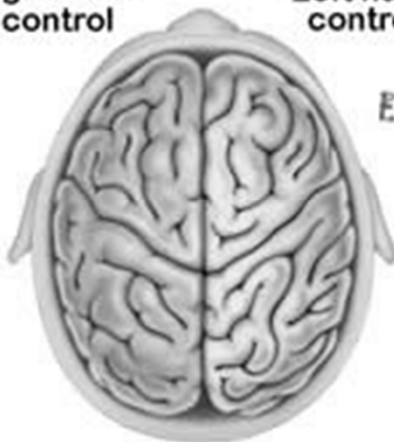
The Way Your Brain Is Organised



Right hand control



Left hand control



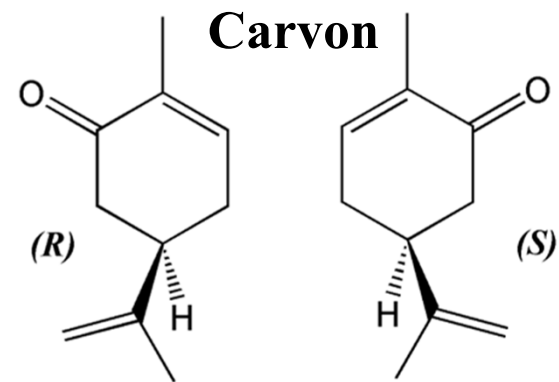
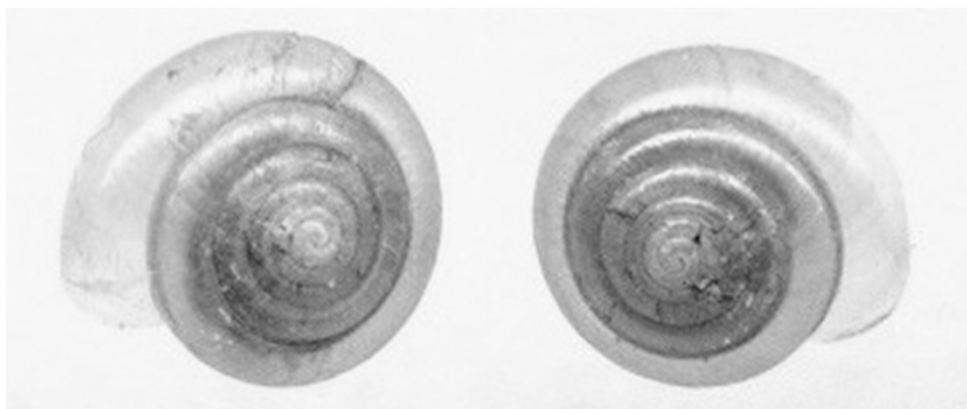
Writing
Language
Scientific skills
Mathematics
Lists
Logic

Emotional expression
Spatial awareness
Music
Creativity
IMAGINATION
Dimension
Gestalt (whole picture)

