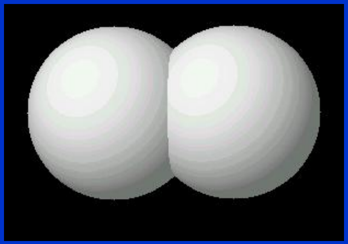
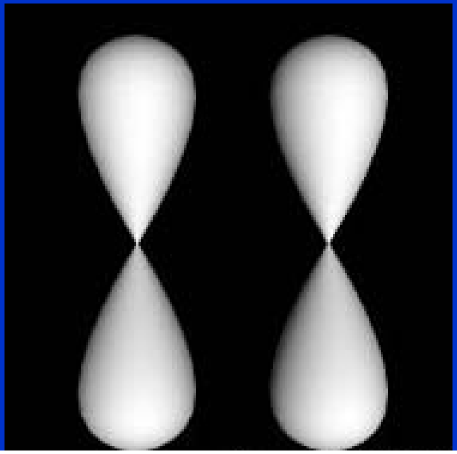
Překryv orbitalů

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

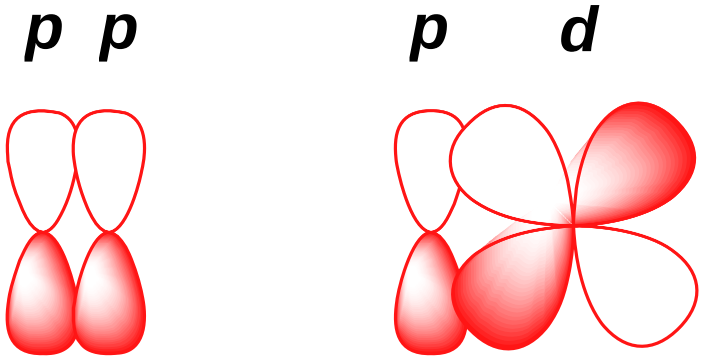
Elektronová hustota lokalizována na spojnici jader

Spojnici jader obvykle značíme jako osu z

Pi vazba, π

Elektronová hustota lokalizována mimo spojnici jader

Jedna uzlová rovina

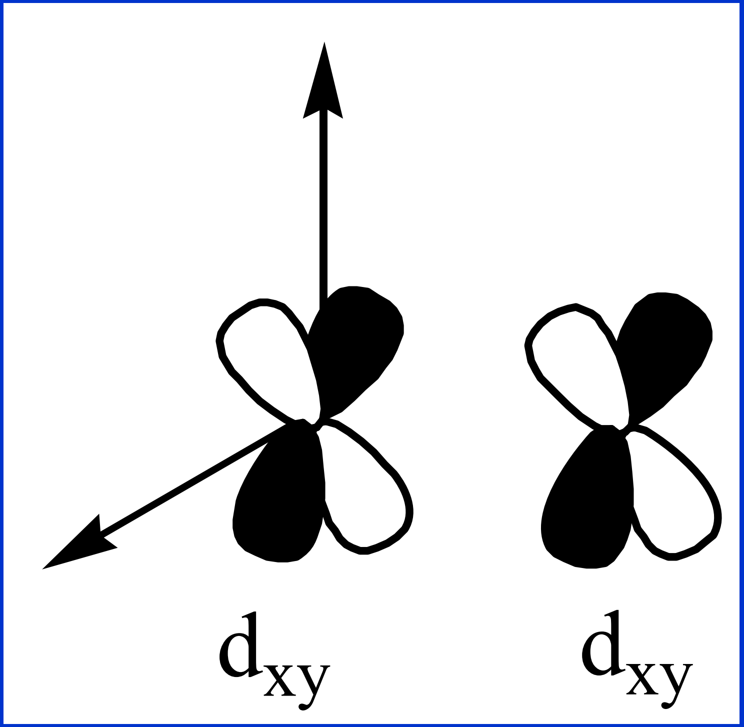


Typy překryvu orbitalů

Delta vazba, δ

Elektronová hustota lokalizována mimo spojnici jader

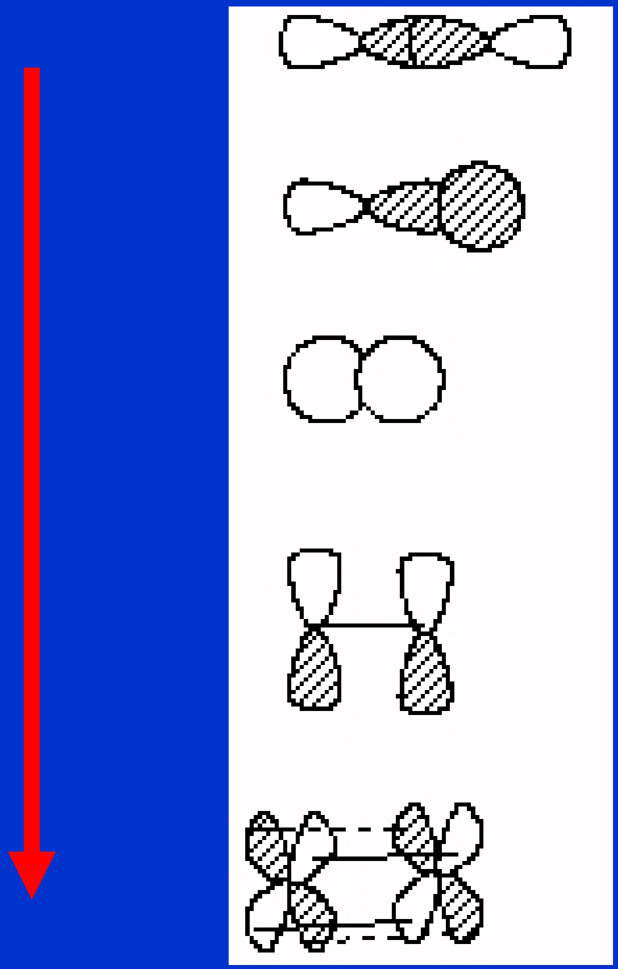
Dvě uzlové roviny



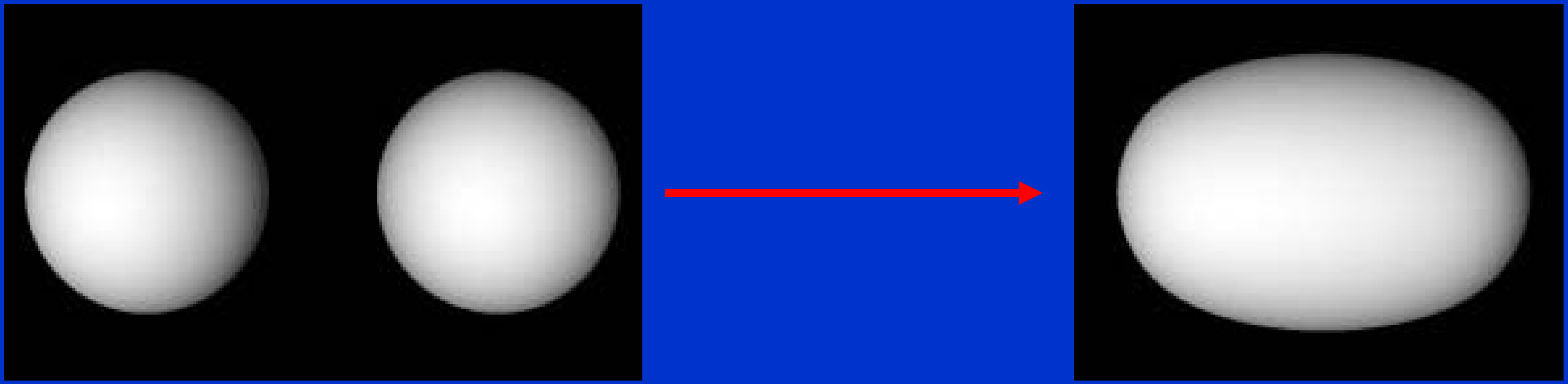
Typy překryvu orbitalů

Překryv klesá

slabší vazba



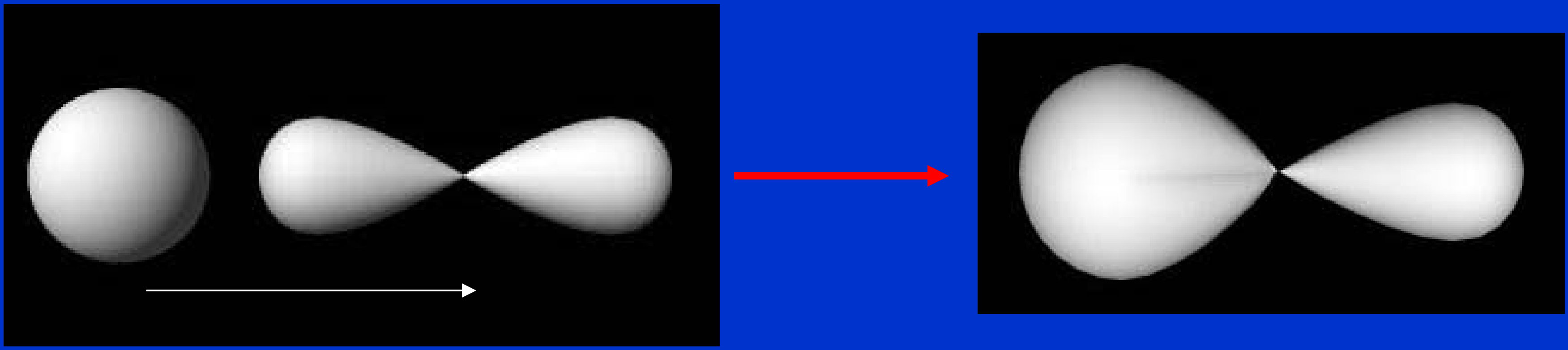
Sigma vazba, σ_{ss}



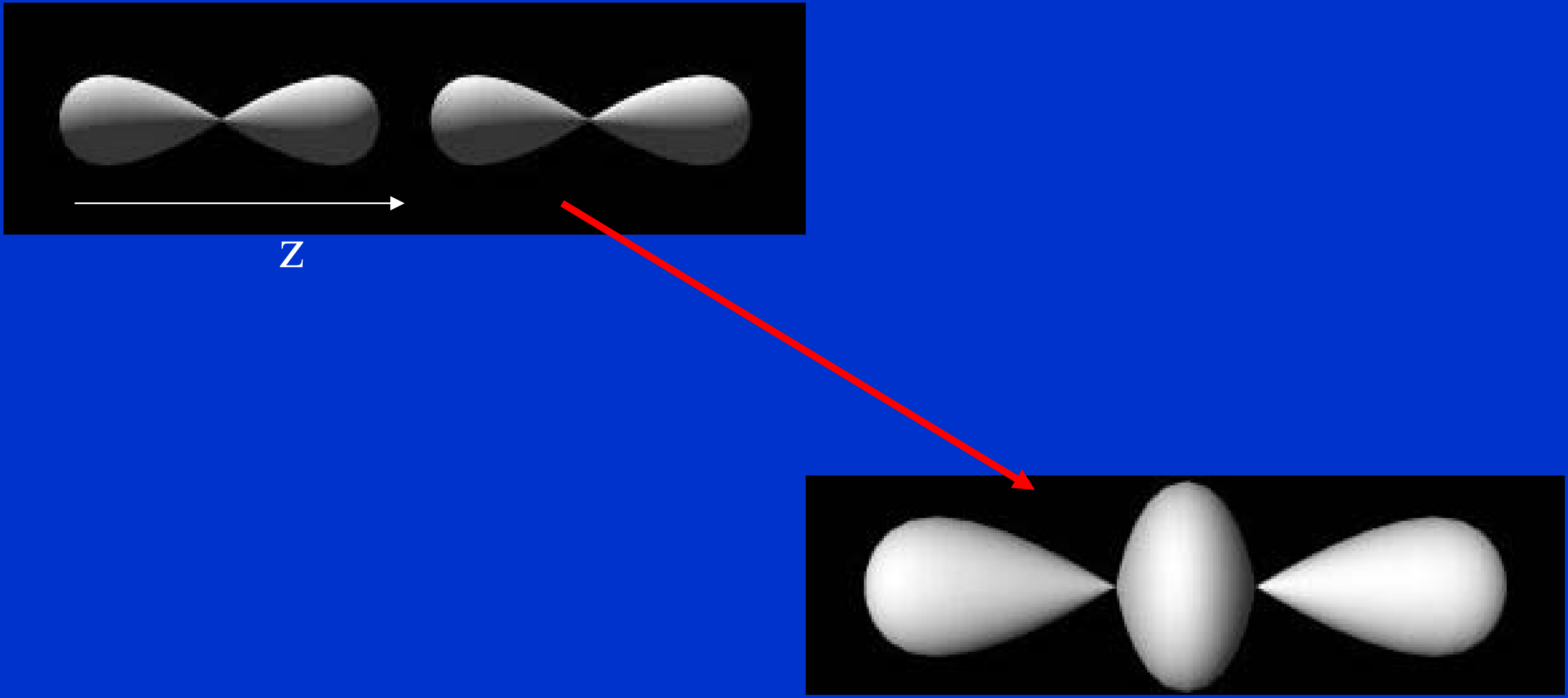
σ_{ss}

Elektronová hustota lokalizována na spojnici jader

Sigma vazba, σ_{sp}



Sigma vazba, σ_{pp}

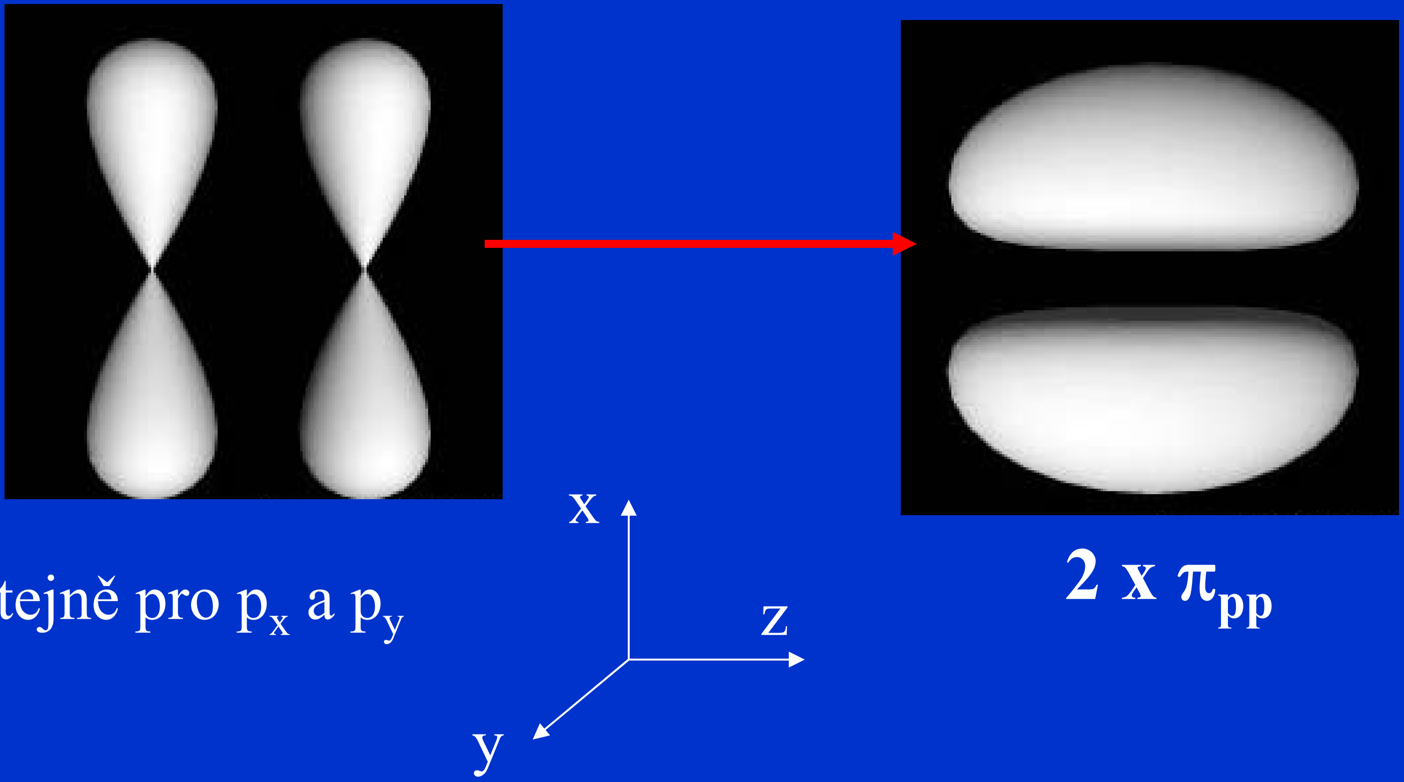


σ_{pp}

Pi vazba, π

Elektronová hustota lokalizována mimo spojnici jader

Jedna uzlová rovina



Stejně pro p_x a p_y

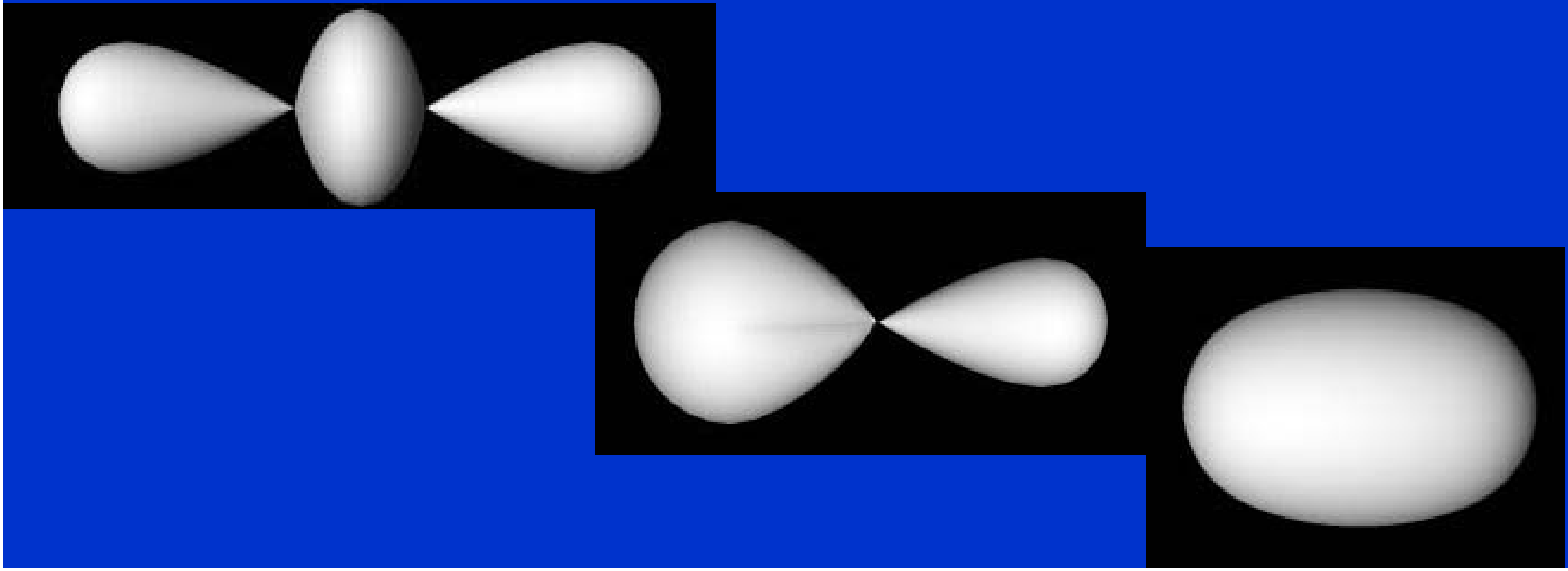
2 x π_{pp}

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	

↓ Polarita vazby roste

		t. tání, °C
Ge-Ge	188	937
Si-Si	226	1412
C-C	347	3827

Vazebné parametry

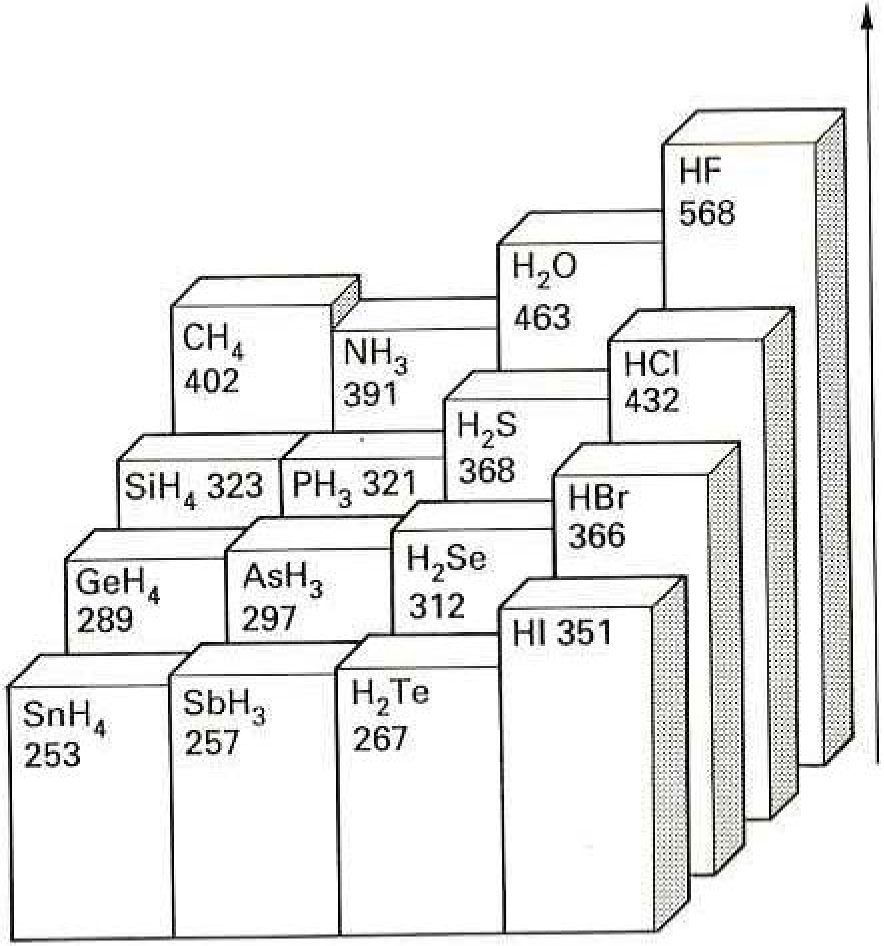
Vazba	**E, kJ mol^{-1}**	**délka, Å**
C-I	240	2.16
C-Br	276	1.91
C-Cl	339	1.79
C-F	485	1.40

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

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

Schomaker-Stevenson

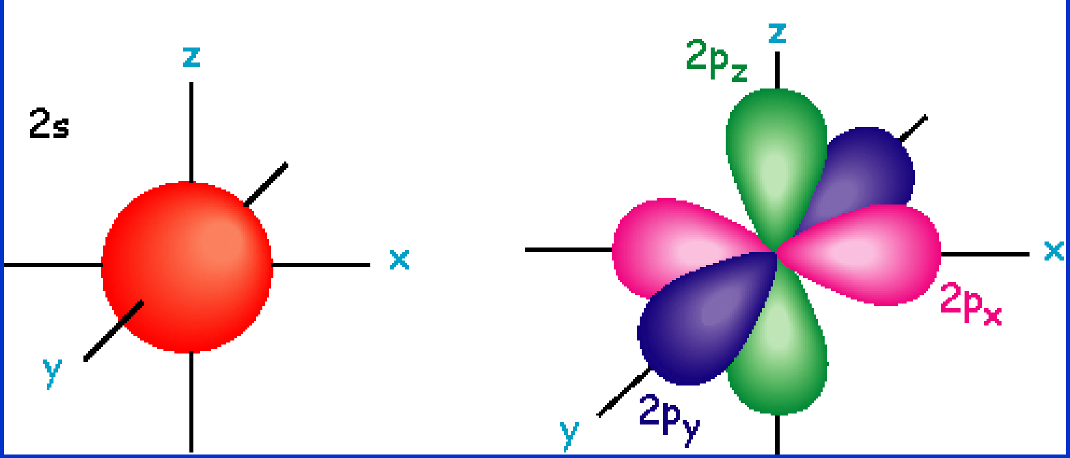
$$r_{AB} = r_A + r_B - 0.09\ |\chi_A - \chi_B|$$



