Chapter 10

Molecular Geometry

CHAPTER OUTLINE

- Molecular Geometry
- Molecular Polarity
- VSEPR Model
- Summary of Molecular Shapes
- Hybridization
- Molecular Orbital Theory
- Bond Angles

MOLECULAR GEOMETRY

- **Molecular geometry of a molecule indicates the relative positions of its nuclei and can be determined experimentally.**
- **All diatomic molecules are linear.**

H–H

H–Cl

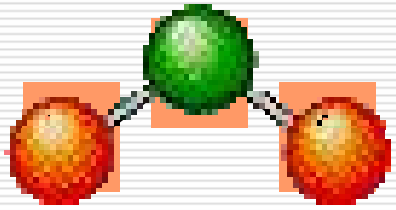
Cl–Cl

N≡N

MOLECULAR GEOMETRY

- **Triatomic molecules may have the following shapes:**

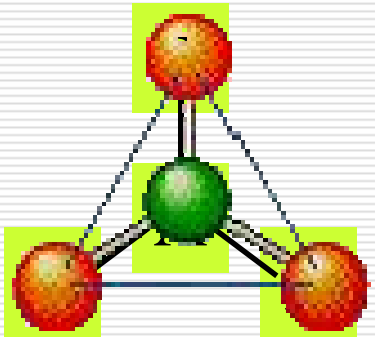
linear



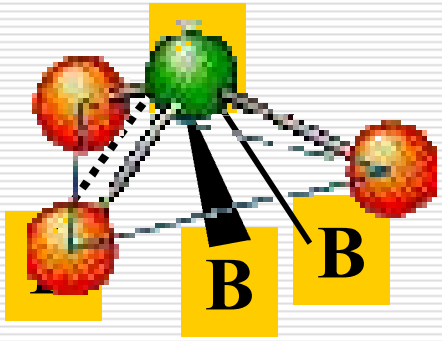
bent

MOLECULAR GEOMETRY

- **Tetraatomic molecules may have the following shapes:**



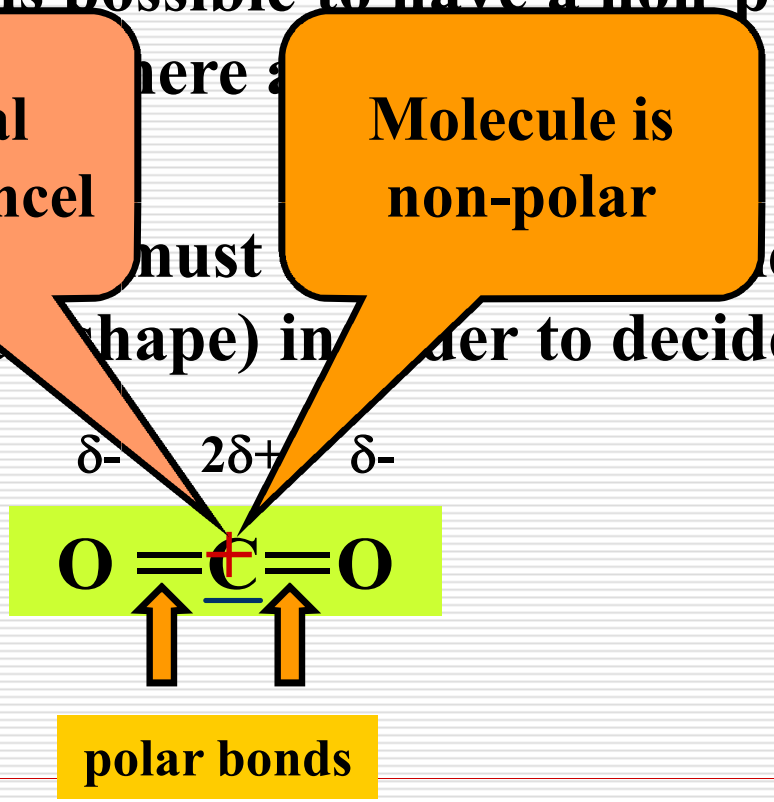
trigonal planar



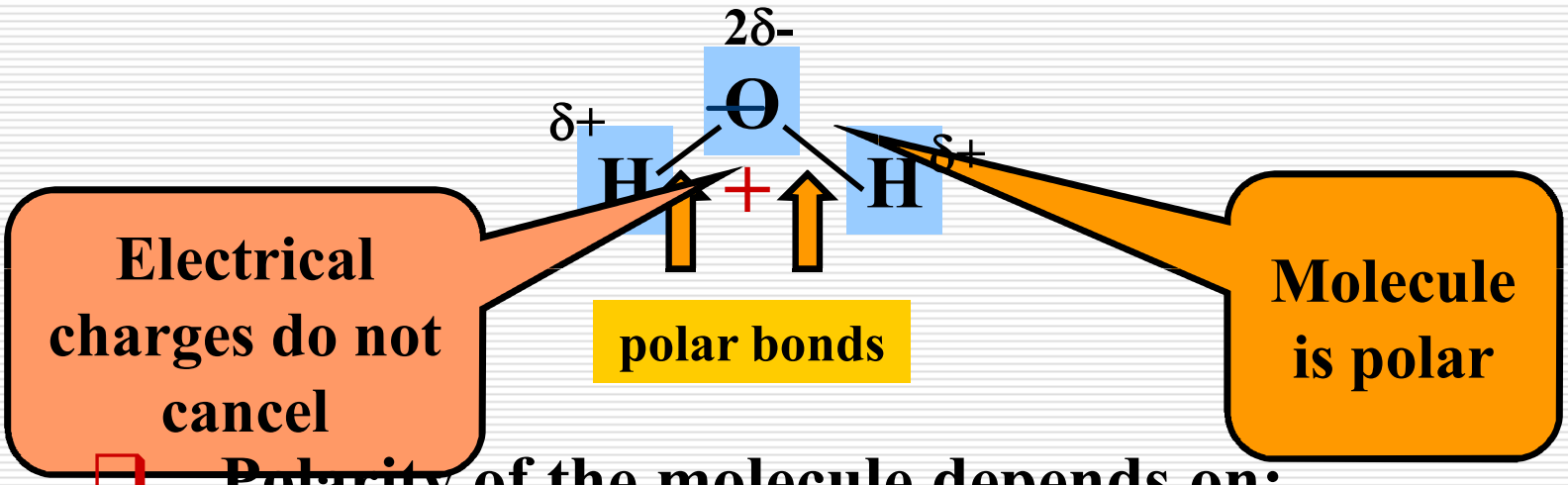
trigonal pyramidal

MOLECULAR POLARITY

- When a molecule contains more than two atoms bonded together it is possible to have a non-polar molecu… here a… present…
- In these… must … ecular geometry (molecul… hape) in… der to decide if it is polar or not.



MOLECULAR POLARITY



- Polarity of the molecule depends on:

Bond polarity

Molecular geometry

MOLECULAR POLARITY

- **Molecules containing like atoms (nonpolar bonds) are nonpolar.**

- **Molecules containing unlike atoms (polar bonds)**

  A. **are NONPOLAR if the molecular shape is SYMMETRICAL**

  B. **are POLAR if the molecular shape is ASYMMETRICAL**

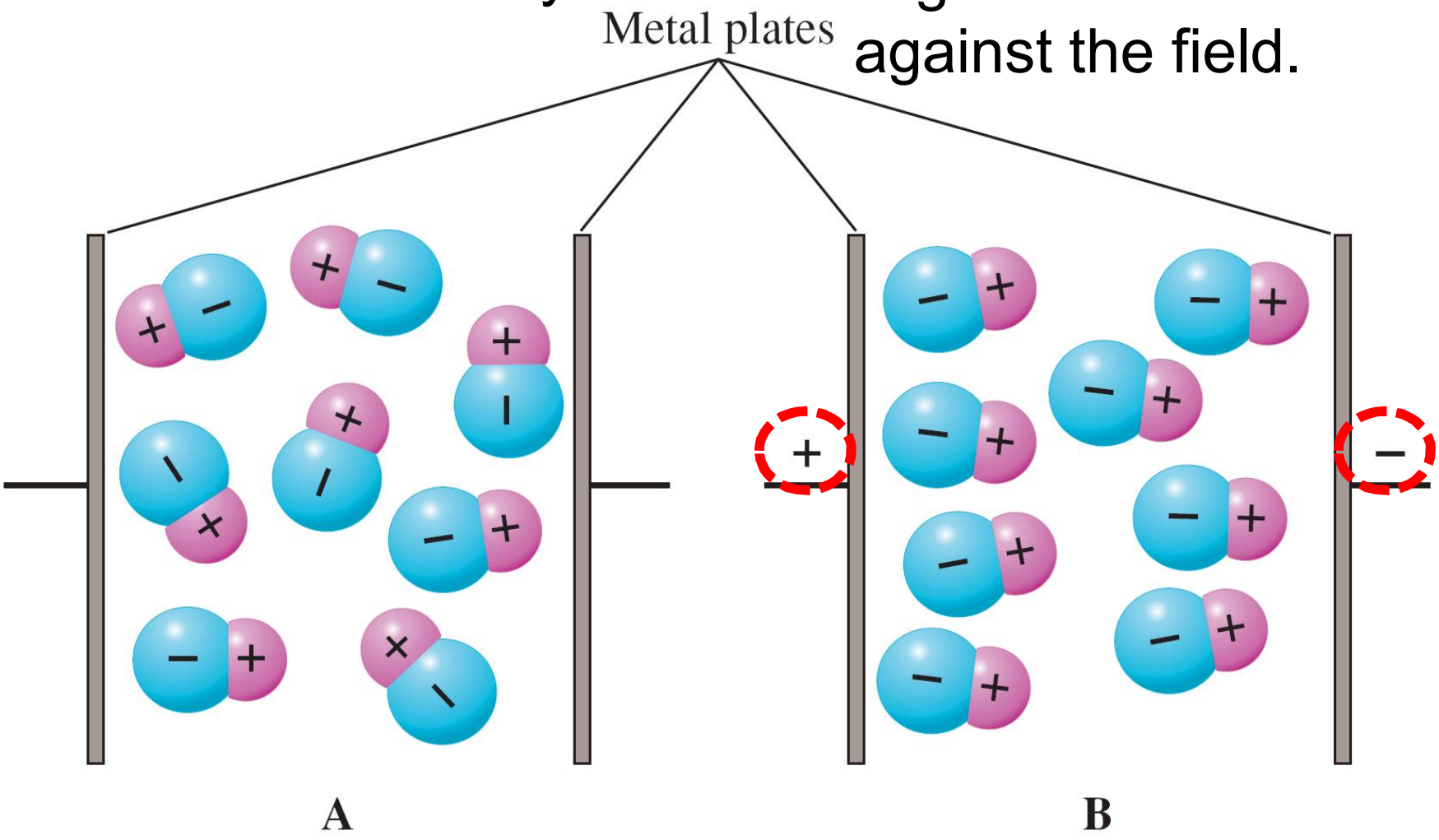
DIPOLE MOMENT

A quantitative measure of the degree of charge separation in a molecule.

Measurements are based on the fact that polar molecules are oriented by an electric field. This orientation affects the capacitance of the charged plates that create the electric field.

In part A, there is no electric field; molecules are oriented randomly.

In part B, there is an electric field; molecules align themselves against the field.

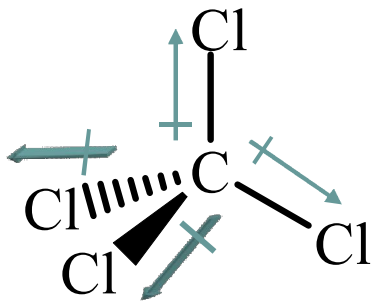


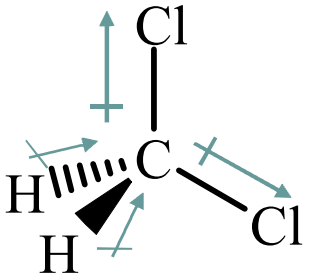
A polar bond is characterized by separation of electrical charge.