LEFT HEMISPHERE
LINEAR THINKING MODE

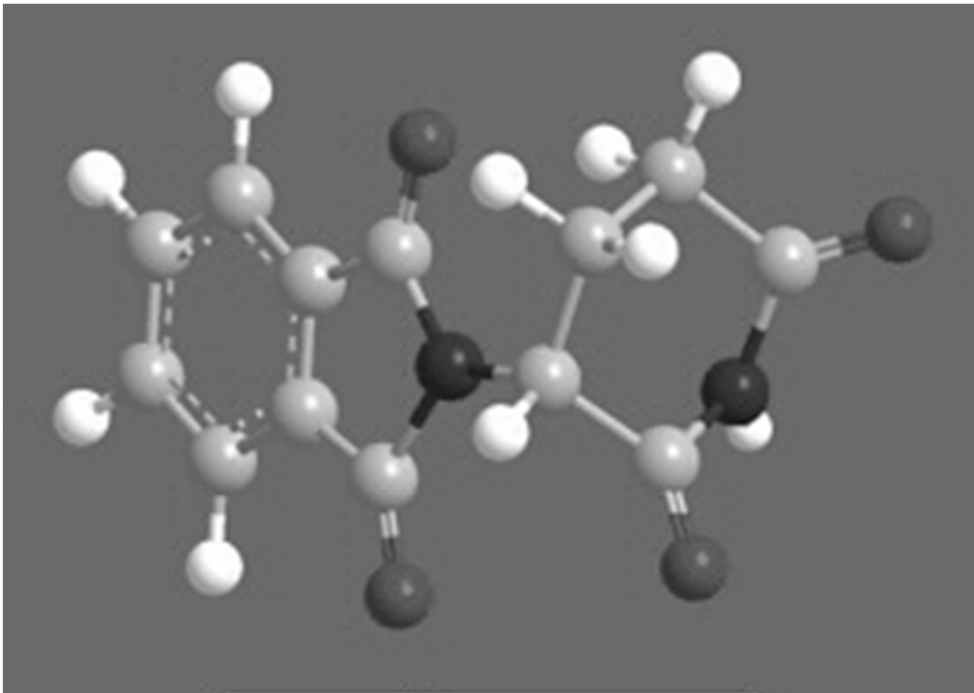
RIGHT HEMISPHERE
HOLISTIC THINKING MODE

© The Left-Handers Club (www.lefthandersday.com)



