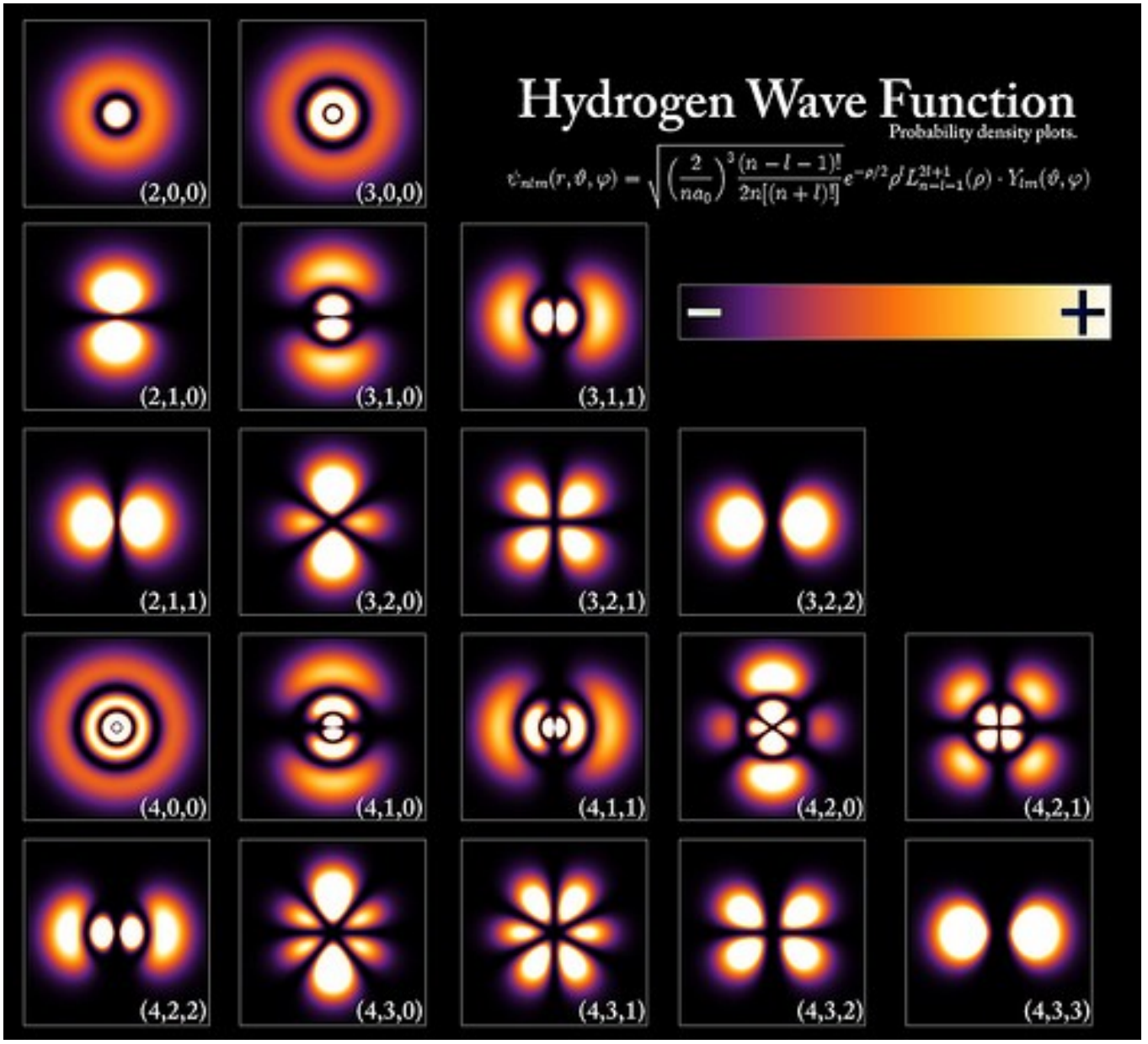
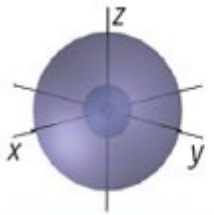
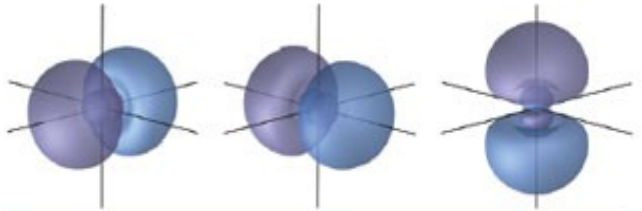

Hydrogen Wave Function
Probability density plots.
$\psi_{nlm}(r,\theta,\varphi) = \sqrt{\left(\frac{2}{na_0}\right)^3 \frac{(n-l-1)!}{2n[(n+l)!]}} e^{-\rho/2} \rho^l L_{n-l-1}^{2l+1}(\rho) \cdot Y_{lm}(\theta,\varphi)$
−
+
(2,0,0)
(3,0,0)
(2,1,0)
(3,1,0)
(3,1,1)
(2,1,1)
(3,2,0)
(3,2,1)
(3,2,2)
(4,0,0)
(4,1,0)
(4,1,1)
(4,2,0)
(4,2,1)
(4,2,2)
(4,3,0)
(4,3,1)
(4,3,2)
(4,3,3)

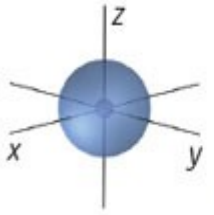
Atomové orbitaly



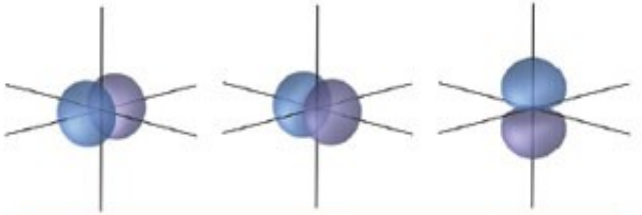
3s



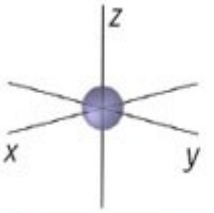
$3p_x$ $3p_y$ $3p_z$



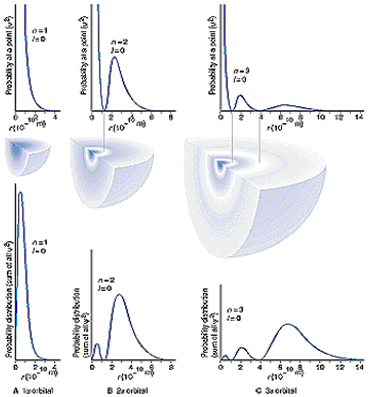
2s

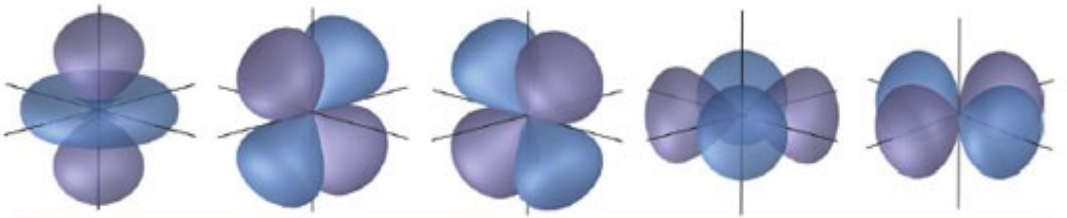


$2p_x$ $2p_y$ $2p_z$



1s

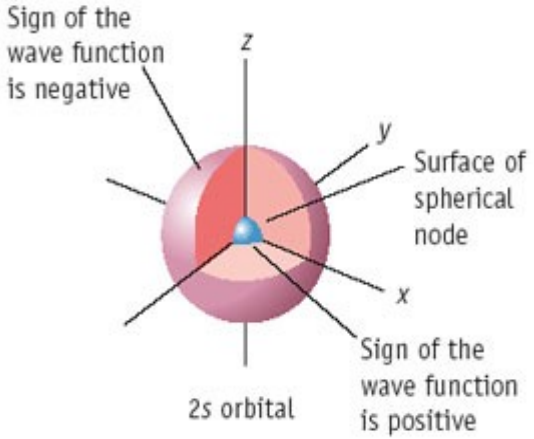


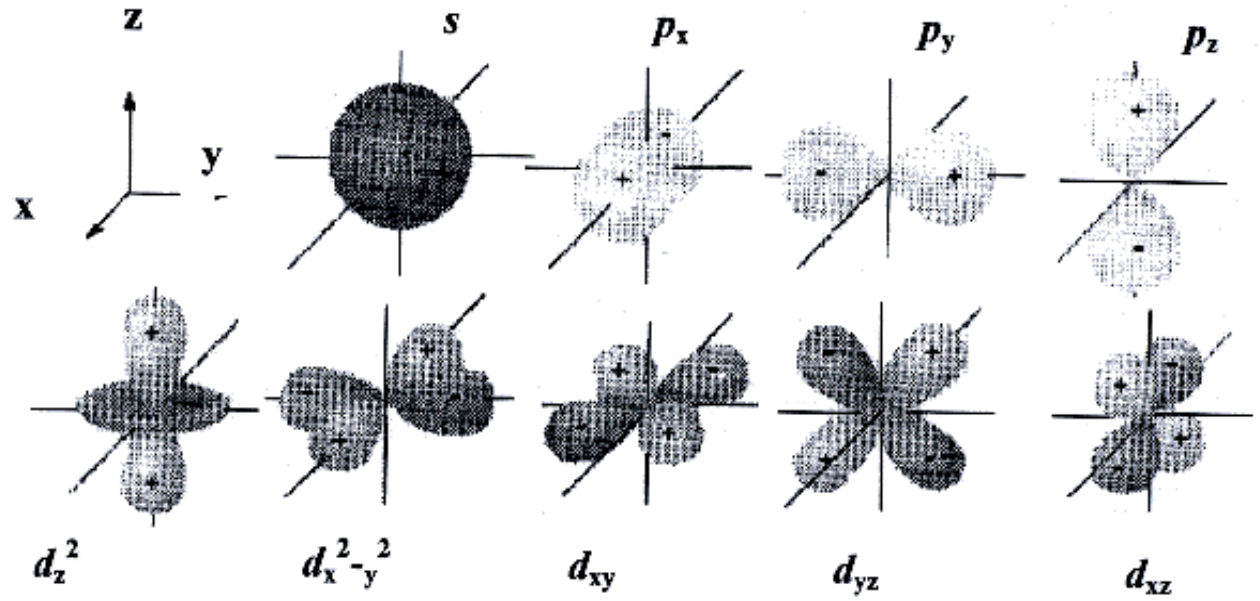


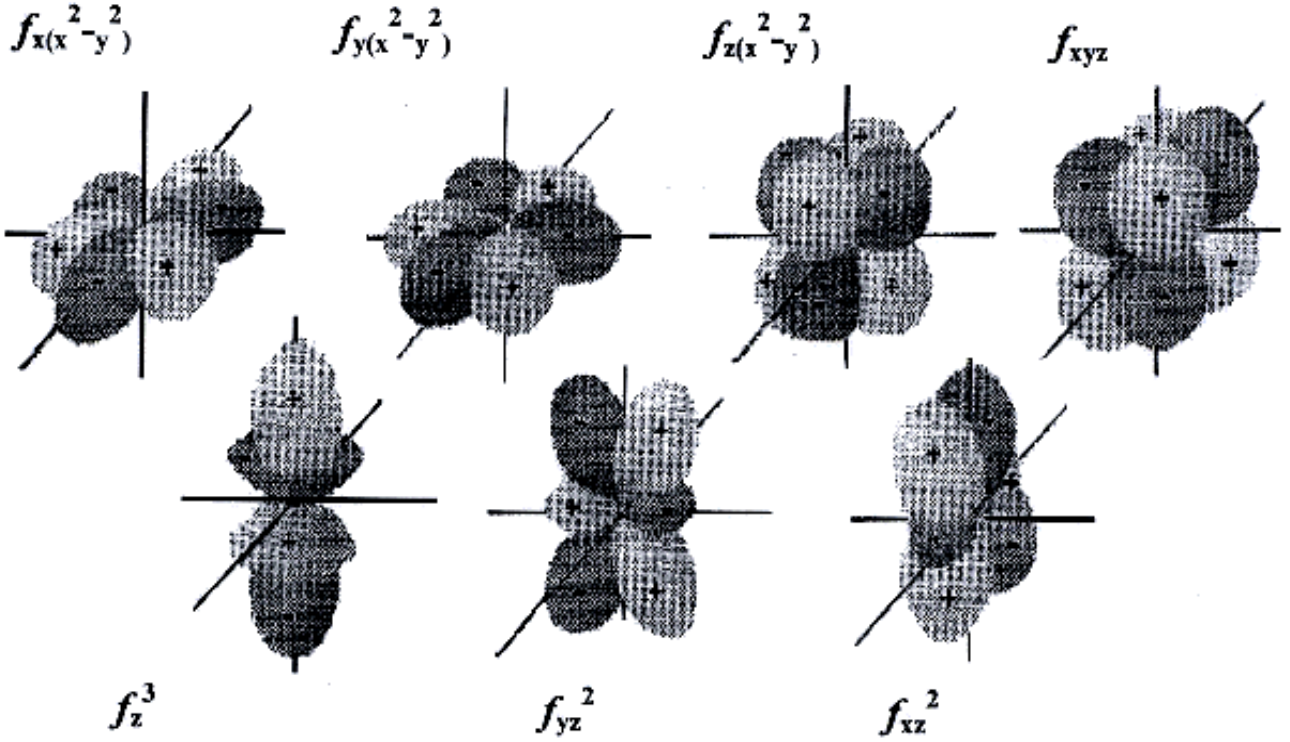
$3d_{z^2}$ $3d_{xz}$ $3d_{yz}$ $3d_{xy}$ $3d_{x^2-y^2}$

Spherical Nodes

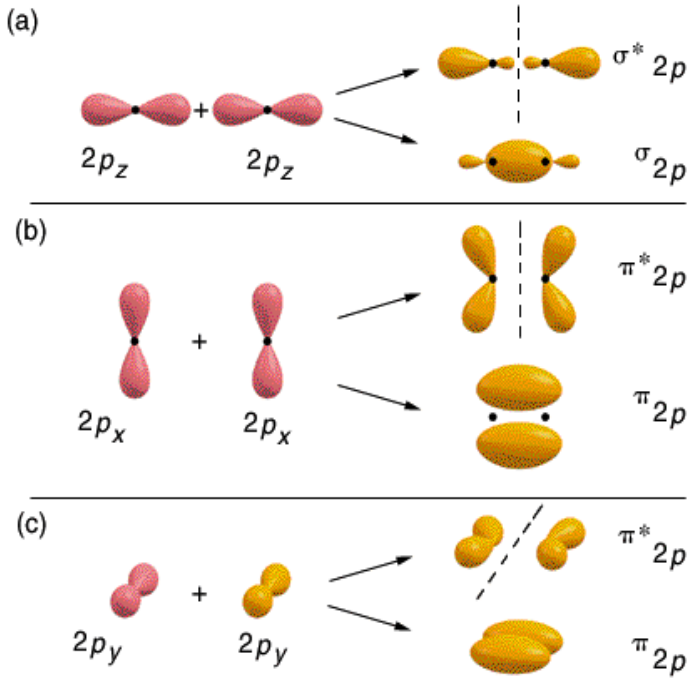
The drawings of the 2*s* and 3*s* orbitals show that they consist of nested spheres because these orbitals (as well as *p* orbitals with $n > 2$ and *d* orbitals with $n > 3$) have spherical nodes. For a 2s orbital the wave function has a positive value close to the nucleus, but it has a negative value at greater distances. That is, the wave function has a zero value, a node, at this point. The node occurs at the same distance from the nucleus regardless of direction so the node occurs on a spherical surface. The number of spherical nodes for any orbital is $n - \ell - 1$.

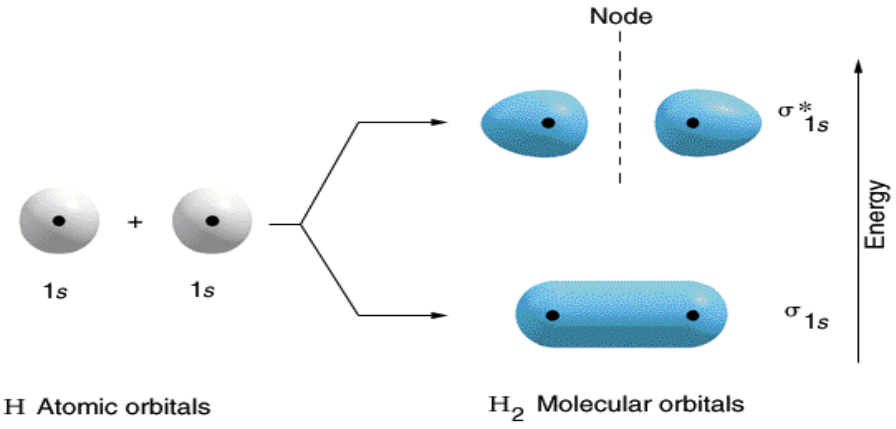


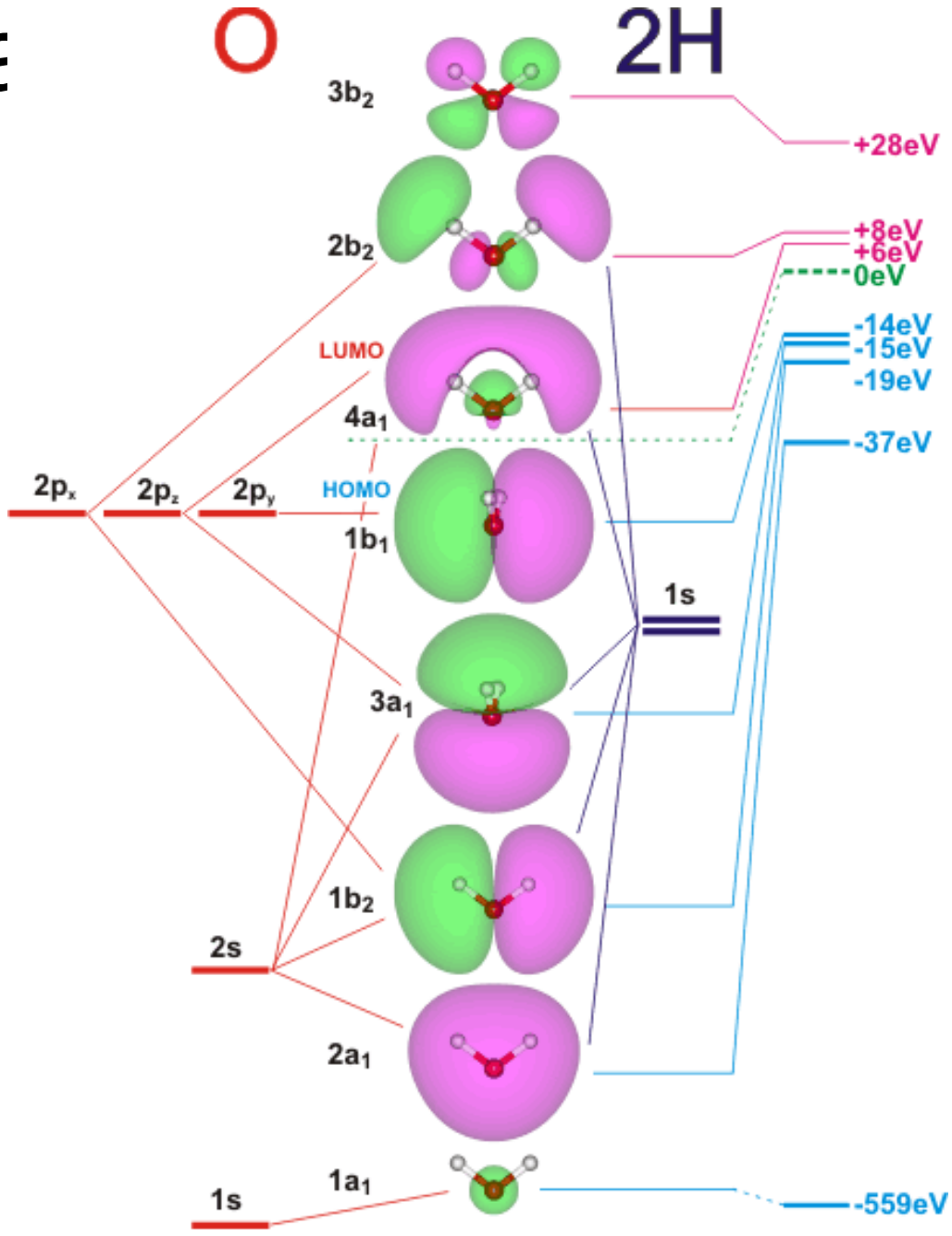

z
y
x
s
p_x
p_y
p_z
d_{z^2}
$d_{x^2-y^2}$
d_{xy}
d_{yz}
d_{xz}

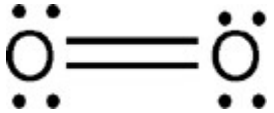

$f_{x(x^2-y^2)}$
$f_{y(x^2-y^2)}$
$f_{z(x^2-y^2)}$
f_{xyz}
f_{z^3}
f_{yz^2}
f_{xz^2}

