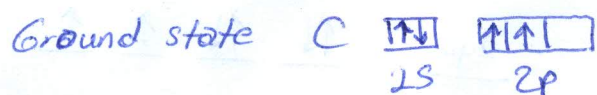


Introduction to the Valence-Bond Method

A description of covalent bond formation in terms of atomic orbital overlap is called the valence-bond method. The creation of a covalent bond in the valence-bond method is normally based on the overlap of half-filled orbitals. But some times such an overlap involves a filled orbital on one atom and an empty orbital on another.

Hybridization of Atomic Orbitals

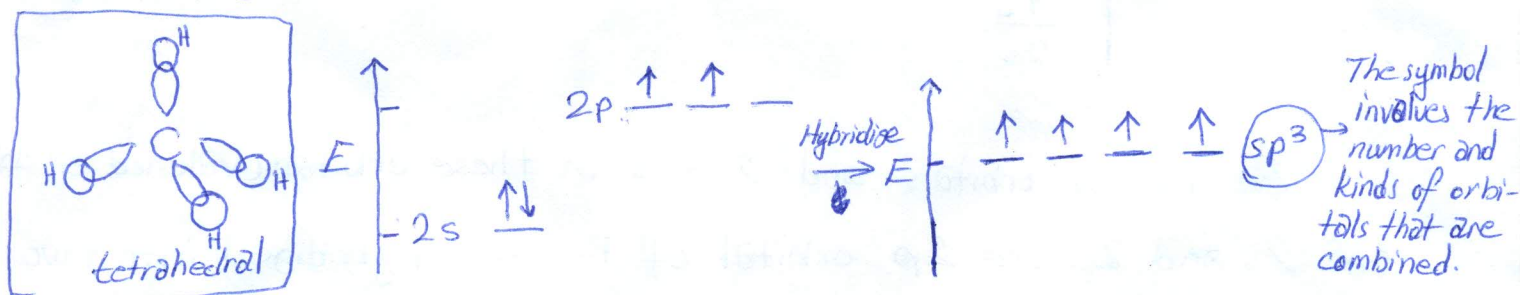
Based on the ground-state  $\bar{e}$  configuration of the C atom, it is not possible the formation of  $\text{CH}_2$  molecule.



C atom has two half-filled orbitals and it can form  $\text{CH}_2$  molecule based on this  $\bar{e}$  configuration. But the simplest molecule formed by C is  $\text{CH}_4$ .

To obtain  $\text{CH}_4$  molecule by the valence-bond theory we need four unpaired  $\bar{e}$ 's. These 4 half-filled orbitals are formed by mixing of atomic orbitals.

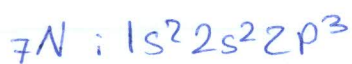
\* The process of mixing atomic orbitals is called hybridization and the new orbitals formed by hybridization are called hybrid orbitals.



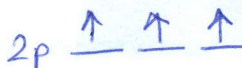
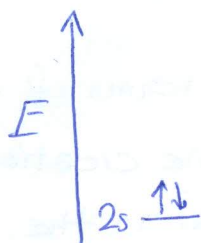
The number of hybrid orbitals equal to the total number of atomic orbitals that are combined.

\* Hybrid orbitals have energies, that are intermediate between the 2s and 2p orbitals.

## NH<sub>3</sub> molecule:

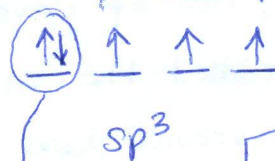


Ground state

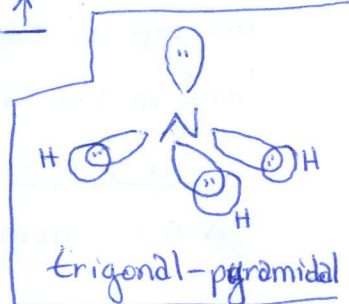


Hyb.

