Orbital Overlap

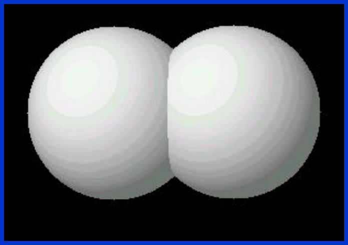
Formation of a bond by overlapping orbitals on two different atoms A, B

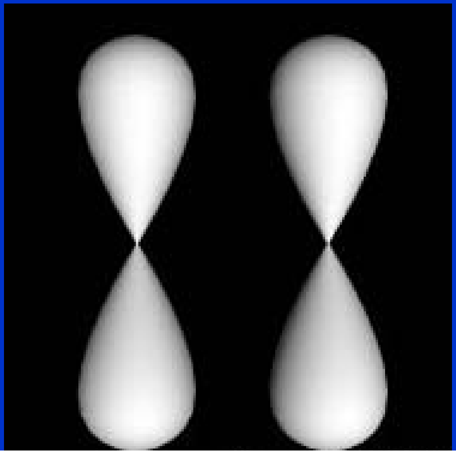
Occupied by a pair of electrons

$Y = Y_A \times Y_B$

Overlap conditions:

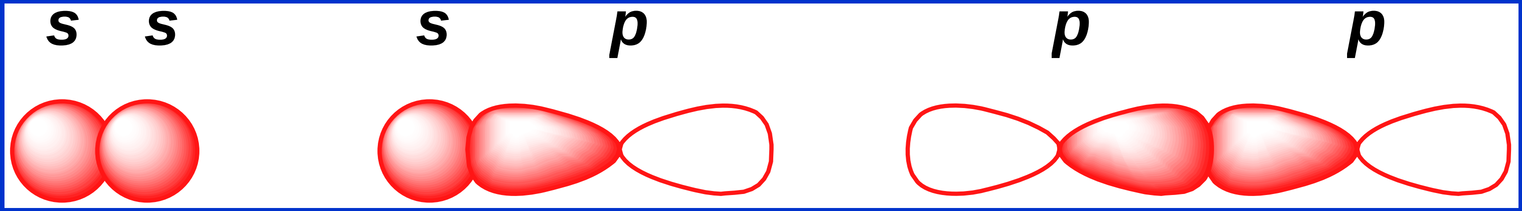
- Proper symmetry, sign of wave functions
- Suitable energies, comparable, not too disparate



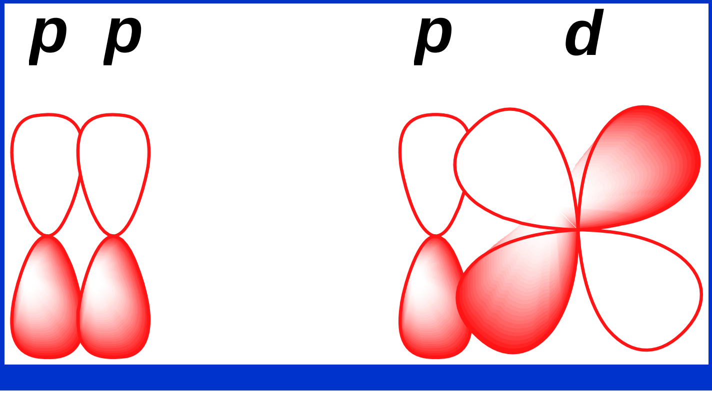


Types of Orbital Overlap

Sigma bond, σ
Electron density localized on the connection line between atoms, customarily assigned as *z*



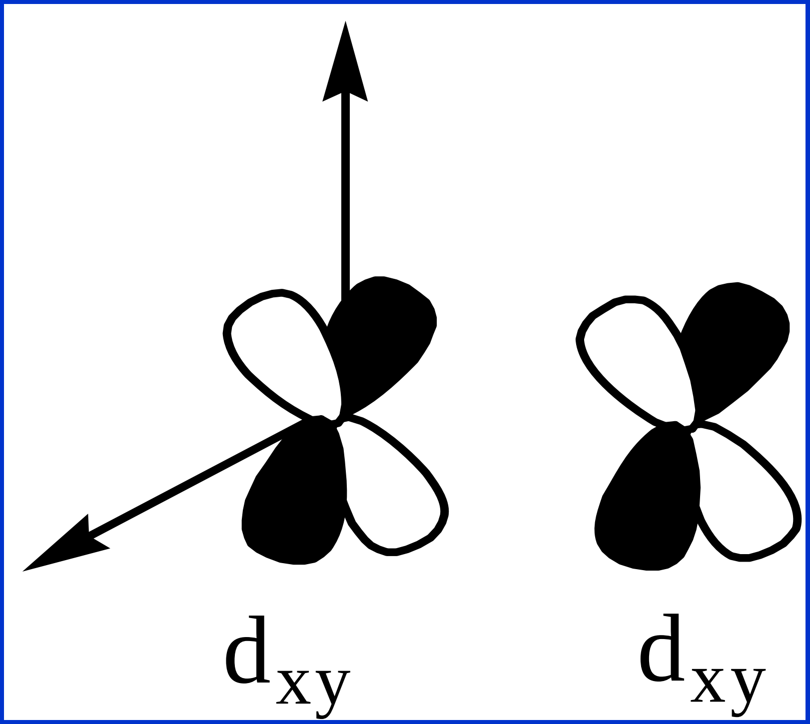
Pi bond, π
Electron density localized above and below the connection line between atoms, one nodal plane



Types of Orbital Overlap

Delta bond, δ

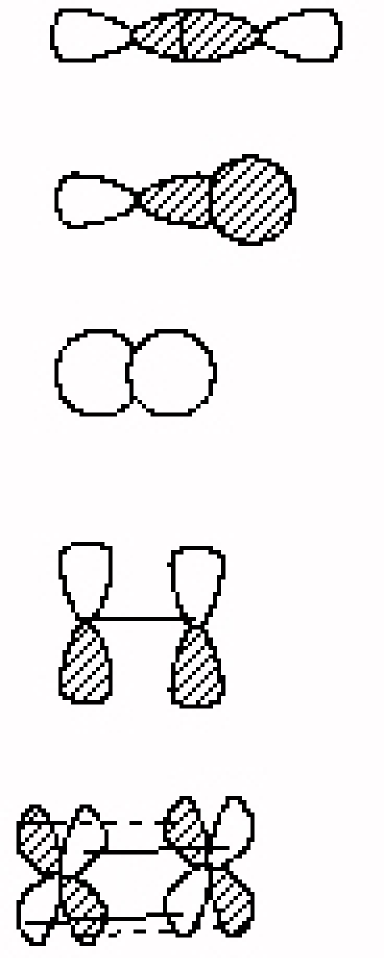
Electron density localized off the connection line between atoms, two nodal planes



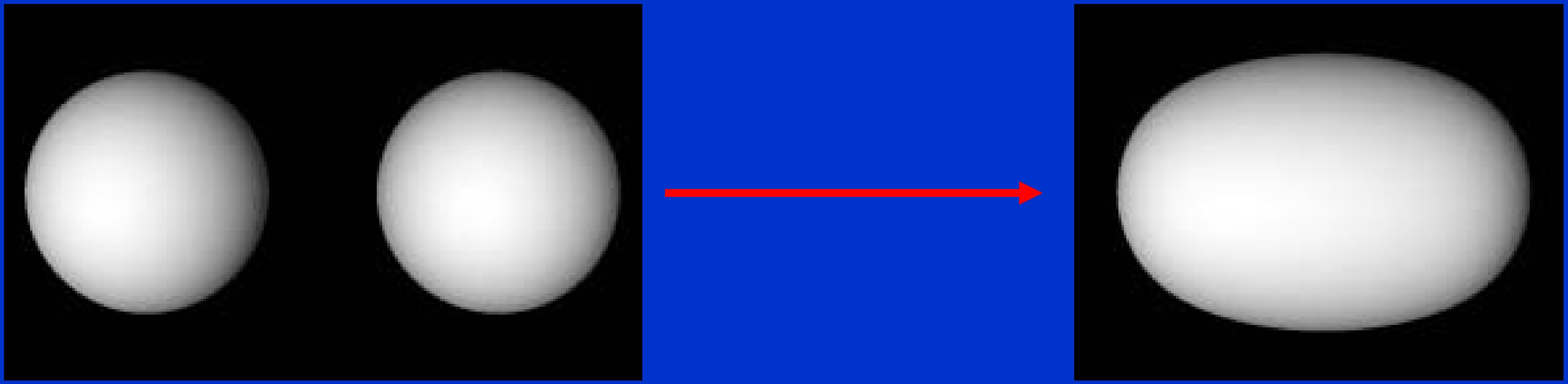
Types of Orbital Overlap

Overlap
decreases

Weaker bonds



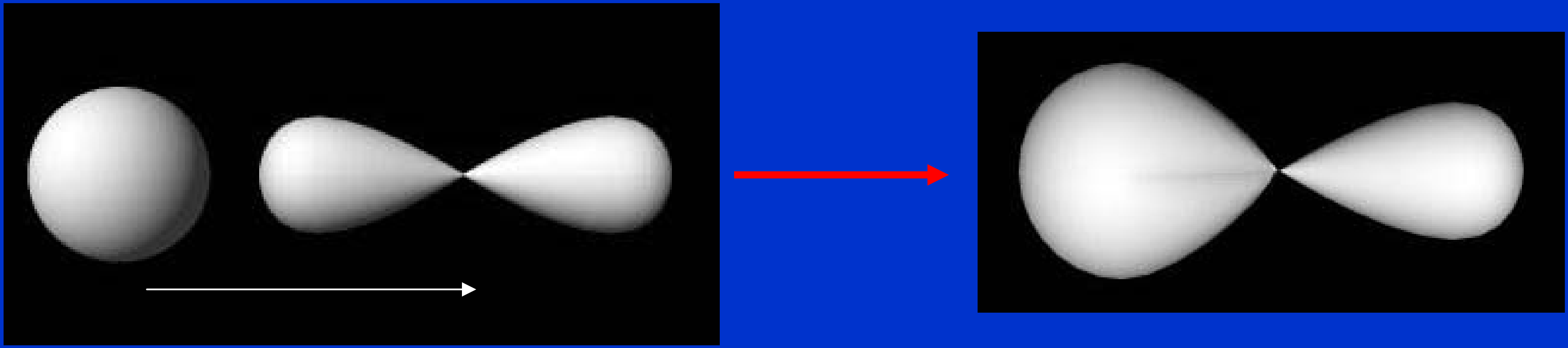
Sigma Bond, σ_{ss}



σ_{ss}

Electron density localized on the connection line between atoms

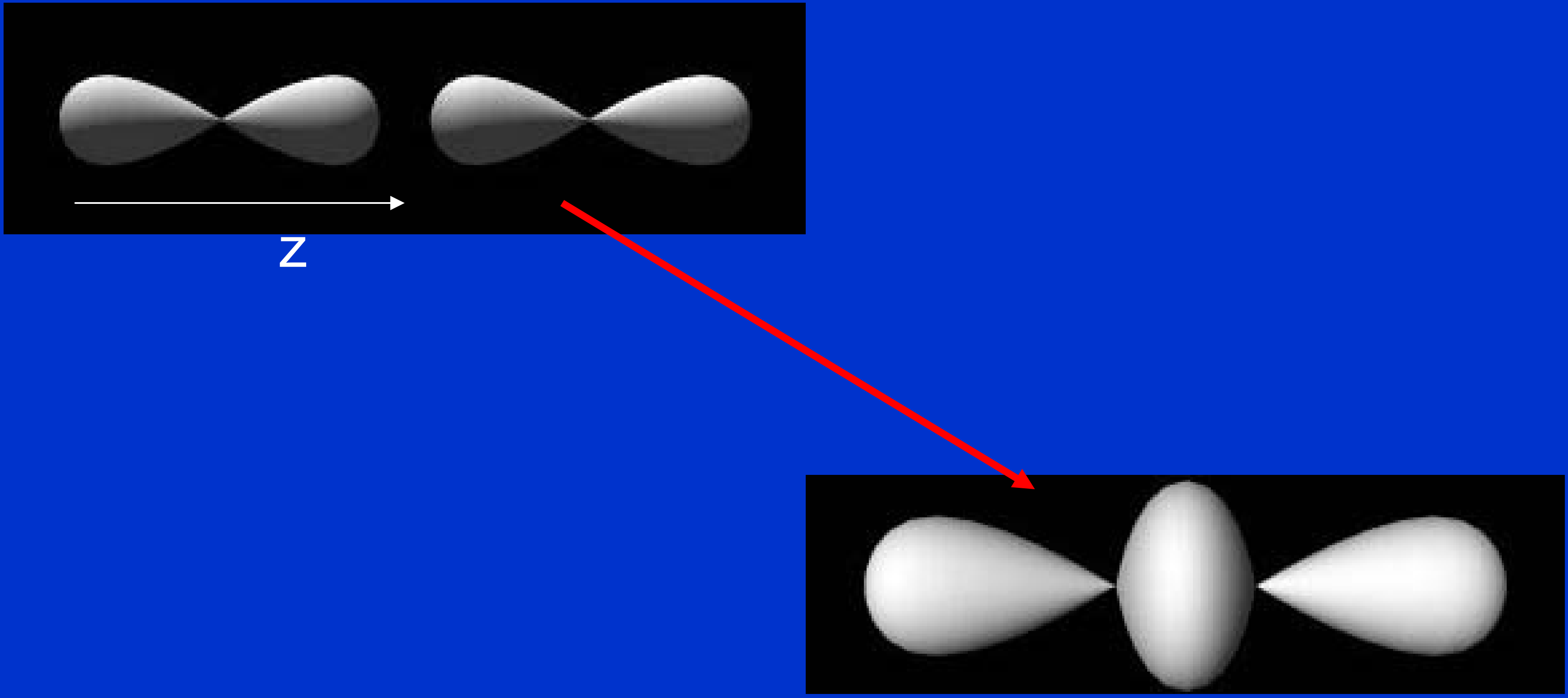
Sigma Bond, σ_{sp}



z

σ_{sp}

Sigma Bond, σ_{pp}

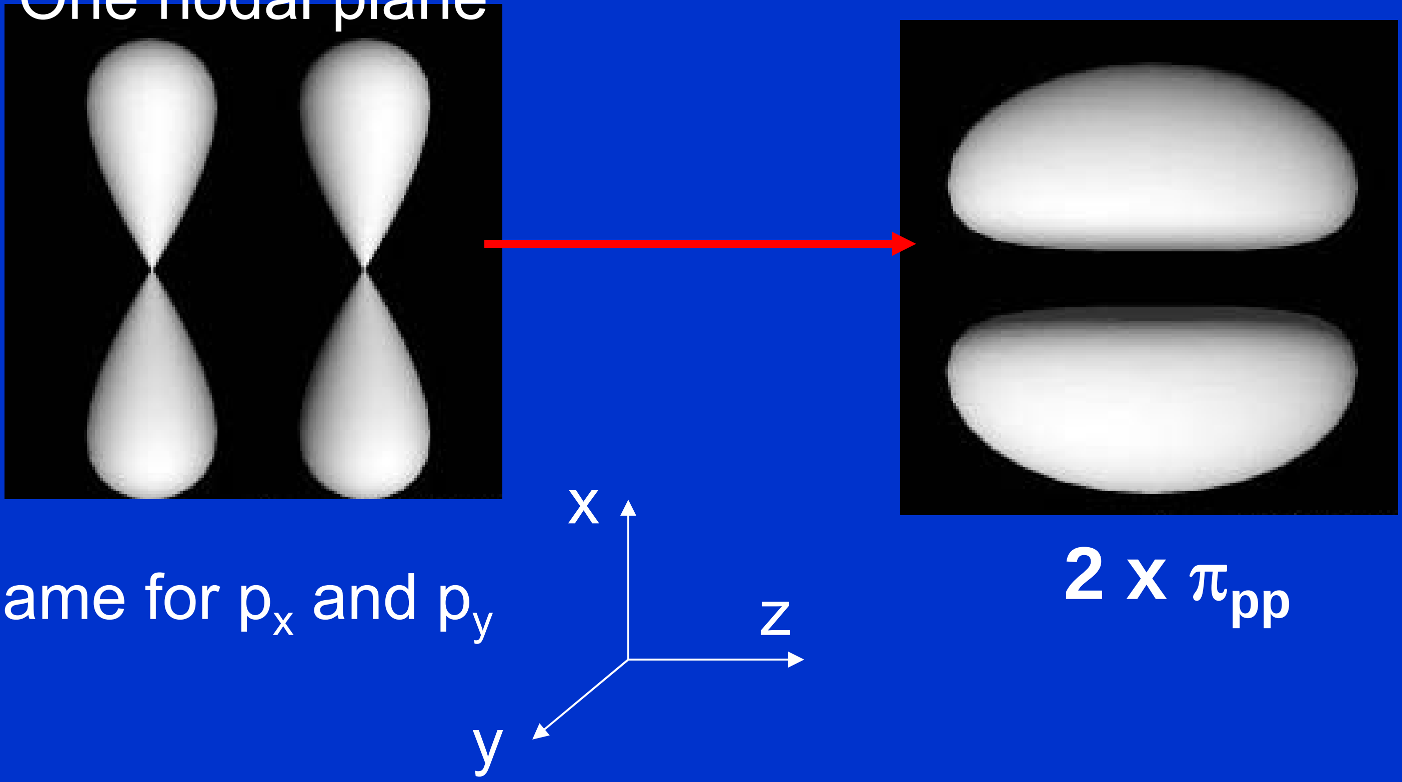


σ_{pp}

Pi vazba, π

Electron density localized above and below the connection line between atoms

One nodal plane



Same for p_x and p_y

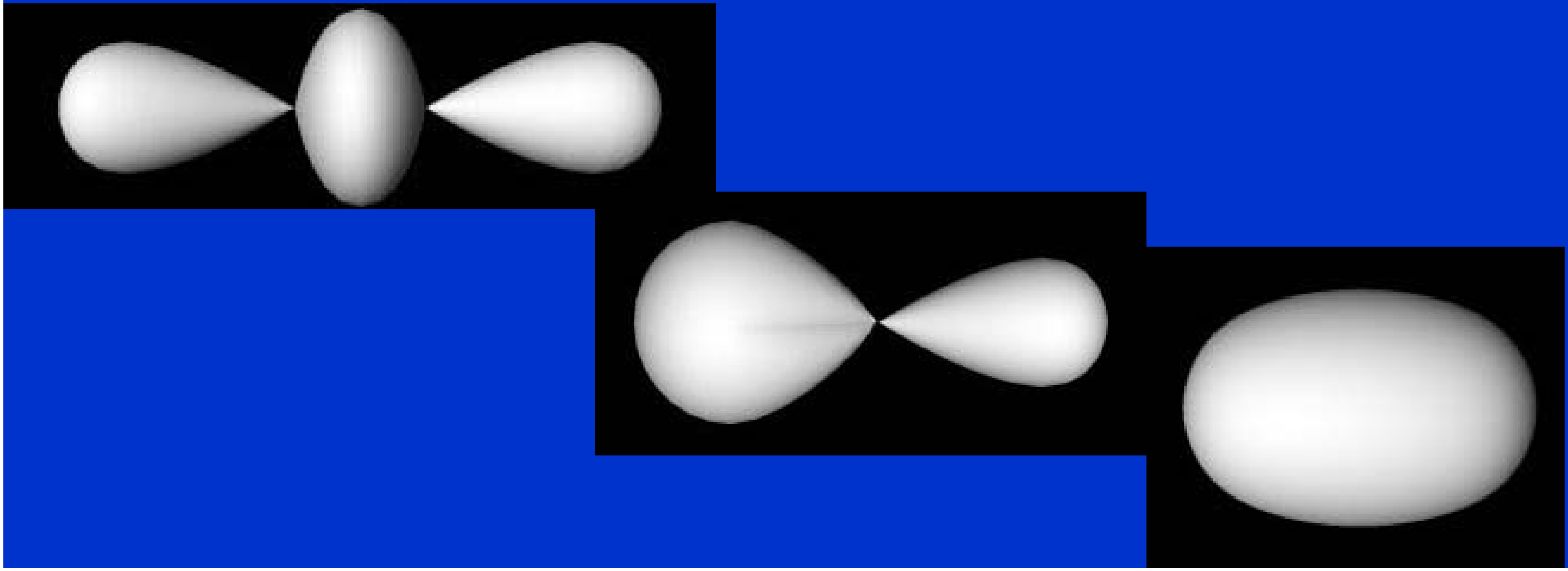
2 x π_{pp}

Effectivity of Orbital Overlap

Shorter distance = Better orbital overlap

At the same distance : $\sigma > \pi > \delta$

For σ: p_z-p_z > p_z-s > s-s



Bonding Parameters

Anion	Bond Order	Bond Distance, 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

Bond Order increases

Bond Distance decreases

Bonding Parameters

Bond	Distance Å]	Energy [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

Bond	E, kJ mol^{-1}	Bond Polarity
H-H	431	Nonpolar
F-F	155	Nonpolar
H-F	565	Polar
C-I	240	↓ Bond polarity increases
C-Br	276	
C-Cl	339	
C-F	485	
		m.p, °C
Ge-Ge	188	937
Si-Si	226	1412
C-C	347	3827

Bonding Parameters

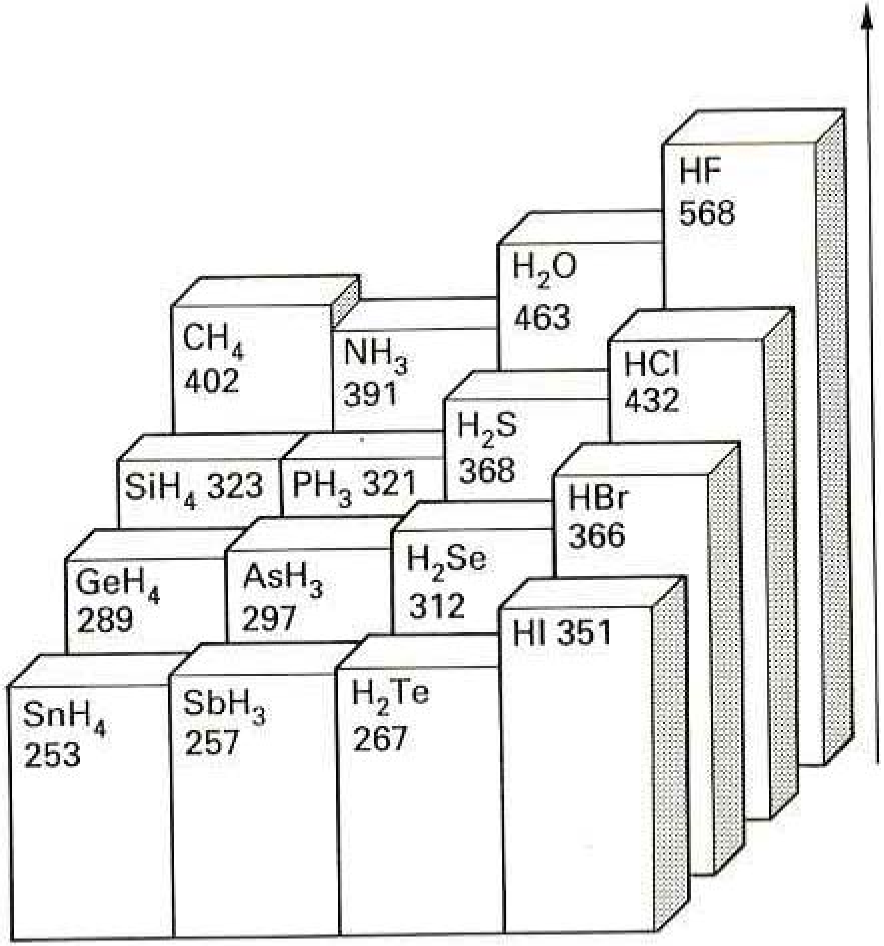
Bond	**E, kJ mol^{-1}**	**Length, Å**
C-I	240	2.16
C-Br	276	1.91
C-Cl	339	1.79
C-F	485	1.40