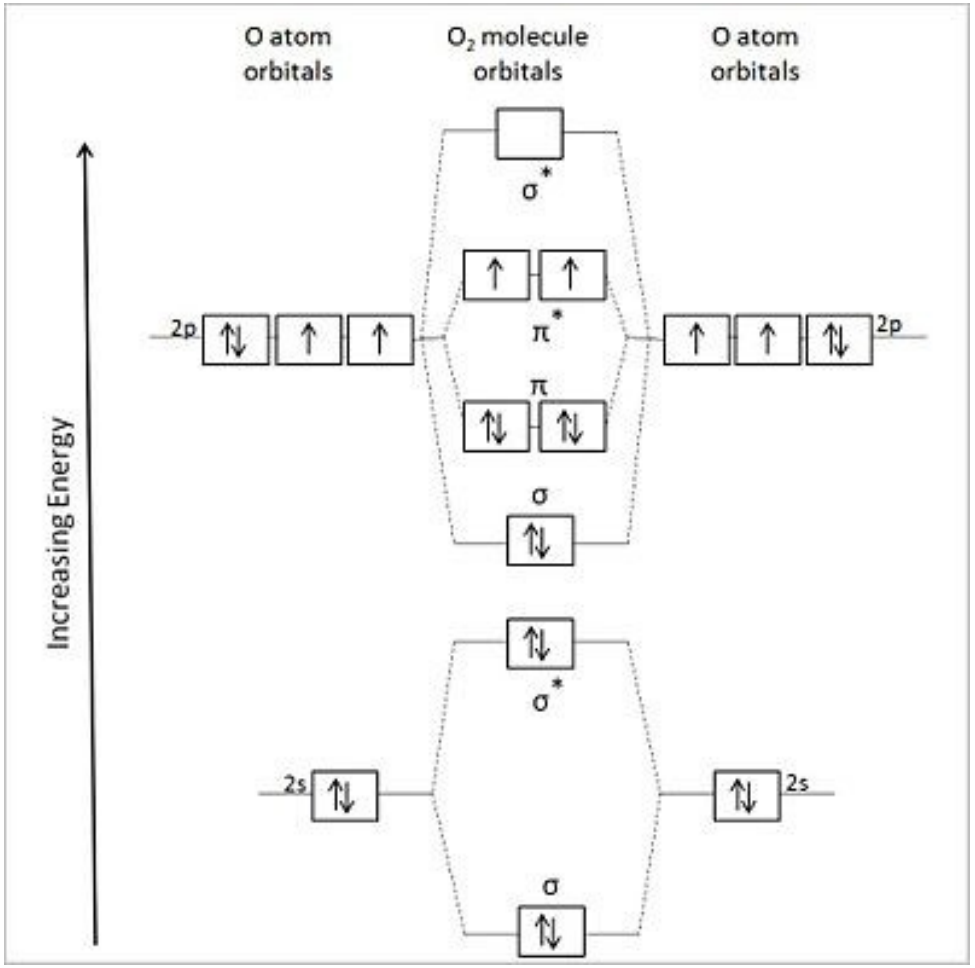
Molekulové orbita



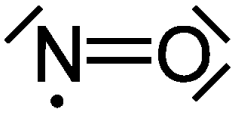


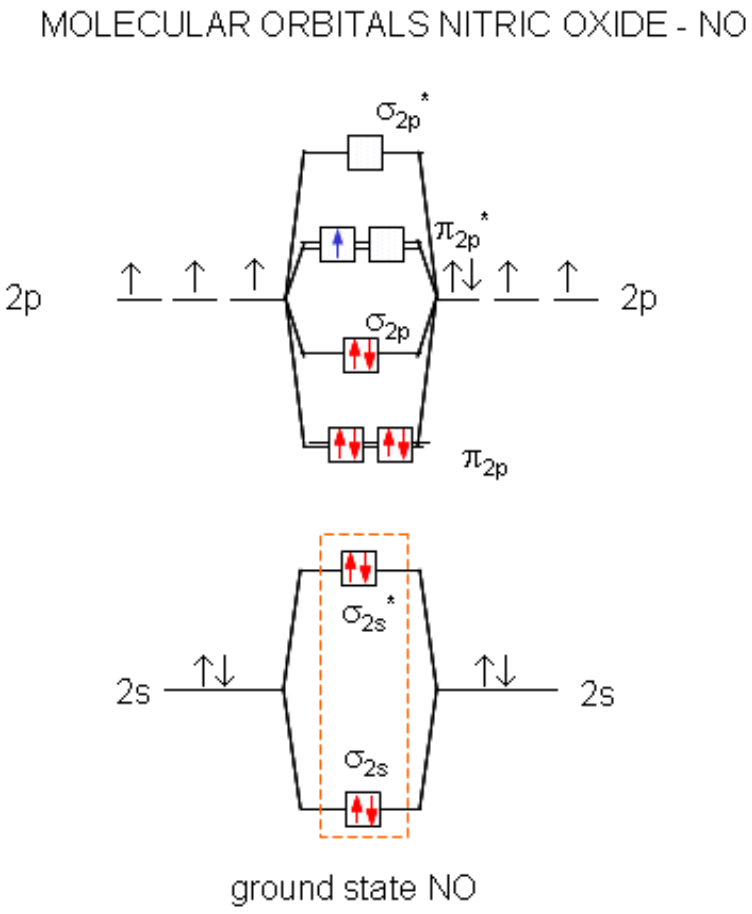




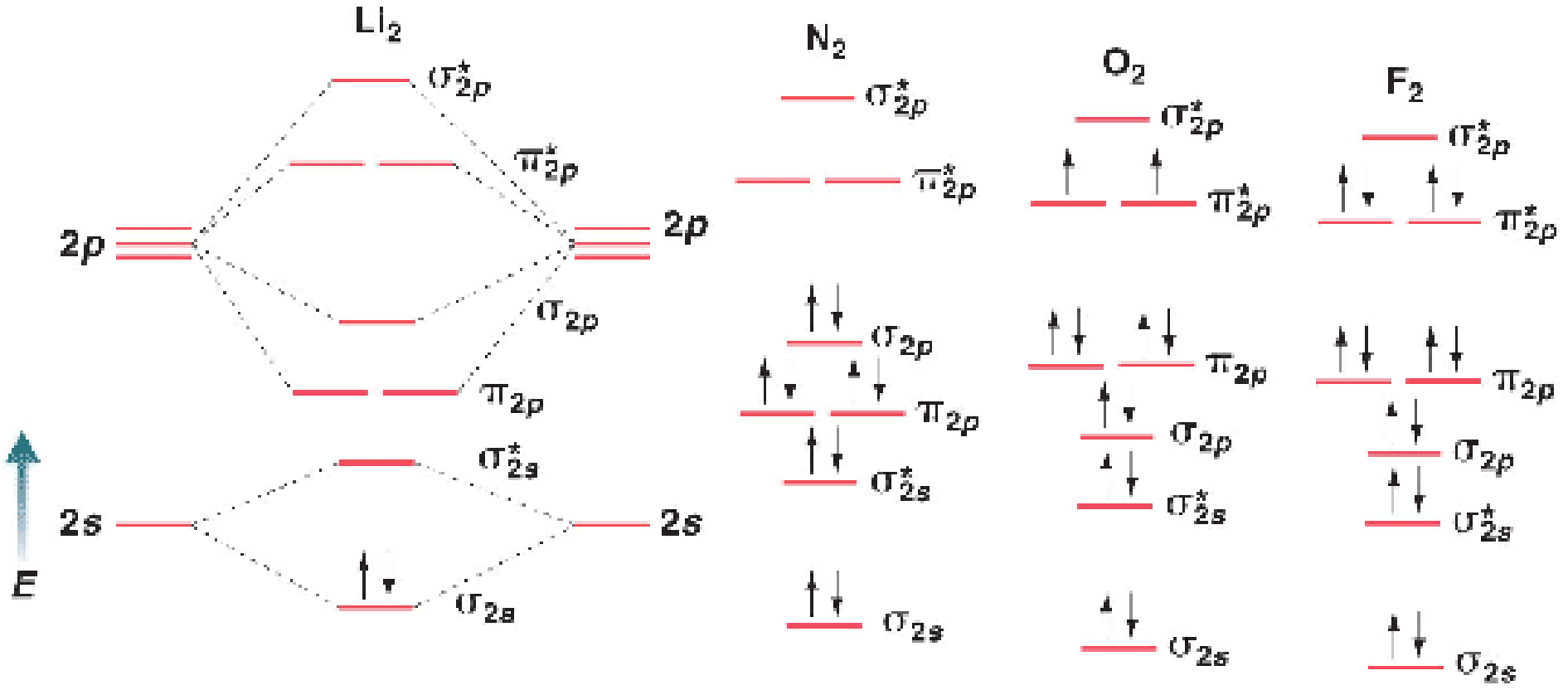


Bez interakce s-p_z



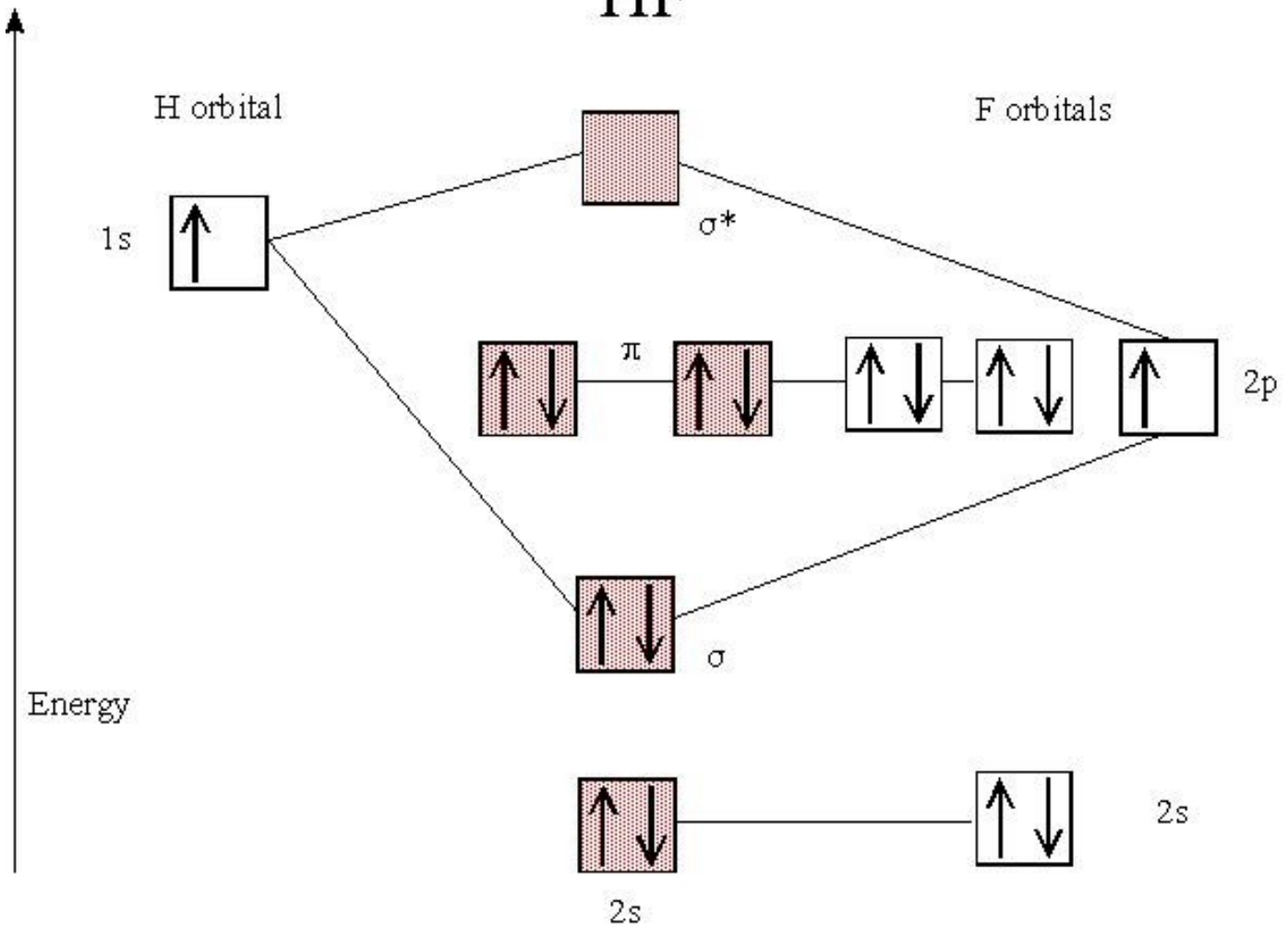


S interakcí s-p_z

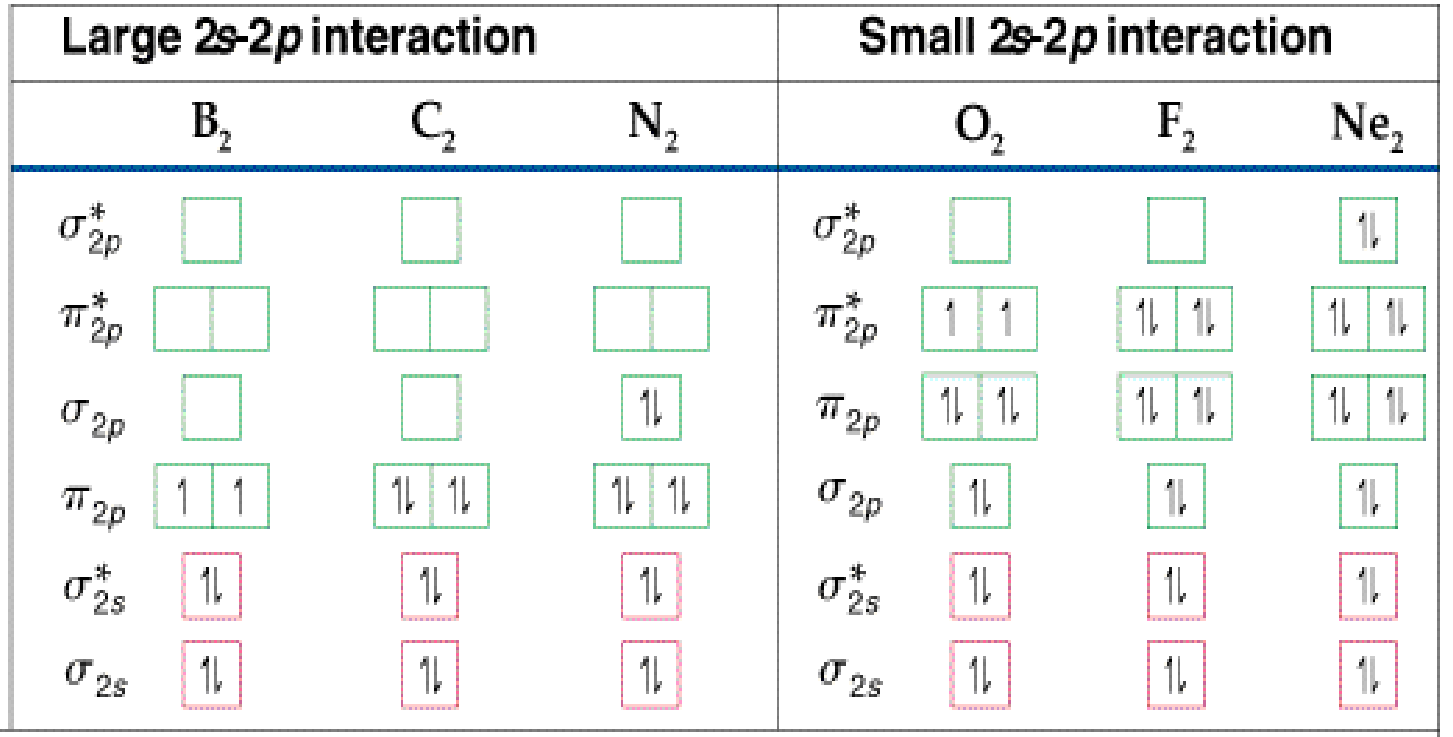


	Li_2	N_2	O_2	F_2
Bond order	$\frac{2-0}{2} = 1$	$\frac{8-2}{2} = 3$	$\frac{8-4}{2} = 2$	$\frac{8-6}{2} = 1$
Bond energy	1.05 eV	9.76 eV	5.12 eV	1.60 eV
Bond length	2.67 Å	1.10 Å	1.21 Å	1.41 Å

HF



Molekulové orbitaly



	B_2	C_2	N_2	O_2	F_2	Ne_2
Bond order	1	2	3	2	1	0
Bond energy (kJ/mol)	290	620	941	495	155	—
Bond length (Å)	1.59	1.31	1.10	1.21	1.43	—
Magnetic behavior	Paramagnetic	Diamagnetic	Diamagnetic	Paramagnetic	Diamagnetic	—

Lewisovy struktury

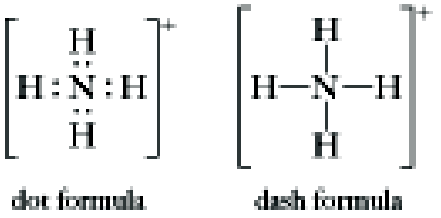
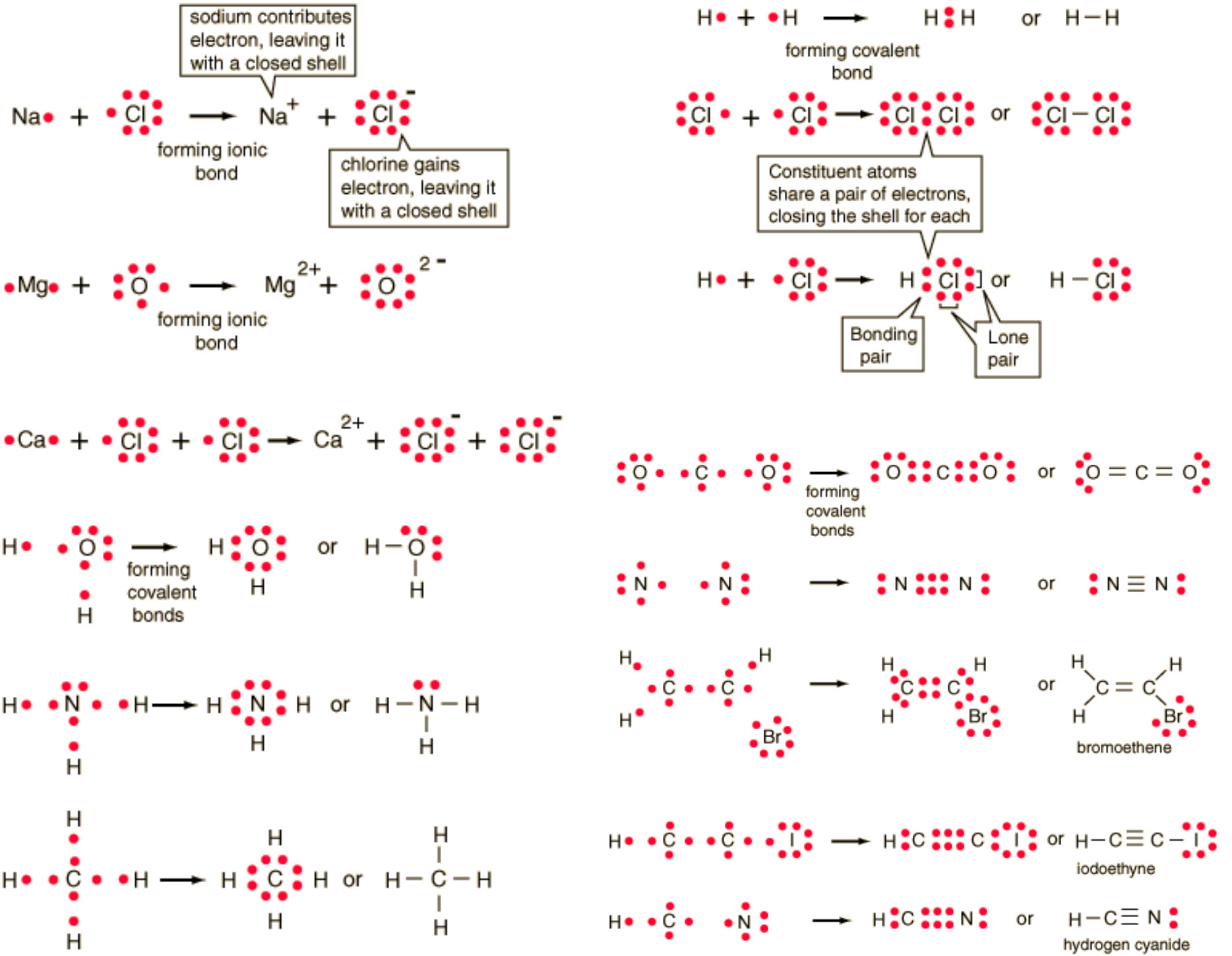


