

SHAPES OF MOLECULES (VSEPR MODEL)

Valence Shell Electron-Pair Repulsion model

- Electron pairs surrounding atom spread out as to minimize repulsion.
- Electron “pairs” can be bonding pairs (including multiple bonds) or nonbonding pairs.
- Arrangement of all the atoms surrounding central atom depends on electron pairs surrounding central atom.
- Electron domain is a better term than electron pair.

Two similar, but different geometries

1. Electron domain geometry
 - arrangement of e^- domain around central atom
 - remember: multiple bonds count as a single e^- domain
2. Molecular geometry
 - arrangement of atoms around central atom

****A molecular geometry is decided only after an electron domain geometry has been determined.****

- need to write Lewis structure to determine number of electron domains.

Geometries with two e^- domains about central atom.

1. electron domain geometry – linear



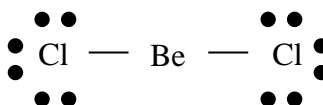
- angle between e^- domains is 180°

2. possible molecular geometries

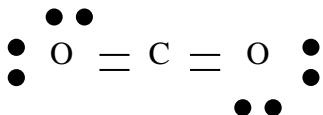
a) Linear

- only linear geometry is possible with two electron domains

Example: BeCl_2

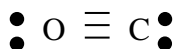


Example: CO_2



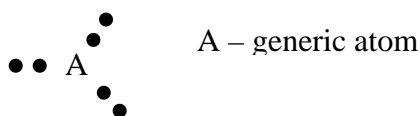
- Note: Only two electron domains around central atom since multiple bonds count as a single domain.

Example: CO



Geometries with three e⁻ domains about central atom.

1. electron domain geometry – trigonal planar



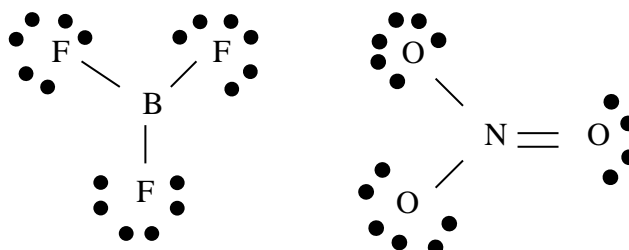
- angle between e⁻ domains is 120 °

2. possible molecular geometries

a) Trigonal Planar

- all three electron domains are bonding pairs

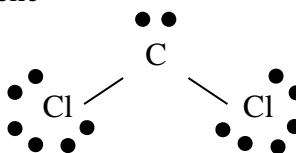
Examples: BF₃ and NO₃⁻



b) Bent (V-shaped)

- two bonding pairs and one nonbonding pair

Example: dichlorocarbene



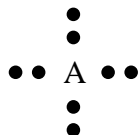
Nonbonding e- pairs take up more room than bonding pairs. Therefore bond angle between chlorine atoms is slightly less than 120°.

Geometries with four e⁻ domains about central atom.

1. electron domain geometry – tetrahedral

- tetrahedron is three dimensional object

- angle between electron domains is 109.47°



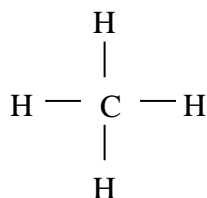
Caution! Representation is 2-D,
not 3-D, bond angle between e⁻
pairs is **not** 90°

2. possible molecular geometries

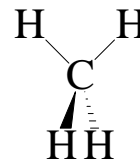
a) Tetrahedral

- all four electron domains are bonding pairs

Example: CH_4

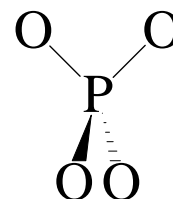
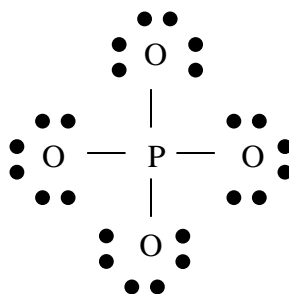


2-D picture



3-D picture

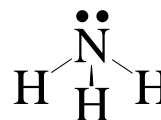
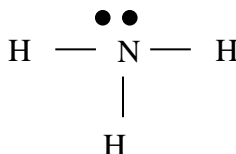
Example: PO_4^{3-}



b) Trigonal Pyramidal

- 3 bonding pairs and 1 nonbonding pair

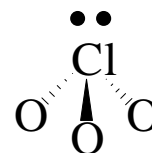
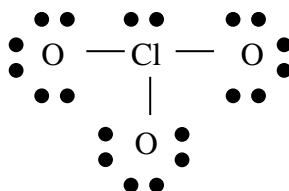
Example: NH_3



- Bond angle is 107° . (specifically for NH_3)

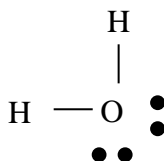
- Bond angle is less than 109.47° because nonbonding pair takes more room than bonding pair.

Example: ClO_3^-



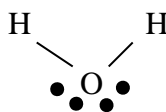
- c) Bent (V-shaped)
 - two bonding pairs and two nonbonding pairs

Example: H_2O

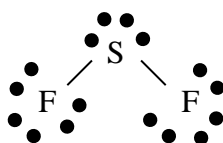


- Bond angle is 104.5° .

Redraw H_2O to show tetrahedral angle.



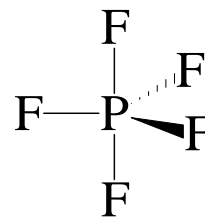
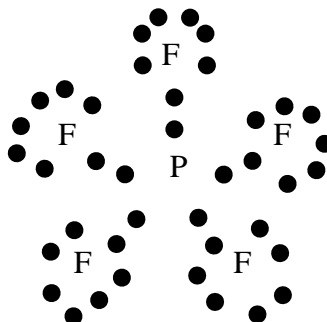
Example: SF_2



Geometries with five e^- domains about central atom.