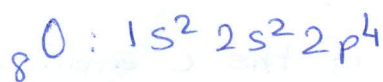
used for covalent bond formation



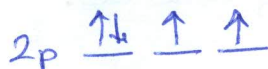
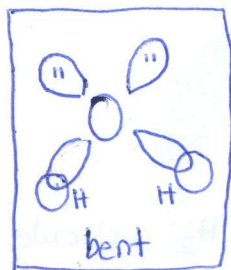
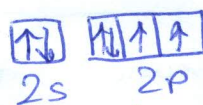
lone-pair  $e^-$ 's



## H<sub>2</sub>O molecule:



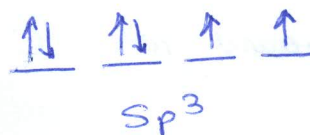
Ground state



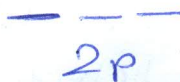
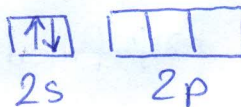
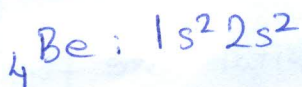
hyb.

lone-pair  $e^-$ 's

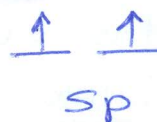
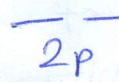
bond forming  $e^-$ 's



## sp Hybrid Orbitals

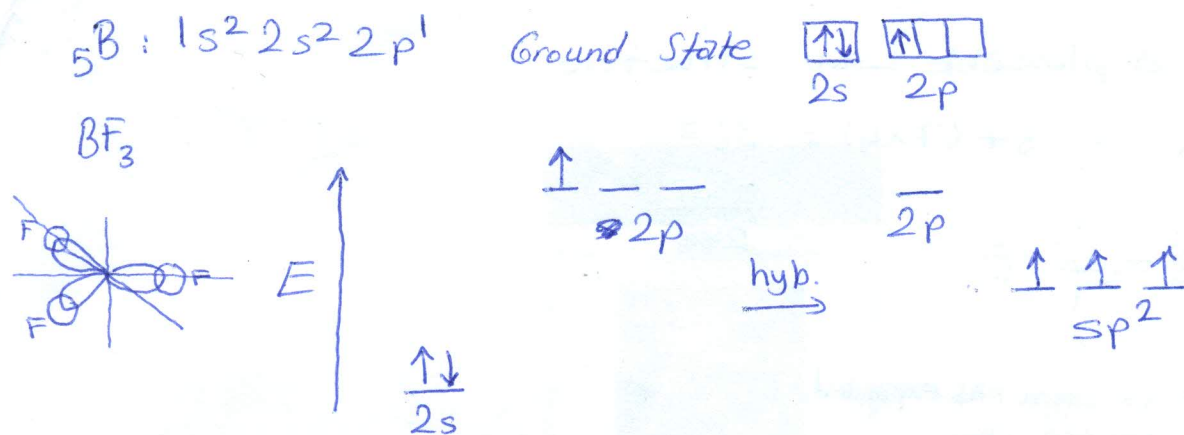
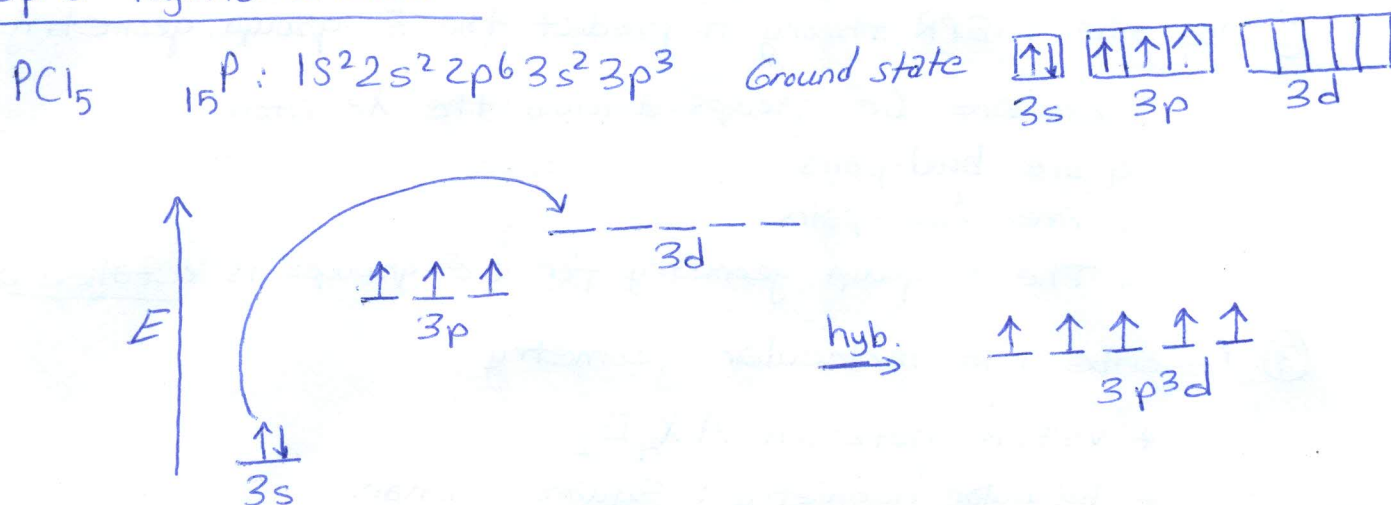
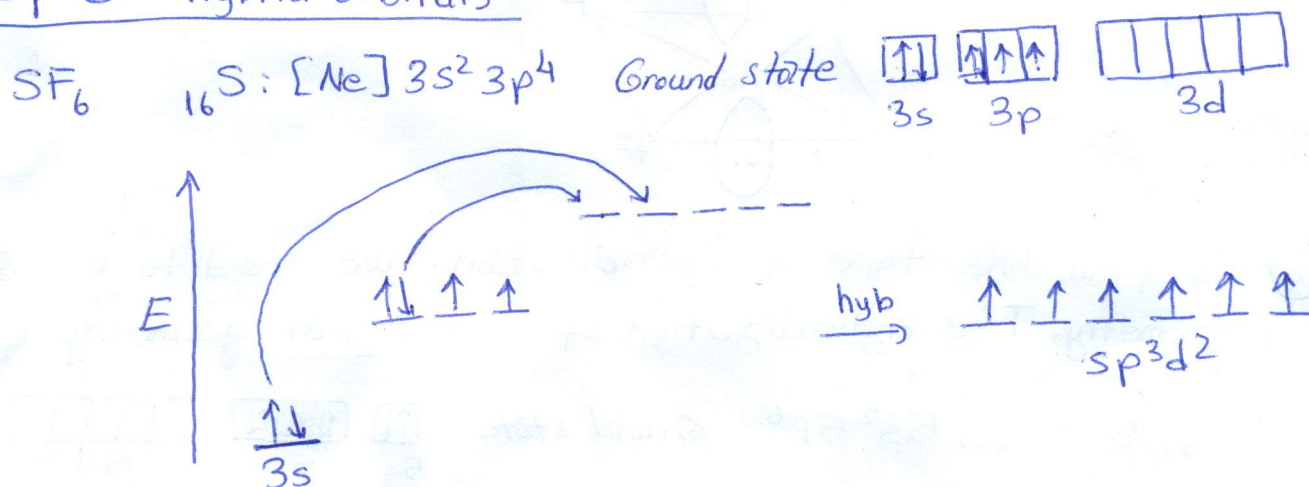


hyb.



Be has 4 orbitals and 2  $e^-$ 's in these orbitals (valence orbitals).  
one 2s and ~~two~~ one 2p orbital of Be are hybridized into two sp hybrid orbitals. The remaining two 2p orbitals are left unhybridized.