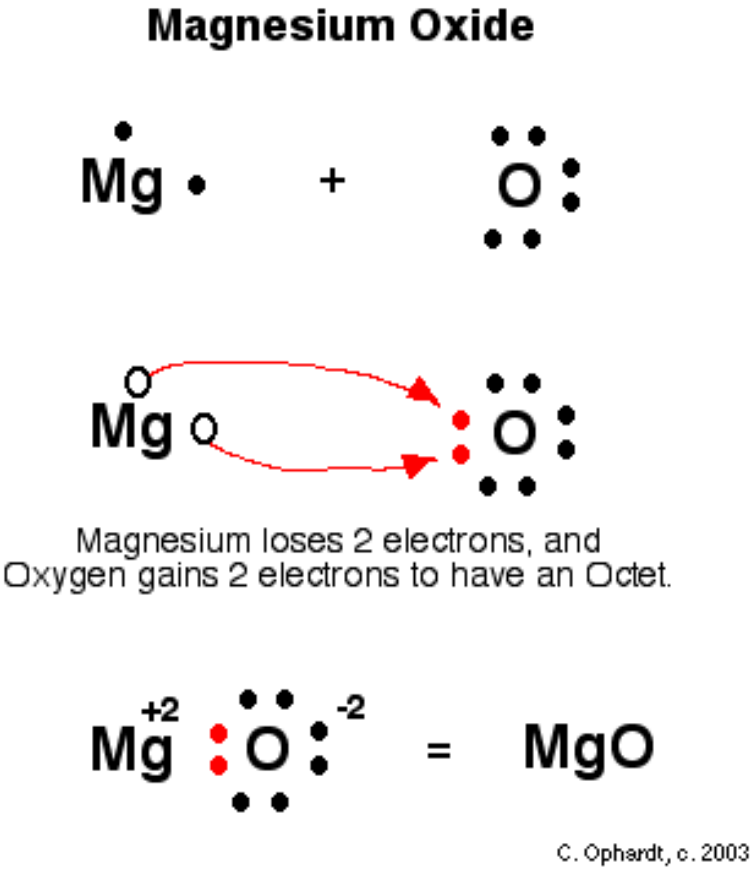
TABLE 7-1 *Lewis Dot Formulas for Representative Elements*

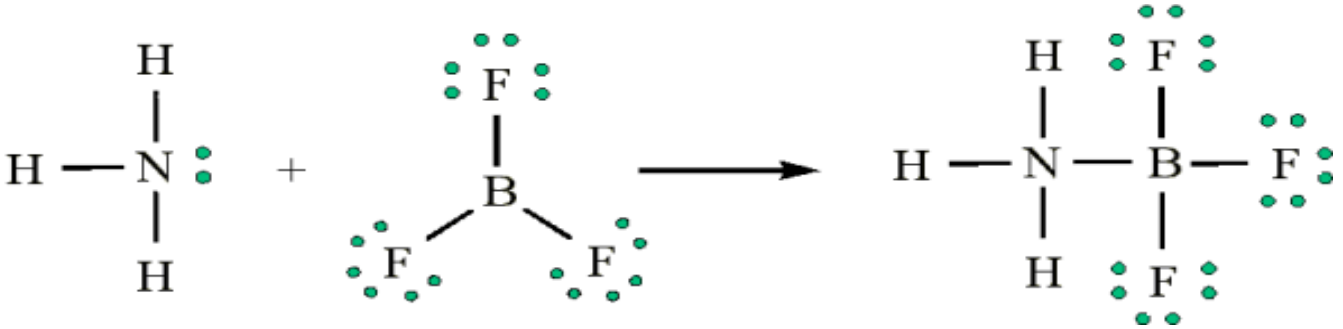
Group	IA	IIA	IIIA	IVA	VA	VIA	VIIA	VIIIA
Number of electrons in valence shell	1	2	3	4	5	6	7	8 (*except He*)
Period 1	H ·							He :
Period 2	Li ·	Be :	·· B ·	·· C ·	·· · N ·	·· · O :	·· · F :	·· : Ne :
Period 3	Na ·	Mg :	·· Al ·	·· Si ·	·· · P ·	·· · S :	·· · Cl :	·· : Ar :
Period 4	K ·	Ca :	·· Ga ·	·· Ge ·	·· · As ·	·· · Se :	·· · Br :	·· : Kr :
Period 5	Rb ·	Sr :	·· In ·	·· Sn ·	·· · Sb ·	·· · Te :	·· · I :	·· : Xe :
Period 6	Cs ·	Ba :	·· Tl ·	·· Pb ·	·· · Bi ·	·· · Po :	·· · At :	·· : Rn :
Period 7	Fr ·	Ra :						


sodium contributes electron, leaving it with a closed shell
Na + Cl → Na+ + Cl−
forming ionic bond
chlorine gains electron, leaving it with a closed shell
Mg + O → Mg2+ + O2−
forming ionic bond
Ca + Cl + Cl → Ca2+ + Cl− + Cl−
H + O → H O H or H−O−H
forming covalent bonds
H + N + H → H N H or H−N−H
H
H + C + H → H C H or H−C−H
H
H + H → H H or H−H
forming covalent bond
Cl + Cl → Cl Cl or Cl−Cl
Constituent atoms share a pair of electrons, closing the shell for each
H + Cl → H Cl or H−Cl
Bonding pair
Lone pair
O C O → O C O or O=C=O
forming covalent bonds
N N → N N or N≡N
H C C H → H C C H or
Br Br
bromoethene
H C C I → H C C I or H−C≡C−I
iodoethyne
H C N → H C N or H−C≡N
hydrogen cyanide

Oktetové pravidlo

Ve většině sloučenin zaujímají prvky stabilní konfiguraci vzácného plynu. Týká se pouze prvků 2. a 3. periody.





Výjimky z oktetového pravidla

Table 9.7 Lewis Structures in Which the Central Atom Exceeds an Octet

Group 4A	Group 5A	Group 6A	Group 7A	Group 8
SiF_5^-	PF_5	SF_4	ClF_3	XeF_2
SiF_6^{2-}	PF_6^-	SF_6	BrF_5	XeF_4

Formální náboj

FC = (č. skupiny) - [(počet vazeb) + (počet nevazeb. el.)]

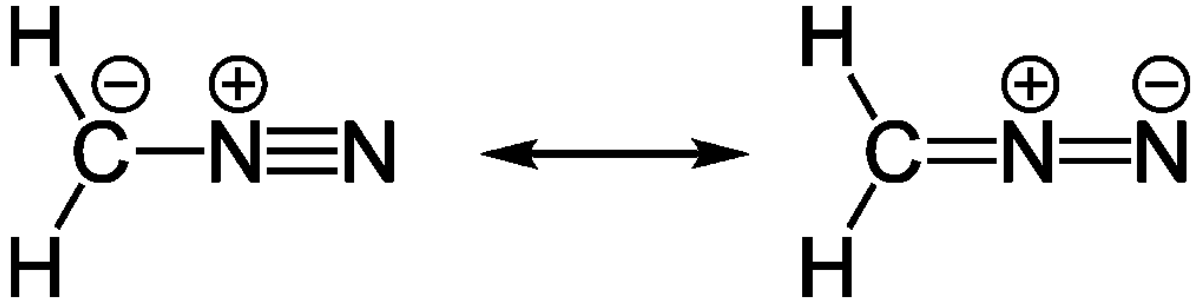
(i) 

For Cl, FC = 7 − (2 + 4) = +1
For N, FC = 5 − (3 + 2) = 0
For O, FC = 6 − (1 + 6) = −1

(ii) 

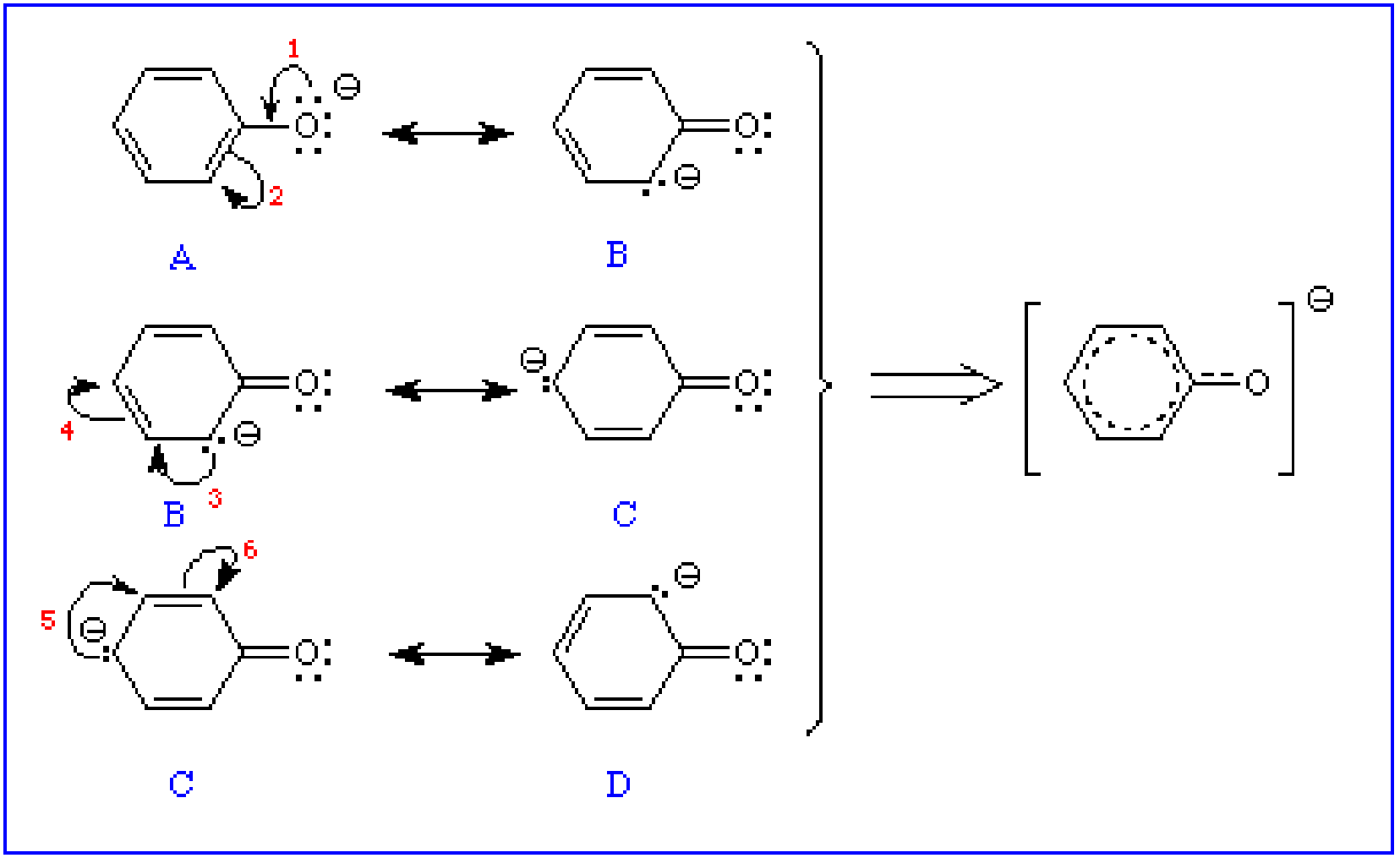
For Cl, FC = 7 − (1 + 6) = 0
For N, FC = 5 − (3 + 2) = 0
For O, FC = 6 − (2 + 4) = 0

diazomethan



Rezonance

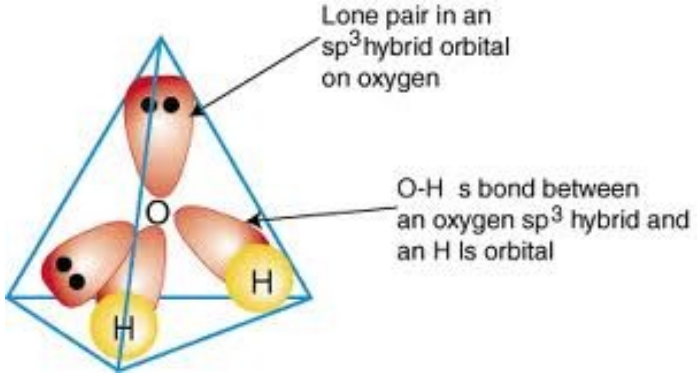
(fenolát)

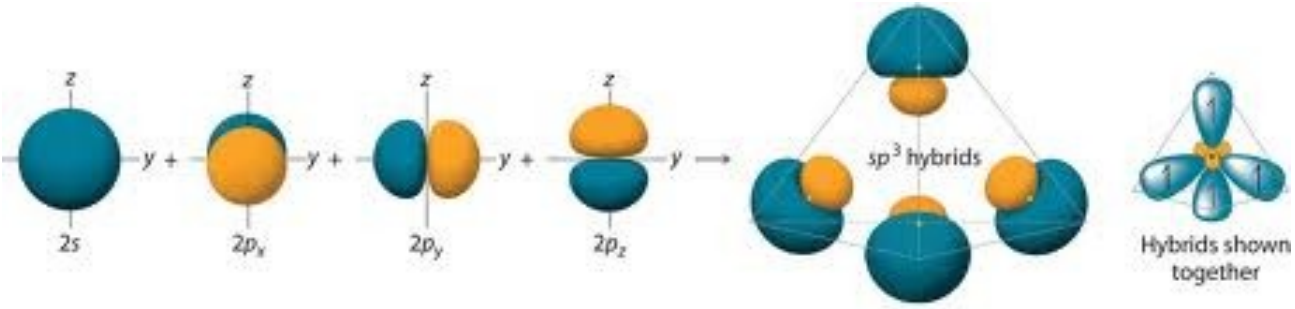


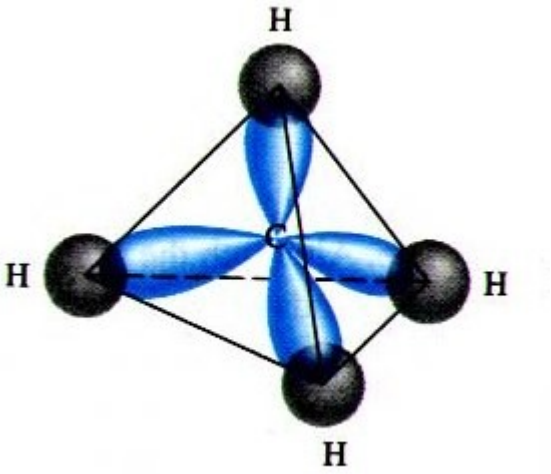
Hybridizace

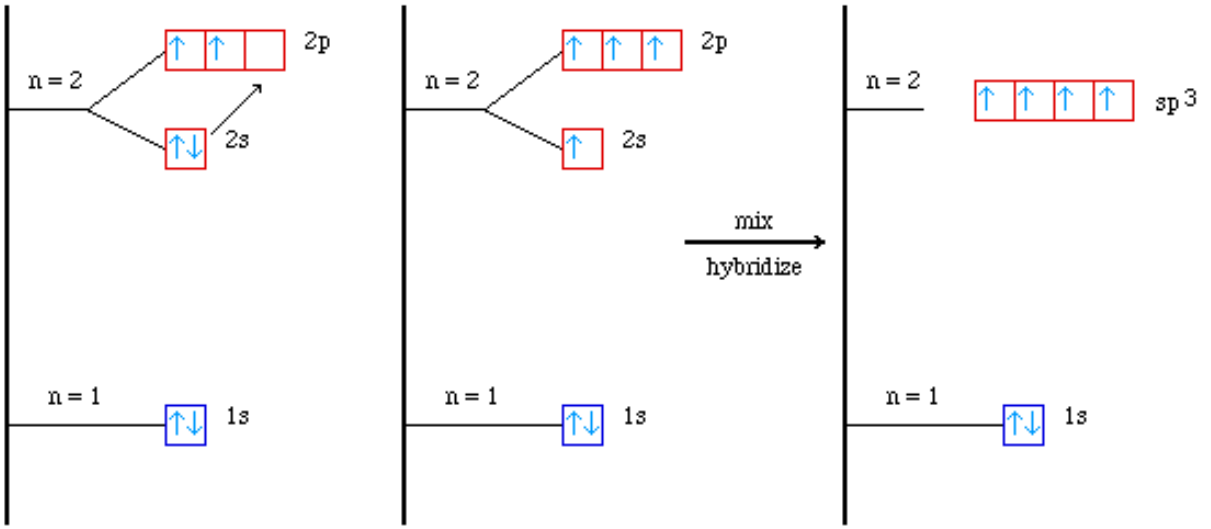
TABLE 8-2 *Relation Between Electronic Geometries and Hybridization*

Regions of High Electron Density	Electronic Geometry	Atomic Orbitals Mixed from Valence Shell of Central Atom	Hybridization
2	linear	one *s*, one *p*	*sp*
3	trigonal planar	one *s*, two *p*'s	sp^2
4	tetrahedral	one *s*, three *p*'s	sp^3
5	trigonal bipyramidal	one *s*, three *p*'s, one *d*	sp^3d
6	octahedral	one *s*, three *p*'s, two *d*'s	sp^3d^2





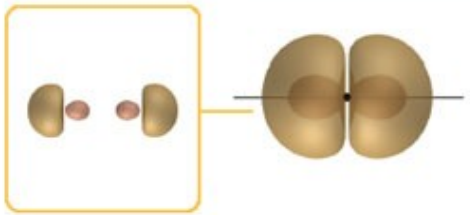
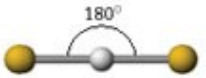
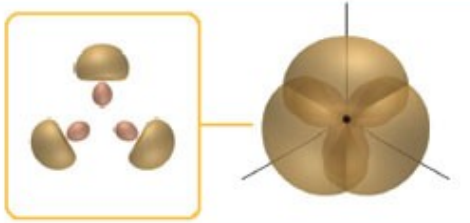
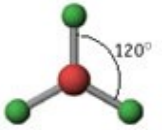
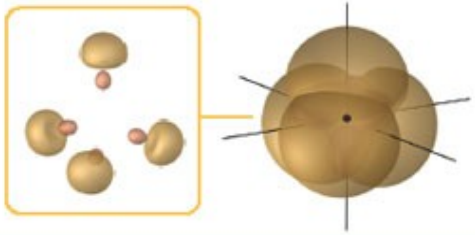
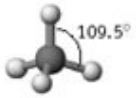
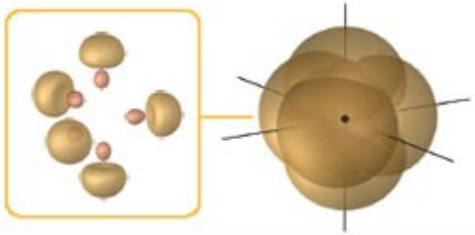
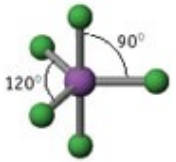
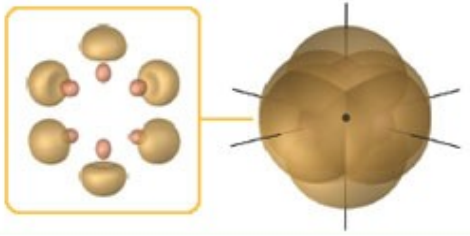
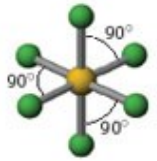