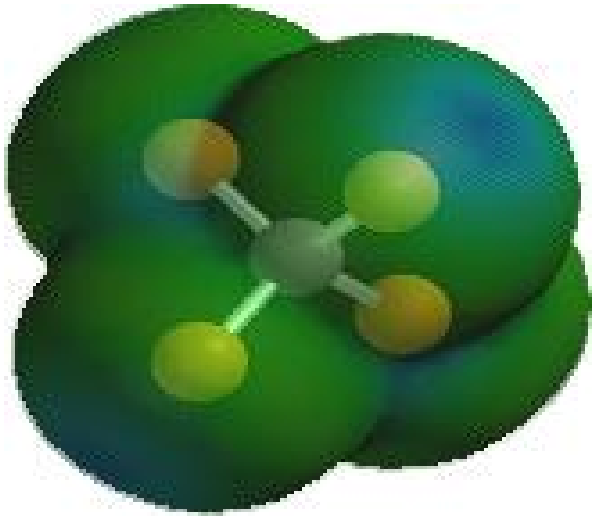
For HCl, we can represent the charge separation using $\delta+$ and $\delta-$ to indicate partial charges. Because Cl is more electronegative than H, it has the $\delta-$ charge, while H has the $\delta+$ charge.

$$\delta+ \quad \delta-$$
$$H\text{——}Cl$$

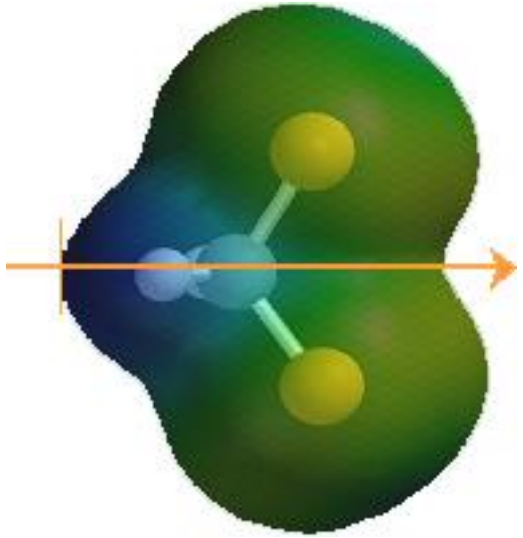
- To determine whether a molecule is polar, we need to determine the electron-dot formula and the molecular geometry. We then use vectors to represent the charge separation. They begin at $\delta+$ atoms and go to $\delta-$ atoms. Vectors have both magnitude and direction.
- We then sum the vectors. If the sum of the vectors is zero, the dipole moment is zero. If there is a net vector, the molecule is polar.







CCl_4
$\mu = 0.0$ D



CH_2Cl_2
$\mu = 2.0$ D

Adding Dipole Moments

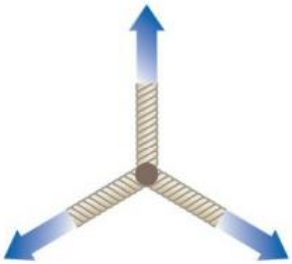
Nonpolar

Two identical polar bonds pointing in opposite directions will cancel. The molecule is nonpolar.

Polar

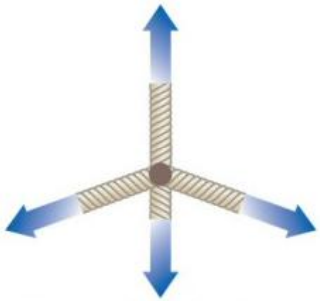
Two polar bonds with an angle of less than 180° between them will not cancel. The molecule is polar.

Nonpolar



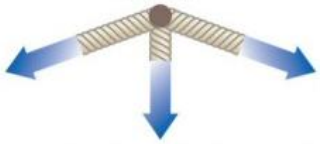
Three identical polar bonds at 120° from each other will cancel. The molecule is nonpolar.

Nonpolar



Four identical polar bonds in a tetrahedral arrangement (109.5° from each other) will cancel. The molecule is nonpolar.

Polar



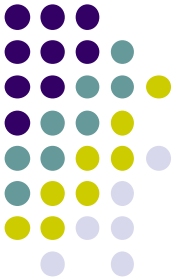
Three polar bonds in a trigonal pyramidal arrangement (109.5°) will not cancel. The molecule is polar.

Note: In all cases where the polar bonds cancel, the bonds are assumed to be identical. If one or more of the bonds are different than the other(s), the bonds will not cancel and the molecule is polar.

VSEPR MODEL

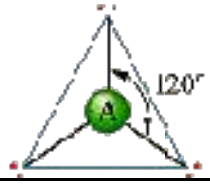
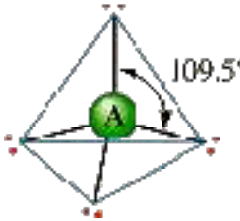
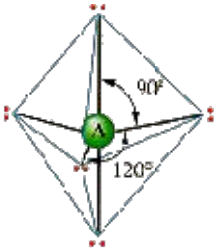
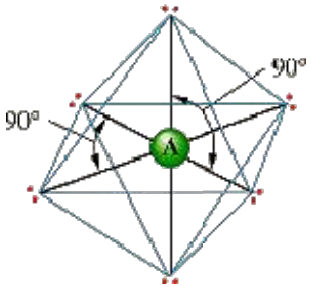
- **VSEPR Theory**
  - **V**alence **S**hell **E**lectron **P**air **R**epulsion
- The shape around the central atom(s) can be predicted by assuming that the areas of electrons on the central atom will try to get as far from each other as possible
  - areas of negative charge will repel
  - thus the shape minimizes the repulsion between the bond pairs.

Areas of Electrons

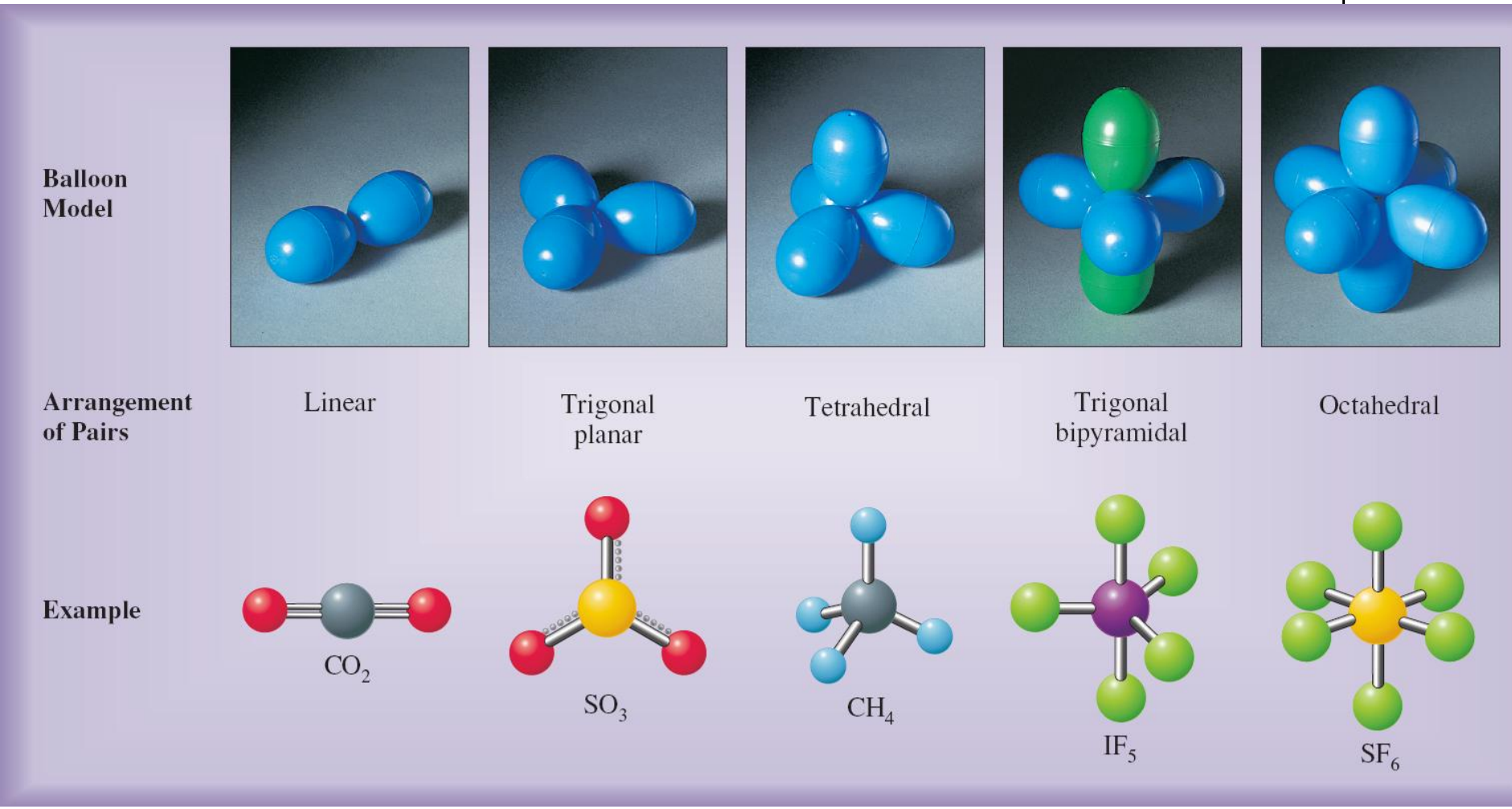


- Each Bond counts as 1 area of electrons
  - single, double or triple all count as 1 area
- Each Lone Pair counts as 1 area of electrons
  - Even though lone pairs are not attached to other atoms, they do “occupy space” around the central atom
- Lone pairs take up slightly more space than bonding pairs
  - Effects bond angles

Valence Shell Electron Pair Repulsion Theory

Number of Electron Pairs	Arrangement of Electron Pairs	Geometry of Molecule
2		Linear
3		Trigonal Planar
4		Tetrahedral
5		Trigonal Bipyramidal
6		Octahedral

These arrangements are illustrated below with balloons and models of molecules for each.