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

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

Schomaker-Stevenson

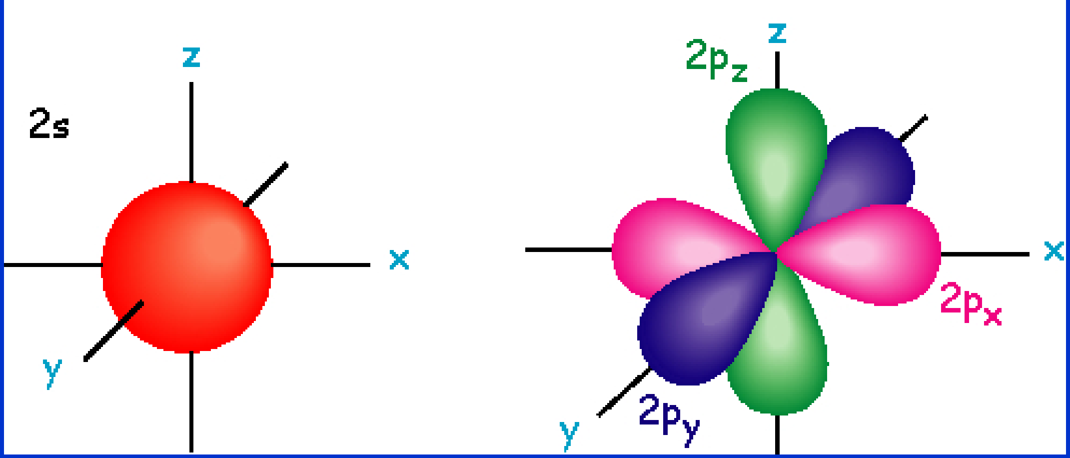
$$r_{AB} = r_A + r_B - 0.09\ |\chi_A - \chi_B|$$



Bond Energy

kJ mol^{-1}

Hybridization



Bond angles 90° are rare for main group elements, common values are 109, 120, 180°

Hybridization = energetical mixing and directional change of atomic orbitals on the same atom

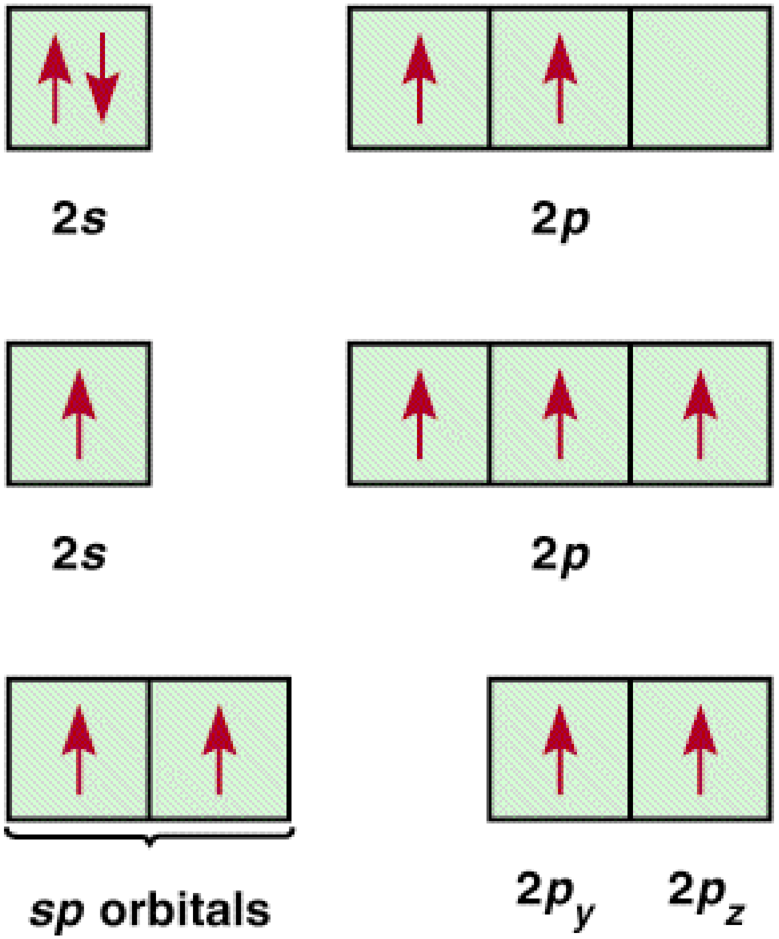
Number of hybrid orbitals = Number of mixed atomic orbitals