1. electron domain geometry – trigonal bipyramidal
 - two different positions in a trigonal bipyramid
 - axial – two position along axis
 - equatorial – three positions along equator
 - angle between equatorial positions is 120°
 - axial positions are 90° from equator
 - * - nonbonding pairs prefer equatorial position*
2. possible molecular geometries
 - a. Trigonal Bipyramidal
 - all five electron domains are bonding pairs

Example: PF_5

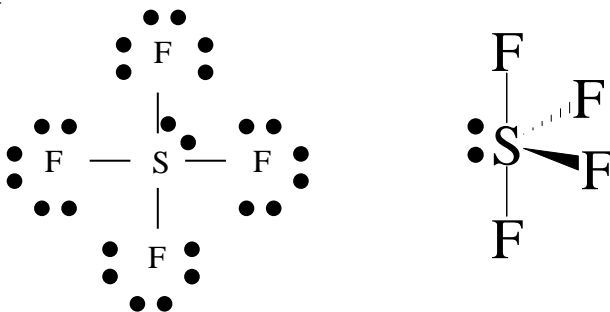


Note: axial bond lengths are almost always longer than equatorial bond lengths

b. Seesaw

- four electron domains are bonding pairs and one nonbonding pair

Example: SF_4

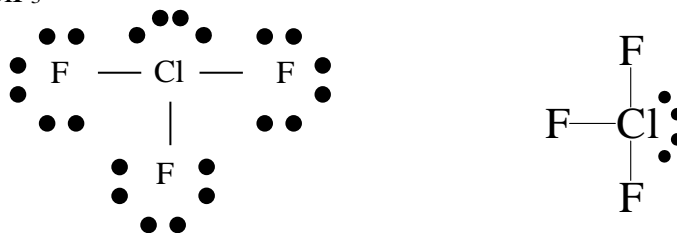


- remember lone pairs prefer equatorial position

c. T-shaped

- three electron domains are bonding pairs and two are nonbonding pairs

Example: ClF_3

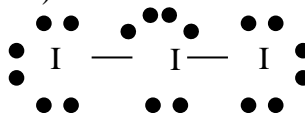


- both lone pairs occupy an equatorial position

d. Linear

- two electron domains are bonding pairs and three are nonbonding pairs

Example: I_3^- (triiodide ion)

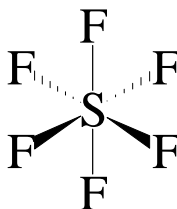


- all three lone pairs occupy equatorial positions

Geometries with six e^- domains about central atom.

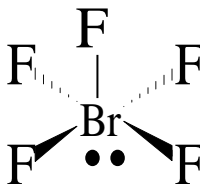
1. electron domain geometry – octahedral
 - angle between electron domains is 90°
2. possible molecular geometries
 - a.) Octahedral
 - all six electron domains are bonding pairs

Example: SF_6



- b.) Square pyramidal
 - five electron domains are bonding pairs with one lone pair

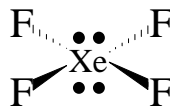
Example: BrF_5



- note angles will be slightly less than 90°

- c.) Square planar
 - four electron domains are bonding pairs with two lone pairs

Example: XeF_4



- What are angles between fluorine atoms?

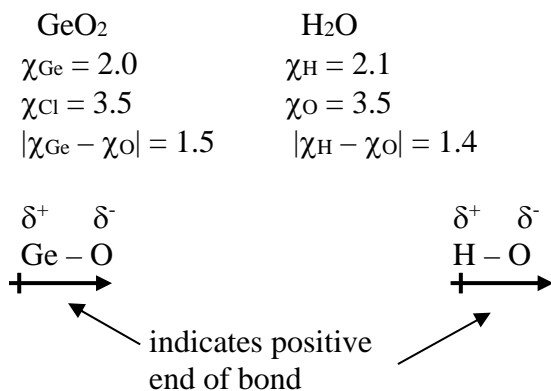
POLAR MOLECULES

A polar molecule has one side slightly positive and the other slightly negative.

Two conditions must be met in a polar molecule.

- 1.) Polar covalent bonds
- 2.) Correct geometry

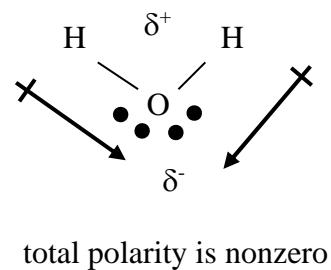
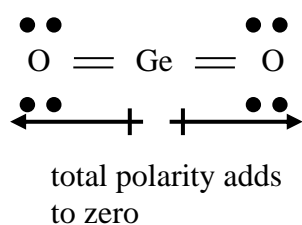
To emphasize necessity of correct geometry, compare two examples.



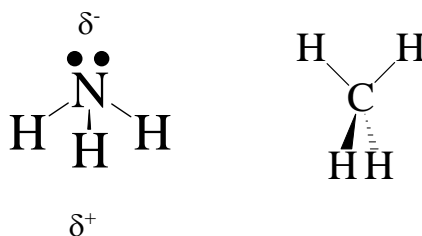
Ge – O bond is more polar than H – O bond; however, GeO_2 is **nonpolar** molecule and H_2O is a **polar** molecule.

Question: How can this be?

Answer: GeO_2 has a linear geometry and H_2O has a bent geometry.



Example: Is either ammonia or methane a polar molecule?



Answer: Ammonia is a polar molecule, but methane is a nonpolar molecule.

Nonequivalent polar bonds can affect overall polarity.

CF_4 is a nonpolar molecule. CF_3Cl is a polar molecule.



Dipole Moment - μ

When equal and opposite charges, $\pm Q$, are separated by a distance, d ; the dipole moment is defined as

$$\mu = Q \times d$$

Since a polar molecule has a separation of charge, it has a dipole moment.

Polarity of molecule is usually considered via its dipole moment.

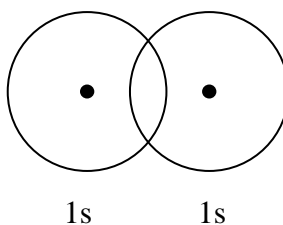
Scheme: Chemical formula \rightarrow Lewis structure \rightarrow e^- domain geometry
 \rightarrow molecular geometry \rightarrow polarity

VALENCE BOND THEORY

Bond Overlap

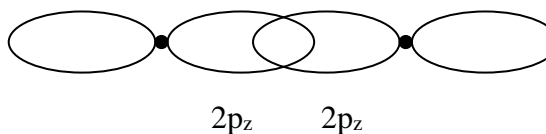
Molecular bonds form when atomic orbitals overlap.

Hydrogen – H_2



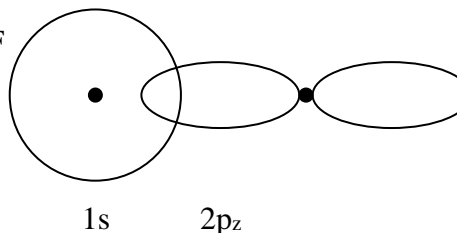
- Bond is overlap of two 1s orbitals.

Fluorine – F_2



- Bond is overlap of two 2p_z orbitals.