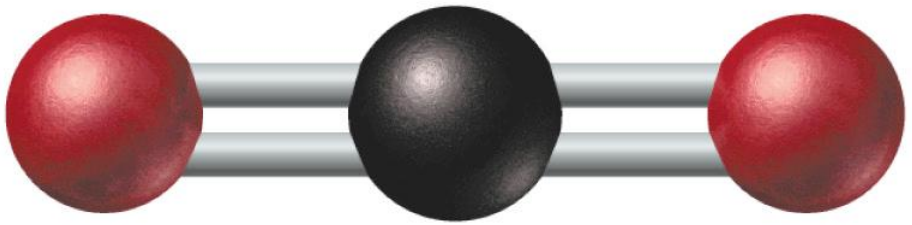
SUMMARY OF SHAPES PREDICTED BY VSEPR

No. of electron pair groups		Notation	Molecular Shape	Bond Angle	Example
Bonding	Non-bonding				
2	0	AX_2	Linear	180	CO_2
3	0	AX_3	Trigonal planar	120	BF_3
2	1	AX_2E	Bent	120	SO_2

Molecular Geometry: Linear

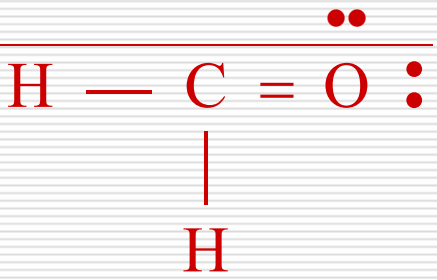
- Electron Groups Around Central Atom = 2
- Bonding Groups = 2
- Lone Pairs = 0
- Electron Geometry = Linear
- Bond Angle = 180°

AX_2

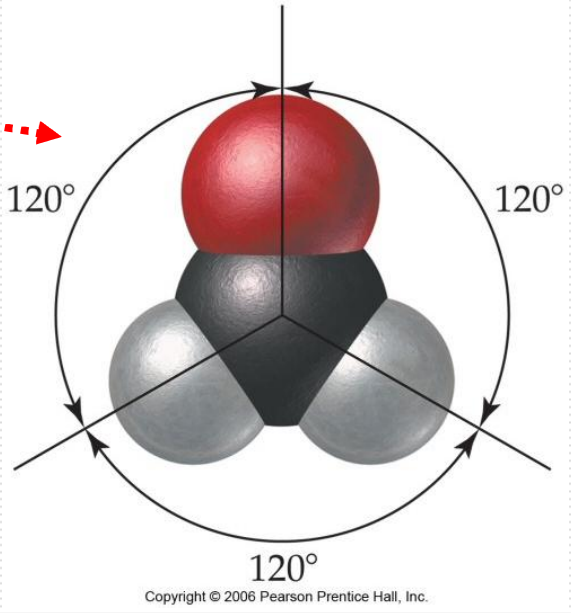


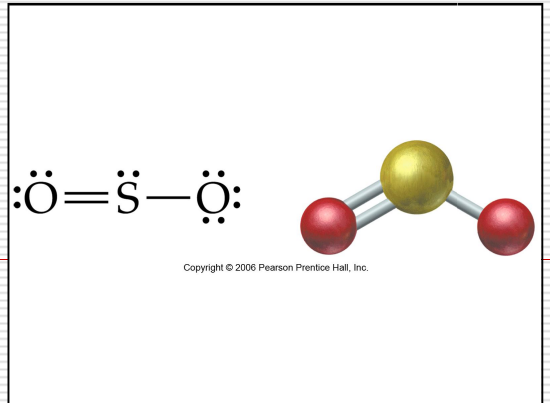
Nonpolar

Trigonal Planar Shapes: Electron Pair Geometry



- **Trigonal Planar**
  - 3 areas of electrons around the central atom
  - 120° bond angles
  - All Bonding = **trigonal planar**
  - 2 Bonding + 1 Lone Pair = **bent**

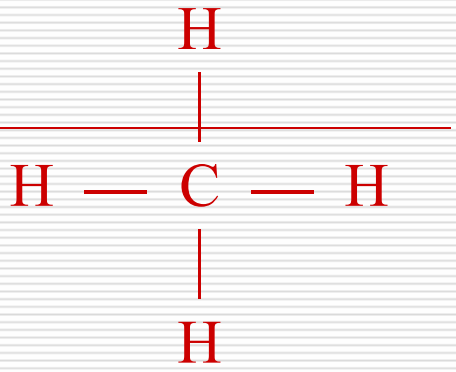




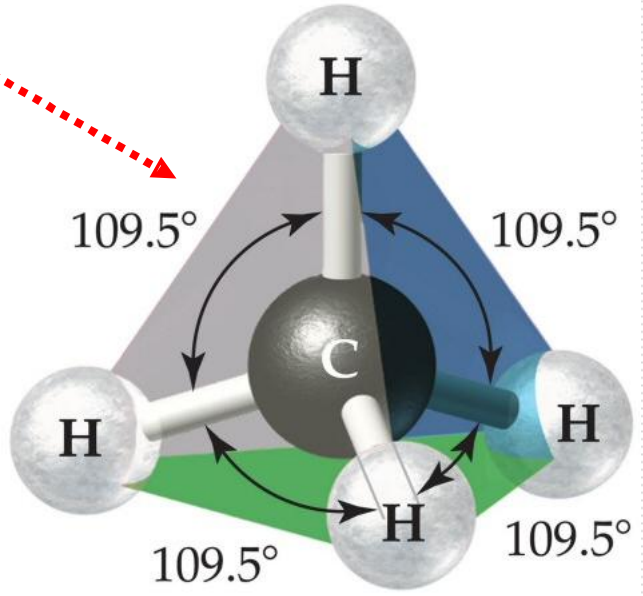
SUMMARY OF SHAPES PREDICTED BY VSEPR

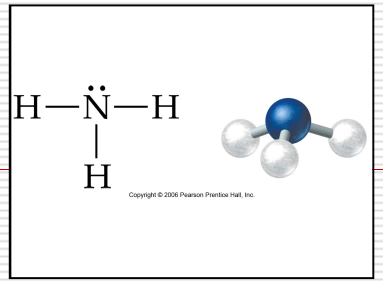
No. of electron pair groups		Notation	Molecular Shape	Bond Angle	Example
Bonding	Non-bonding				
4	0	AX_4	Tetrahedral	109.5	CH_4
3	1	AX_3E	Trigonal pyramidal	109.5	NH_3
2	2	AX_2E_2	Bent	109.5	H_2O

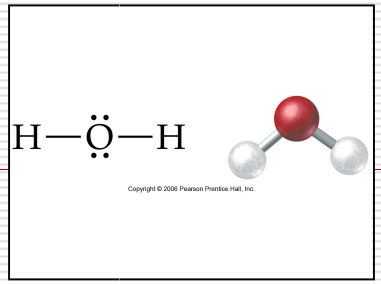
Tetrahedral Shapes: Electron Pair Geometry



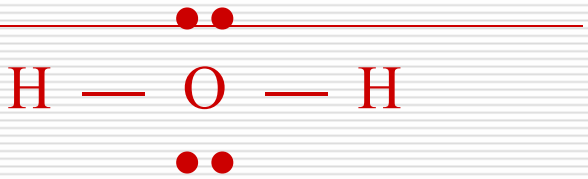
- **Tetrahedral**
  - 4 areas of electrons around the central atom
  - 109.5° bond angles
  - All Bonding = **tetrahedral**
  - 3 Bonding + 1 Lone Pair = **trigonal pyramidal**
  - 2 Bonding + 2 Lone Pair = **bent**

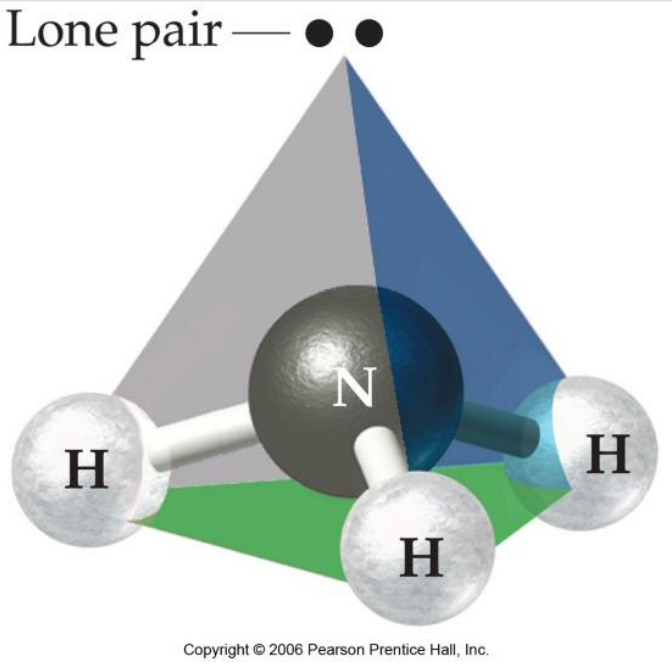


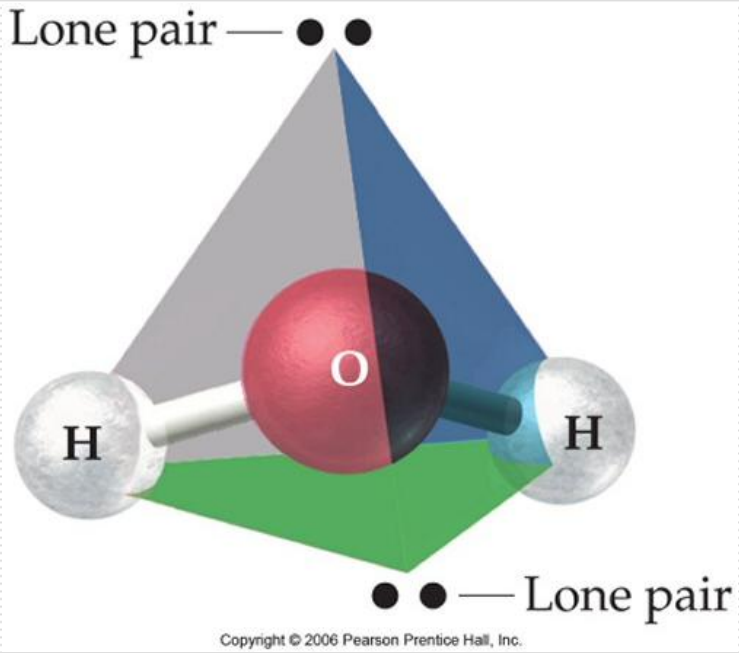




Tetrahedral Derivatives







trigonal pyramidal **bent**

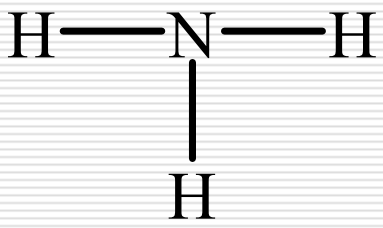
Determine if NH_3 is polar:

Lewis Structure

bond polarity & molecular shape

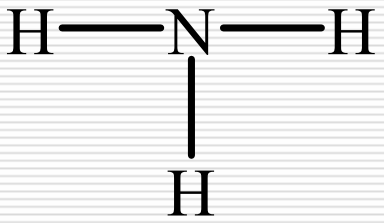
✓Draw the Lewis Structure

➢write skeletal structure



✓Draw the Lewis Structure

➢count valence electrons



N = 5

H = 3 · 1

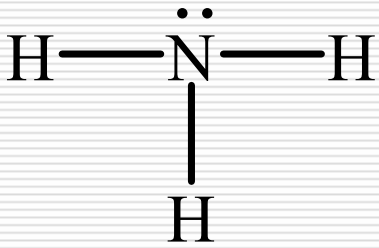
total NH_3 = 8

start 8 e^-

use 6 e^-

left 2 e^-

➢complete octets



start 2 e^-

use 2 e^-

left 0 e^-

Electronegativity

N = 3.0

H = 2.1

✓Determine if Bonds are Polar

3.0 – 2.1 = 0.9

∴ polar covalent

✓Determine Shape of Molecule

4 areas of electrons around N;

3 bonding areas

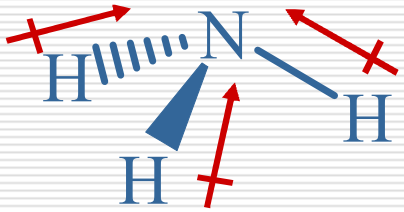
1 lone pair

shape = trigonal pyramid

✓Determine Molecular Polarity

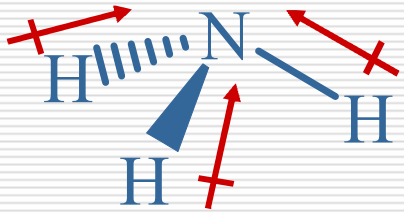
bonds = polar

shape = trigonal pyramid



molecule = polar

bonds = polar
shape = trigonal pyramid



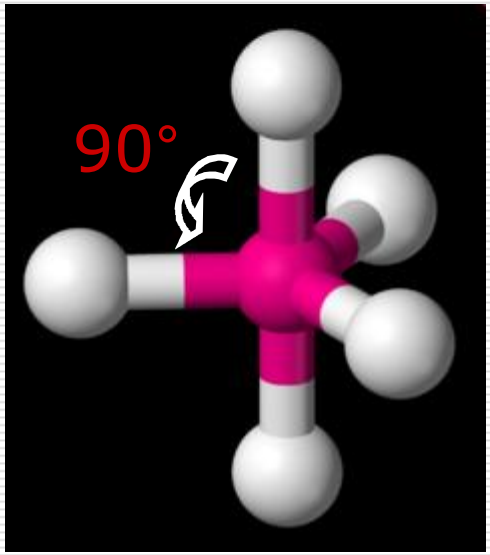
The Lewis structure is correct. The bonds are polar and the shape is asymmetrical, thus the molecule is polar.