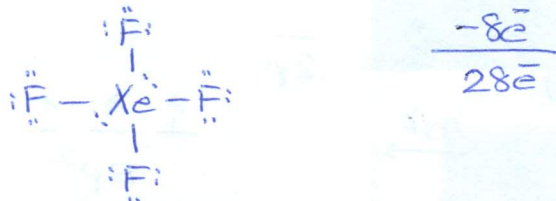
sp<sup>2</sup> Hybrid Orbitals:sp<sup>3</sup>d Hybrid Orbitals:sp<sup>3</sup>d<sup>2</sup> Hybrid Orbitals

→ Hybrid orbitals	Geometric Orientation	Example	$\bar{e}$ group
sp	linear	$\text{BCl}_2$	2
sp <sup>2</sup>	trigonal-planar	$\text{BF}_3$	3
sp <sup>3</sup>	tetrahedral	$\text{CH}_4$	4
sp <sup>3</sup> d	trigonal-bipyramidal	$\text{PCl}_5$	5
sp <sup>3</sup> d <sup>2</sup>	octahedral	$\text{SF}_6$	6

Example: Predict the shape of  $\text{XeF}_4$  molecule and a hybridized scheme consistent with this prediction.

① Write a plausible Lewis structure

$$\text{tn.v.e} = 8 + (7 \times 4) = 36\bar{e}$$



\* Xe atom has expanded valence shell.

② Describe the molecular geometry.

② Use the VSEPR theory to predict the  $\bar{e}$ -group geometry

There are  $6\bar{e}$  groups around the Xe atom.

4 are bond-pairs

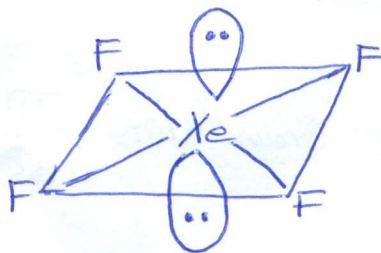
2 are lone-pairs

\* The  $\bar{e}$ -group geometry for  $6\bar{e}$ -groups is octahedral.

③ Describe the molecular geometry

\* VSEPR notation:  $\text{AX}_4\text{E}_2$

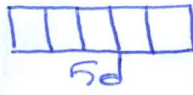
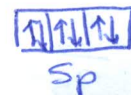
\* Molecular geometry: Square-planar.



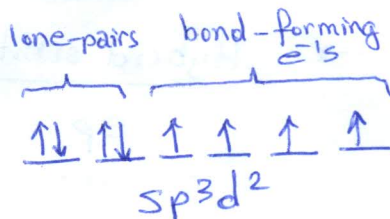
④ To find the type of hybridization, we need to use  $\bar{e}$ -group geometry. The hybridization of octahedral geometry is  $\text{sp}^3\text{d}^2$ .