Hydrogen Fluoride – HF

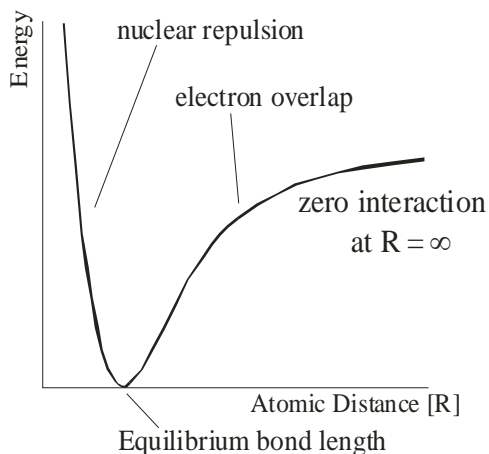


- Bond is overlap of a 1s orbital and a 2p_z orbital.

Concepts of bond overlap

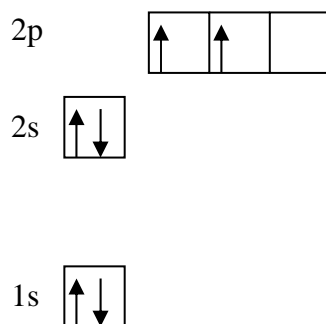
- Energy of molecule is lowered when overlap of singly occupied orbitals occurs.
- As atoms approach each other, increasing overlap has a limit. Nuclei start to repel each other.
- Bond distance is a compromise between increasing overlap and increasing nuclear repulsion.

Potential Energy Curve for Diatomic Bonding



HYBRIDIZATION

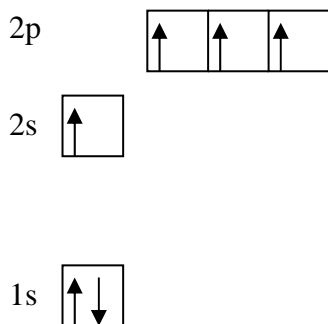
Consider the orbital diagram of the ground state carbon atom.



Since bonding occurs from the overlap of atomic orbitals, one would naïvely think that the carbon would form only two bonds coming from the overlap of the two 2p electrons with orbitals from other atoms.

However, we know (from a huge number of experiments) that carbon forms four bonds. How can this be?

Perhaps a small input of energy causes one of the 2s electrons to enter the empty 2p orbital.



Now the carbon atom can form four bonds; however, we have another problem.

In a compound such as methane, CH_4 , all the bonds surrounding the carbon atom are identical. There is no way to differentiate between the four bonds.

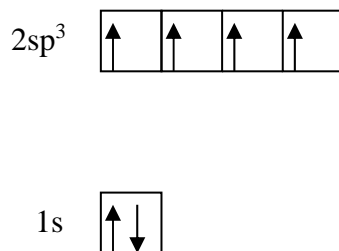
-Again, there is a boatload of experimental evidence demonstrating the equivalence of all of the bonds.

Once again, how can this be? We should have

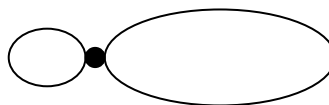
- 3 bonds from the overlap of carbon 2p orbitals and hydrogen 1s orbitals
- 1 bond from the overlap of a carbon 2s orbital and a hydrogen 1s orbital

To rationalize the fact that all of the bonds are equivalent, we invoke the concept of **hybridization**.

The three 2p orbitals and the one 2s orbital hybridize, i.e., blend, together to form four identical orbitals, labeled in this specific case as sp^3 orbitals.



The shape of an sp^3 is a lopsided dumbbell.

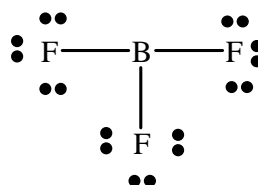


All four sp^3 orbitals point a different corner of a tetrahedron.

Thus there exists an intimate connection between the electron domain geometry of an atom and the hybridization of the orbitals on that atom.

Electron domain geometry	Number of identical orbitals	Hybridization of atomic orbitals
Linear	2	sp
Trigonal planar	3	sp^2
Tetrahedral	4	sp^3
Trigonal bipyramidal	5	sp^3d
Octahedral	6	sp^3d^2

Example: What is the hybridization of the valence orbitals of the boron atom in BF_3 ?



3 e^- domains \rightarrow Trigonal planar $\rightarrow sp^2$ hybridization

Example: What is the hybridization of the valence orbitals of the fluorine atoms in BF_3 ?

4 e^- domains \rightarrow Tetrahedral $\rightarrow sp^3$ hybridization

Example: What orbitals are overlapping to create the covalent bonds in BF_3 ?

$2sp^2$ orbital of boron overlapping with $2sp^3$ orbital of fluorine.

Hybridization of Expanded Octets

The phosphorus atom in PCl_5 can “expand its octet” to form a trigonal bipyramidal shape with sp^3d hybridized orbitals.

Q: If PCl_5 can exist, why can't NCl_5 exist?

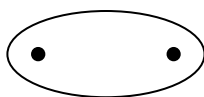
A: (Adequate) The sp^3d orbitals come from blending one 3s, three 3p and one 3d orbitals. NCl_5 can't exist because there is no 2d orbital!

A: (Better!) Nitrogen is too small to fit five electron domains about it.

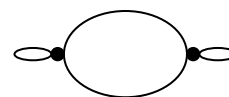
COVALENT BOND ORBITALS (sigma and pi bonds)

Sigma bonds - σ

- first covalent bond between atoms
- bond is directly between nuclei

H₂

σ bond from overlap of 1s orbitals

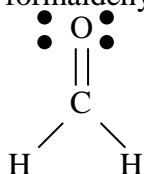
F₂

σ bond from overlap of 2sp³ orbitals

- strongest covalent bond

Pi bonds - π

- double bond, extra bonds after sigma bond
- consider formaldehyde



1 σ C – O bond

1 π C – O bond

2 σ C – H bonds

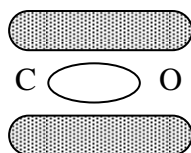
- also triple bonds
- consider carbon monoxide



1 σ C – O bond

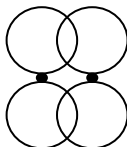
2 π C – O bonds

- Bond is outside of internuclear axis.



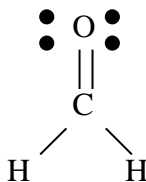
π bond – both parts belong to one pi bond.

- Bond comes from overlap of perpendicular p orbitals.



- Pi bonds are weaker than sigma bonds.

Reexamine bonding in formaldehyde

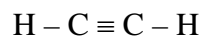


Q: What is hybridization of carbon orbitals?

A: One p orbital is used in formation of π bond; therefore, other orbitals hybridize to form sp^2 orbitals.

- Note: sp^2 hybridization is consistent with trigonal planar geometry.