SUMMARY OF SHAPES PREDICTED BY VSEPR

No. of electron pair groups		Notation	Molecular Shape	Bond Angle	Example
Bonding	Non-bonding				
5	0	AX_5	Trigonal bipyramidal	90, 120, 180	PCl_5
4	1	AX_4E	See-saw	90, 120, 180	SF_4
3	2	AX_3E_2	T-shaped	90, 180	ClF_3
2	3	AX_2E_3	Bent	180	XeF_2

Trigonal Bipyramidal: Electron Pair Geometry

- **Trigonal Bipyramidal**
  - 5 areas of electrons around the central atom
  - 120° and 90° bond angles
  - All Bonding = **Trigonal bipyramidal**
  - 4 Bonding + 1 Lone Pair = **Seesaw**
  - 3 Bonding + 2 Lone Pair = **T-shaped**
  - 2 Bonding + 3 Lone Pair = **Linear**

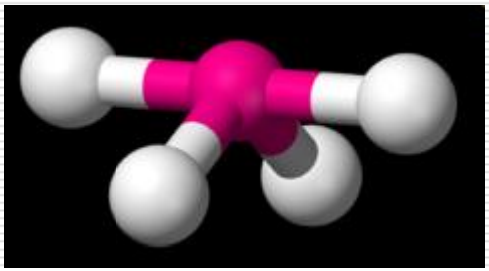


Molecular Geometry: Seesaw and T-shaped

- Bond Angles = 120° and 90° **Seesaw**

AX_4E

E = lone pair

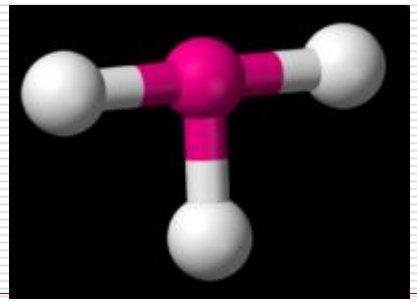


Polar

- Bond Angles = 90° **T-shaped**

AX_3E_2

E = lone pair



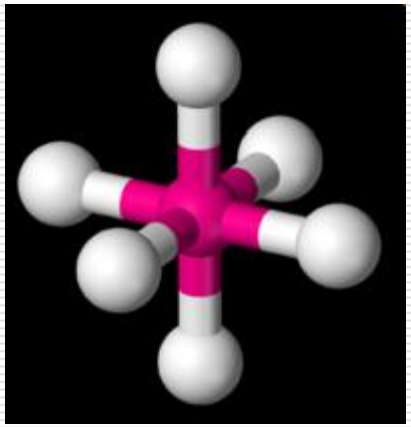
Polar

SUMMARY OF SHAPES PREDICTED BY VSEPR

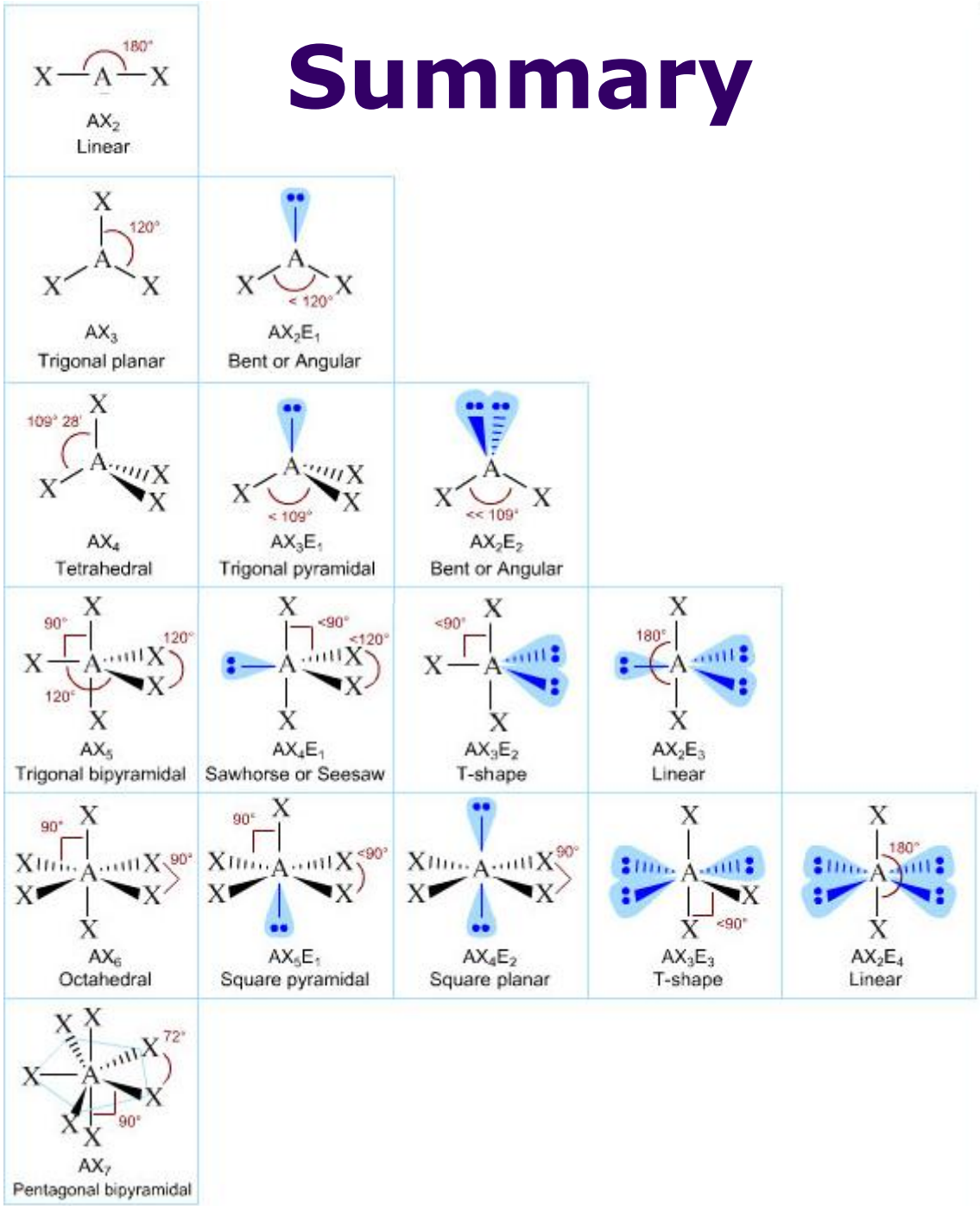
No. of electron pair groups		Notation	Molecular Shape	Bond Angle	Example
Bonding	Non-bonding				
6	0	AX_6	Octahedral	90	SF_6
5	1	AX_5E	Square pyramidal	90	BrF_5
4	2	AX_4E_2	Square planar	90	XeF_4

Octahedral: Electron Pair Geometry

- **Octahedral**
  - 6 areas of electrons around the central atom
  - 90° bond angles
  - All Bonding = **Octahedral**
  - 5 Bonding + 1 Lone Pair = Square pyramidal
  - 4 Bonding + 2 Lone Pair = **Square planar**



Summary


180°
AX2
Linear
120°
AX3
Trigonal planar
< 120°
AX2E1
Bent or Angular
109° 28'
AX4
Tetrahedral
< 109°
AX3E1
Trigonal pyramidal
<< 109°
AX2E2
Bent or Angular
90°
120°
120°
AX5
Trigonal bipyramidal
<90°
<120°
AX4E1
Sawhorse or Seesaw
<90°
AX3E2
T-shape
180°
AX2E3
Linear
90°
90°
AX6
Octahedral
90°
<90°
AX5E1
Square pyramidal
90°
AX4E2
Square planar
<90°
AX3E3
T-shape
180°
AX2E4
Linear
72°
90°
AX7
Pentagonal bipyramidal

SUMMARY OF SHAPES PREDICTED BY VSEPR

Symmetrical Molecules

Linear

Trigonal planar

Tetrahedral

Trigonal bipyramidal

Octahedral

Square planar

Could be polar if atoms are not all the same

SUMMARY OF SHAPES PREDICTED BY VSEPR

Asymmetrical Molecules

Bent

Trigonal pyramidal

See-saw

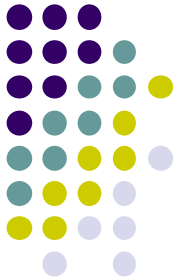
T-shaped

Square pyramidal

Polar bonds

Polar molecules

BOND ANGLES



- Bond angles between atoms can be approximately predicted from the VSEPR model.
- Some deviations from the predicted bond angles have been determined experimentally.
- These deviations are caused by 2 factors:

Effect of lone pairs

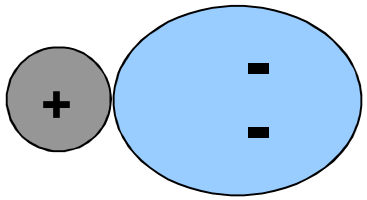
Effect of multiple bonds

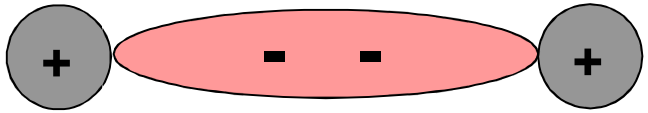
BOND ANGLES

Effect of Lone Pairs

- A lone pair tends to require more space than a bonding pair.
- A lone pair of electrons is attracted to only one atomic core, whereas a bonding pair is attracted to two.
- The lone pair is larger, while the bonding pair is drawn more tightly to the nuclei.