(R): Máta (S): Kmín

Thalidomide

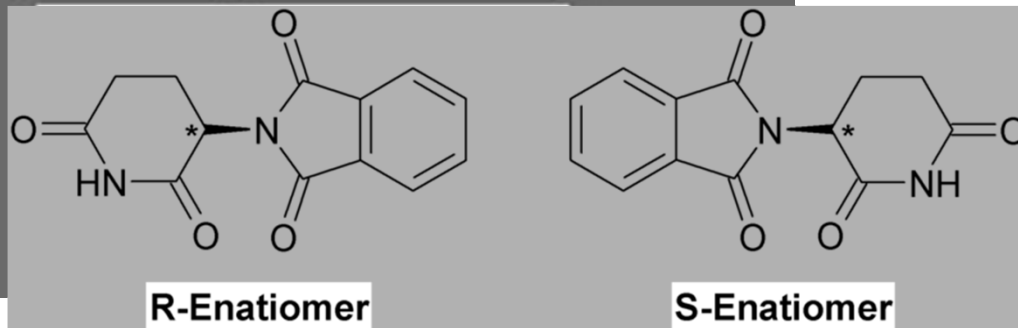


(*R*)-enantiomer

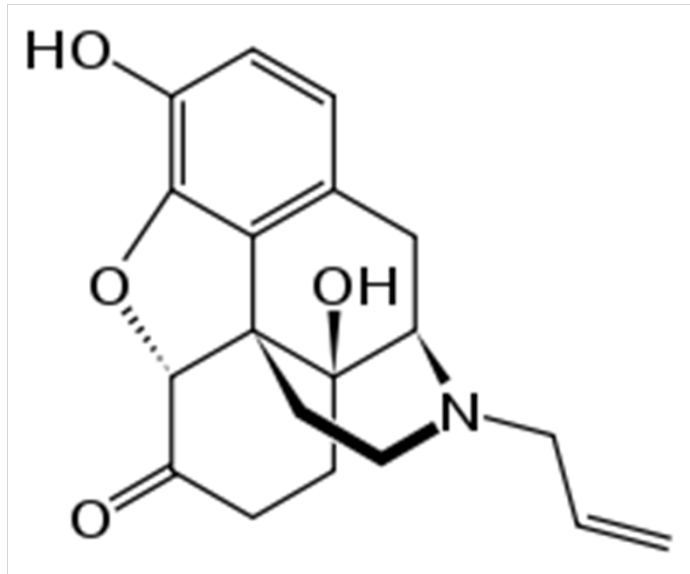
lék na ranní nevolnost

(*S*)-enantiomer

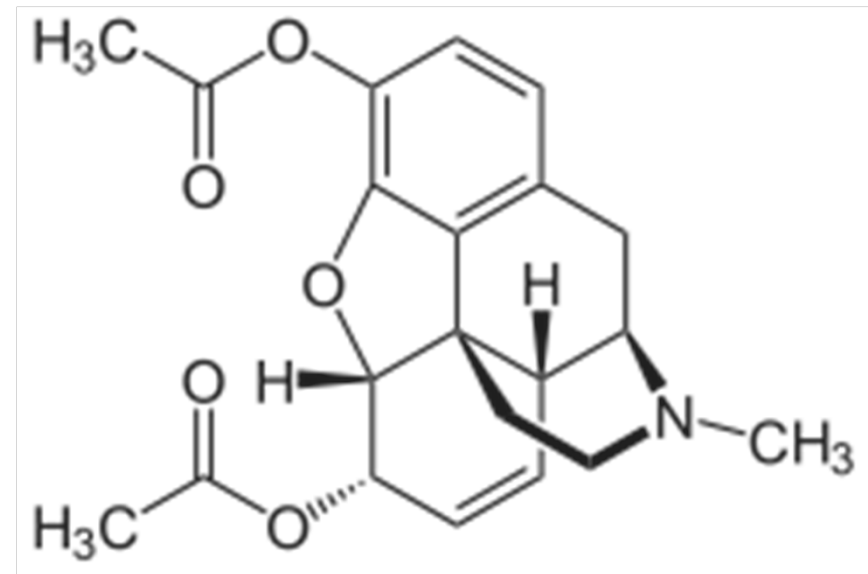
je teratogenní



Chiralita



Naloxone

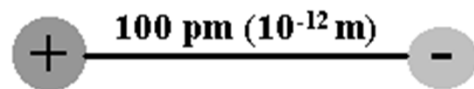


Heroin

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

$$\mu = q L = (1.60 \cdot 10^{-19} \text{ C})(1.00 \cdot 10^{-10} \text{ m})$$

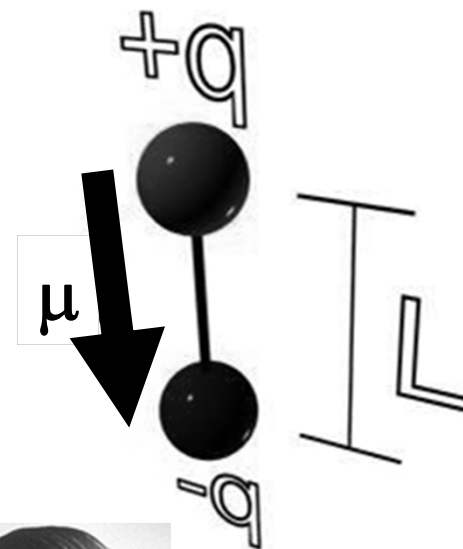
$$= 1.60 \cdot 10^{-29} \text{ C m} = \mathbf{4.80 \text{ D}}$$

dipolový moment **4.80 D**

je referenční hodnota, čisté +1 a -1

náboje vzdálené 100 pm, vazba mezi nimi

je 100% iontová



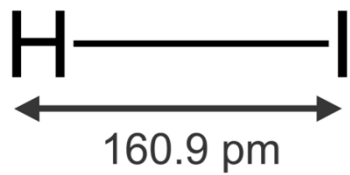
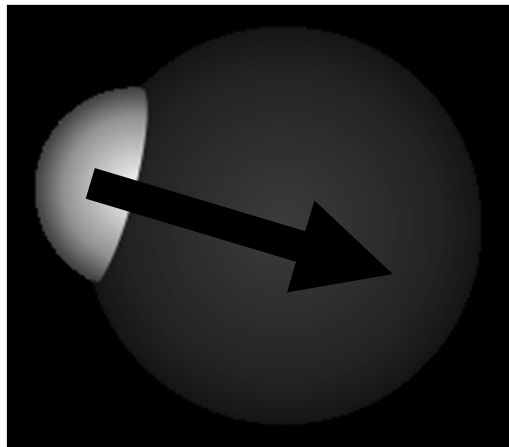
Peter Debye (1884-1966)