Vazebná energie

kJ mol^{-1}

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

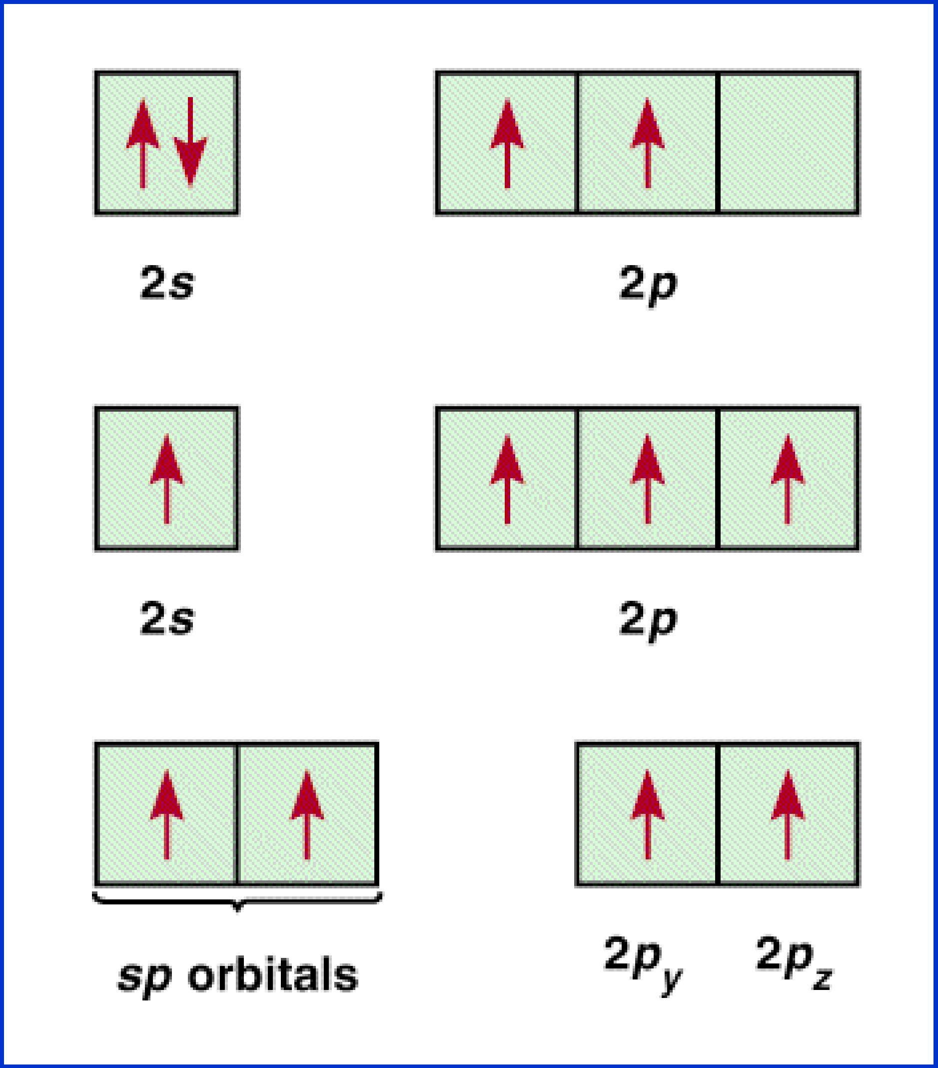
Počet hybridních orbitalů = počet smísených atomových orbitalů

Hybridizace sp

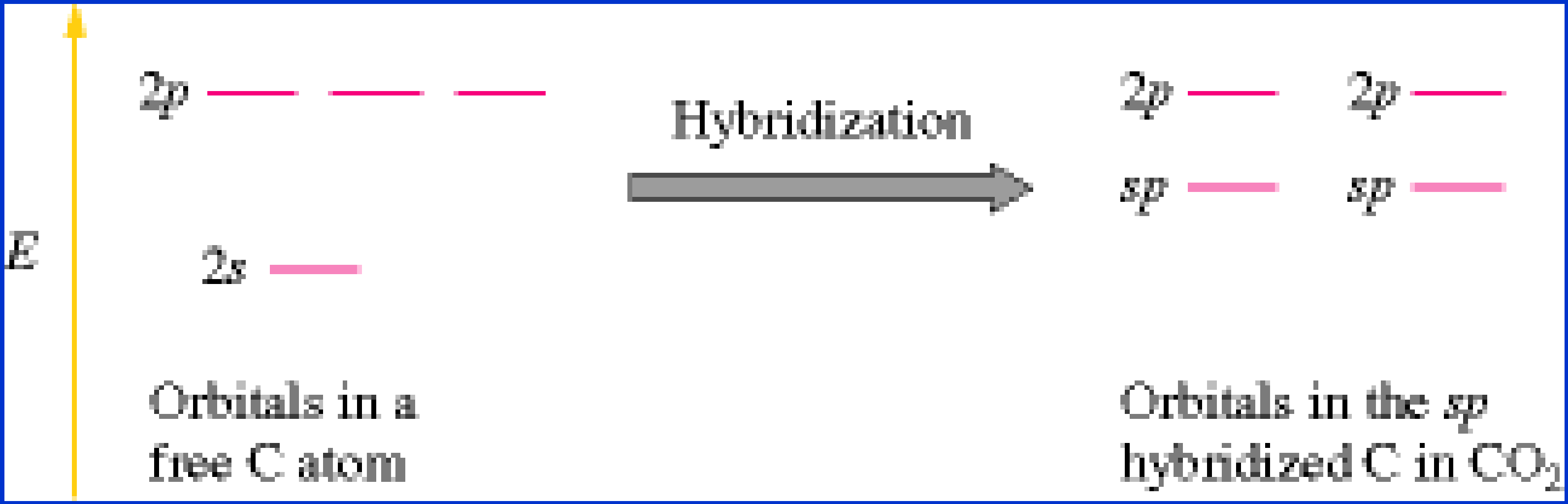
Základní stav

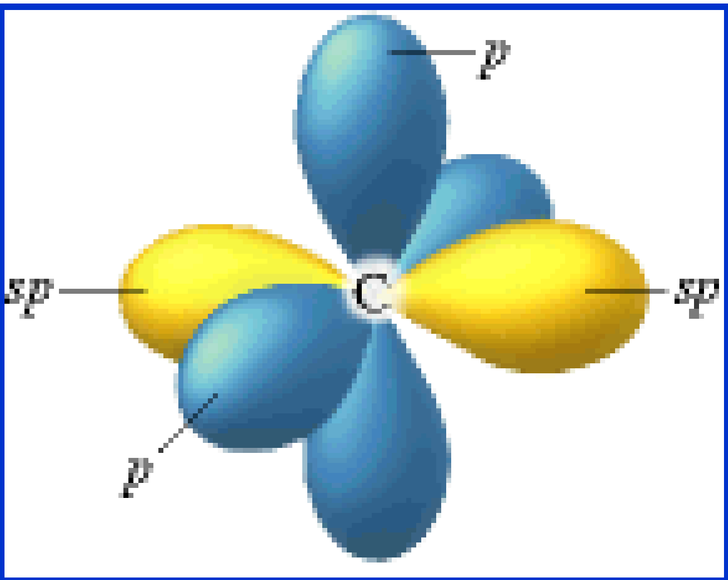
Excitovaný stav

Hybridizovaný stav

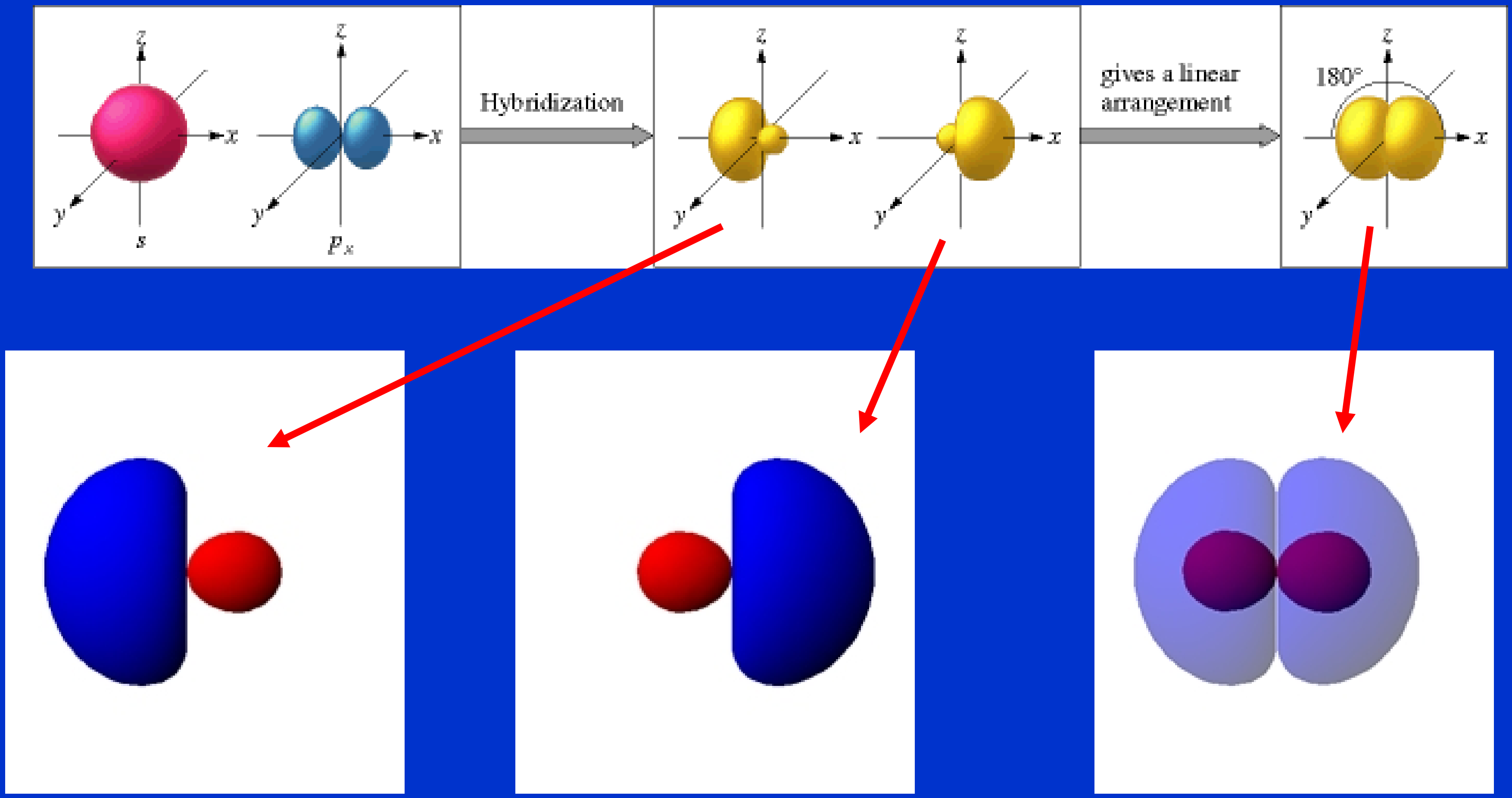


Hybridizace sp

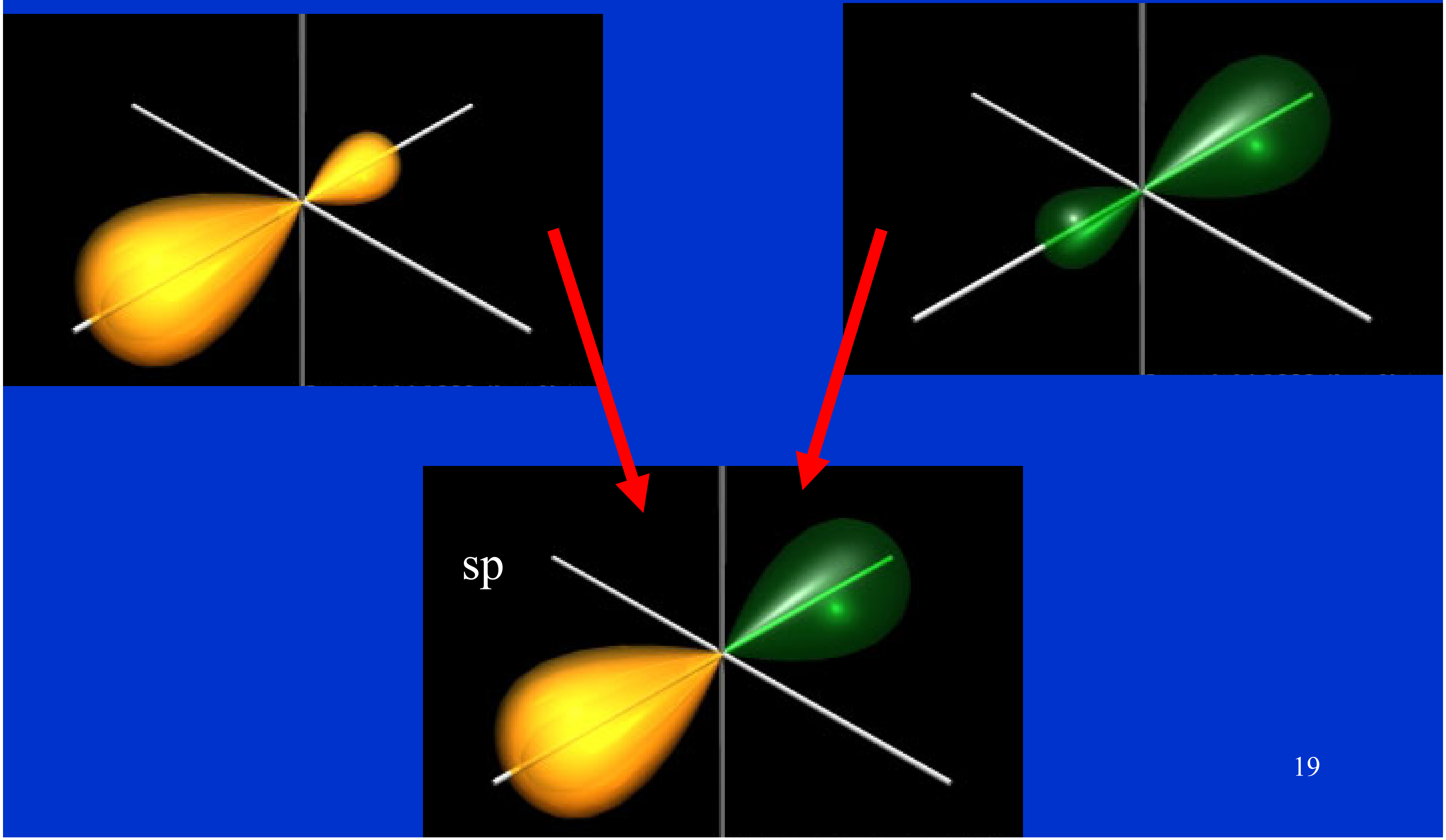




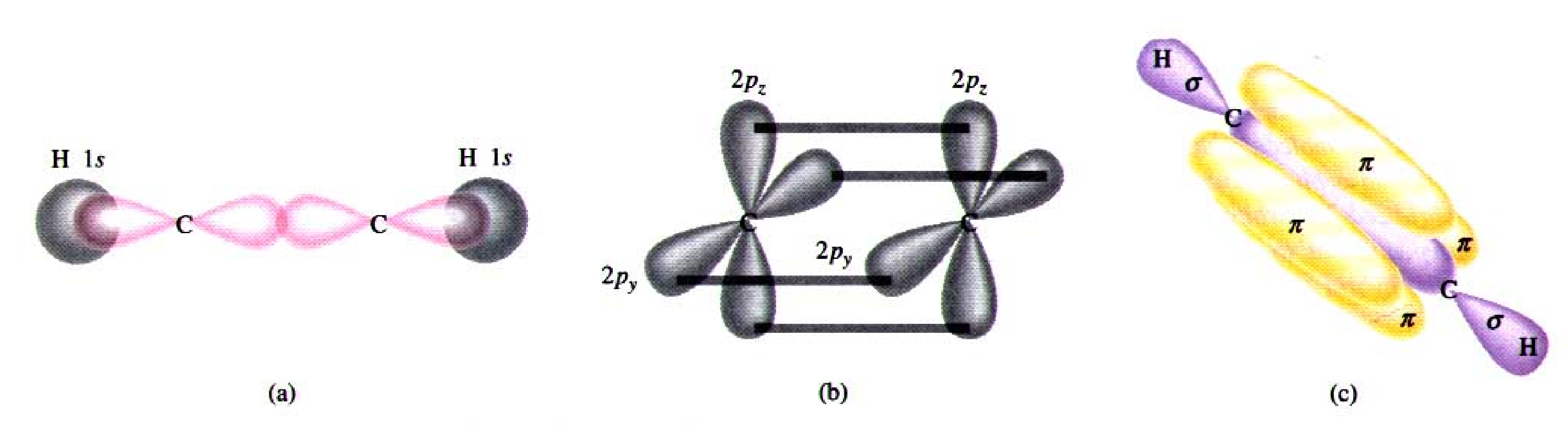
Hybridizace sp



Hybridizace sp

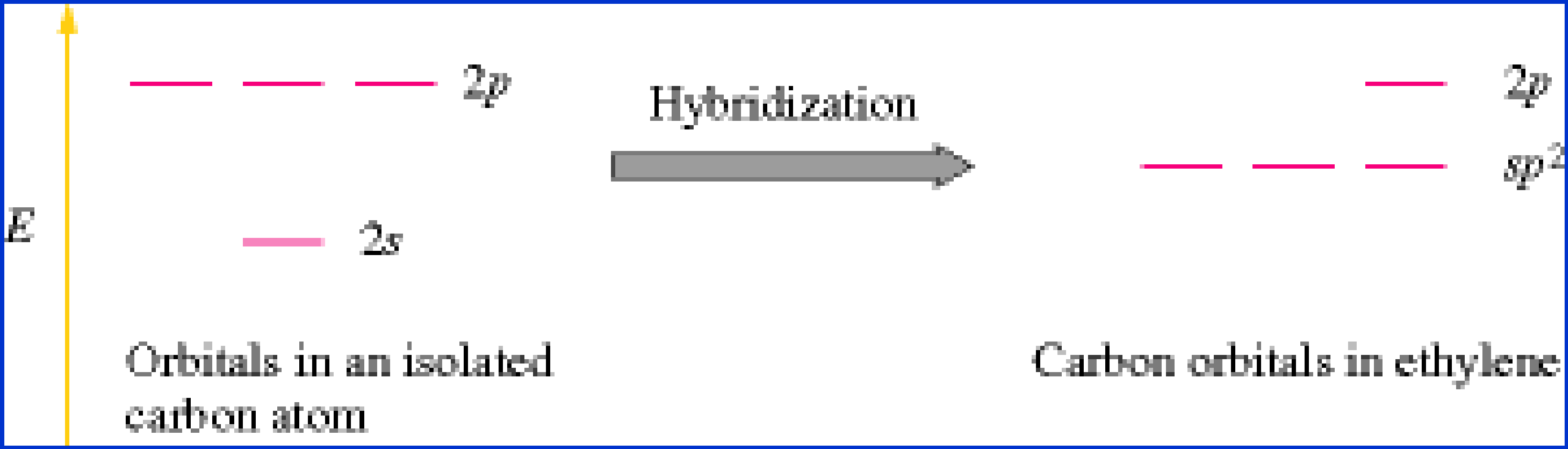


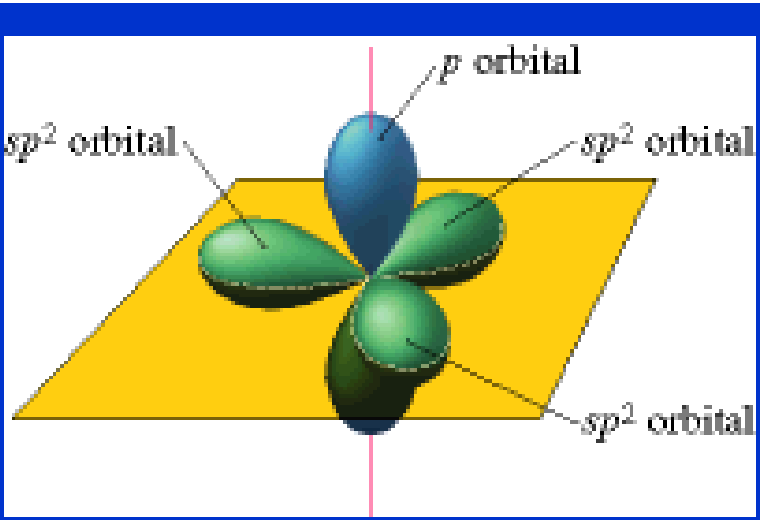
Acetylen



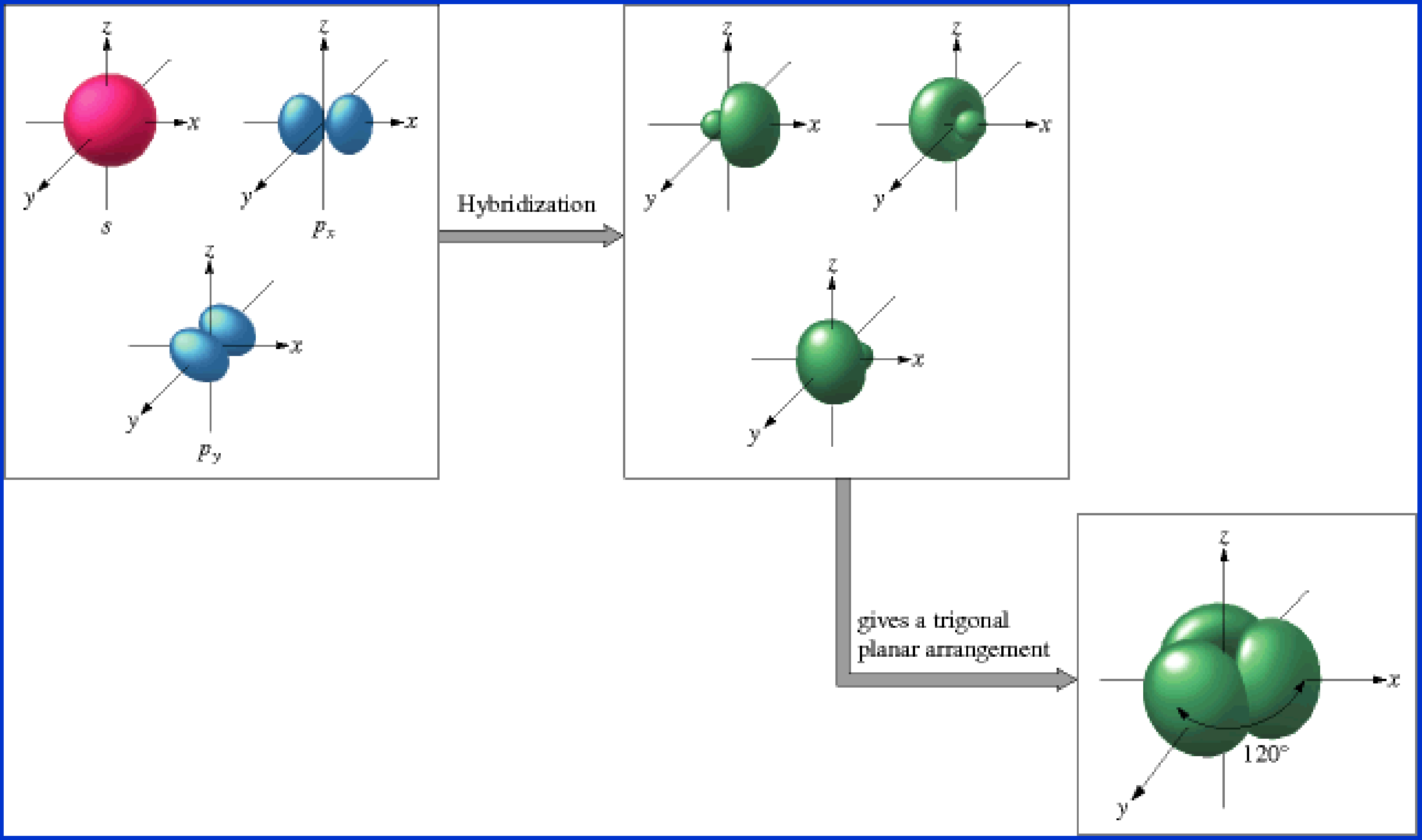
- 2 σ vazby překryvem C(sp)–H(s)
- 1 σ vazba překryvem C(sp)–C(sp)
- 2 navzájem kolmé π-vazby (x, y) překryvem C(p)–C(p)