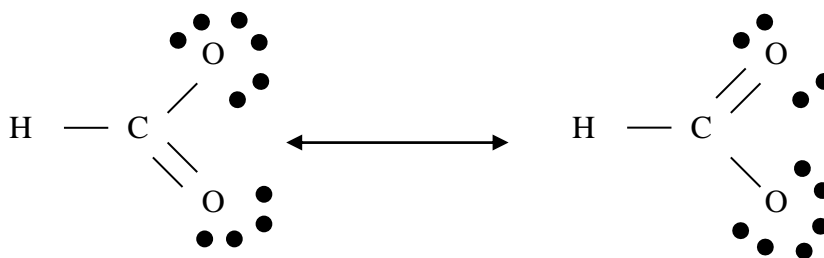
Examine bonding in acetylene, C_2H_2



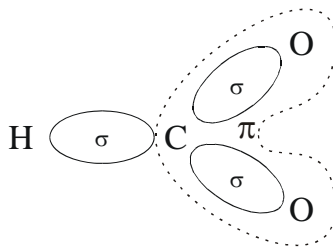
- Two π bonds means each carbon is using two p orbitals for π bonds; therefore, hybridization is sp .
- Note: hybridization matches linear geometry.
- Two π bonds are perpendicular to each other.

RESONANCE AND DELOCALIZATION

Consider resonance of formate ion, HCO_2^-



- π bond is delocalized over both C – O sigma bonds.



- Resonance always indicates delocalization of bonds.

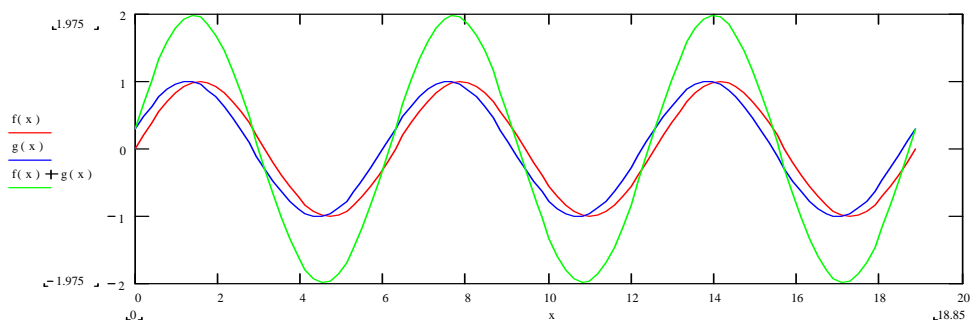
MOLECULAR ORBITAL THEORY

Wave Interference

- When two waves are put together, two types of interferences (i. e. mixing) occurs.

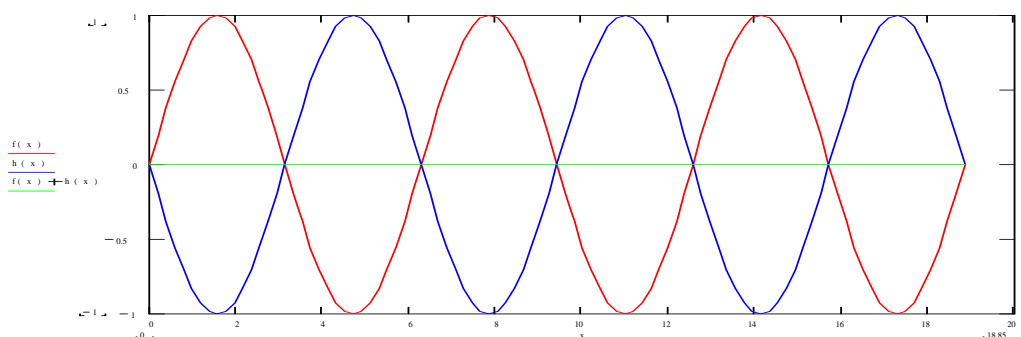
1. Constructive interference

- Two waves add together to reinforce each other.



2. Destructive interference

- Two waves add together to destroy each other.



Molecular Orbitals

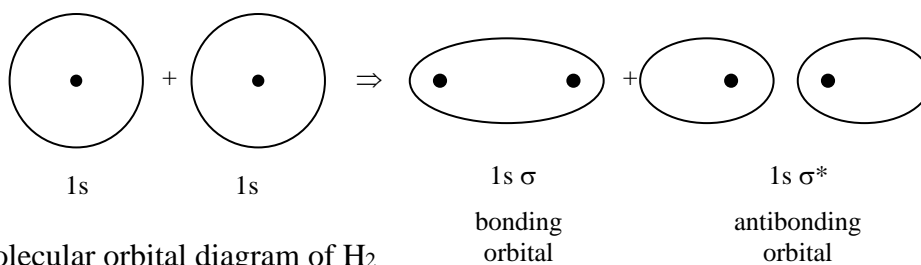
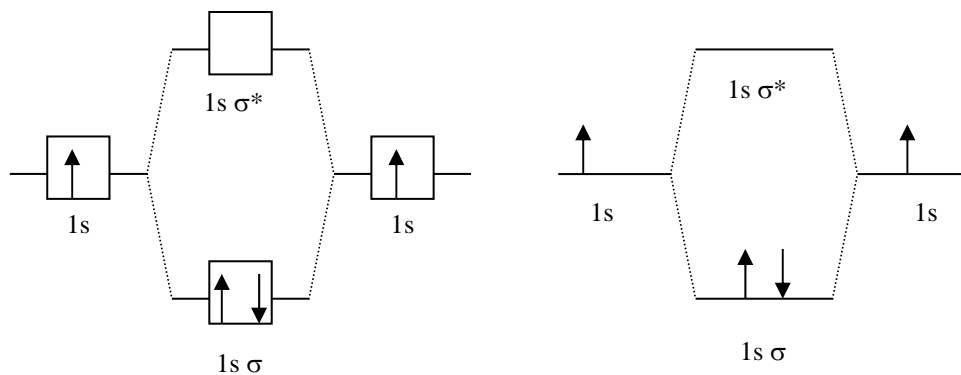
When two atomic orbitals are put together, they interfere with each other, and two molecular orbitals result.