$54\text{Xe} : \dots 5s^2 5p^6$

Ground state



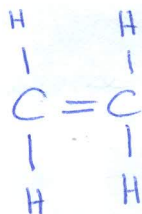
hyb.  $\rightarrow$



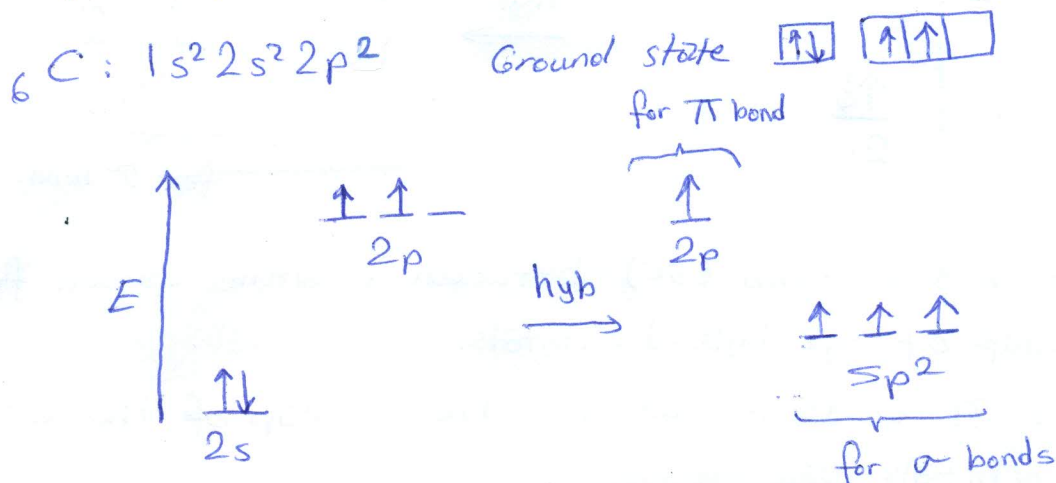


## Multiple Covalent Bonds

Bonding in  $C_2H_4$ : Ethylene has a carbon-to-carbon double bond in its Lewis structure.

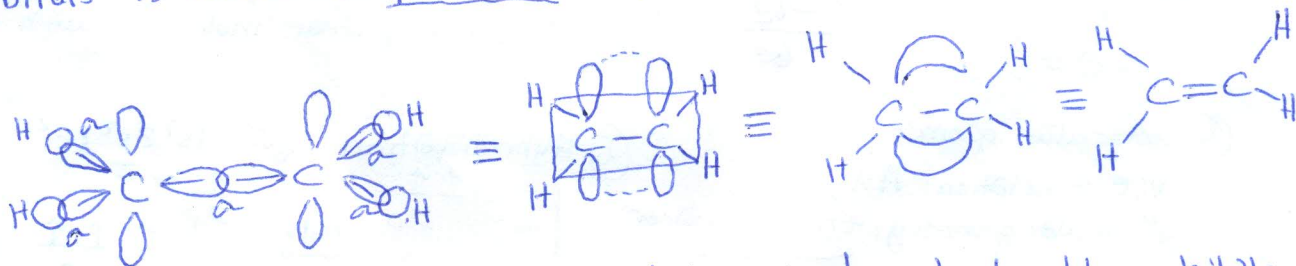


According to VSEPR theory, each C atom has  $3 \bar{e}$  groups in a trigonal-planar arrangement. The hybridization scheme with a trigonal-planar orientation is  $sp^2$ .



→ One of the bond, between the C atoms result from the overlap of  $sp^2$  hybrid orbitals. This overlap occurs along the line joining the nuclei of the two atoms. Orbitals that overlap in this end-to-end fashion produce a sigma ( $\sigma$ ) bond.

→ A second bond between the C atoms result from the overlap of the unhybridized p orbitals. There is a region of high  $\bar{e}$  density above and below the plane of the  $CH_2$  atoms. The bond produced by this side-to-side overlap of two parallel orbitals is called a pi bond ( $\pi$ ).



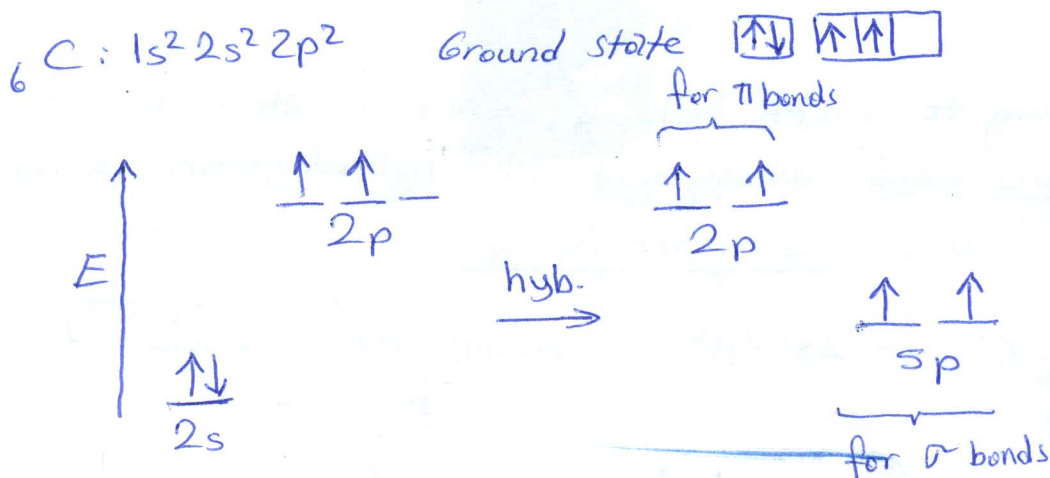
\* The shape of a molecule is determined only by the orbitals forming  $\sigma$  bonds.