Lone pair

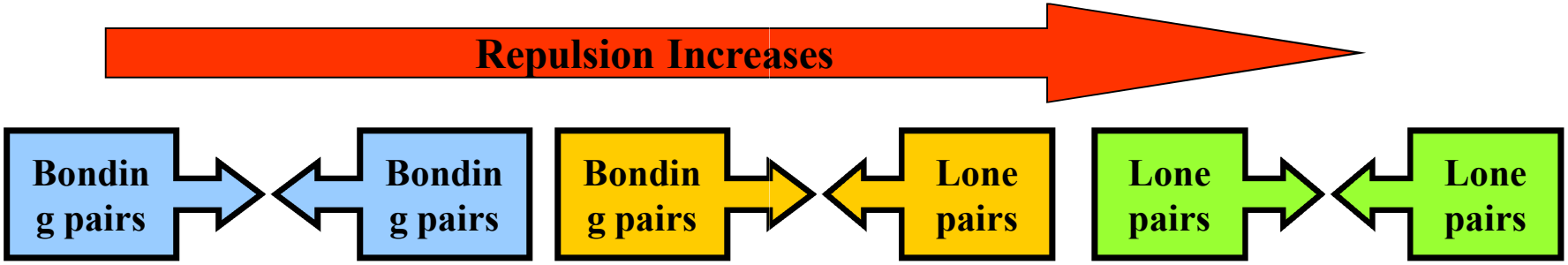




Bonding Pair

BOND ANGLES

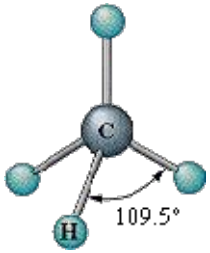
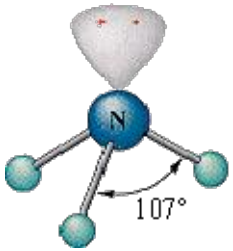
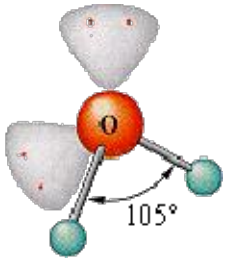
- Lone pairs repel each other stronger than Bonding Pairs.
- As a result, the repulsions between electron pairs depend on the type of electron pairs involved.



Weakest Repulsion

Strongest Repulsion

Effects of Lone Pairs on Bond Angles

	CH_4	NH_3	H_2O
			
Electron Pair Geometry	Tetrahedral	Tetrahedral	
Expected Bond Angle	109.5°	109.5°	
Bonding Pairs	4	3	
Lone Pairs	0	1	
Actual Bond Angle	109.5°	107°	105°

Bond angles decrease as the number of lone pairs increase

BOND ANGLES

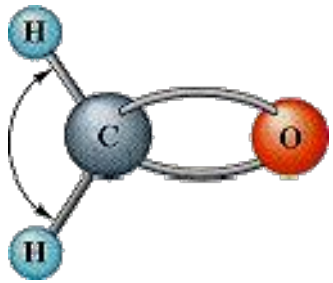
Effect of Multiple Bonds

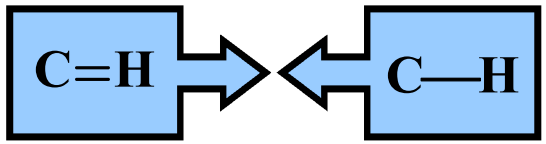
- Multiple bonds require more space than single bonds because of the greater number of electrons

Electron Pair Geometry: Trigonal Planar

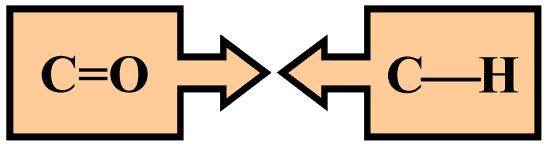
Expected Bond Angle: 120°

Actual Bond Angle: 116°





Weaker Repulsion



Stronger Repulsion

VALENCE BOND THEORY

- **Valence bond theory is used to explain covalent bonds by quantum mechanics.**

- **This basic theory describes bonds formed between two atoms when:**

1. An orbital of one atom overlaps with the orbital of another atom.

2. the total number of electrons in both orbitals does not exceed two.

HYBRID ORBITALS

- **Hybrid orbitals are orbitals used to describe the bonding that is obtained by taking combinations of the atomic orbitals of the isolated atoms.**

- **The number of hybrid orbitals formed always equals the number of atomic orbitals used.**

HYBRID ORBITALS

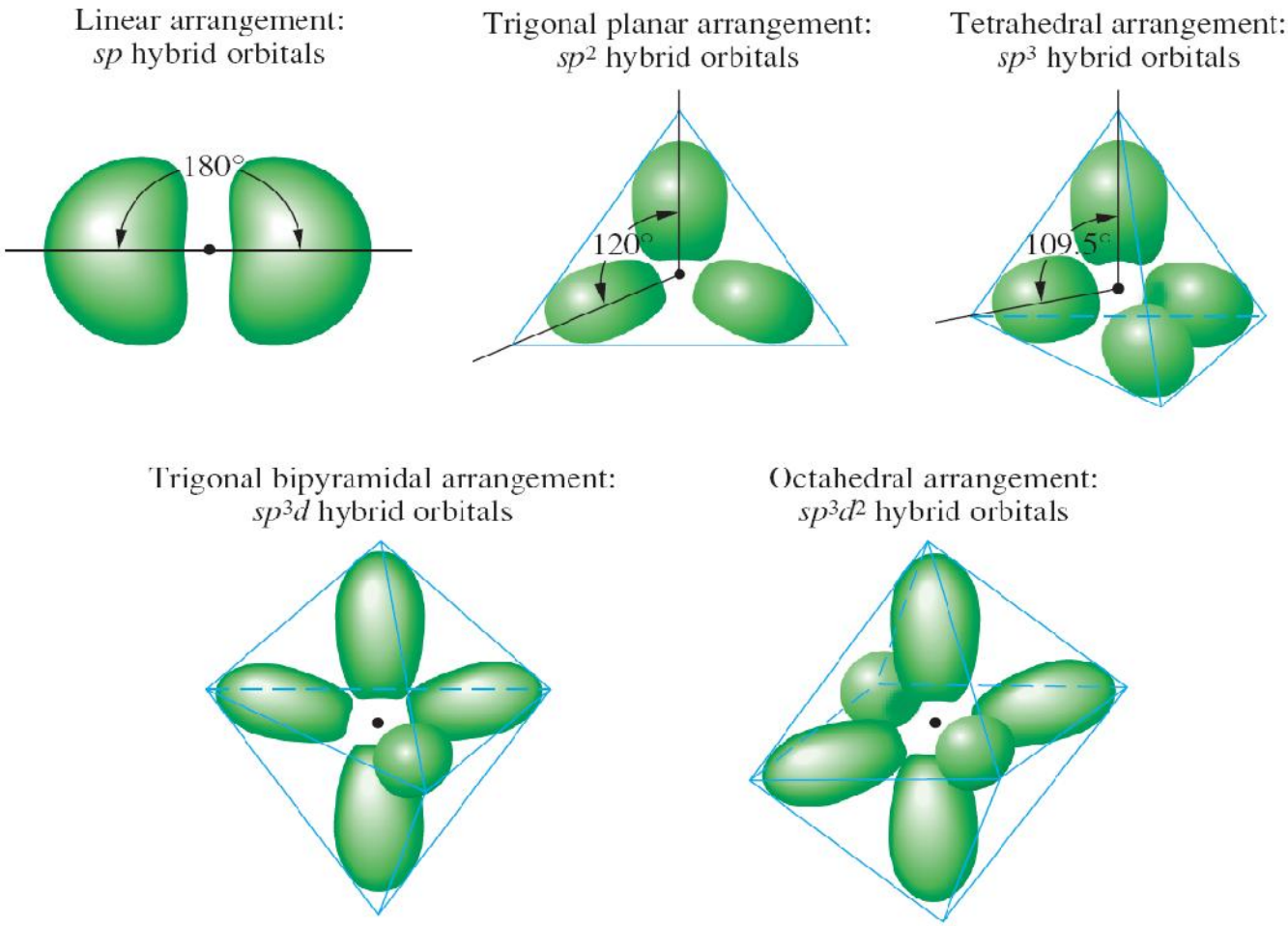
- Hybrid orbitals are named by using the atomic orbitals that combined:
- one *s* orbital + one *p* orbital gives two *sp* orbitals
- one *s* orbital + two *p* orbitals gives three sp^2 orbitals
- one *s* orbital + three *p* orbitals gives four sp^3 orbitals
- one *s* orbital + three *p* orbitals + one *d* orbital gives five sp^3d orbitals
- one *s* orbital + three *p* orbitals + two *d* orbitals gives six sp^3d^2 orbitals

Hybrid orbitals have definite directional characteristics, as described in Table 10.2.

TABLE 10.2 Kinds of Hybrid Orbitals

Hybrid Orbitals	Geometric Arrangement	Number of Orbitals	Example
sp	Linear	2	Be in BeF_2
sp^2	Trigonal planar	3	B in BF_3
sp^3	Tetrahedral	4	C in CH_4
sp^3d	Trigonal bipyramidal	5	P in PCl_5
sp^3d^2	Octahedral	6	S in SF_6

HYBRID ORBITALS

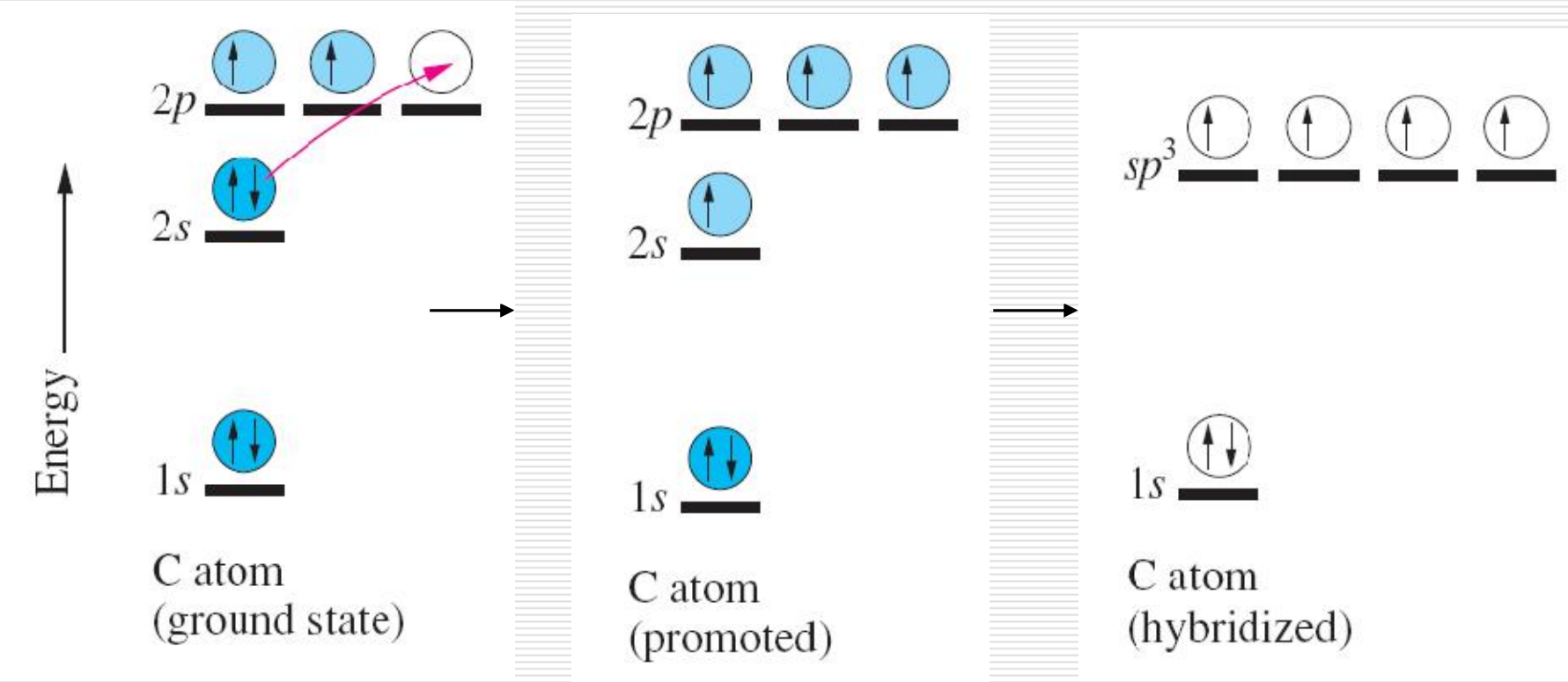


Hybrid Orbitals

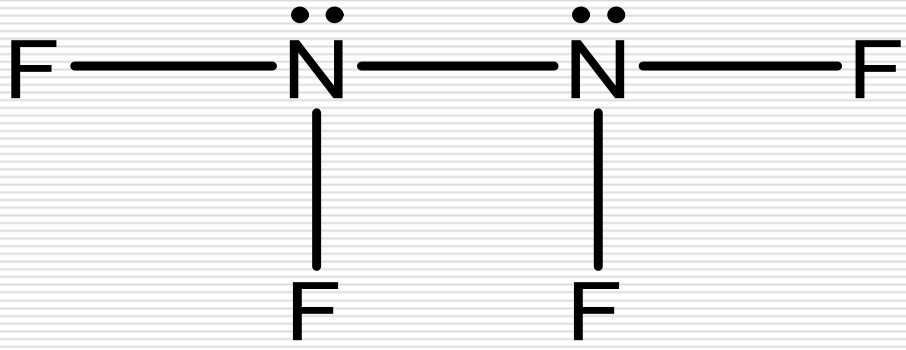
- Let's look at the methane molecule, CH_4. Simply using the atomic orbital diagram, it is difficult to explain its four identical C—H bonds.