sp-Hybridization

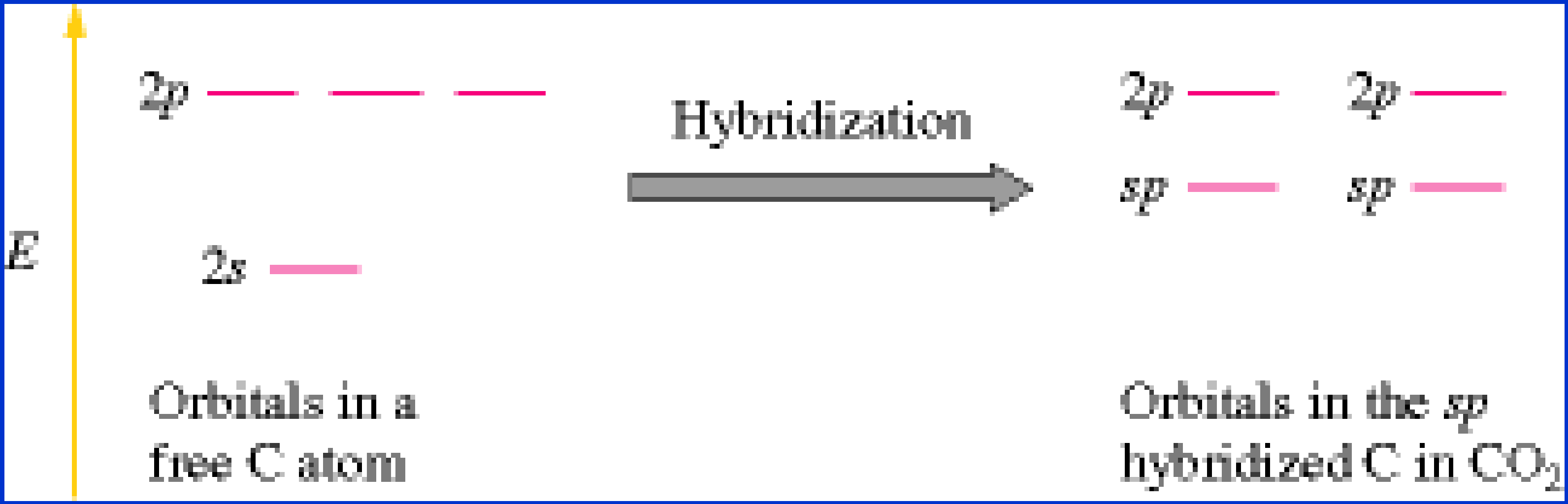
Ground state

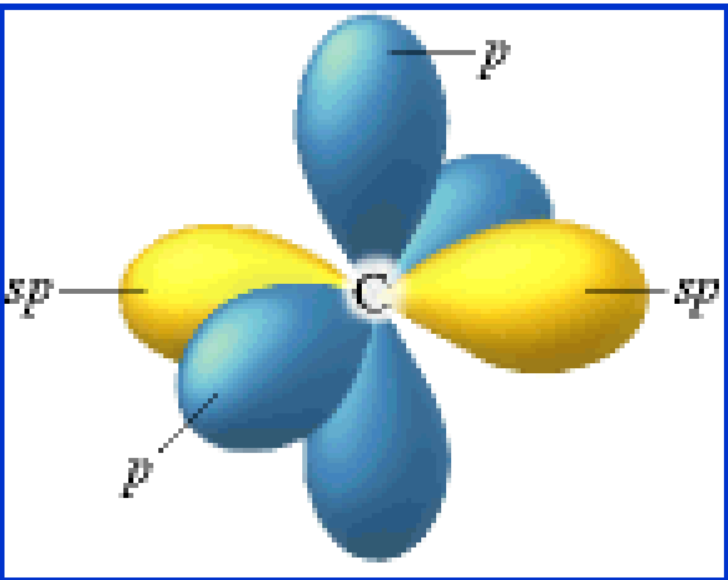
Excited state

Hybridized state

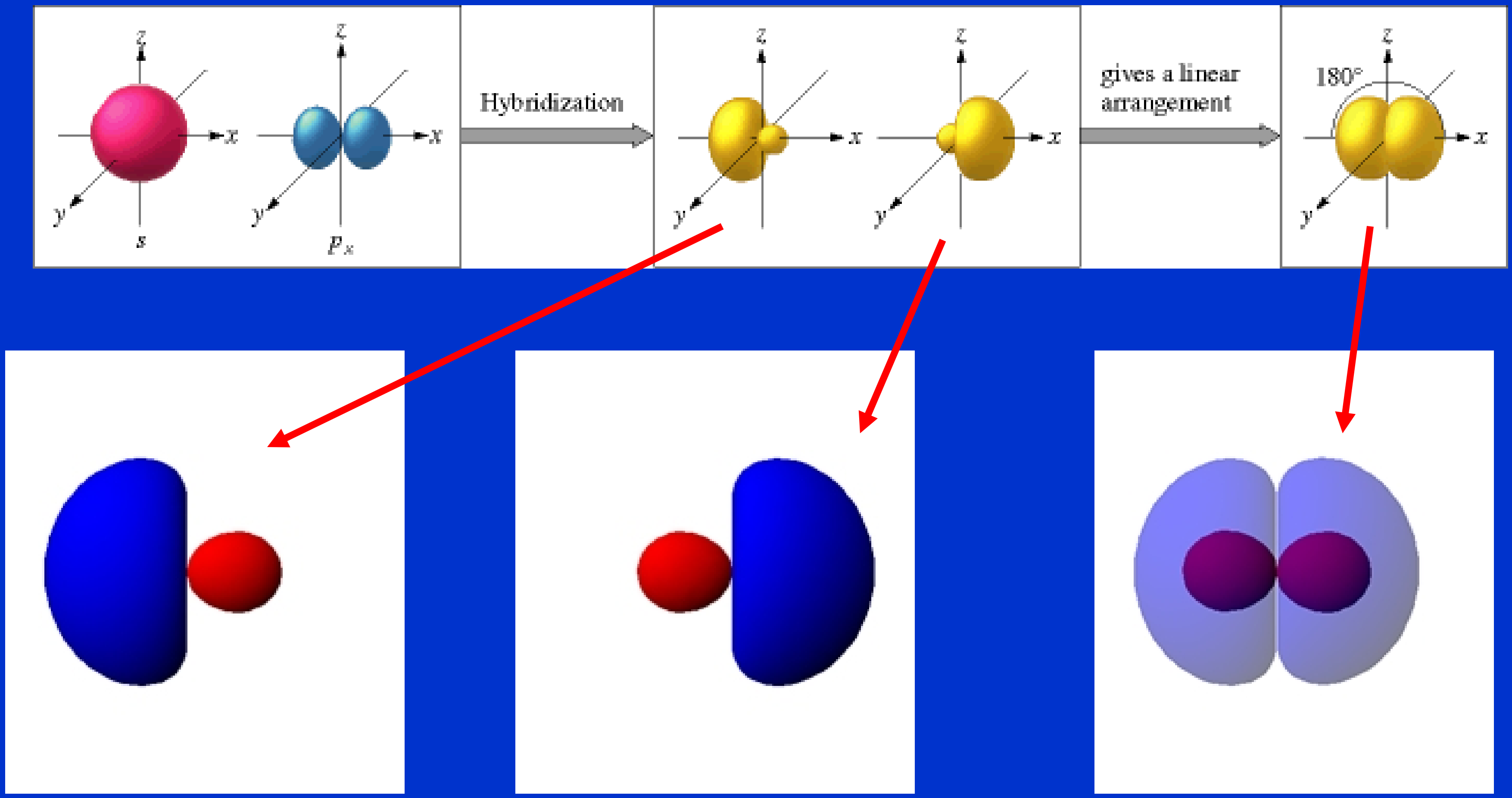


sp-Hybridization

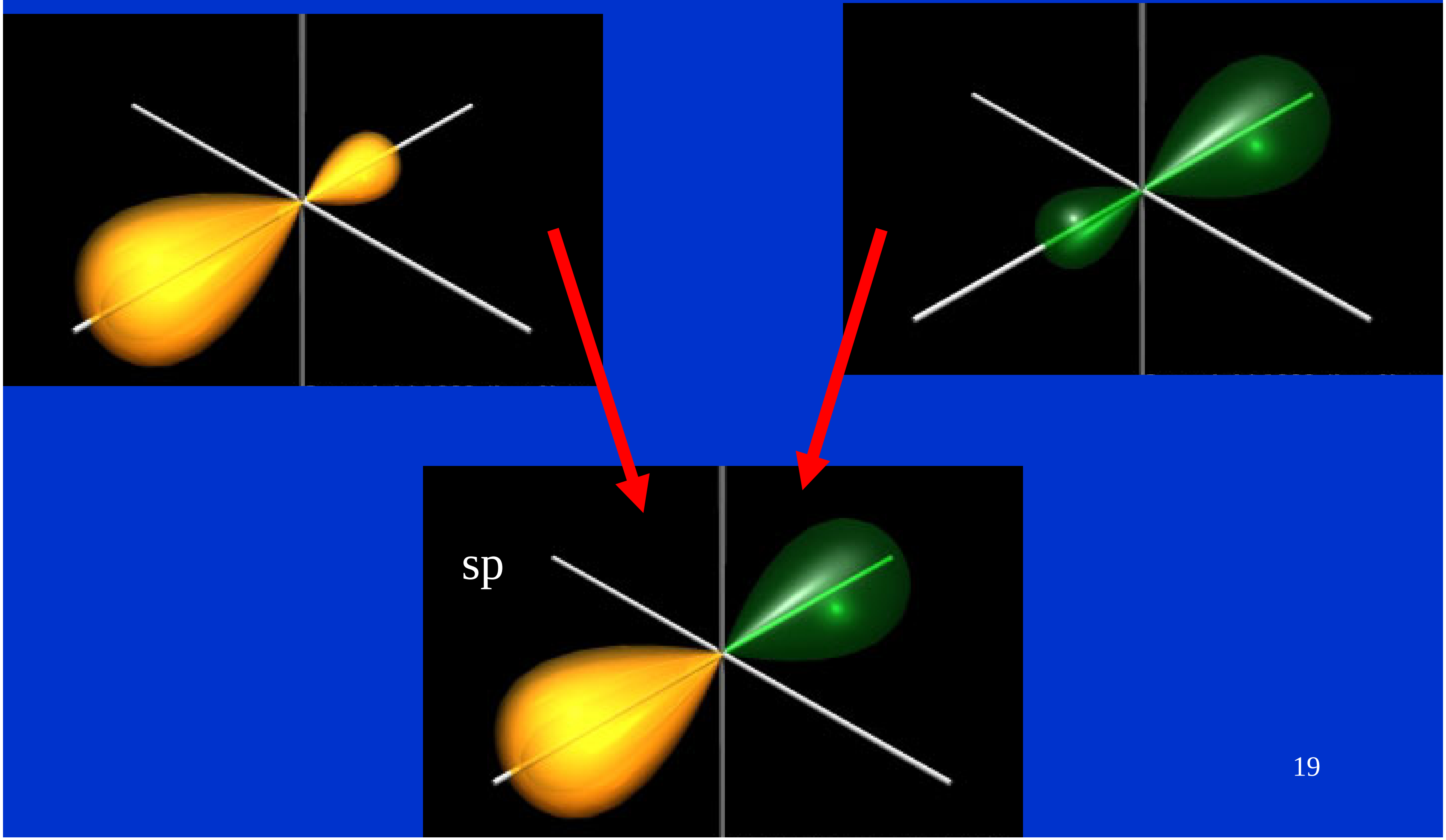




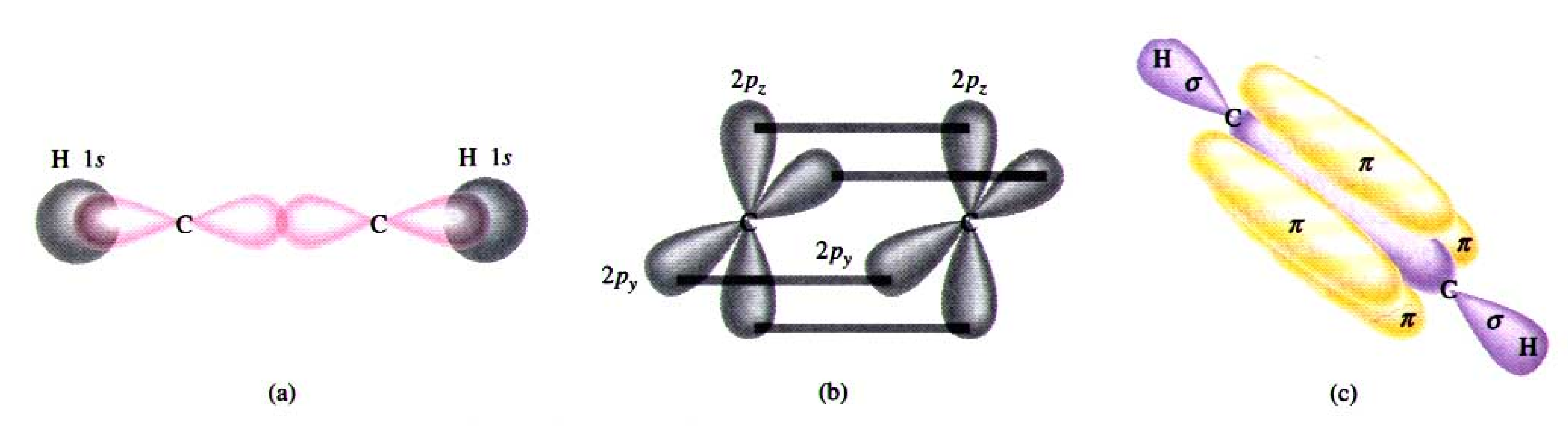
sp-Hybridization



sp-Hybridization

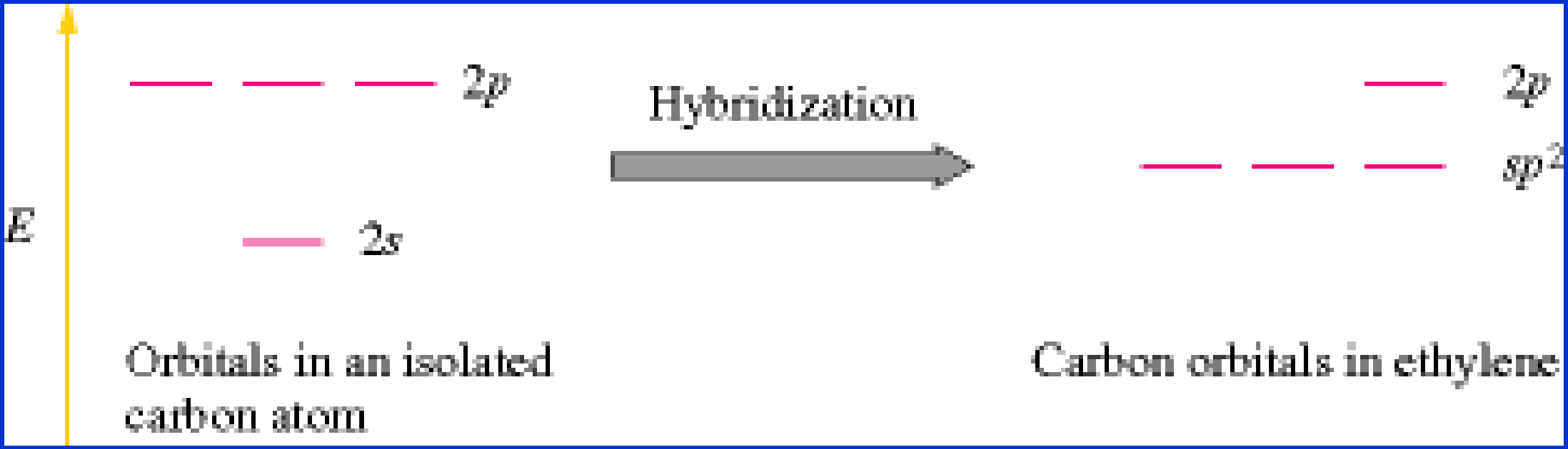


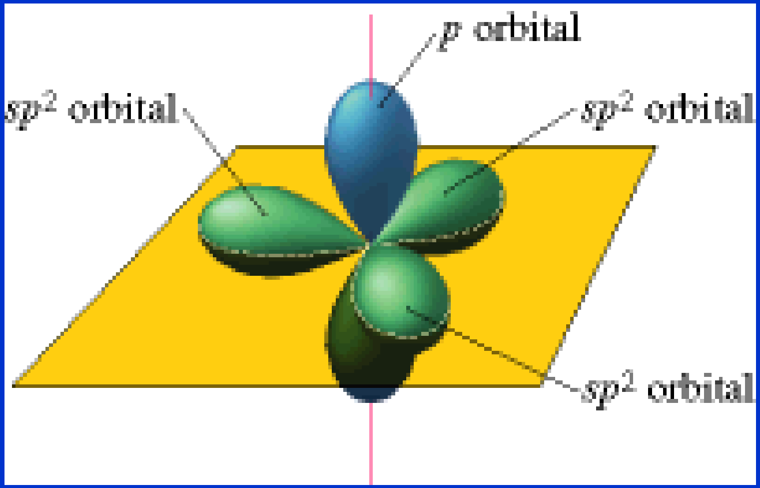
Acetylene



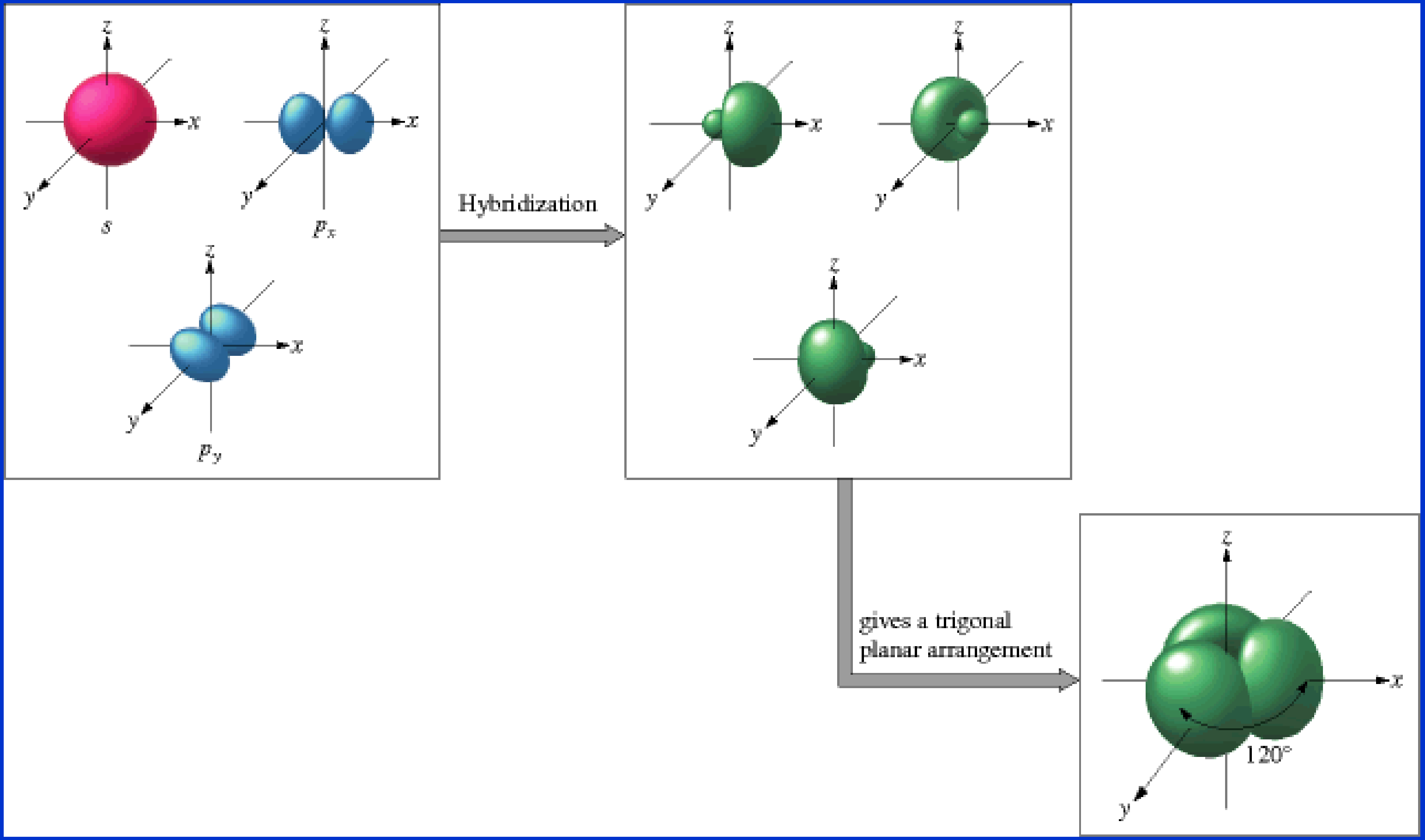
- 2 σ bonds - C(sp)–H(s) overlap
- 1 σ bond - C(sp)–C(sp) overlap
- 2 perpendicular π- bonds (x, y), C(p)–C(p) overlap

sp^2-Hybridization

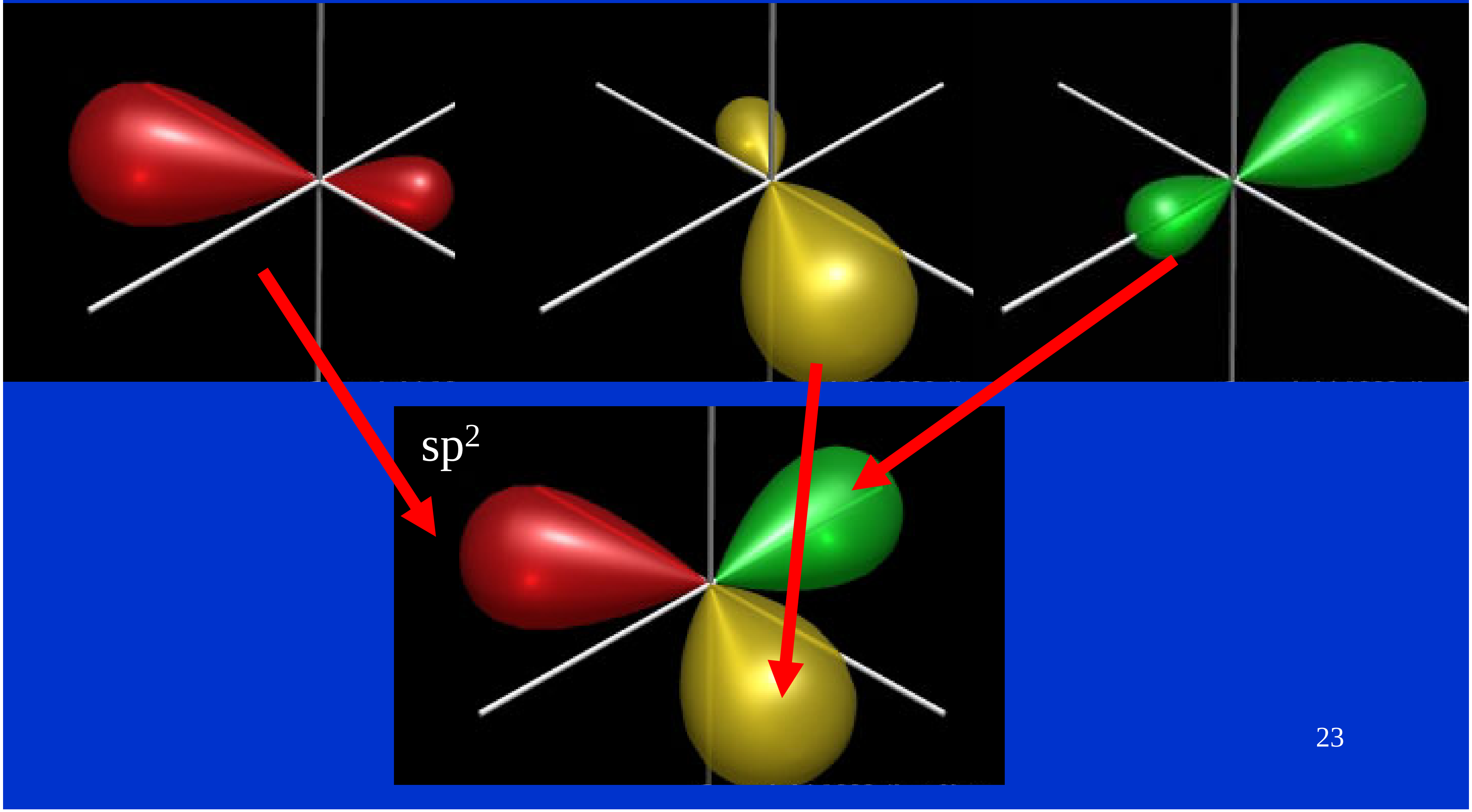




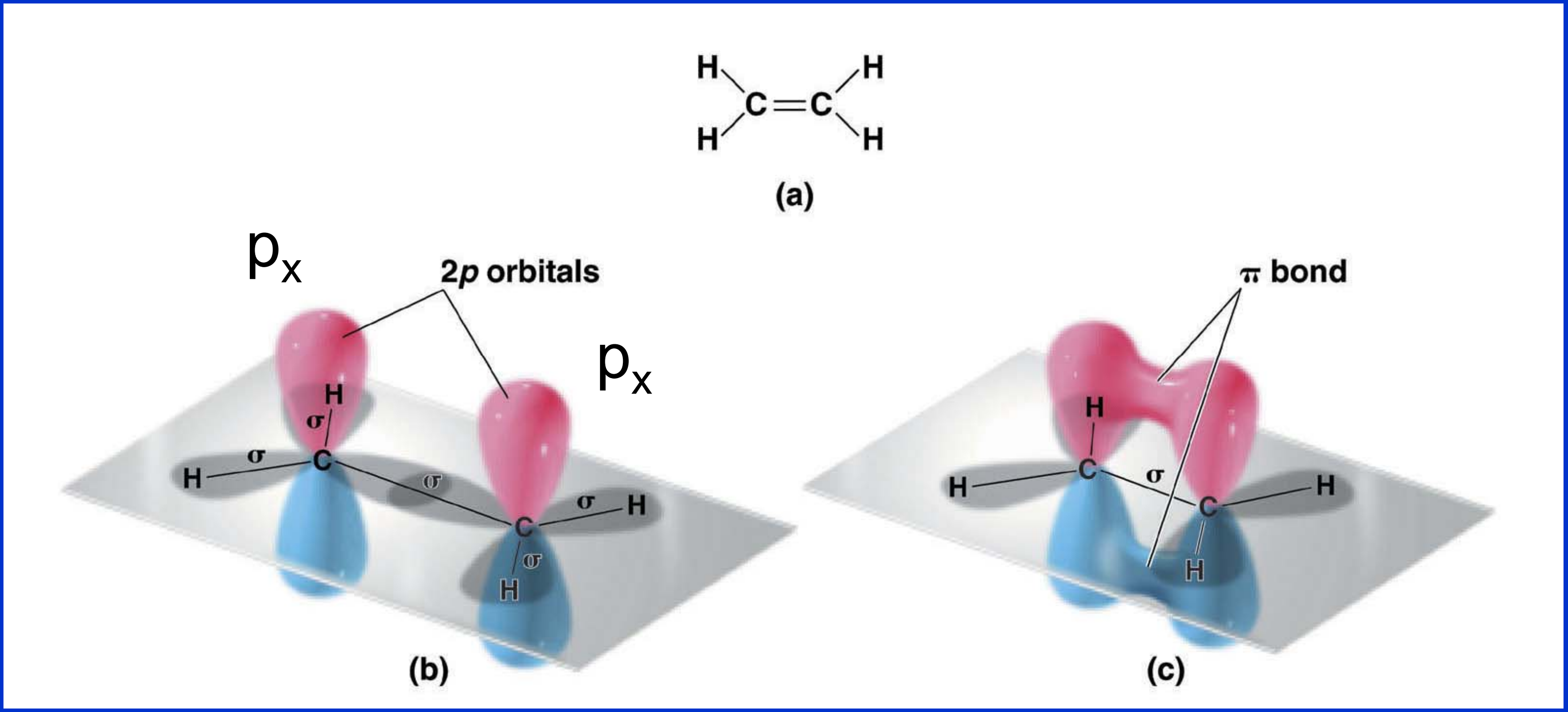
sp^2-Hybridization



sp^2-Hybridization

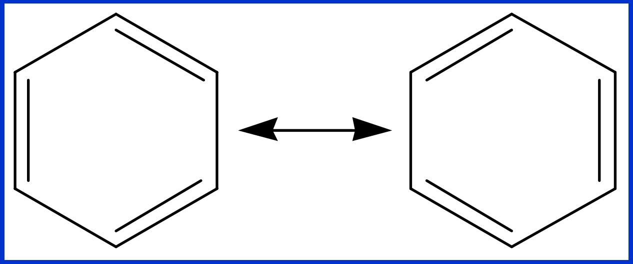


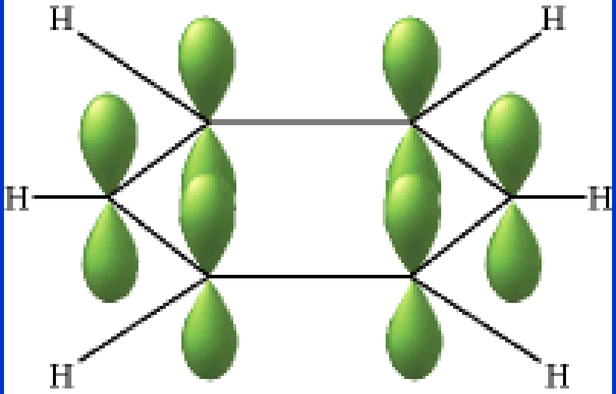
Ethylene

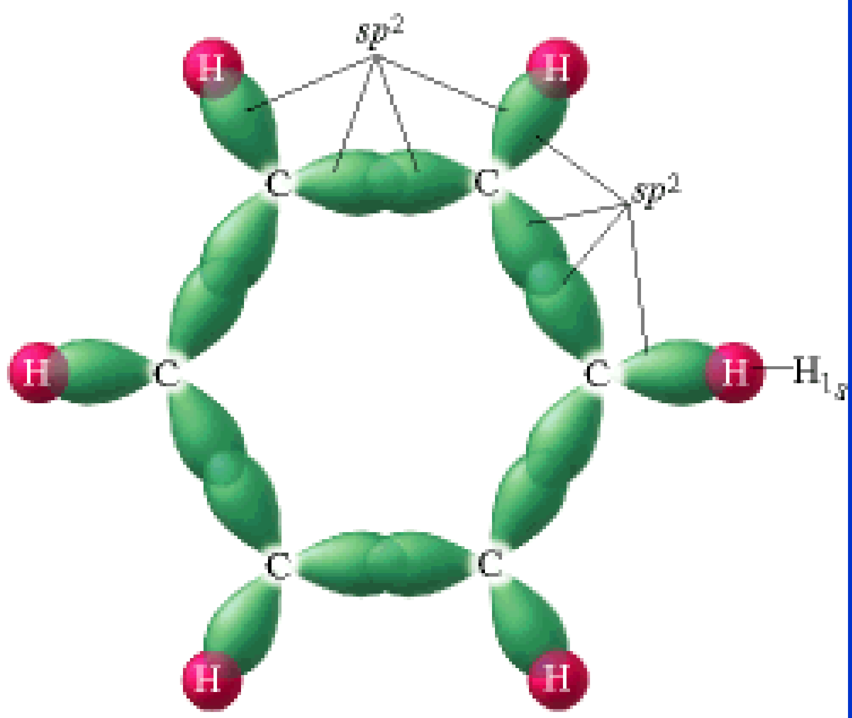


- 4 σ bonds - C(sp^2)–H(s) overlap
- 1 σ bond - C(sp^2)–C(sp^2) overlap
- 1 π bond - C(p_x)–C(p_x) overlap

