

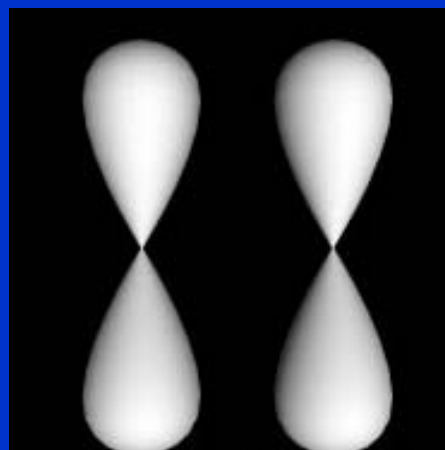
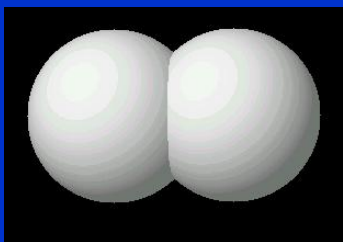
## Překryv orbitalů

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, $\sigma$

Elektronová hustota lokalizována na spojnici jader

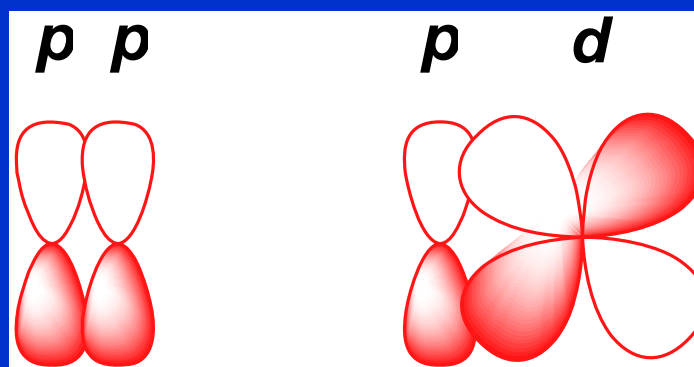
Spojnicí jader obvykle značíme jako osu  $z$



### Pi vazba, $\pi$

Elektronová hustota lokalizována mimo spojnici jader

Jedna uzlová rovina

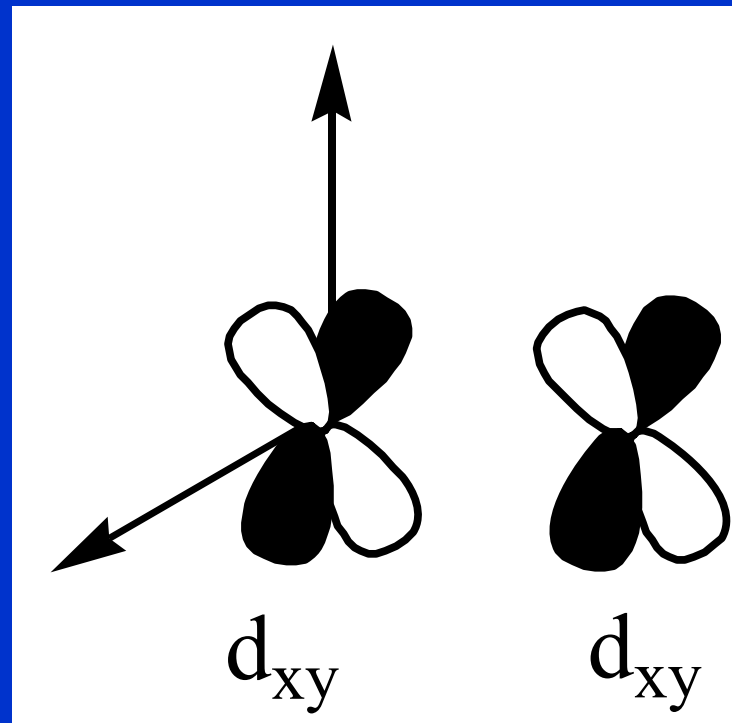


# Typy překryvu orbitalů

## Delta vazba, $\delta$

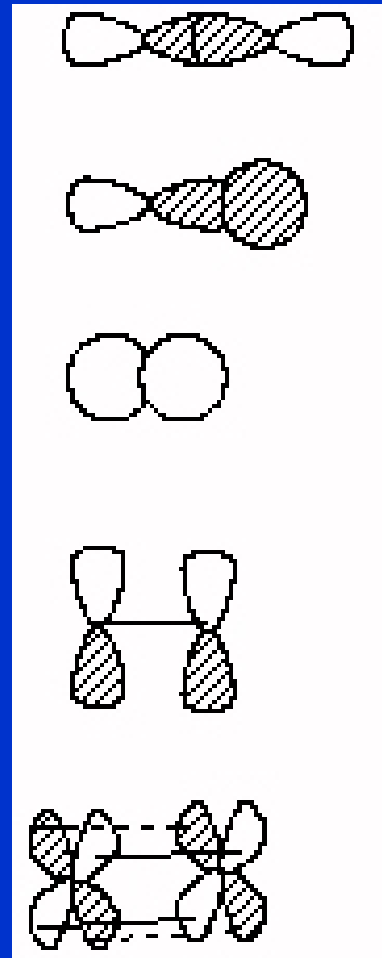
Elektronová hustota lokalizována mimo spojnici jader

Dvě uzlové roviny

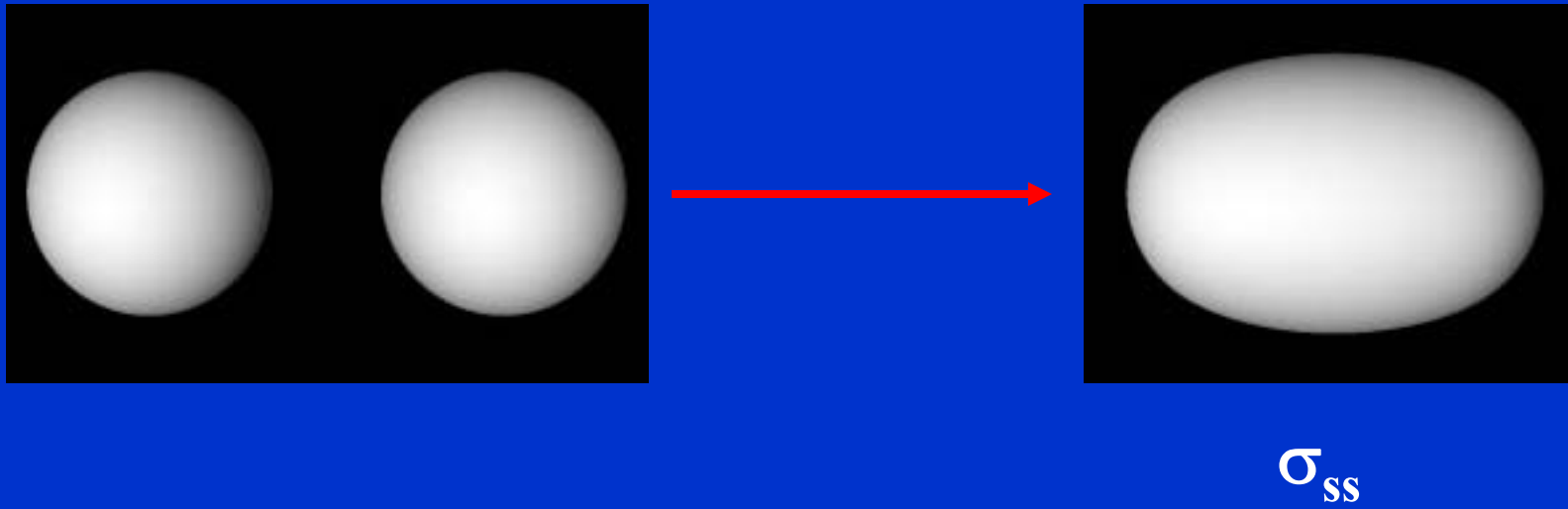


# Typy překryvu orbitalů

Překryv klesá  
slabší vazba

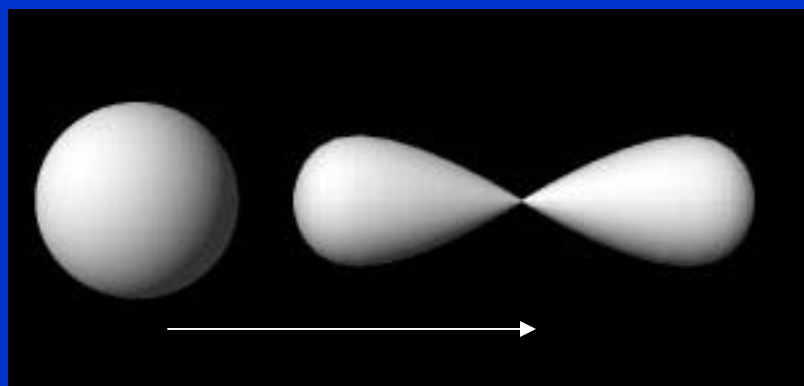


## Sigma vazba, $\sigma_{ss}$

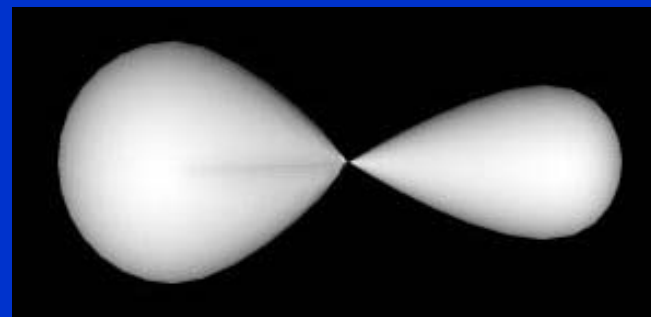


Elektronová hustota lokalizována na spojnici jader

# Sigma vazba, $\sigma_{sp}$

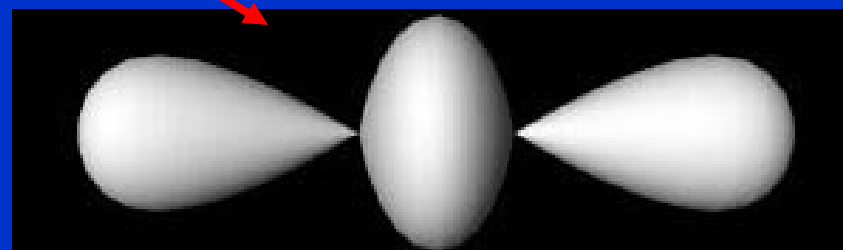
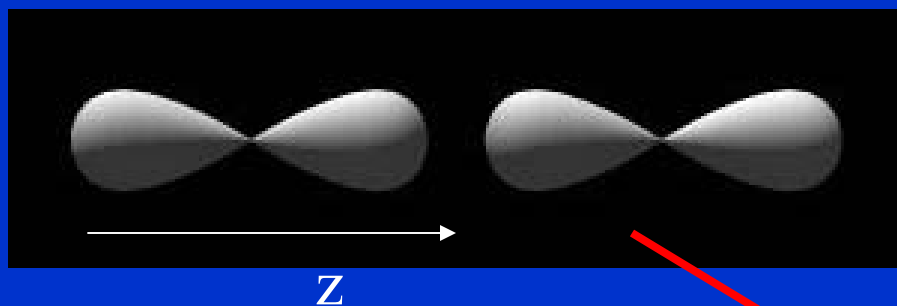


$z$



$\sigma_{sp}$

# Sigma vazba, $\sigma_{pp}$

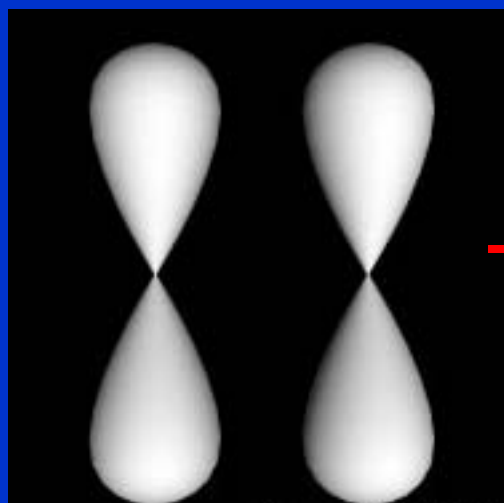


$\sigma_{pp}$

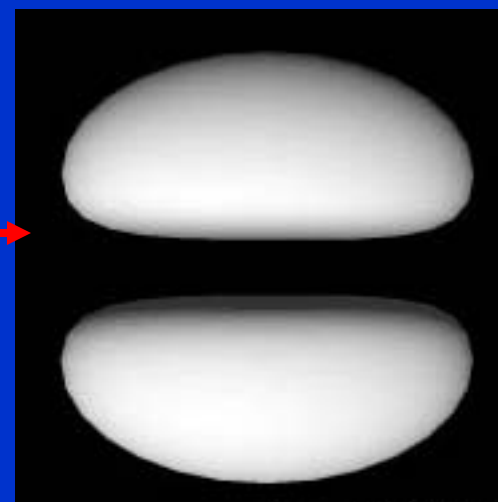
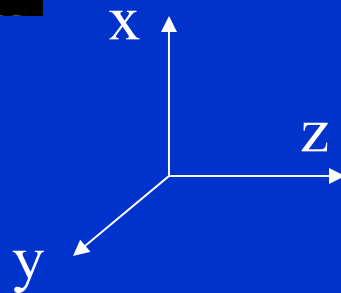
## Pi vazba, $\pi$

Elektronová hustota lokalizována mimo spojnici jader

Jedna uzlová rovina



Stejně pro  $p_x$  a  $p_y$



$2 \times \pi_{pp}$

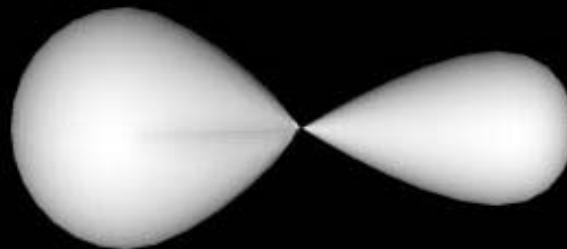
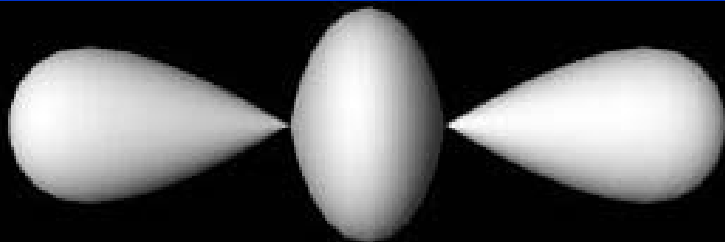


# Účinnost překryvu orbitalů

Kratší vzdálenost = lepší překryv

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

Pro  $\sigma$ :  $p_z-p_z > p_z-s > s-s$



## Vazebné parametry


Anion	Řád vazby	Vazebná délka, Å
$\text{ClO}^-$	1.0	1.67
$\text{ClO}_2^-$	1.50	1.58
$\text{ClO}_3^-$	1.67	1.49
$\text{ClO}_4^-$	1.75	1.43
$\text{ClO}_2^+$	2.0	1.39

Řád vazby roste

Vazebná délka klesá

## Vazebné parametry

vazba	délka [ $\text{\AA}$ ]	energie [ $\text{kJ mol}^{-1}$ ]
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 <sup>-1</sup>	Polarita vazby
H-H	431	Nepolární
F-F	155	Nepolární
H-F	565	Polární
C-I	240	 Polarita vazby roste
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

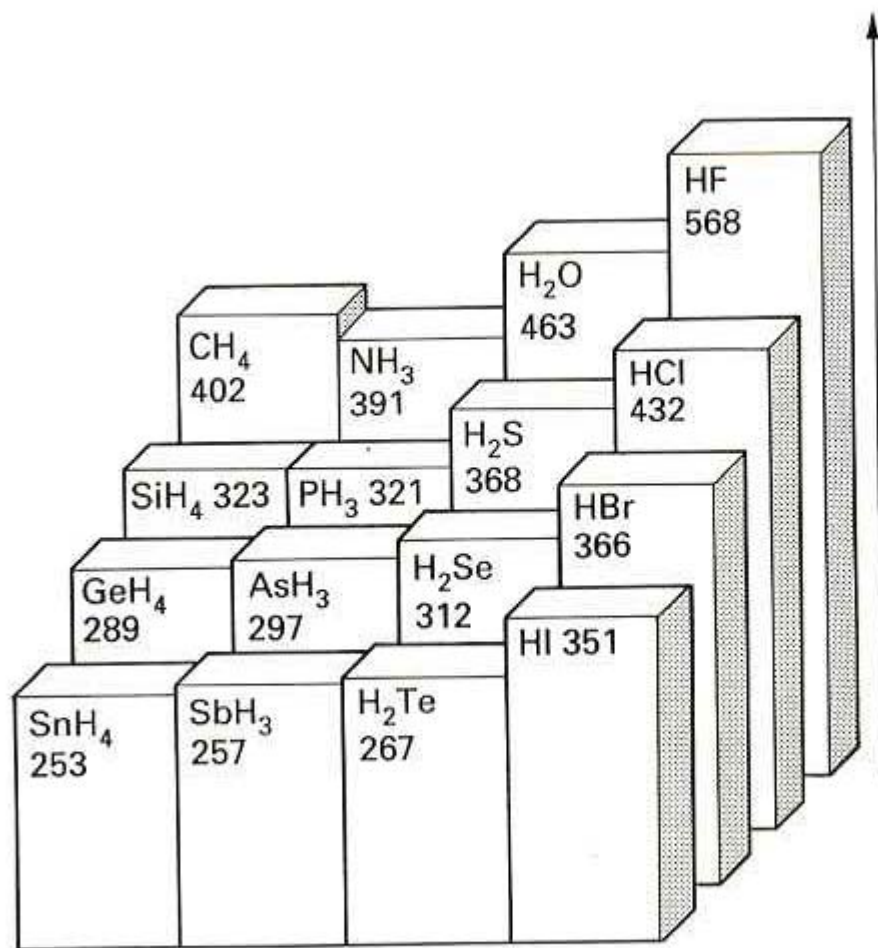
Vazba	E, kJ mol <sup>-1</sup>	délka, Å
C-I	240	2.16
C-Br	276	1.91
C-Cl	339	1.79
C-F	485	1.40

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

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

Schomaker-Stevenson

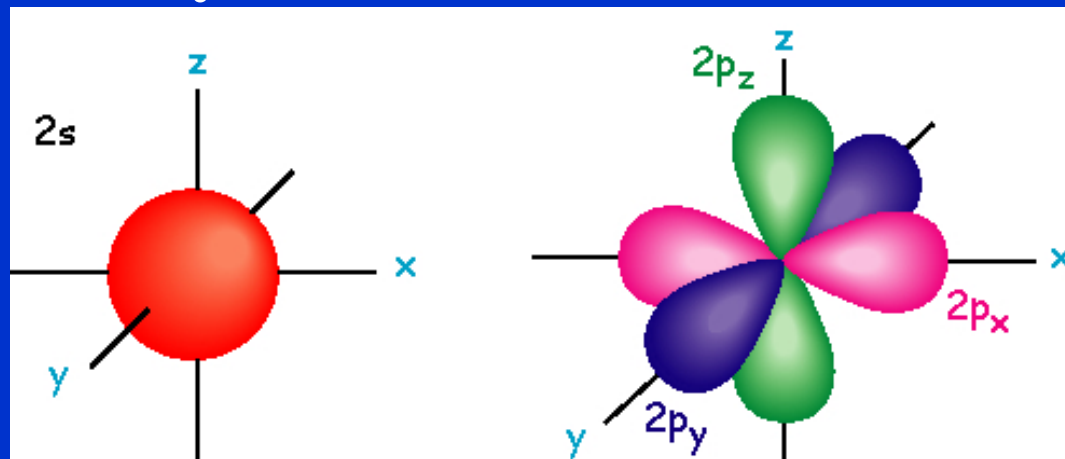
$$r_{AB} = r_A + r_B - 0.09 |\chi_A - \chi_B|$$



Vazebná energie  
kJ mol<sup>-1</sup>



## Hybridizace



Vazebné úhly  $90^\circ$  jsou vzácné (u prvků hlavních skupin), obvyklé úhly jsou  $109$ ,  $120$ ,  $180^\circ$