- The valence bond theory allows us to explain this in two steps: promotion and hybridization.

- One paired 2*s* electron is promoted to the unfilled 2P orbital.
- Each orbital has one electron.
- These orbitals are hybridized → four sp^3 hybrid orbitals.



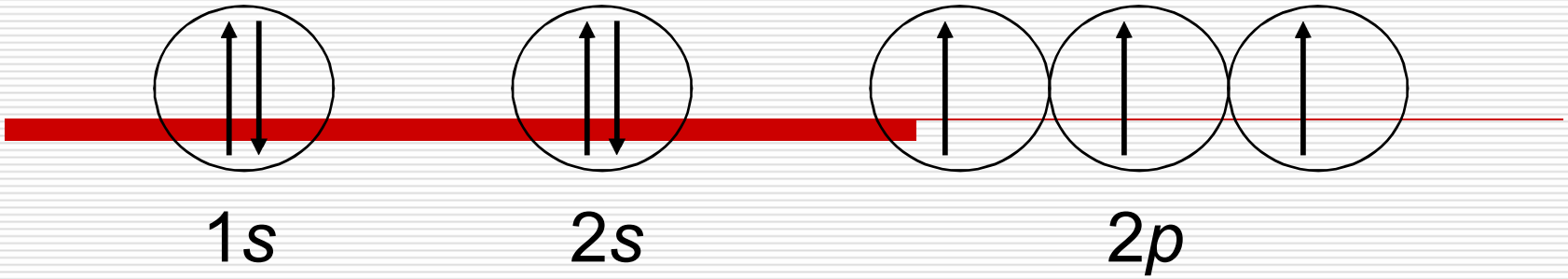
Use valence bond theory to describe the bonding about an N atom in N_2F_4.



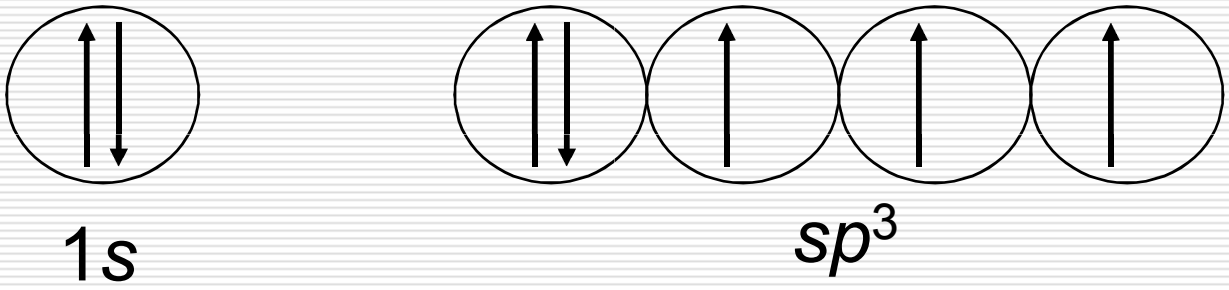
The Lewis electron-dot structure shows three bonds and one lone pair around each N atom. They have a tetrahedral arrangement.

A tetrahedral arrangement has sp^3 hybrid orbitals.

The orbital diagram of the ground-state N atom is



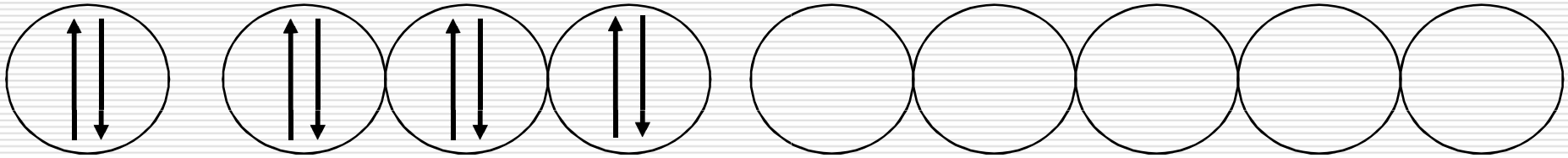
The sp^3 hybridized N atom is



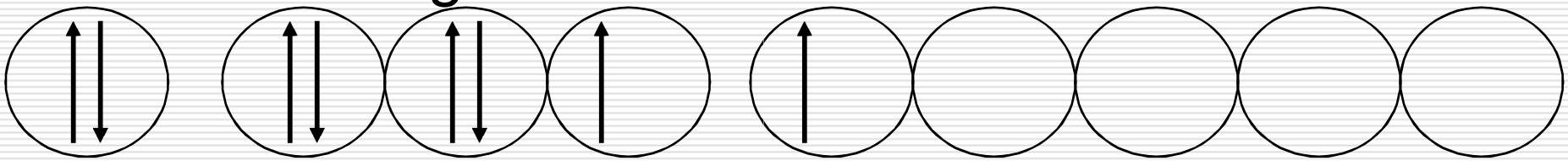
Consider one N in N_2F_4: the two N—F bonds are formed by the overlap of a half-filled sp^3 orbital with a half-filled $2p$ orbital on F. The N—N bond forms from the overlap of a half-filled sp^3 orbital on each. The lone pair occupies one sp^3 orbital.

Use valence bond theory to describe the bonding in the ClF_2^- ion.

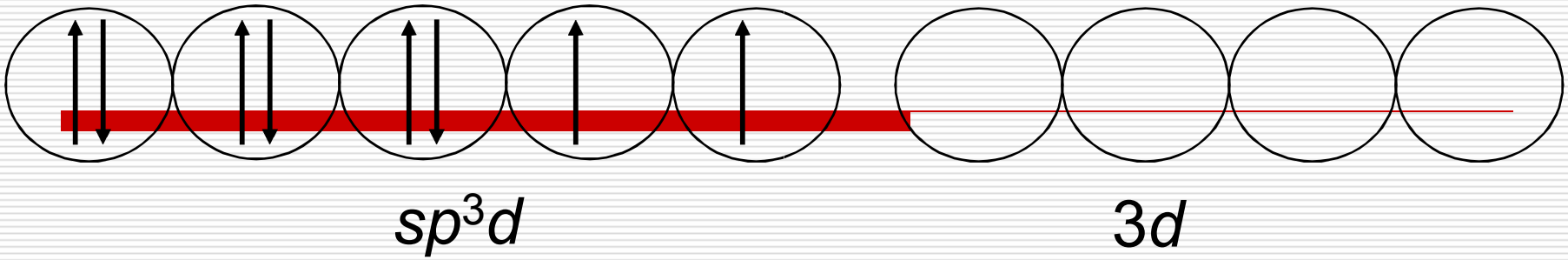
The valence orbital diagram for the Cl^- ion is



After the promotion to get two half-filled orbitals, the orbital diagram is



The sp^3d hybridized orbital diagram is



- Two Cl—F bonds are formed from the overlap of two half-filled sp^3d orbitals with half-filled 2p orbitals on the F atom. These use the axial positions of the trigonal bipyramid.

- Three lone pairs occupy three sp^3d orbitals. These are in the equatorial position of the trigonal bipyramid.

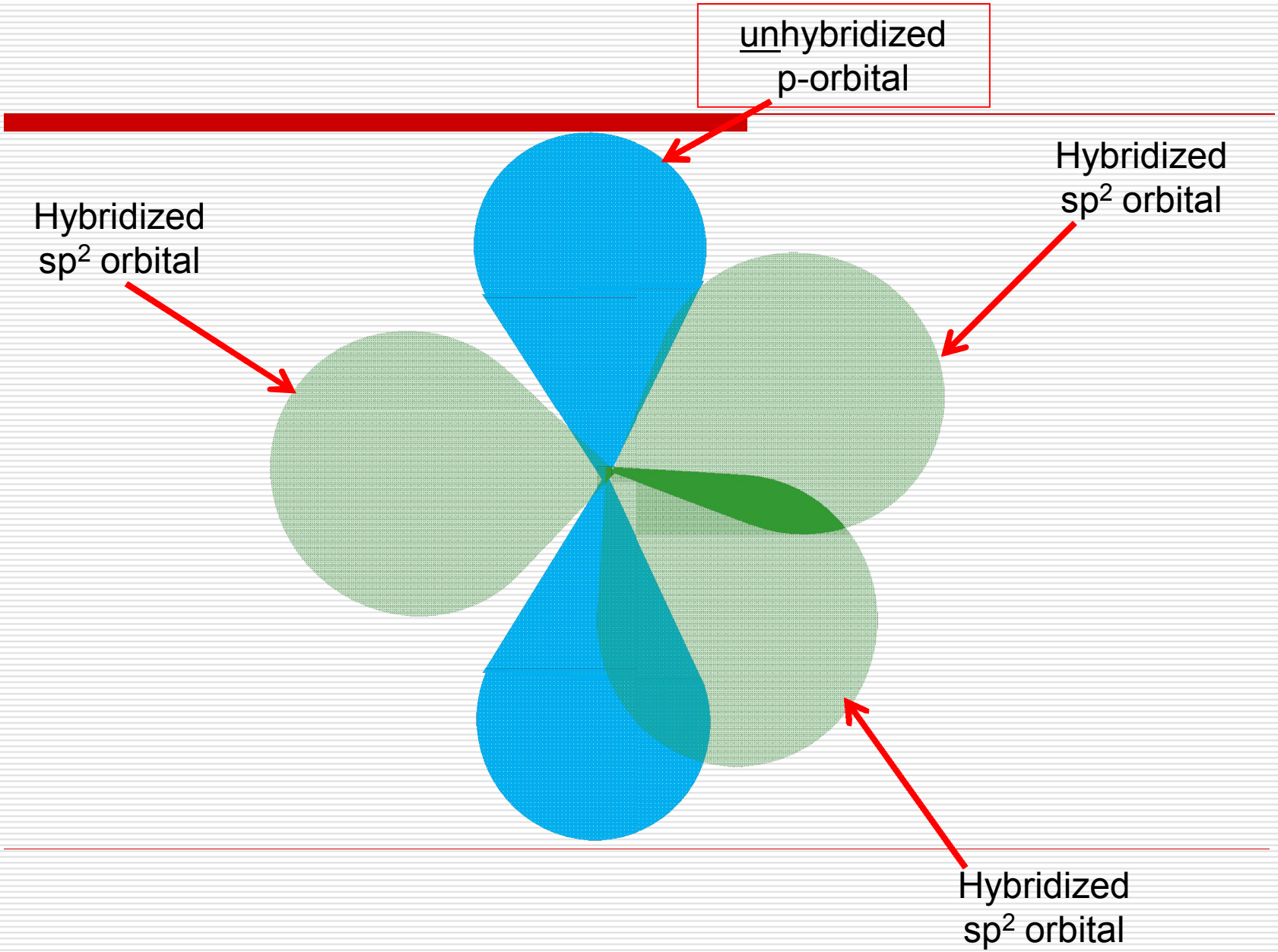
- One hybrid orbital is required for each bond (whether a single or a multiple bond) and for each lone pair.