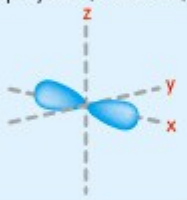
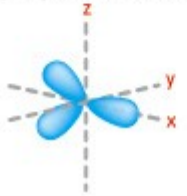
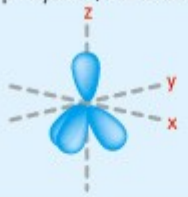
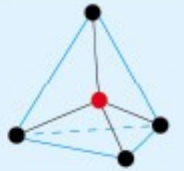
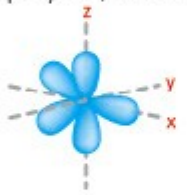
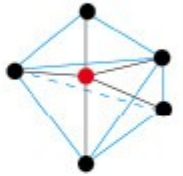
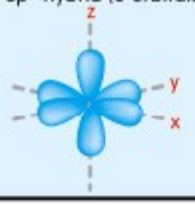
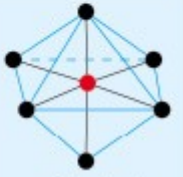


Energy level diagram for carbon

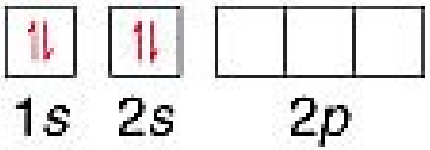
promotion of a 2*s* electron

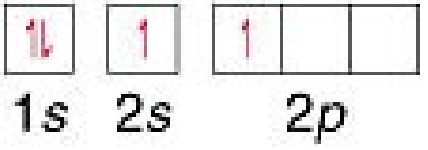
four hybrid sp^3 orbitals are formed

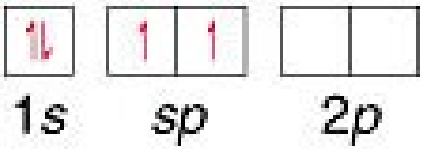
Arrangement of Hybrid Orbitals	Geometric figure	Example
Two electron pairs *sp*		Linear	 $BeCl_2$
Three electron pairs sp^2		Trigonal-planar	 BF_3
Four electron pairs sp^3		Tetrahedral	 CH_4
Five electron pairs sp^3d		Trigonal-bipyramidal	 PF_5
Six electron pairs sp^3d^2		Octahedral	 SF_6

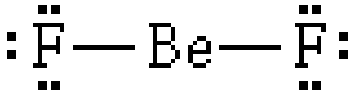
Atomic orbitals combined	Hybrid orbitals formed	Bonding electron pairs and lone pairs around central atom	VSEPR geometry
1 *s* orbital & **1** *p* orbital	sp hybrid (2 orbitals) 	2	 linear
1 *s* orbital & **2** *p* orbitals	sp^2 hybrid (3 orbitals) 	3	 trigonal planar
1 *s* orbital & **3** *p* orbitals	sp^3 hybrid (4 orbitals) 	4	 tetrahedral
1 *s* orbital & **3** *p* orbitals & **1** *d* orbital	dsp^3 hybrid (5 orbitals) 	5	 trigonal bipyramidal
1 *s* orbital & **3** *p* orbitals & **2** *d* orbitals	d^2sp^3 hybrid (6 orbitals) 	6	 octahedral

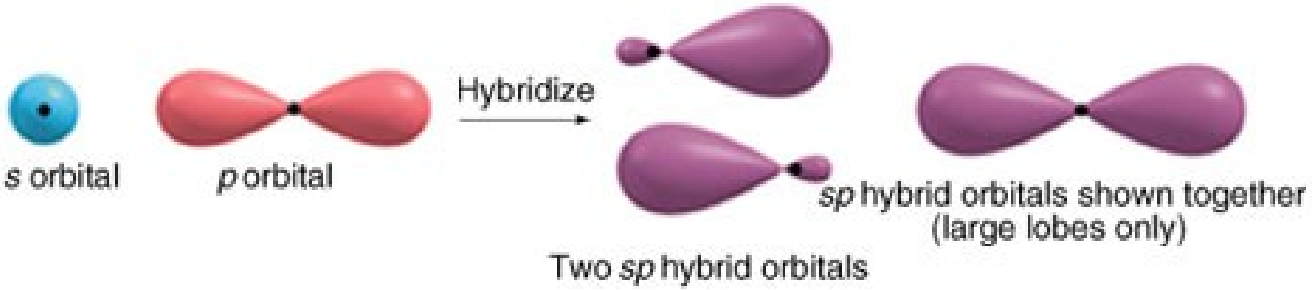
sp

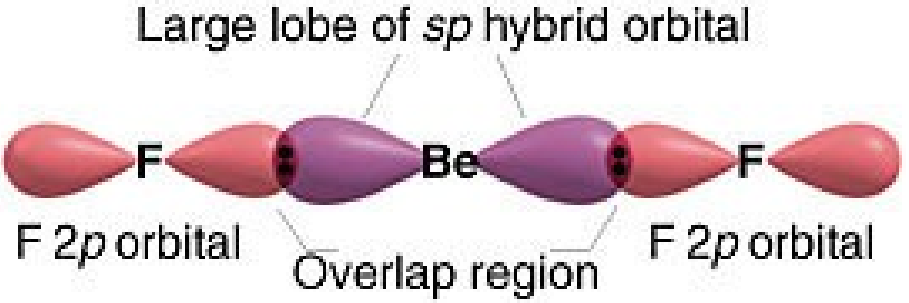

1s
2s
2p


1s
2s
2p

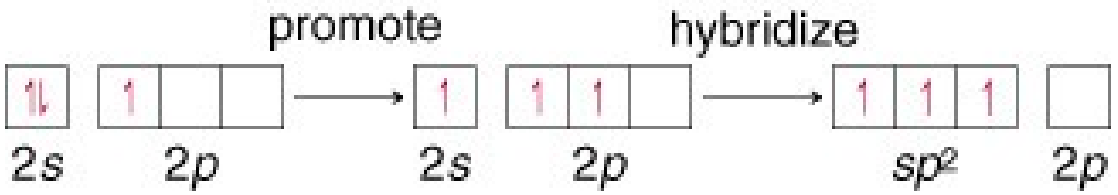

1s
sp
2p

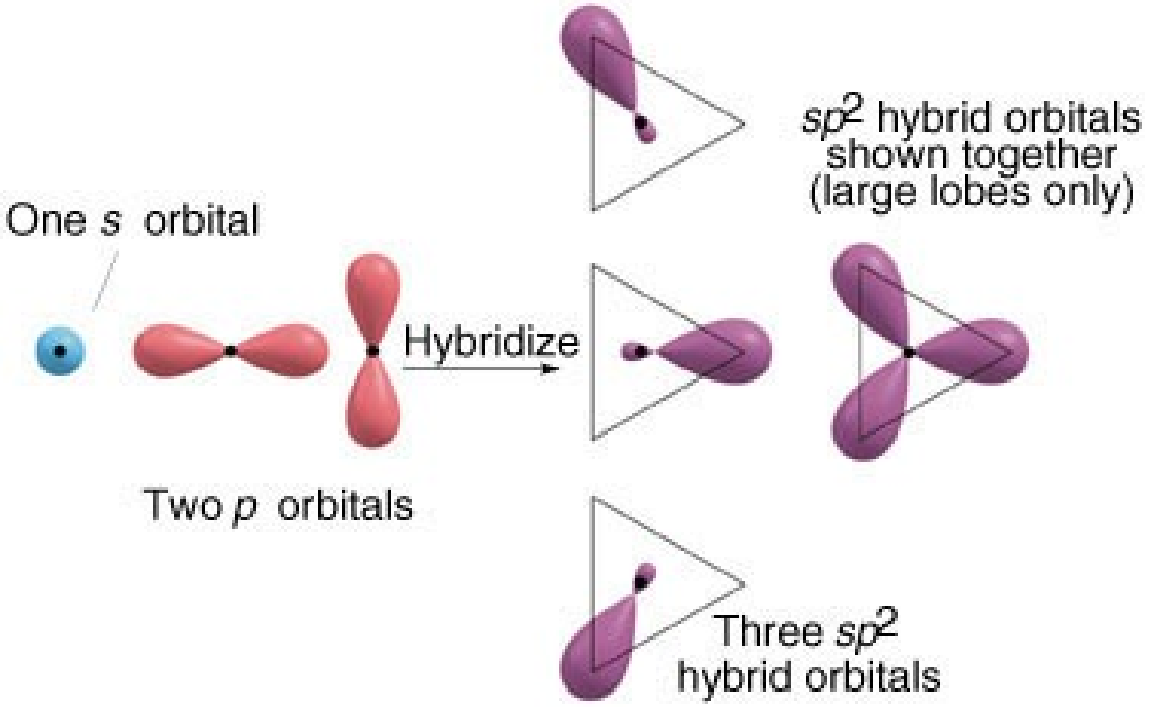

F
Be
F


Hybridize
s orbital
p orbital
sp hybrid orbitals shown together
(large lobes only)
Two sp hybrid orbitals

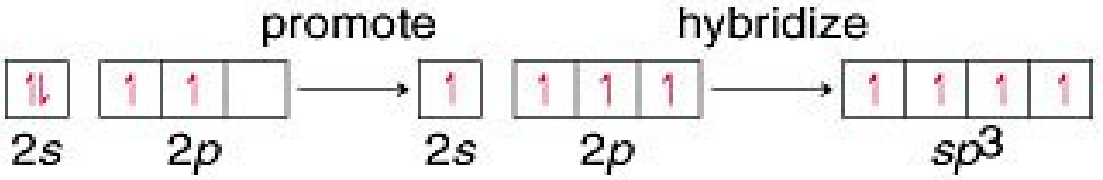

Large lobe of sp hybrid orbital
F
Be
F
F 2p orbital
Overlap region
F 2p orbital

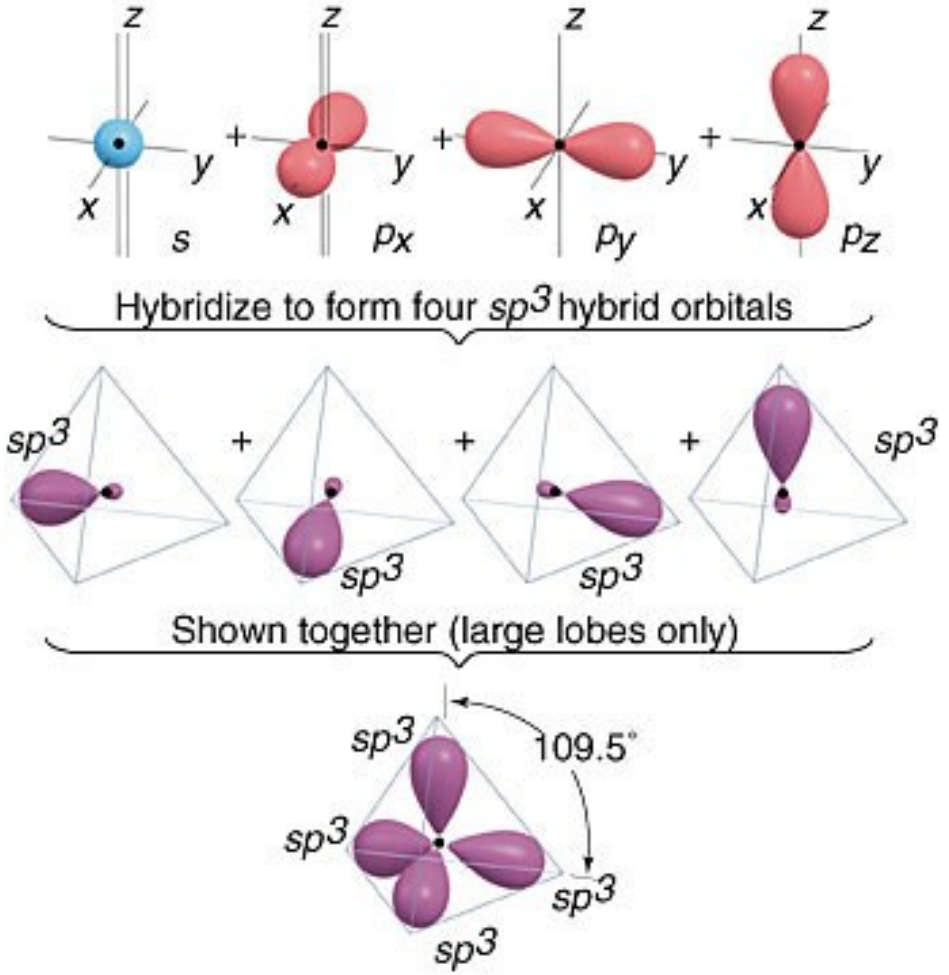
sp^2

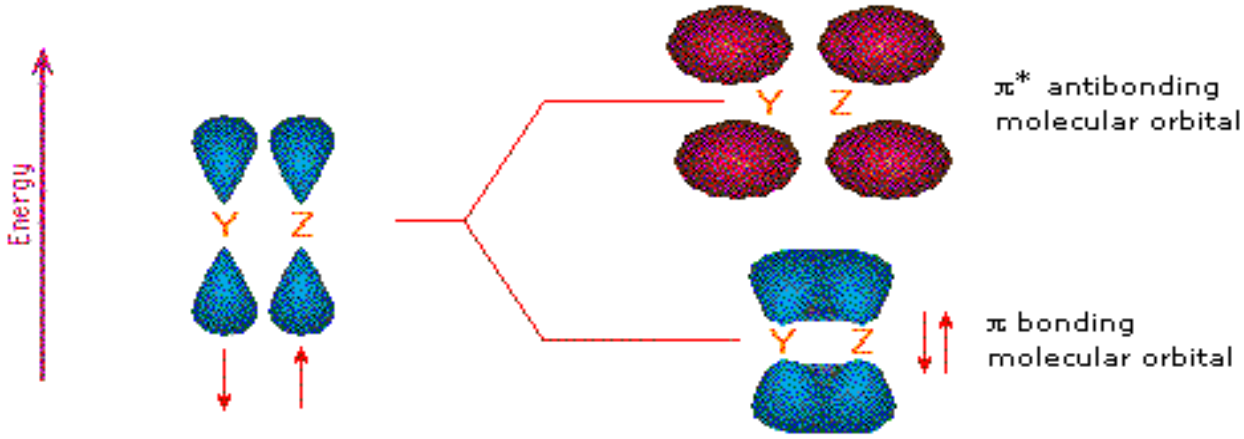

promote
hybridize
2s
2p
2s
2p
sp2
2p


sp2 hybrid orbitals
shown together
(large lobes only)
One s orbital
Hybridize
Two p orbitals
Three sp2
hybrid orbitals

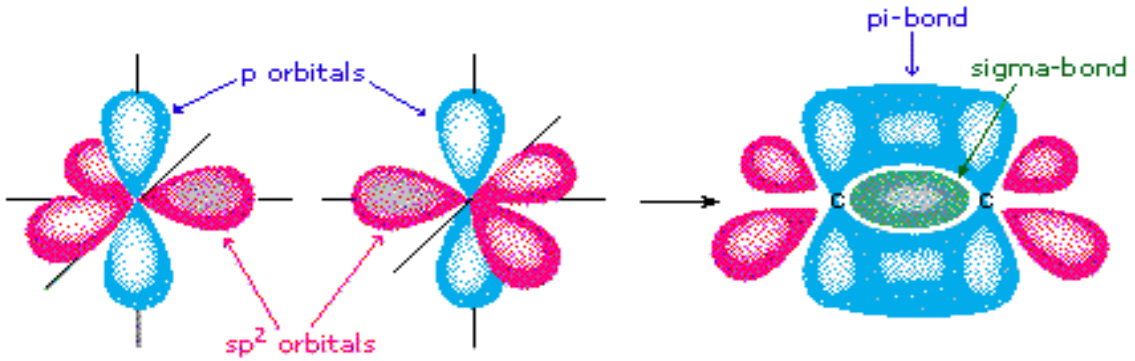
sp^3


promote
hybridize
2s
2p
2s
2p
sp3

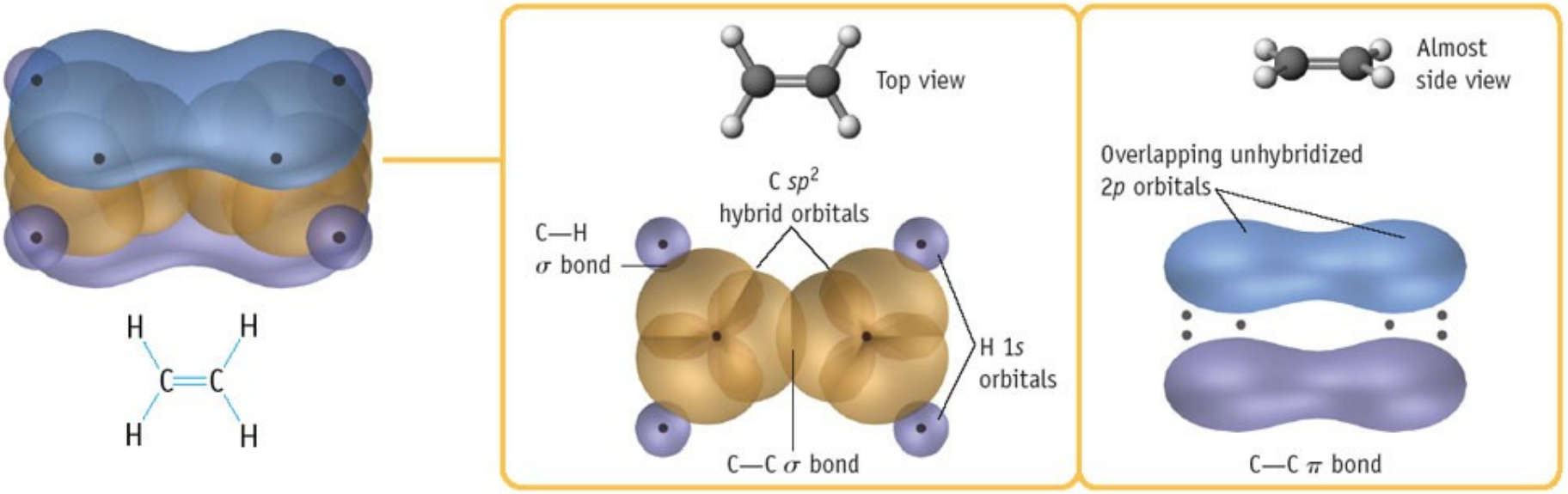

z
y
x
s
px
py
pz
Hybridize to form four sp3 hybrid orbitals
sp3
Shown together (large lobes only)
109.5°