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

Počet hybridních orbitalů = počet smísených atomových orbitalů

# Hybridizace sp

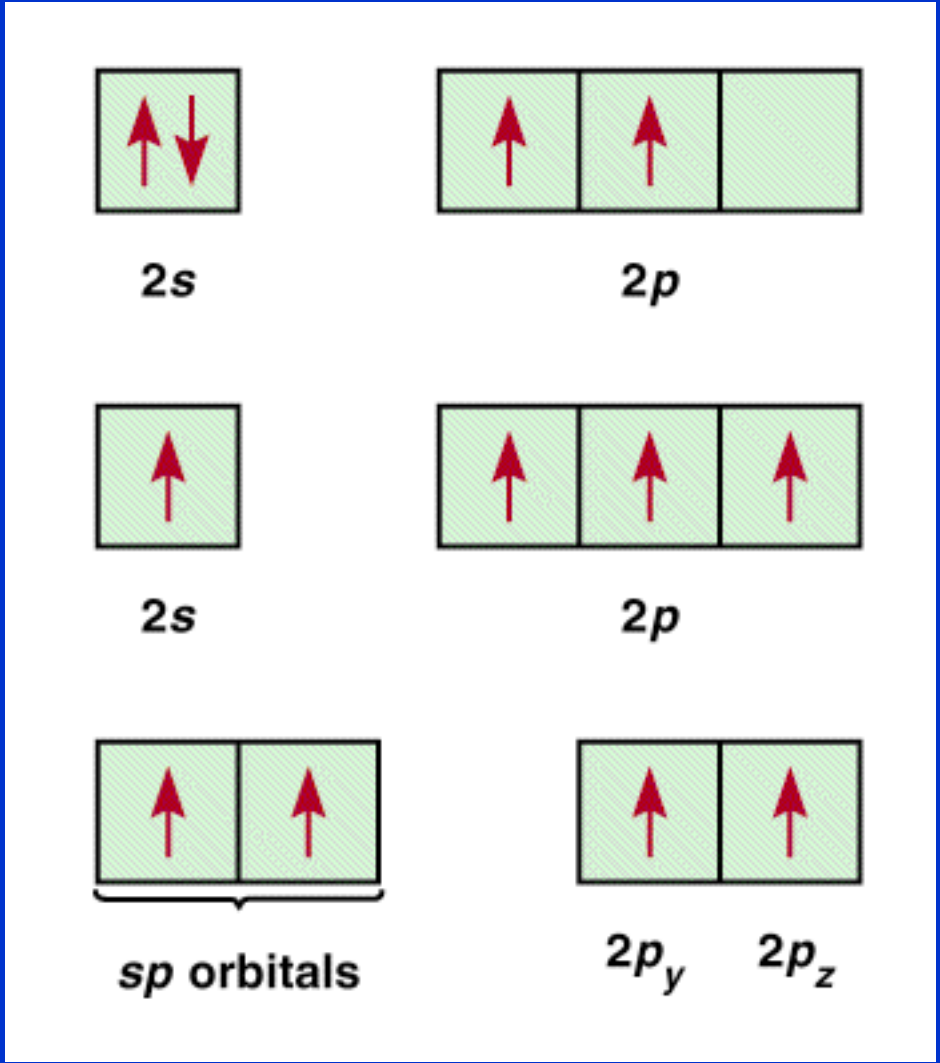
Základní stav



Excitovaný stav

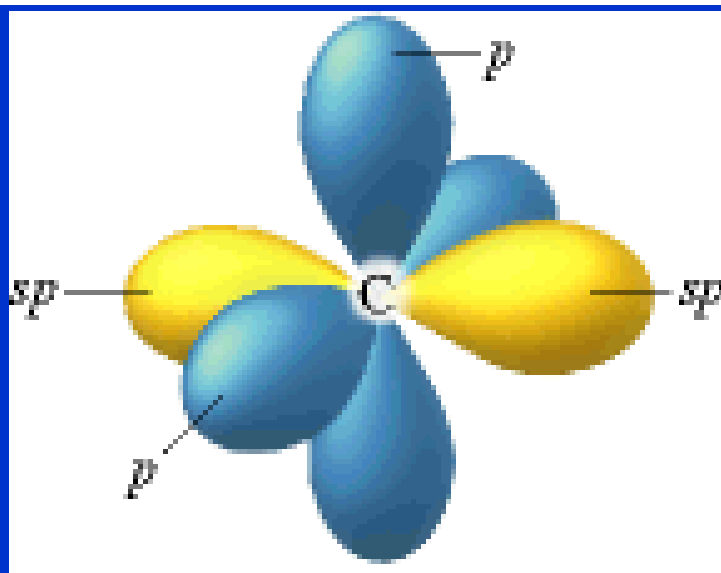
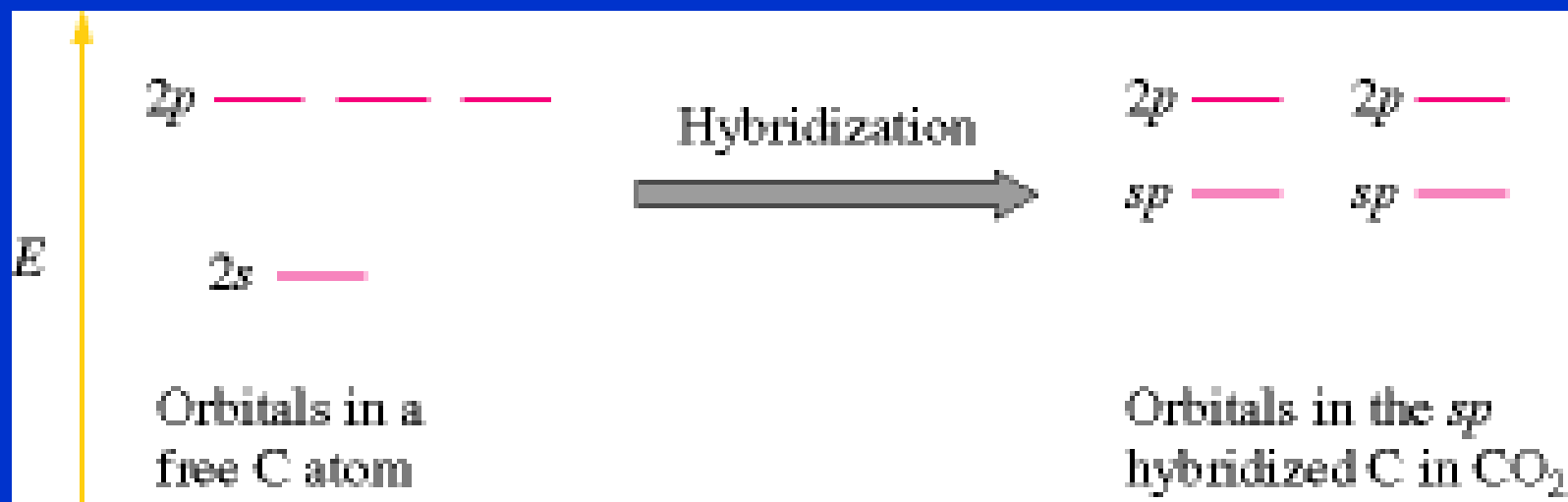


Hybridizovaný stav

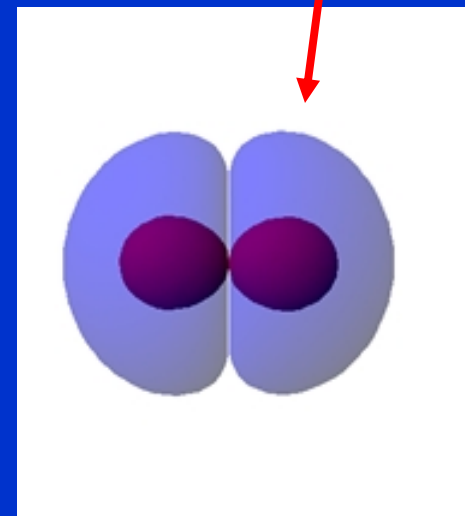
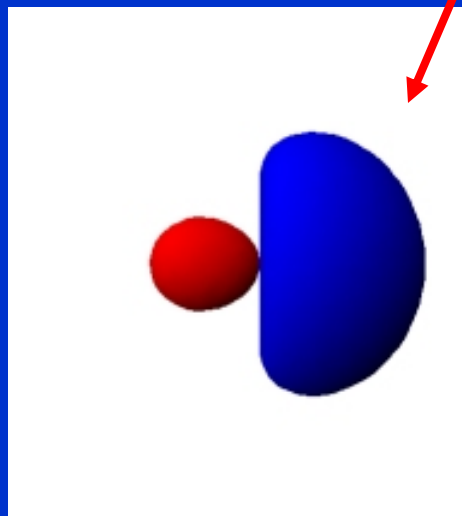
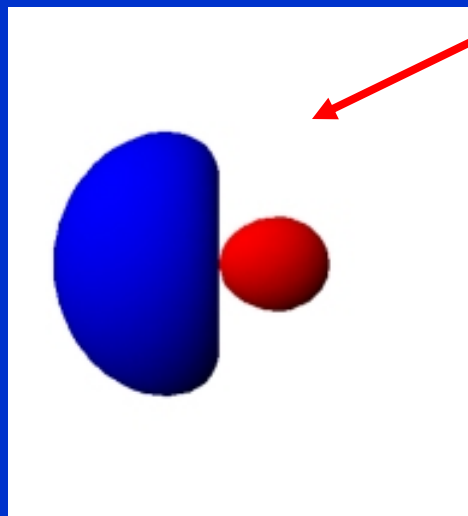
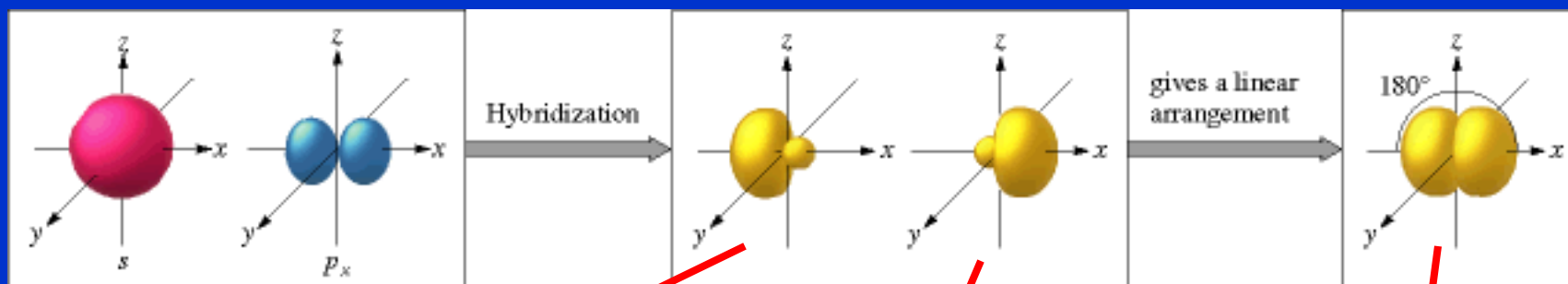




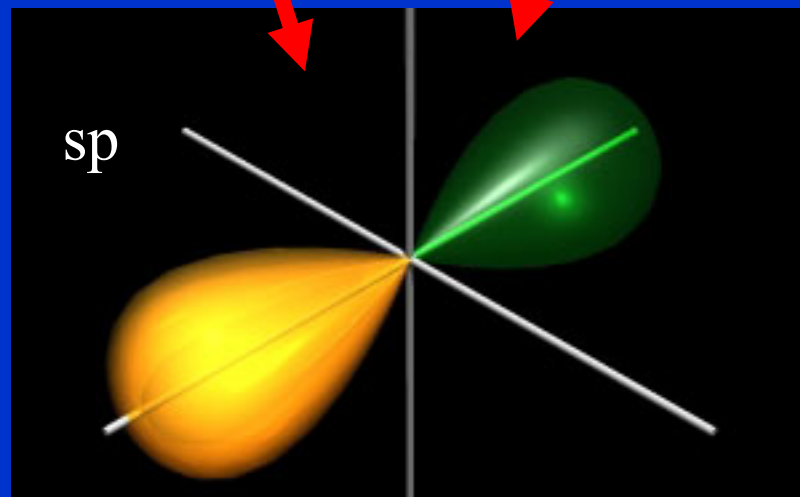
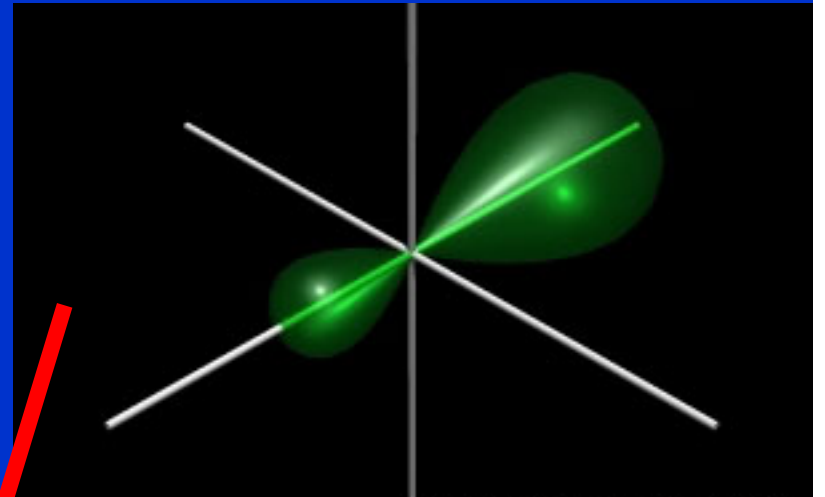
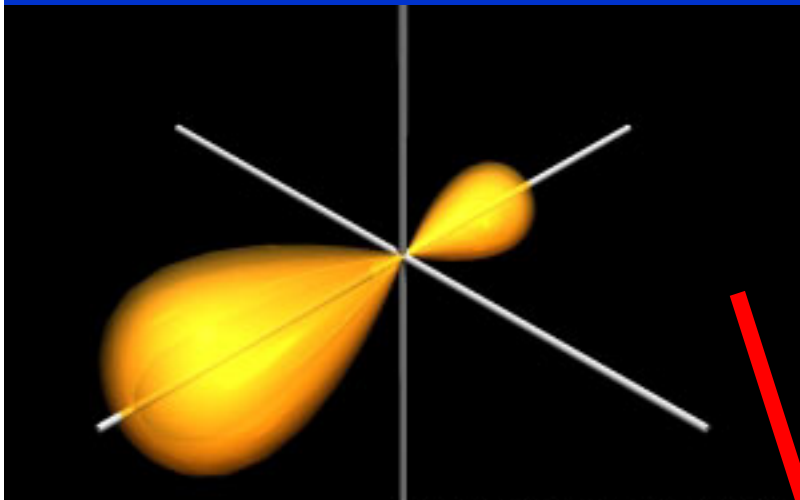
# Hybridize $sp$



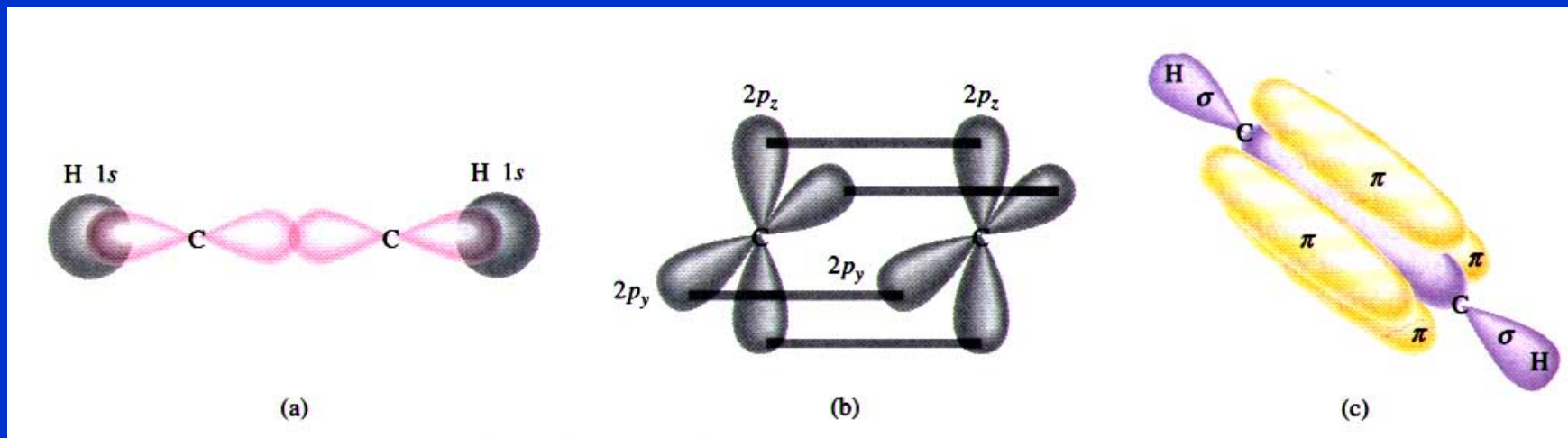
# Hybridizace sp



# Hybridizace sp

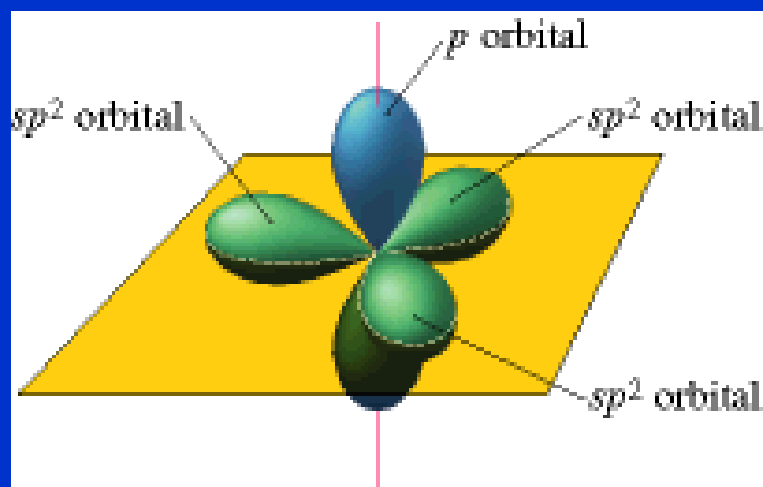
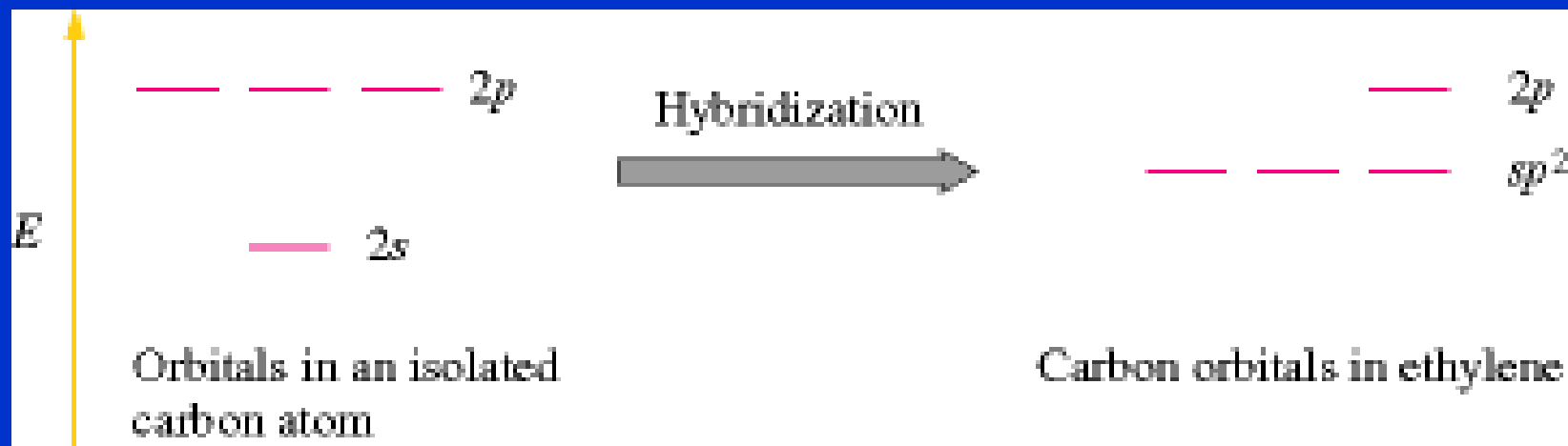


# Acetylen

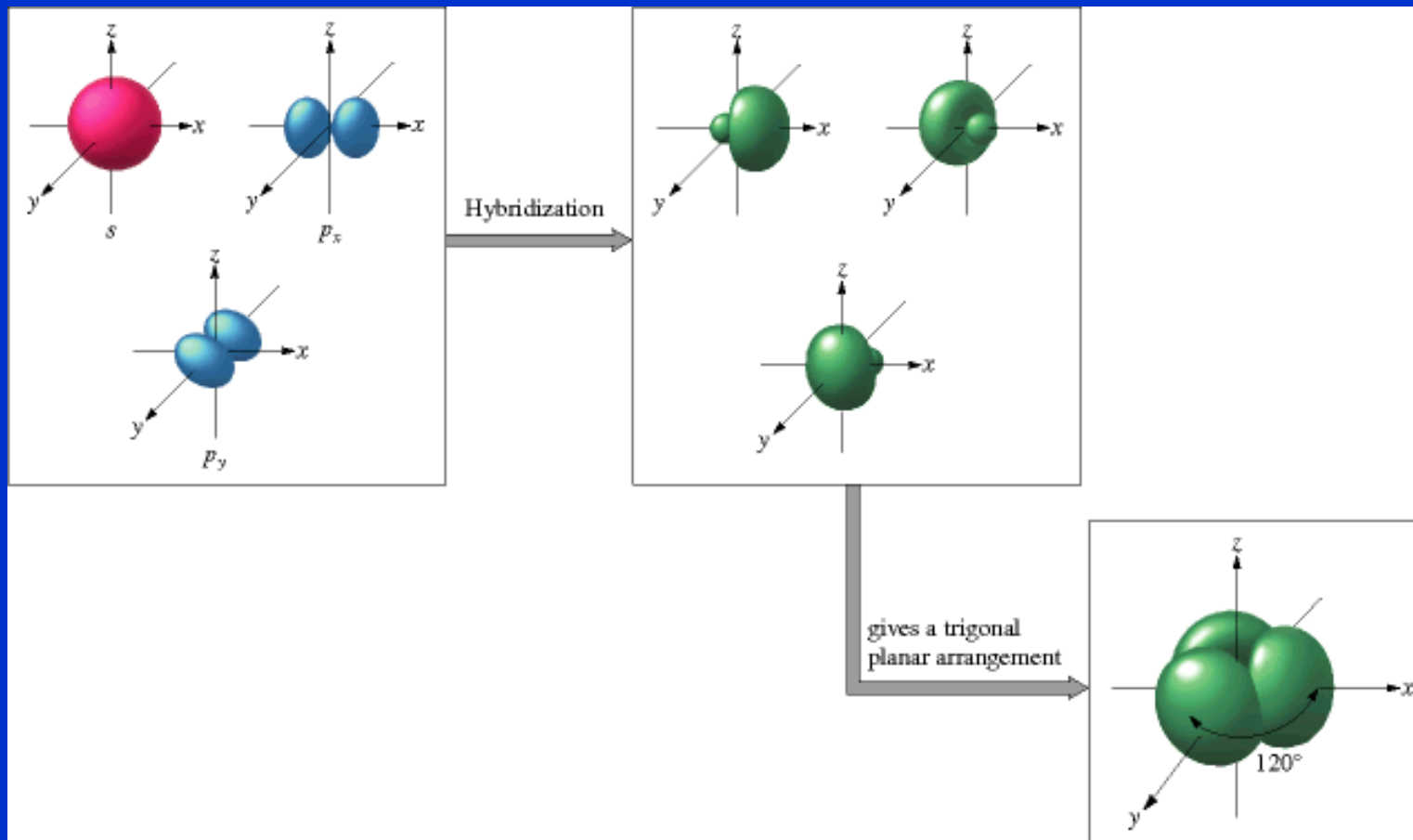


- 2  $\sigma$  vazby překryvem C(sp)–H(s)
- 1  $\sigma$  vazba překryvem C(sp)–C(sp)
- 2 navzájem kolmé  $\pi$ -vazby (x, y) překryvem C(p)–C(p)