- Multiple bonding involves the overlap of one hybrid orbital and one (for a double bond) or two (for a triple bond) nonhybridized *p* orbitals.

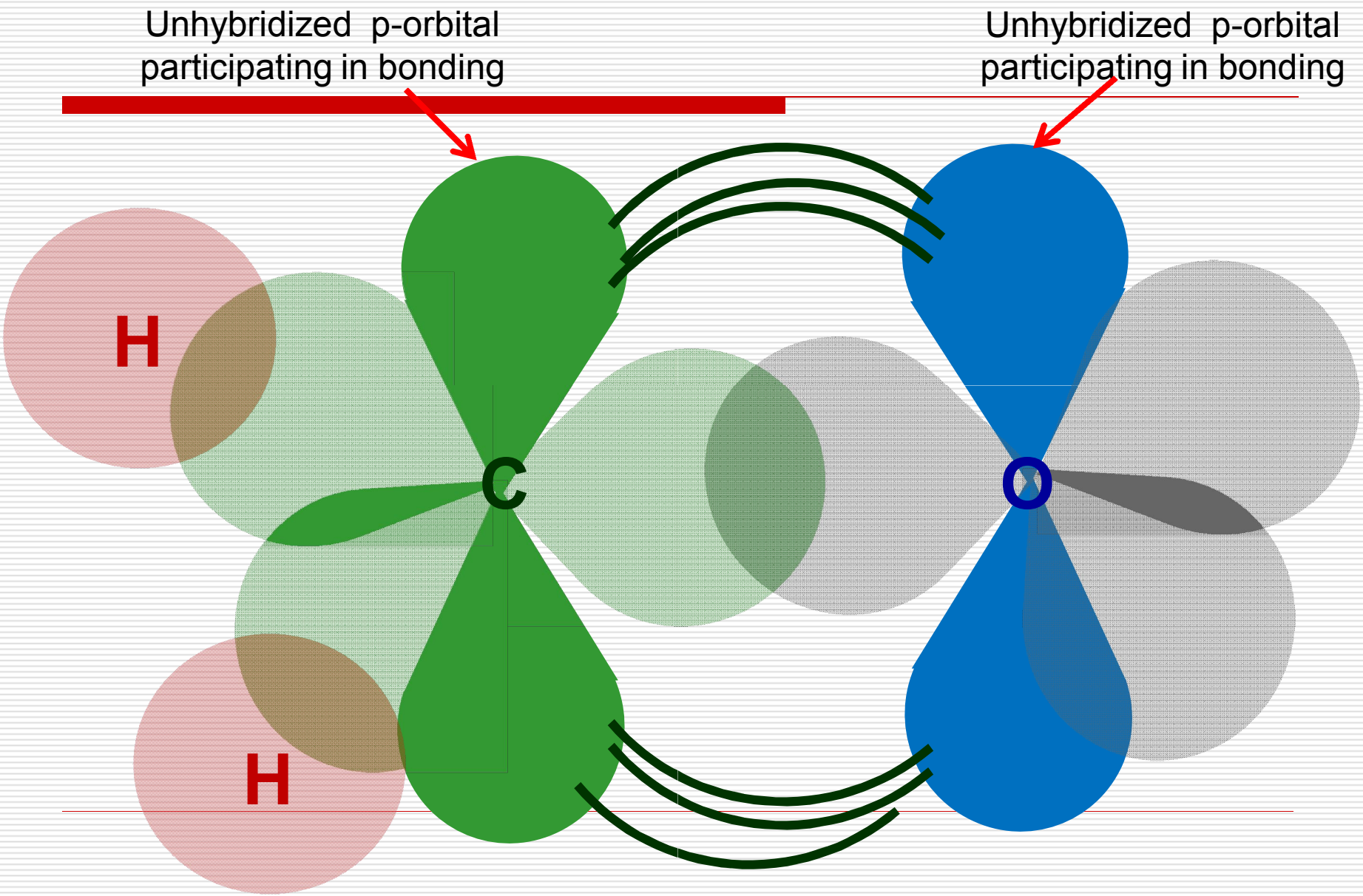
- To describe a multiple bond, we need to distinguish between two kinds of bonds.

- A σ **bond** (sigma) has a cylindrical shape about the bond axis. It is formed either when two *s* orbitals overlap or with directional orbitals (*p* or hybrid), when they **overlap along their axis.**

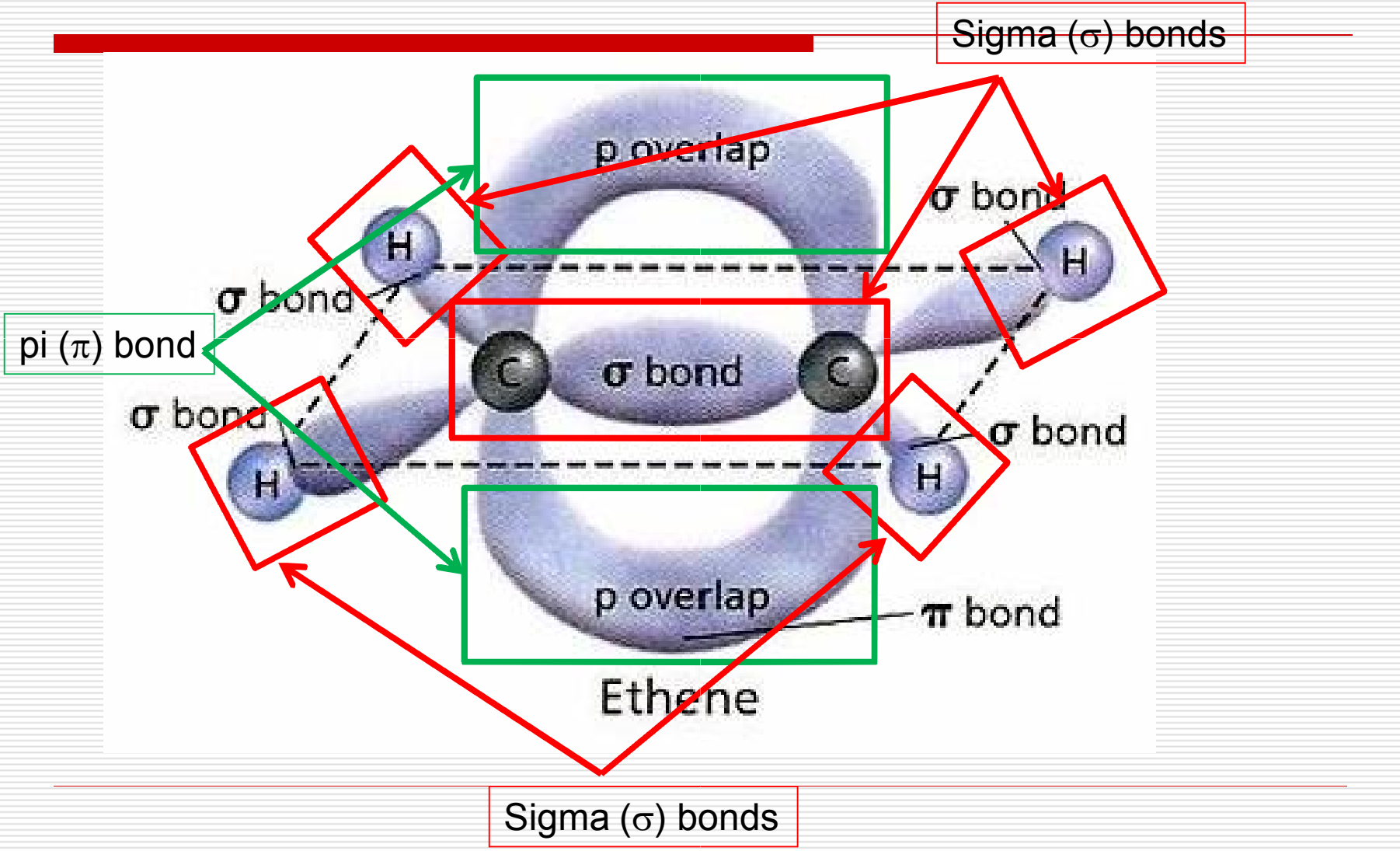
- A π **bond** (pi) has an electron distribution above and below the bond axis. It is formed by the **sideways overlap** of two parallel *p* orbitals. This overlap occurs when two parallel half-filled *p* orbitals are available after σ bonds have formed.


unhybridized
p-orbital
Hybridized
sp2 orbital
Hybridized
sp2 orbital
Hybridized
sp2 orbital

CH_2O Structure

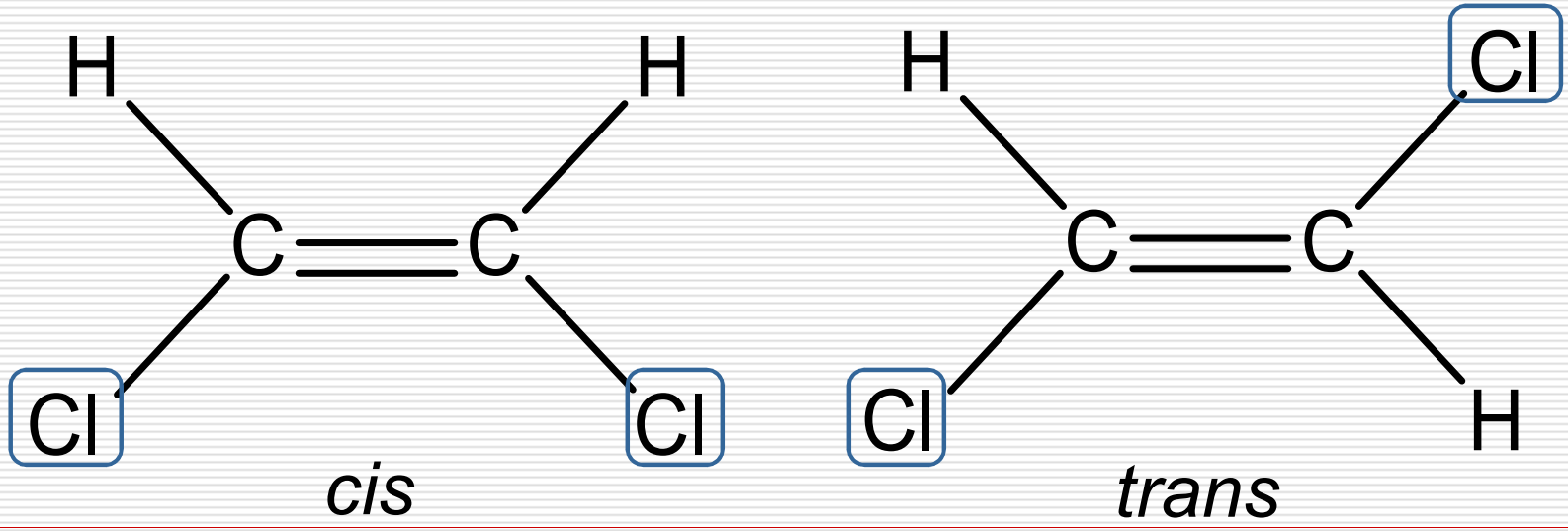


C_2H_4 Structure

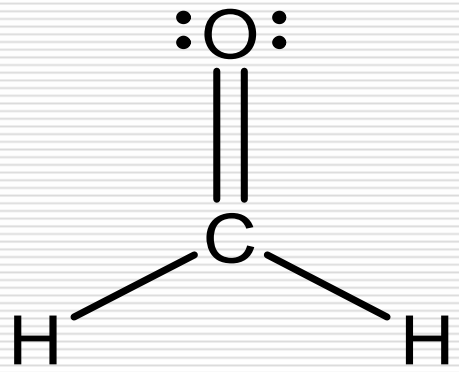


The description of a π bond helps to explain the *cis*-*trans* isomers of 1,2-dichloroethene.