1. Bonding orbitals – σ , π

- when filled with e^- , they draw atoms together.
- result of constructive interference
- electron density increases between atoms

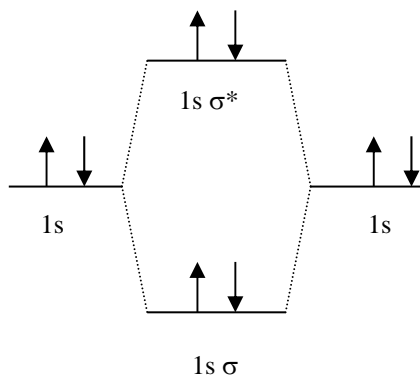
2. Antibonding orbitals – σ^* , π^*

- when filled with e^- , they push atoms apart
- result of destructive interference
- electron density decreases between atoms
 - antibonding orbitals have **node** between nuclei
- effect of antibonding orbital slightly greater than bonding orbital
- always higher energy than similar bonding orbital

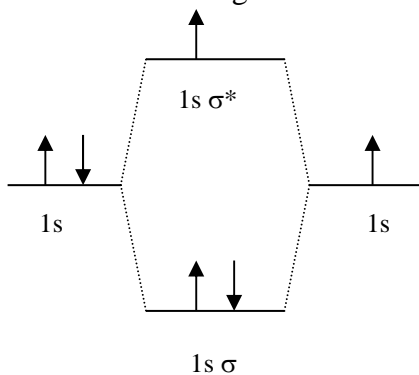
Molecular orbitals (MO) of H_2 Molecular orbital diagram of H_2 

Note one bonding orbital is filled; therefore, **bond order** is one.

$$\text{Bond order} = \frac{1}{2}(\# \text{ of bonding } e^- - \# \text{ antibonding } e^-)$$

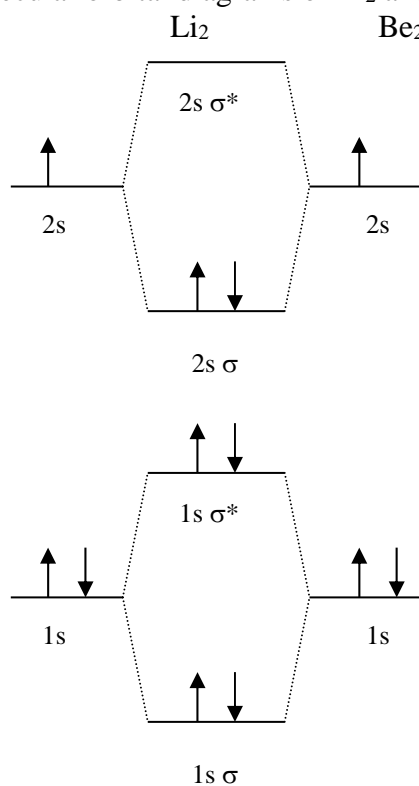
Molecular orbital diagram of He_2 

One bonding orbital and one antibonding orbital are filled; therefore, bond order is zero.

Molecular orbital diagram of He_2^+ or H_2^- 

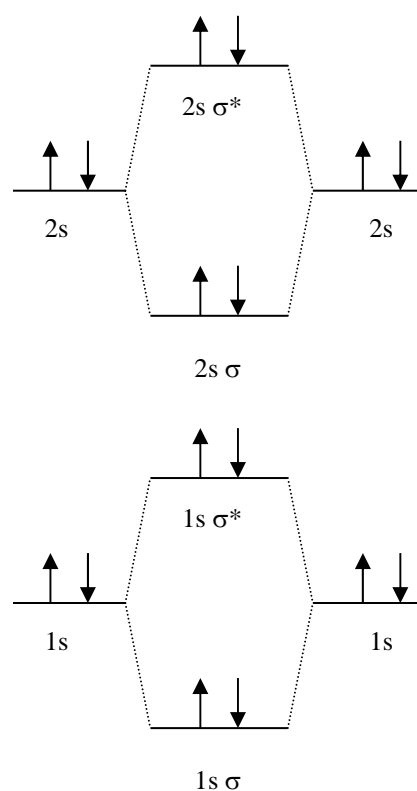
He_2^+ exists!!
However the atoms are lightly bonded together.

Two bonding e^- and one antibonding e^- ; therefore, bond order is $\frac{1}{2}$.

Molecular orbital diagrams of Li_2 and Be_2 

$$\text{Bond Order} = 2 \text{ bonds} - 1 \text{ antibond} = 1$$

Li_2 exists. Though not as crystal, only as gas.



$$\text{Bond Order} = 2 \text{ bonds} - 2 \text{ antibonds} = 0$$

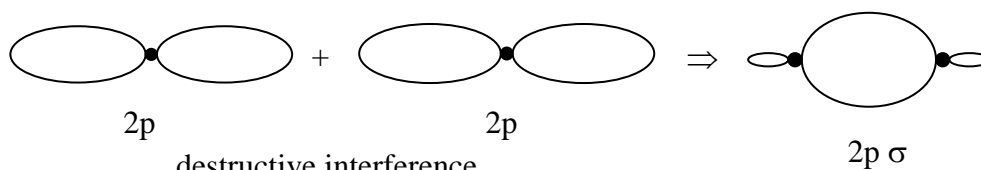
Be_2 does not exist.

Note: Two atomic orbitals making two molecular orbitals must be close in energy.
- As a consequence, 1s and 2s orbitals do not mix together very much.