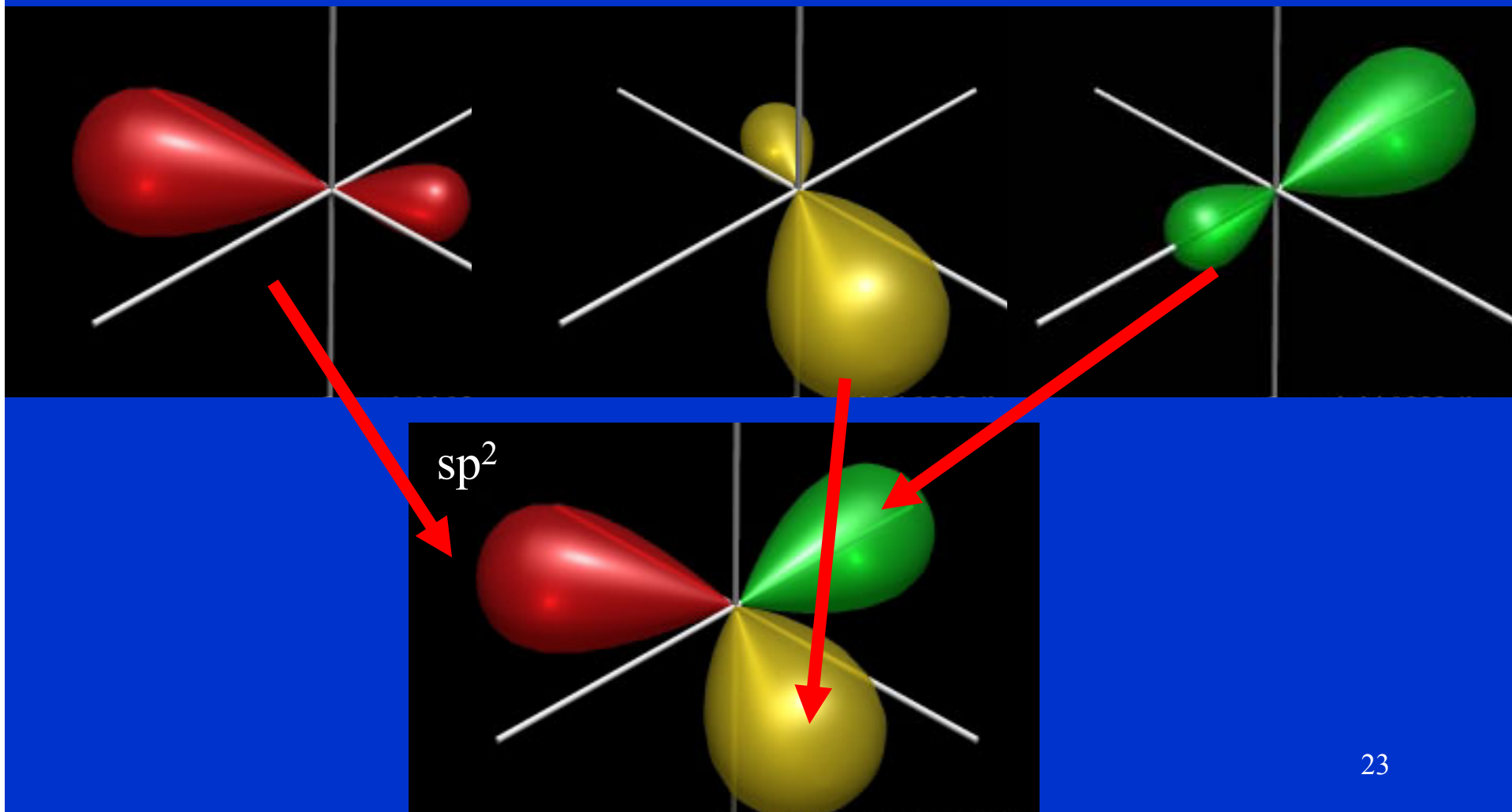
# Hybridizace $sp^2$



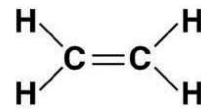
# Hybridizace $sp^2$



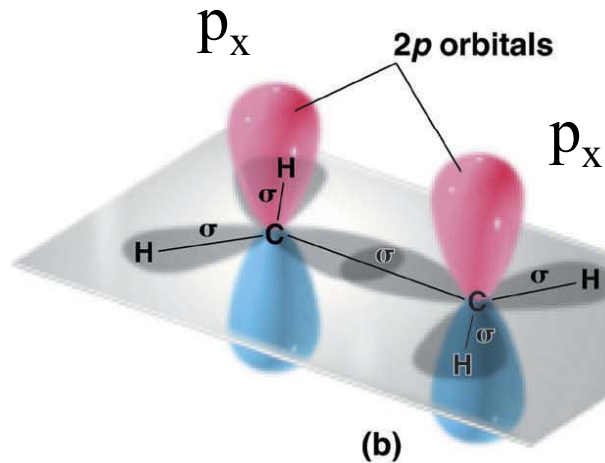
# Hybridizace $sp^2$



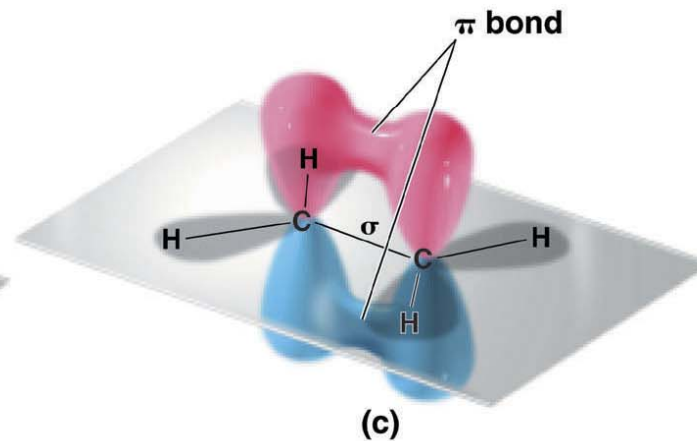
# Ethylen



(a)



(b)

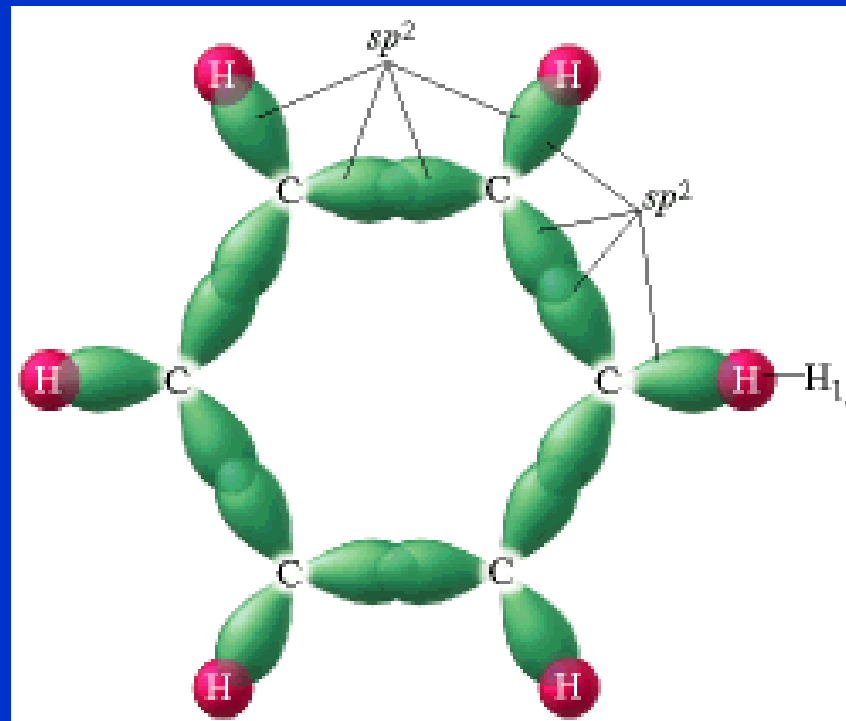
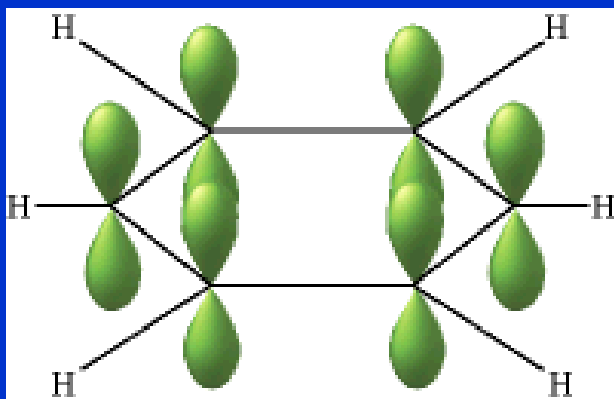
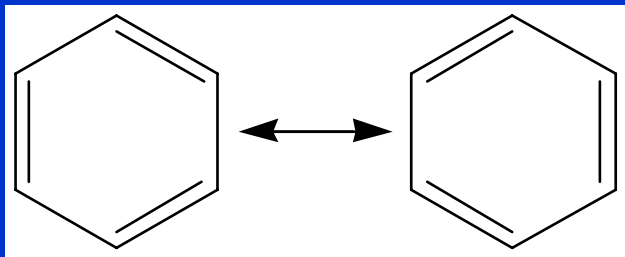


(c)

- 4  $\sigma$  vazby překryvem  $C(sp^2)-H(s)$
- 1  $\sigma$  vazba překryvem  $C(sp^2)-C(sp^2)$
- 1  $\pi$ -vazba překryvem  $C(p_x)-C(p_x)$



# Benzen

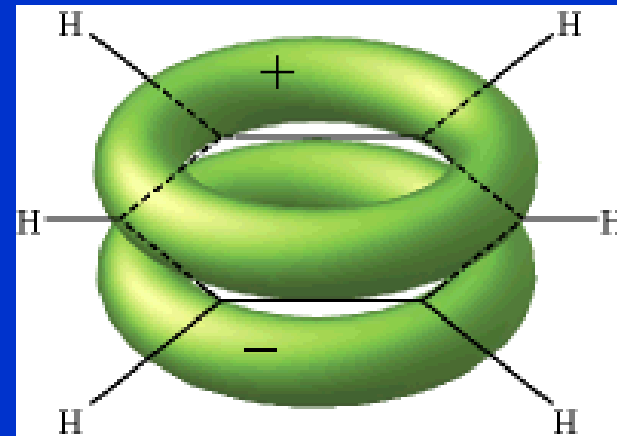


- Každý C použije 3  $sp^2$  orbitaly pro 3  $\sigma$ -vazby  
2 C – C vazby a 1 C – H vazba
- 1  $2p_x$  orbital na každém C zůstane nepoužitý (pro  $\sigma$ -vazby)

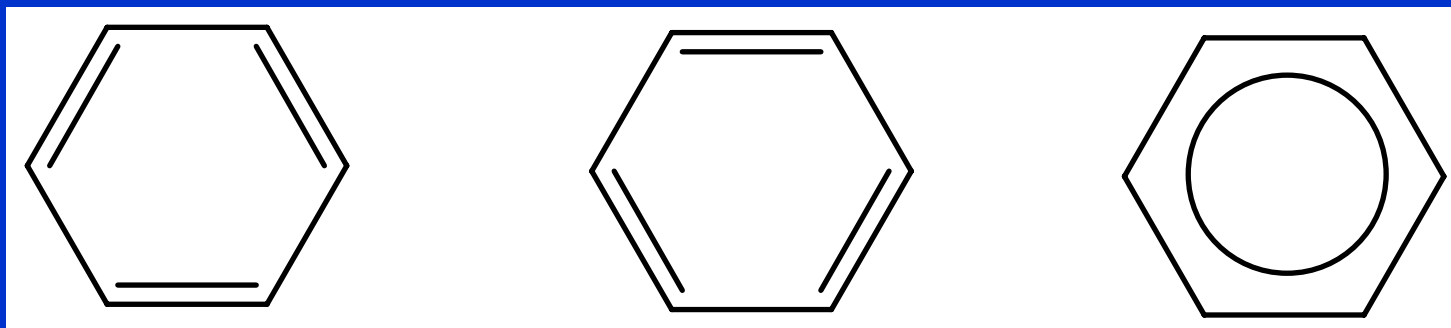
# Benzen



6 C  $2p_x$  orbitalů použito pro 3  $\pi$ -vazby



# Benzen



(a) Localized  $\pi$  bonds

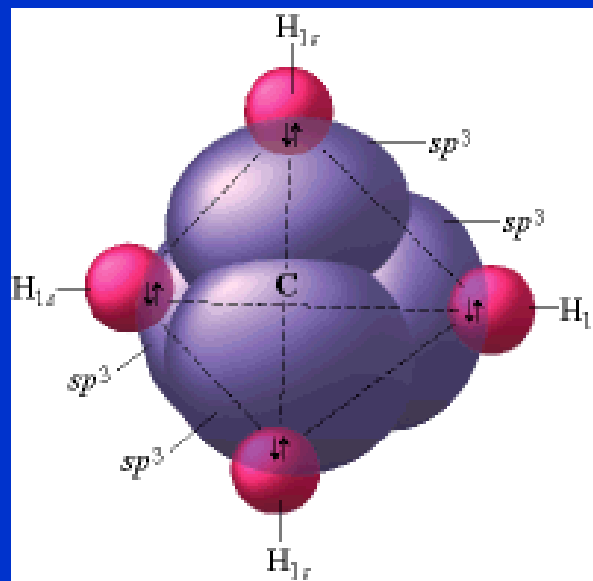
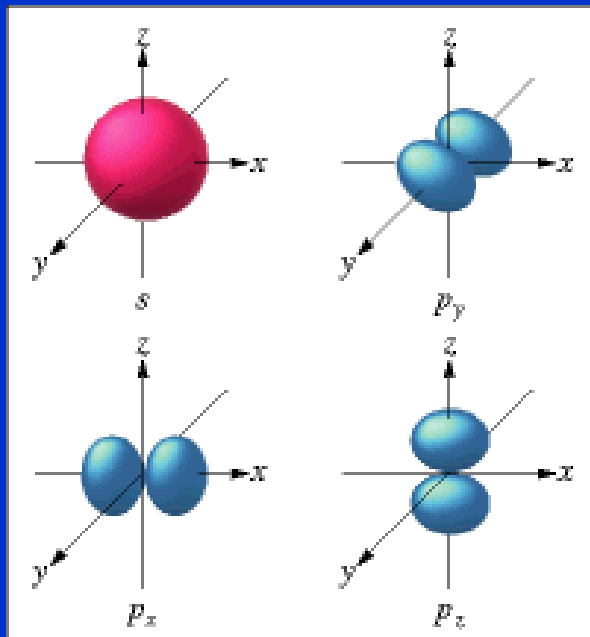
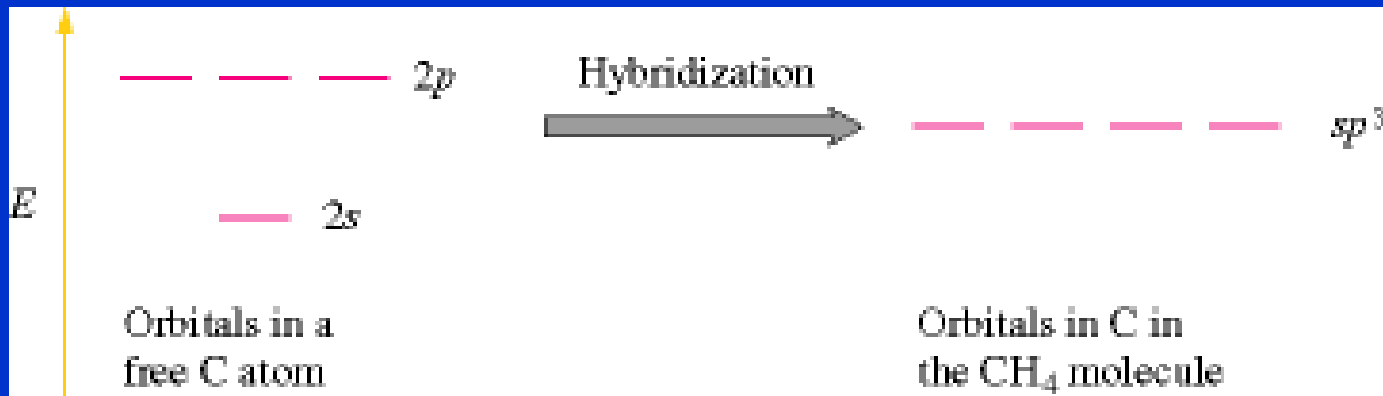


(b) Localized  $\pi$  bonds

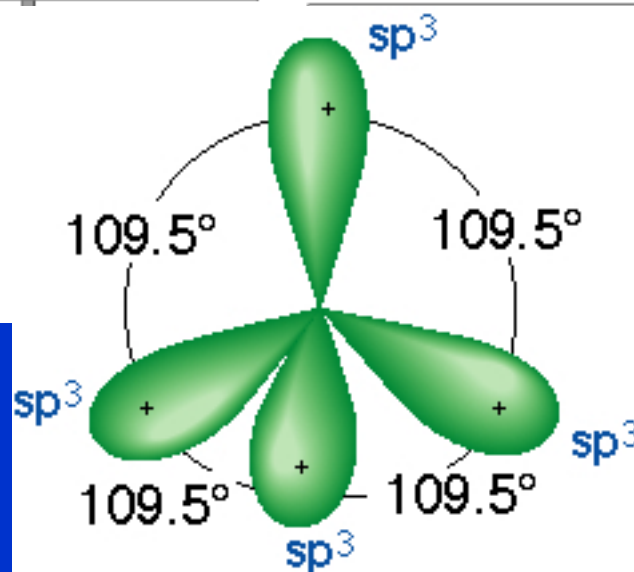
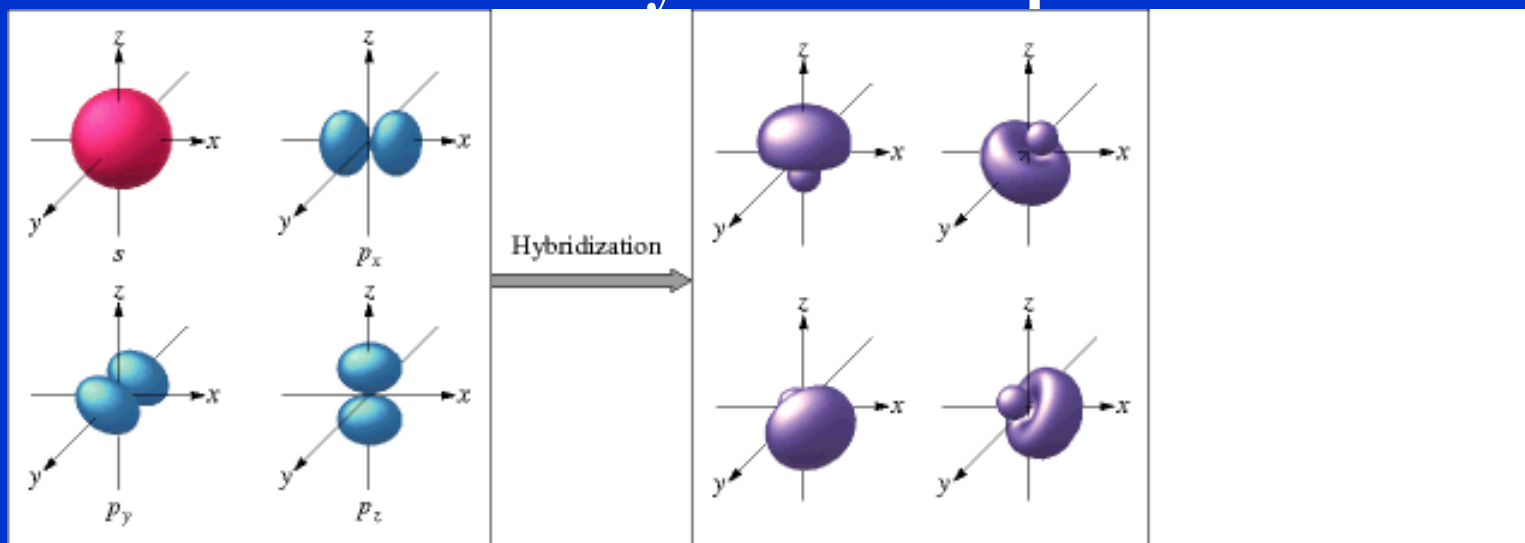