\* Rotation about the double bond is severely restricted.  $C=C$  double bond ( $\sigma + \pi$ ) is stronger than single  $\sigma$  bond.

Bonding in  $C_2H_2$ : Acetylene  $C_2H_2$  has a carbon-to-carbon triple bond in its Lewis structure.

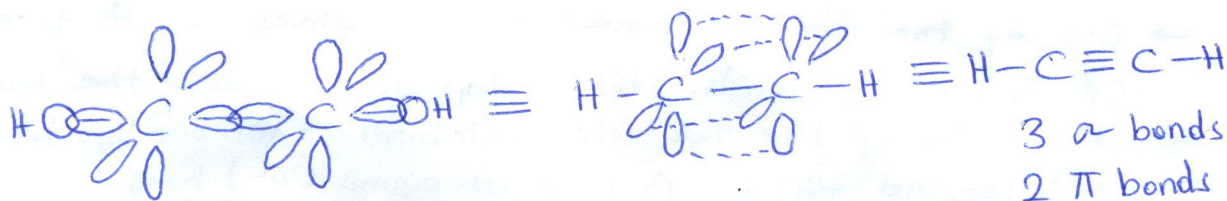


According to VSEPR theory each C atom has 2 e<sup>-</sup> group in a linear geometry. Because of the linear geometry its hybridization scheme is  $sp$ .



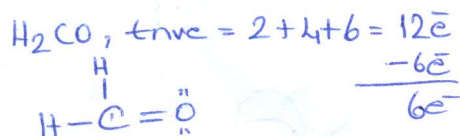
$\rightarrow$  One of the bond ( $\sigma$ ) between C atoms result from the overlap of  $sp$  hybrid orbitals.

$\rightarrow$  Two  $\pi$ -bonds result from the overlap of the unhybridized  $p$  orbitals.



Example: Describe the molecular geometry and bonding scheme for the  $H_2CO$  (formaldehyde) molecule.

① Lewis structure



② e<sup>-</sup> group geometry of the central atom

e<sup>-</sup> group number = 3

trigonal-planar molecule with  $120^\circ$  bond angles.