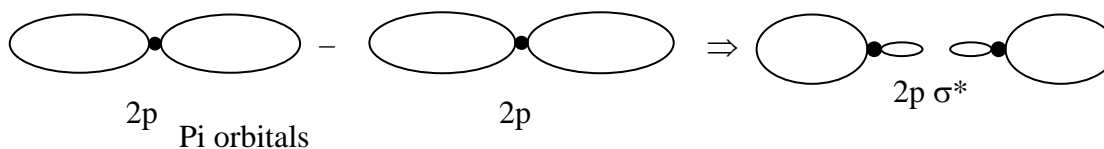
Molecular orbitals from p orbitals

Sigma orbitals

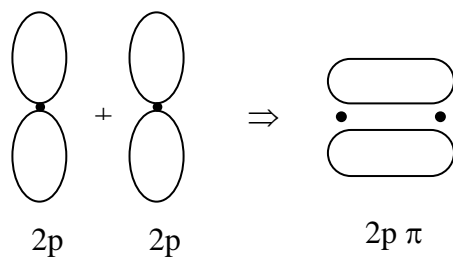
constructive interference



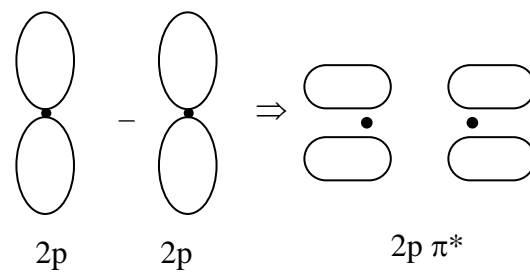
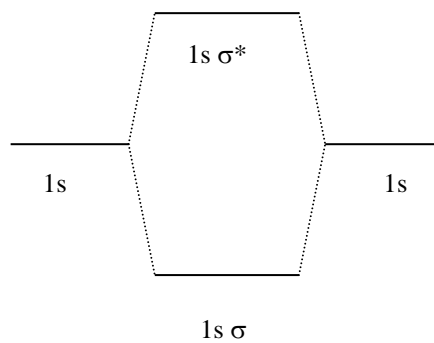
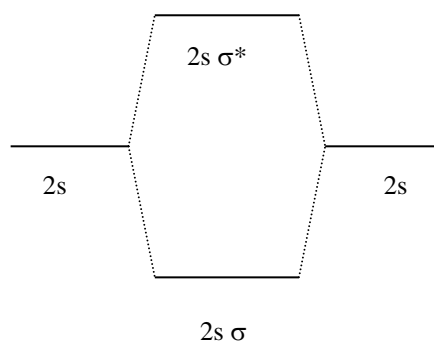
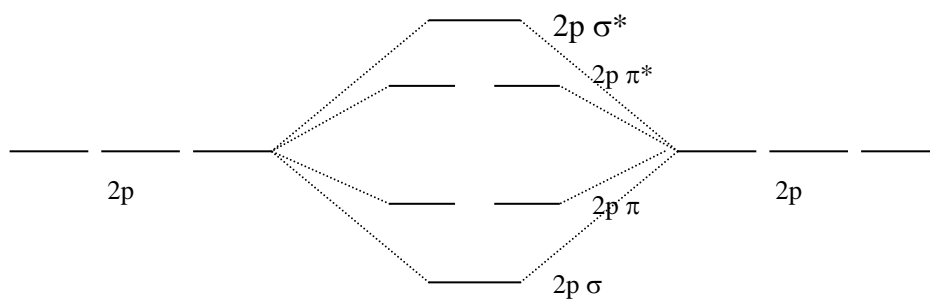
destructive interference

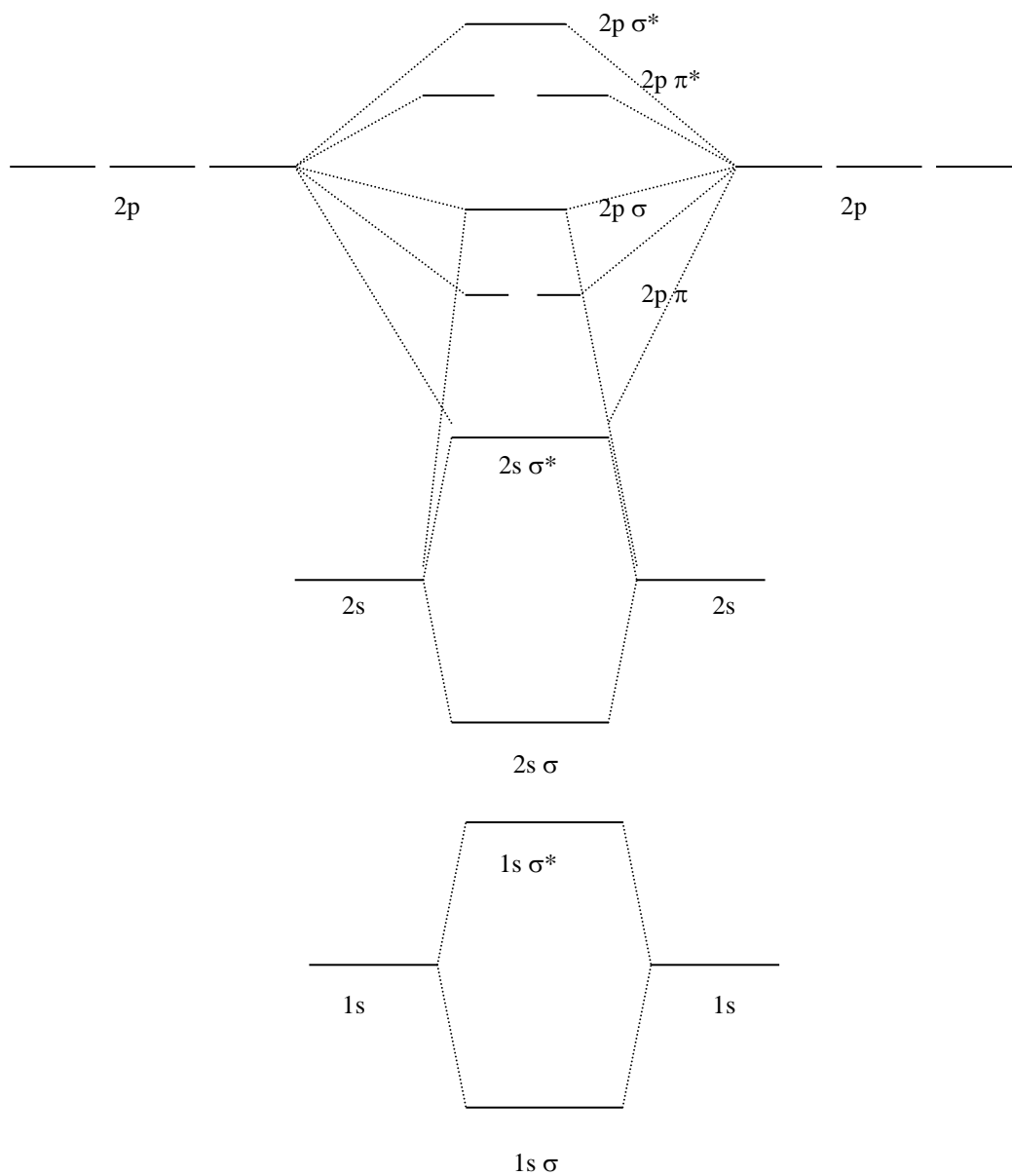


constructive interference



destructive interference

MO Diagrams of O_2 , F_2 , Ne_2 

MO Diagrams of B₂, C₂, N₂

- 2s and 2p orbital hybridize causing σ and π orbitals to be “out of order”

Using MO Theory to predict bonding and magnetic properties

One of the great successes of MO theory is that it correctly predicts the magnetic properties of diatomic molecules.