(c) Delocalized  $\pi$  bonds

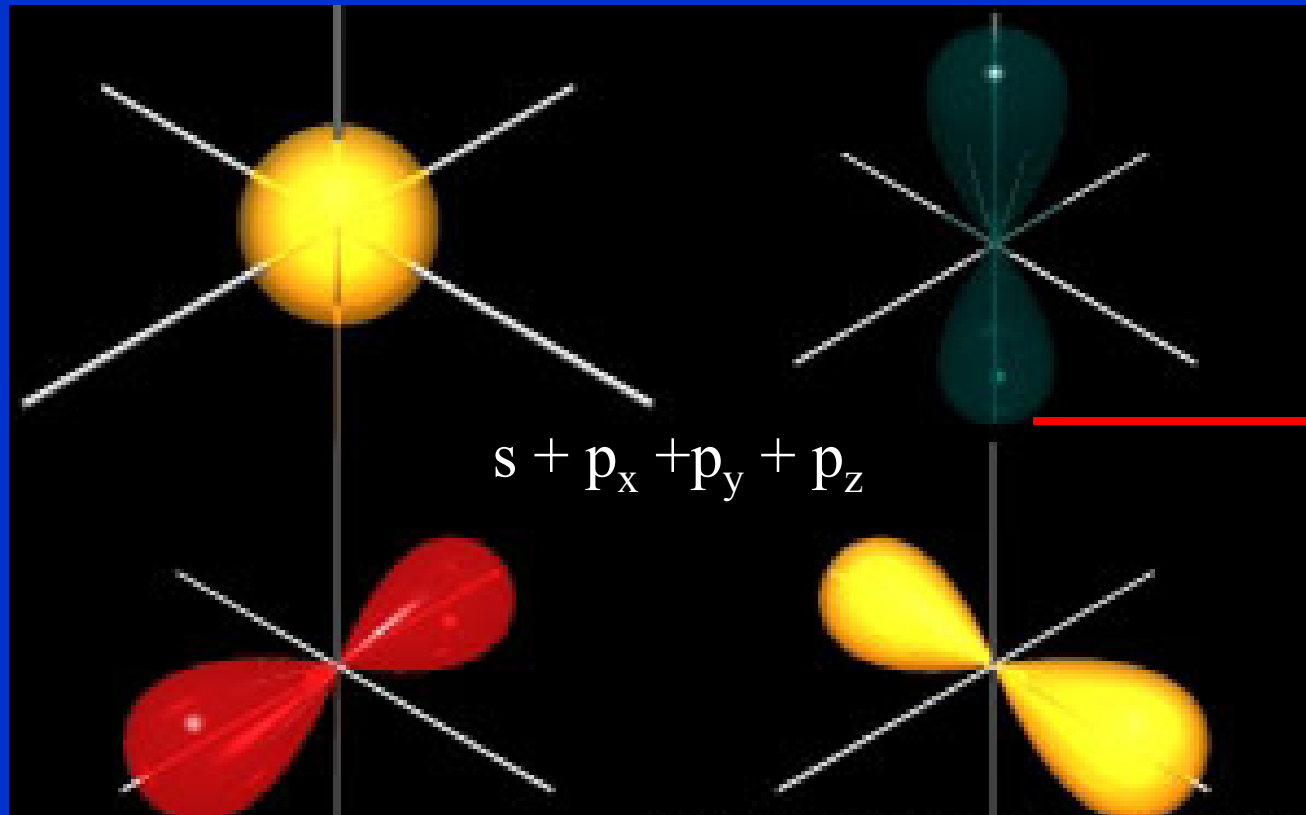
# Hybridizace $sp^3$

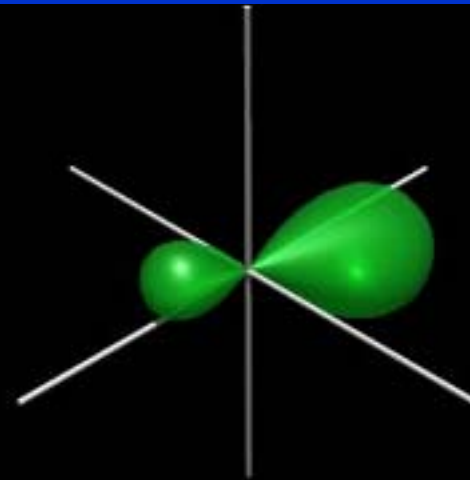
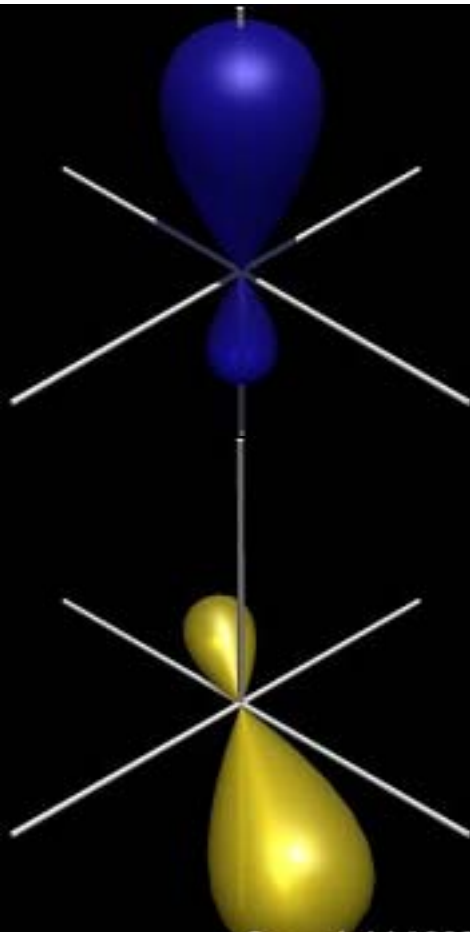
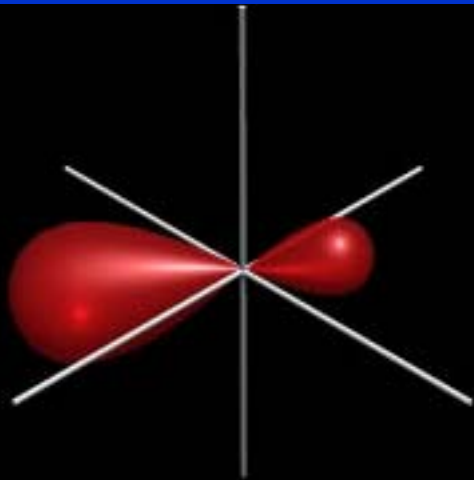


# Hybridizace $sp^3$

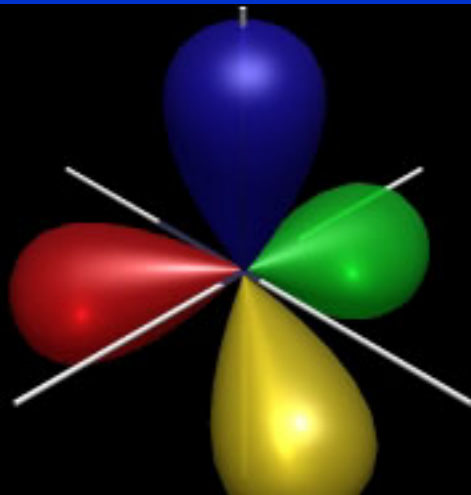


# Hybridizace $sp^3$



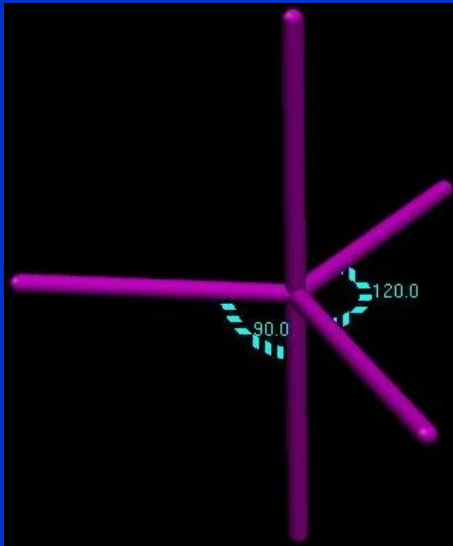


$sp^3$

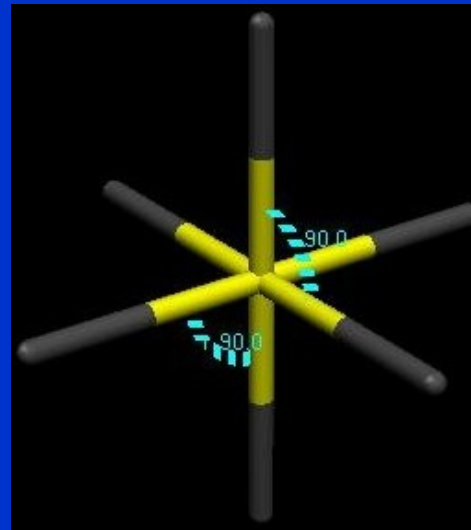


# Hybridizace

$sp^3d$

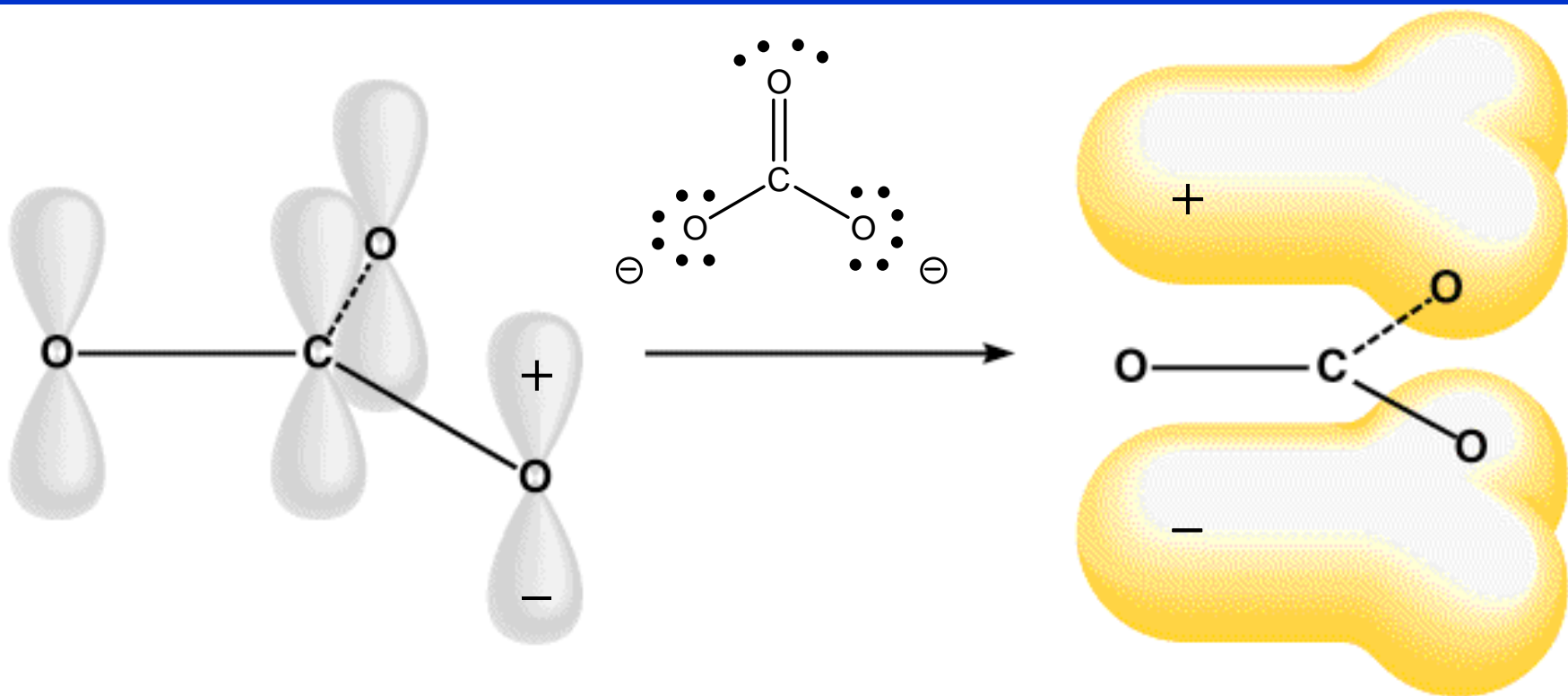


$sp^3d^2$



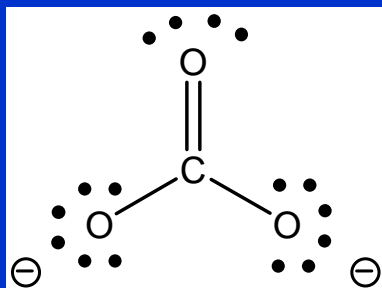


## Vazba v $\text{CO}_3^{2-}$ a $\text{NO}_3^-$



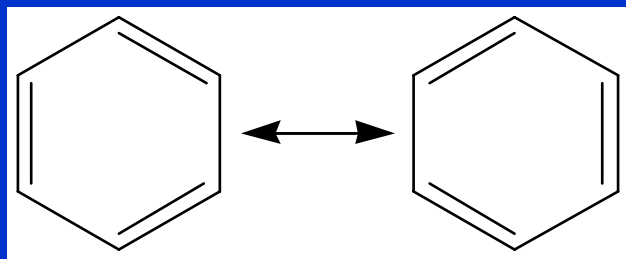
3  $\sigma$  vazby překryvem  $\text{C}(sp^2)\text{--O}(sp^2)$   
1  $\pi$ -vazba překryvem  $\text{C}(p_x)\text{--O}(p_x)$

## Řád vazby



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

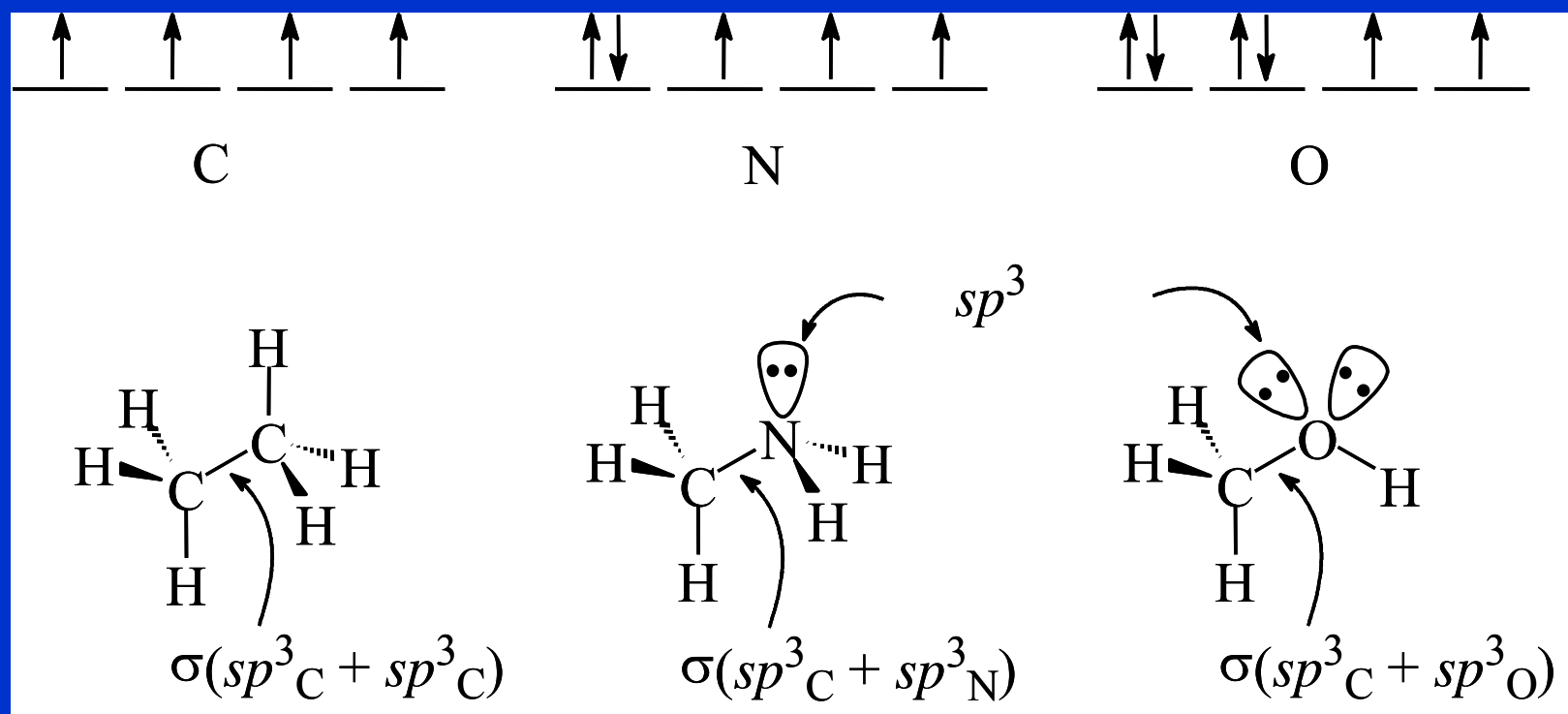
Řád vazby = 1.3333



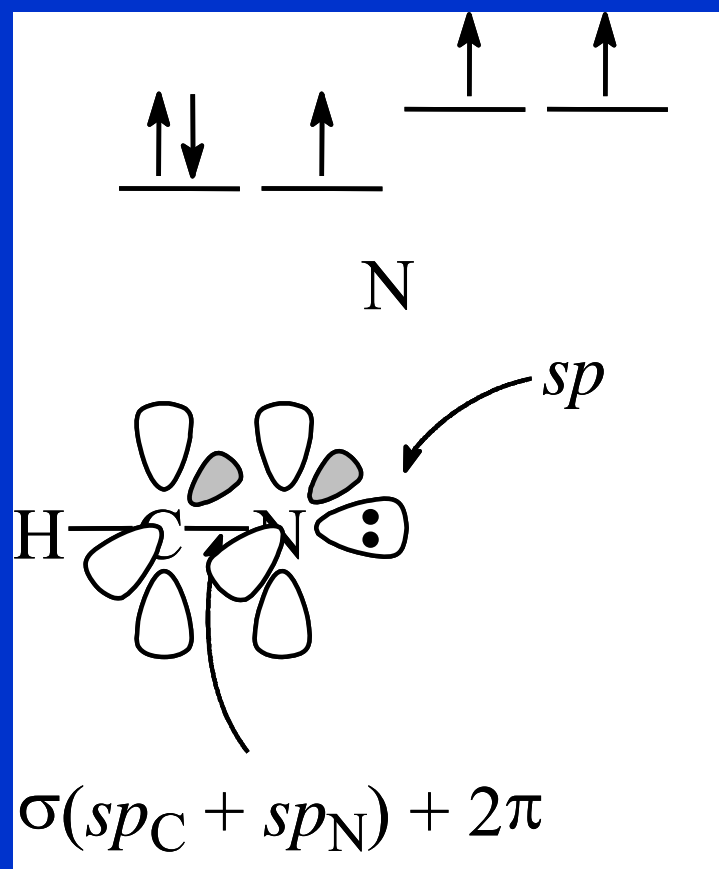
9 (6+3) vazebných elektronových párů / 6 vazeb

Řád vazby = 1.5

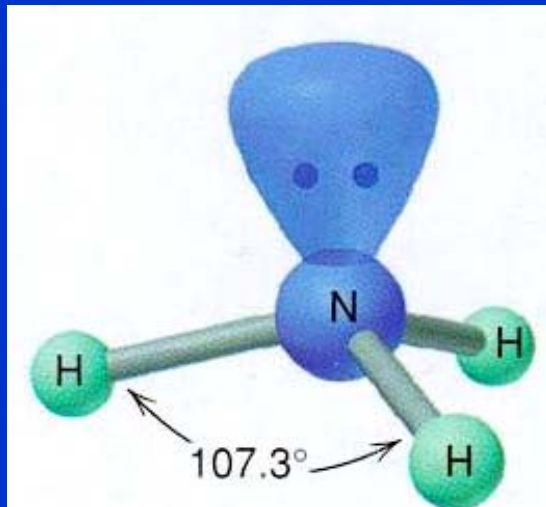
# Vazba v $C_2H_6$ , $CH_3NH_2$ a $CH_3OH$



## Vazba v HC≡N



# Elektronegativita a vazebné úhly



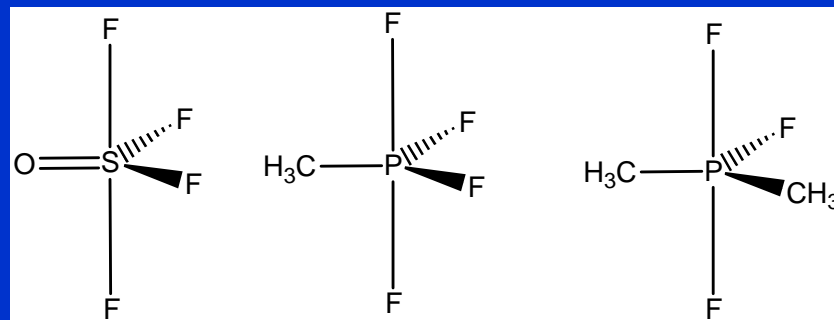
Vazebný úhel Hybridizace

NH <sub>3</sub>	107.3°	sp <sup>3</sup>
PH <sub>3</sub>	93.8°	
AsH <sub>3</sub>	91.8°	
SbH <sub>3</sub>	91.3°	
		s + 3p
NF <sub>3</sub>	102.5°	
OH <sub>2</sub>	104.5°	
OF <sub>2</sub>	103.2°	

Rostoucí  $\Delta\chi$  snižuje vazebné úhly

## Bentovo pravidlo

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

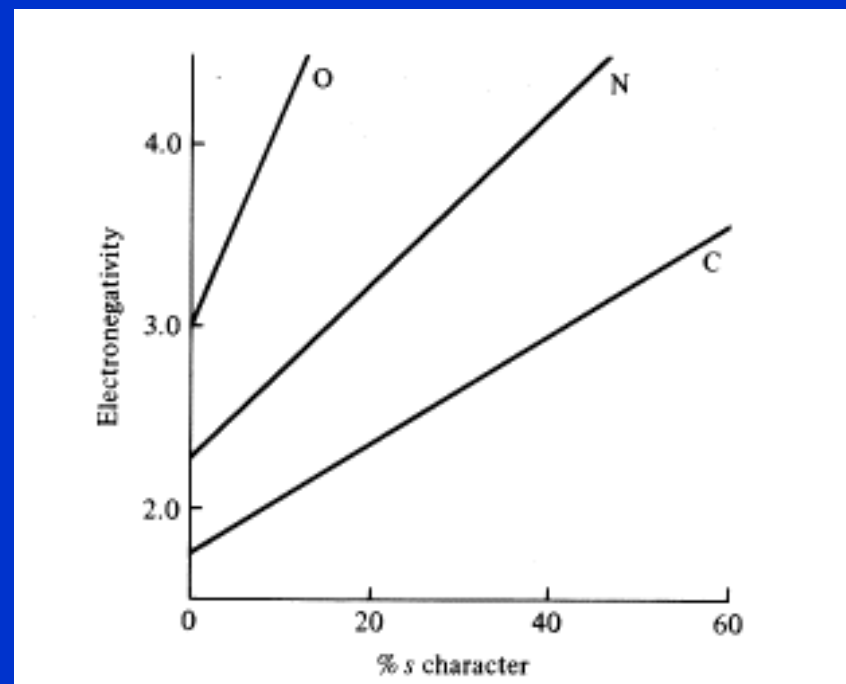


Lepší donory obsazují ekvatoriální rovinu v TBP a bazální rovinu v SP.