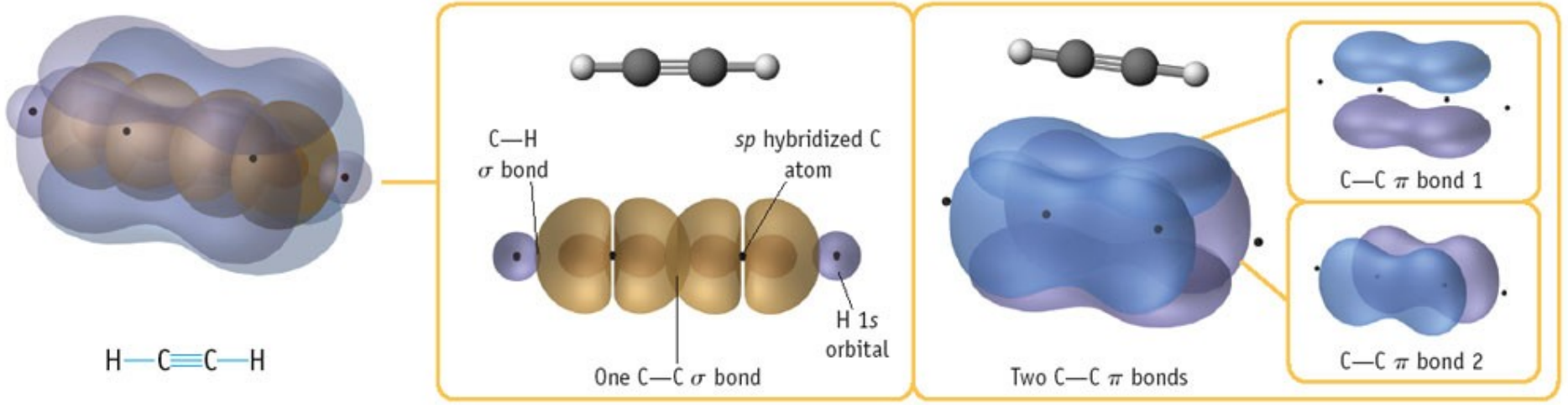


A π-orbital formation from two p-orbitals

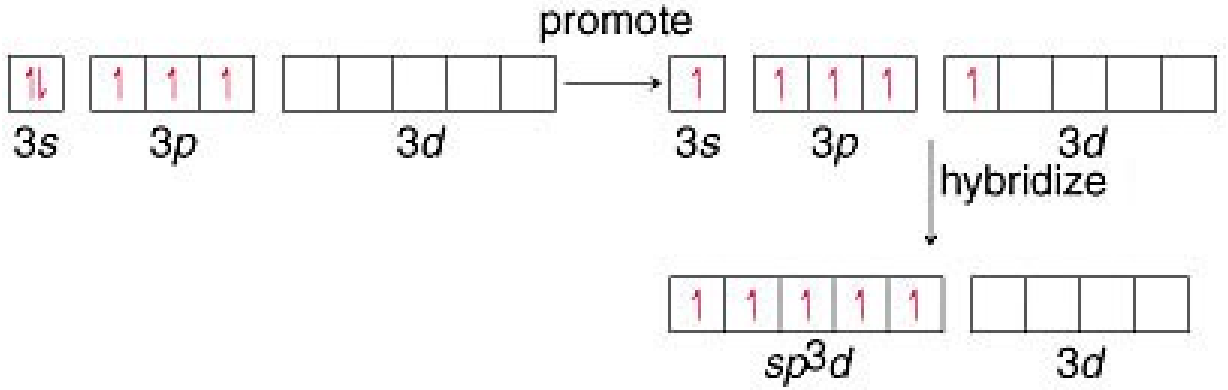


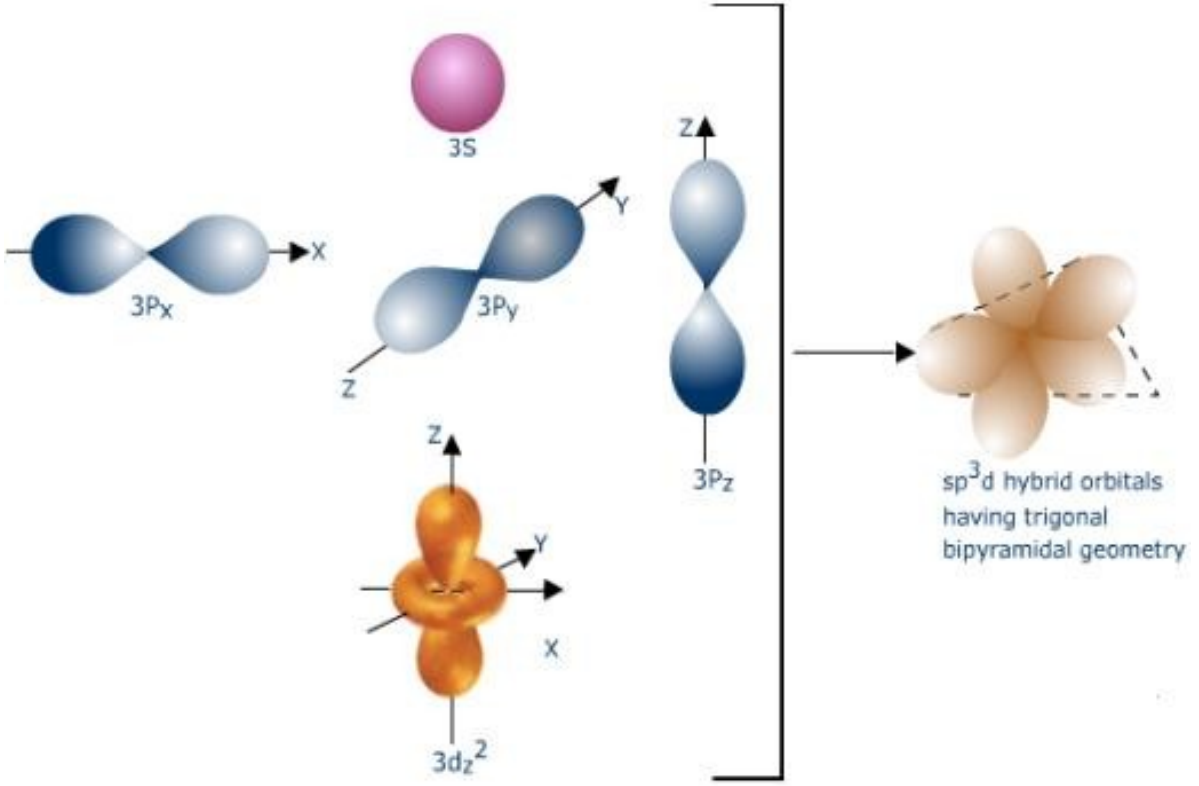
B Formation of σ- and π- molecular orbitals from two sp^2 hybridized carbon atoms



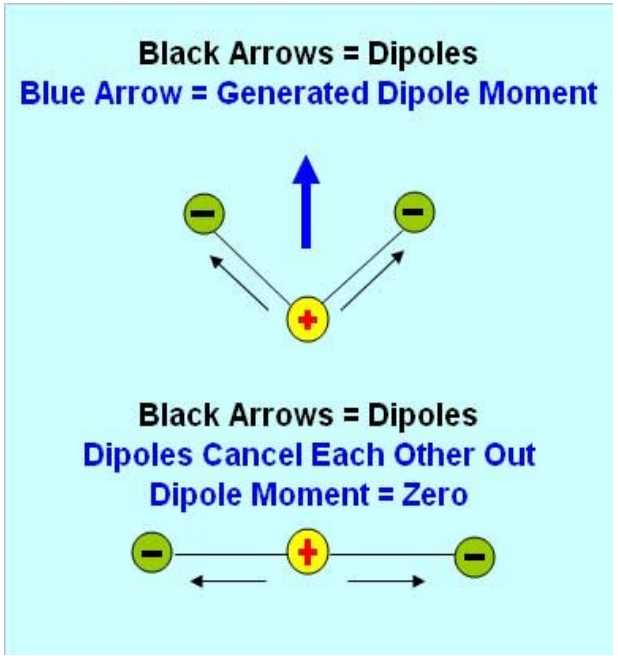


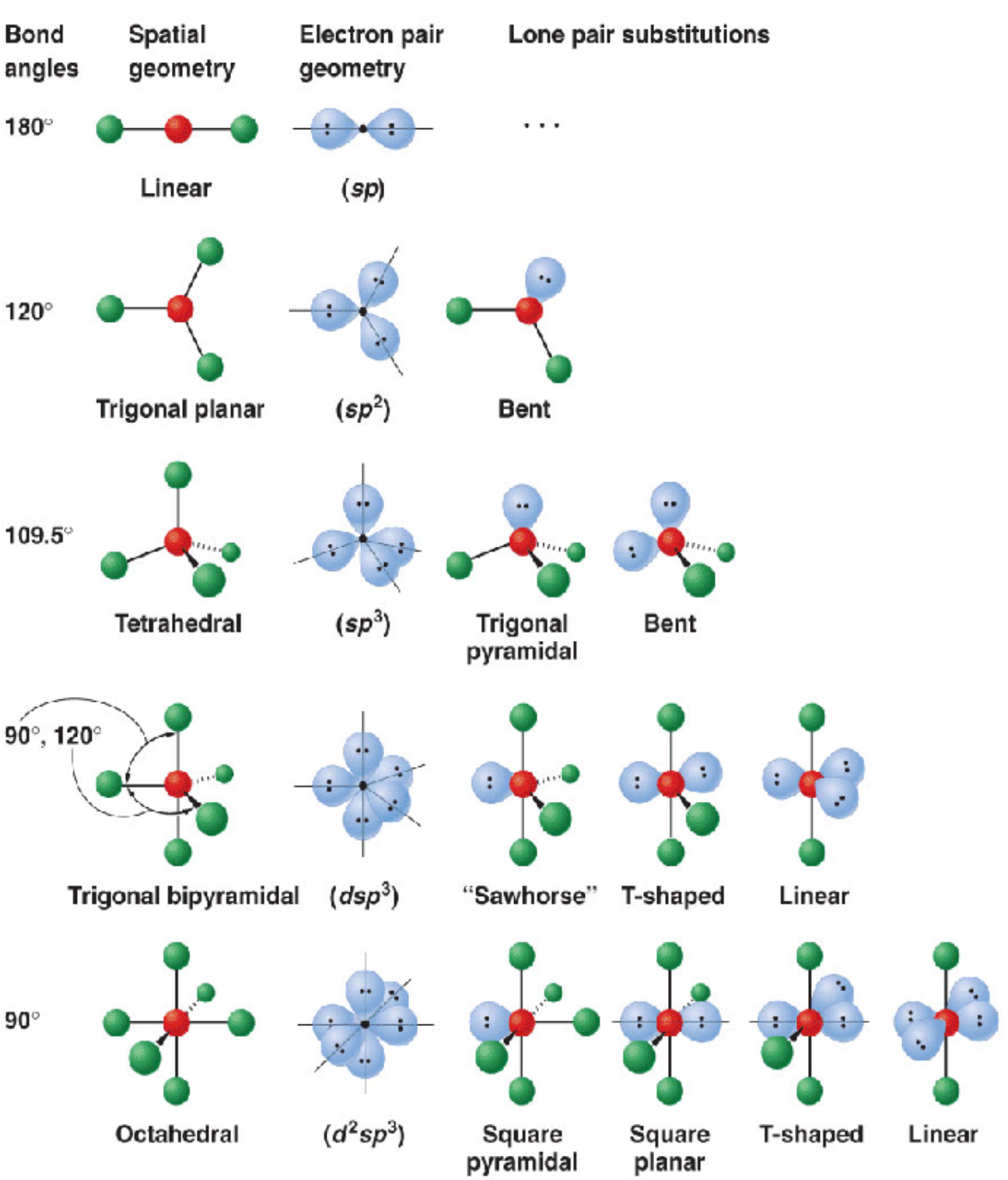
d- orbitaly


promote
3s
3p
3d
3s
3p
3d
hybridize
sp3d
3d

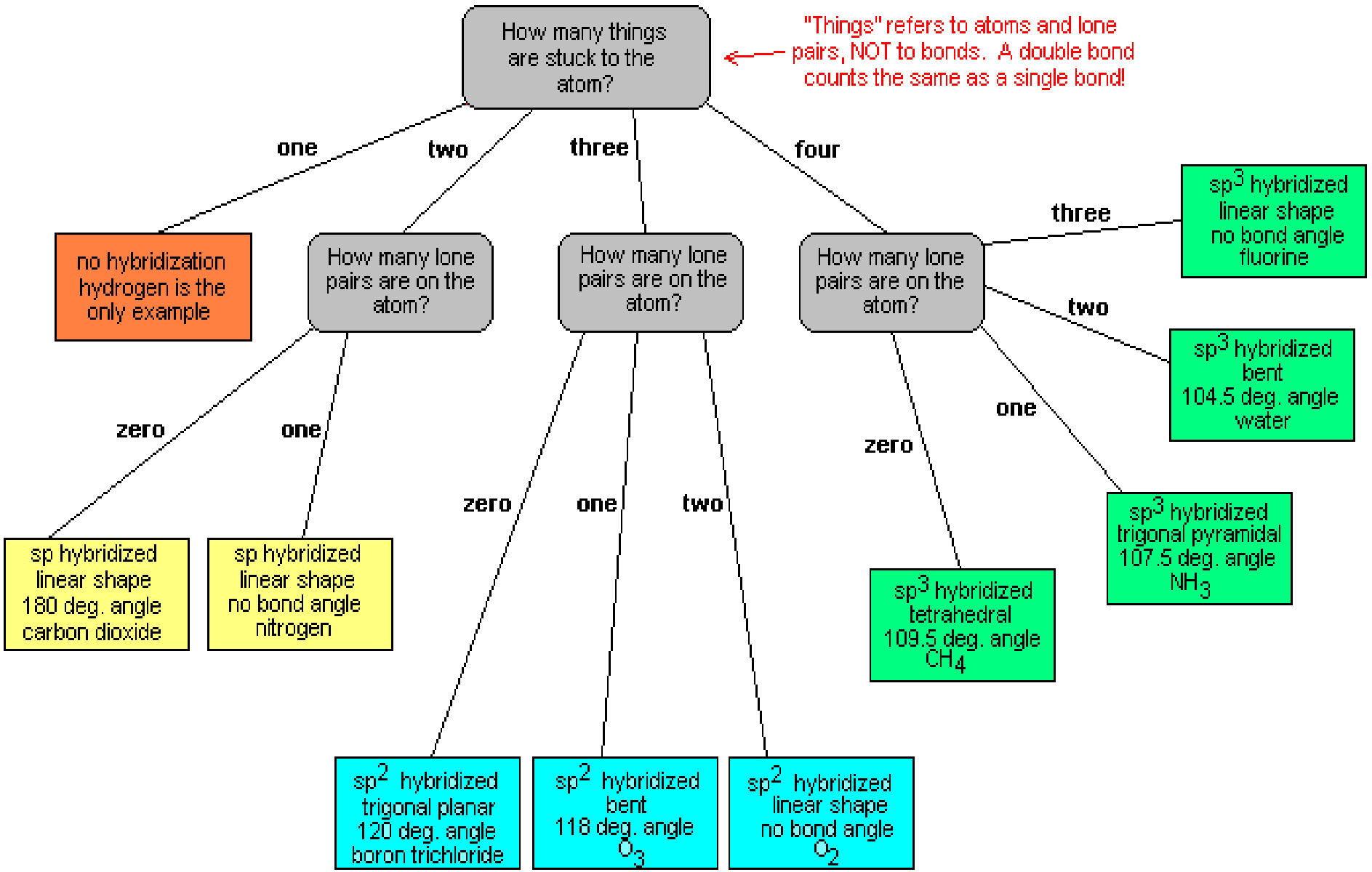

3S
3Px
3Py
3Pz
3dz2
X
Y
Z
sp3d hybrid orbitals
having trigonal
bipyramidal geometry

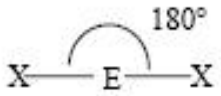
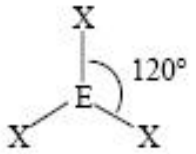
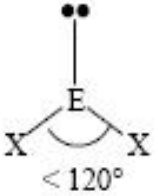
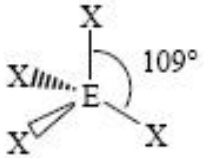
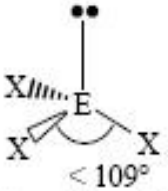
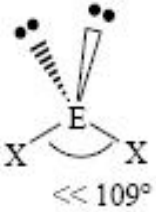
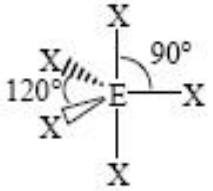
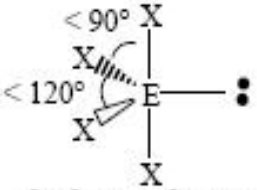
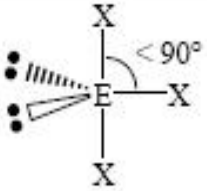
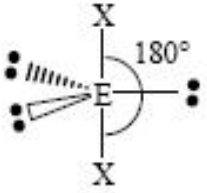
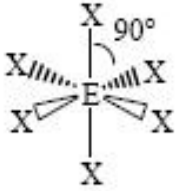
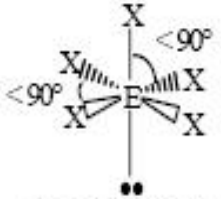
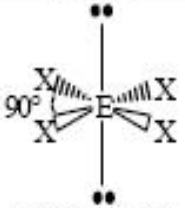
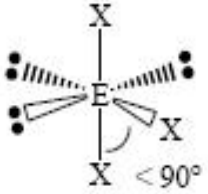
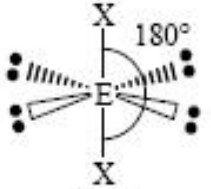
VSEPR



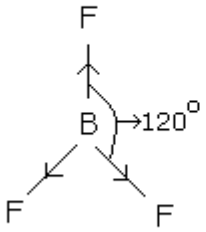


VSEPR

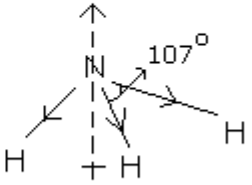

How many things are stuck to the atom?
"Things" refers to atoms and lone pairs, NOT to bonds. A double bond counts the same as a single bond!
one
two
three
four
no hybridization hydrogen is the only example
How many lone pairs are on the atom?
How many lone pairs are on the atom?
How many lone pairs are on the atom?
three
two
one
zero
sp3 hybridized linear shape no bond angle fluorine
sp3 hybridized bent 104.5 deg. angle water
sp3 hybridized trigonal pyramidal 107.5 deg. angle NH3
zero
one
zero
one
two
zero
sp hybridized linear shape 180 deg. angle carbon dioxide
sp hybridized linear shape no bond angle nitrogen
sp3 hybridized tetrahedral 109.5 deg. angle CH4
sp2 hybridized trigonal planar 120 deg. angle boron trichloride
sp2 hybridized bent 118 deg. angle O3
sp2 hybridized linear shape no bond angle O2

VSEPR Geometries					
Steric No.	Basic Geometry 0 lone pair	1 lone pair	2 lone pairs	3 lone pairs	4 lone pairs
2	 **Linear**				
3	 **Trigonal Planar**	 **Bent or Angular**			
4	 **Tetrahedral**	 **Trigonal Pyramid**	 **Bent or Angular**		
5	 **Trigonal Bipyramid**	 **Sawhorse or Seesaw**	 **T-shape**	 **Linear**	
6	 **Octahedral**	 **Square Pyramid**	 **Square Planar**	 **T-shape**	 **Linear**