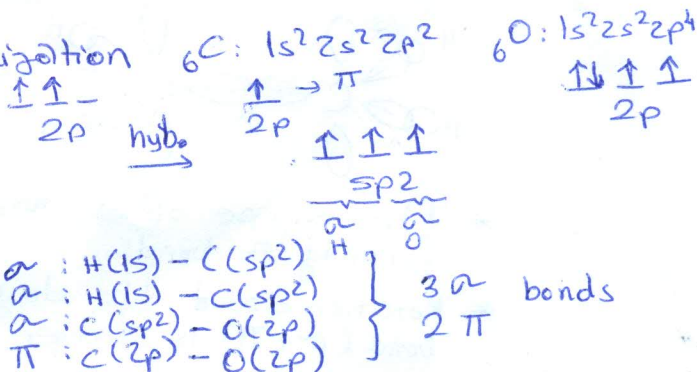
③ Molecular geometry

VSEPR notation:  $AX_3$

Molecular geometry: trigonal-planar

$sp^2$

④ Hybridization





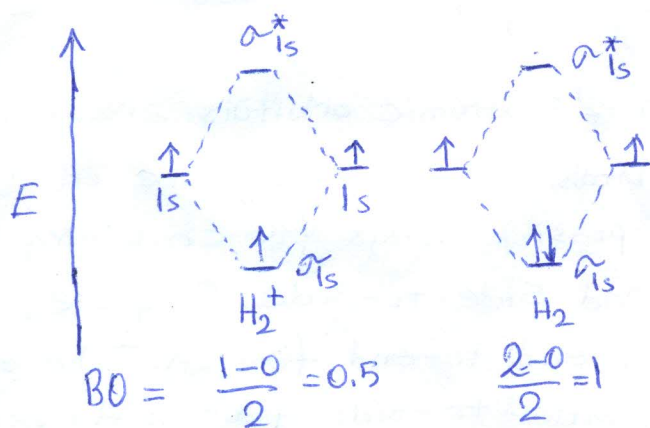
MOLECULAR ORBITAL THEORY

- 1) Atomic orbitals come together to form molecular orbitals (MO).
- 2) The number of molecular orbitals must be equal to the number of atomic orbitals.
- 3) A MO can accommodate only two  $\bar{e}$ 's. and the  $\bar{e}$ 's must have opposite spins.
- 4) The addition of two atomic orbitals in phase to form "bonding MOs"  
       "      "      "      "      "      "      " out of phase to form "antibonding MOs"

The energy of bonding MO is lower than the antibonding MO.

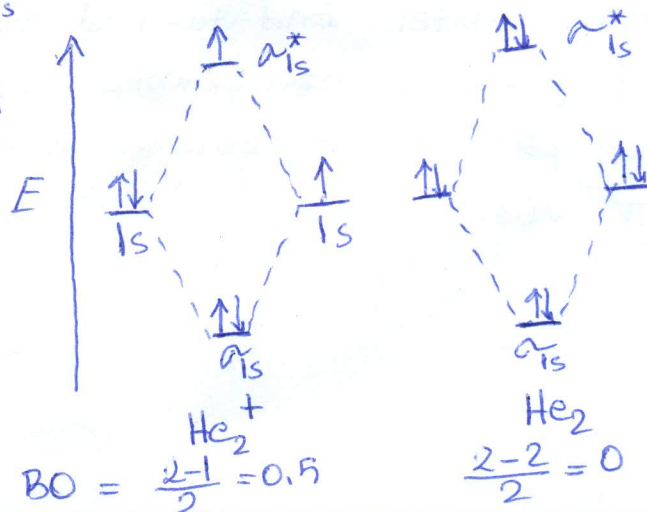
- 5) In ground-state configurations, electrons enter the lowest energy MOs available.
- 6) In ground-state configurations, electrons enter MOs of identical energies singly before they pair up (Hund's rule)

$$\text{Bond order (BO)} = \frac{\text{no. of } \bar{e} \text{ in bonding MOs} - \text{no. of } \bar{e} \text{ in antibonding MO}}{2}$$

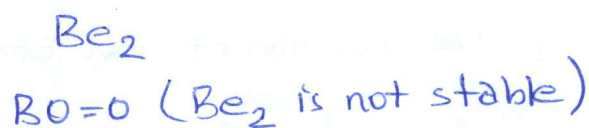
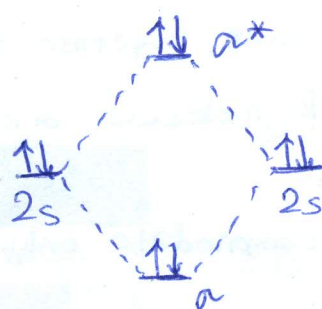
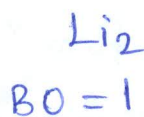
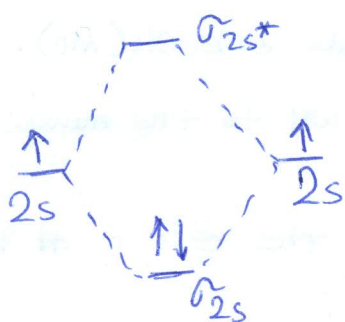
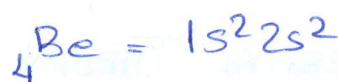
Diatomic Molecules of the First-Period Elements