Volný elektronový pár je nejlepší donor = substituent s nulovou elektronegativitou

## Hybridizace a elektronegativita

Hybridizace	% s	% p
sp	50	50
sp <sup>2</sup>	33	66
sp <sup>3</sup>	25	75



↑  
s-charakter

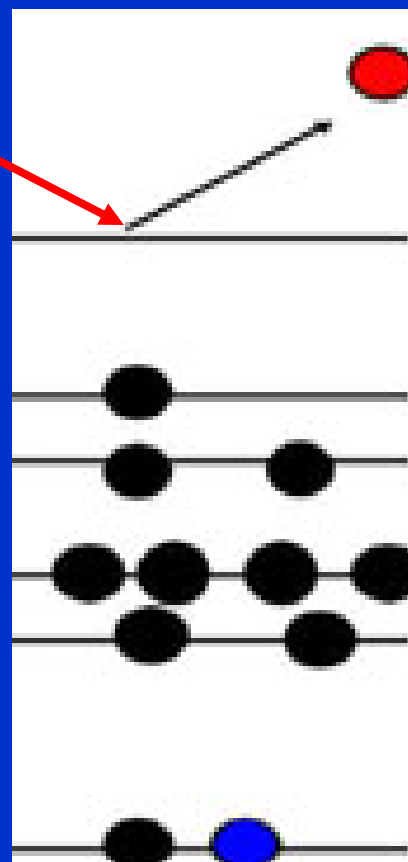
↑  
p-charakter

Elektron v s-orbitalu je vázán pevněji než v p-orbitalu  
Orbital s vyšším s-charakterem má vyšší elektronegativitu

# PES = Fotoelektronová spektroskopie

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

$h\nu$



$E_{\text{kin}}$

měříme

## X-ray Fotoelektronová Spektroskopie (XPS)

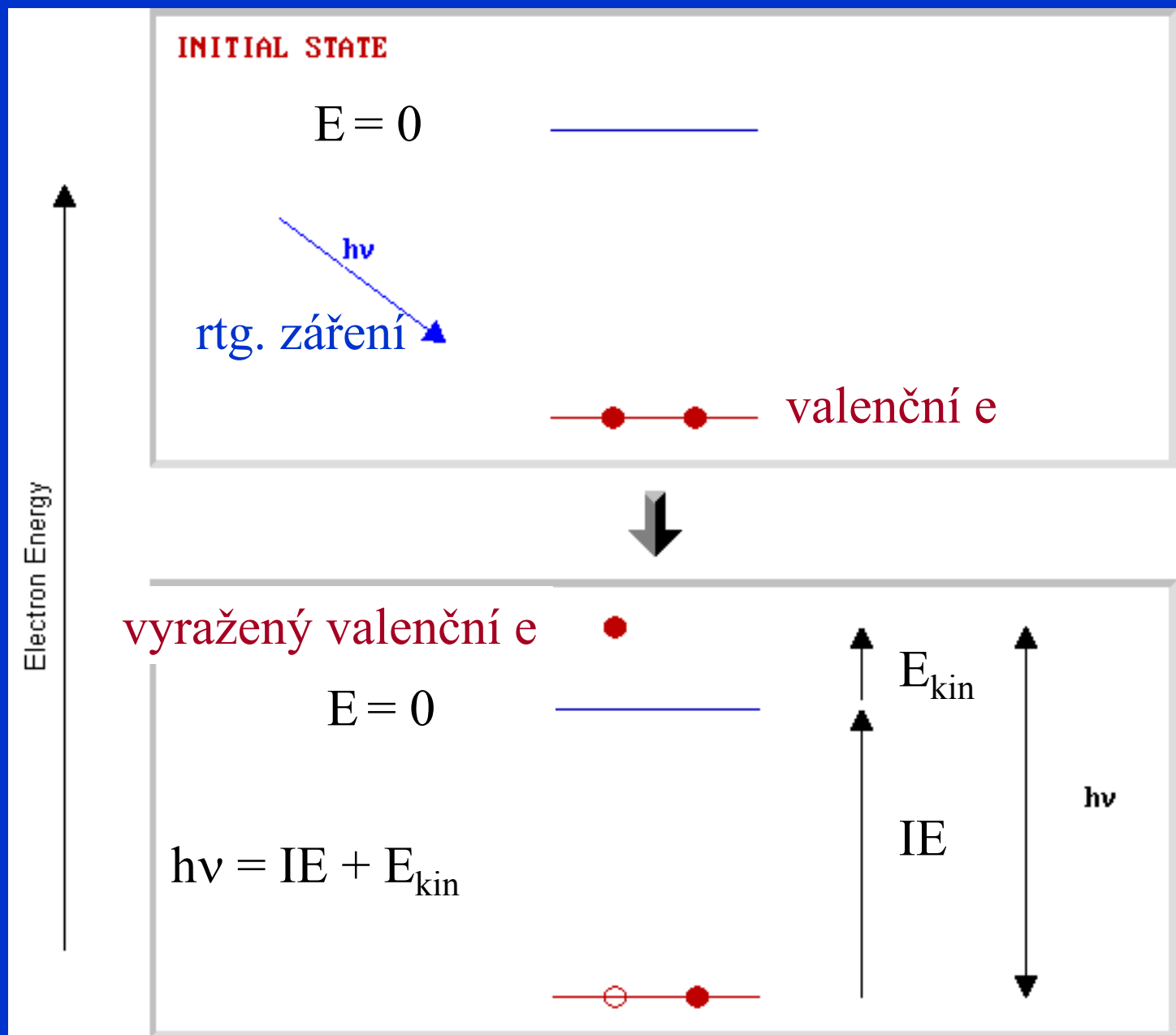
- měkké rtg. záření (200-2000 eV)

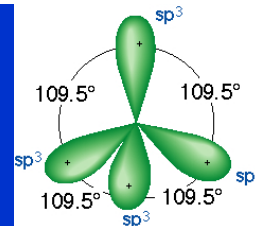
vyráží vnitřní e

## UV Fotoelektronová Spektroskopie (UPS)

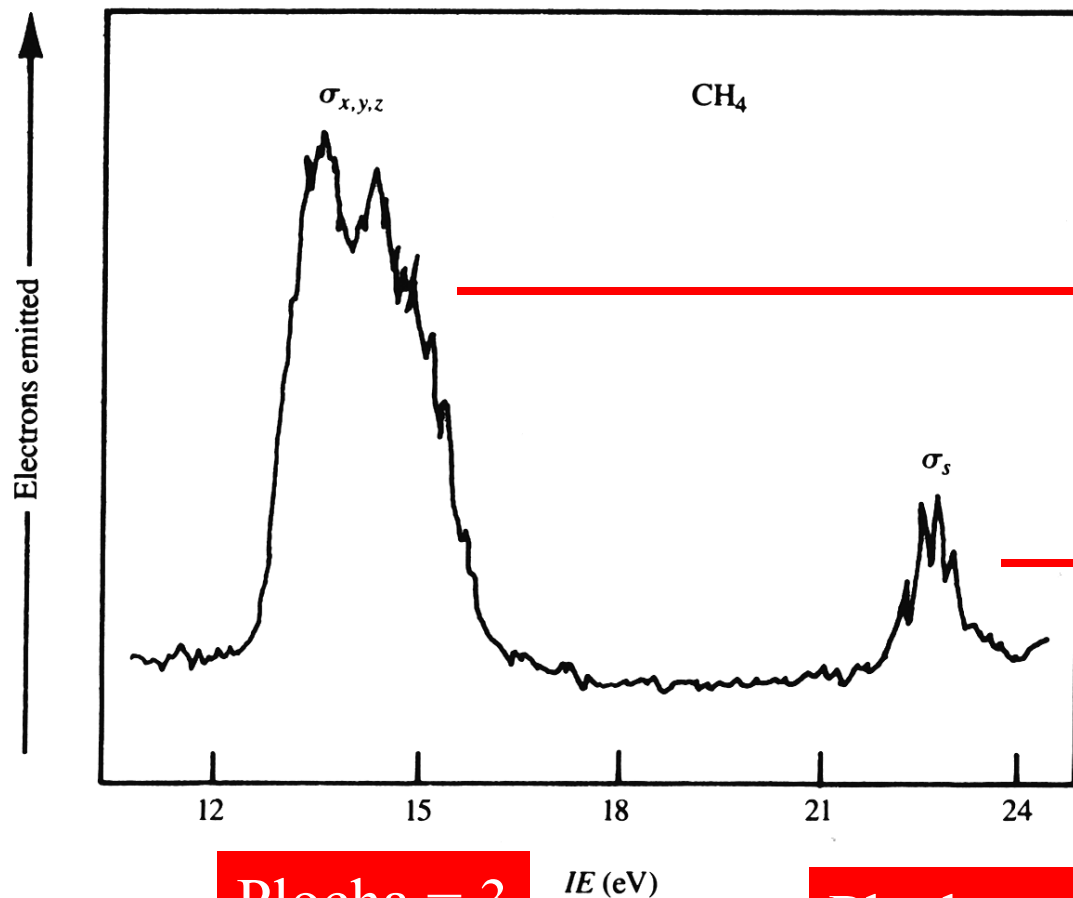
- vakuové UV záření (10-45 eV) vyráží valenční e.





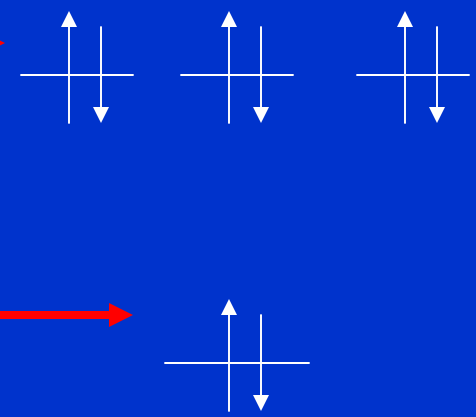


# PES methanu nesouhlasí s modelem 4 $sp^3$

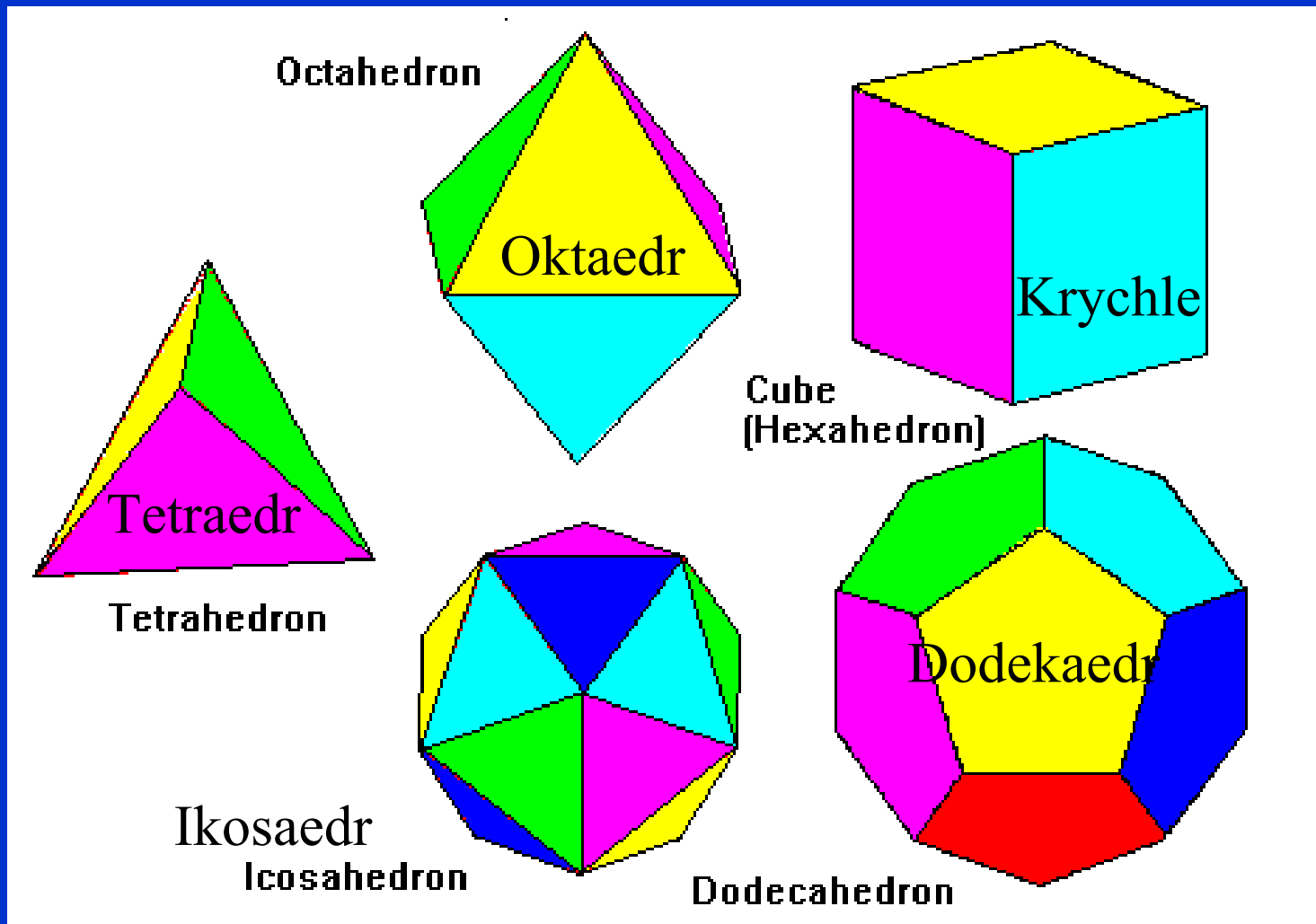


Plocha = 3

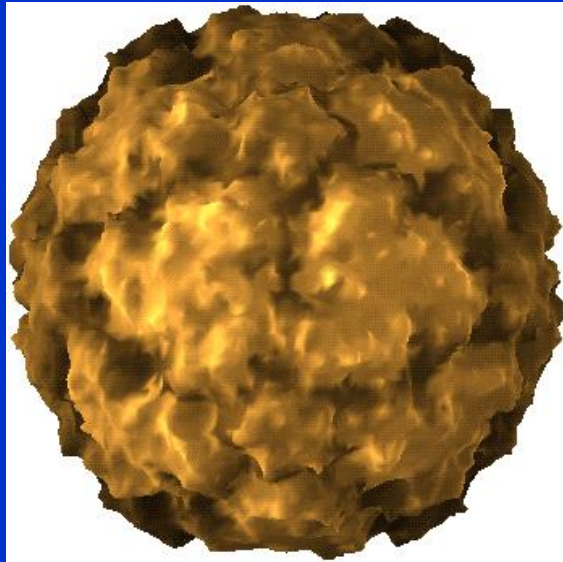
Plocha = 1



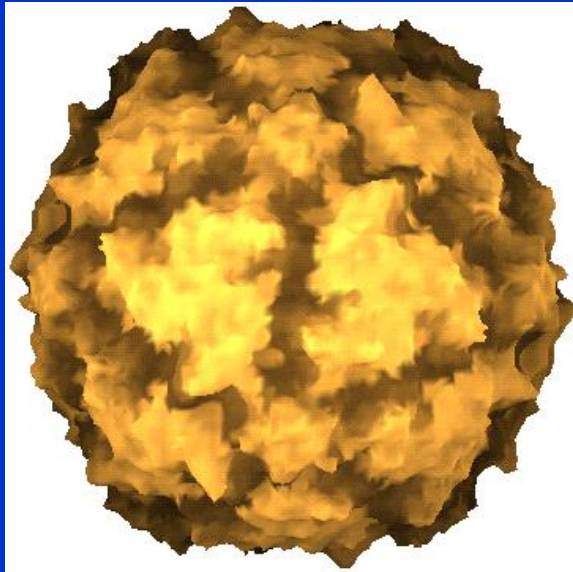
# Symetrie – Platonovská tělesa



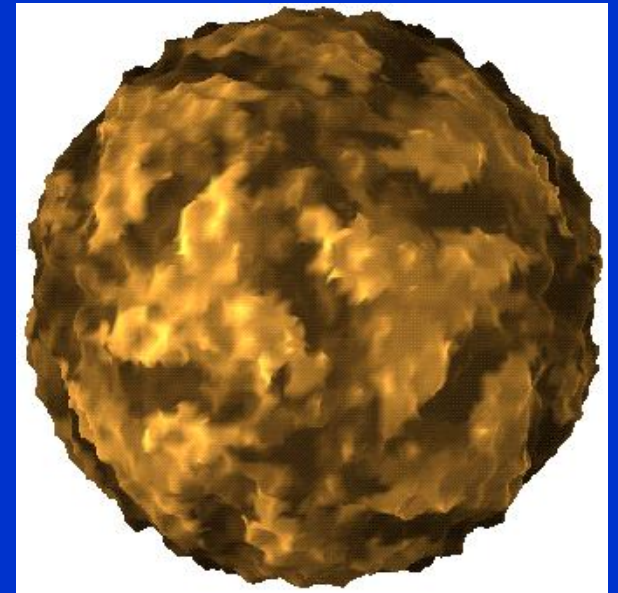
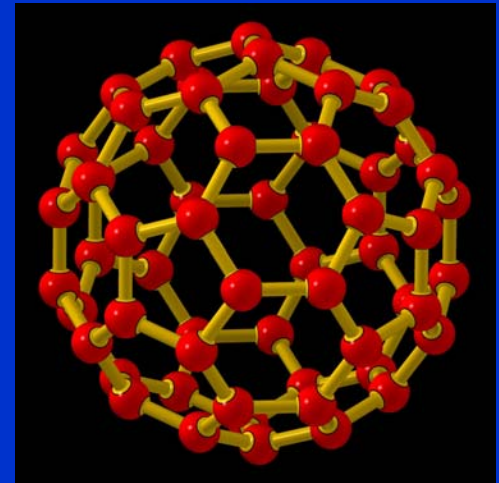
# Symetrie



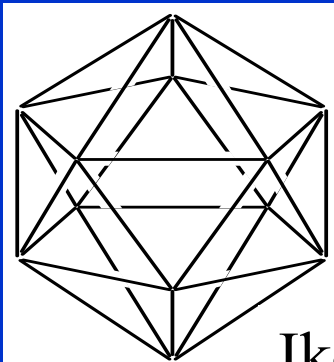
Virus rýmy



Virus obrny



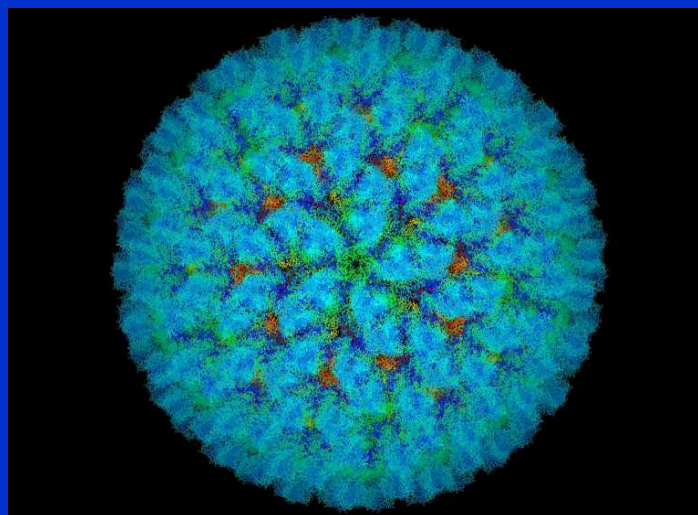
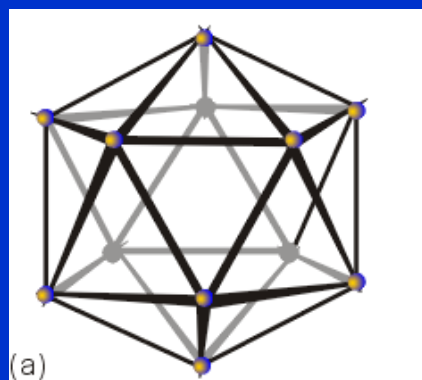
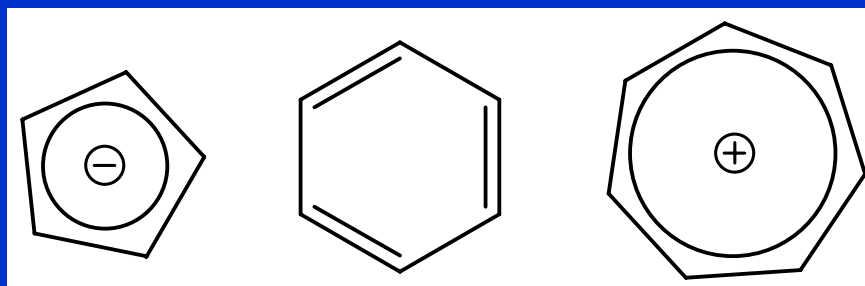
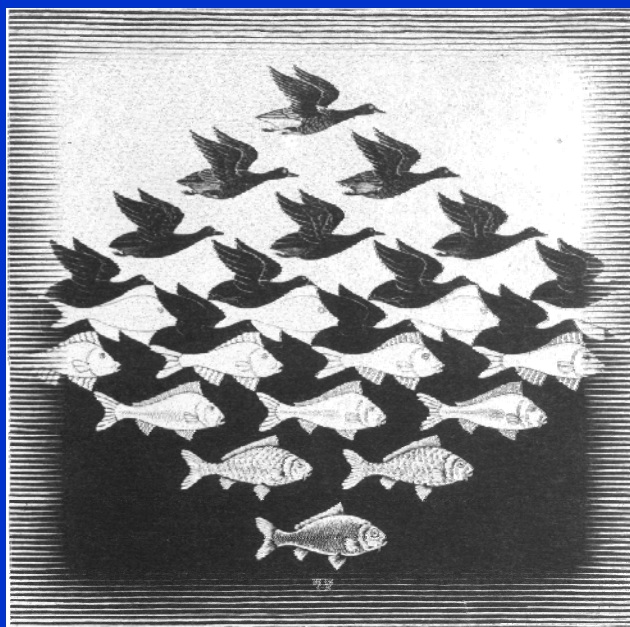
Virus slintavky a kulhavky