Dipólový moment



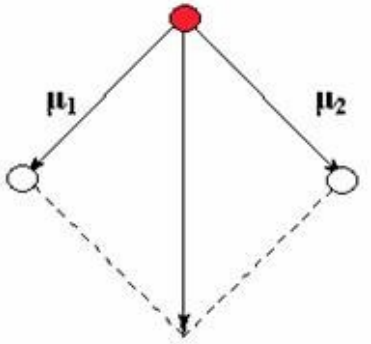
$\mu = 0$



$\mu = 1.49$ D

CO_2 $\mu = 0$ vyruší se

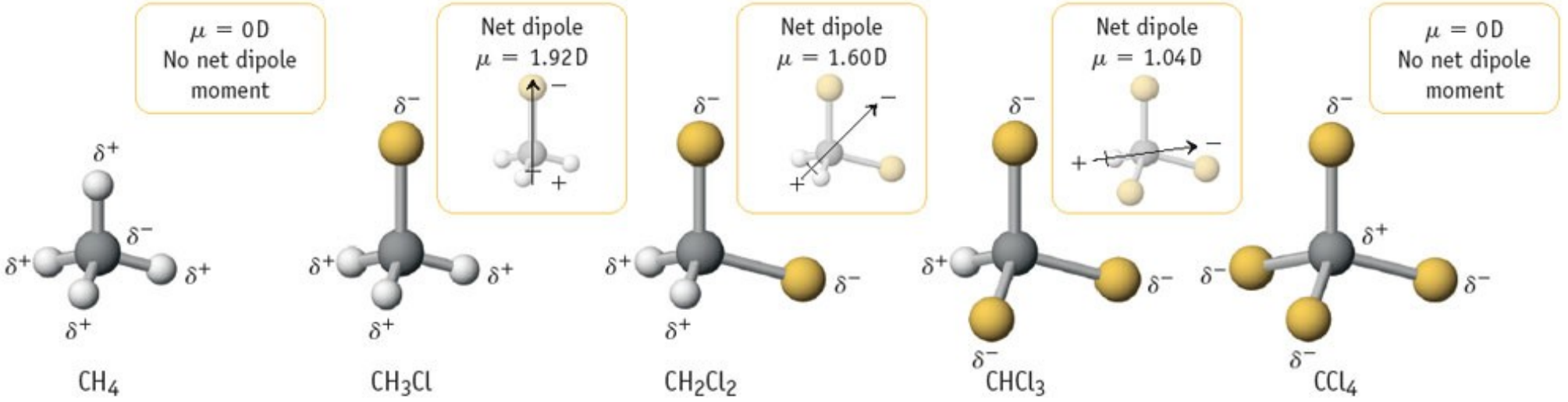
příklad nepolární molekuly

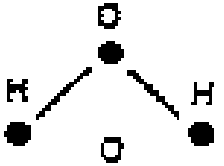
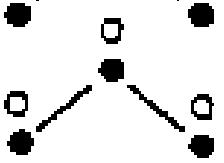
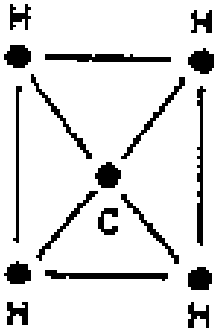


H_2O $\mu \neq 0$

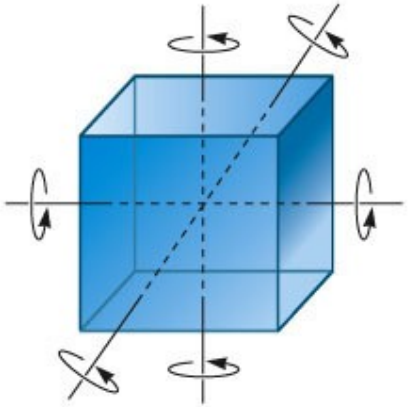
příklad polární molekuly

● C ○ H ● O

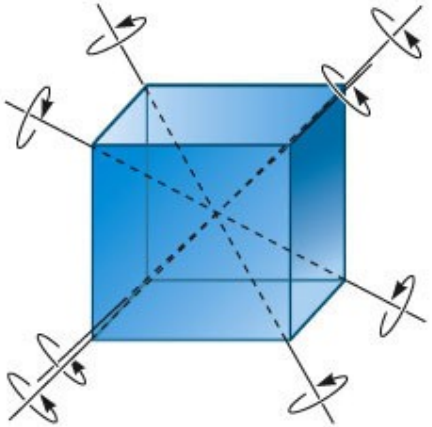


Molecule	Arrangement	Permanent Dipole Moment
N_2		No
O_2		No
CO		Yes
CO_2		No
N_2O		Yes
H_2O		Yes
O_3		Yes
CH_4		No

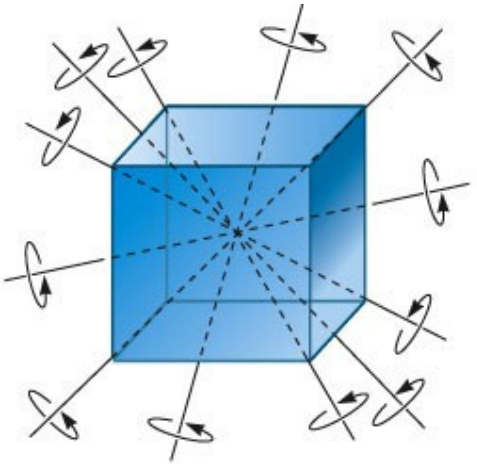
Symetrie



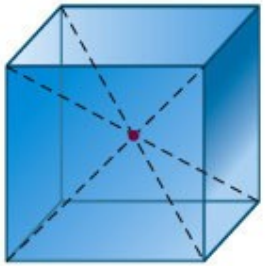
Three 4-fold axes



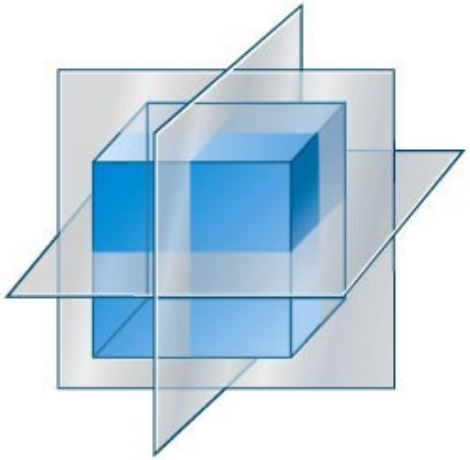
Four 3-fold axes

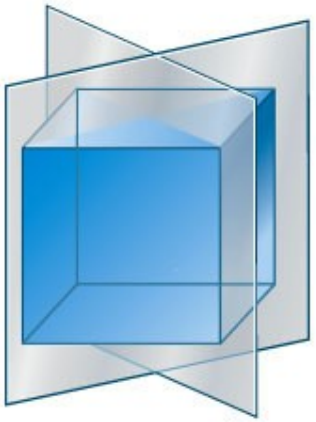


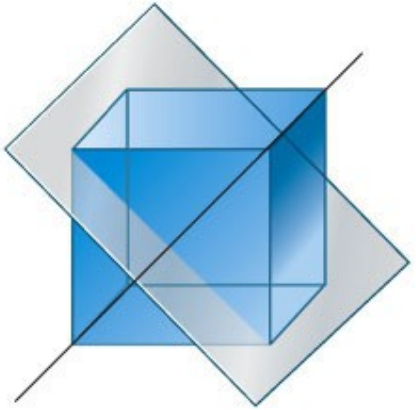
Six 2-fold axes

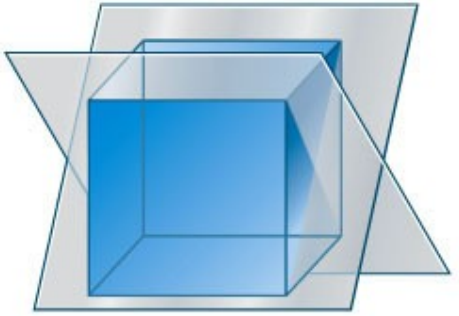


Center of inversion



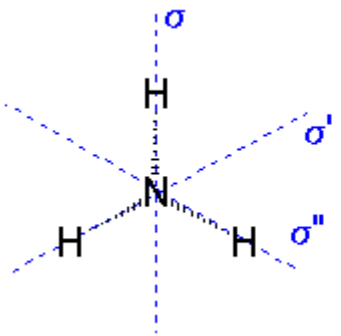




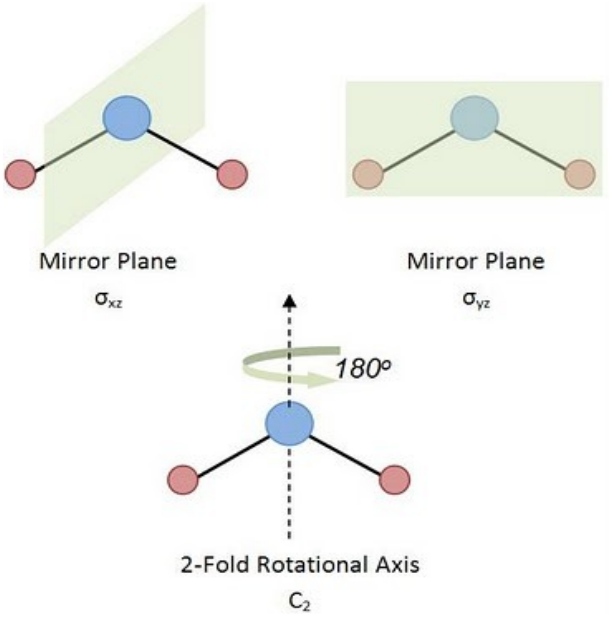


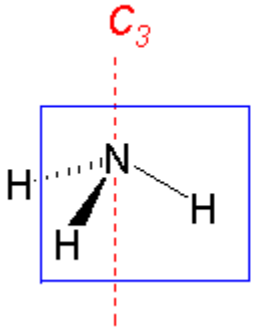
Nine mirror planes

Symetrie

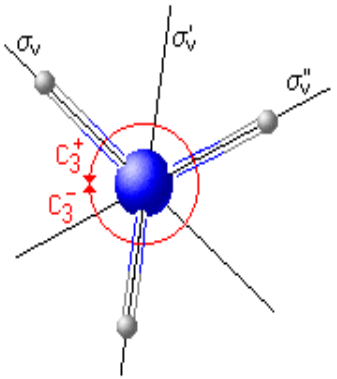


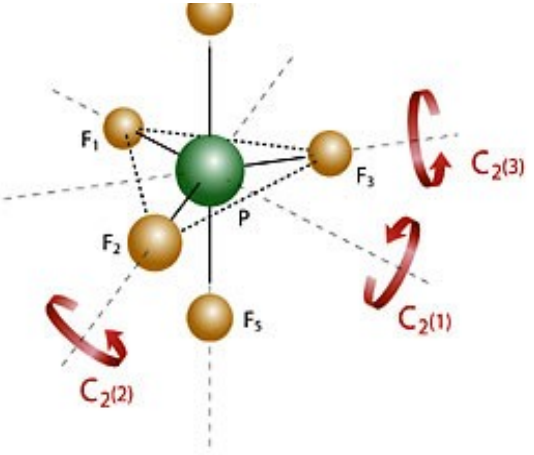
Top view, there is a plane of symmetry along each NH bond as shown by the blue broken lines

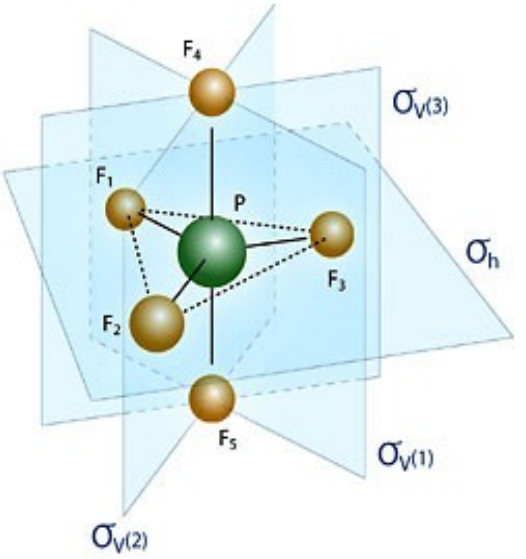




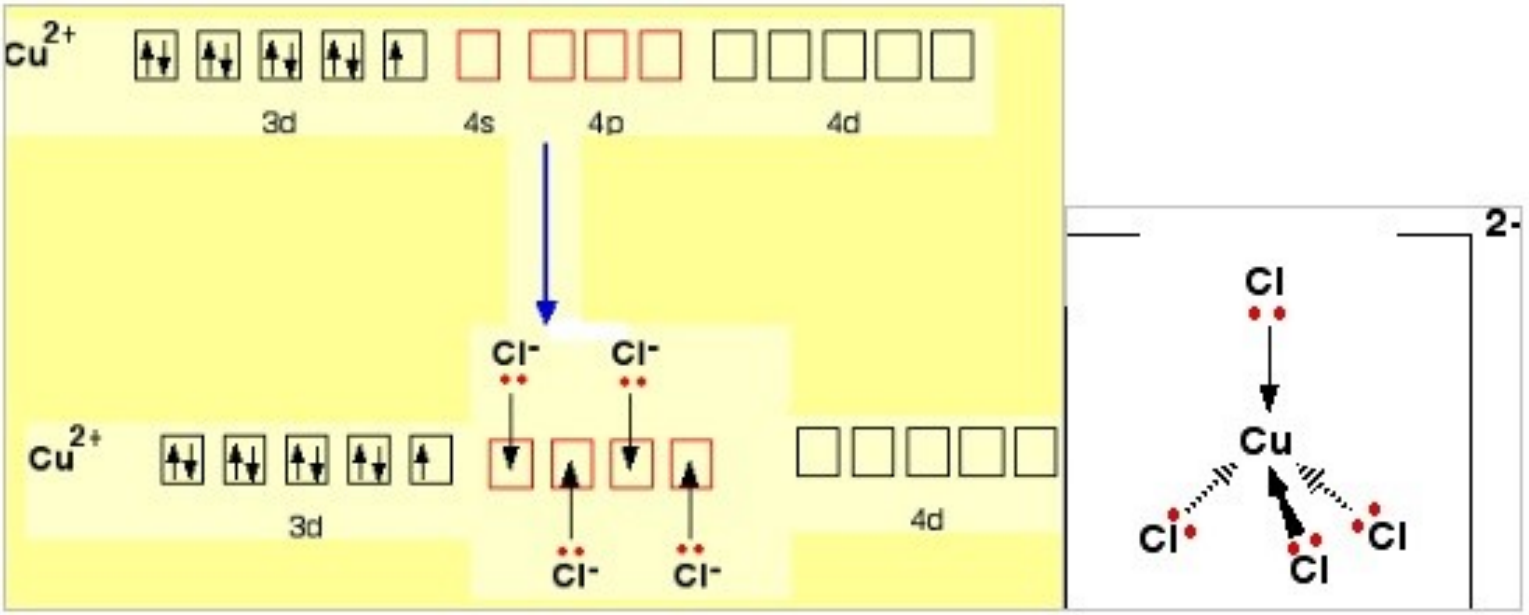
Side view, showing the C_3 axis (broken red line) and one of the three planes of symmetry (blue box)