1936 NP za chemii

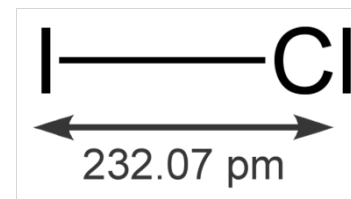
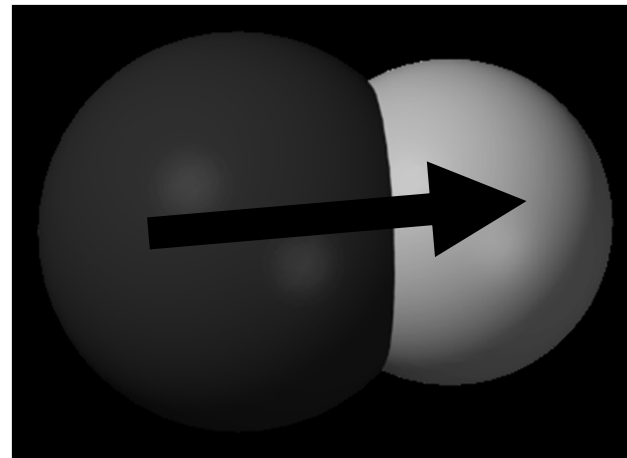
Zahřívání v MW