$$\text{BO} = \frac{2-0}{2} = 1$$

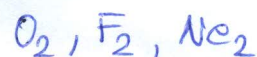
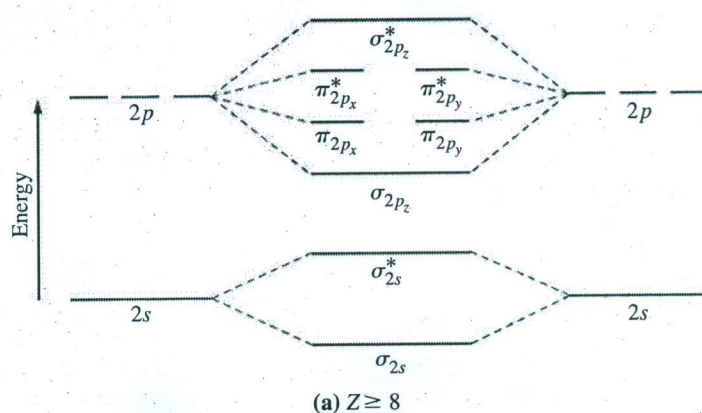
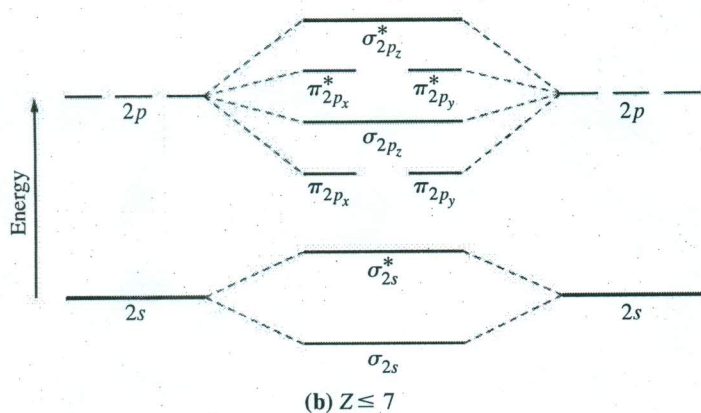
\* The BO of  $\text{He}_2$  is 0.  
 No bond produced. It means  $\text{He}_2$  is not a stable species.



$$\text{BO} = \frac{2-2}{2} = 0$$



## Molecular Orbitals of the Second-Period Elements

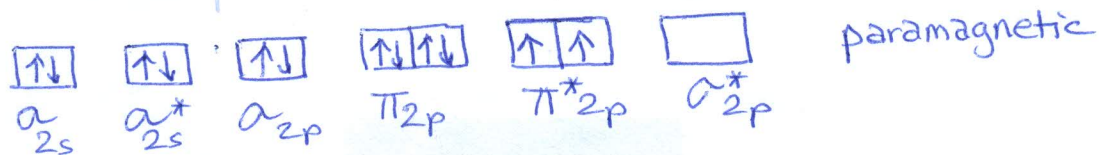


In the second-period elements we must work with  $2s$  and  $2p$  orbitals.

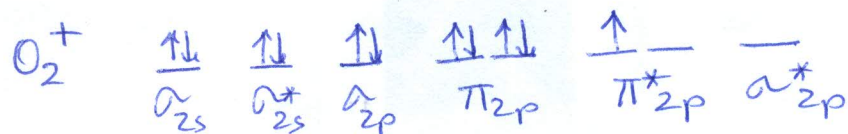
The MOs formed by combining  $2s$  atomic orbitals are similar to those from  $1s$  atomic orbitals, except they are at a higher energy level. There are two possible ways for combining  $2p$  atomic orbitals: End-to-End and Side-to-Side. Only one pair of  $p$  orbitals can combine in end-to-end fashion. The other two pairs must combine in side-to-side fashion to produce  $\pi$  MOs.



Example:  $O_2$   $8O: 1s^2 2s^2 2p^4$



$$BO = \frac{8-4}{2} = 2$$



$$BO = \frac{8-3}{2} = 2.5$$