Hybridizace sp^2

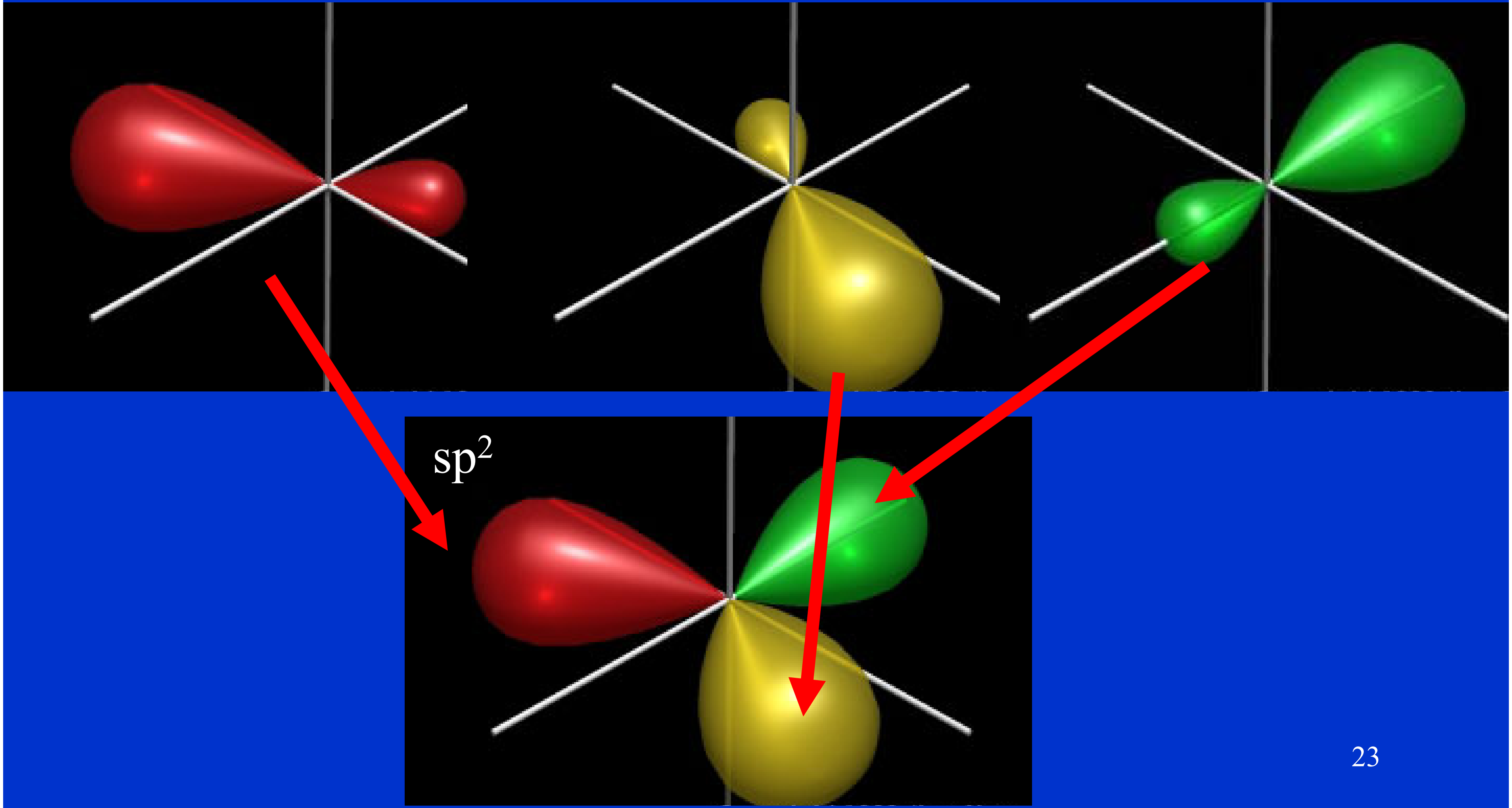




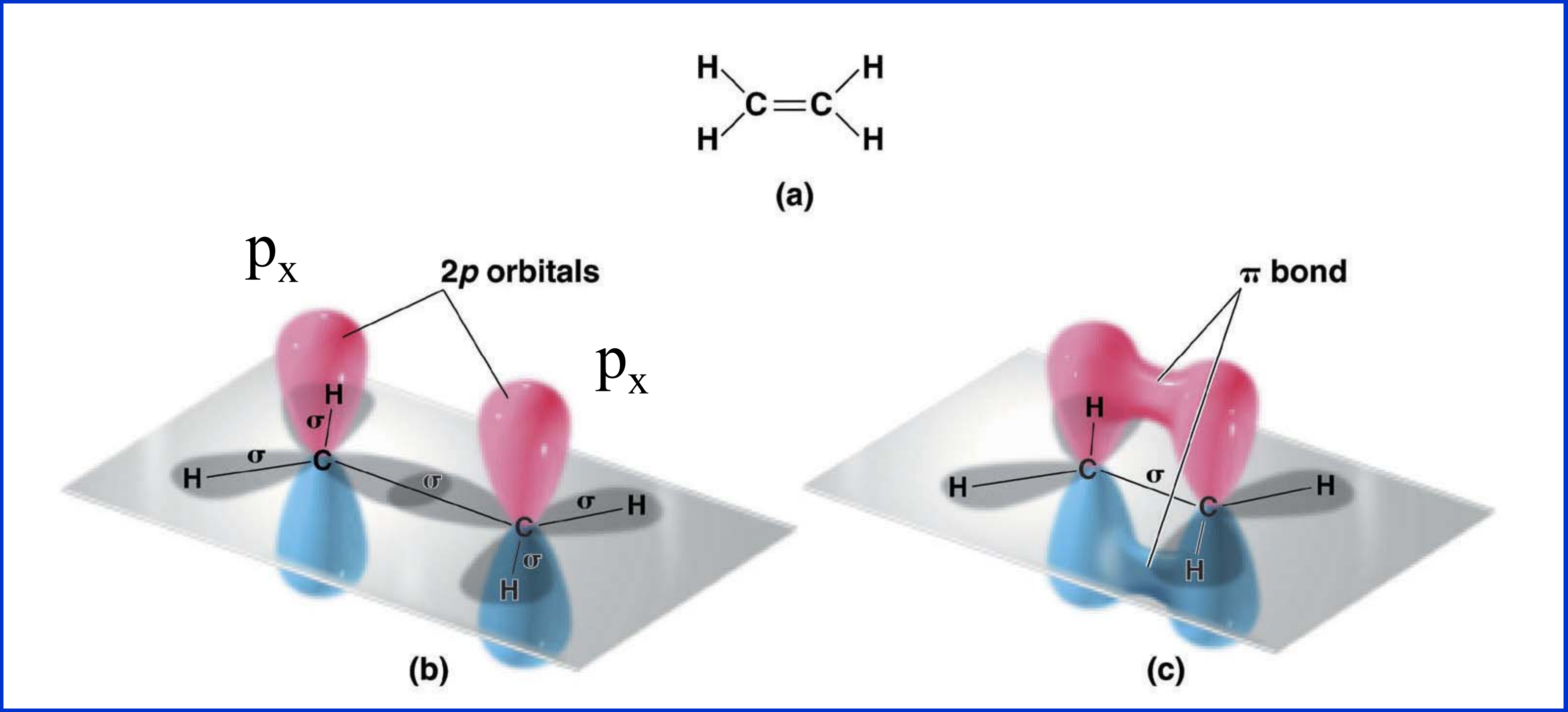
Hybridizace sp^2



Hybridizace sp^2

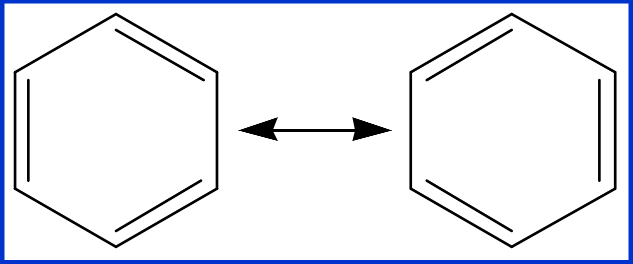


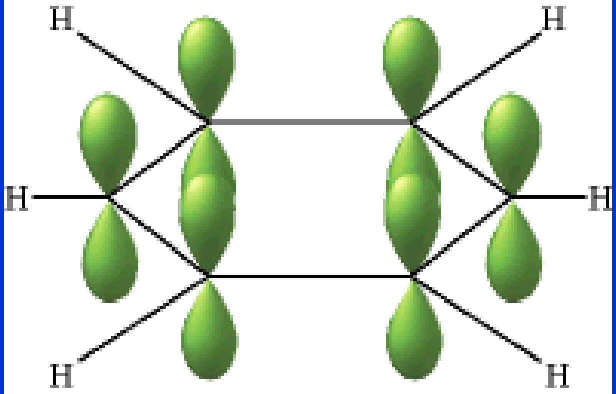
Ethylen

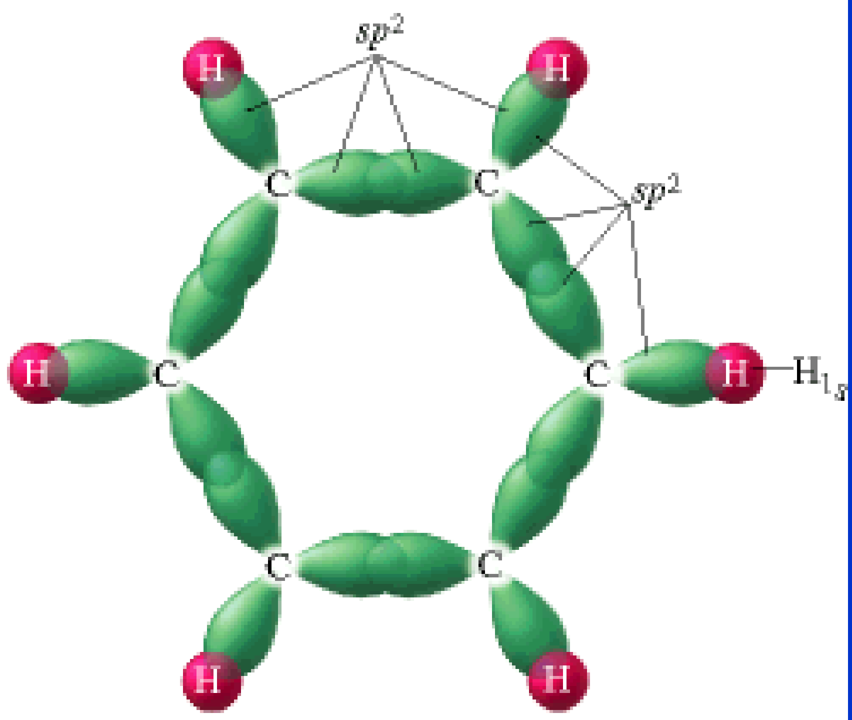


- 4 σ vazby překryvem C(sp^2)–H(s)
- 1 σ vazba překryvem C(sp^2)–C(sp^2)
- 1 π-vazba překryvem C(p_x)–C(p_x)

Benzen





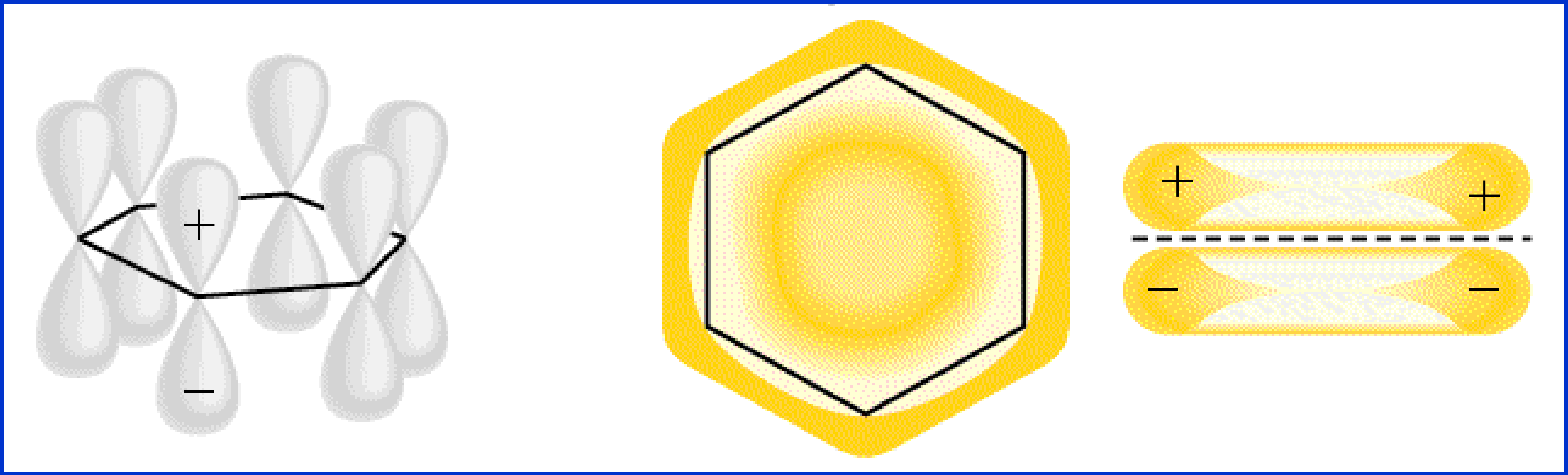


- Každý C použije 3 sp^2 orbitaly pro 3 σ-vazby

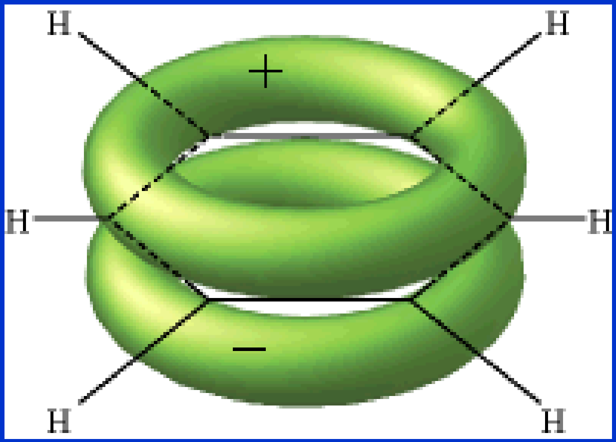
2 C – C vazby a 1 C – H vazba

- 1 $2p_x$ orbital na každém C zůstane nepoužitý (pro σ-vazby)