Magnetic Molecules

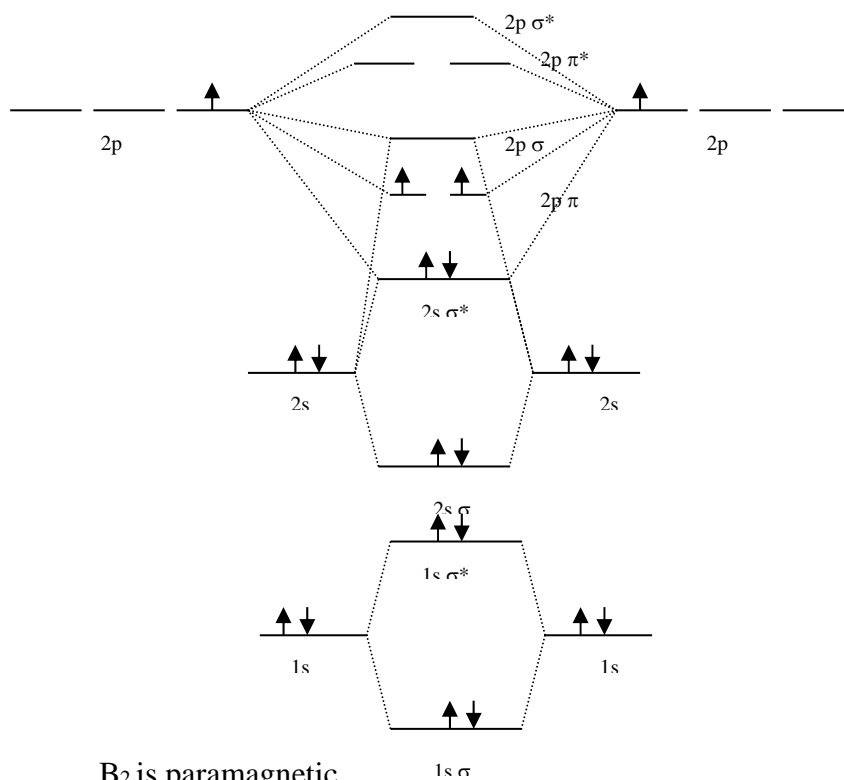
Diamagnetic

- molecule with no unpaired e^-
- molecule not attracted to magnet
- in fact, slightly repelled by magnet

Paramagnetic

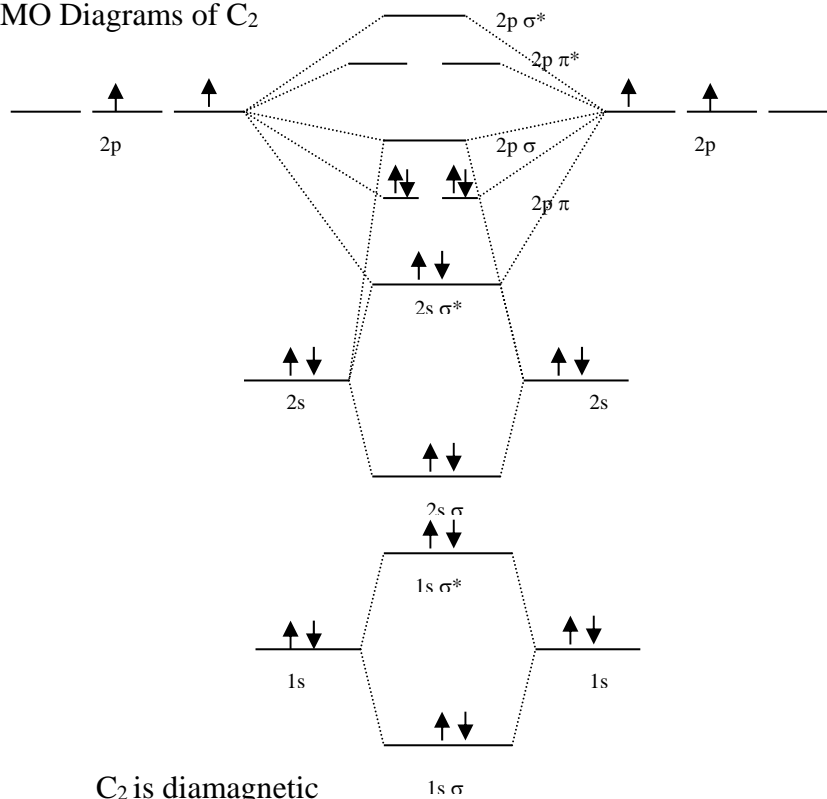
- molecule with unpaired e^-
- spinning e^- acts like bar magnet
 - e^- has **magnetic moment**
- molecule behaves as if it is magnet, it is attracted to other magnets