Benzene





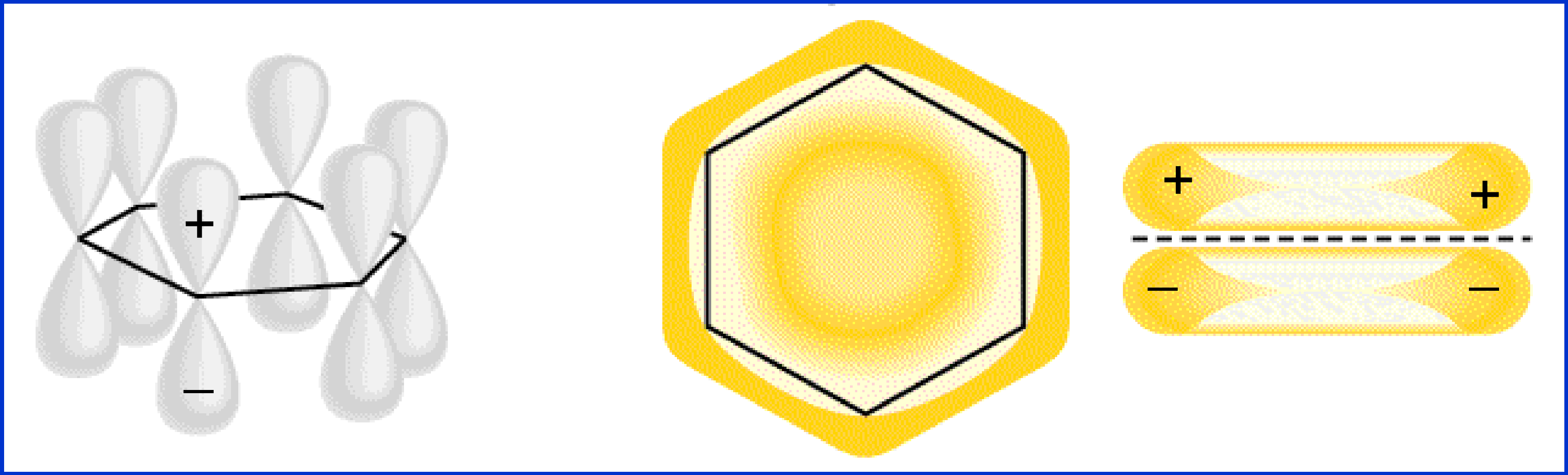


- Each C uses 3 sp^2 orbitals for 3 σ-bonds

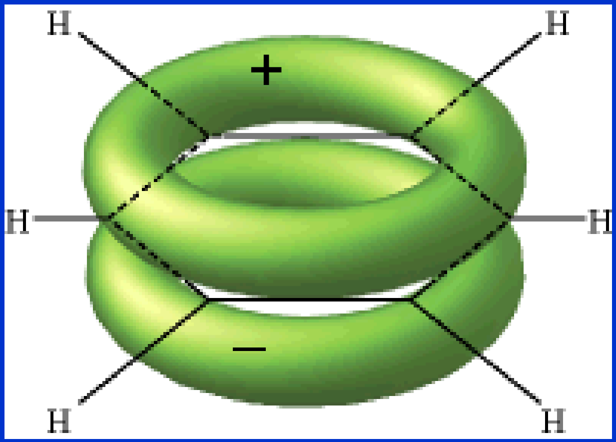
2 C–C bonds and 1 C–H bond

- One $2p_x$ orbital on each C remains unused for σ-bonding

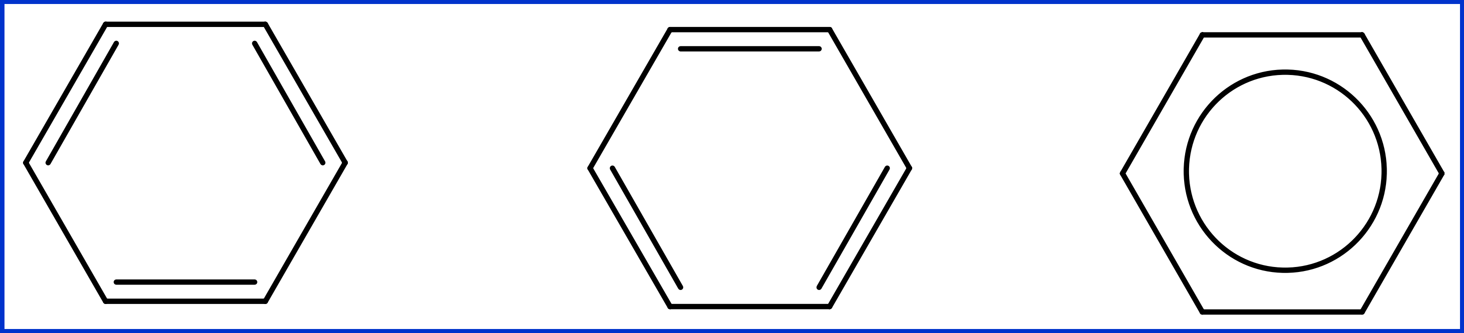
Benzene



Six C $2p_x$ orbitals used for 3 π-bonds

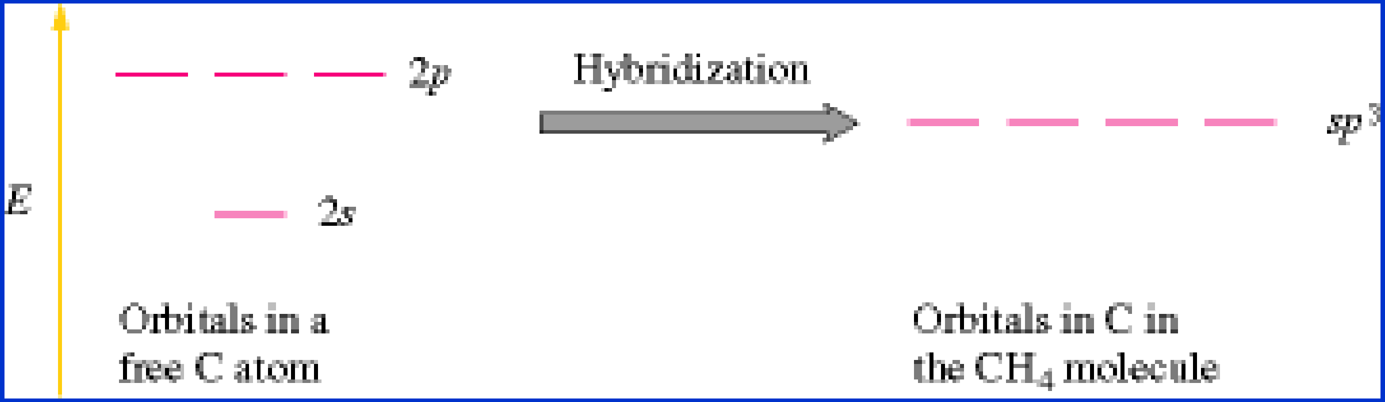


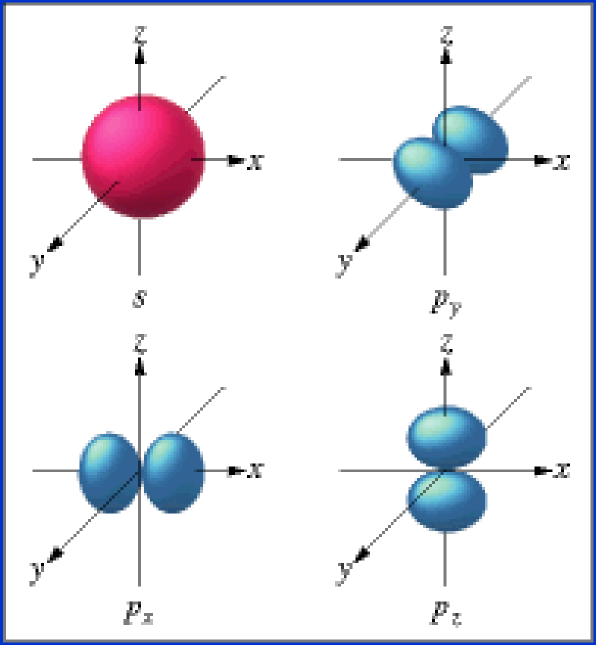
Benzene

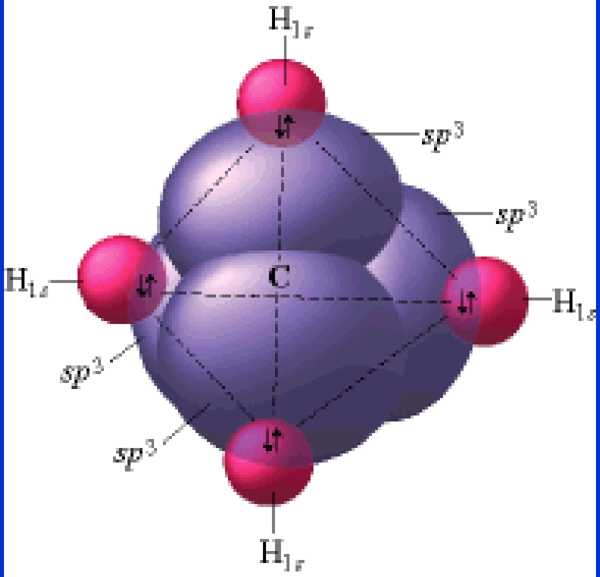


(a) Localized π bonds (b) Localized π bonds (c) Delocalized π bonds

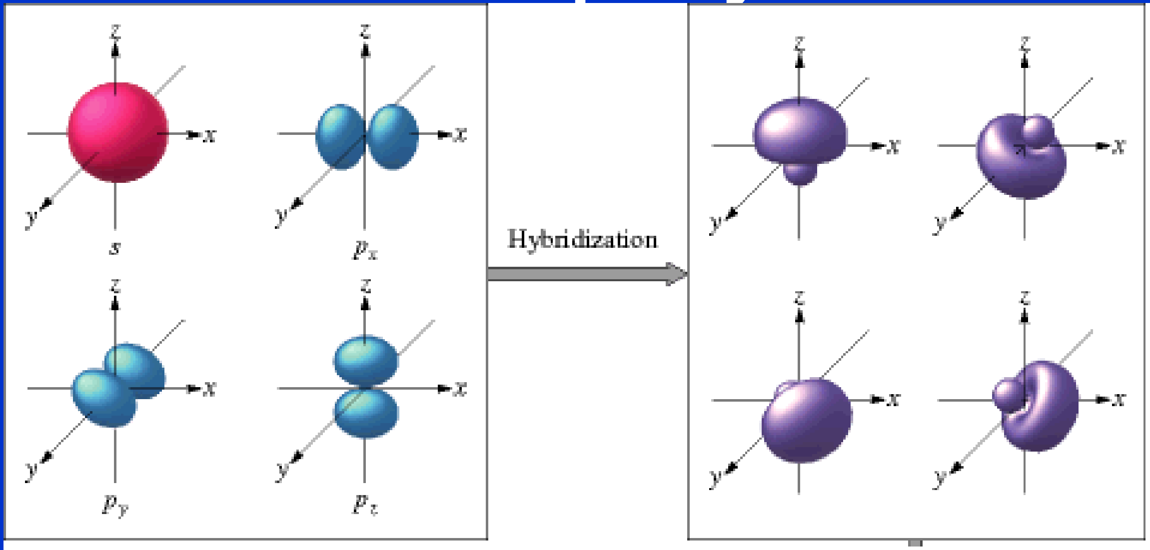
sp^3-Hybridization

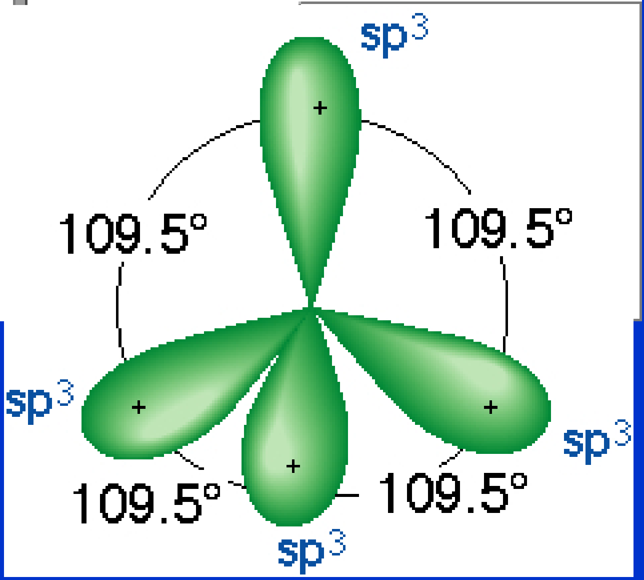




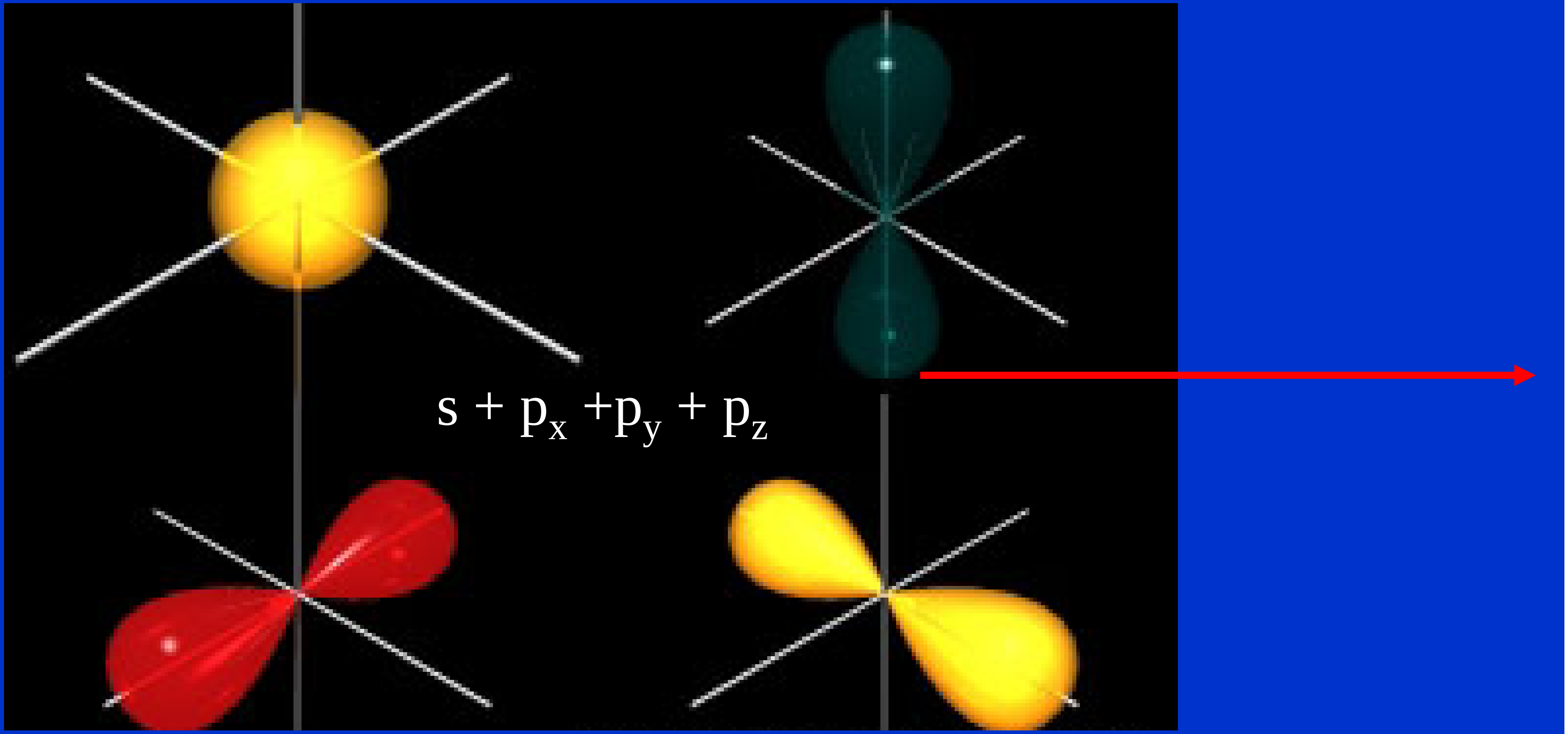


sp^2-Hybridization

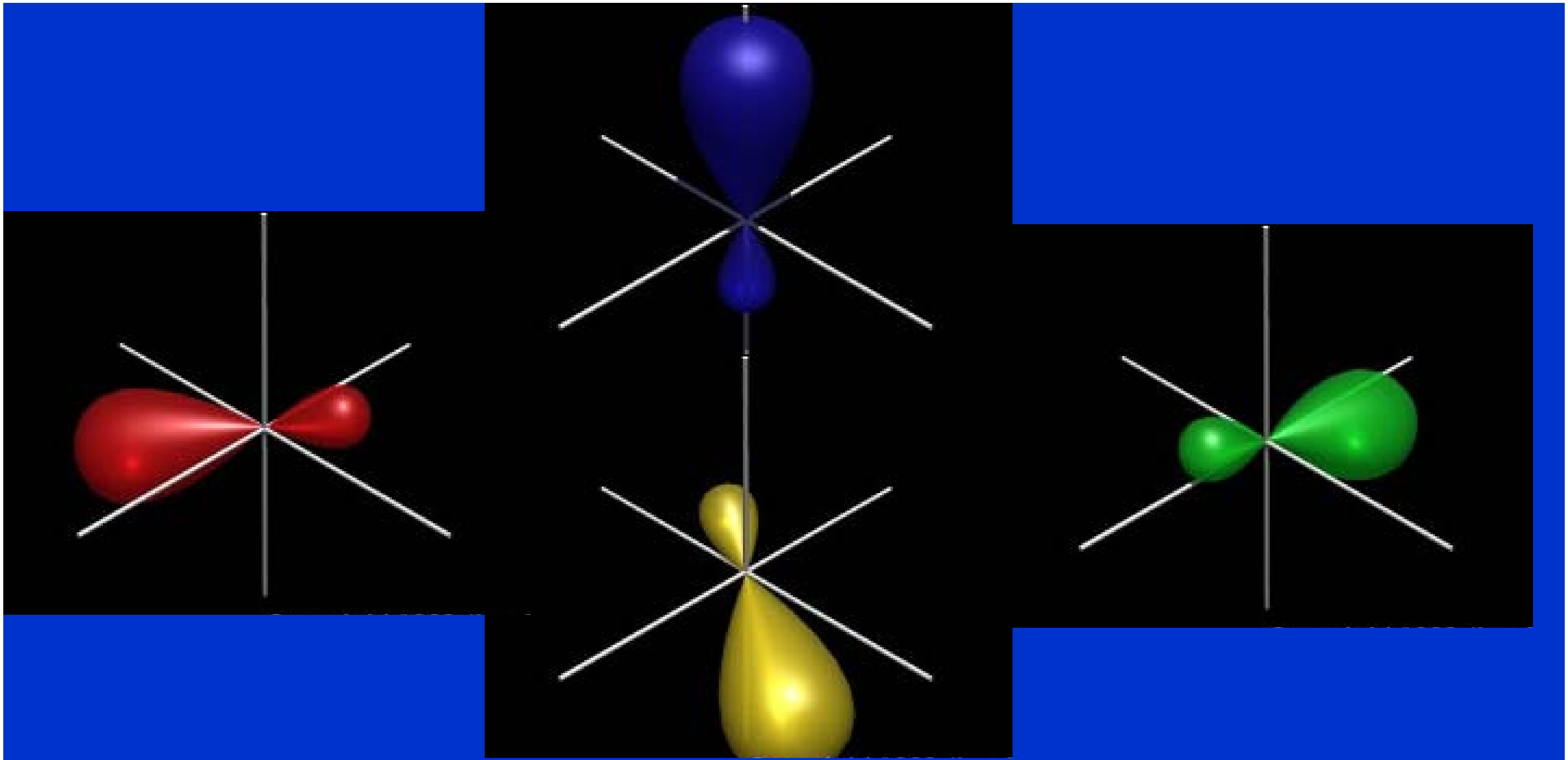


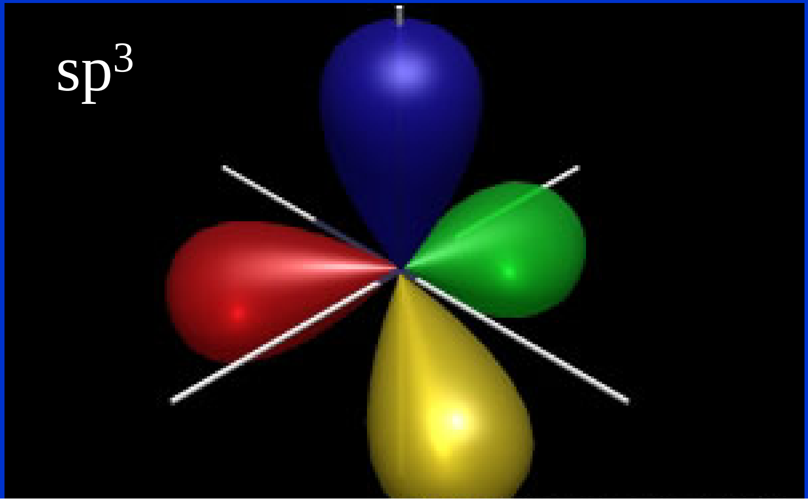


sp^2-Hybridization



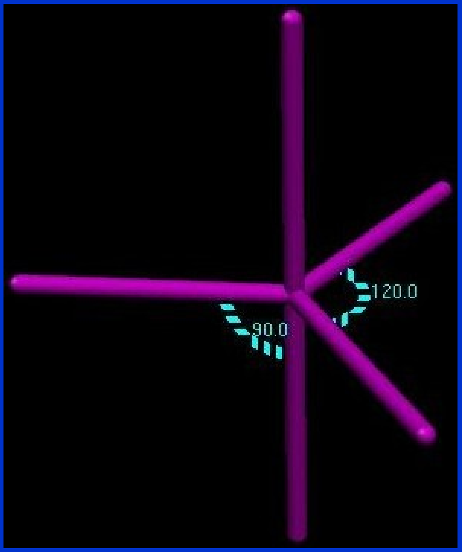
$s + p_x + p_y + p_z$



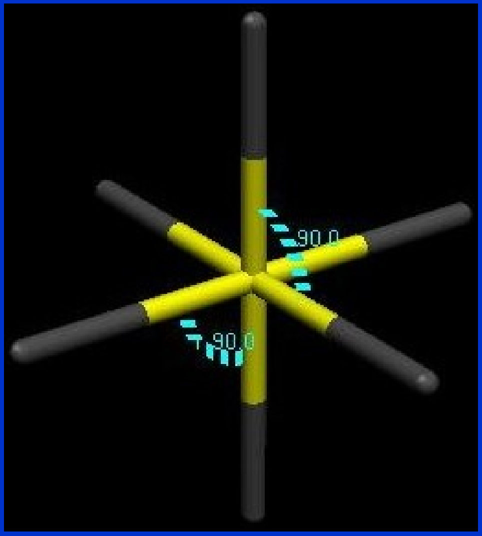

sp^3

sp^3d^n - Hybridization

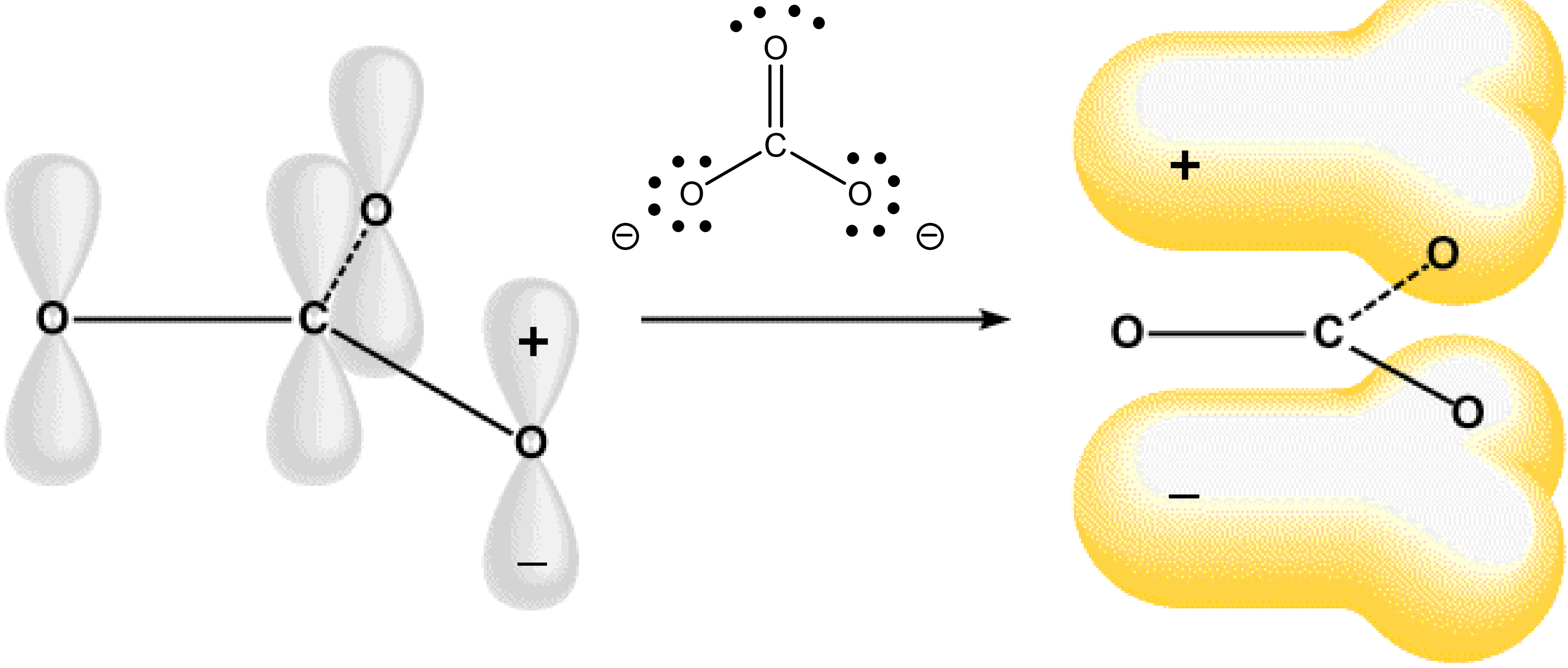
sp^3d



sp^3d^2



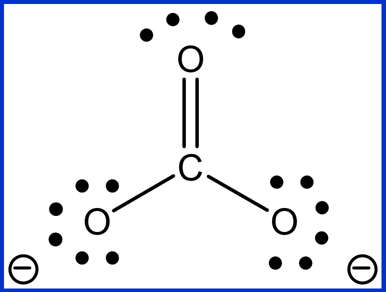
Bonding in CO_3^{2-} and NO_3^{-}



3 σ bonds - C(sp^2)–O(sp^2) overlap

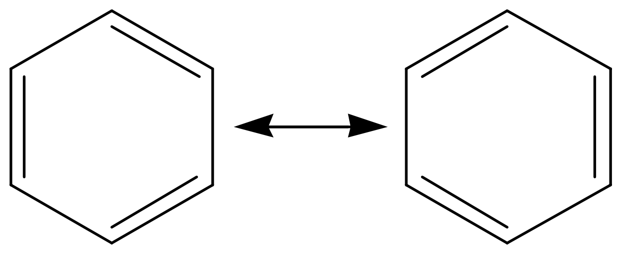
1 π-bond - C(p_x)–O(p_x) overlap

Bond Order



4 (3+1) bonding electron pairs / 3 bonds

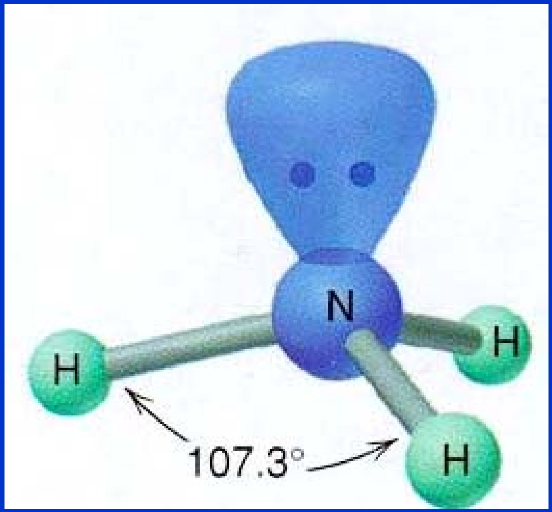
Bond Order = 1.3333



9 (6+3) bonding electron pairs / 6 bonds

Bond Order = 1.5

Electronegativity and Bonding Angles

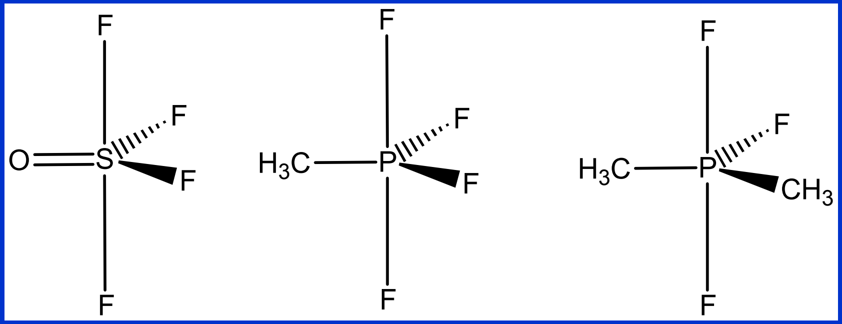


	Bonding Angle	Hybridization
NH_3	107.3°	sp^3
PH_3	93.8°	↓
AsH_3	91.8°	
SbH_3	91.3°	s + 3p
NF_3	102.5°	
OH_2	104.5°	
OF_2	103.2°	

Incr. $\Delta\chi$ decreases bonding angles

Bent’s Rule

More electronegative substituents prefer hybrid orbitals with smaller s-contribution and conversely, electropositive substituents (better donors) prefer hybrid orbitals with higher s-contribution