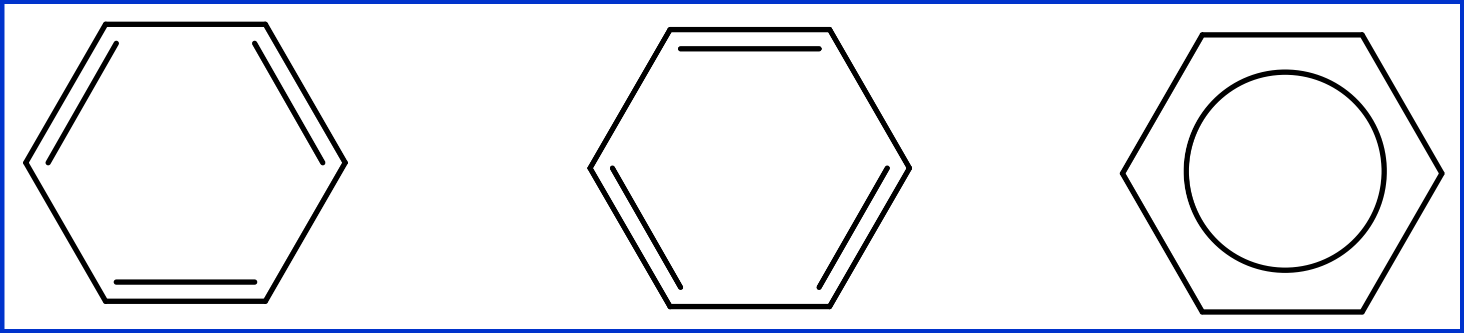
Benzen

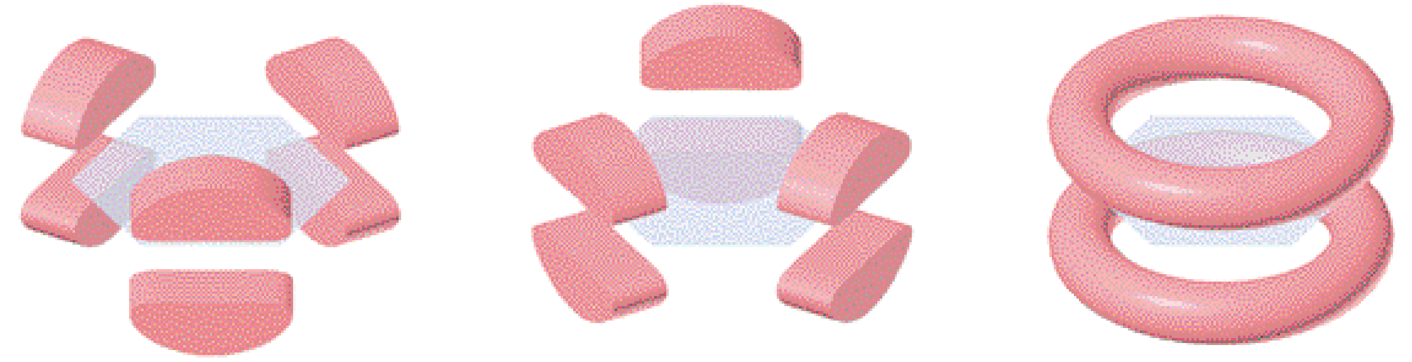


6 C $2p_x$ orbitalů použito pro 3 π-vazby



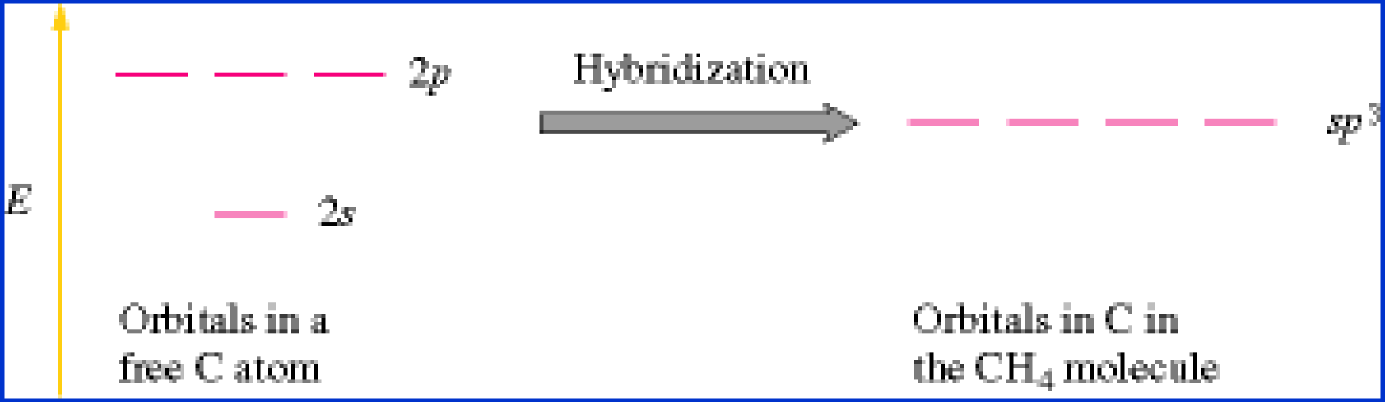
Benzen

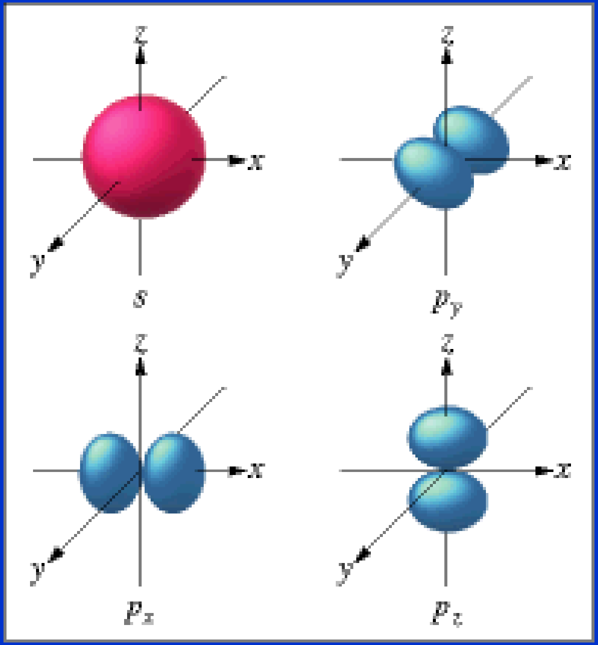


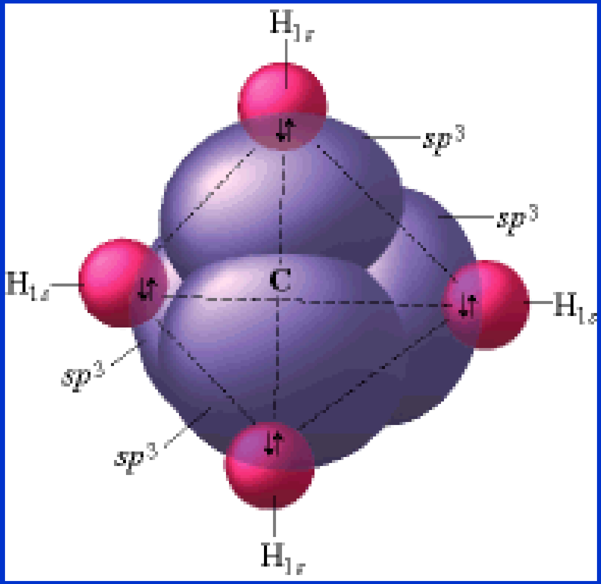


(a) Localized π bonds (b) Localized π bonds (c) Delocalized π bonds

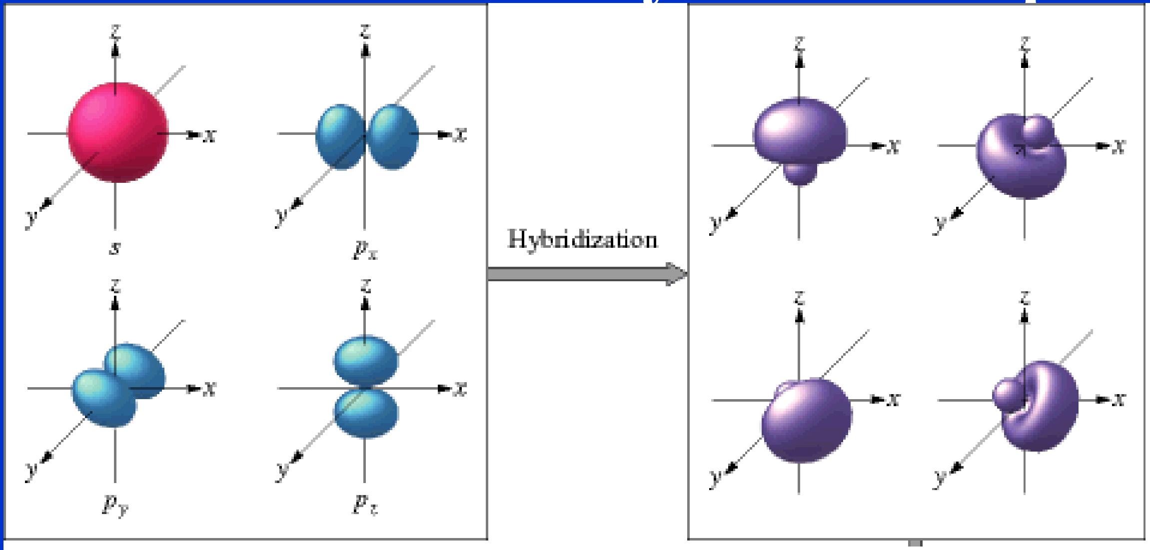
Hybridizace sp^3

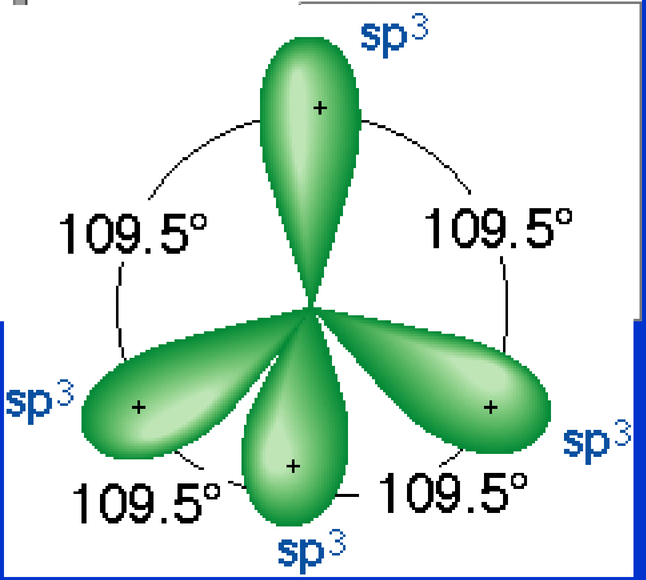




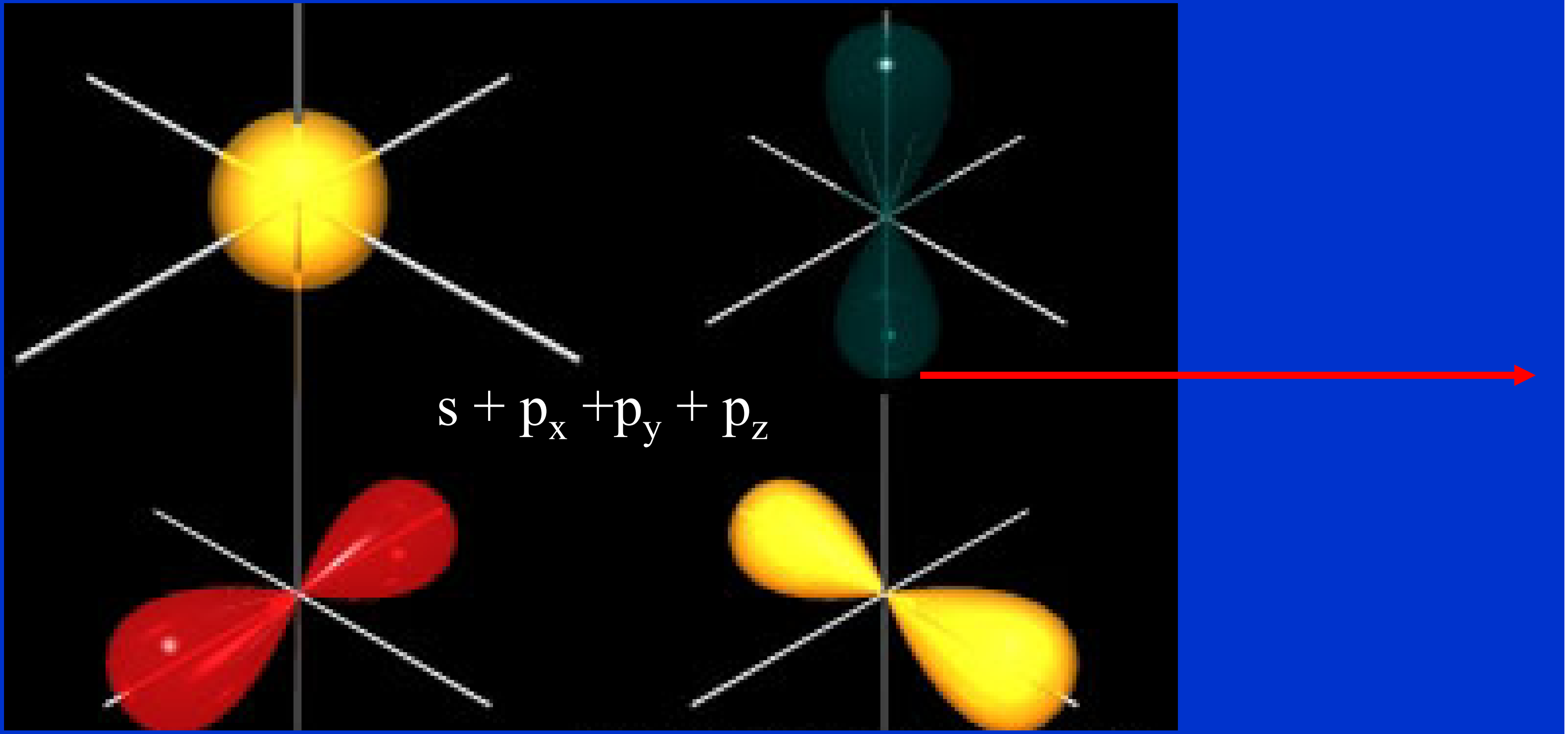


Hybridizace sp^3

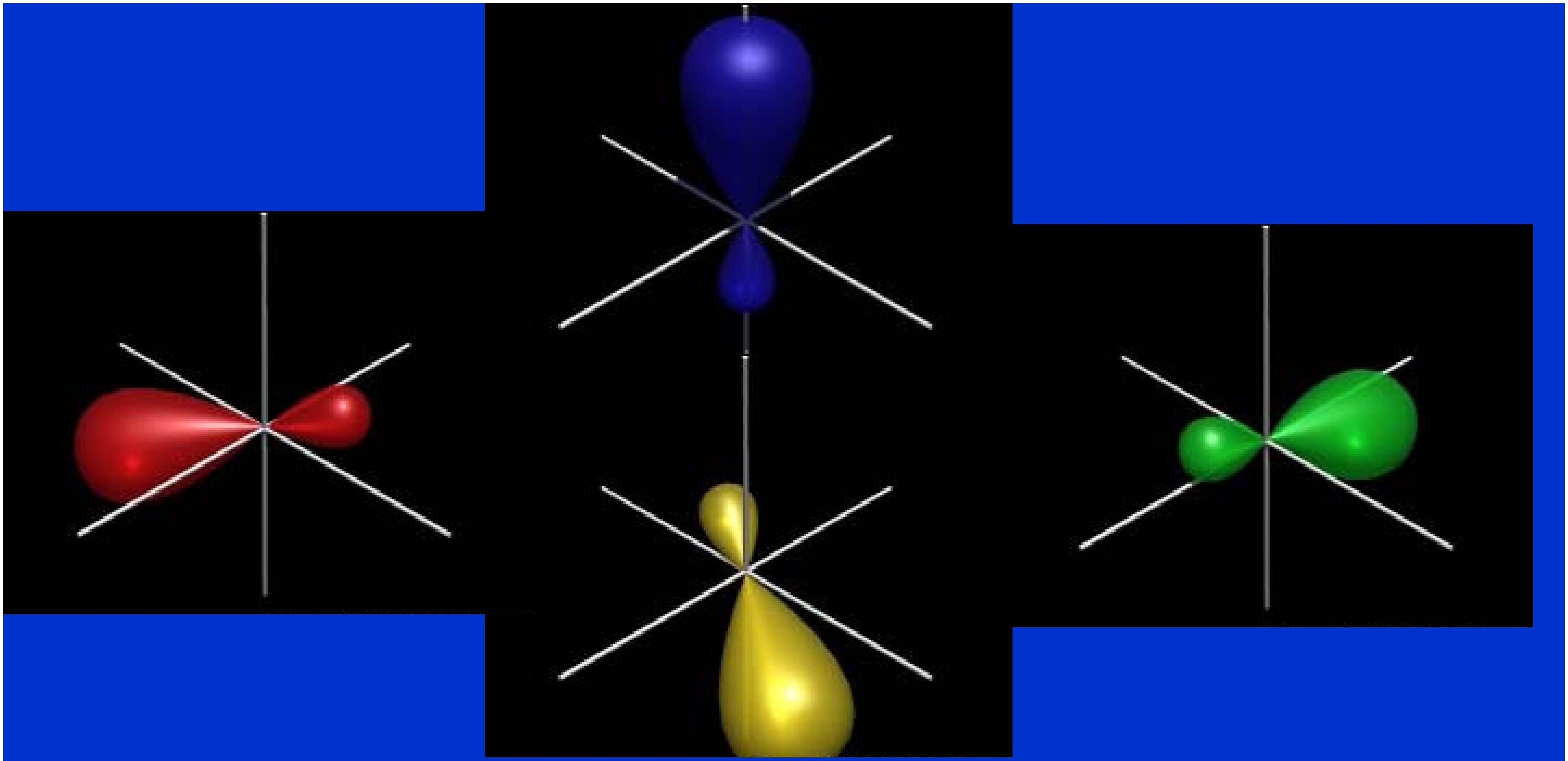


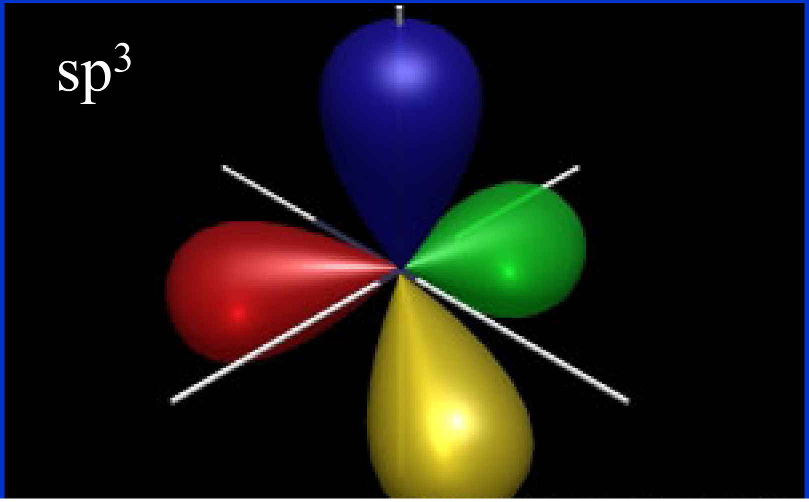


Hybridizace sp^3



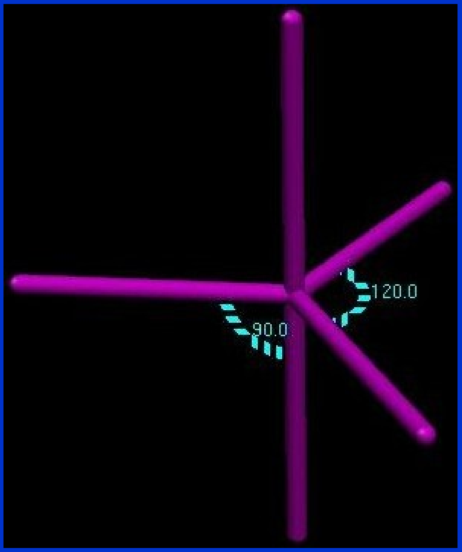
$s + p_x + p_y + p_z$



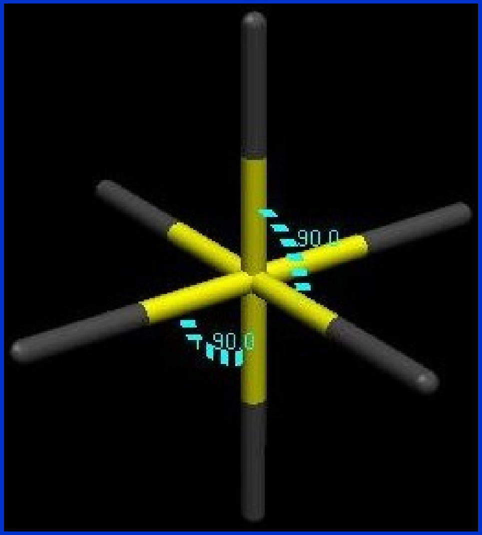

sp^3

Hybridizace

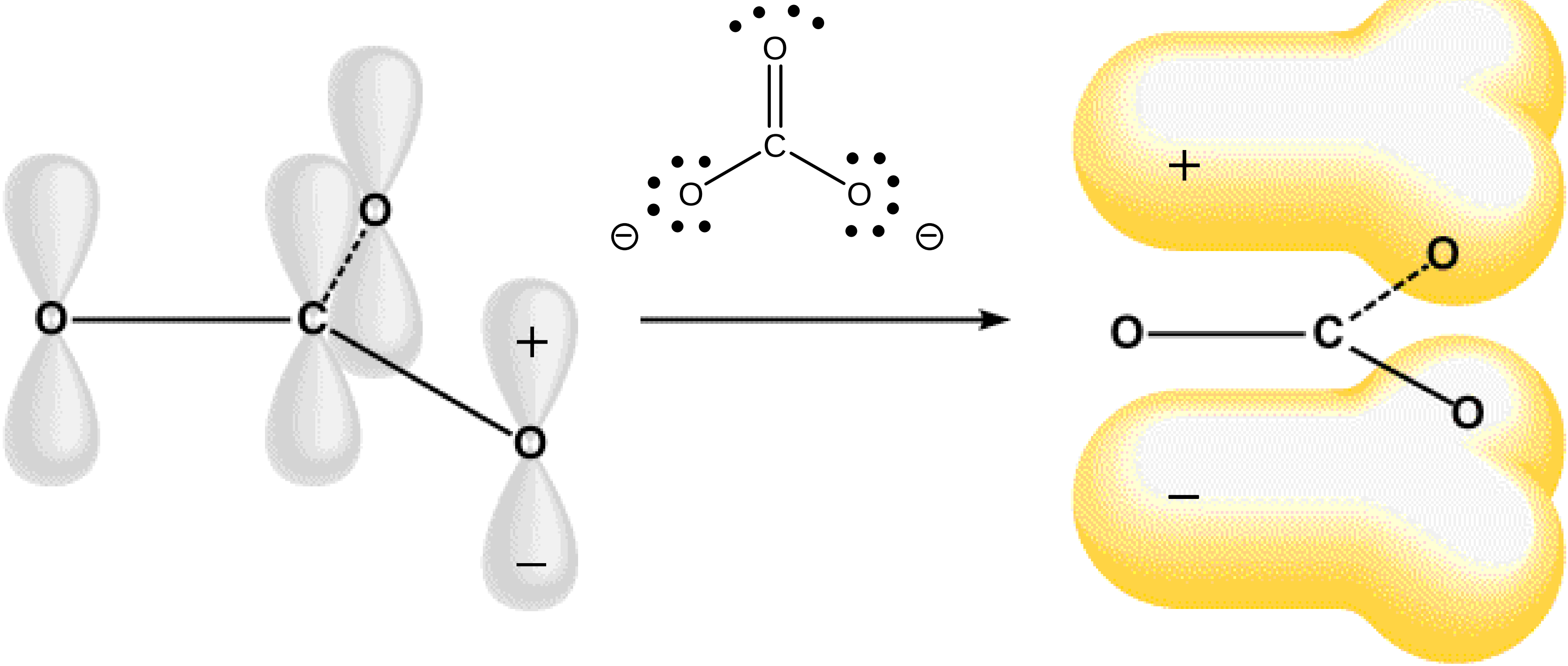
sp^{3}d



sp^{3}d^2



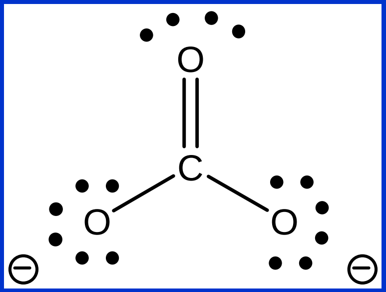
Vazba v CO_3^{2-} a NO_3^-



3 σ vazby překryvem C(sp^2)–O(sp^2)

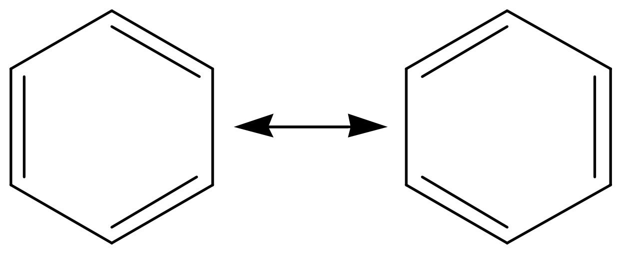
1 π-vazba překryvem C(p_x)–O(p_x)

Řád vazby



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

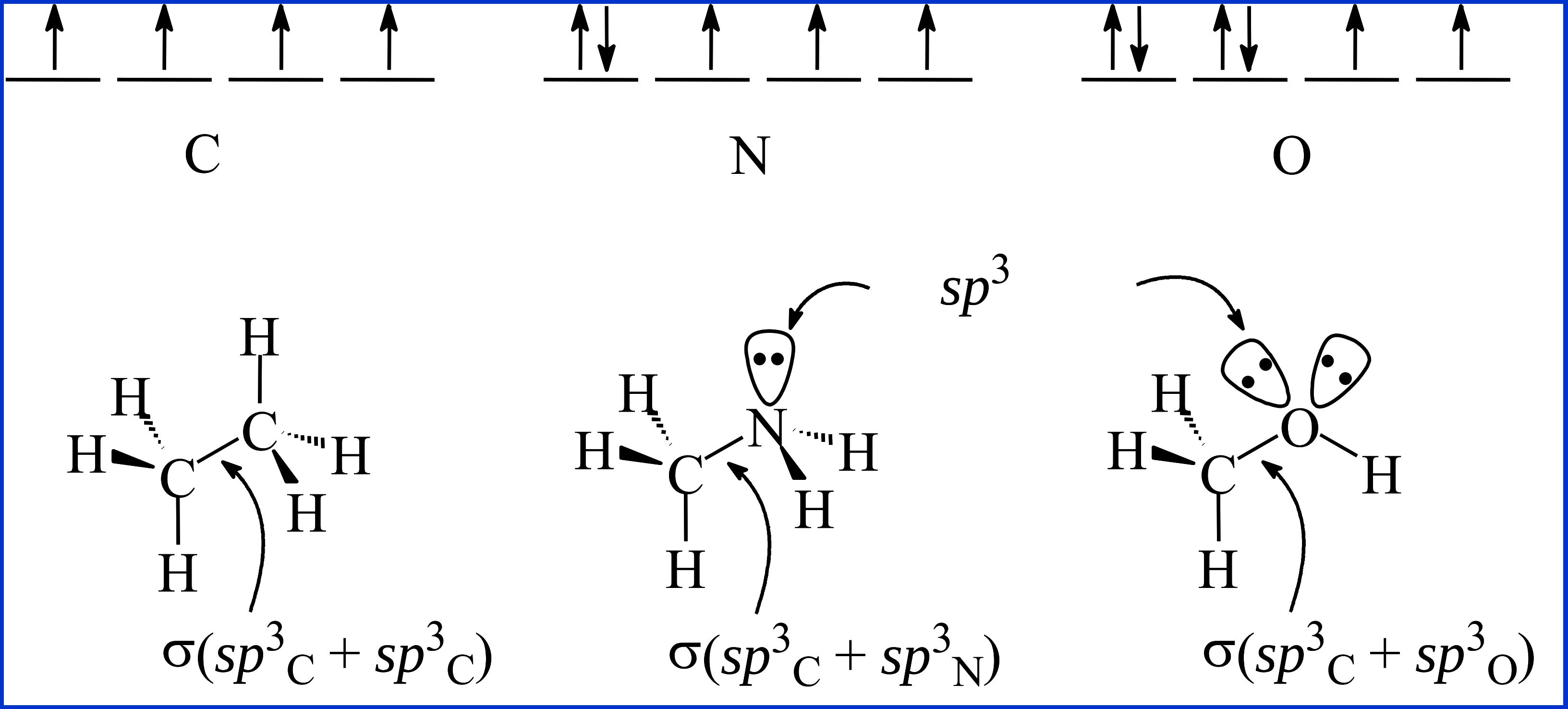
Řád vazby = 1.3333



8 (2+3) vazebných elektronových párů / 6 vazeb

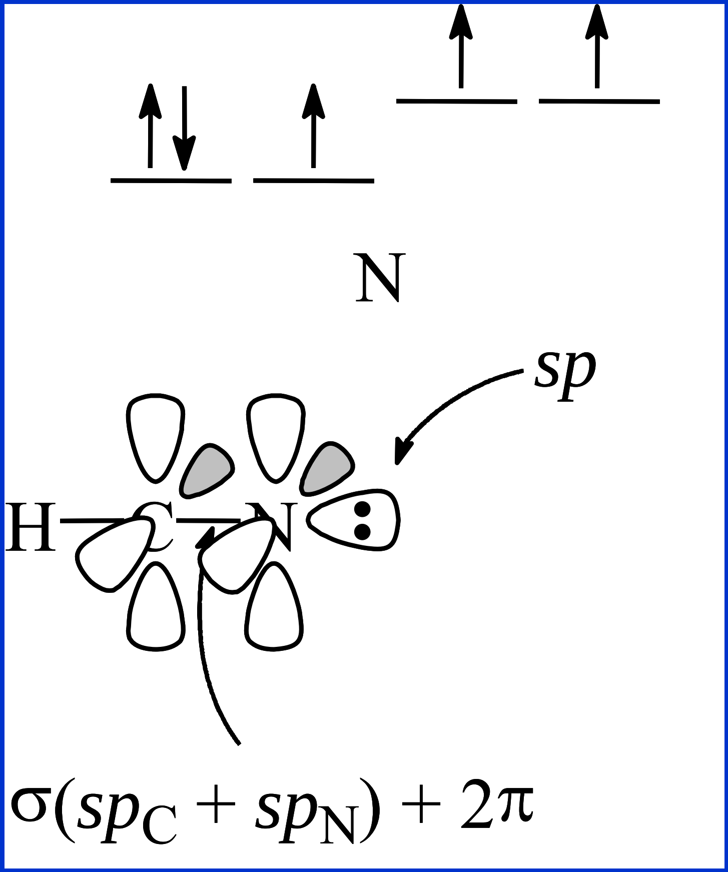
Řád vazby = 1.5

Vazba v C_2H_6, CH_3NH_2 a CH_3OH



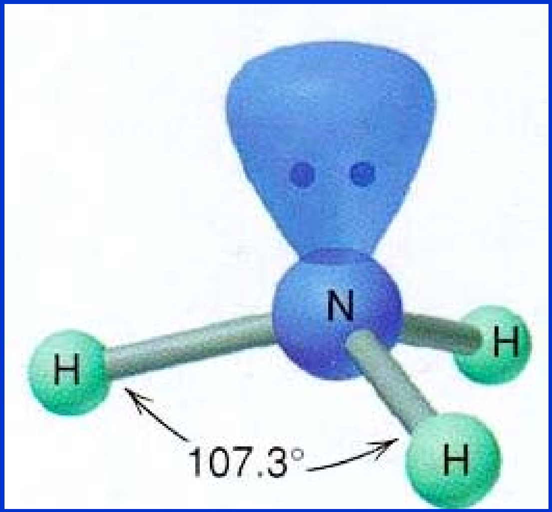
$\sigma(sp^3_C + sp^3_C)$ $\sigma(sp^3_C + sp^3_N)$ $\sigma(sp^3_C + sp^3_O)$

Vazba v HC≡N



$\sigma(sp_C + sp_N) + 2\pi$

Elektronegativita a vazebné úhly

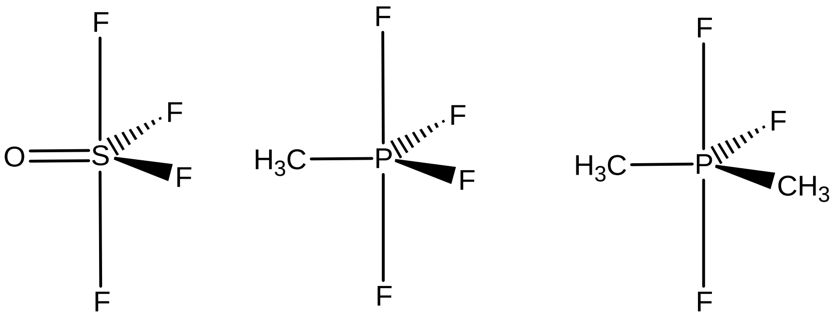


	Vazebný úhel	Hybridizace
NH_3	107.3°	sp^3
PH_3	93.8°	↓
AsH_3	91.8°	
SbH_3	91.3°	s + 3p
NF_3	102.5°	
OH_2	104.5°	
OF_2	103.2°	

Rostoucí Δχ 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.