Ikosaedr

# Symetrie molekul

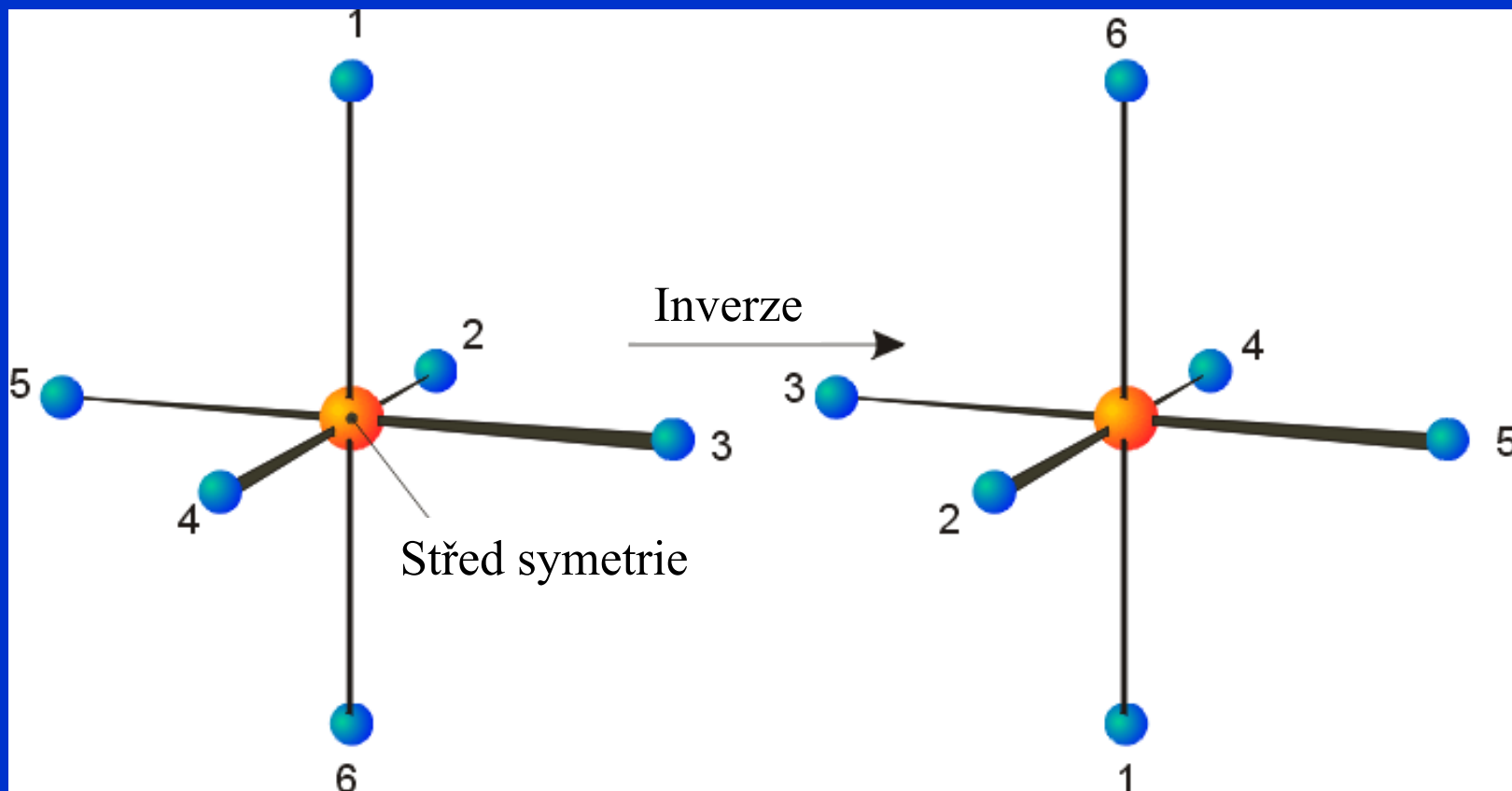
Jak jsou atomy v molekule uspořádány = ekvivalentní atomy



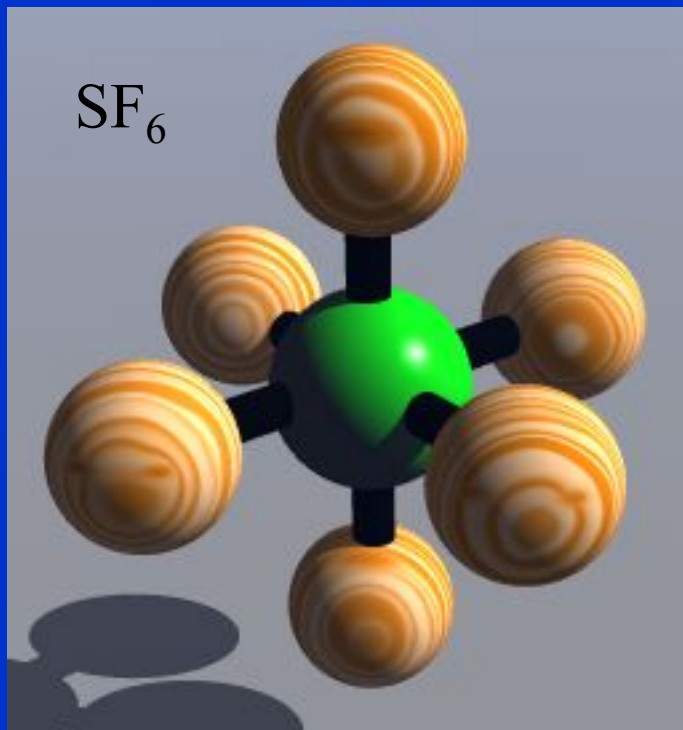
## Prvky a operace symetrie

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
$\sigma$	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

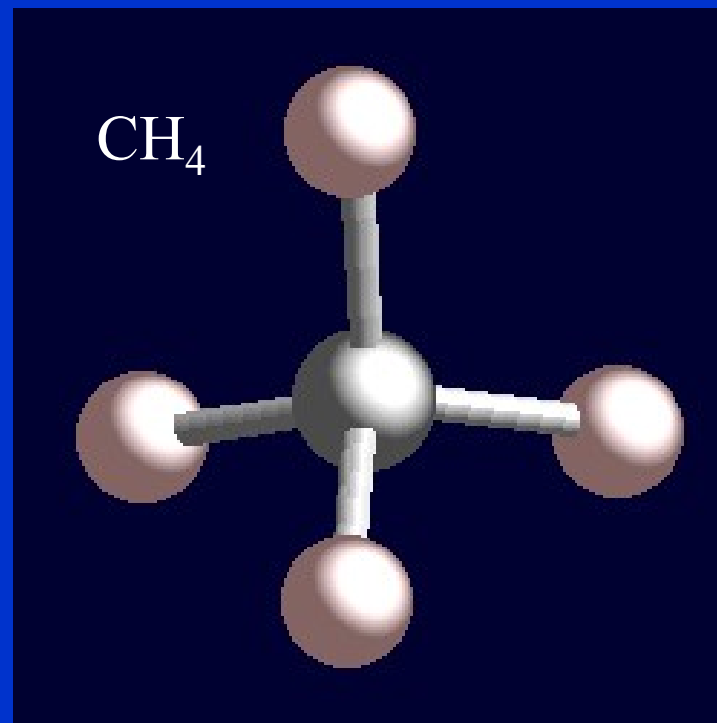
# Střed symetrie



## Střed symetrie

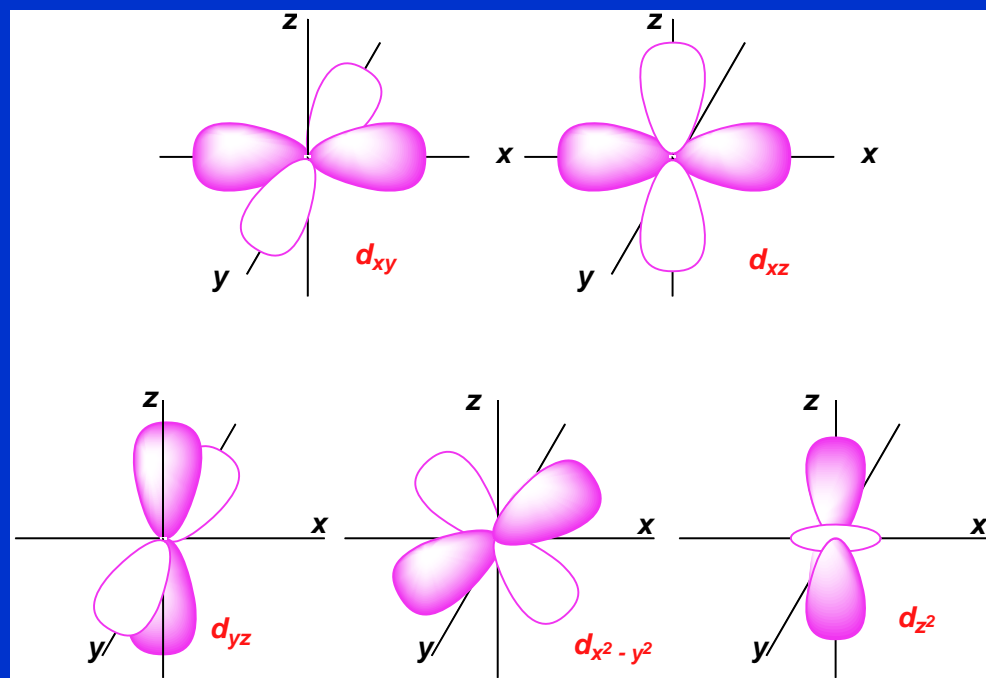
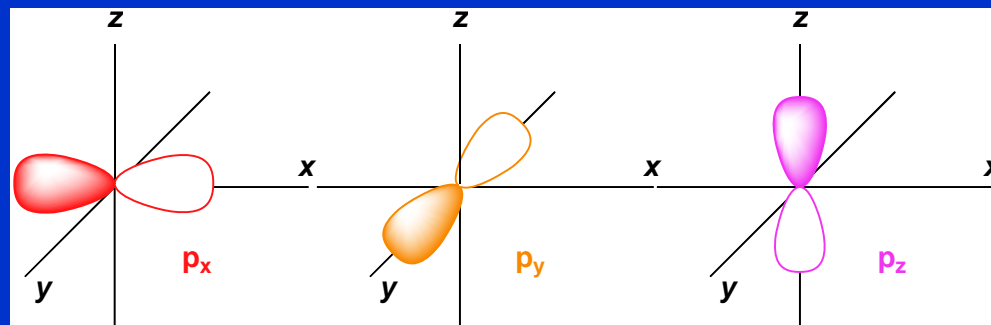
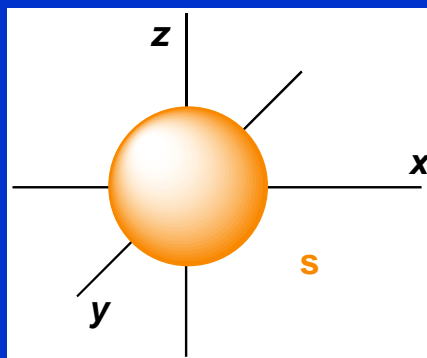


$S$  = střed symetrie



Nemá střed symetrie

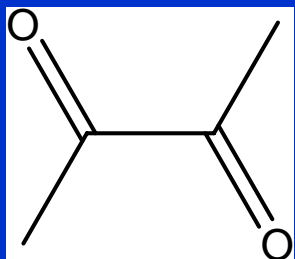




## Orbitaly

s a d mají *i* (střed symetrie)

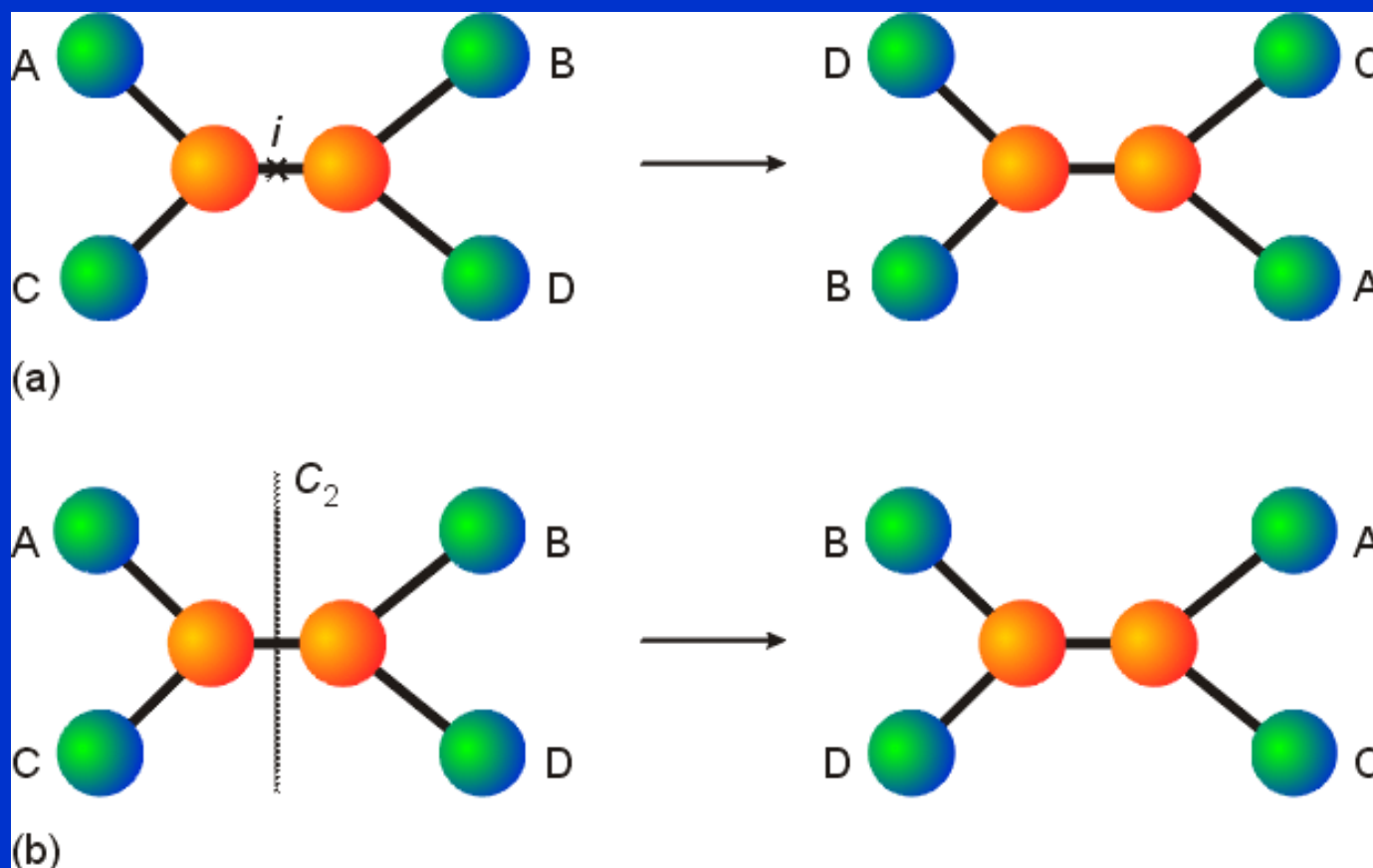
p a f nemají *i* (střed symetrie)



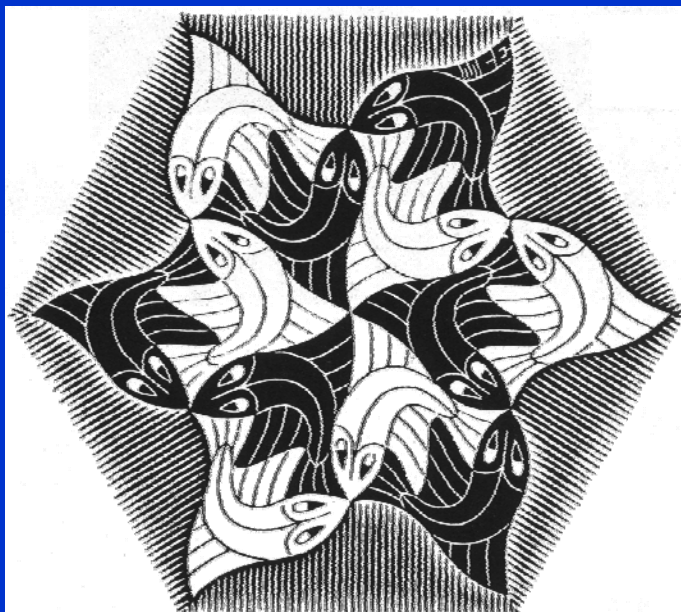
## Rotační osa $C_2$



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

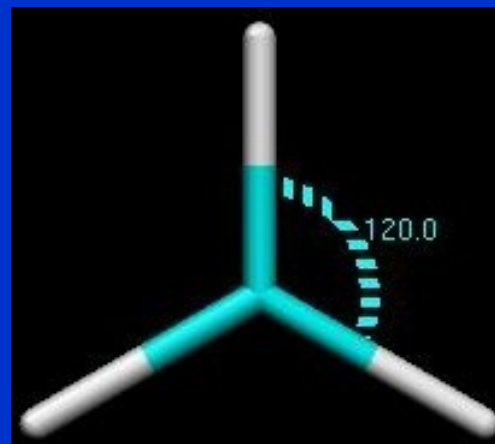


## Rotační osa $C_3$



Rotace o úhel  $360/n$

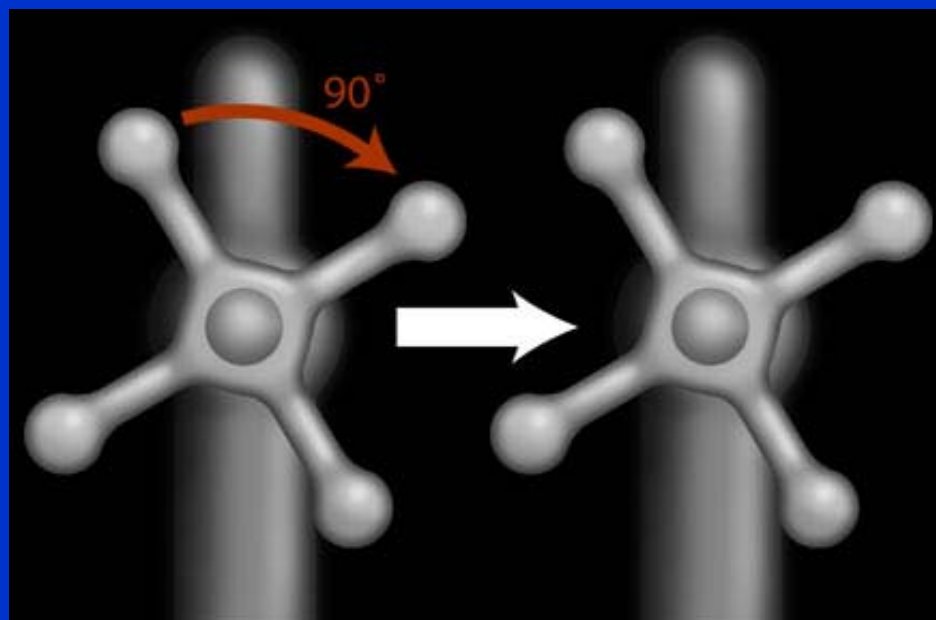
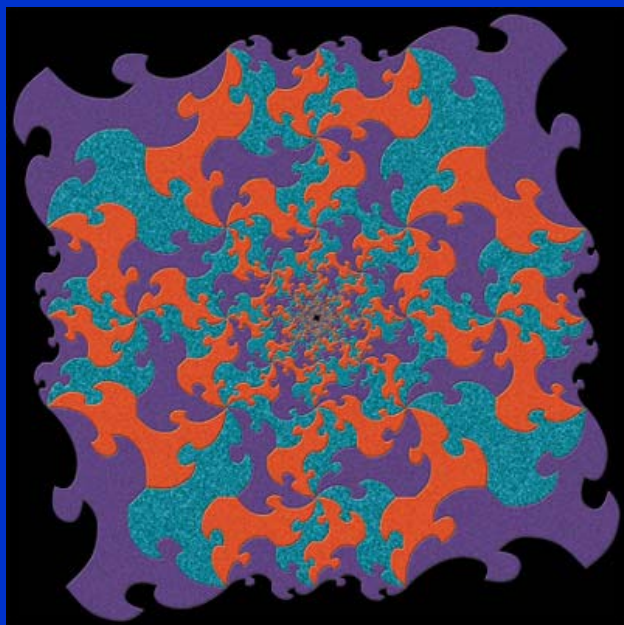
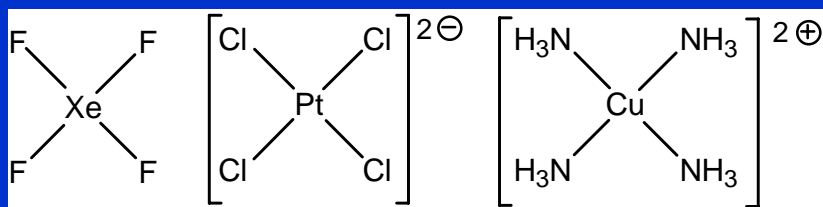
Vzniklá situace je  
nerozlišitelná od výchozí



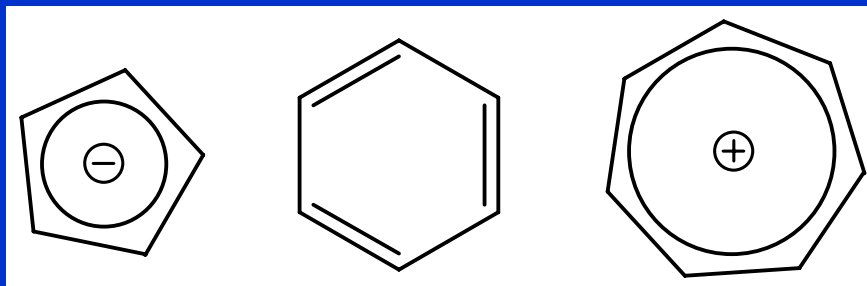
## Rotační osa $C_4$

Rotace o úhel  $360/4$ .