Dipolové momenty diatomických molekul

H-I



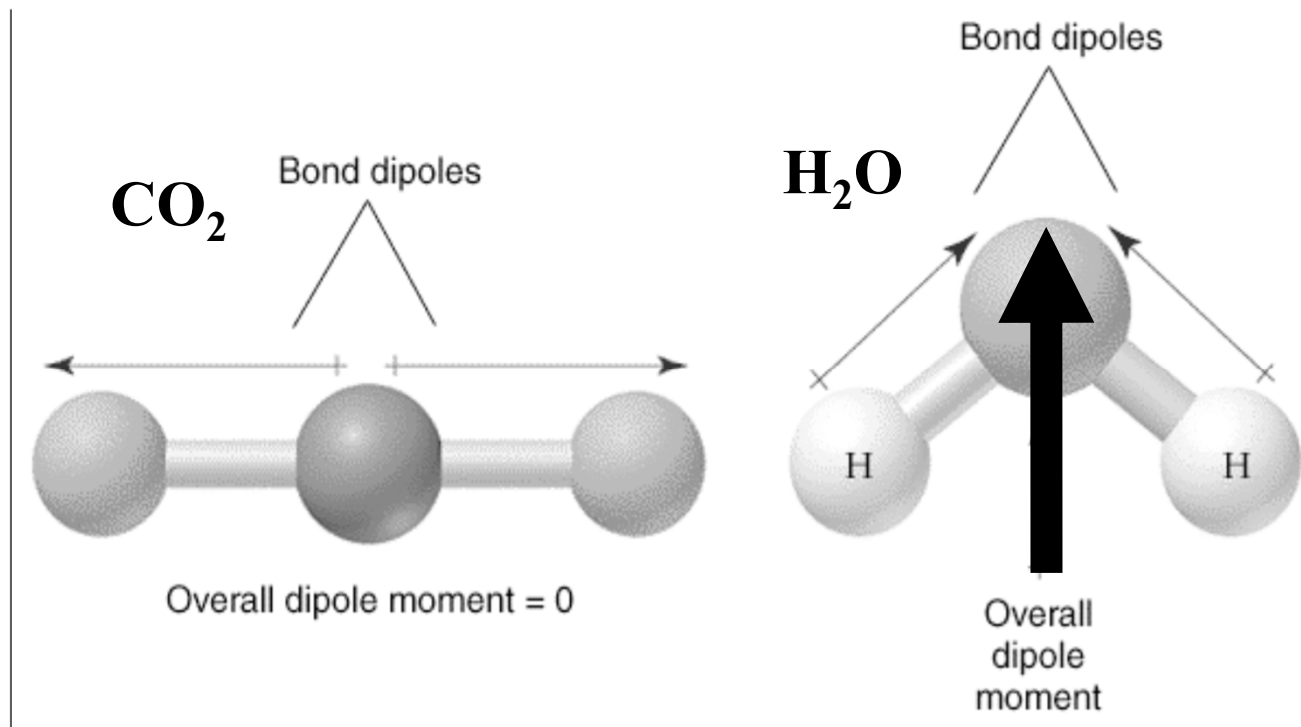
I-Cl



Dipolový moment polyatomické molekuly

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

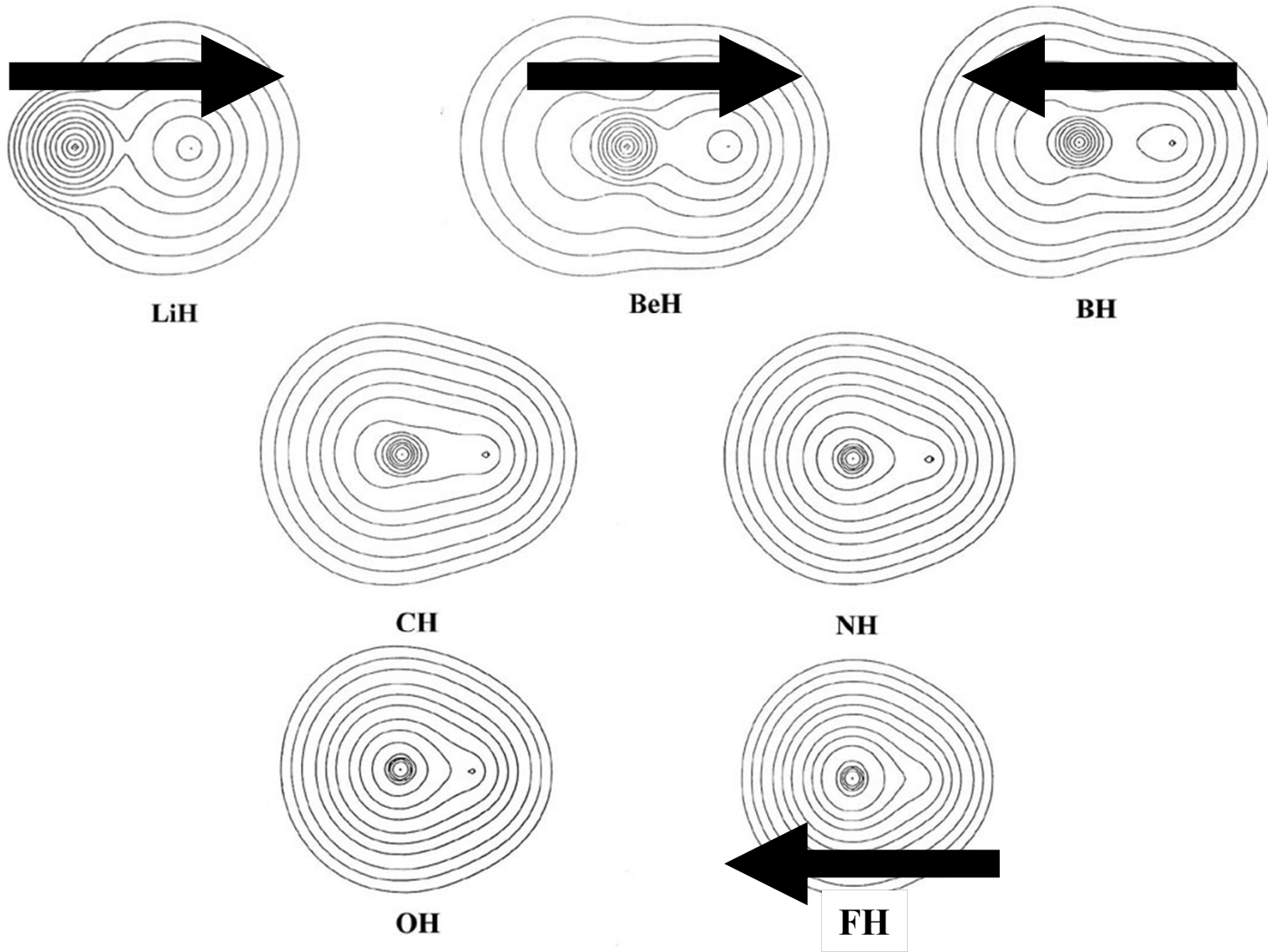
Míra nerovnoměrnosti rozložení náboje v molekule



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.