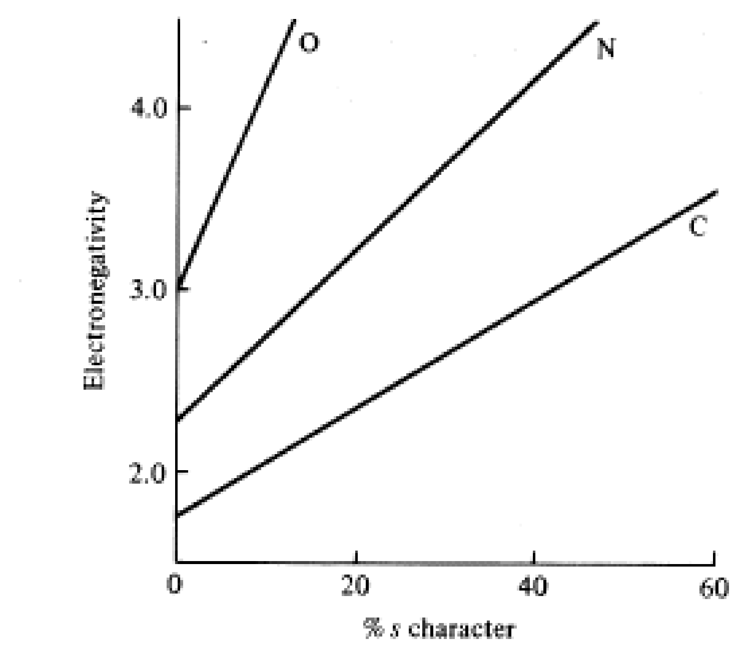


Lepší donory obsazují ekvatoriální rovinu v TBP a bazální rovinu v SP.

Volný elektronový pár je nejlepší donor = substituent s nulovou elektronegativitou

Hybridizace a elektronegativita

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



s-charakter

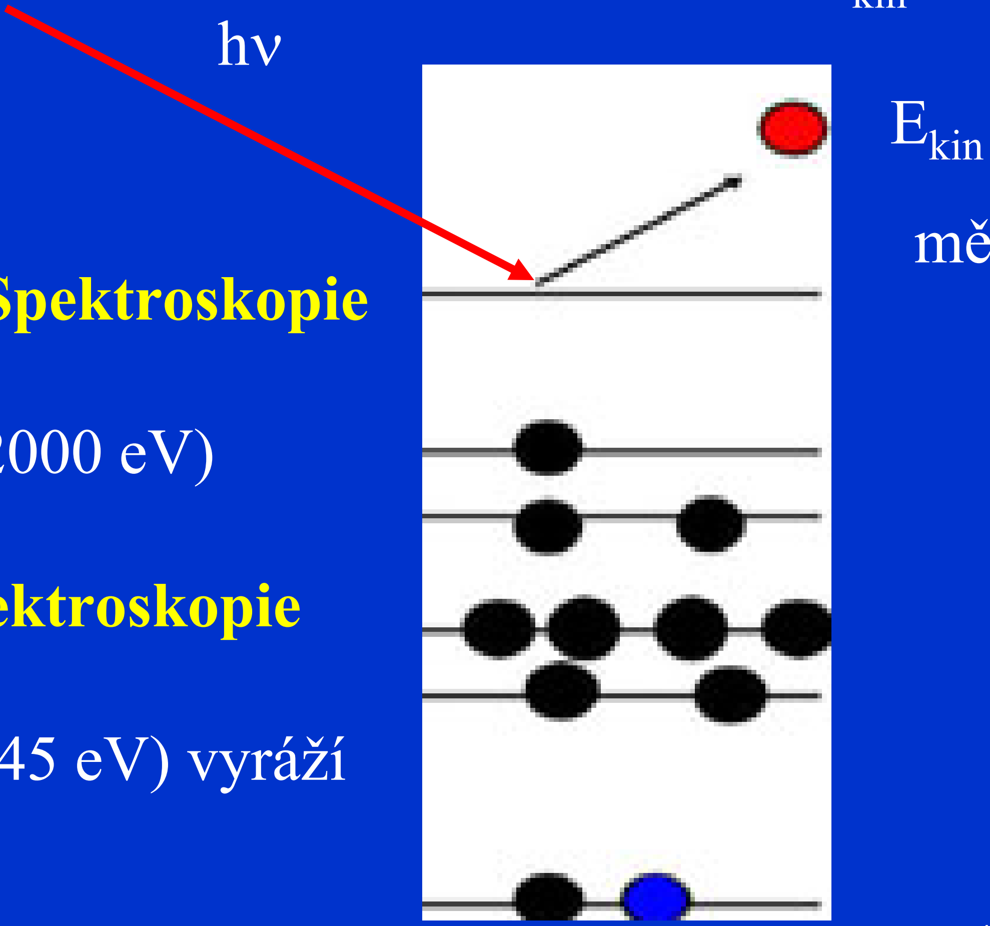
p-charakter

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

Orbital s vyšším s-charakterem má vyšší elektronegativitu

PES = Fotoelektronová spektroskopie

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

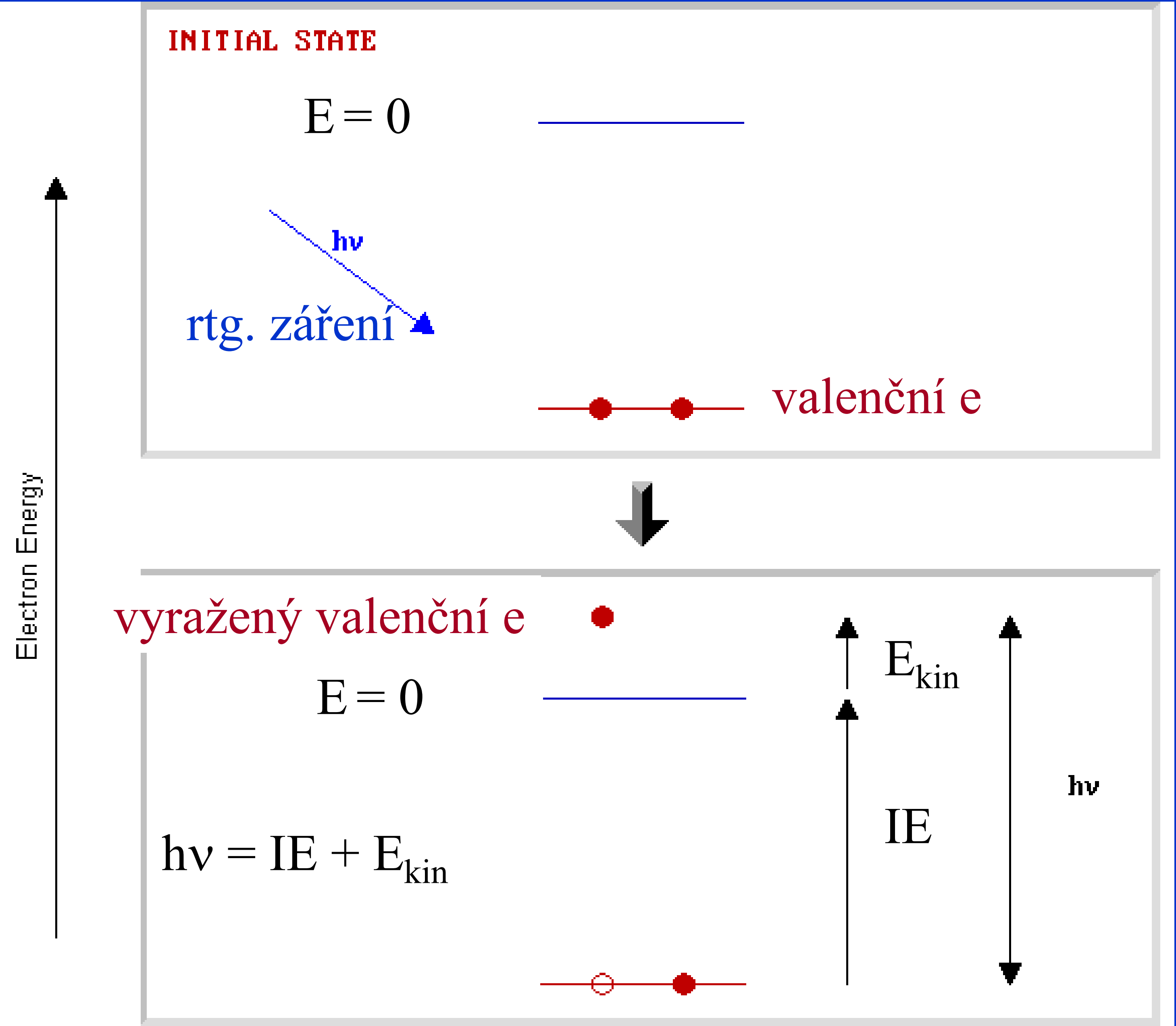


X-ray Fotoelektronová Spektroskopie (XPS)

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

UV Fotoelektronová Spektroskopie (UPS)