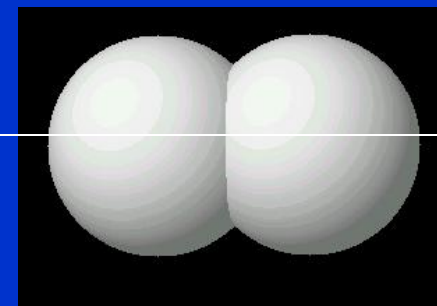
Vzniklá situace je nerozlišitelná od výchozí.



## Rotační osa $C_n$



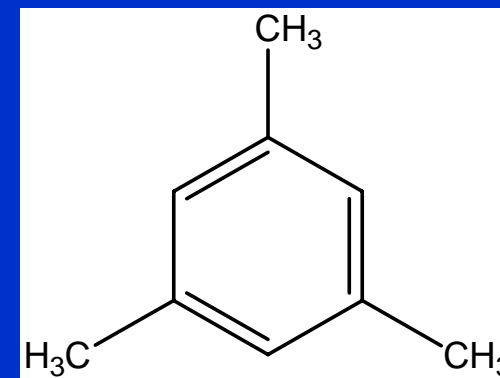
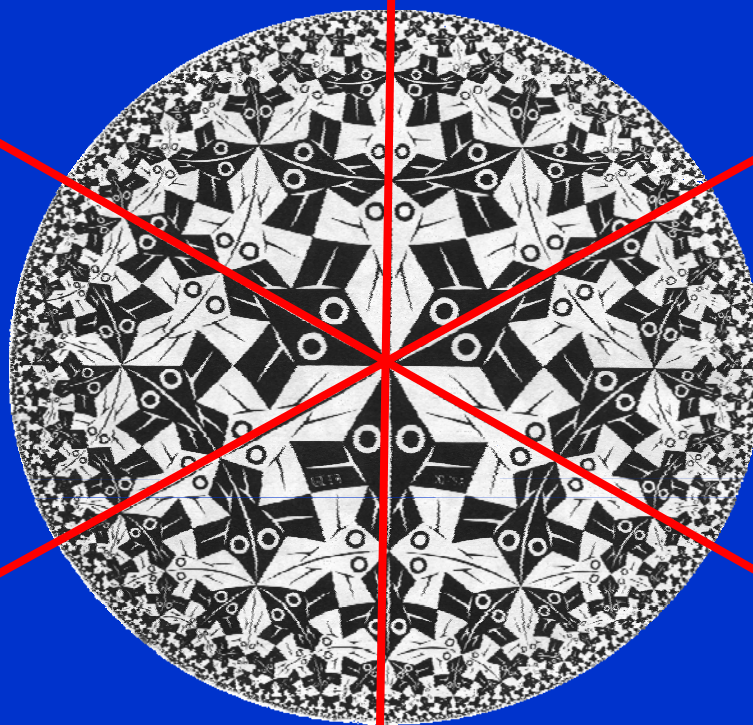
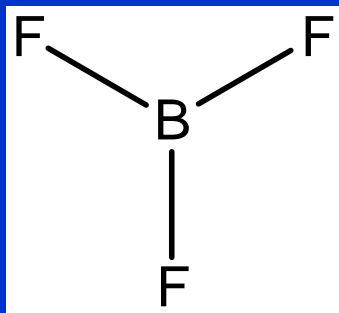
$C_5, C_6, C_7, \dots, C_\infty$



Lineární molekuly



# Rovina symetrie $\sigma$



## Roviny symetrie $\sigma$

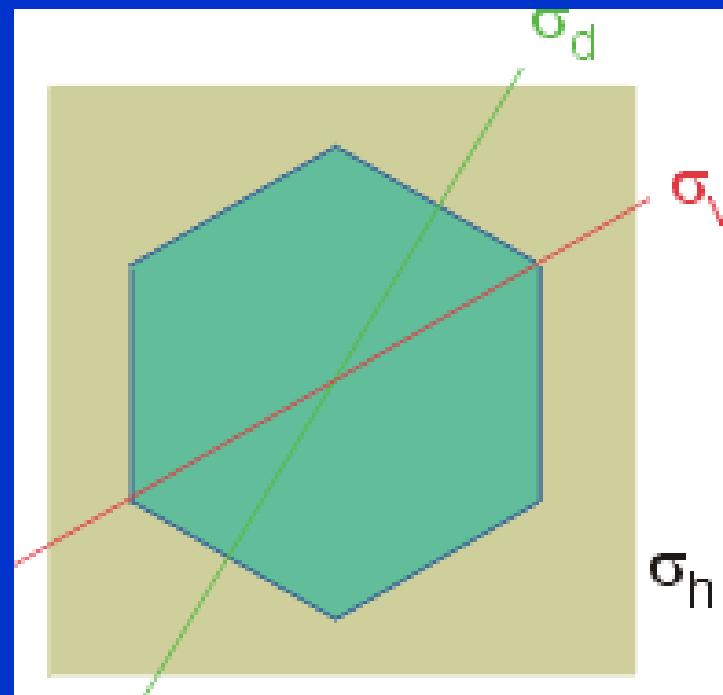
Každá planární molekula má rovinu symetrie ve které leží

$\sigma_h$  = kolmá k hlavní rotační ose

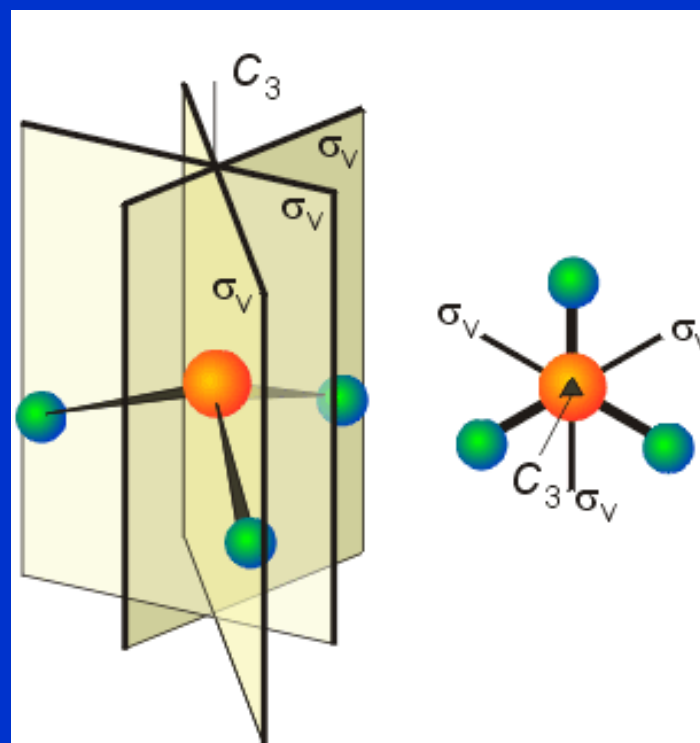
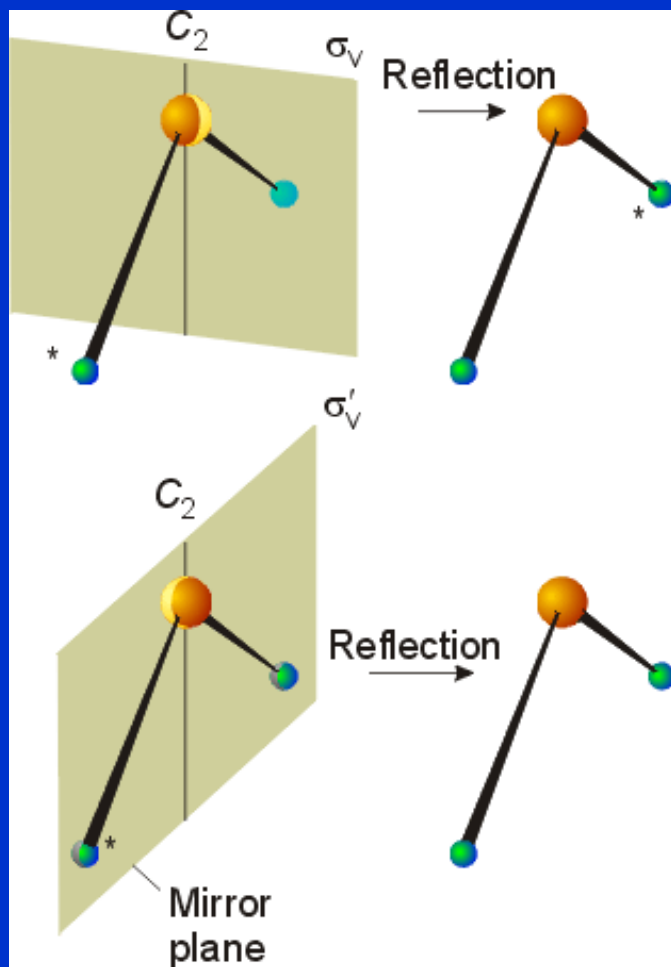
$\sigma_v$  = obsahuje hlavní rotační osu, protíná nejvíce atomů

$\sigma_d$  = obsahuje hlavní rotační osu, pŕlí úhly mezi  $C_2$  osami kolnými na hlavní rotační osu

Všechny  $\sigma$  prochází počátkem



# Roviny symetrie $\sigma$



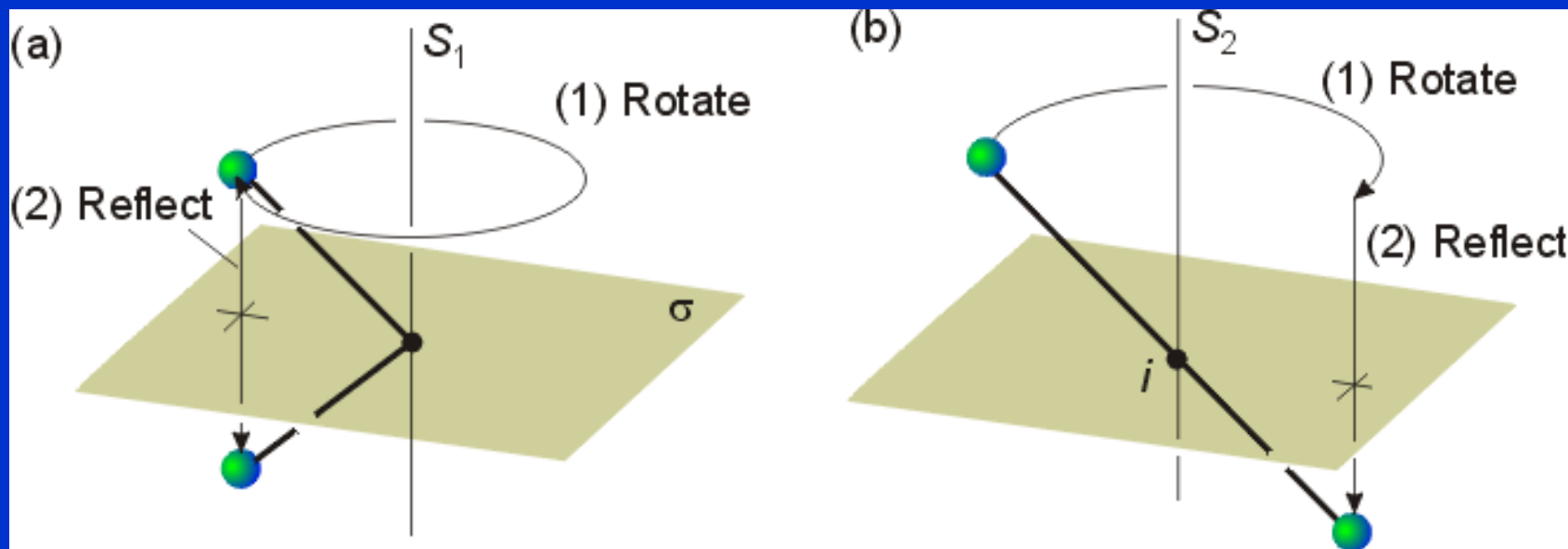


## Zrcadlově-rotační osa $S_n$

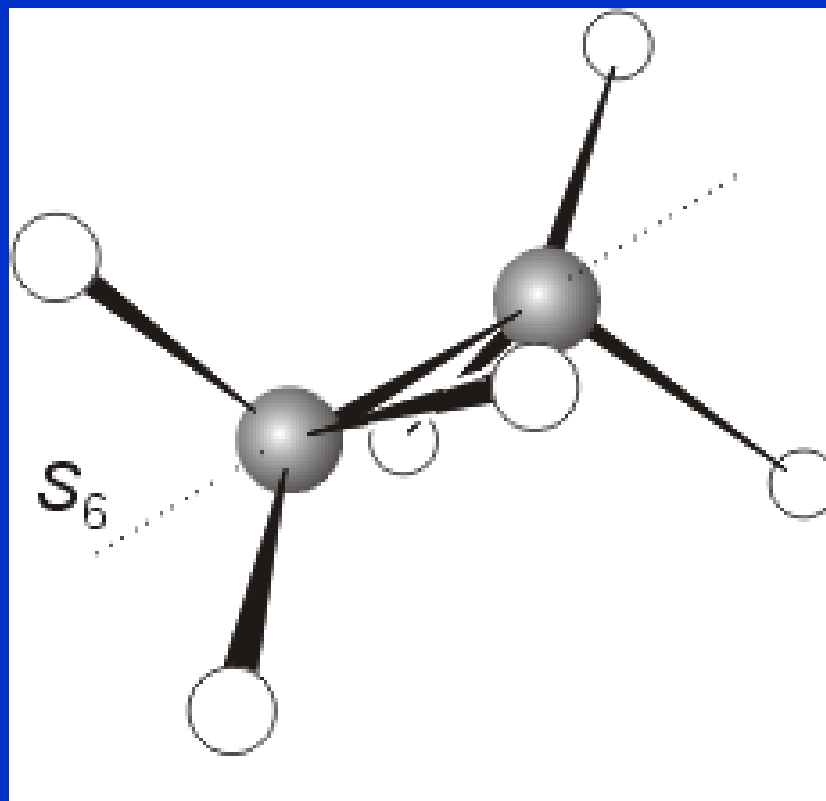
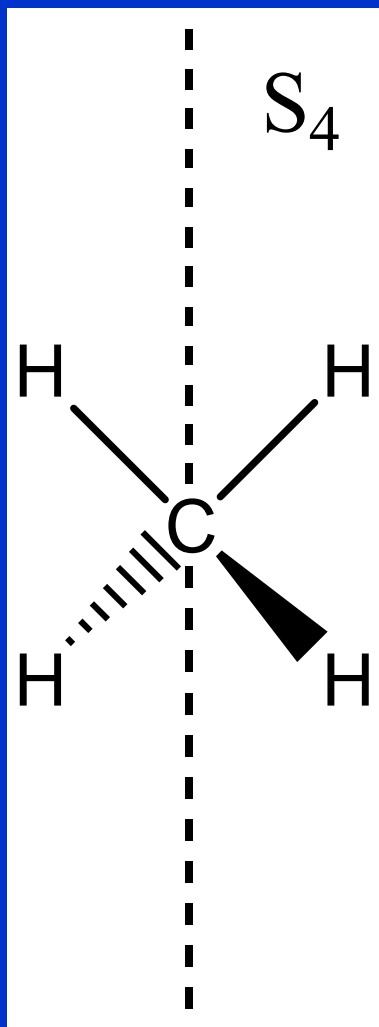
Postupné provedení dvou operací – rotace a zrcadlení

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

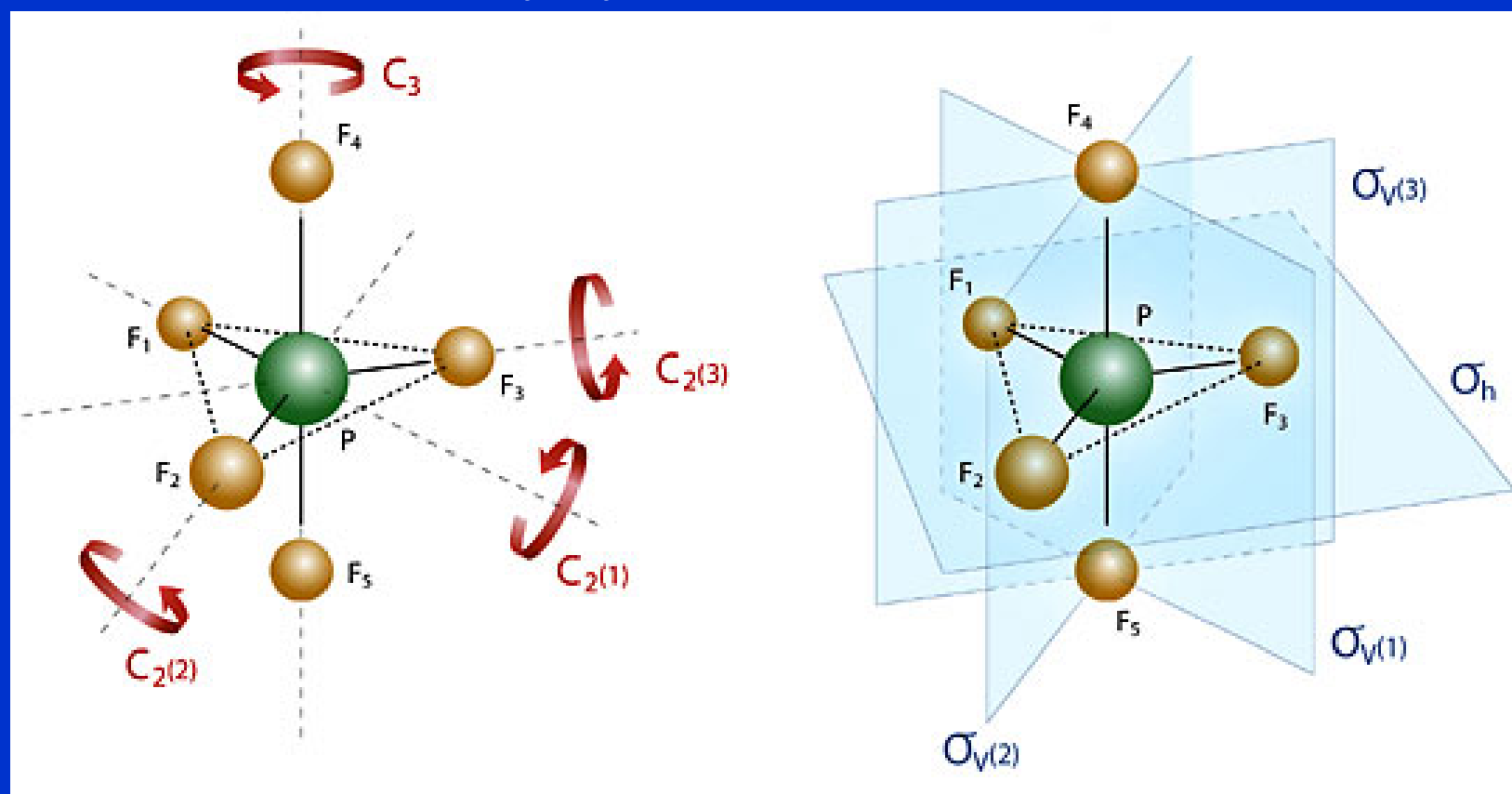
$$S_2 = C_2 \times \sigma = i$$



## Zrcadlově-rotační osa $S_n$



## Prvky symetrie v molekule



Ekvivalentní atomy = jsou zaměňovány operacemi symetrie

$$F_4 = F_5 \quad F_1 = F_2 = F_3$$

## Chiralita



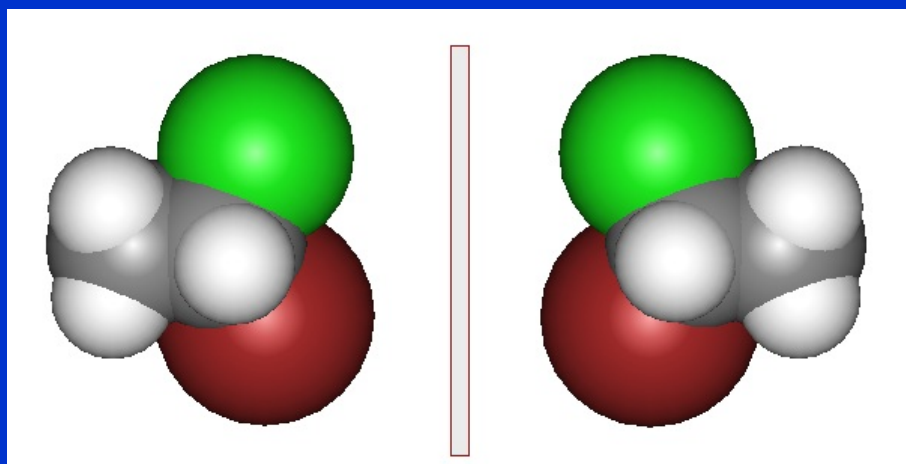
**Figure 2.** The Founding Fathers. R. M. Barrer (1910–1996) (right) and R. M. Milton (1920–2000) photographed