MO Diagrams of B_2

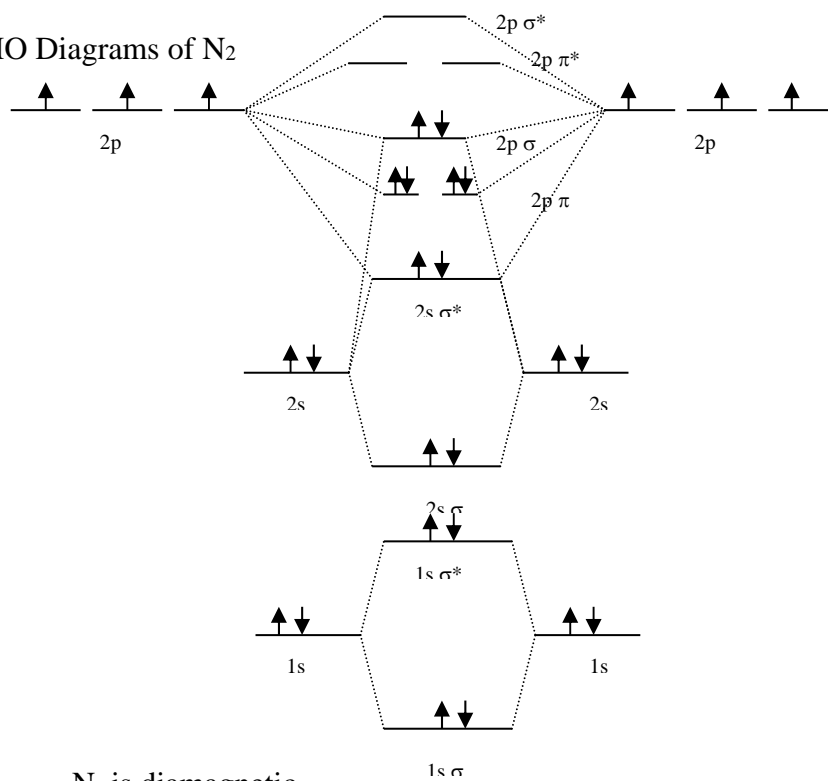


B_2 is paramagnetic

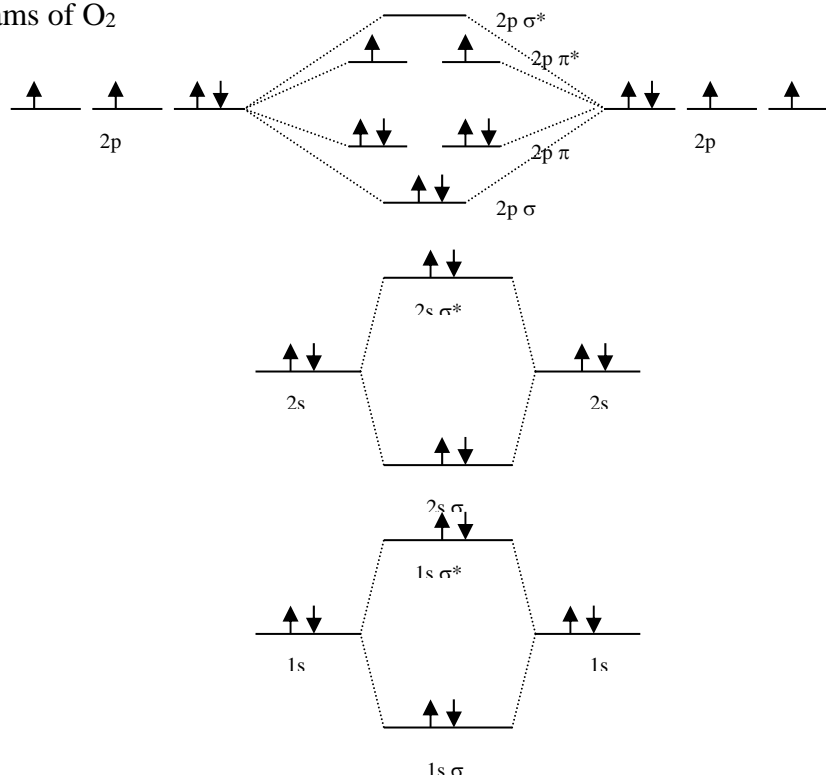
Bond order = 1

MO Diagrams of C_2 

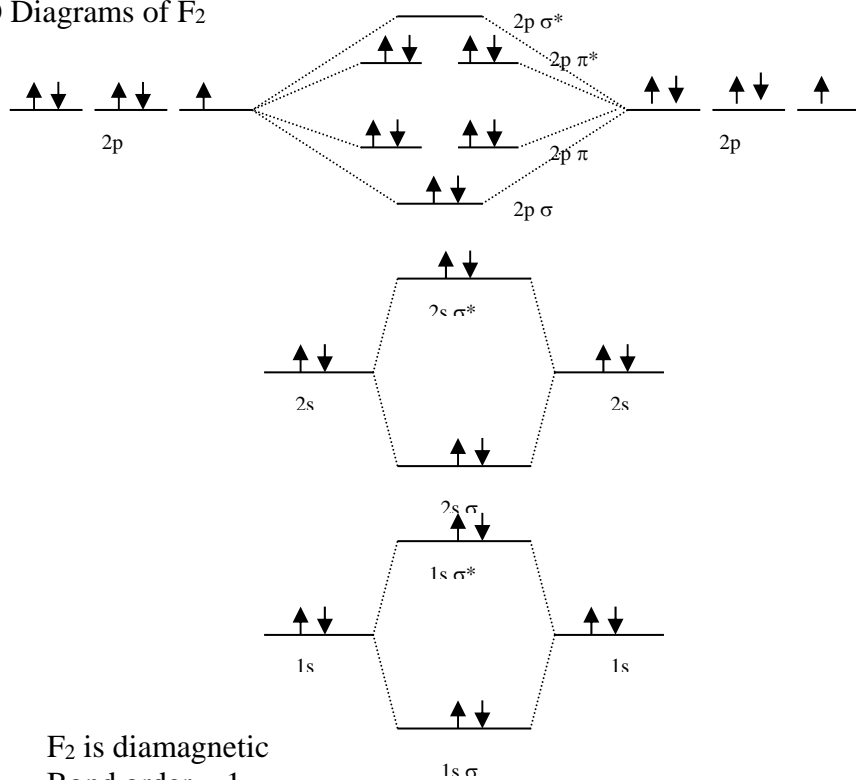
C_2 is diamagnetic
Bond order = 2

MO Diagrams of N_2 

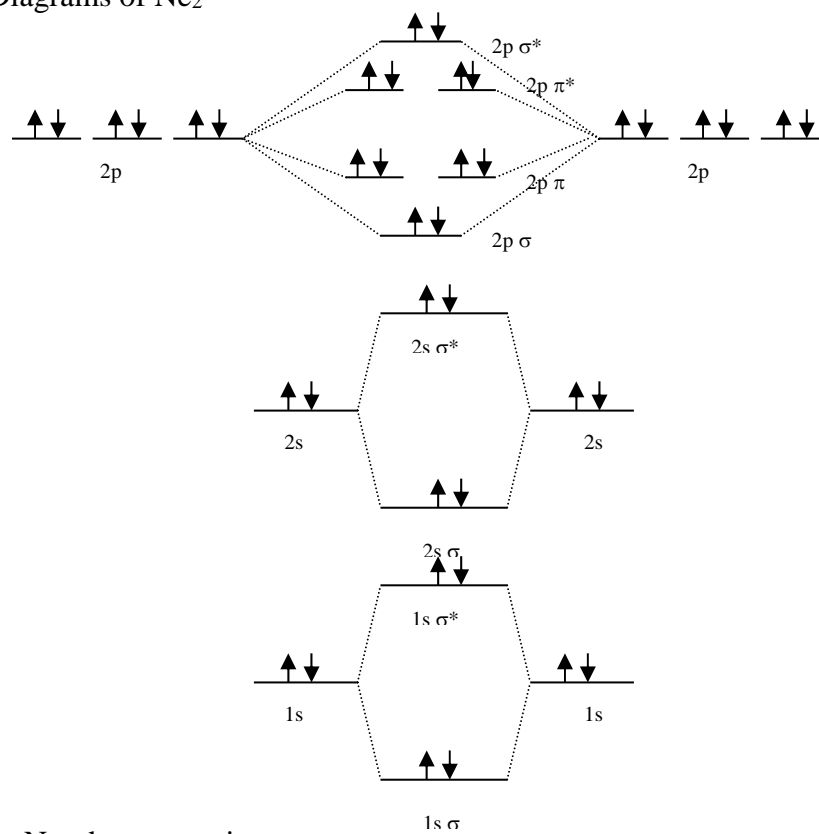
N_2 is diamagnetic
Bond order = 3

MO Diagrams of O₂

O₂ is paramagnetic Bond order = 2

MO Diagrams of F₂

F₂ is diamagnetic
Bond order = 1

MO Diagrams of Ne₂

Ne₂ does not exist
Bond order = 0