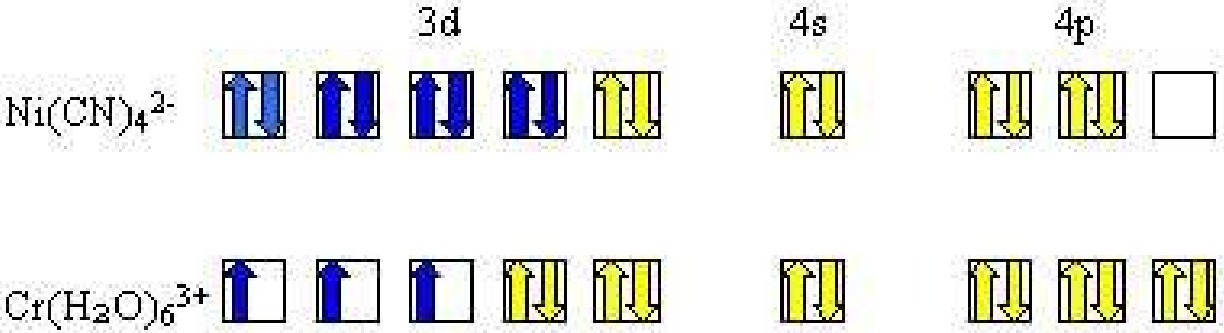


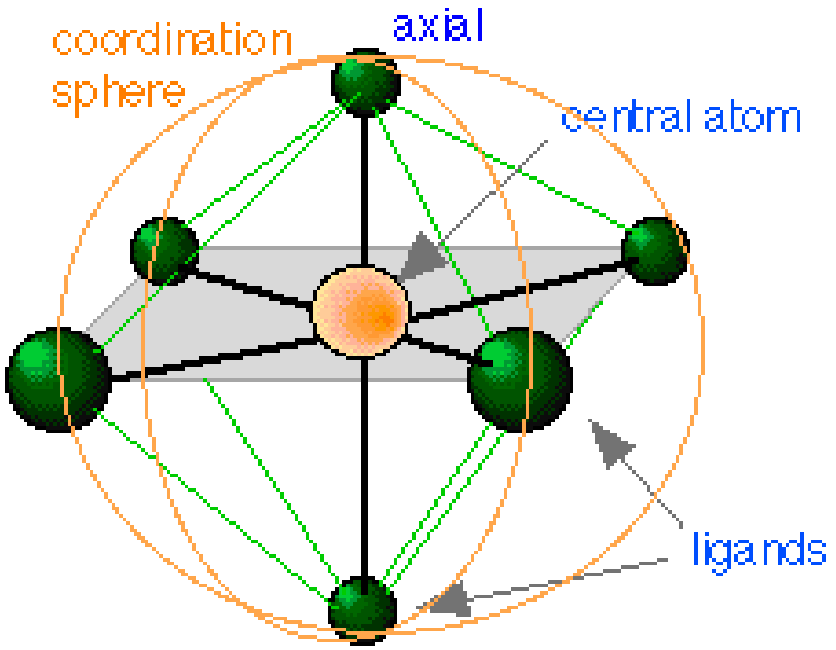




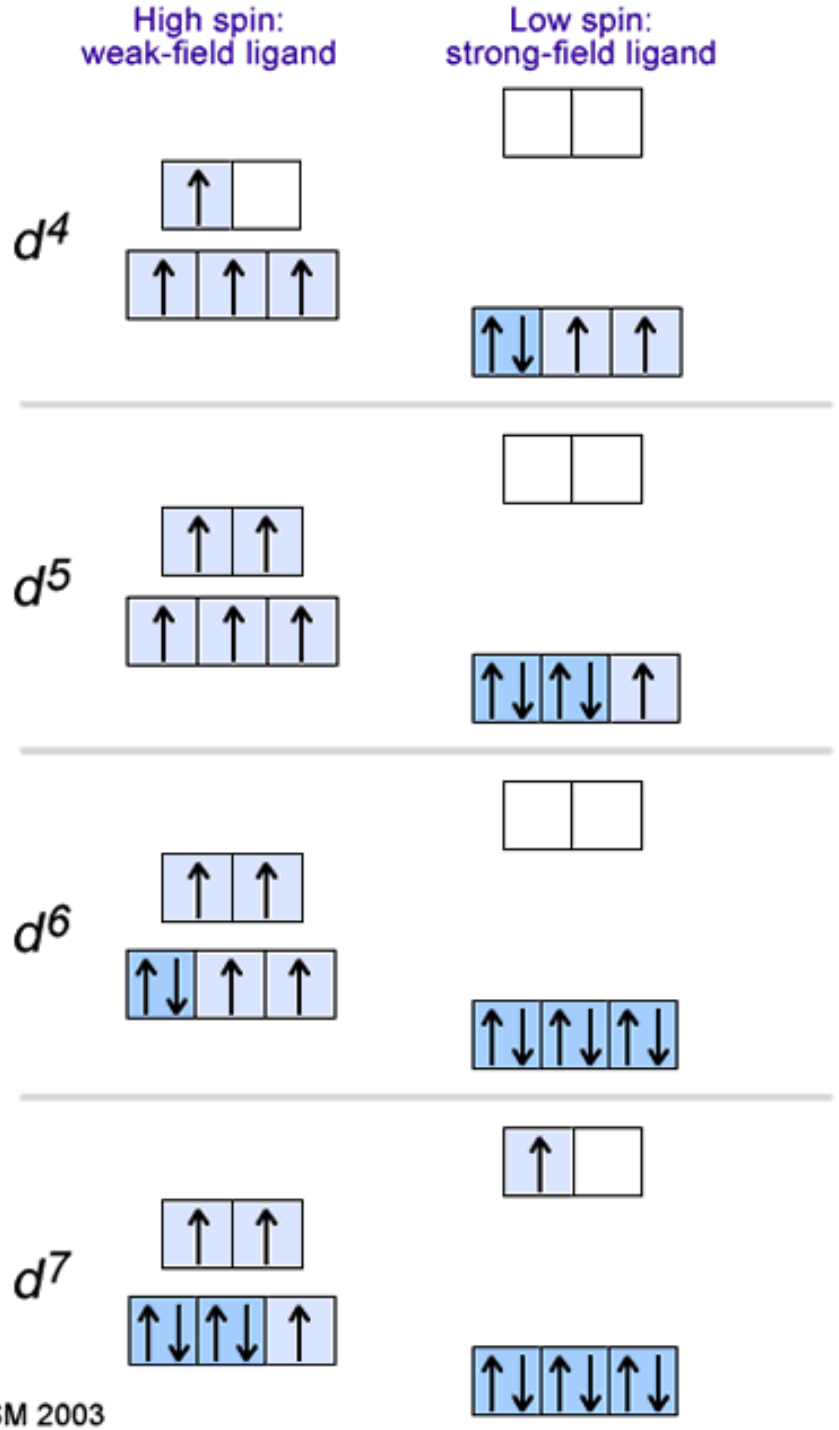
KOMPLEXY

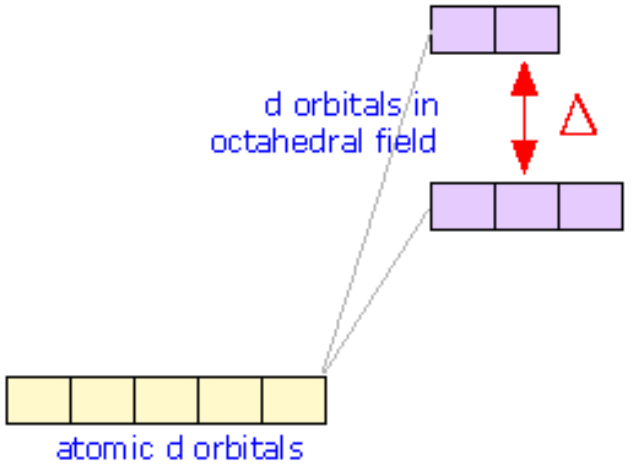

Cu2+
3d
4s
4p
4d
Cl-
Cl-
Cu2+
3d
4d
Cl-
Cl-
2-
Cl
Cu
Cl
Cl
Cl

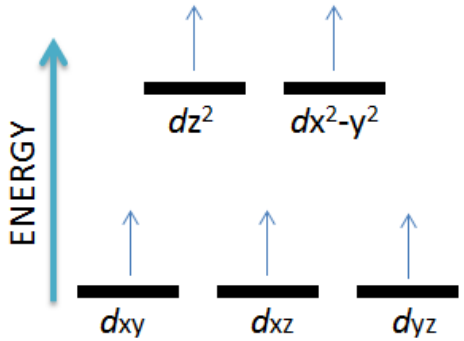

3d
4s
4p
Ni(CN)4 2-
Cr(H2O)6 3+

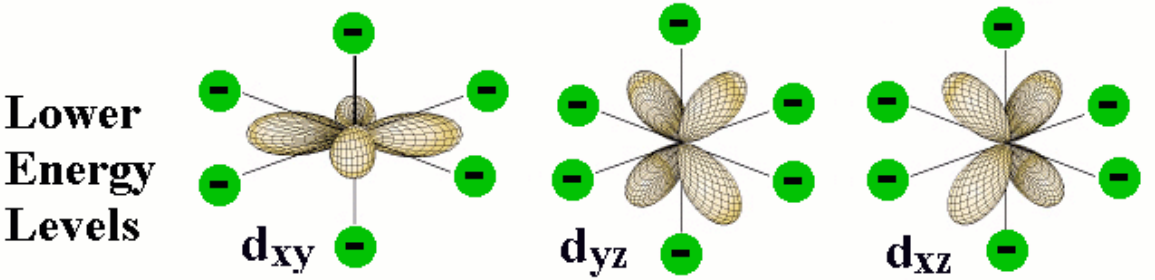


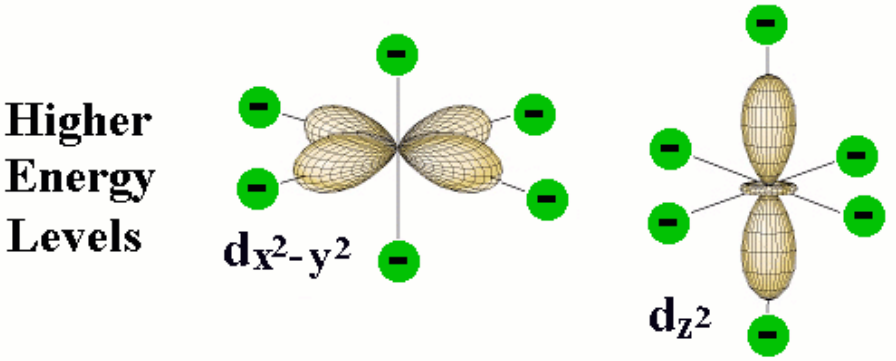
d1	d2	d3	d4	d5	d6	d7	d8	d9	d10
Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg
3	4	5	6	7	8	9	10	11	12

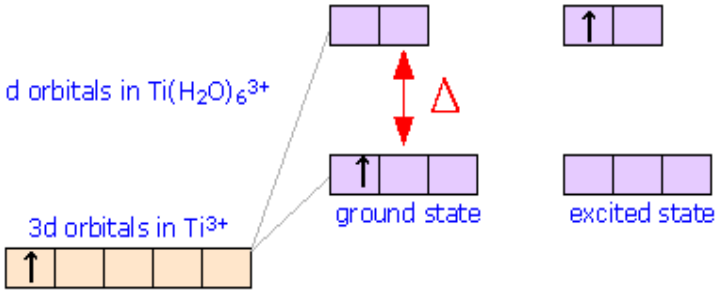


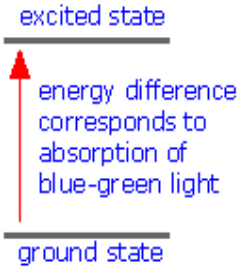


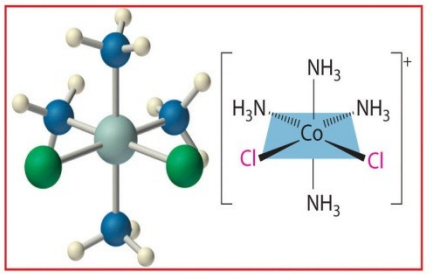




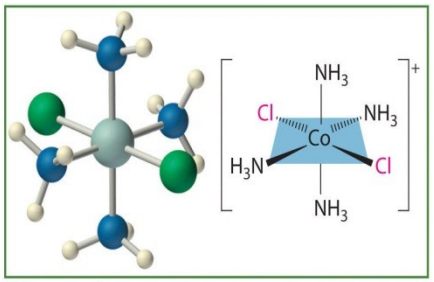




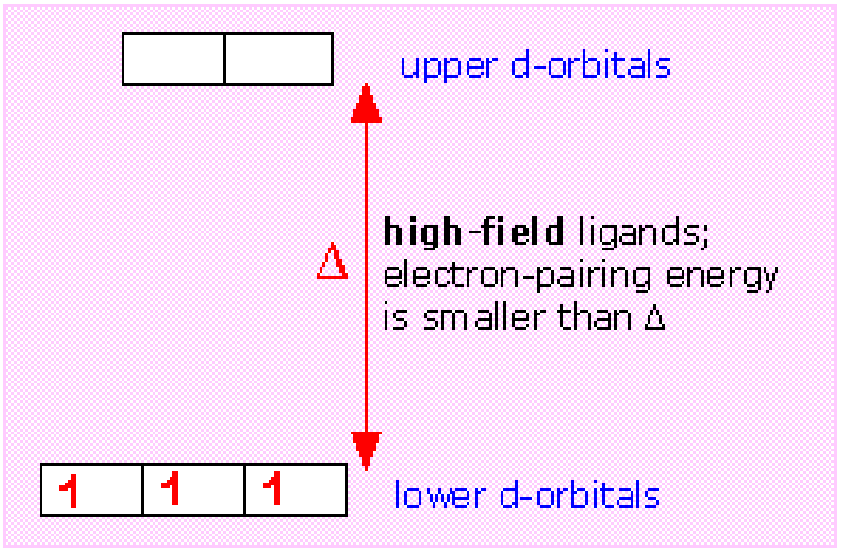


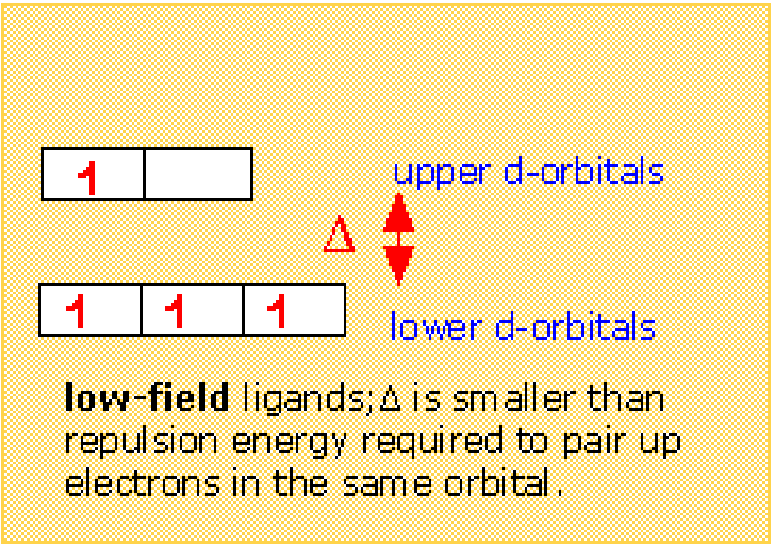


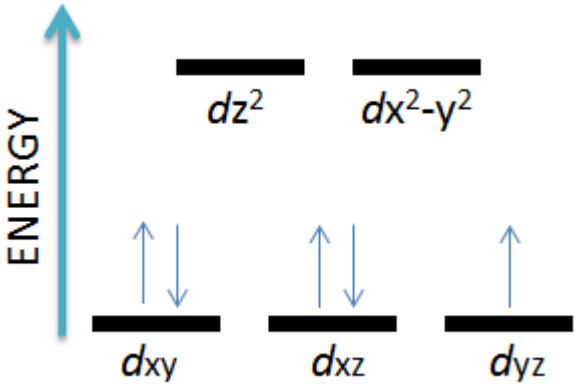
(a) Red form

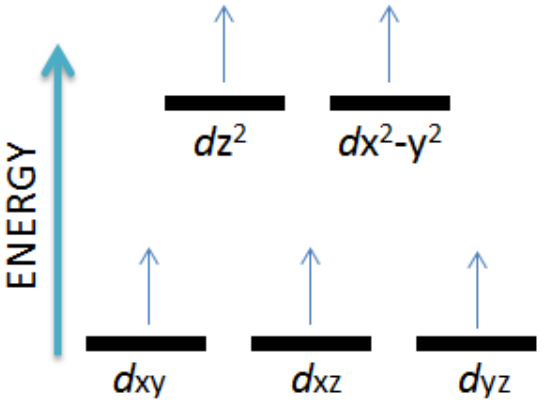


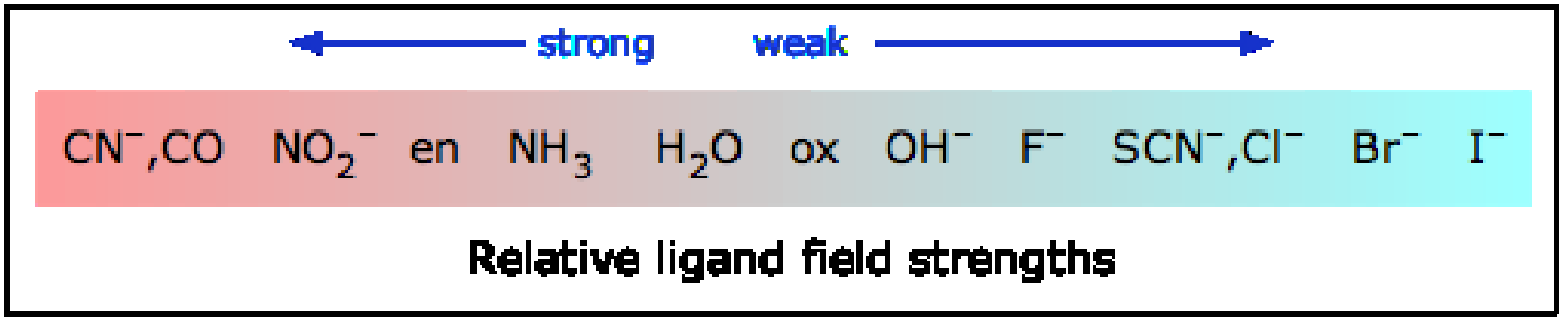
(b) Green form


upper d-orbitals
Δ
high-field ligands;
electron-pairing energy
is smaller than Δ
1
1
1
lower d-orbitals

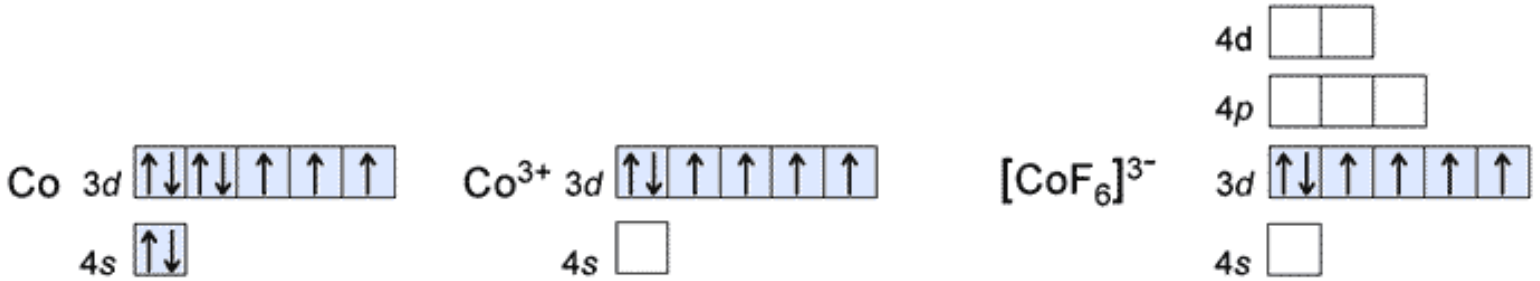

1
upper d-orbitals
Δ
1
1
1
lower d-orbitals
low-field ligands; Δ is smaller than
repulsion energy required to pair up
electrons in the same orbital.


ENERGY
dz2
dx2-y2
dxy
dxz
dyz


ENERGY
dz2
dx2-y2
dxy
dxz
dyz

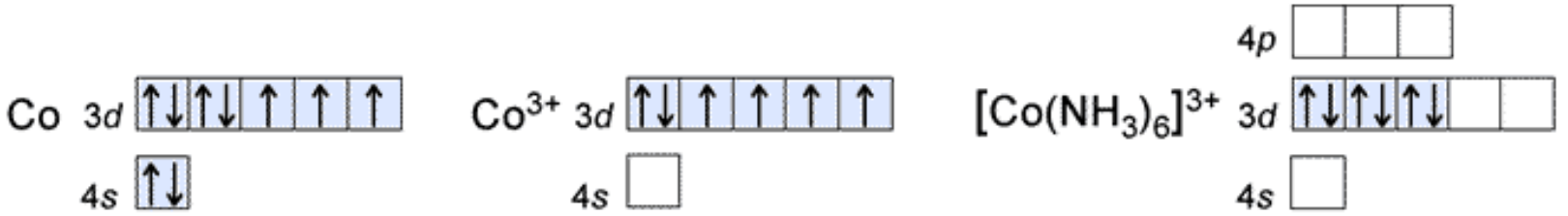

strong
weak
CN⁻,CO
NO2⁻
en
NH3
H2O
ox
OH⁻
F⁻
SCN⁻,Cl⁻
Br⁻
I⁻
Relative ligand field strengths

$[CoF_6]^{3-}$ Octahedral complex sp^3d^2



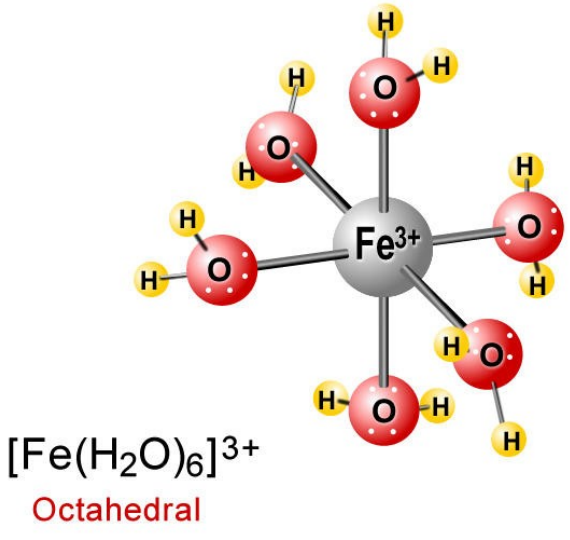
Outer orbital complex
High spin complex
4 unpaired electrons

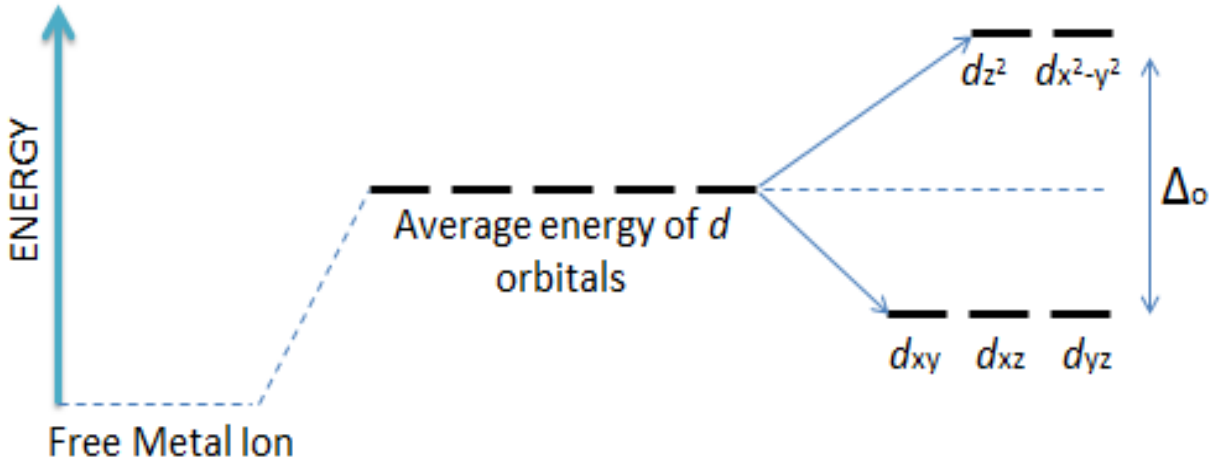
$[Co(NH_3)_6]^{3+}$ Octahedral complex sp^3d^2



Inner orbital complex
Low spin complex
No unpaired electrons

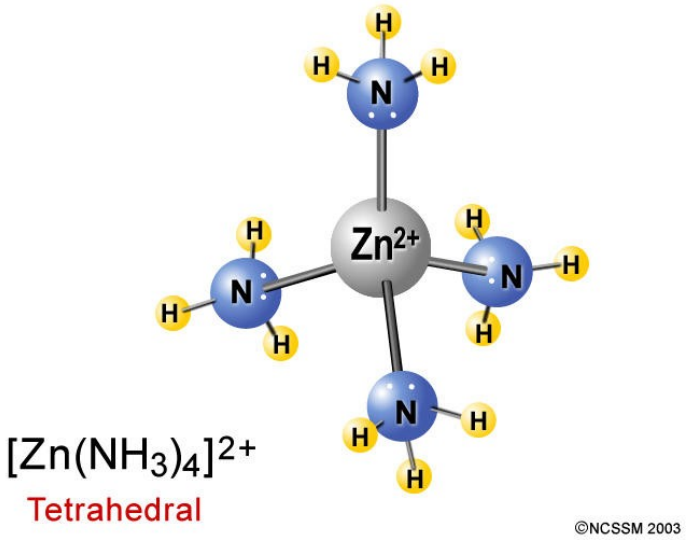
Oktaedrální komplex

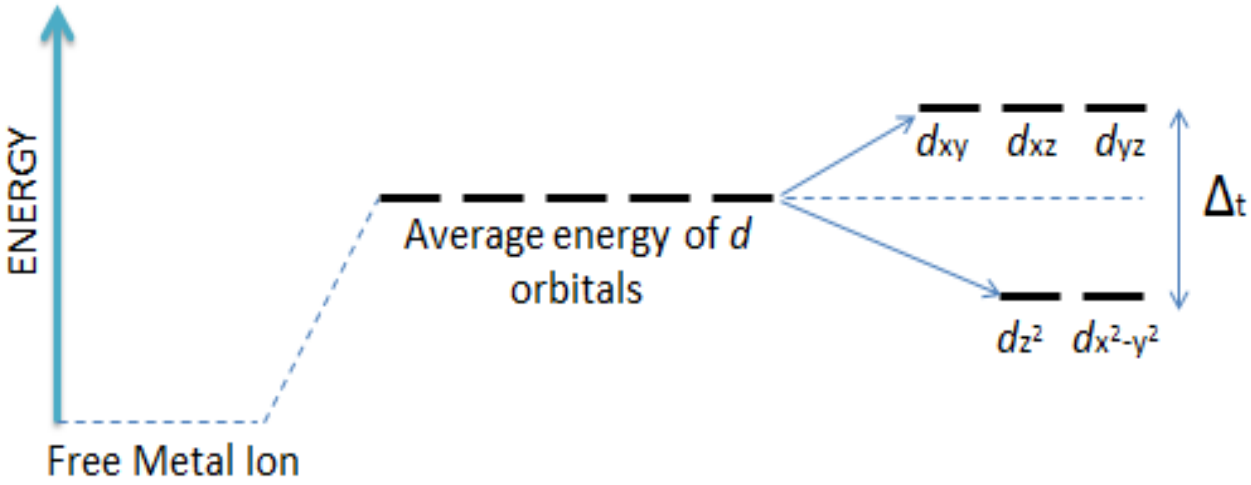




In an octahedral complex, there are six ligands attached to the central transition metal. The d-orbital splits into two different levels. The bottom three energy levels are named d_{xy}, d_{xz}, and d_{yz} (also referred to as t_{2g}). The two upper energy levels are named $d_{x^2-y^2}$, and d_{z^2} (also referred to as eg). The reason they split is because of the electrostatic interactions between the electrons of the ligand and the lobes of the d-orbital. In an octahedral, the electrons are attracted to the axes. Any orbital that has a lobe on the axes moves to a higher energy level. This means that in an octahedral, the energy levels of e_g are higher ($0.6\Delta_o$) while t_{2g} is lower ($0.4\Delta_o$).