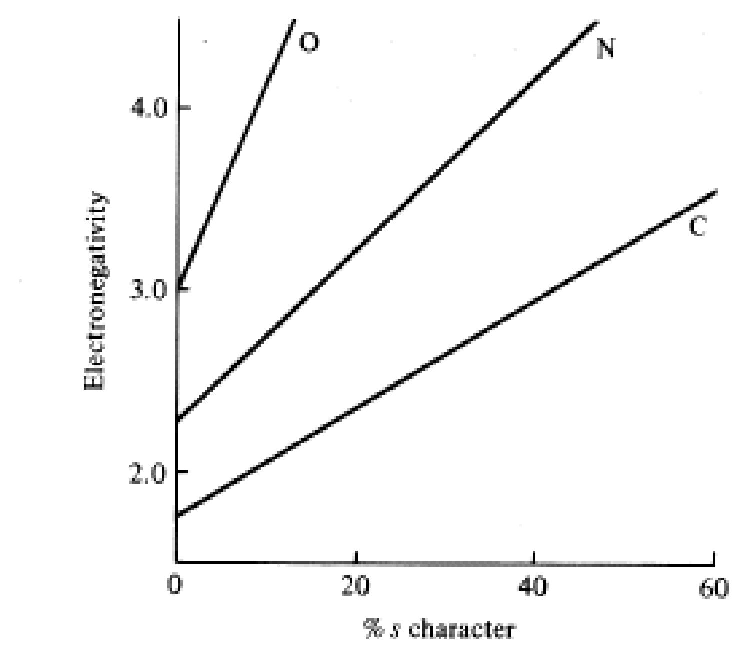


Better donors occupy equatorial plane in TBP and basal plane in SP

Free electron pair is the best donor = substituent with zero electronegativity

Hybridization and Electronegativity

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



s-character

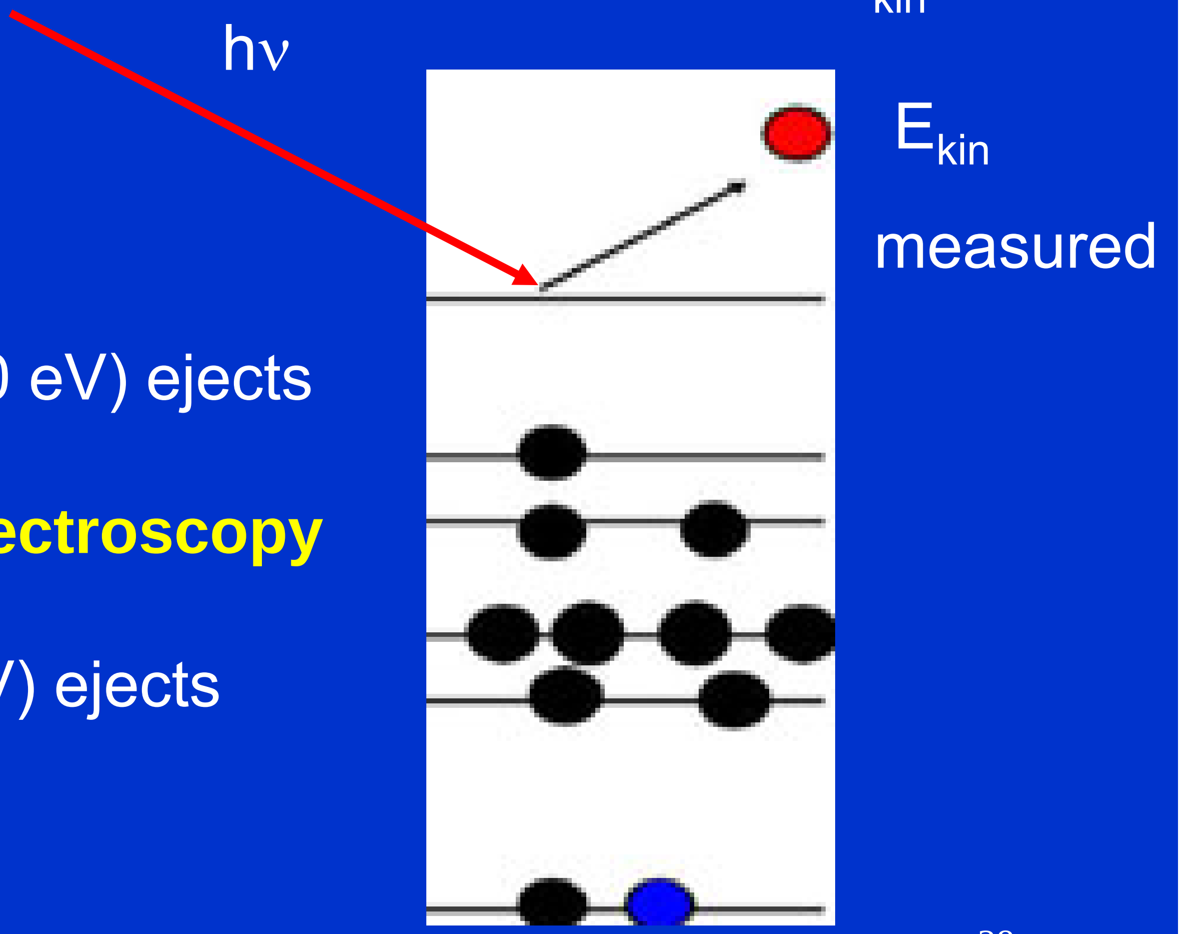
p-character

Electron in an s-orbital is bound more strongly than in a p-orbital

Orbital with higher s-character has a higher electronegativity

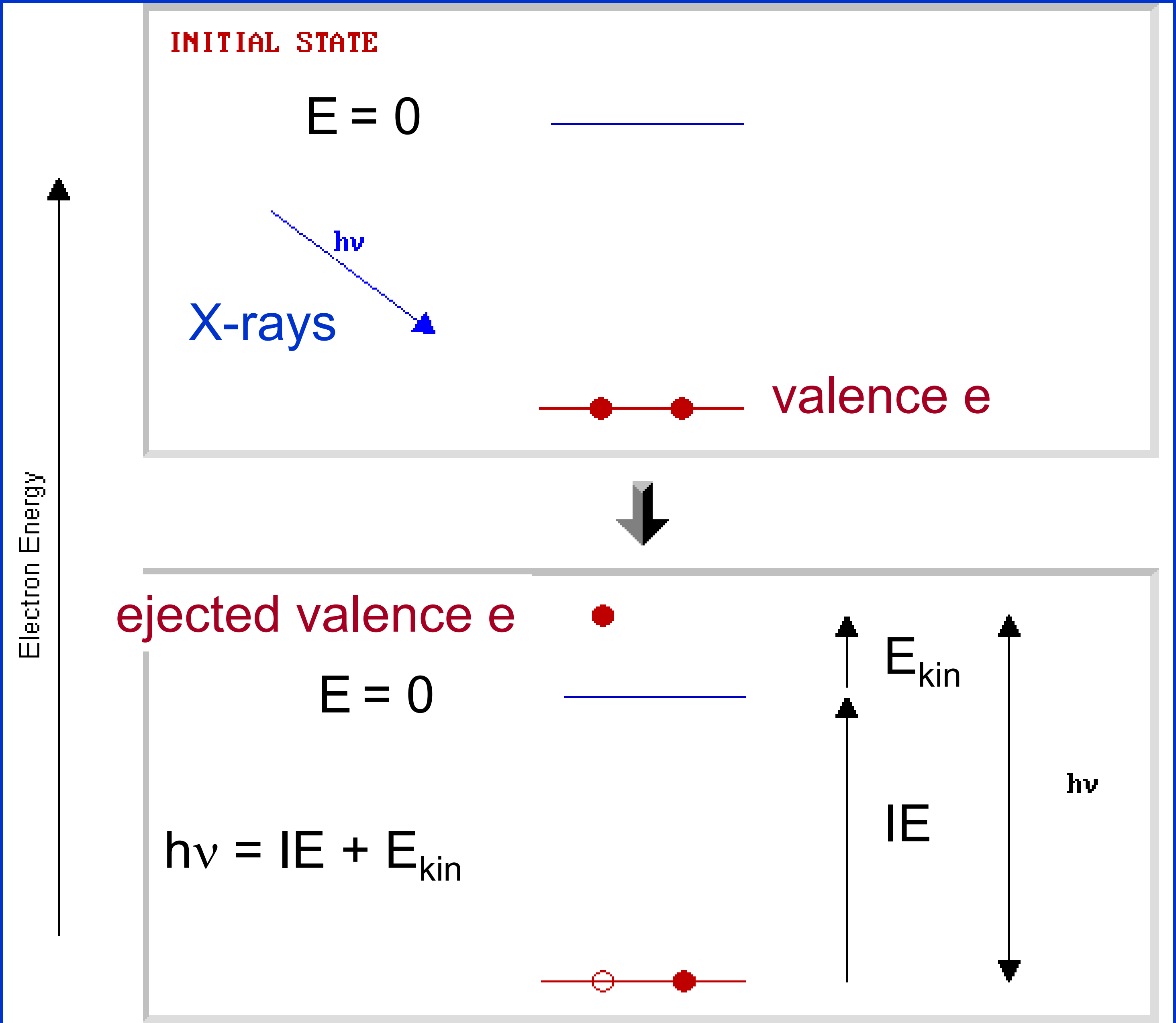
PES = Photoelectron Spectroscopy

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



X-ray Photoelectron Spectroscopy (XPS)
- Soft X-rays (200-2000 eV) ejects inner e