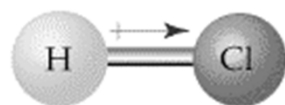
Dipolový moment vazeb

Rozdíl elektronegativit vazebných partnerů

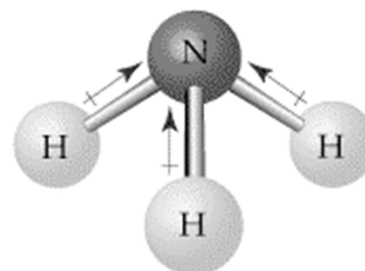
Enlace	$\chi_A - \chi_B$	μ (D)	Enlace	$\chi_A - \chi_B$	μ (D)	Enlace	$\chi_A - \chi_B$	μ (D)
C-H	0.30	0.4	N=C		0.9	Br-P	0.68	0.36
N-H	0.87	1.31	N=C		3.5	I-P	0.15	0
N-D		1.30	O-C	1.00	0.74	O=As		4.2
H-P	0.14	0.36	O=C		2.3	F-As	1.90	2.03
H-As	0	0.10	C-S	0.06	0.9	Cl-As	0.63	1.64
H-Sb	0.38	0.08	C=S		2.6	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			

Dipolové momenty polyatomických molekul

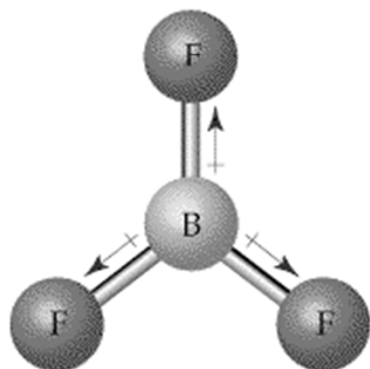
Polární molekula = celkový dipol musí ležet ve všech prvcích symetrie



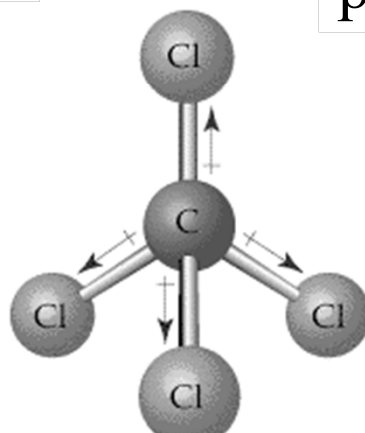
polární



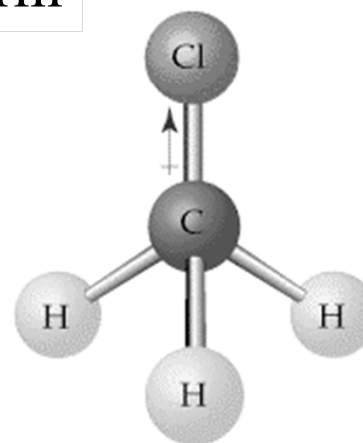
polární



nepolární

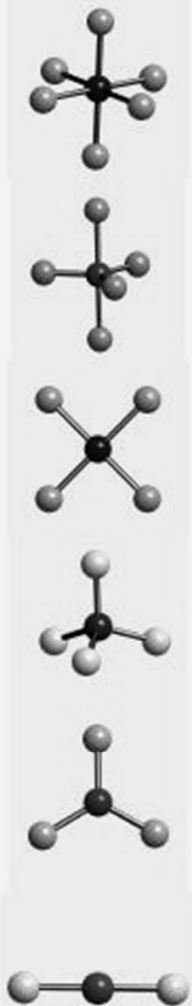


nepolární

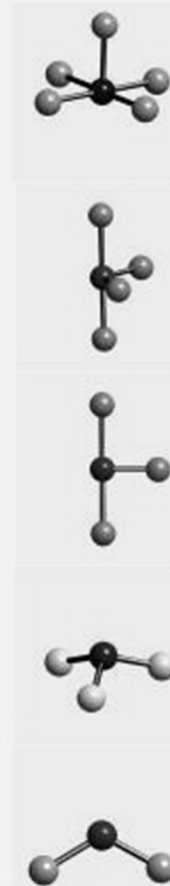


polární

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



$\mu = 0$



$\mu \neq 0$