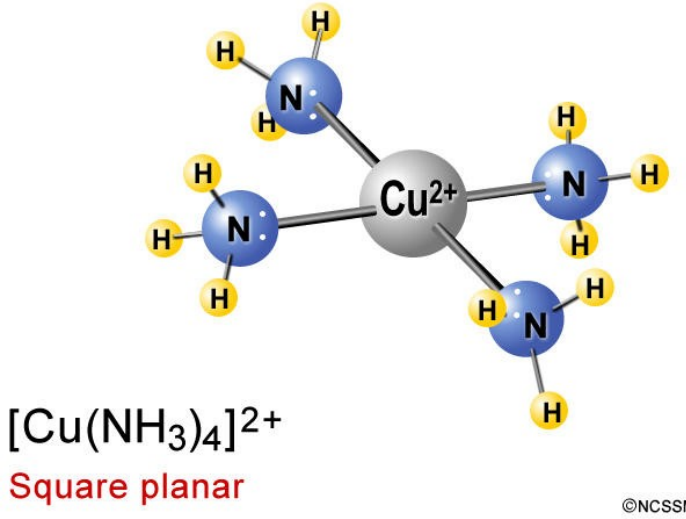
Tetraedrální komplex

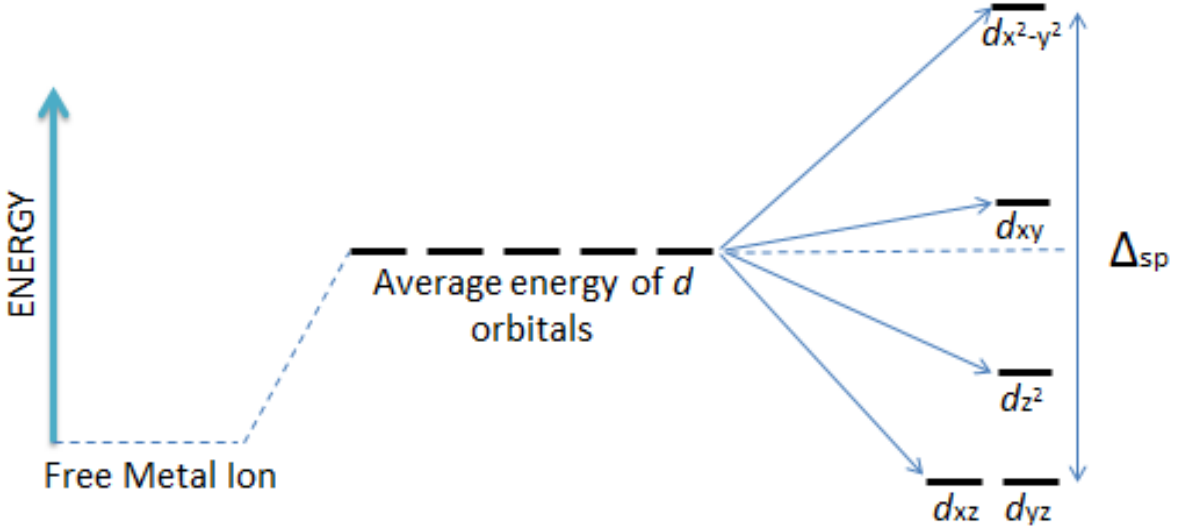




In a tetrahedral, there are four ligands attached to the central metal. The d orbital also splits into two different energy levels. The top three energy levels are named dxy, dxz, and dyz. The two bottom d energy levels are named dx^2-y^2, and dz^2. The reason for this is because the electrons are attracted away from the axes. Any orbital that has a lobe in-between the axes, it moves to a higher energy level. This means that dxy, dxz, and dyz have higher energy levels.

Čtvercový planární komplex





In a square planar, there are four ligands as well. However, the difference is that the electrons of the ligands are only attracted to the xy plane. Any orbital in the xy plane has a higher energy level. There are four different energy levels for the square planar (from the highest energy level to the lowest energy level): $d_{x^2-y^2}$, d_{xy}, d_{z^2}, and both d_{xz} and d_{yz}.

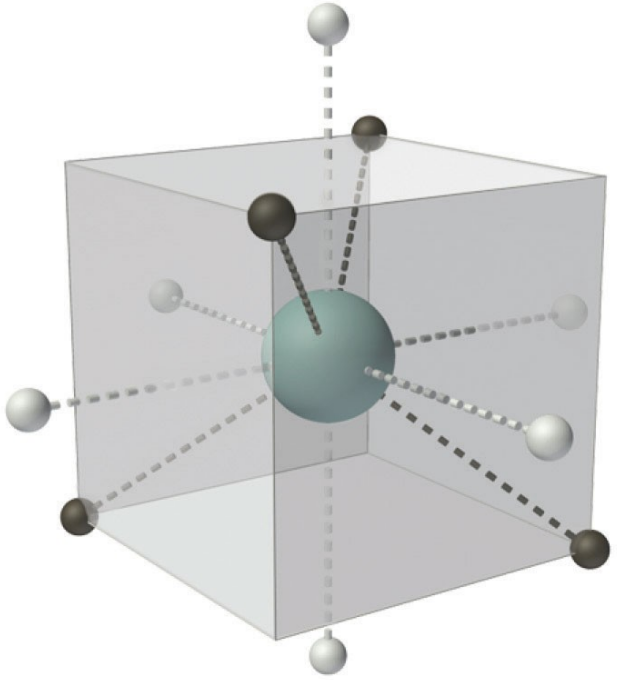
Tetraedr

u komplexů s a p-prvků (např. $[BF_4]^-$) a u těch d-prvků, které buď dosáhly skupinového oxidačního čísla (všechny orbitaly prázdné, např. Mn^{+7} - MnO_4^-), nebo mají konfiguraci d^5 příp. d^{10} (symetrické konfigurace, např. Fe^{+3}, Cu^+ - $[Cu(py)_4]^+$, Ni^0 - $[Ni(CO)_4]$).

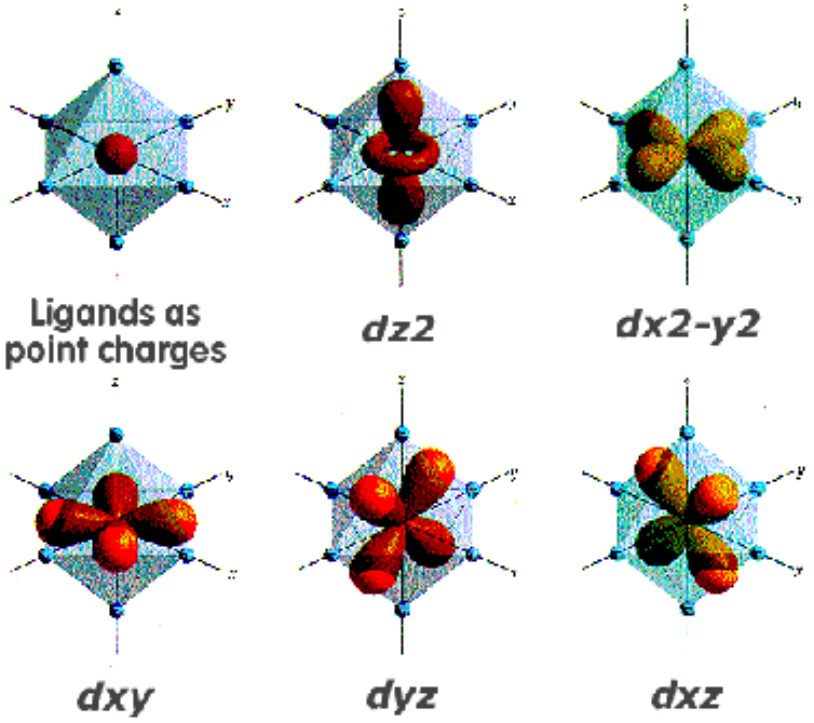
Čtverec

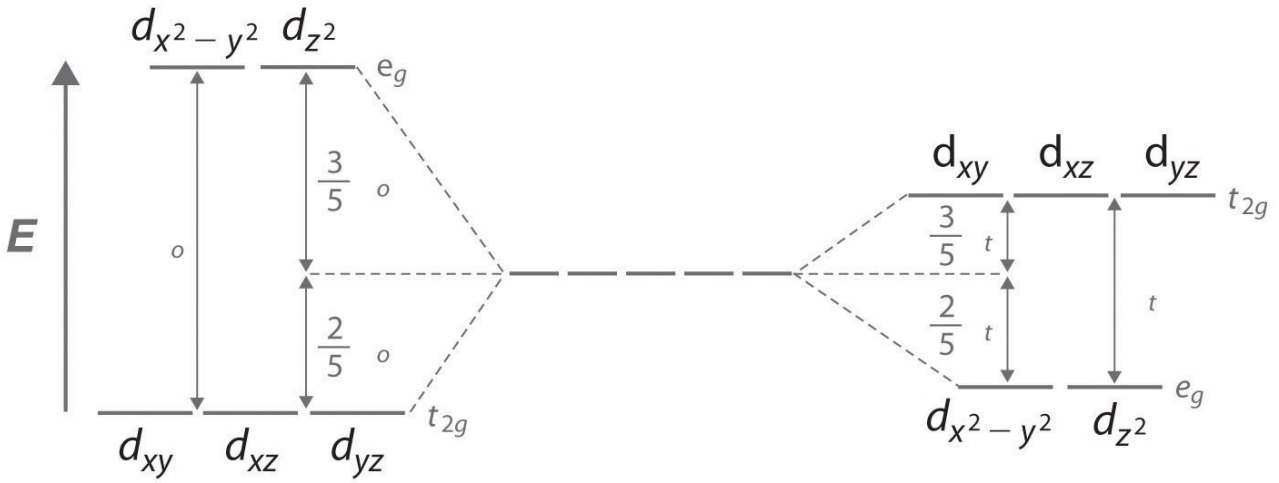
Centrální atomy s jinou konfigurací budou preferovat čtvercové uspořádání komplexů. Platí to především pro konfiguraci d^8 (Pd^{+2}, Pt^{+2}), která ve většině případů vede ke čtvercovému uspořádání (výjimku tvoří Ni^{2+}, který tvoří běžně také tetraedrické komplexy). Čtvercové uspořádání ovšem vyžaduje alespoň jeden volný d-orbital pro hybridizaci dsp^2.

Jsou-li rozdíly v energii mezi čtvercovým a tetraedrickým uspořádáním malé (např. u některých komplexů Ni^{+2} nebo Cu^{+2}), mohou existovat komplexy v obou geometriích nebo může mezi oběma docházet k vzájemné přeměně - $(NH_4)_2[CuCl_4]$ je čtvercový a $Cs_2[CuBr_4]$ je přibližně tetraedrický. Čtverec a tetraedr jsou pak spíše extrémními možnostmi uspořádání ligandů a skutečný tvar leží někde mezi nimi. Tento jev se nazývá konformační izomerií



(a)


Ligands as point charges
dz2
dx2-y2
dxy
dyz
dxz

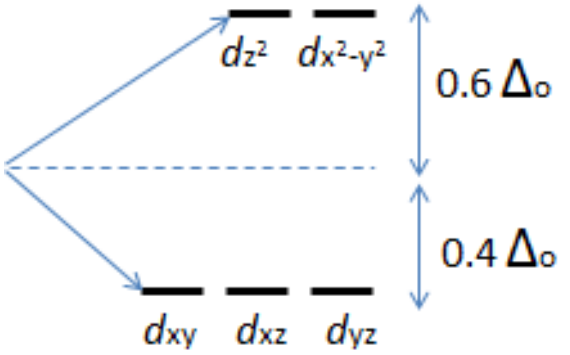

E
$d_{x^2-y^2}$ d_{z^2}
e_g
$\frac{3}{5}$ o
o
$\frac{2}{5}$ o
t_{2g}
d_{xy} d_{xz} d_{yz}
Octahedral
d_{xy} d_{xz} d_{yz}
t_{2g}
$\frac{3}{5}$ t
$\frac{2}{5}$ t
t
e_g
$d_{x^2-y^2}$ d_{z^2}
Tetrahedral

(b)

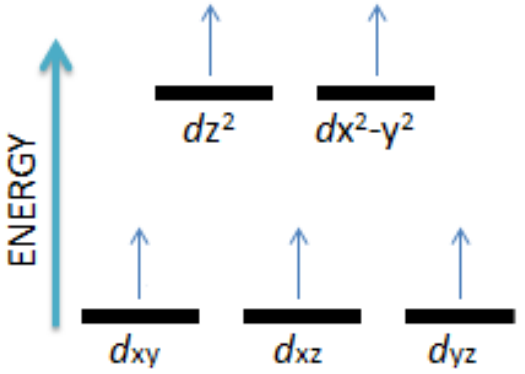
Complex ion $[Fe(Cl)_6]^{3-}$

Step 1: Determine the oxidation state of Fe. Here it is Fe^{3+}. Based on its electron configuration, Fe^{3+} has **5 d-electrons**.

Step 2: Determine the geometry of the ion.
Here it is an octahedral which means the energy splitting should look like:



Step 3: Determine whether the ion is low or high spin by looking at the spectrochemical series. Cl^- is high spin. Therefore, electrons fill all orbitals before being paired.

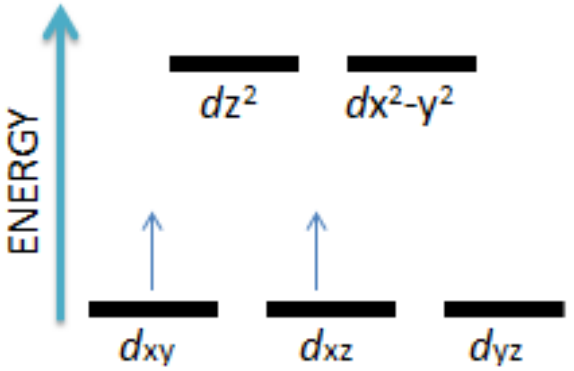


Step 4: Count the number of lone electrons. Here, there are **5 electrons**.

Step 5: lone pairs are paramagnetic. This ion is **paramagnetic**.

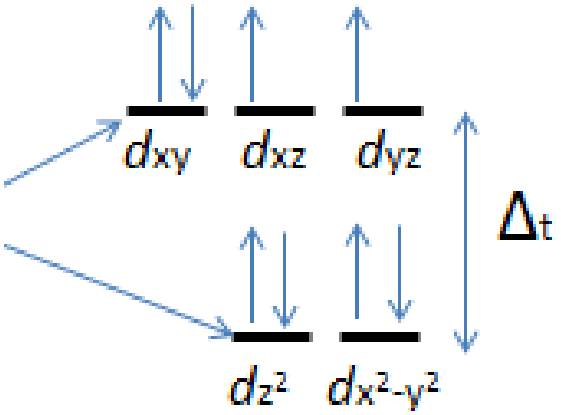
$[Ti(H_2O)_6]^{2+}$

octahedral, paramagnetic



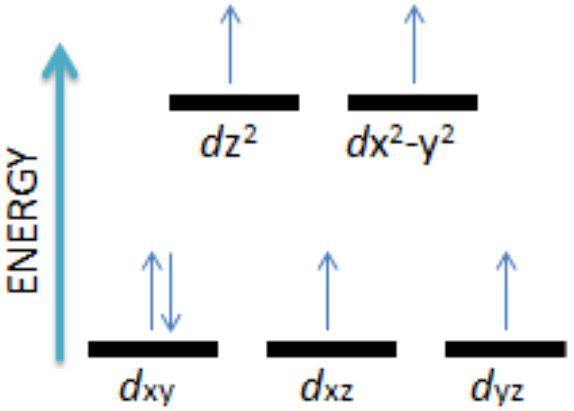
$[NiCl_4]^{2-}$

tetrahedral, paramagnetic

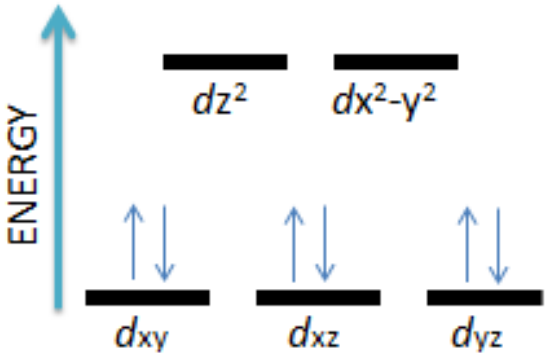


$[CoF_6]^{3-}$

octahedral, paramagnetic, high spin



$[Co(NH_3)_6]^{3+}$



octahedral, diamagnetic, low spin

Example Problem: Which ligand exhibits a stronger magnetism?

1. [Fe(edta)3]^-2

Fe has 6 valence e-
edta is a weaker ligand than CN
that means splitting E is smaller
there are 6 binding sites:
Octahedral

Less e- are paired
More Paramagnetic

2. [Fe(CN)6]^-3

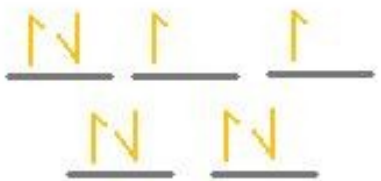
Fe has 5 valence e-
CN- is a stronger ligand
that means splitting E is larger
there are 6 binding sites:
Octahedral

More e- paired
less paramagnetic

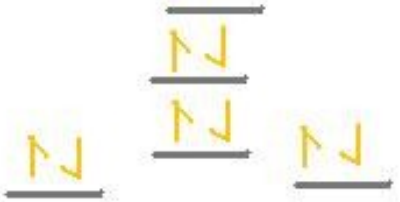
Example Problem: How to predict orbital structure from Magnetic Properties!

[Zn(I)4] has 8 valence e-. It has 4 binding sites and is said to be Diamagnetic. What orbital structure does it exhibit? Is it Tetrahedral or Square planar?

1. Tetrahedral Model



2. Square Planar Model



> Here all e- are paired, the compound is diamagnetic.
> Square Planar is the right structure.

Multiplicita = 2*S + 1

S = celkový spin