UV Photoelectron Spectroscopy (UPS)
- vacuum UV (10-45 eV) ejects valence e



INITIAL STATE

$E = 0$

$h\nu$

X-rays

valence e

Electron Energy

ejected valence e

$E = 0$

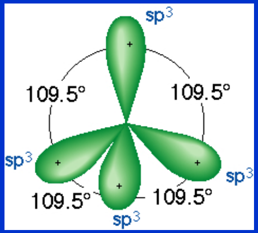
E_{kin}

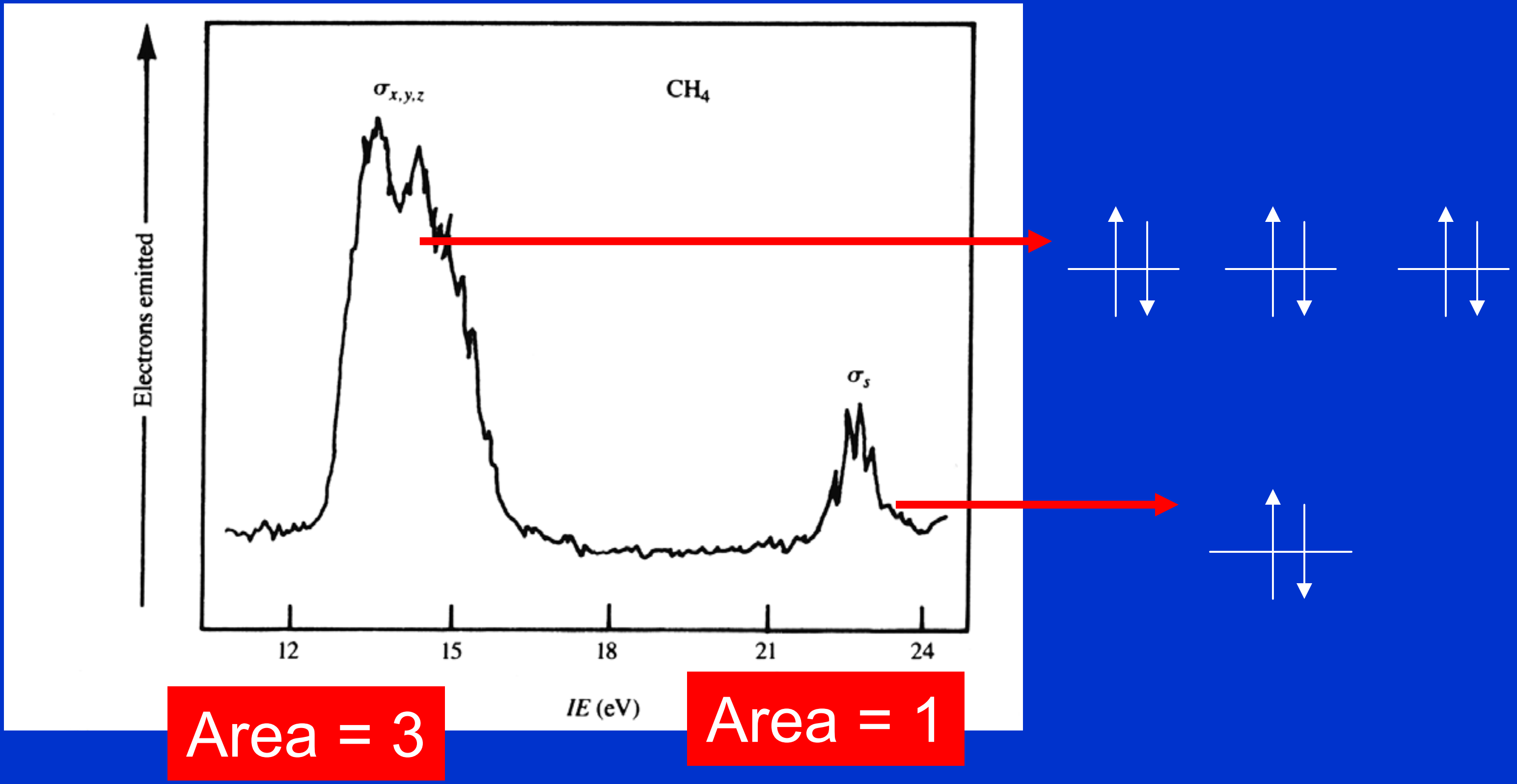
IE

$h\nu$

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

PES of Methane



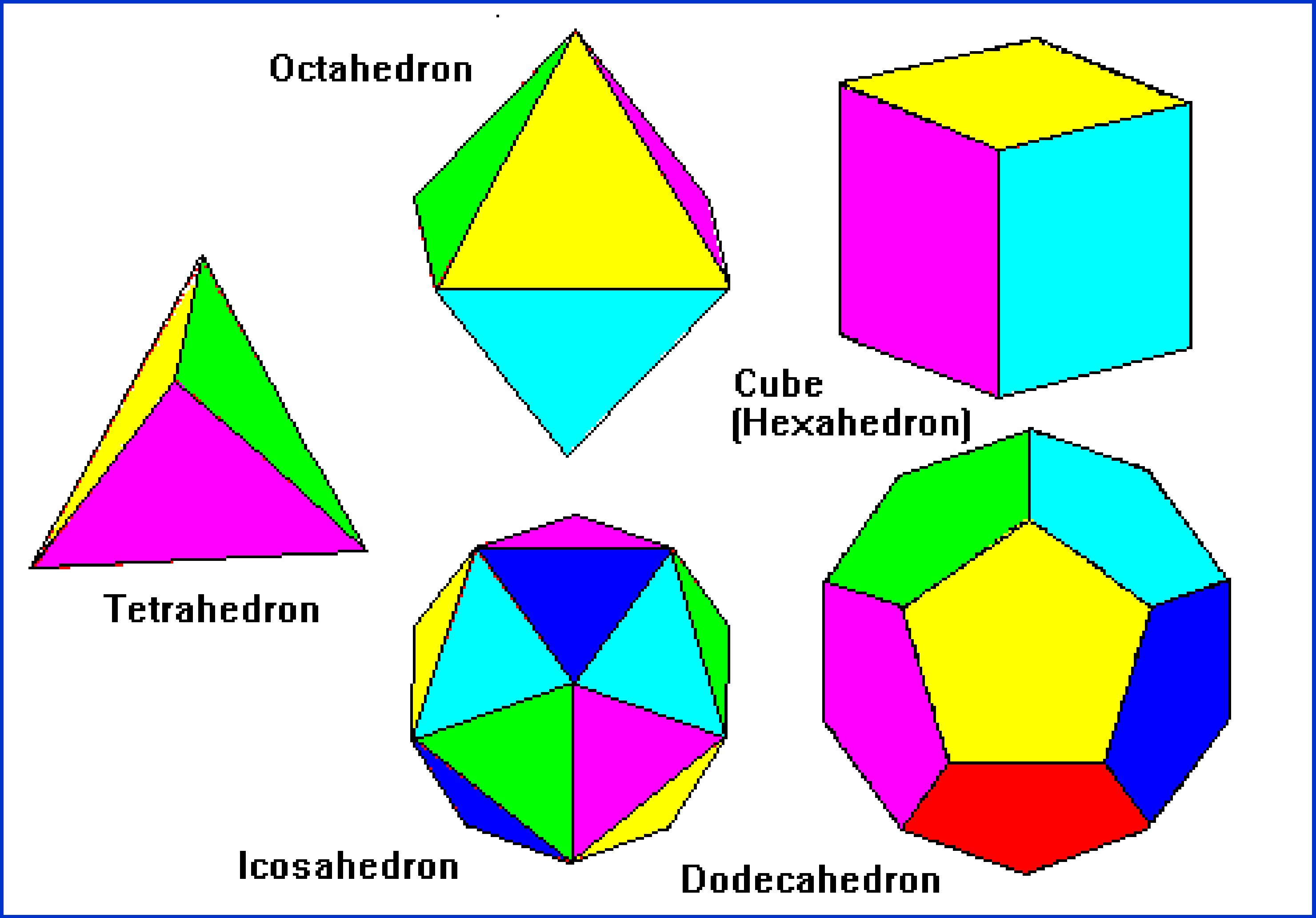


Area = 3

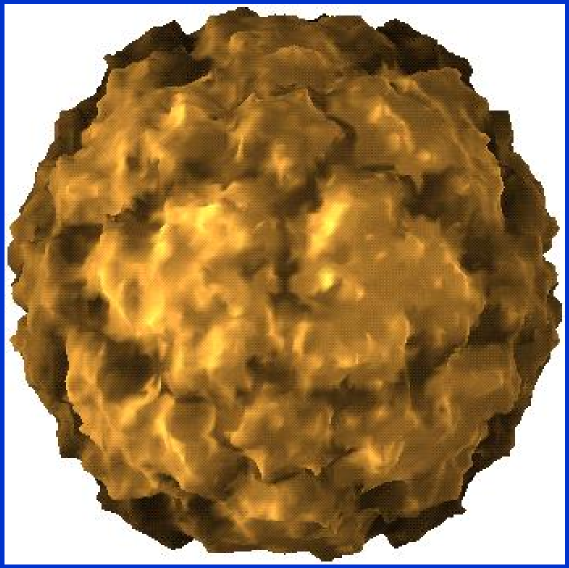
Area = 1

Inconsistent with hybridization model 4 sp^3

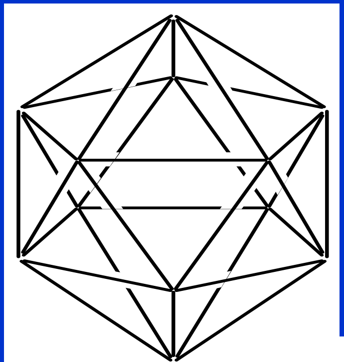
Symmetry – Platonic Solids



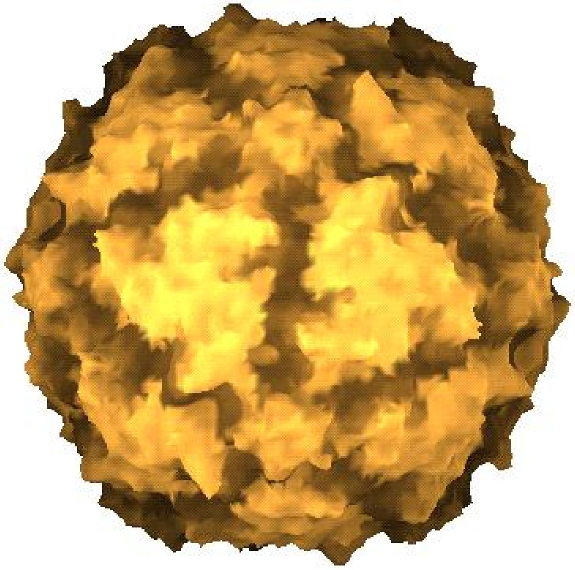
Symmetry



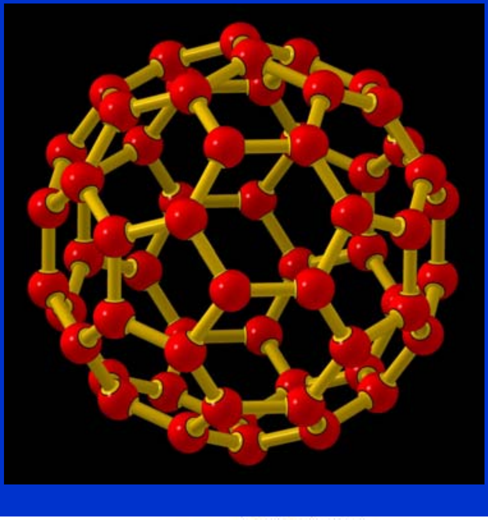
Virus of common cold

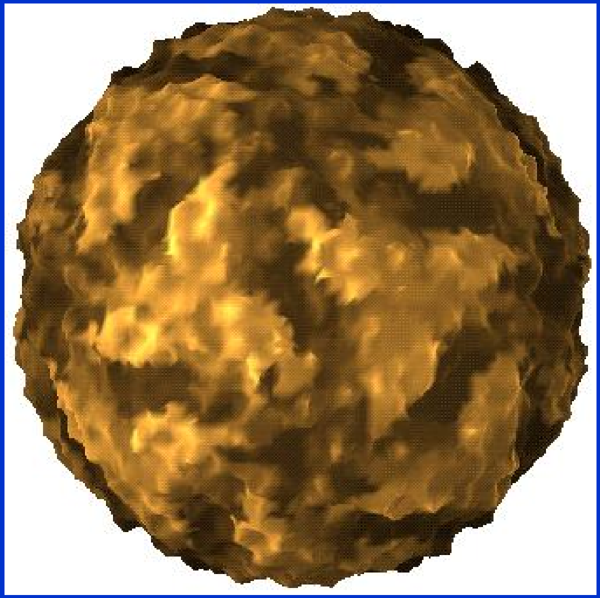


Icosahedron



Virus of polio

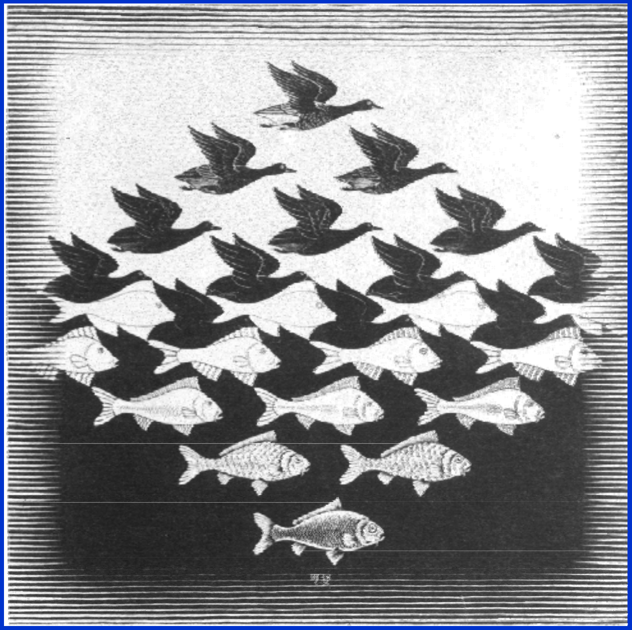


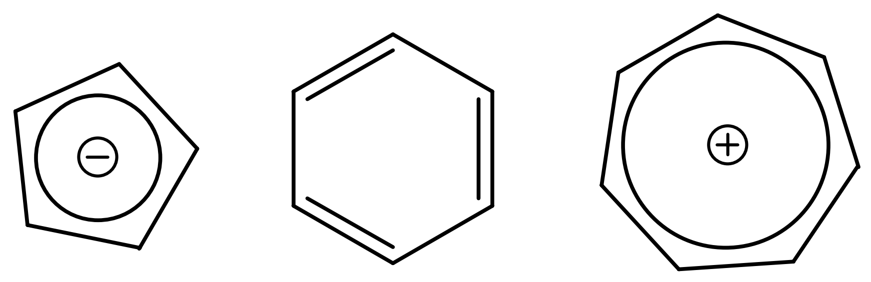


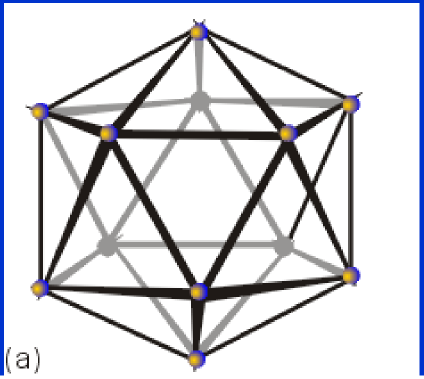
Virus of mouth and foot disease

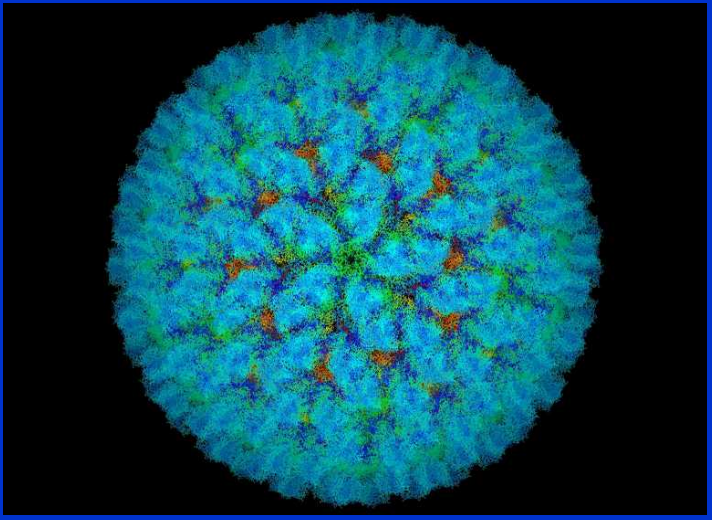
Symmetry of Molecules

Placement of atoms in moleculs = equivalent atoms





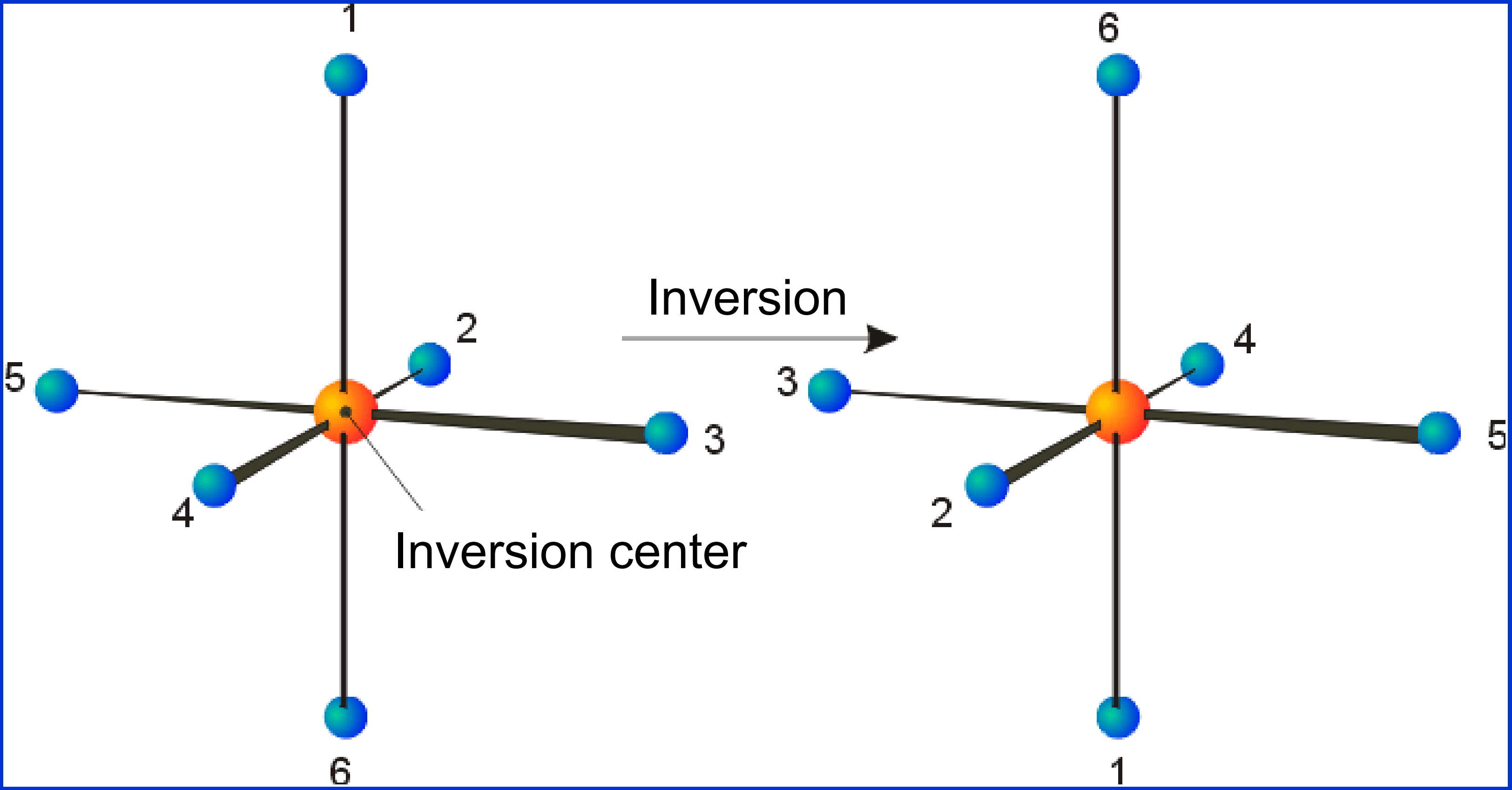




Symmetry Elements and Operations

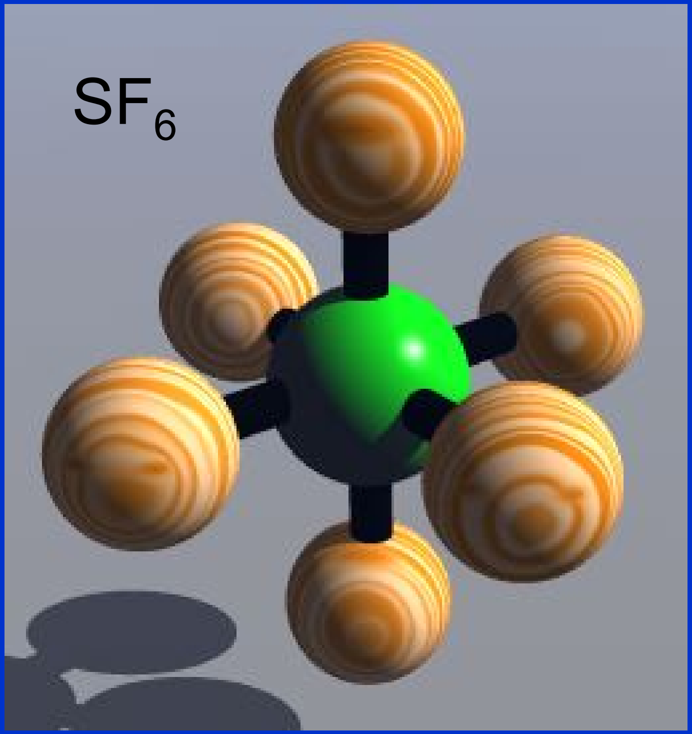
Symbol	Element	Operation	
E	Identity	Identity	No change, (= 1)
i	Inversion center	Inversion	Every point x,y,z translated to -x,-y,-z
C_n	Proper axis	Proper rotation	Rotation about axis by 360/n degrees
σ	Symmetry plane	Reflection	Reflection through plane
S_n	Improper axis	Improper rotation	1. rotation by 360/n 2. reflection through plane perpendicular to rotation axis

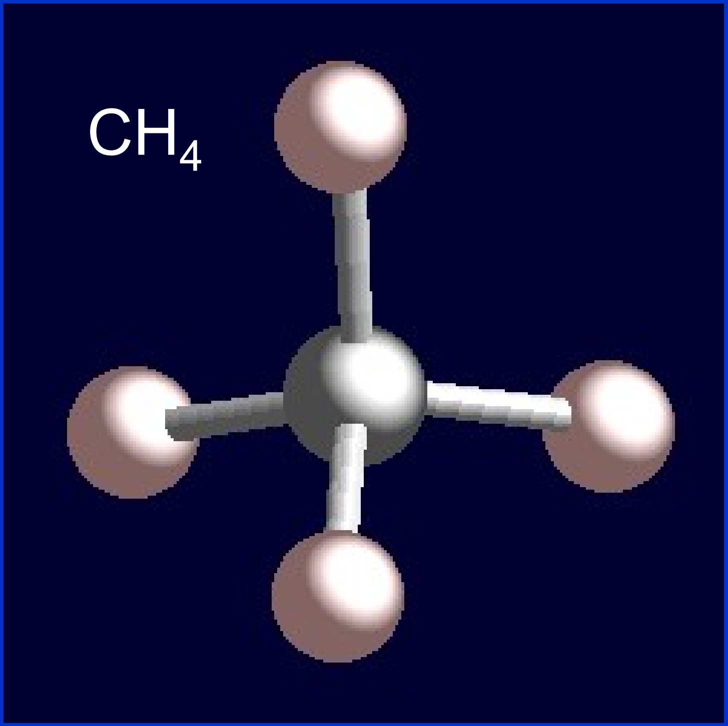
Inversion Center



New situation is indistinquishable from the original

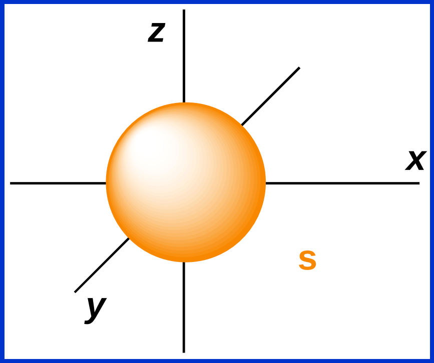
Inversion Center

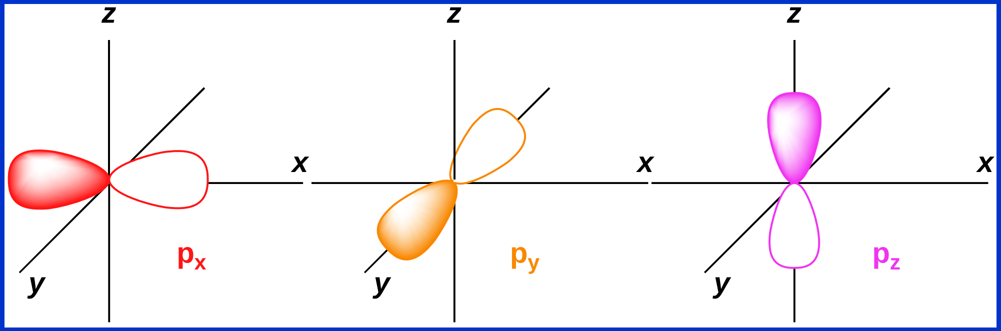


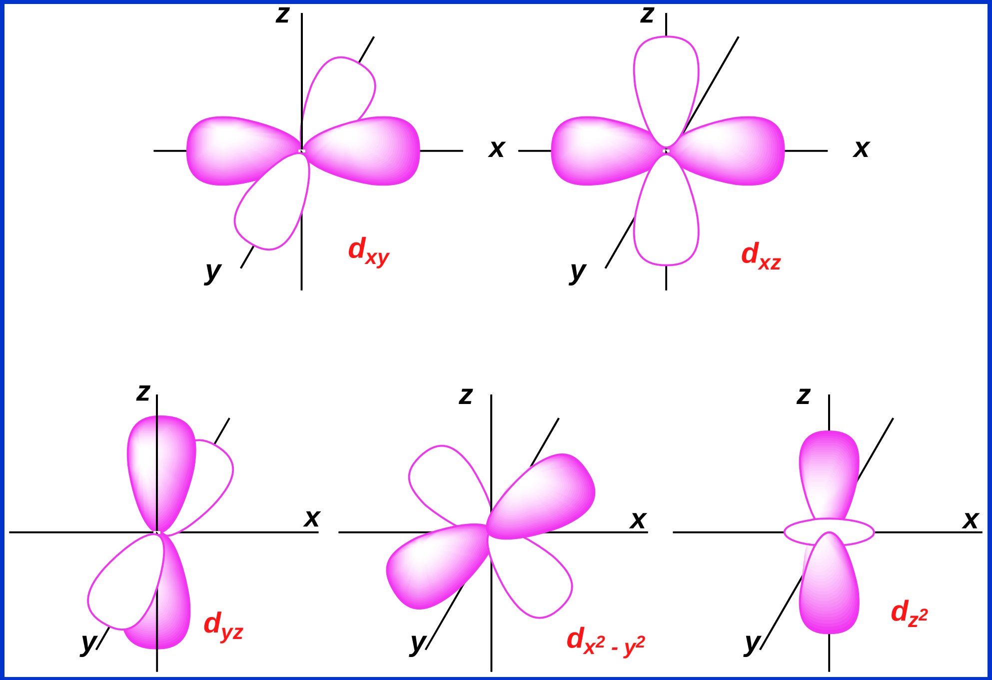


S = Inversion center

NO inversion center



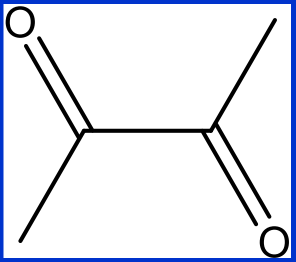




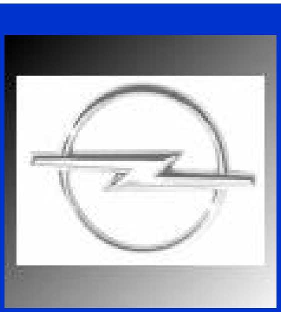
Orbitals

s and d **have** *i*

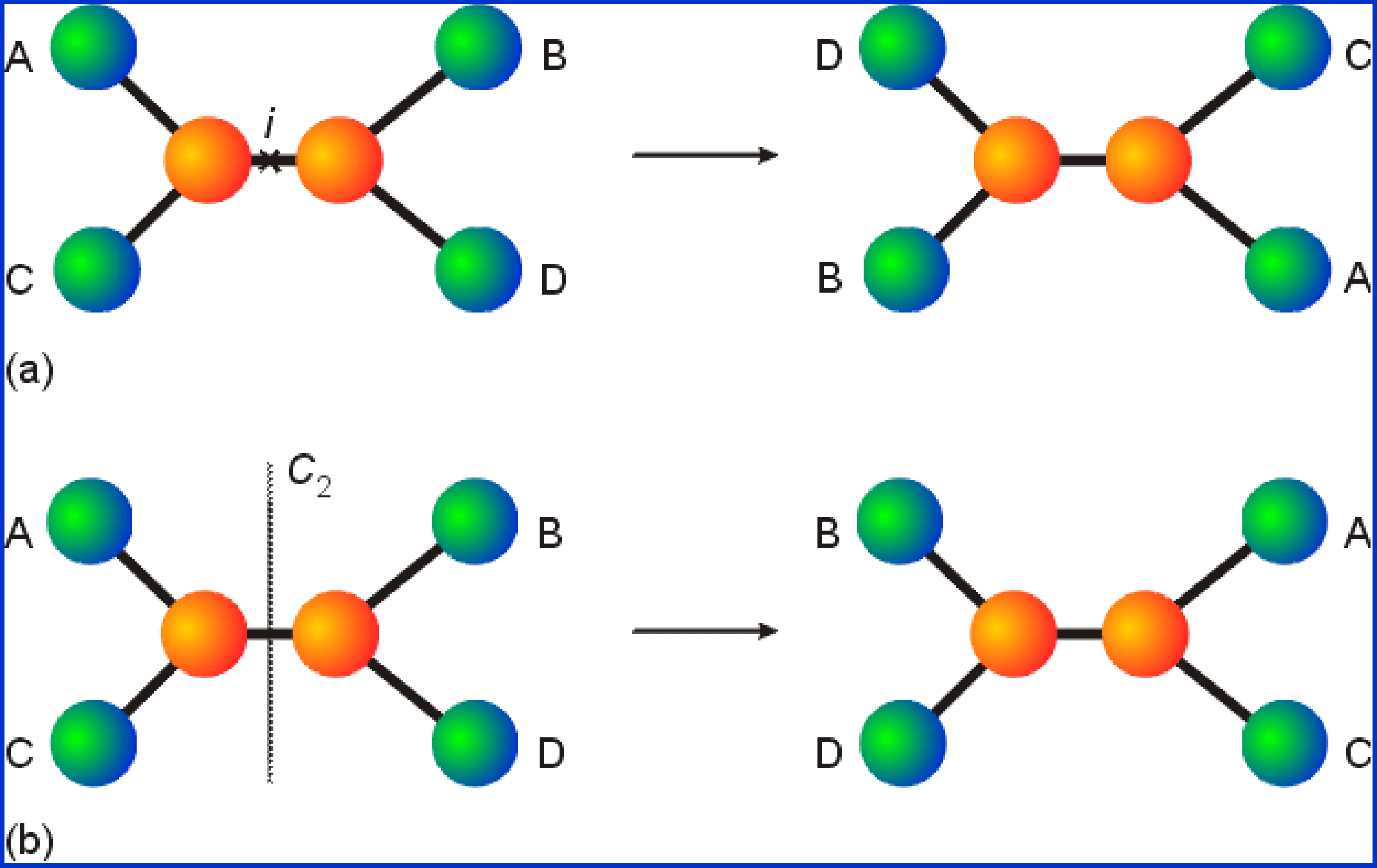
p and f do not have *i*



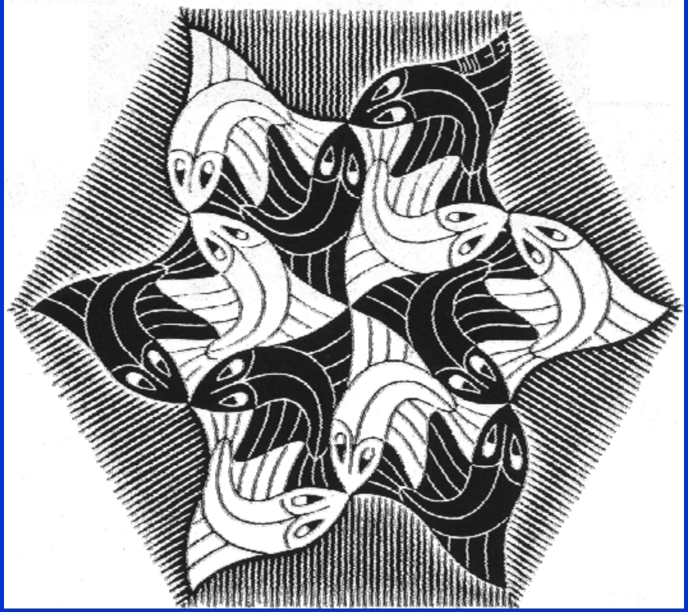
Proper Axis C_2



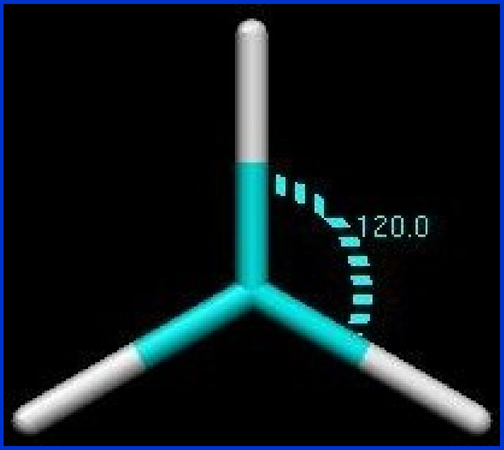
Rotation about axis by 360/2 degrees.
New situation is indistinquishable from the original



Proper Axis C_3

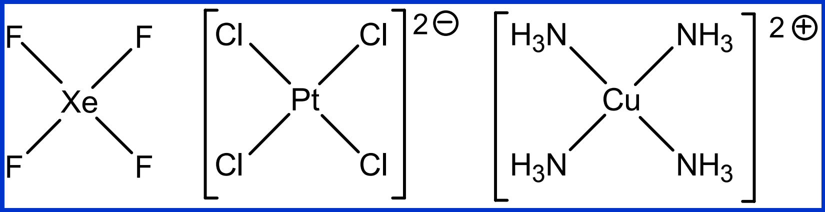


Rotation about axis by 360/3 degrees

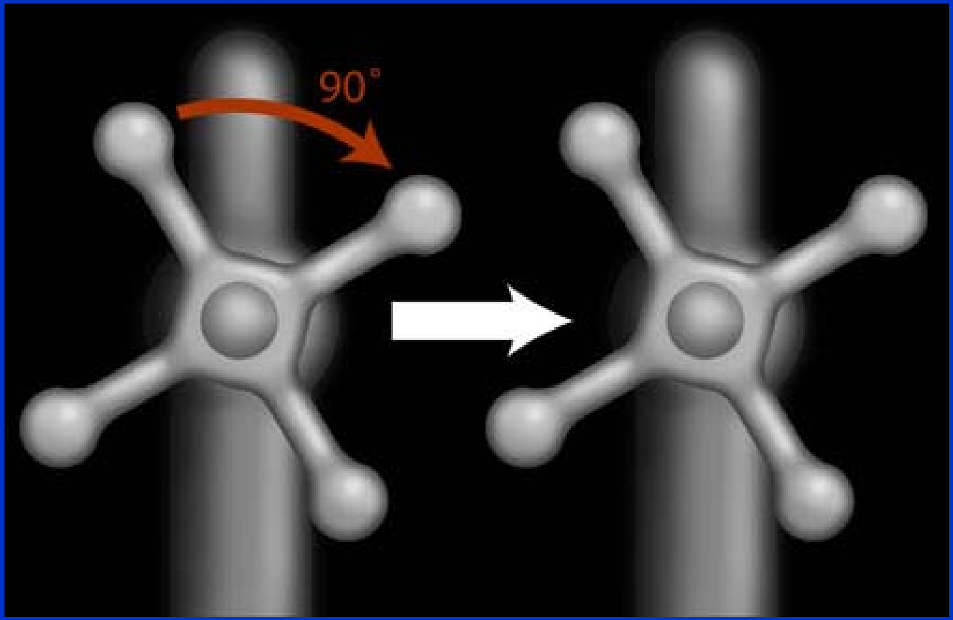


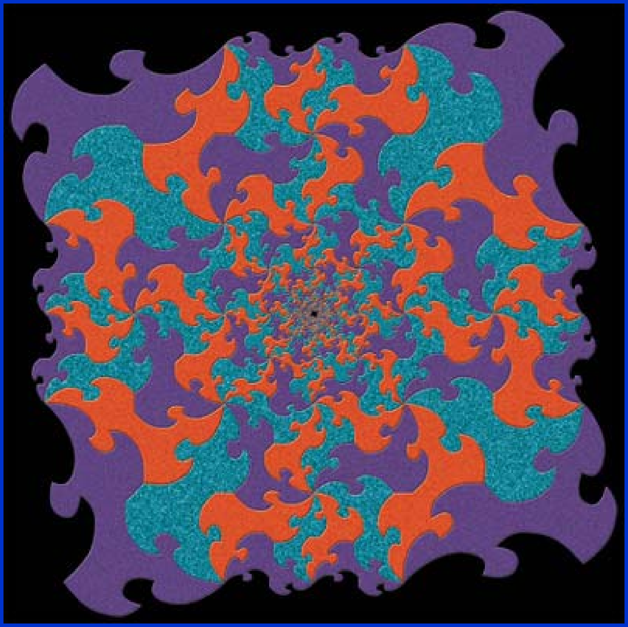
New situation is indistinquishable from the original