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



INITIAL STATE

E = 0

hν

rtg. záření

valenční e

Electron Energy

vyražený valenční e

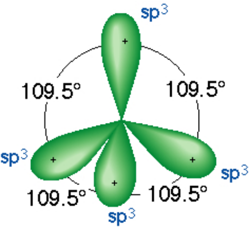
E = 0

E_{kin}

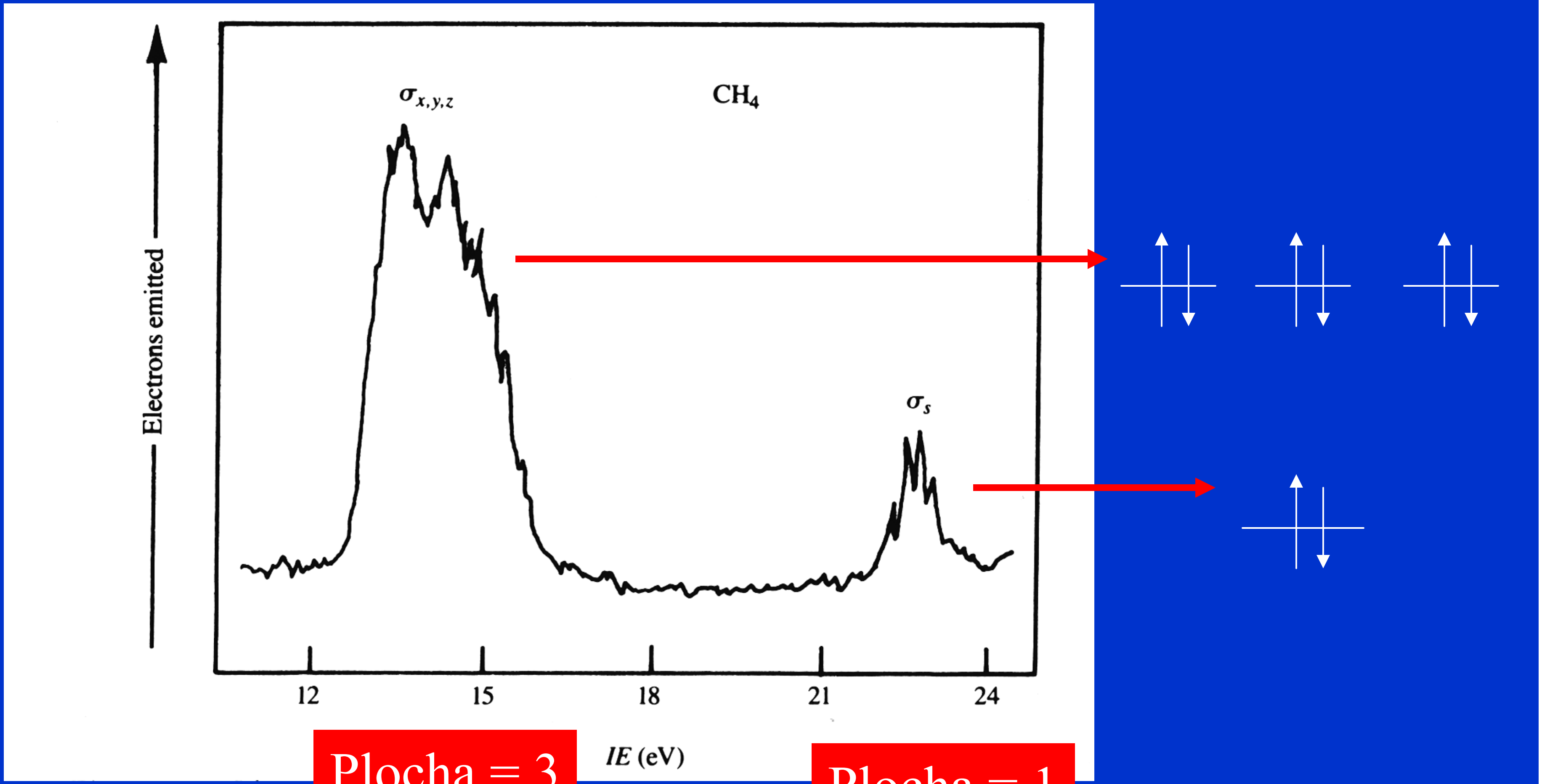
IE

hν

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



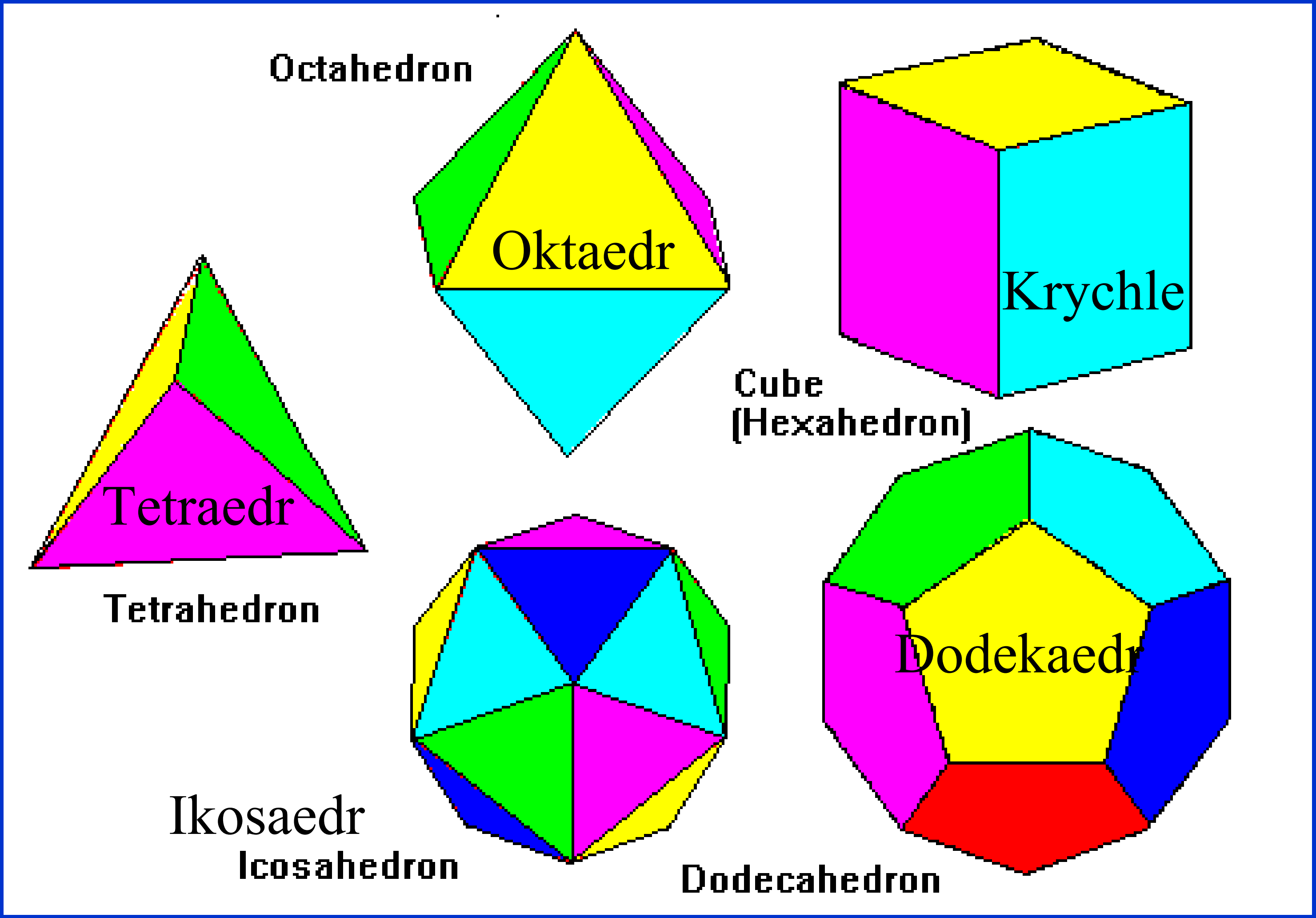
PES methanu nesouhlasí s modelem 4 sp^3



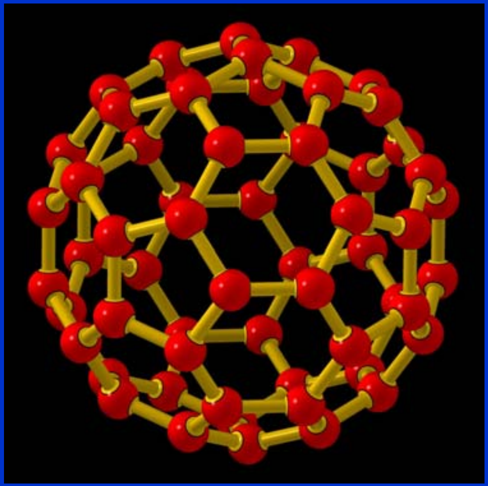
Plocha = 3

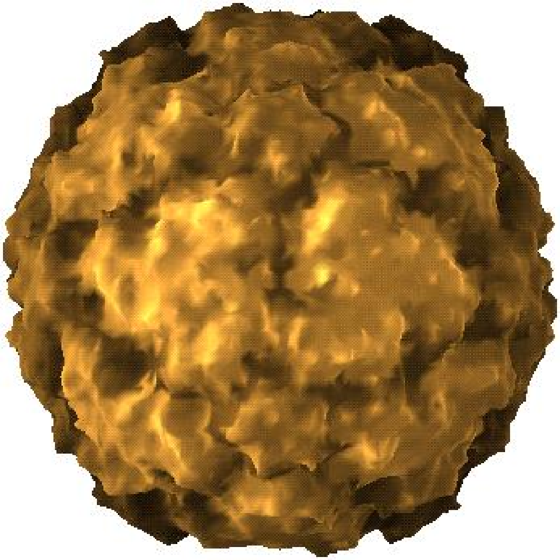
Plocha = 1

Symetrie – Platonovská tělesa

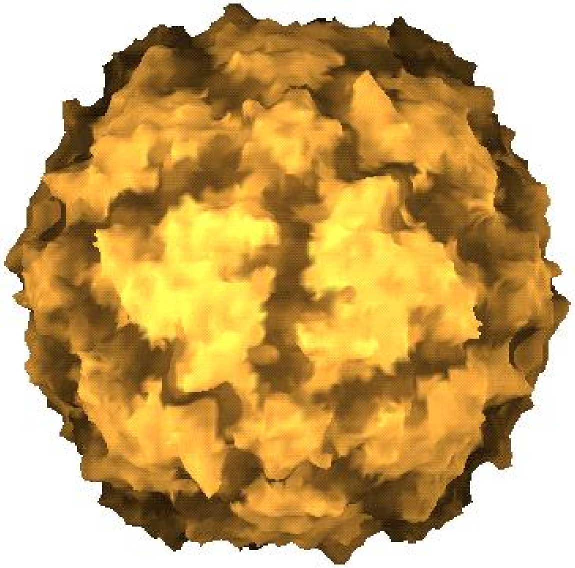


Symetrie

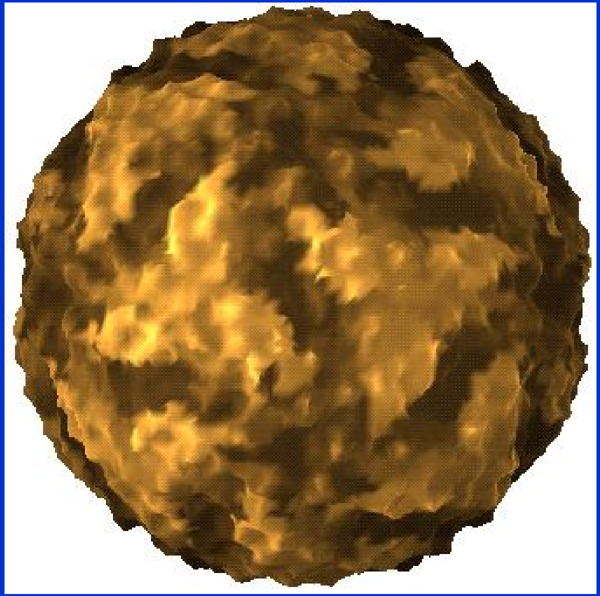




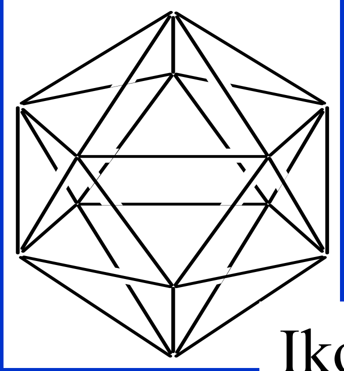
Virus rýmy



Virus obrny



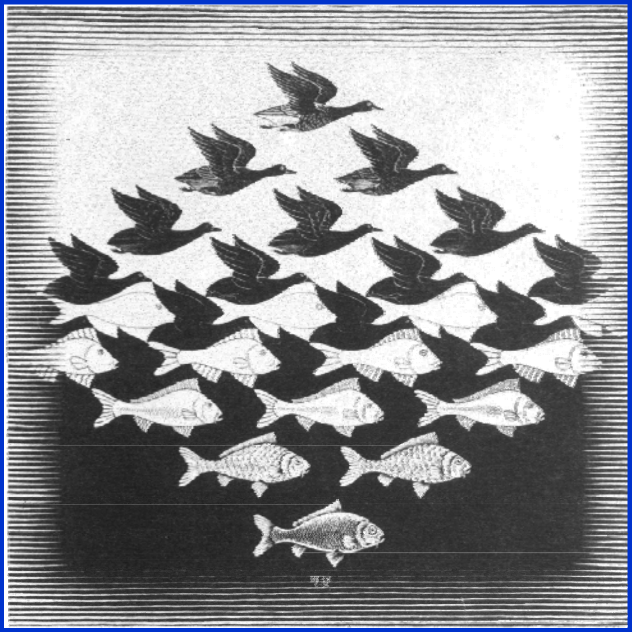
Virus slintavky a kulhavky

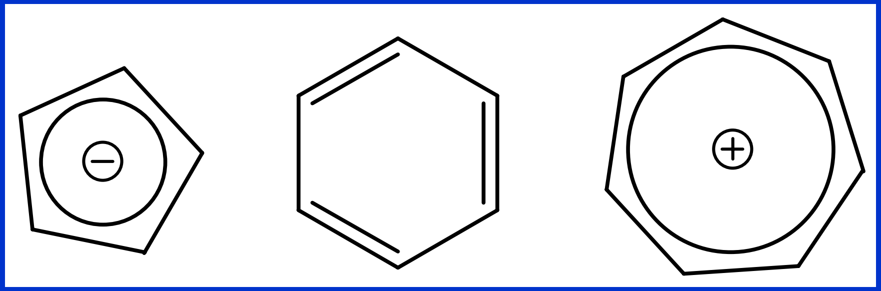


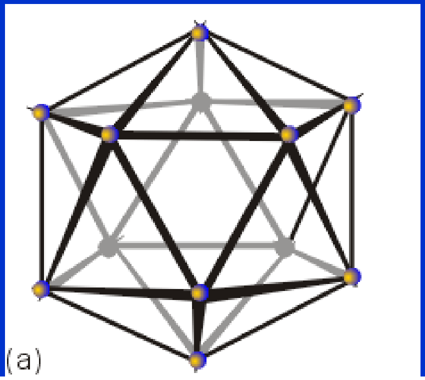
Ikosaedr

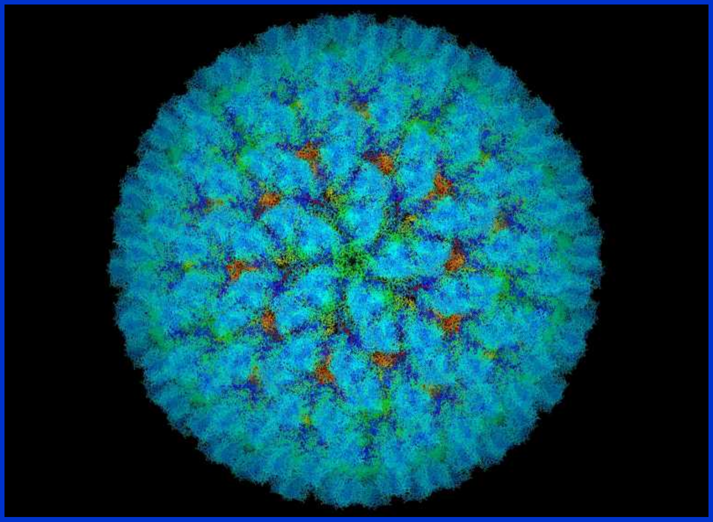
Symetrie molekul

Jak jsou atomy v molekule uspořádány = ekvivalentní atomy





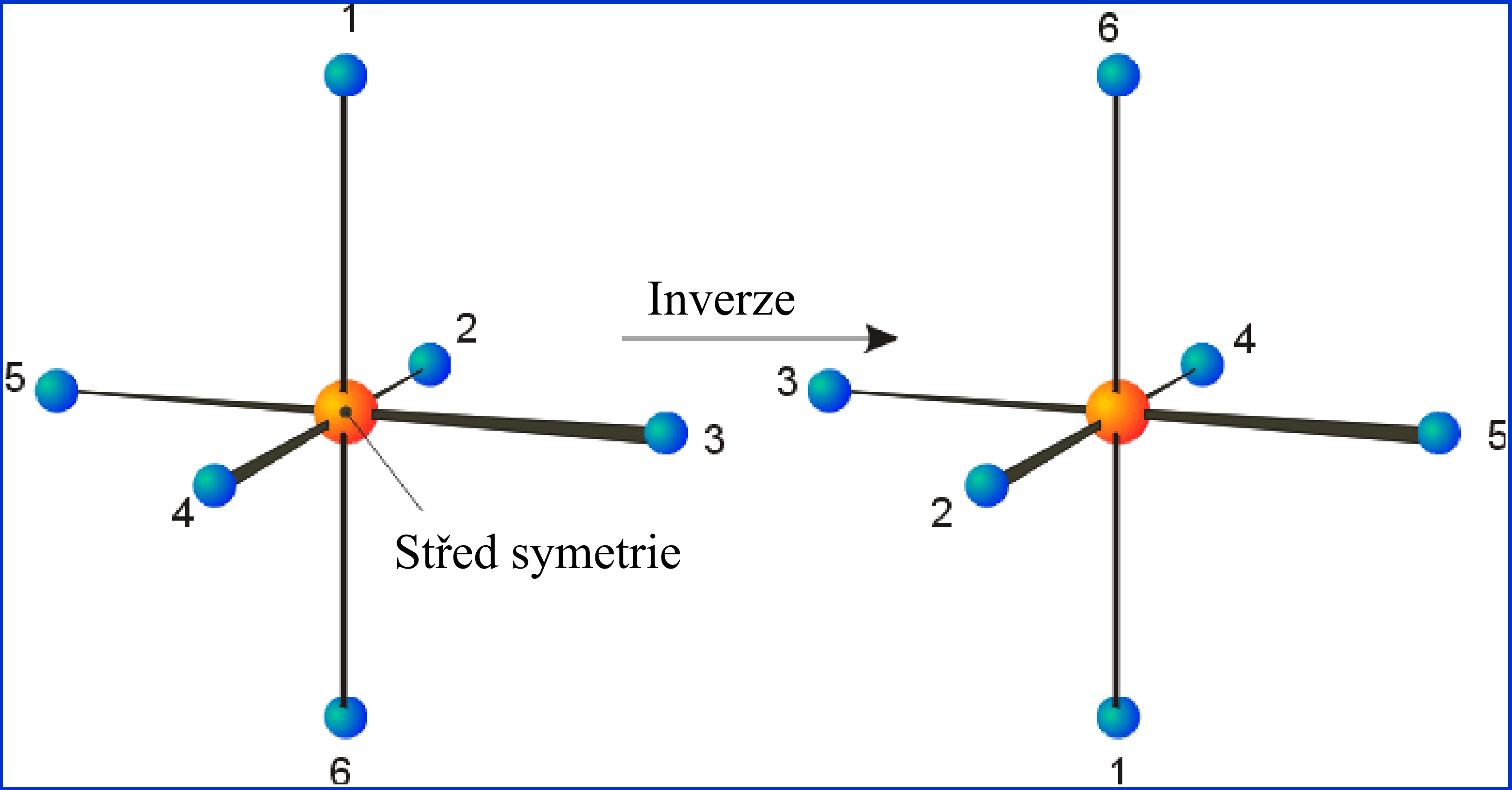




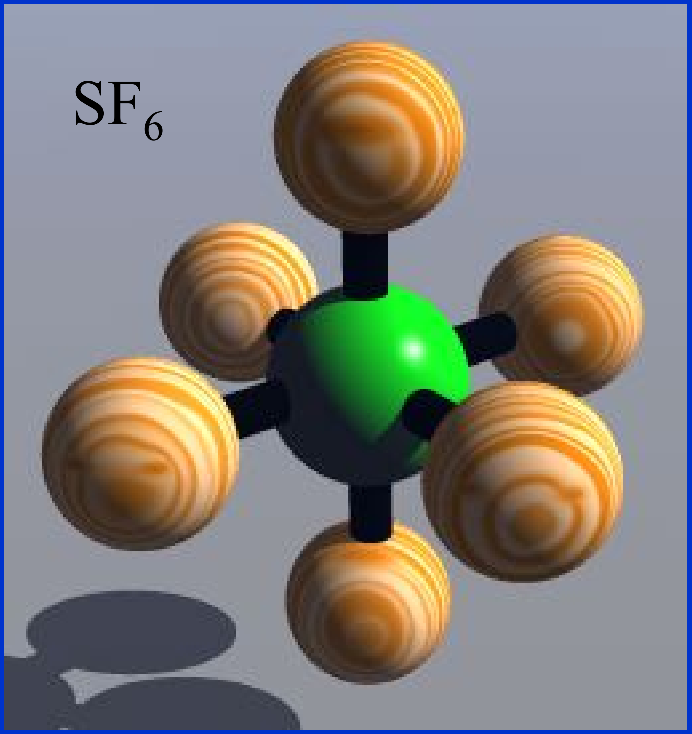
Prvky a operace symetrie

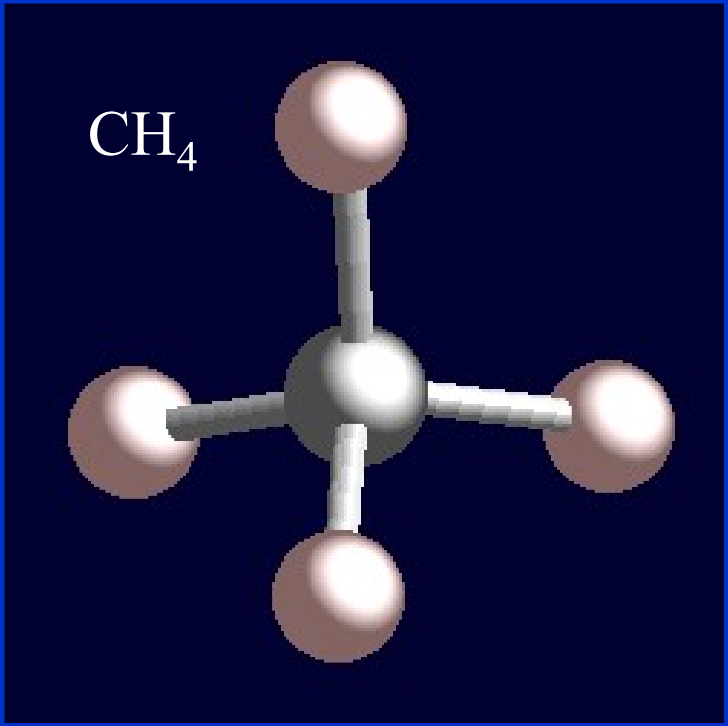
Značka	Prvek	Operace	Pozn.
E	Identita	Identita	Bezezměny, (= 1)
i	Střed symetrie (inverze) BOD	Inverze	Převrácení přes střed
C_n	Rotační osa PŘÍMKA	Pravá (vlastní) rotace	Otočení o úhel 360/n
σ	Rovina symetrie, zrcadlová ROVINA	Zrcadlení, reflexe	Zrcadlení přes rovinu
S_n	Zrcadlově-rotační osa PŘÍMKA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

Střed symetrie



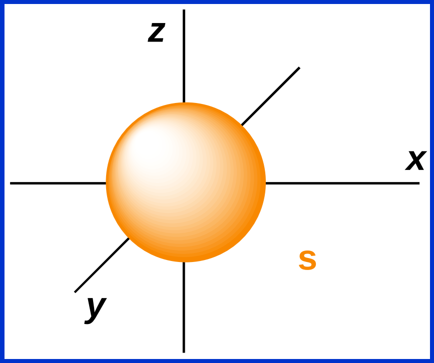
Střed symetrie

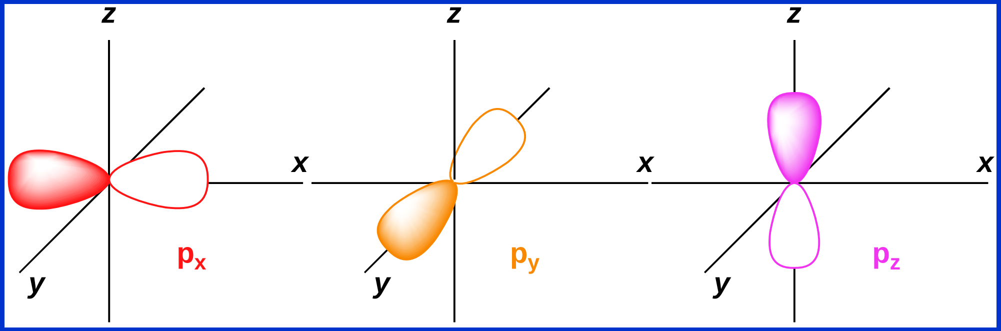


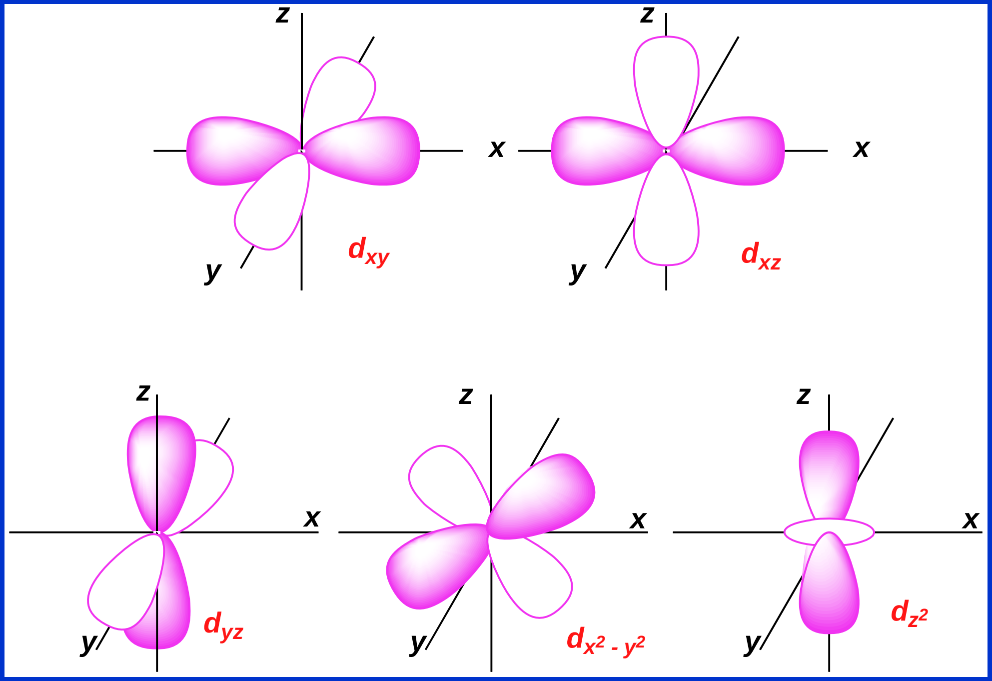


S = střed symetrie

Nemá střed symetrie



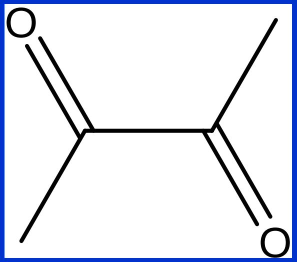




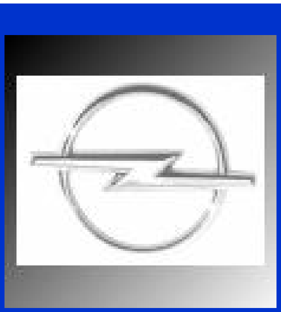
Orbitaly

s a d **mají** *i* (střed symetrie)

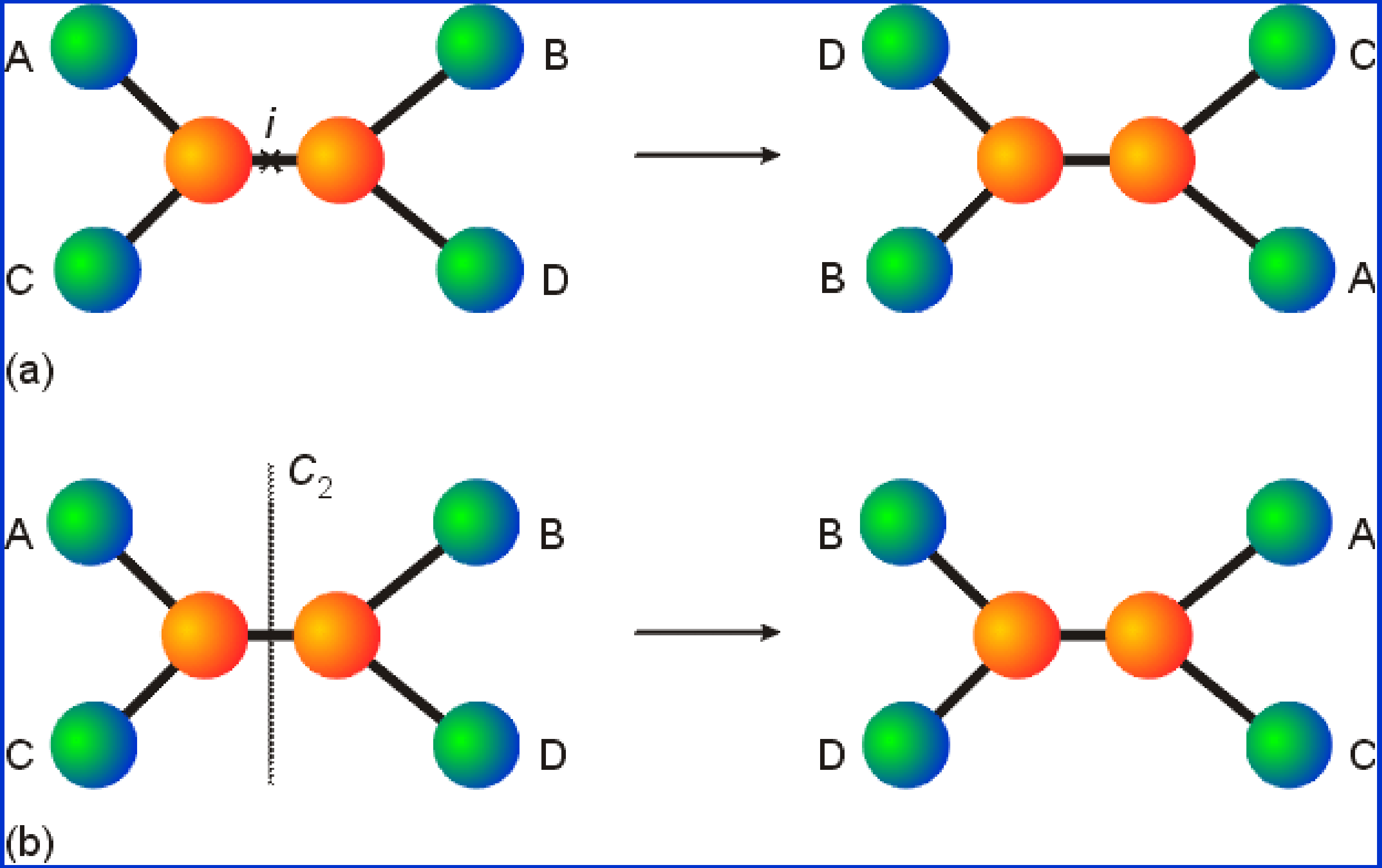
p a f nemají *i* (střed symetrie)



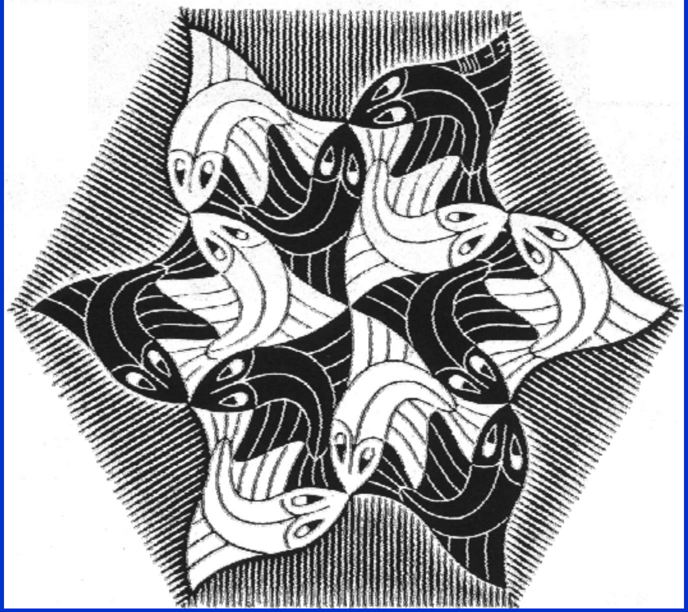
Rotační osa C_2



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

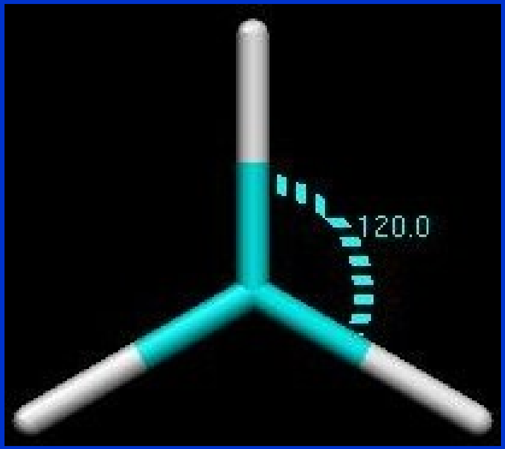


Rotační osa C_3



Rotace o úhel 360/n

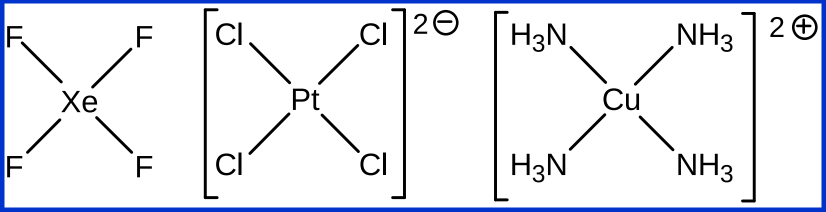
Vzniklá situace je nerozlišitelná od výchozí

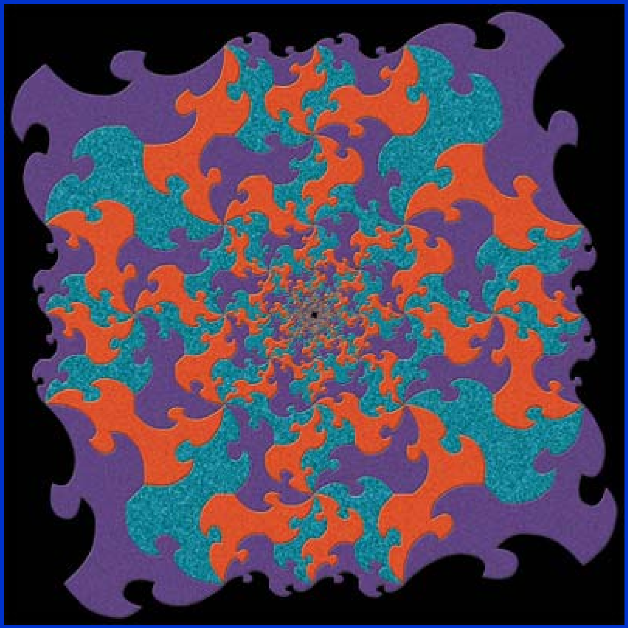


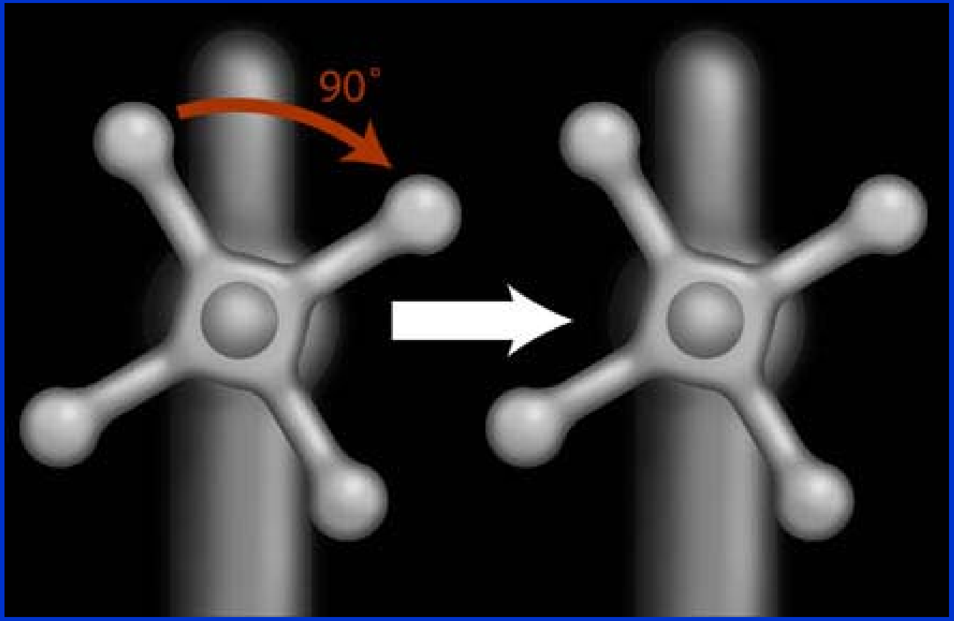
Rotační osa C_4

Rotace o úhel 360/4.