# Chiralita

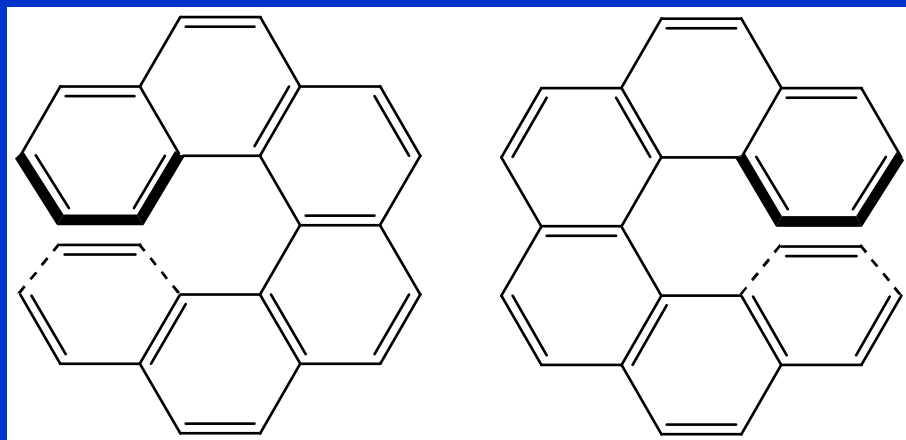
Podmínka chirality: v molekule není přítomna  $S_n$

$$S_1 = \sigma$$

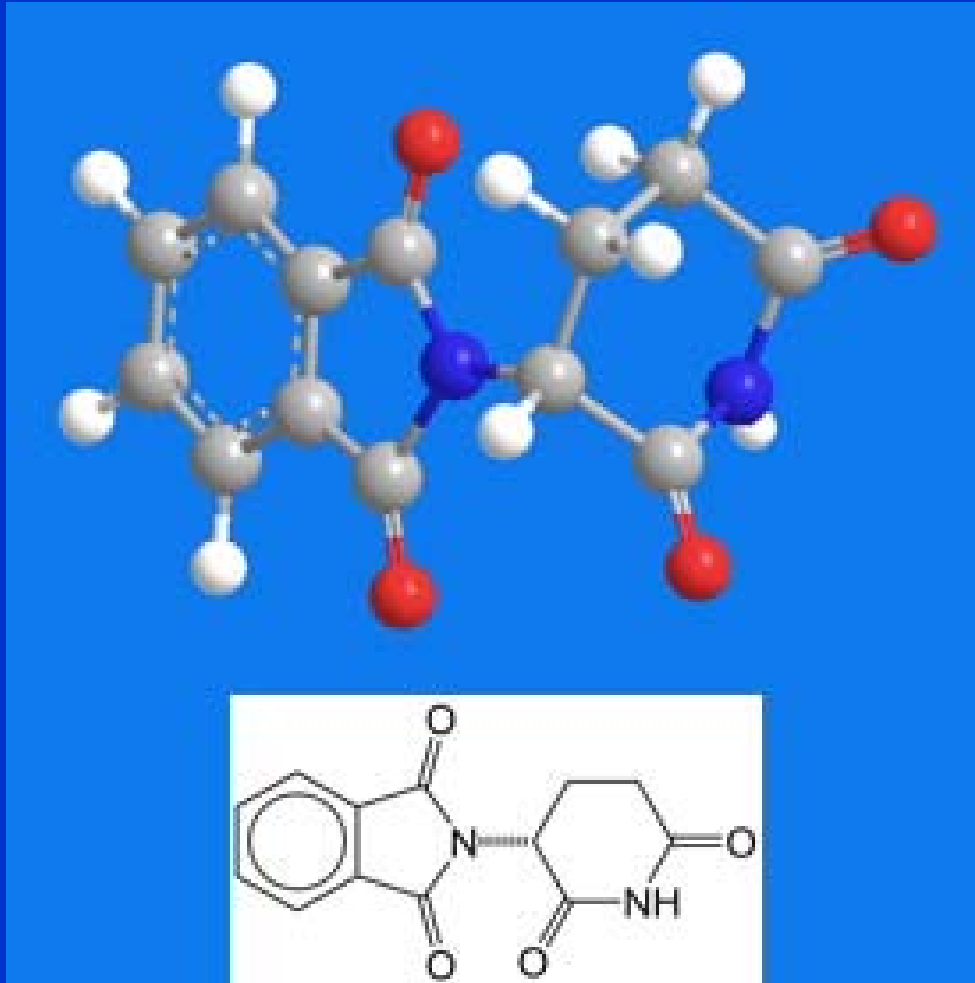
$$S_2 = i$$



$C_2$



# Thalidomide



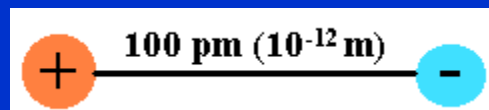
(*R*)-enantiomer  
lék na ranní nevolnost

(*S*)-enantiomer  
je teratogenní

## Dipolový moment

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

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



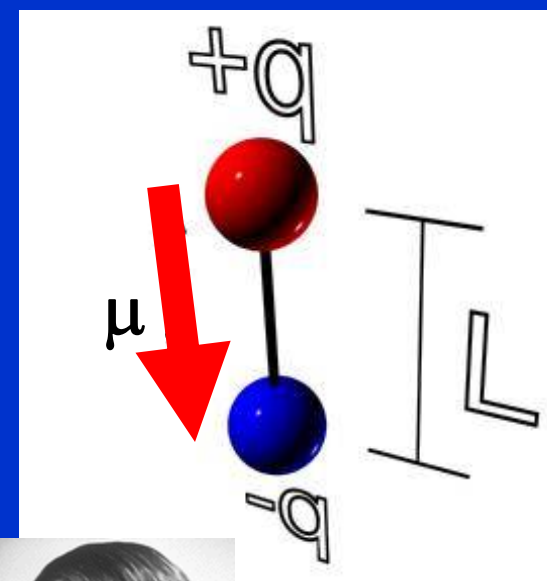
proton a elektron, vzdáleny 1 Å

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

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

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)

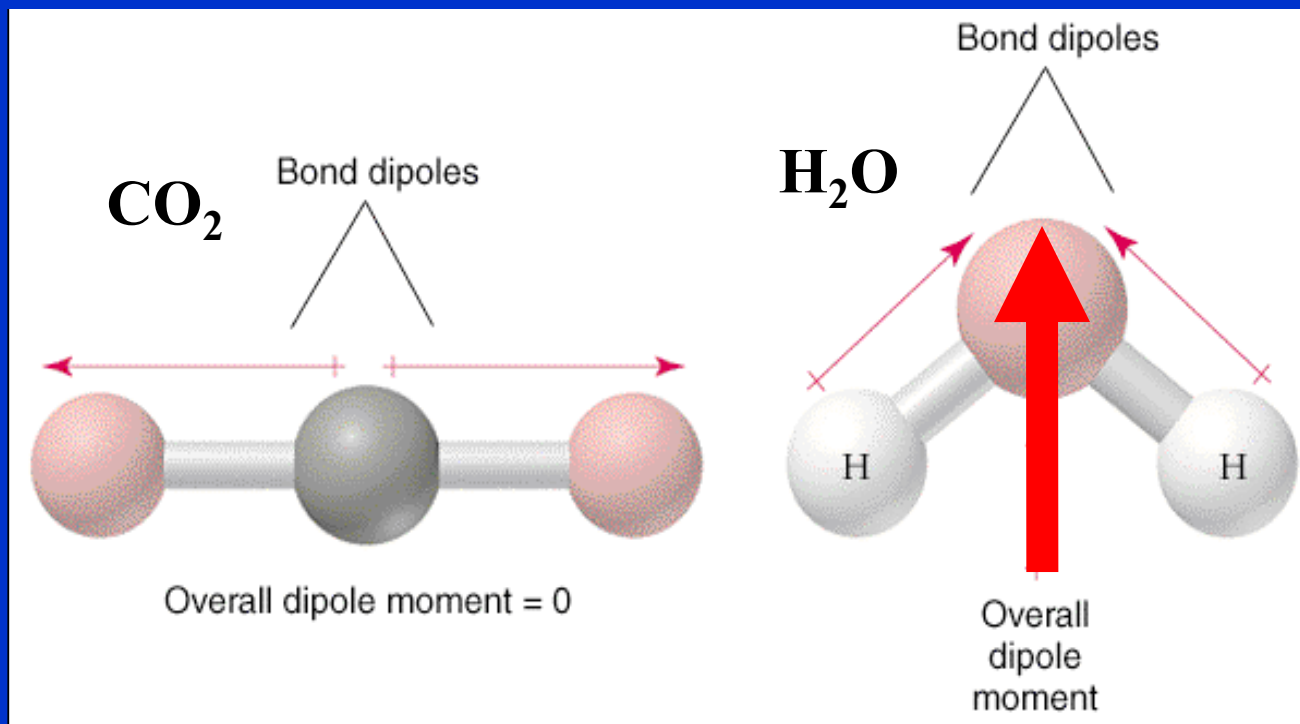
1936 NP za chemii

Zahřívání v MW

## Dipolový moment molekuly

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

Míra nerovnoměrnosti rozložení náboje v molekule

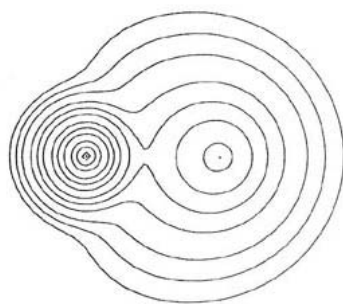




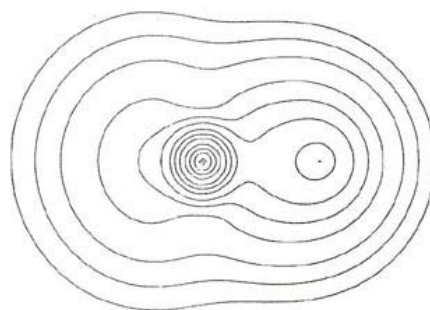
## Dipolové momenty diatomických molekul

AH	$\mu$ (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

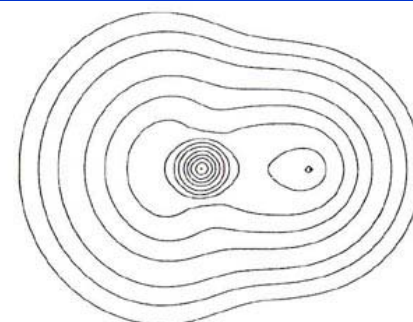
negativní nebo pozitivní znaménko pro  $\mu \Rightarrow$  H je negativní nebo pozitivní konec dipolu.



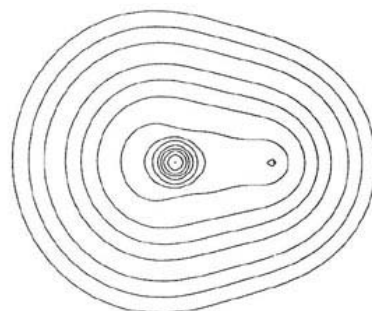
**LiH**



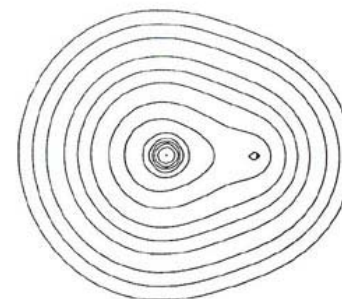
**BeH**



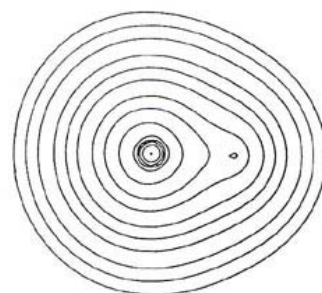
**BH**



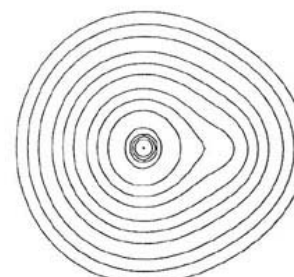
**CH**



**NH**



**OH**



**HF**

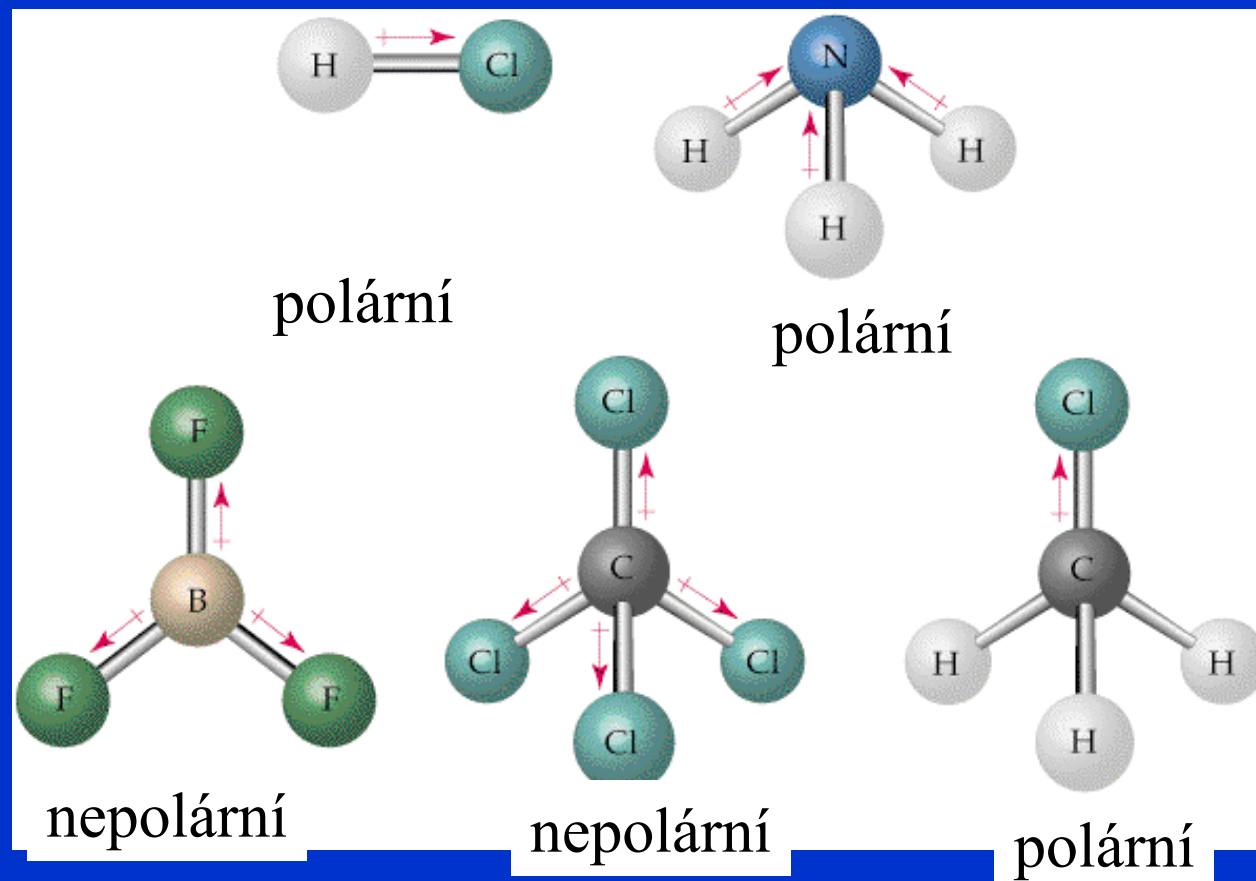
# Dipolový moment vazeb

Rozdíl elektronegativit vazebných partnerů

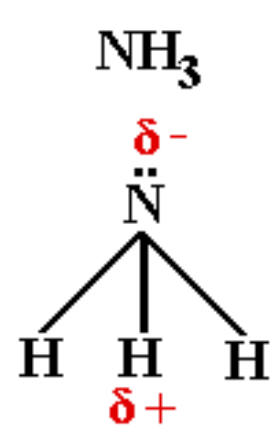
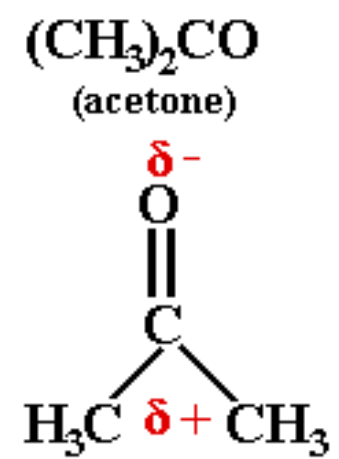
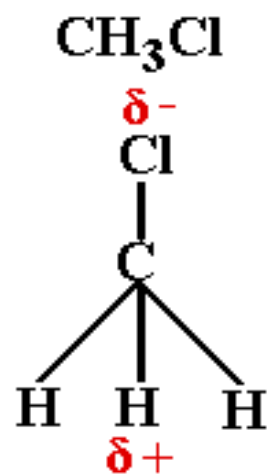
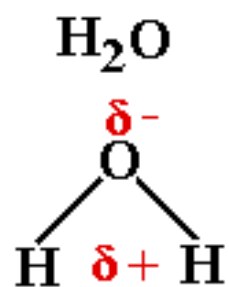
Enlace	$\chi_A - \chi_B$	$\mu$ (D)	Enlace	$\chi_A - \chi_B$	$\mu$ (D)	Enlace	$\chi_A - \chi_B$	$\mu$ (D)
C-H	0.30	0.4	N=C		0.9	Br-P	0.68	0.36
N-H	0.87	1.31	N≡C		3.5	I-P	0.15	0
N-D		1.30	O-C	1.00	0.74	O=As		4.2
H-P	0.14	0.36	O=C		2.3	F-As	1.90	2.03
H-As	0	0.10	C-S	0.06	0.9	Cl-As	0.63	1.64
H-Sb	0.38	0.08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

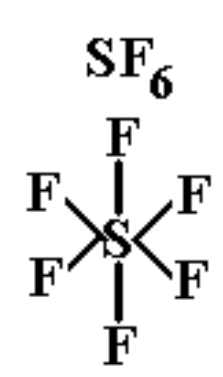
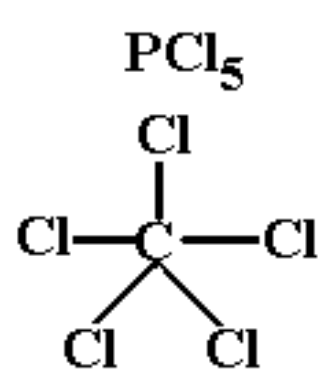
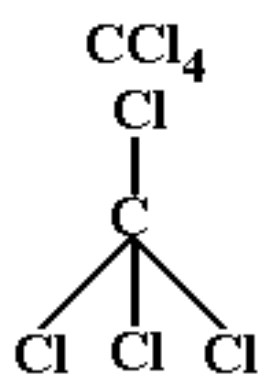
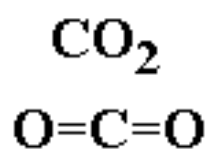
Polární molekula = celkový dipol musí ležet ve všech prvcích symetrie

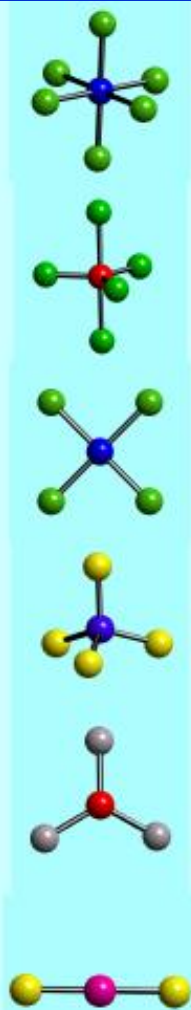


Polární



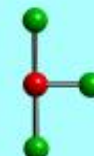
Nepolární





$\mu = 0$

<b>AB<sub>n</sub>E<sub>m</sub></b>	<b>Grupo Puntual</b>	$\mu$	<b>Molekula</b>
AB <sub>2</sub>	D <sub>∞h</sub>	0	CO <sub>2</sub> , BeCl <sub>2</sub> (g), ZnX <sub>2</sub>
AB <sub>3</sub>	D <sub>3h</sub>	0	BX <sub>3</sub> , GaI <sub>3</sub> , In(CH <sub>3</sub> ) <sub>3</sub>
AB <sub>2</sub> E	C <sub>2v</sub>	finito	SnX <sub>2</sub> , PbX <sub>2</sub>
AB <sub>4</sub>	T <sub>d</sub>	0	CX <sub>4</sub> , SiX <sub>4</sub> , ThX <sub>4</sub>
AB <sub>3</sub> E	C <sub>3v</sub>	finito	NH <sub>3</sub> , NX <sub>3</sub> , PX <sub>3</sub>
AB <sub>2</sub> E <sub>2</sub>	C <sub>2v</sub>	finito	H <sub>2</sub> O, SeX <sub>2</sub> , TeX <sub>2</sub>
AB <sub>5</sub>	D <sub>3h</sub>	0	PF <sub>5</sub> , PCl <sub>5</sub> (g), NbCl <sub>5</sub> (g)
AB <sub>4</sub> E	C <sub>2v</sub>	finito	SF <sub>4</sub> , SeF <sub>4</sub>
AB <sub>3</sub> E <sub>2</sub>	C <sub>2v</sub>	finito	ClF <sub>3</sub> , BrF <sub>3</sub>
AB <sub>2</sub> E <sub>3</sub>	D <sub>∞h</sub>	0	XeF <sub>2</sub>
AB <sub>6</sub>	O <sub>h</sub>	0	SF <sub>6</sub> , SeF <sub>6</sub> , MoF <sub>6</sub>
AB <sub>5</sub> E	C <sub>4v</sub>	finito	ClF <sub>5</sub> , BrF <sub>5</sub> , IF <sub>5</sub>
AB <sub>4</sub> E <sub>2</sub>	D <sub>4h</sub>	0	XeF <sub>4</sub>
AB <sub>7</sub>	D <sub>5h</sub>	0	IF <sub>7</sub>



$\mu \neq 0$