Proper Axis C_4



Rotation about axis by 360/4 degrees

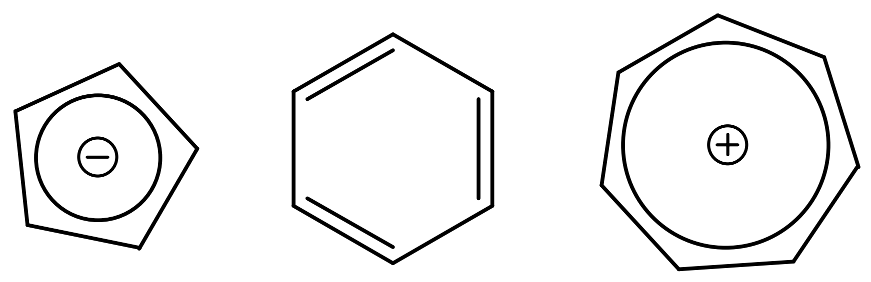


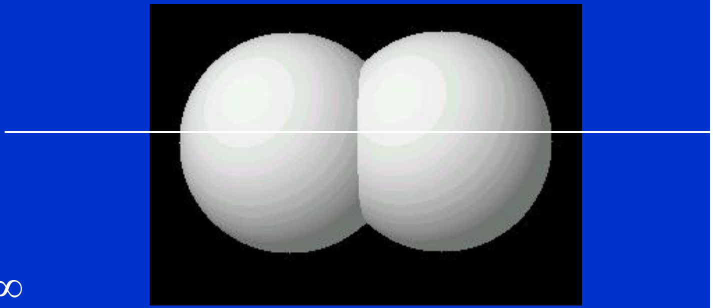


$$C_4^1 \rightarrow C_4^2 \rightarrow C_4^3 \rightarrow C_4^4 = E$$

New situation is indistinquishable from the original

Proper Axis C_n



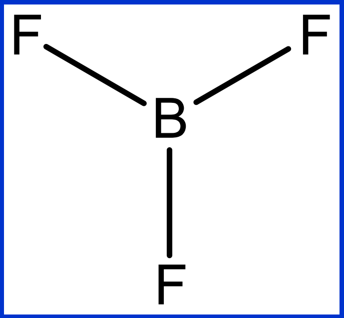


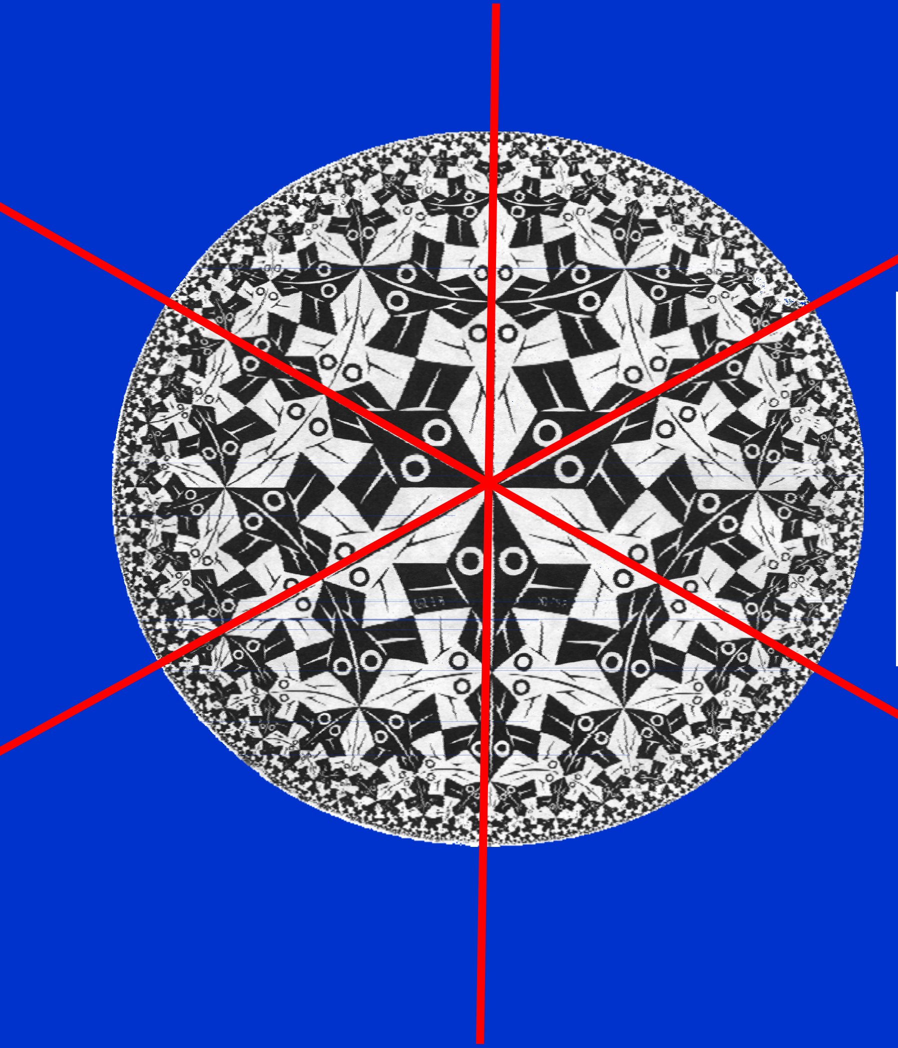
C_5, C_6, C_7,............................ C_∞

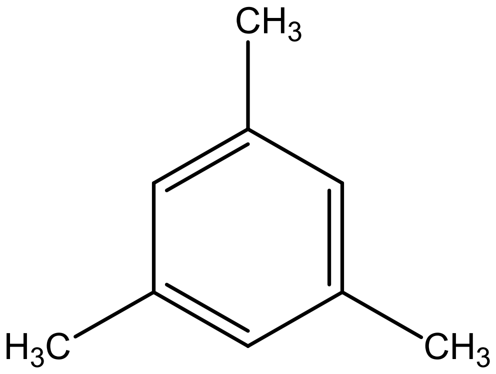
Linear molecules

The main (principal) axis
= the highest *n*

Symmetry Plane σ

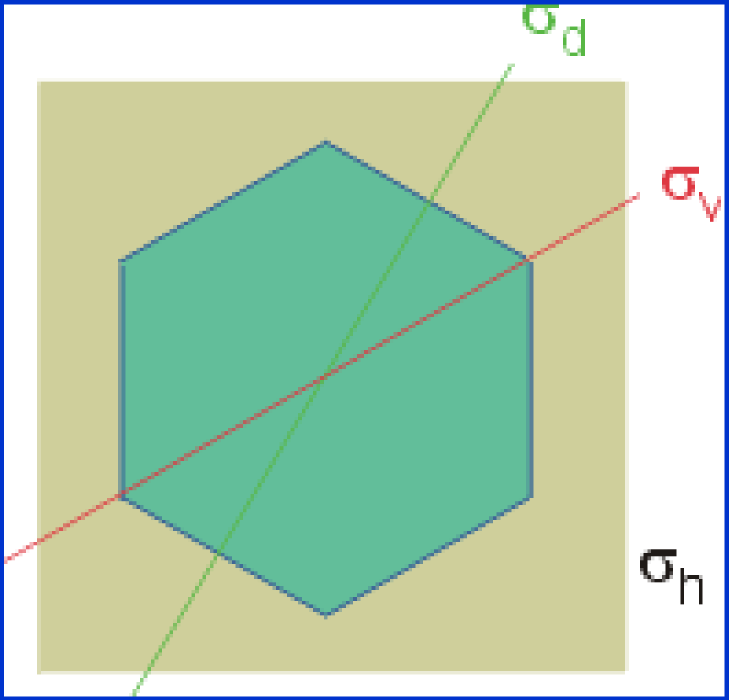






Symmetry Plane σ

Any planar molecule has a symmetry plane

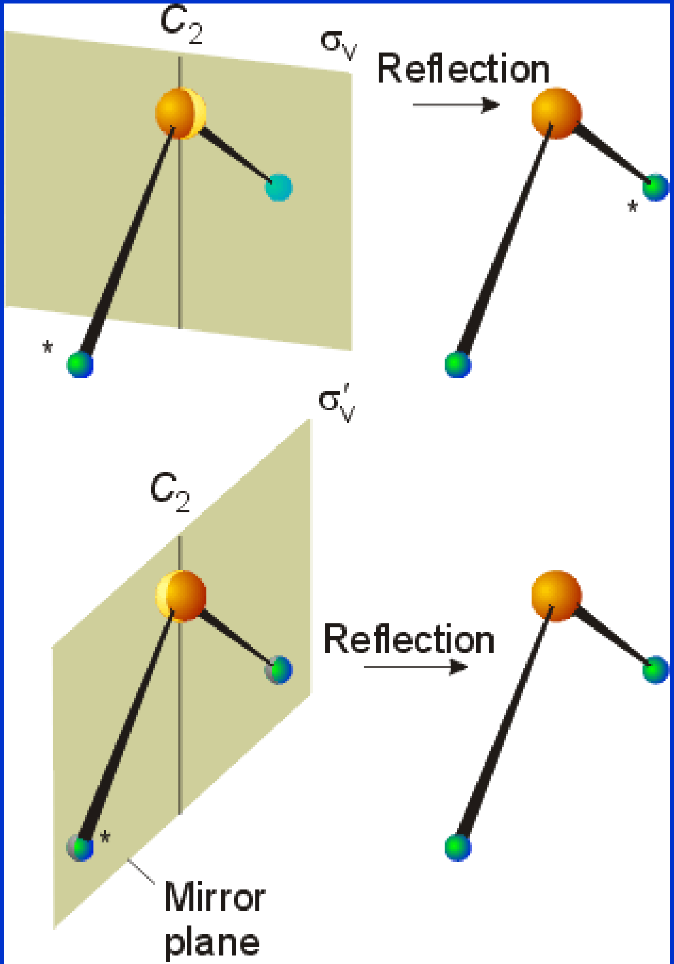


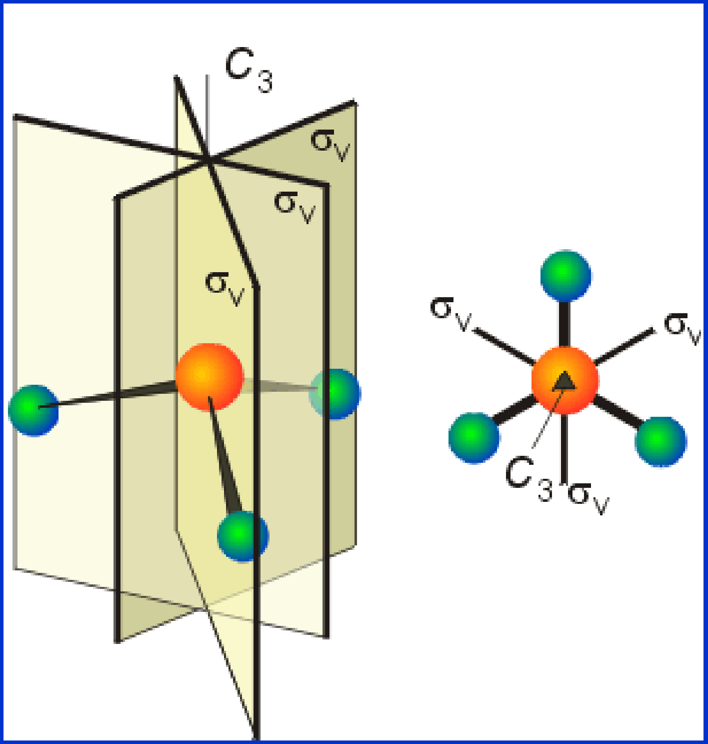
σ_h = perpendicular to the main axis

σ_v = passes thru the main axis, intercepts most atoms

σ_d = passes thru the main axis, bisects the angle between the twofold axes perpendicular to the main axis

Symmetry Plane σ



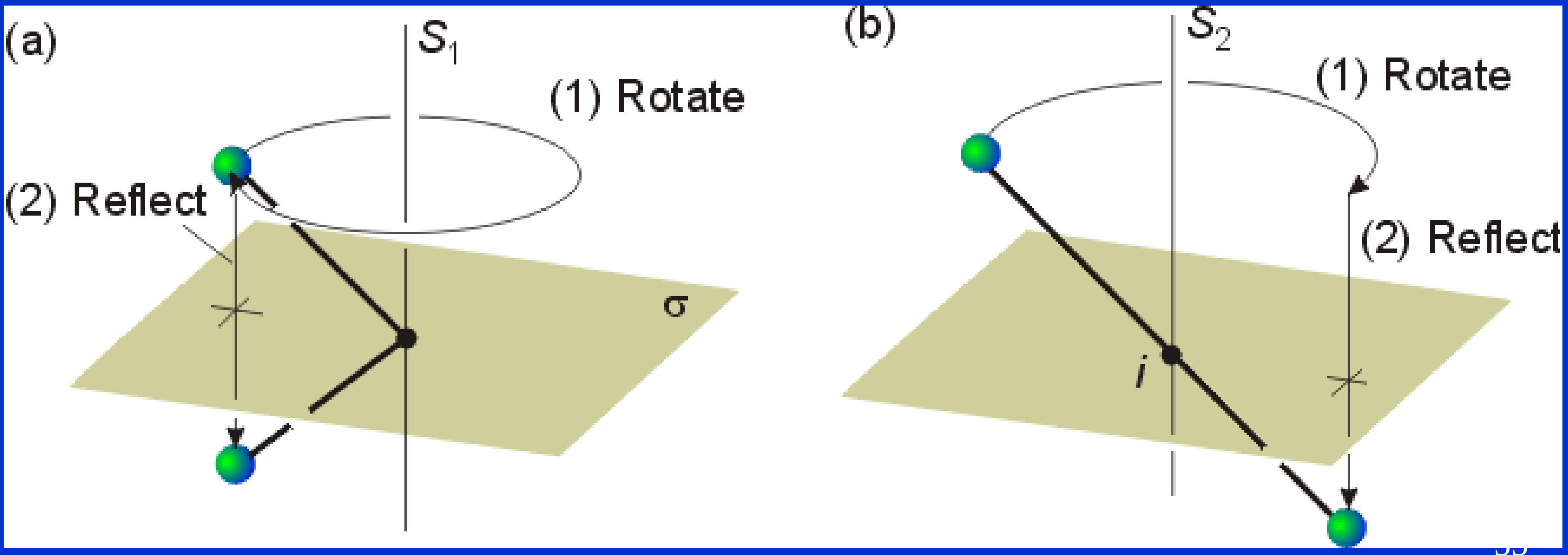


Improper Axis S_n

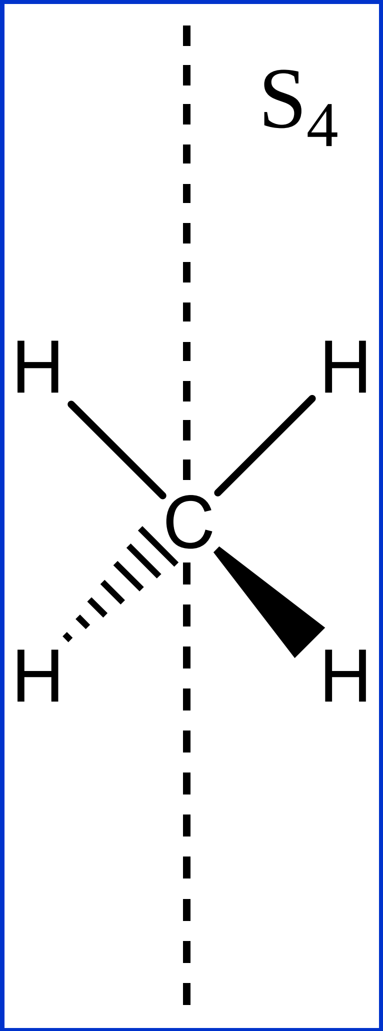
Regular rotations followed by a reflection in the plane perpendicular to the axis of rotation. Also known as rotation-reflection axis.

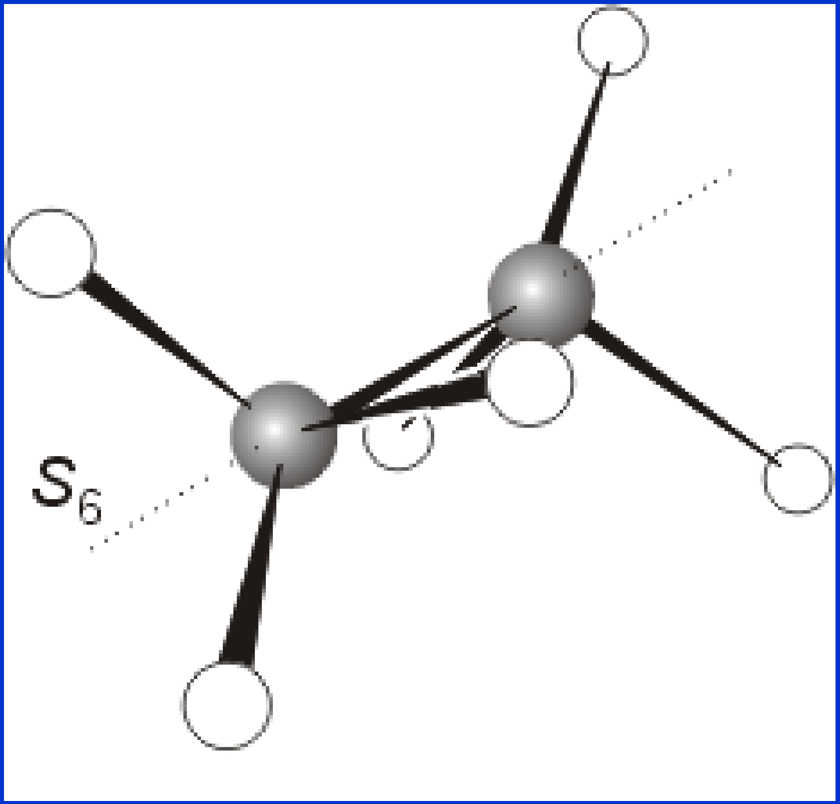
$S_1 = C_1 \times \sigma = \sigma$

$S_2 = C_2 \times \sigma = i$

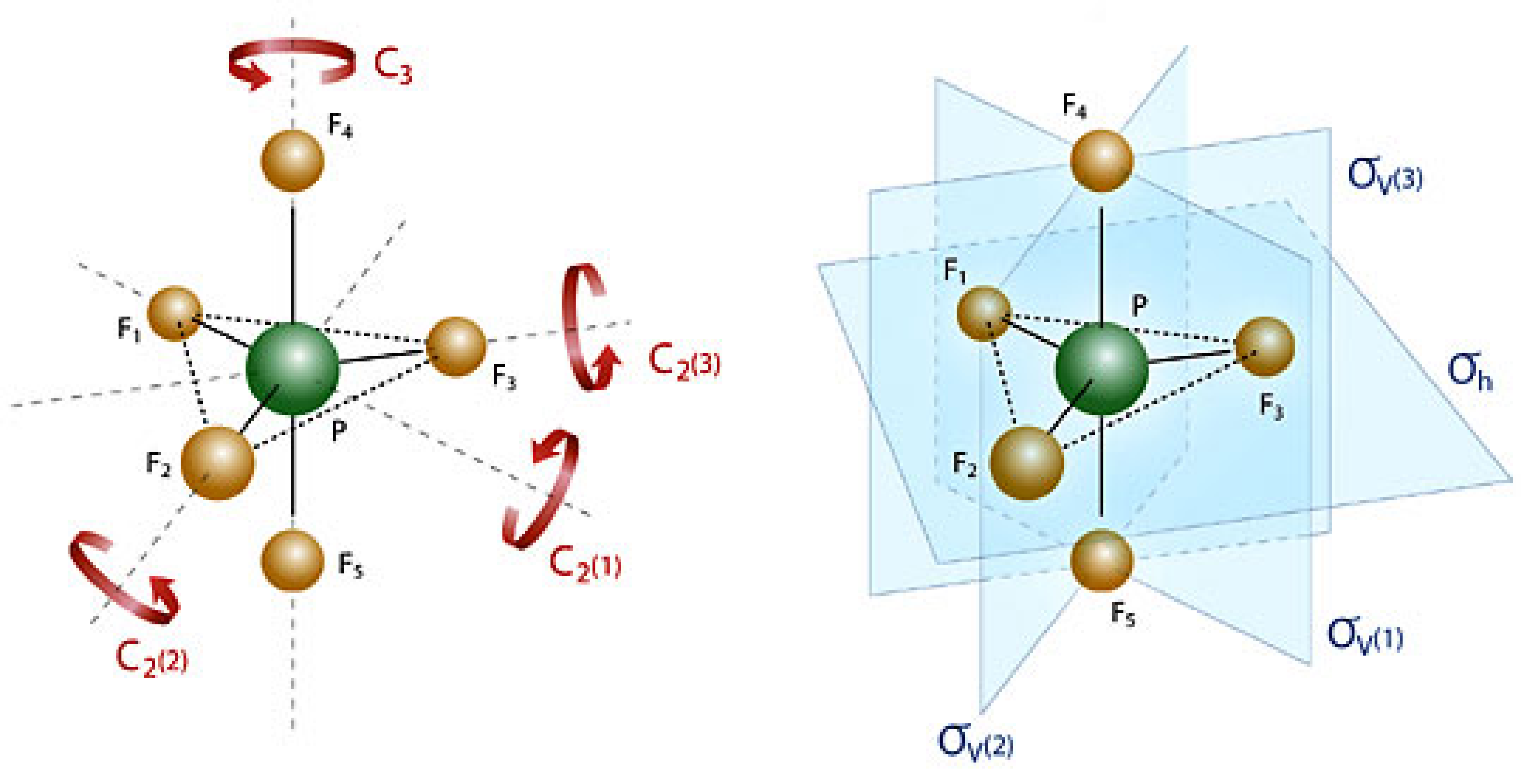


Improper Axis S_n





Symmetry Elements in Molecules



Equivalent atoms = exchanged by symmetry operations

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

Chirality

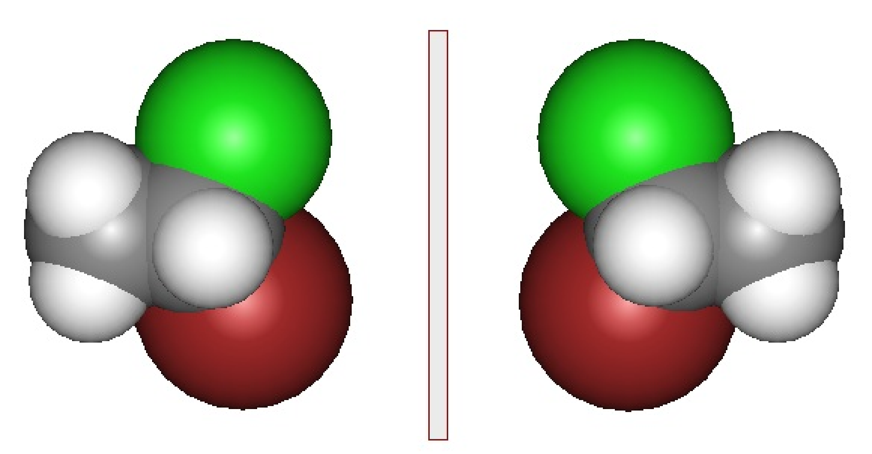
Figure 2. The Founding Fathers. R. M. Barrer (1910–1996) (right) and R. M. Milton (1920–2000) photographed