Vzniklá situace je nerozlišitelná od výchozí.

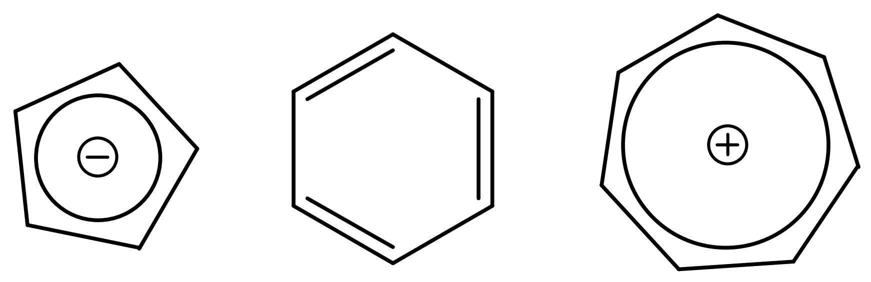


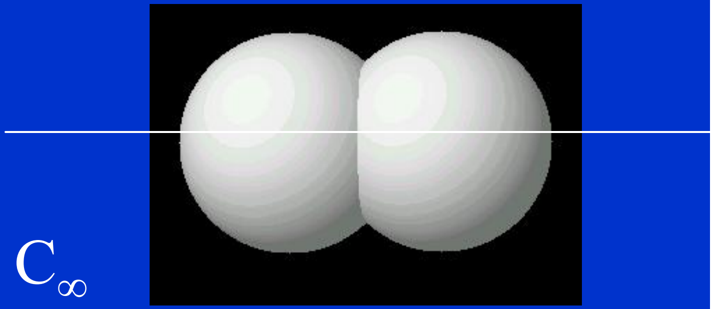




$$C_4^1 \rightarrow C_4^2 \rightarrow C_4^3 \rightarrow C_4^4 = E$$

Rotační osa C_n

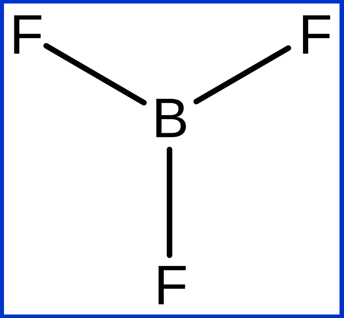


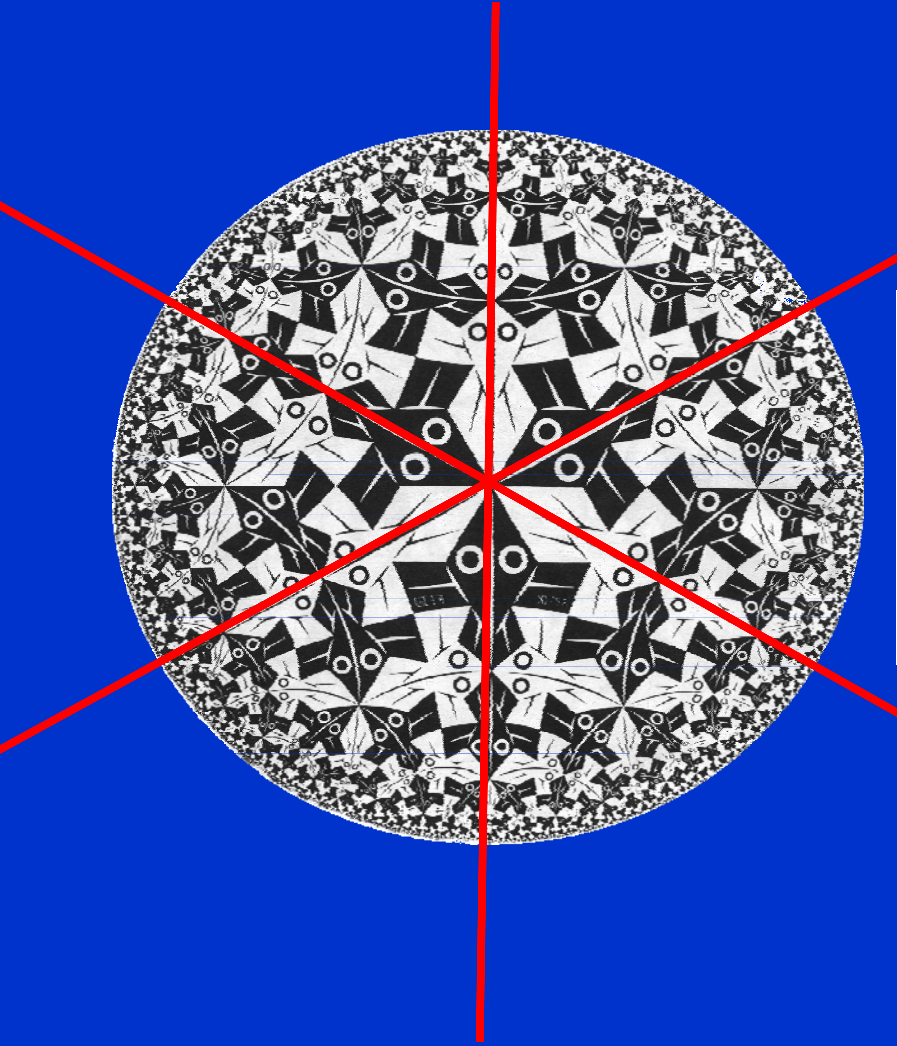


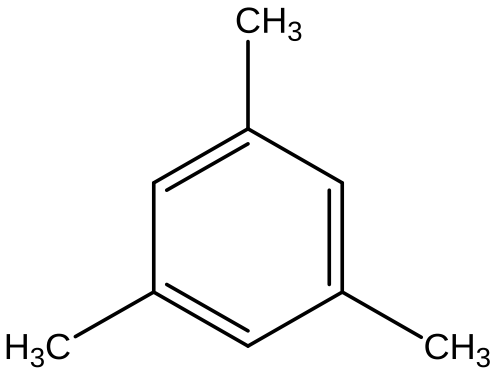
C_5, C_6, C_7,.................................... C_∞

Lineární molekuly

Rovina symetrie σ







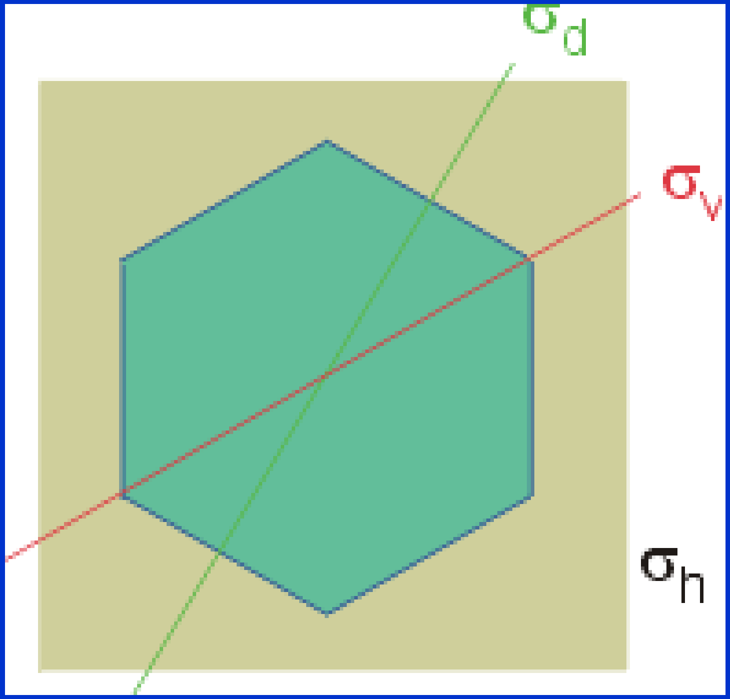
Roviny symetrie σ

Každá planární molekula má rovinu symetrie ve které leží

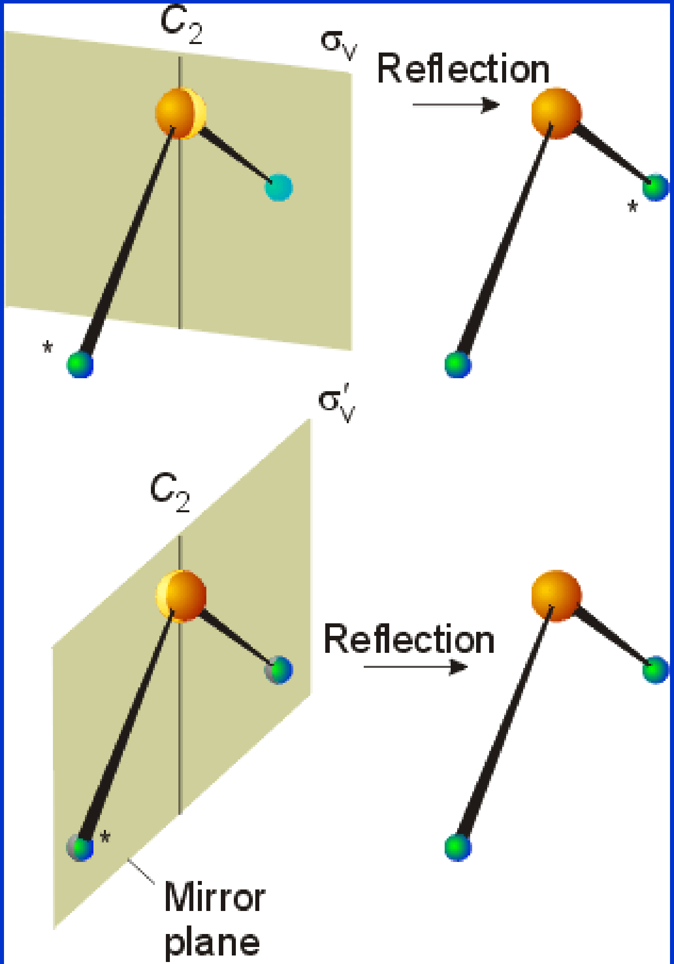
σ_h = kolmá k hlavní rotační ose

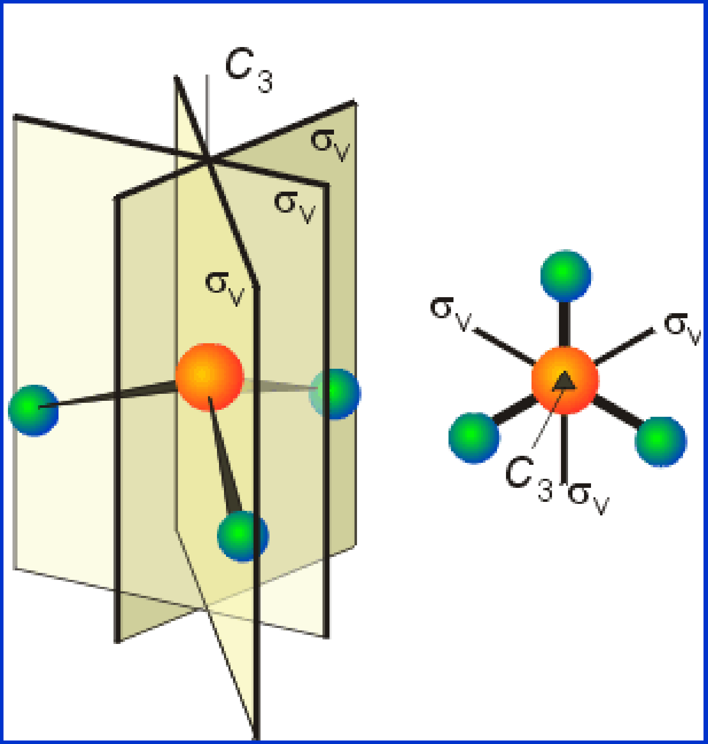
σ_v = protíná nejvíce atomů

σ_d = kolmá k hlavní rotaní ose



Roviny symetrie σ

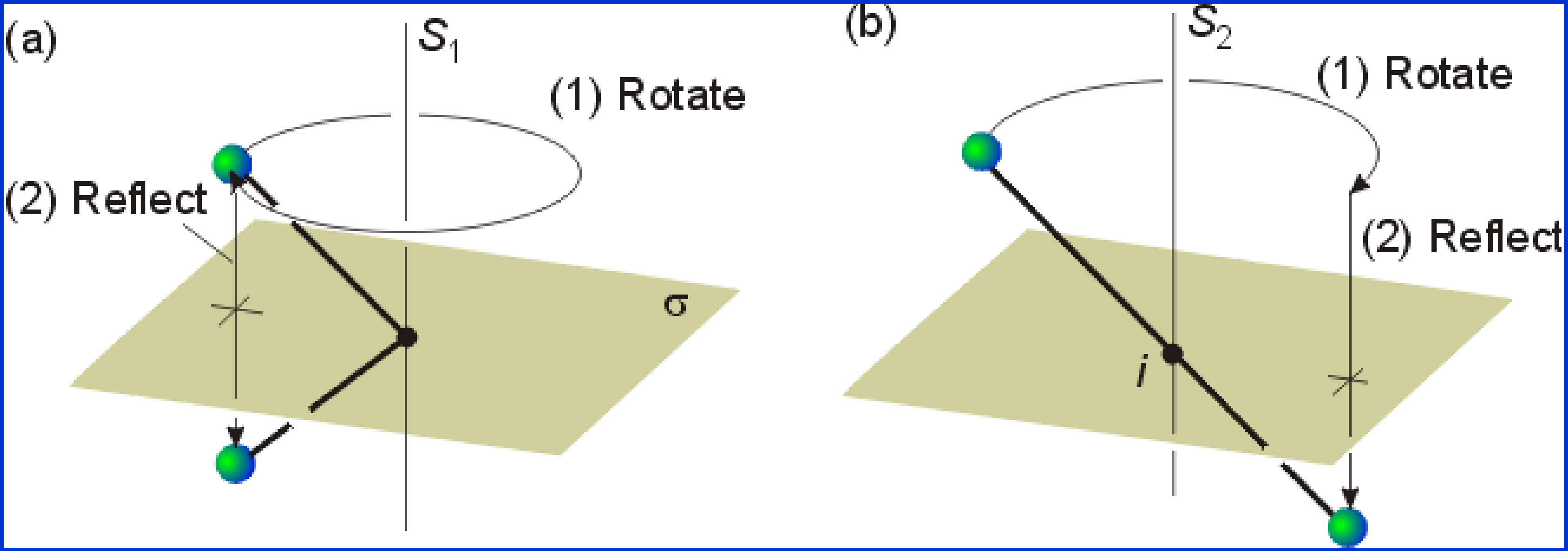




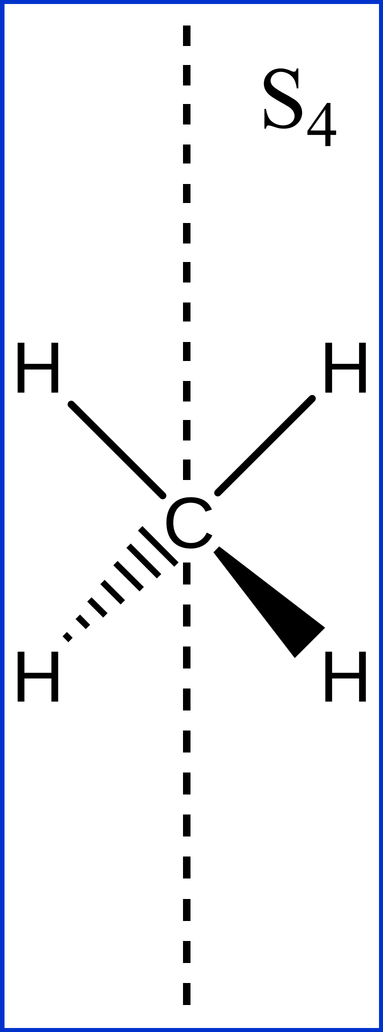
Zrcadlově-rotační osa S_n

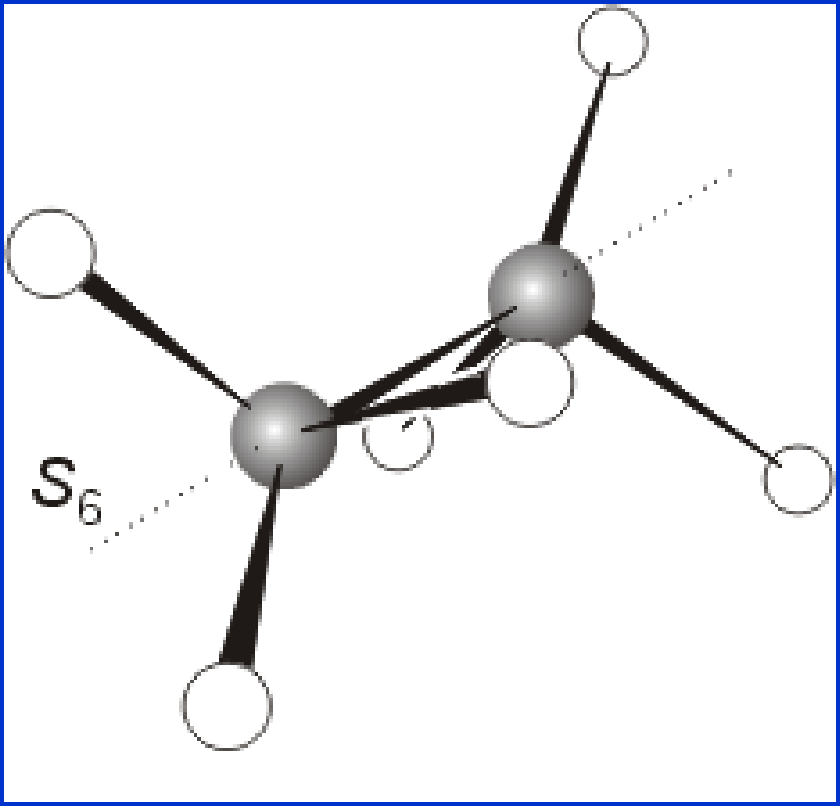
Postupné provedení dvou operací – rotace a zrcadlení

$S_1 = C_1 \times \sigma = \sigma$ $S_2 = C_2 \times \sigma = i$

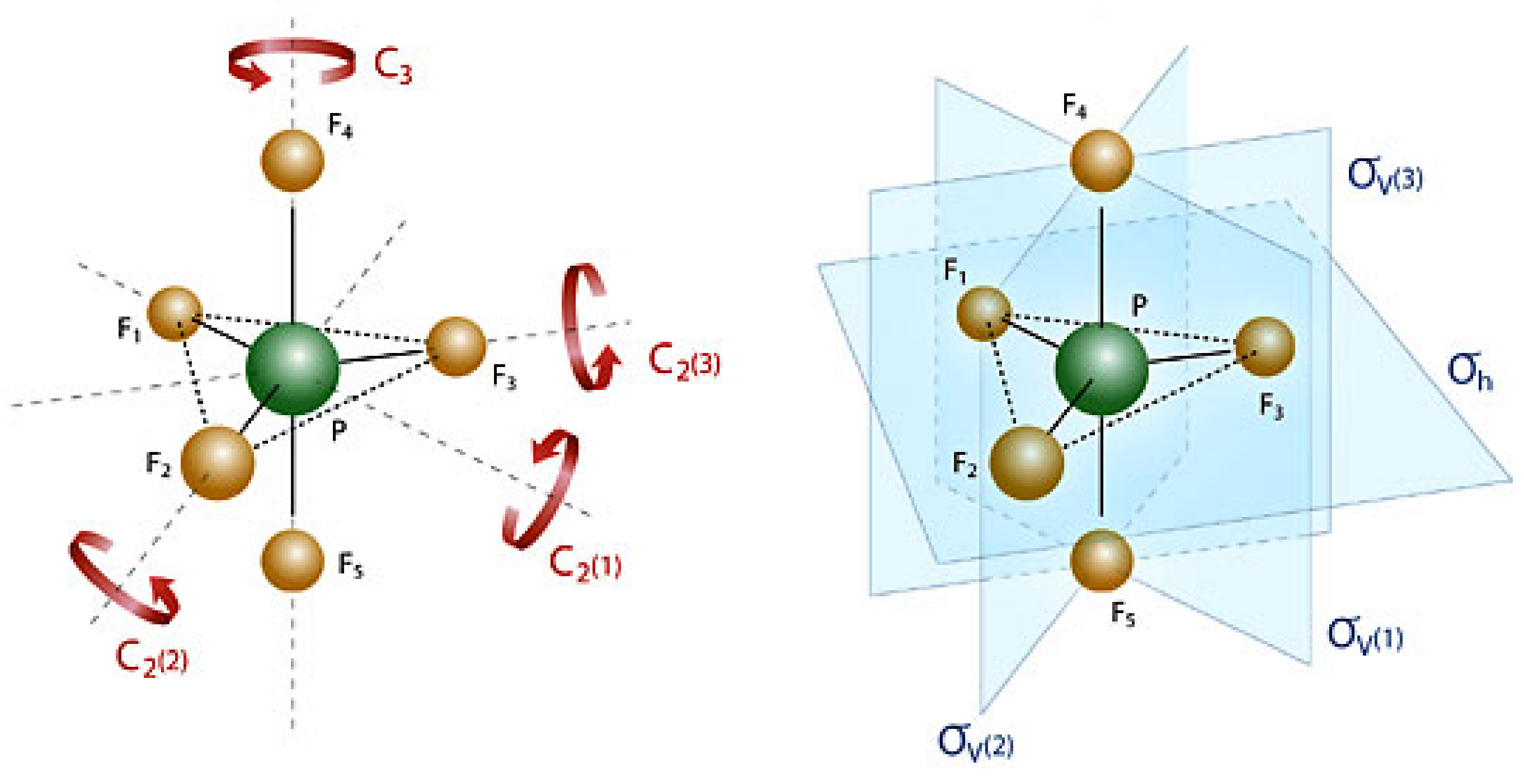


Zrcadlově-rotační osa S_n





Prvky symetrie v molekule



Ekvivalentní atomy = jsou zaměňovány operacemi symetrie

$F_4 = F_5$ $F_1 = F_2 = F_3$

Chiralita

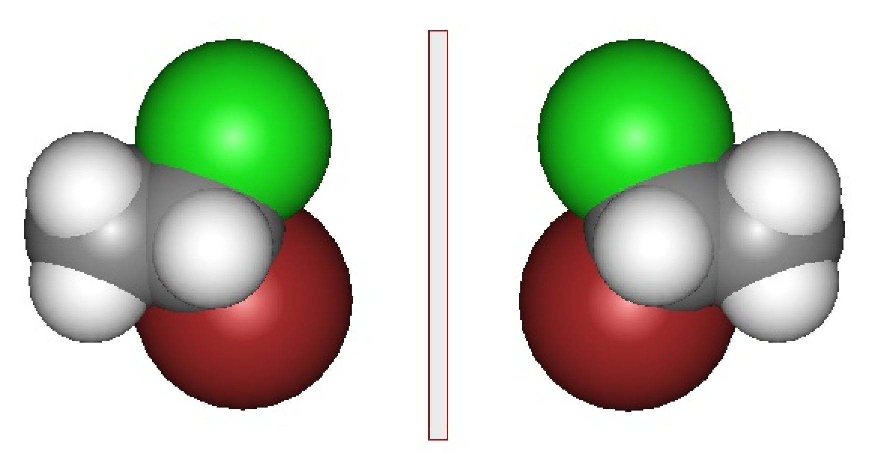
Figure 2. The Founding Fathers. R. M. Barrer (1910–1996) (right) and R. M. Milton (1920–2000) photographed