Chirality

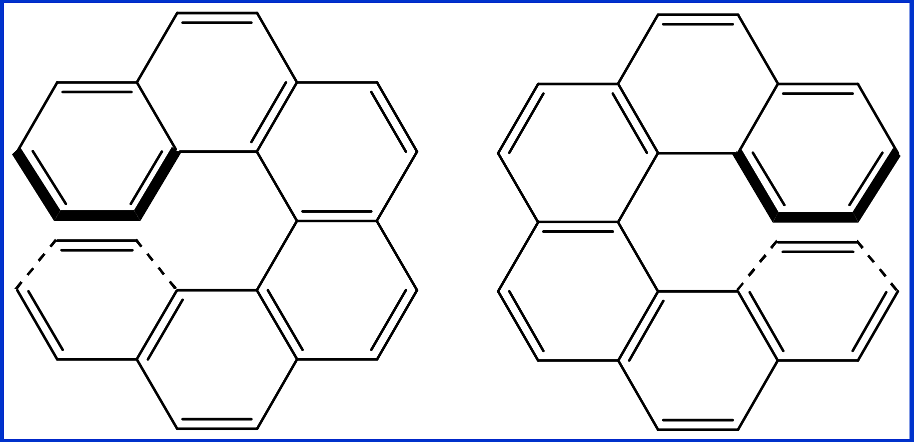
Condition of chirality: absence of S_n in a molecule

$S_1 = \sigma$

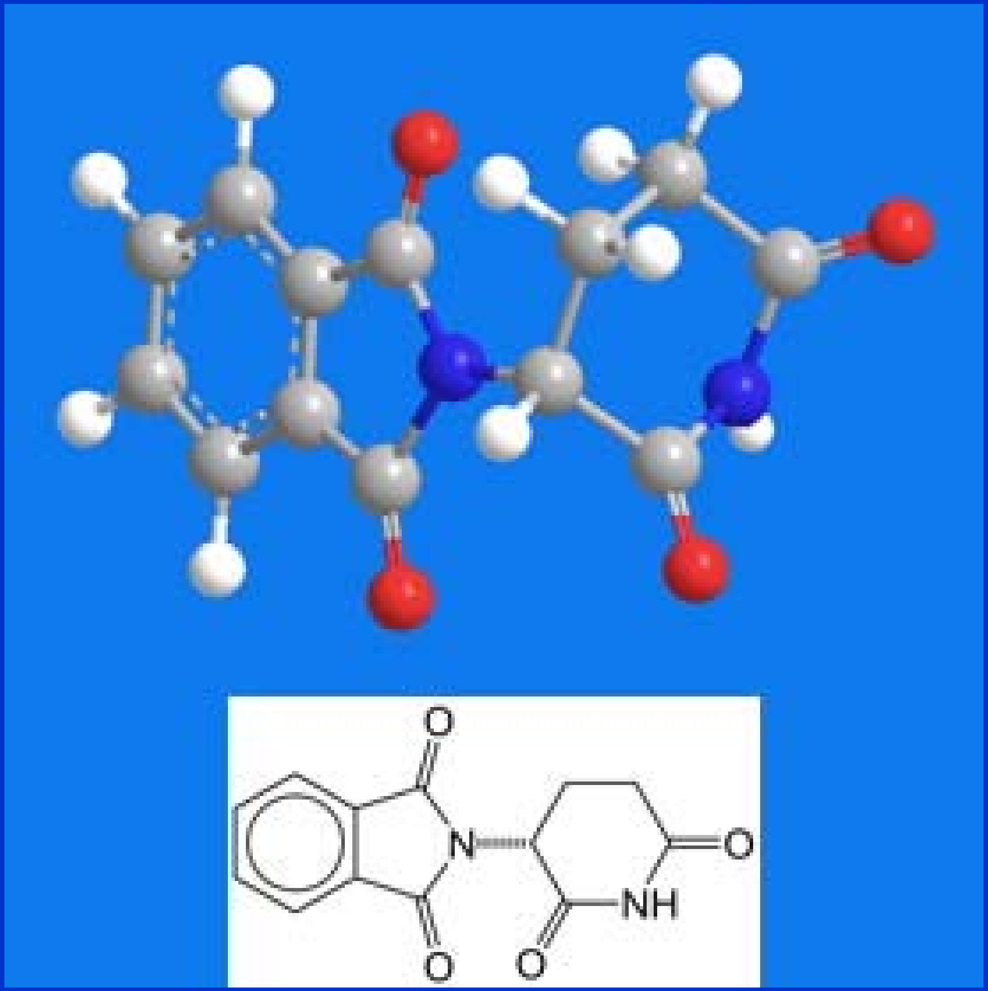
$S_2 = i$



C_2 →



Thalidomide



(*R*)-enantiomer

Morning sickness pill

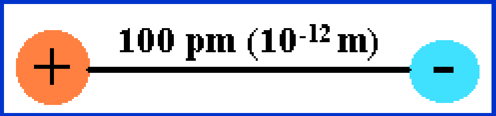
(*S*)-enantiomer

is teratogenic

Dipole Moment

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

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

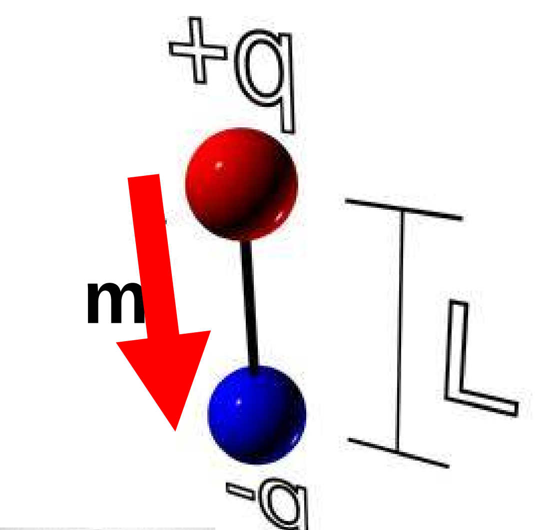


proton and electron, at 1 Å

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

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

dipole moment **4.80 D** reference value, full +1 and –1 charges at 100 pm, bonding between them is 100% ionic



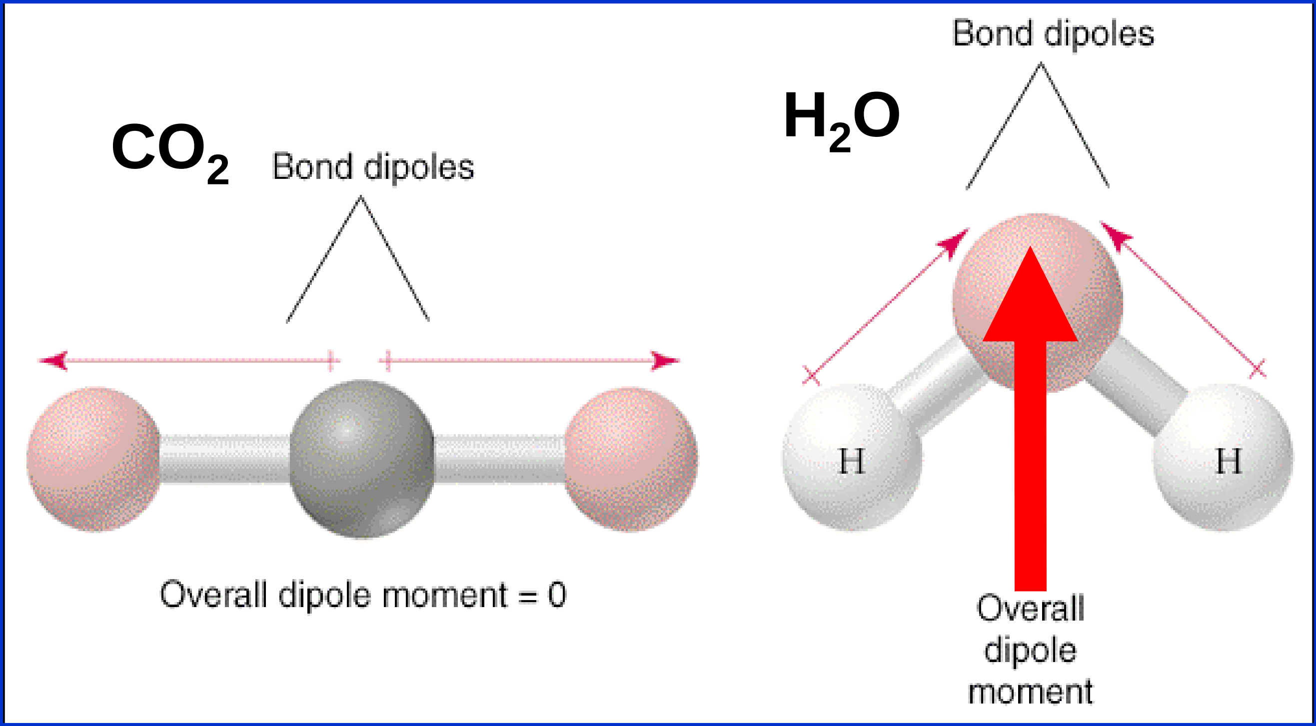
Peter Debye (1884-1966)
1936 NP in Chemistry

MW heating

Dipole Moment in Molecules

Vector sum of dipole moments of all bonds and free electron pairs

Distribution of charge in a molecule

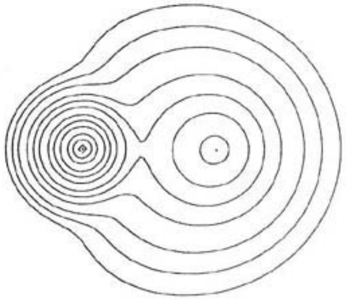


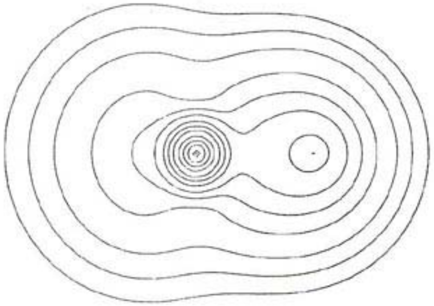
Dipole Moment in Diatomic Molecules

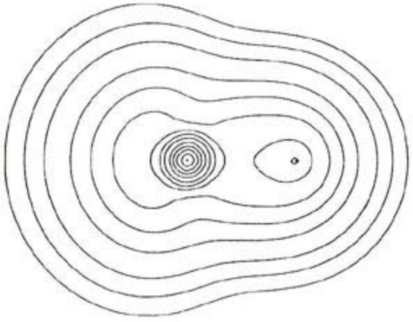
AH	μ (Debye)	R(Å)
LiH	–6.002	1.595
BeH	–0.282	1.343
BH	1.733	1.236
CH	1.570	1.124
NH	1.627	1.038
OH	1.780	0.9705
FH	1.942	0.9171

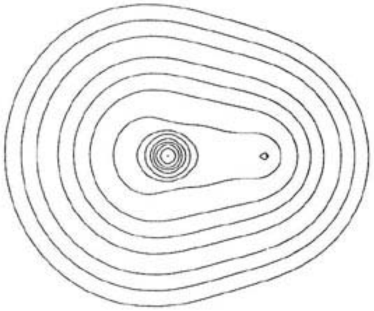
negative or positive sign for $\mu \Rightarrow$ H is negative or positive end of dipole

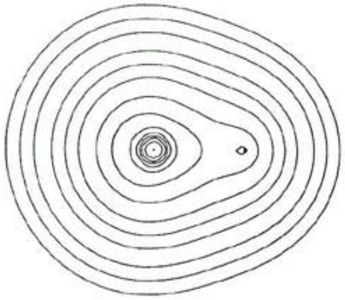
Dipole Moment in Diatomic Molecules

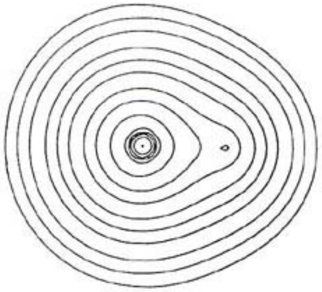

LiH

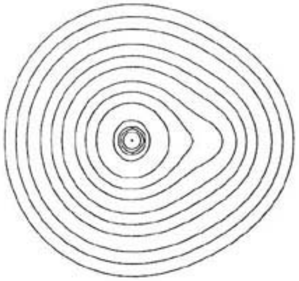

BeH


BH


CH

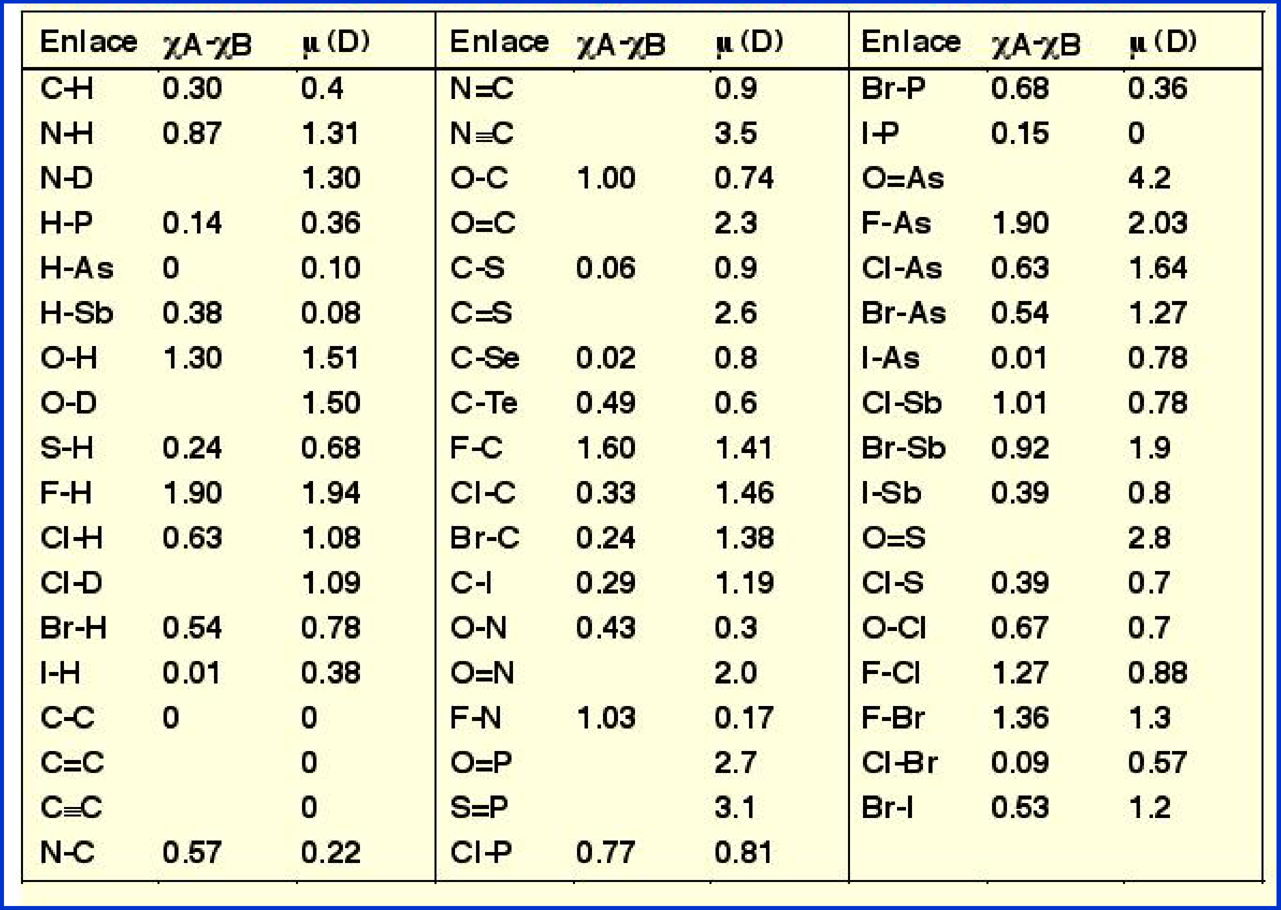

NH


OH


HF

Bond Dipole Moment

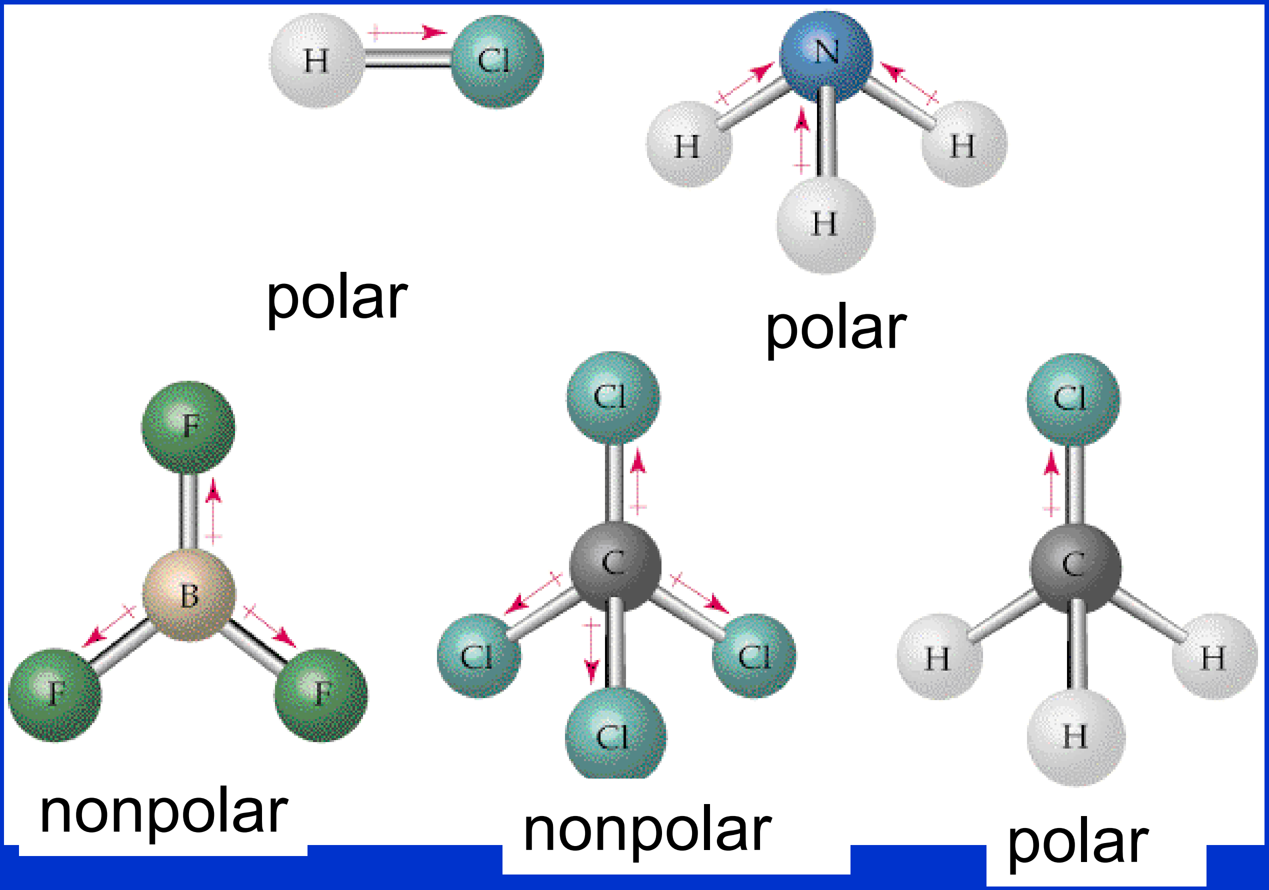
Electronegativity difference in bonds



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			

Dipole Moment and Polarity

Polar molecules = total dipole must lie in all symmetry elements



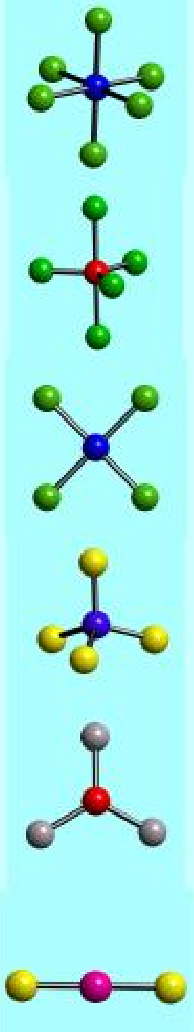
polar

polar

nonpolar

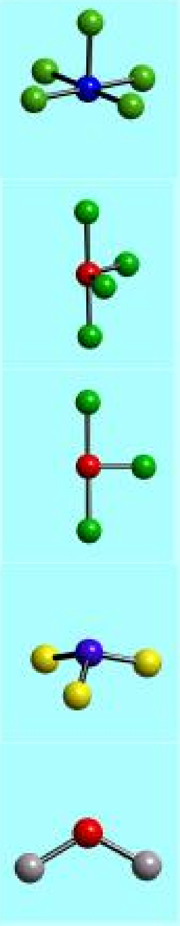
nonpolar

polar



μ = 0

AB_nE_m	Grupo Puntual	μ	Molecule
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



μ ≠ 0