Chiralita

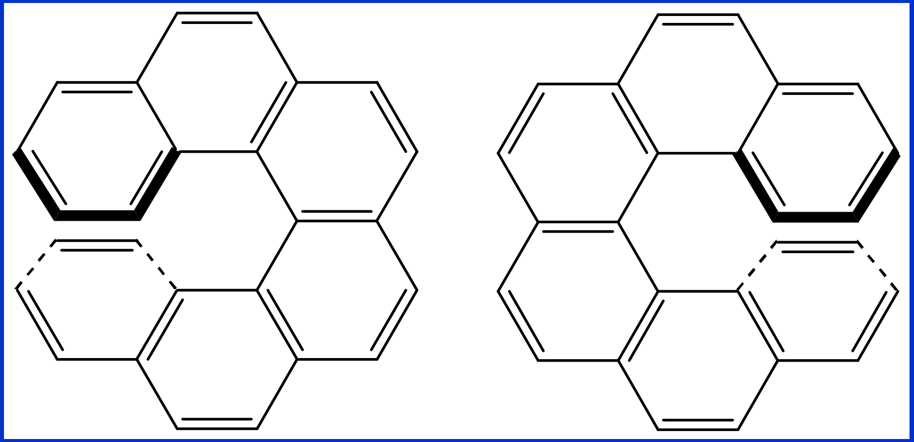
Podmínka chirality: v molekule není přítomna S_n

$S_1 = \sigma$

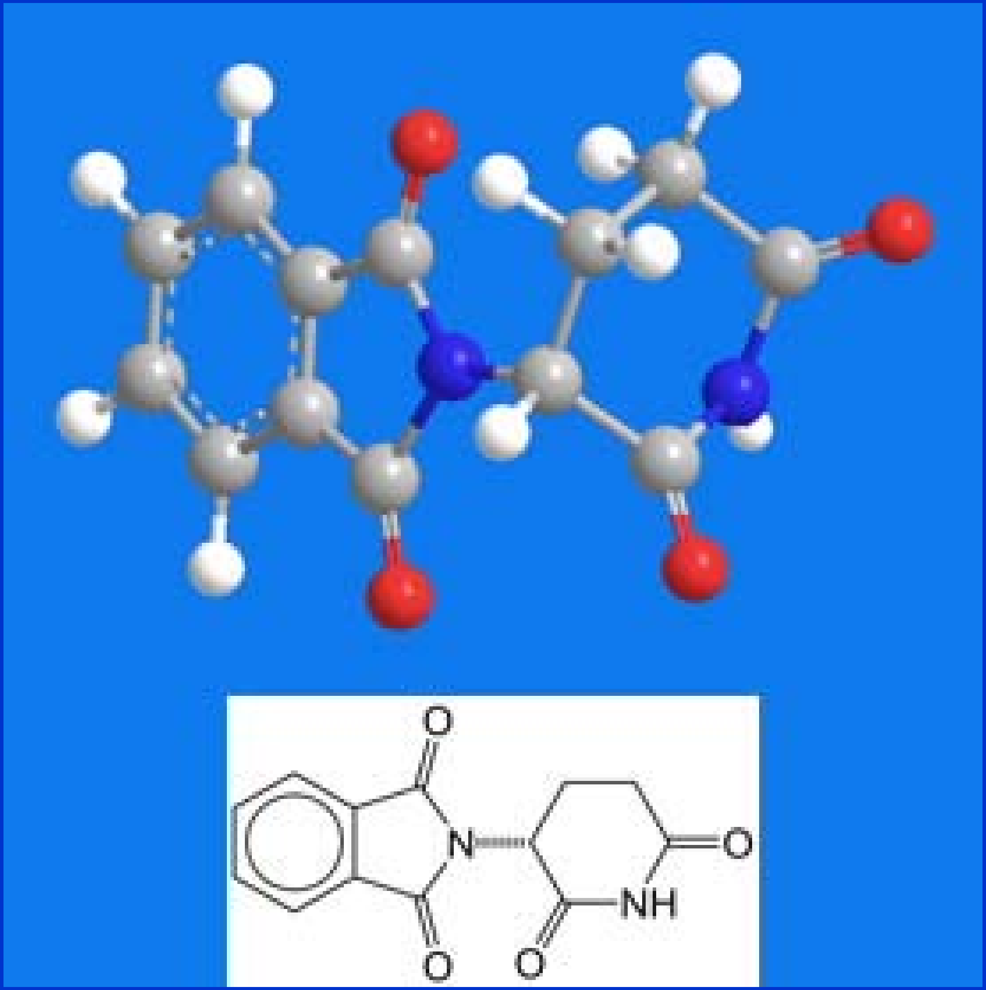
$S_2 = i$



C_2 →



Thalidomide

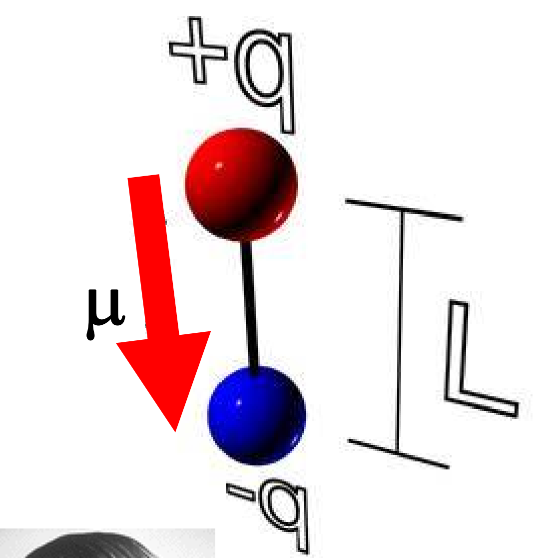


(*R*)-enanciomer

lék na ranní nevolnost

(*S*)-enanciomer

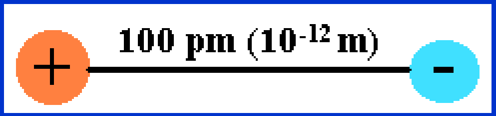
je teratogenní



Dipolový moment

$\mu = q\,L$ vektor [C m]

1 D debye = 3.33564 10^{-30} C m



proton a elektron, vzdáleny 1 Å

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

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

dipolový moment **4.80 D**
je referenční hodnota, čisté +1 a –1
náboje vzdálené100 pm, vazba mezi nimi
je 100% iontová

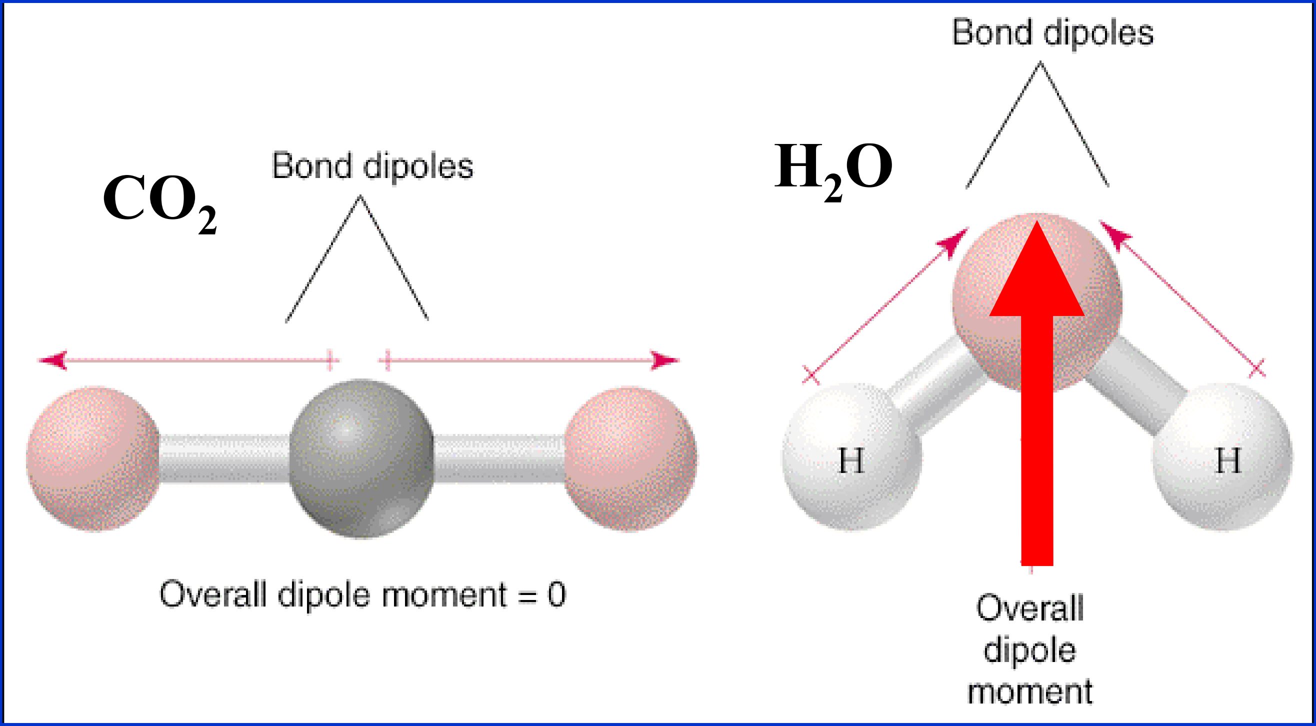
Peter Debye (1884-1966)
1936 NP za chemii

Zahřívání v MW

Dipolový moment molekuly

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

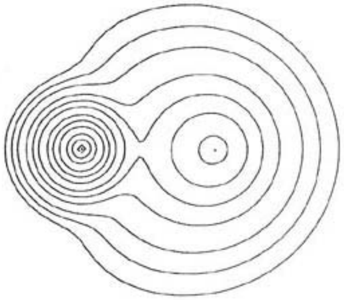
Míra nerovnoměrnosti rozložení náboje v molekule

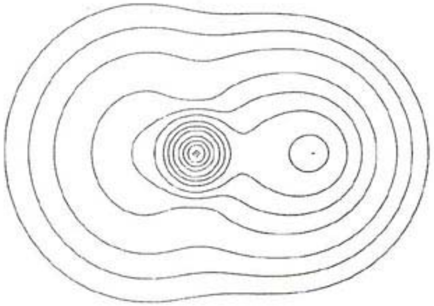


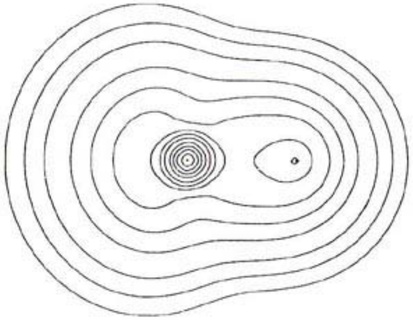
Dipolové momenty diatomických molekul

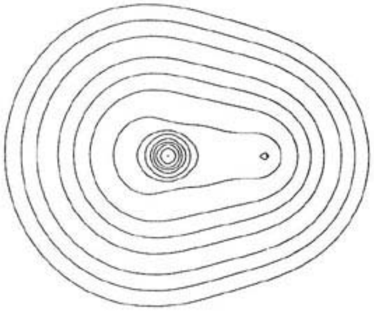
AH	μ (Debye)	R(Å)
LiH	–6.002	1.595
BeH	–0.282	1.343
BH	1.733	1.236
CH	1.570	1.124
NH	1.627	1.038
OH	1.780	0.9705
FH	1.942	0.9171

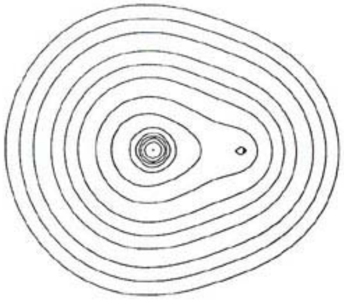
negativní nebo pozitivní znaménko pro μ ⇒ H je negativní nebo pozitivní konec dipolu.

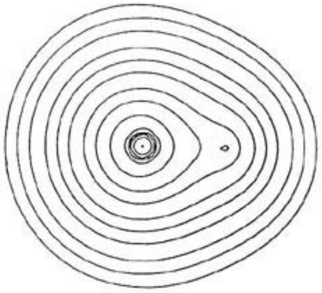

LiH

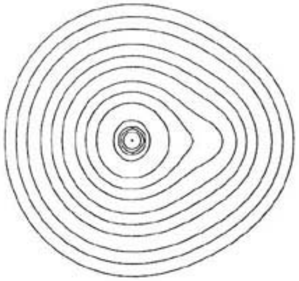

BeH


BH


CH

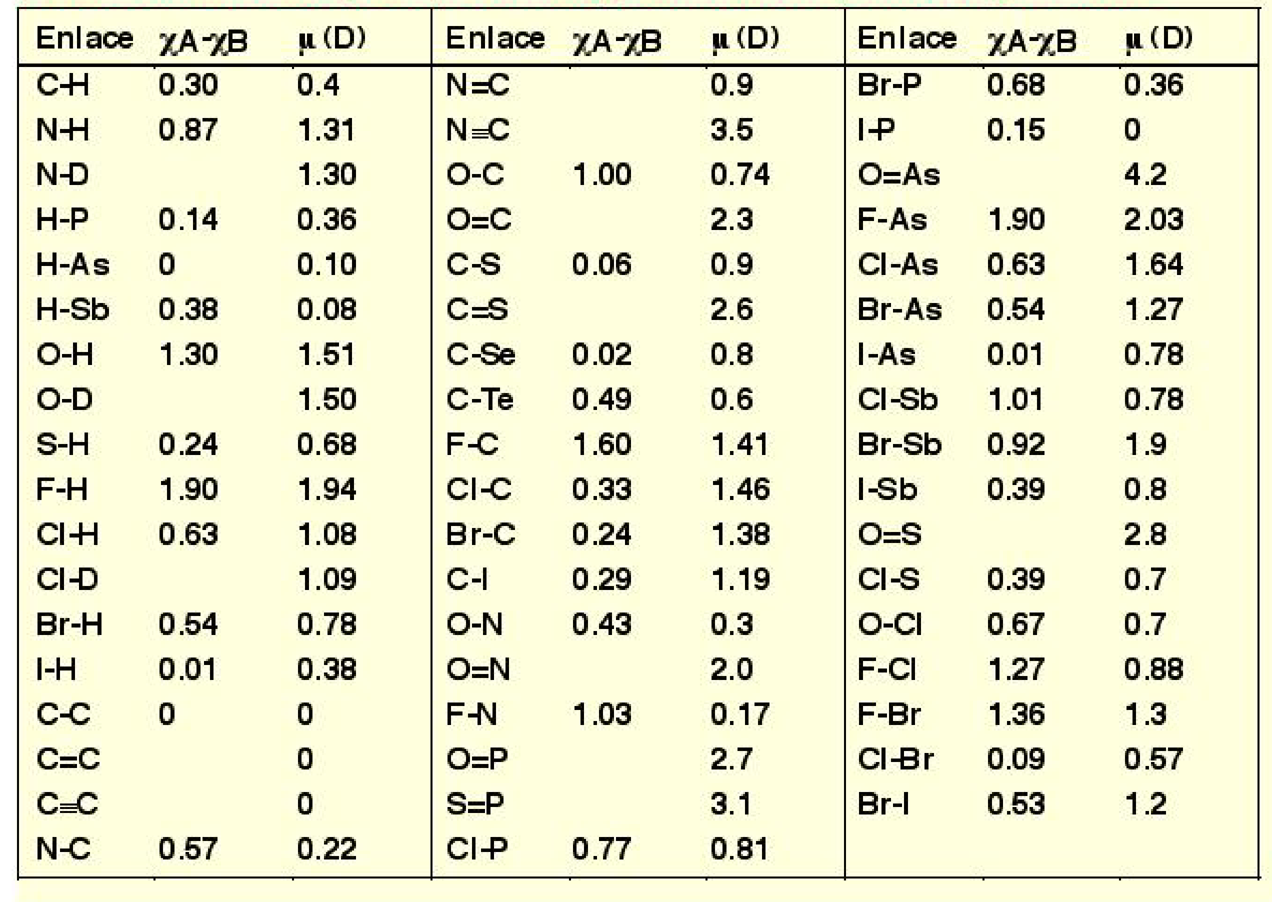

NH


OH


HF

Dipolový moment vazeb

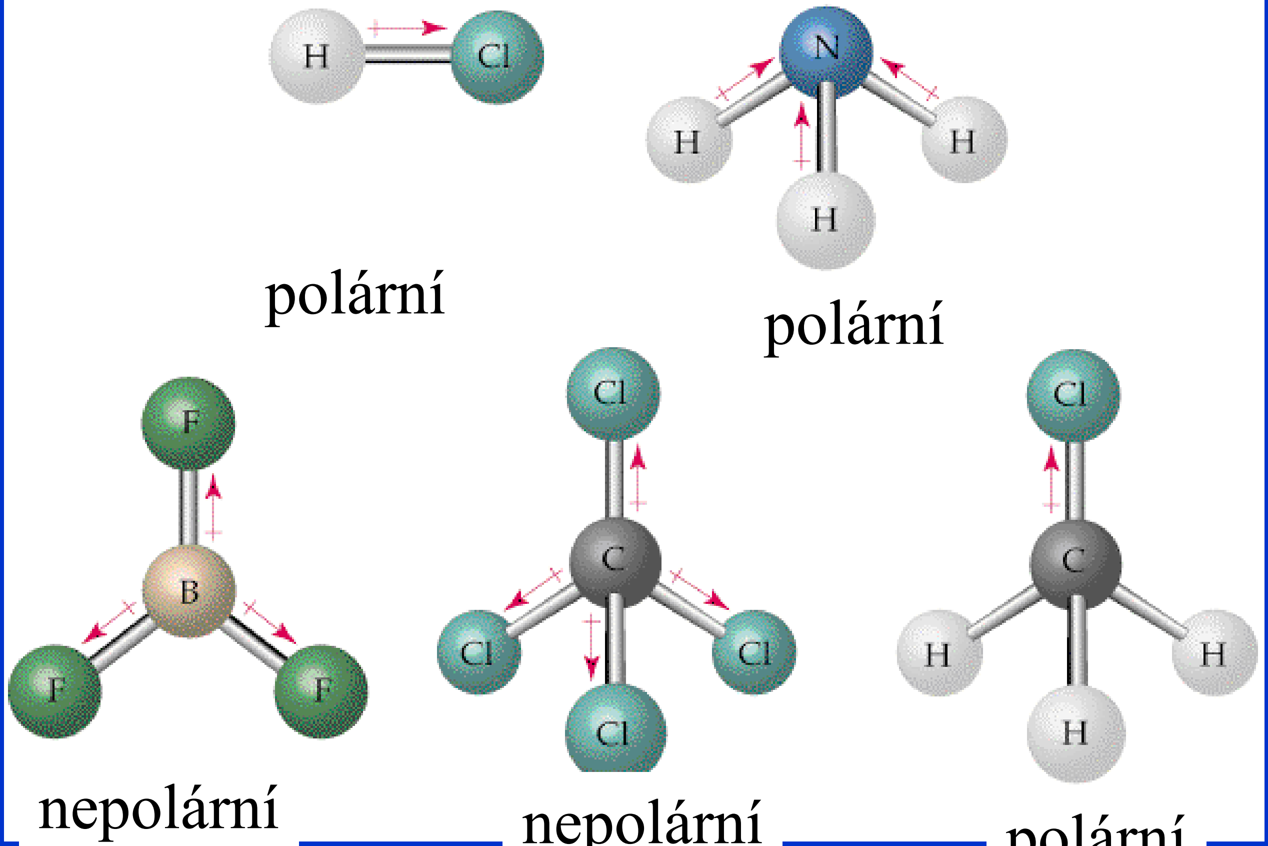
Rozdíl elektronegativit vazebných partnerů



Enlace	χA-χB	μ (D)	Enlace	χA-χB	μ (D)	Enlace	χA-χB	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



polární

polární

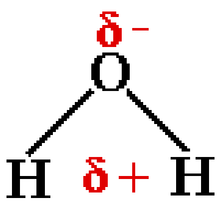
nepolární

nepolární

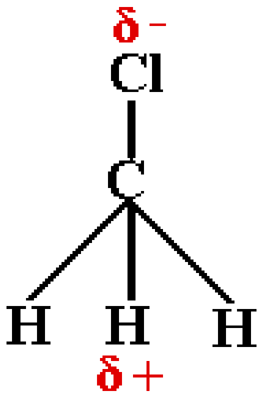
polární

Polární

H_2O

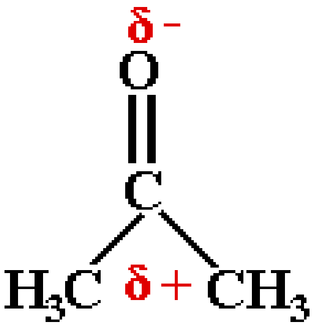


CH_3Cl

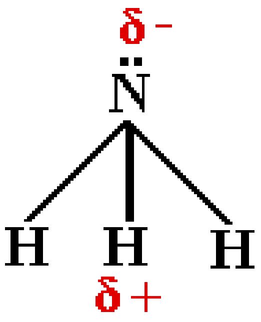


$(CH_3)_2CO$

(acetone)



NH_3

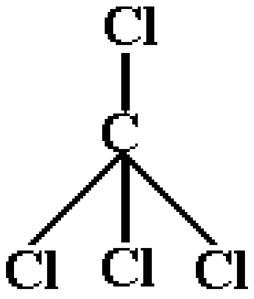


Nepolární

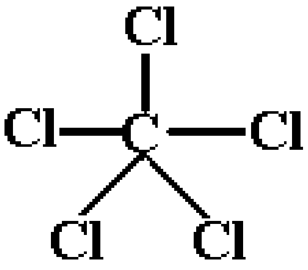
CO_2

O=C=O

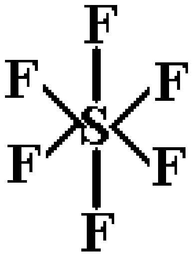
CCl_4

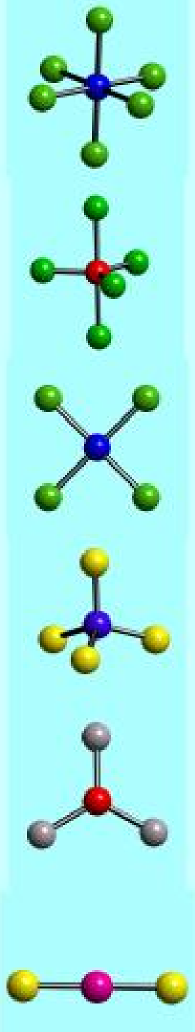


PCl_5



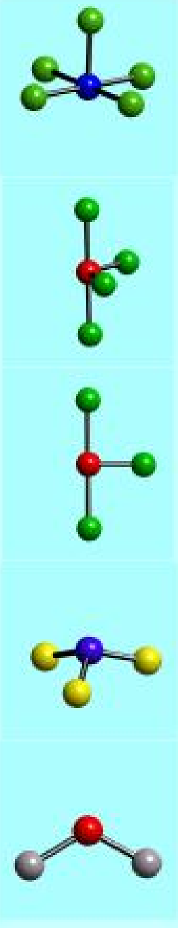
SF_6





$\mu = 0$

AB_nE_m	Grupo Puntual	μ	Molekula
AB_2	$D_{\infty h}$	0	CO_2, $BeCl_2(g)$, ZnX_2
AB_3	D_{3h}	0	BX_3, GaI_3, $In(CH_3)_3$
AB_2E	C_{2v}	finito	SnX_2, PbX_2
AB_4	T_d	0	CX_4, SiX_4, ThX_4
AB_3E	C_{3v}	finito	NH_3, NX_3, PX_3
AB_2E_2	C_{2v}	finito	H_2O, SeX_2, TeX_2
AB_5	D_{3h}	0	PF_5, $PCl_5(g)$, $NbCl_5(g)$
AB_4E	C_{2v}	finito	SF_4, SeF_4
AB_3E_2	C_{2v}	finito	ClF_3, BrF_3
AB_2E_3	$D_{\infty h}$	0	XeF_2
AB_6	O_h	0	SF_6, SeF_6, MoF_6
AB_5E	C_{4v}	finito	ClF_5, BrF_5, IF_5
AB_4E_2	D_{4h}	0	XeF_4
AB_7	D_{5h}	0	IF_7



$\mu \neq 0$