The overlap of the parallel *p* orbitals restricts the rotation around the C=C bond. This fixes the geometric positions of Cl: either on the same side (*cis*) or on different sides (*trans*) of the C=C bond.



Describe the bonding about the C atom in formaldehyde, CH_2O, using valence bond theory.

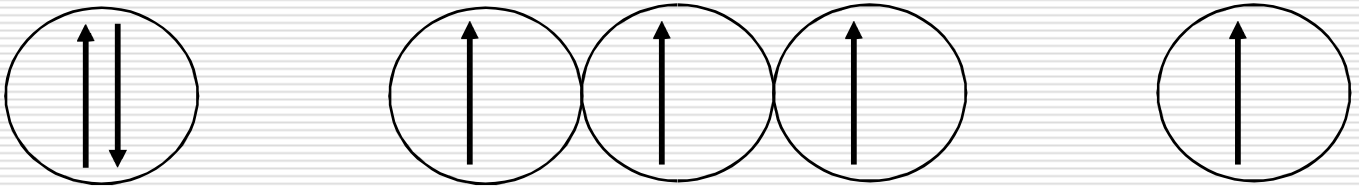


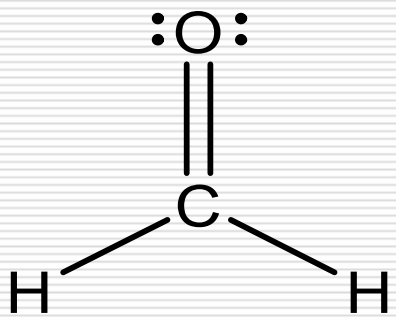
The electron arrangement is trigonal planar using sp^2 hybrid orbitals.

The ground-state orbital diagram for C is

- After promotion, the orbital diagram is

After hybridization, the orbital diagram is





The C—H σ bonds are formed from the overlap of two C sp^2 hybrid orbitals with the 1*s* orbital on the H atoms.

The C—O σ bond is formed from the overlap of one sp^2 hybrid orbital and one O half-filled *p* orbital.

The C—O π bond is formed from the sideways overlap of the C 2*p* orbital and an O 2*p* orbital.

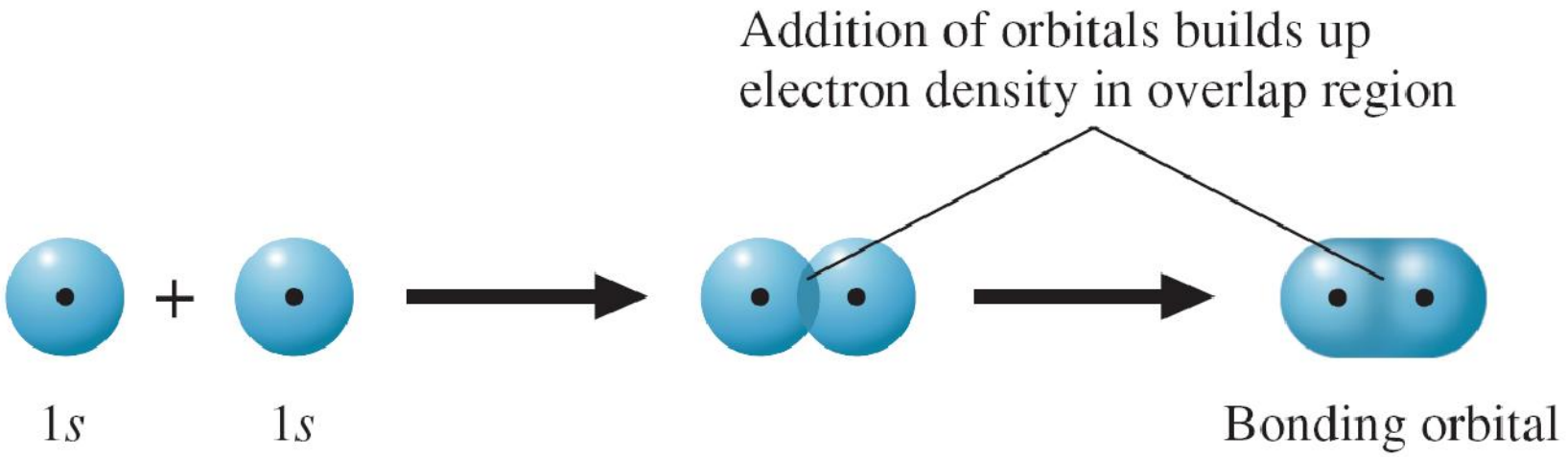
MOLECULAR ORBITAL THEORY

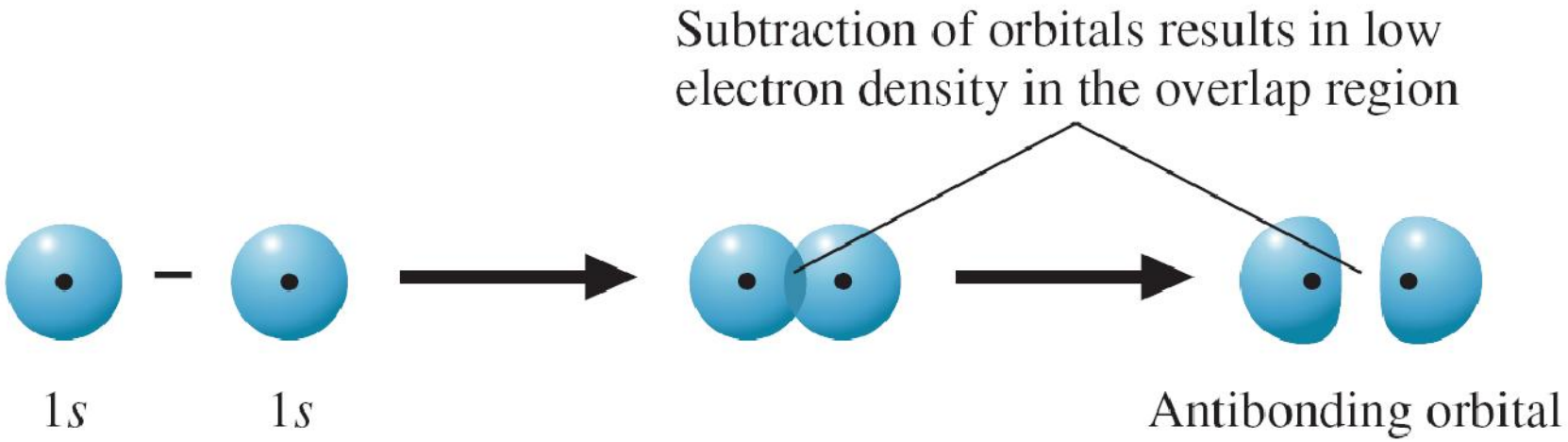
- **The valence bond theory does not satisfactorily describe all molecules.**

- **Molecular orbital theory involves the electronic structure of molecules that relates to molecular orbitals.**

MOLECULAR ORBITAL THEORY

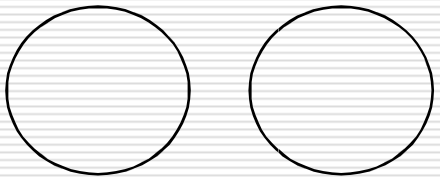
- As atoms approach one another, their atomic orbitals overlap and form molecular orbitals.
- Molecular orbitals concentrated in regions between nuclei are called **bonding orbitals.** They are obtained by adding atomic orbitals.
- Molecular orbitals having zero values in regions between nuclei (and exist in other regions) called **antibonding orbitals.** They are obtained by subtracting atomic orbitals.





MOLECULAR ORBITAL THEORY

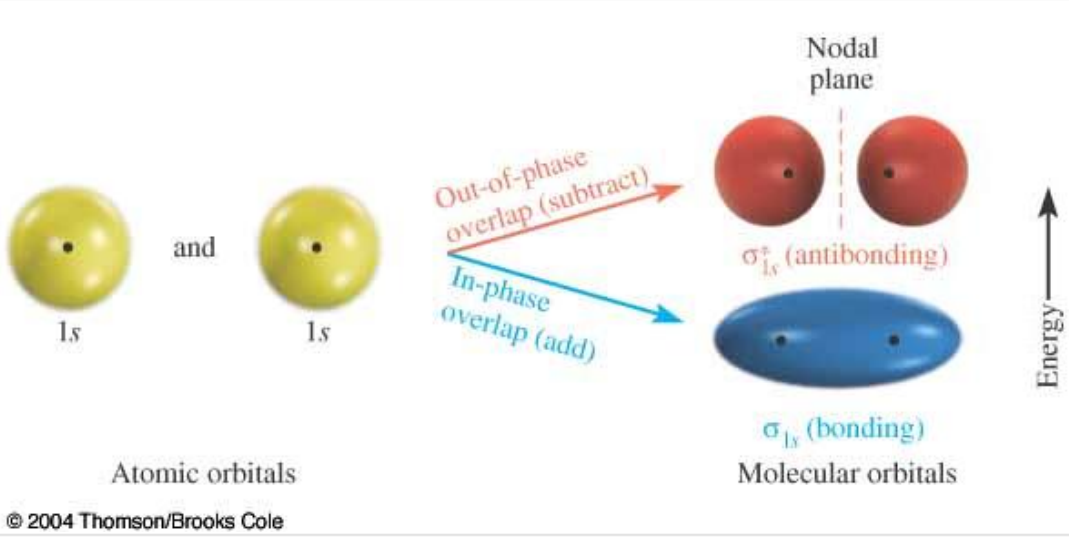
- Once a molecular orbital is formed, it can be occupied in the same way as atomic orbitals.
- When the two 1*s* orbitals combine, they form two σ molecular orbitals.
- The bonding molecular orbital is lower in energy than the antibonding molecular orbital.

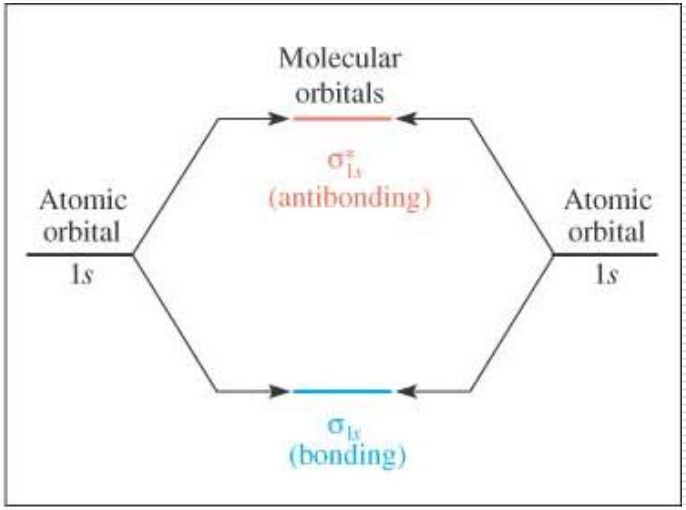


σ_{1s} σ^*_{1s}

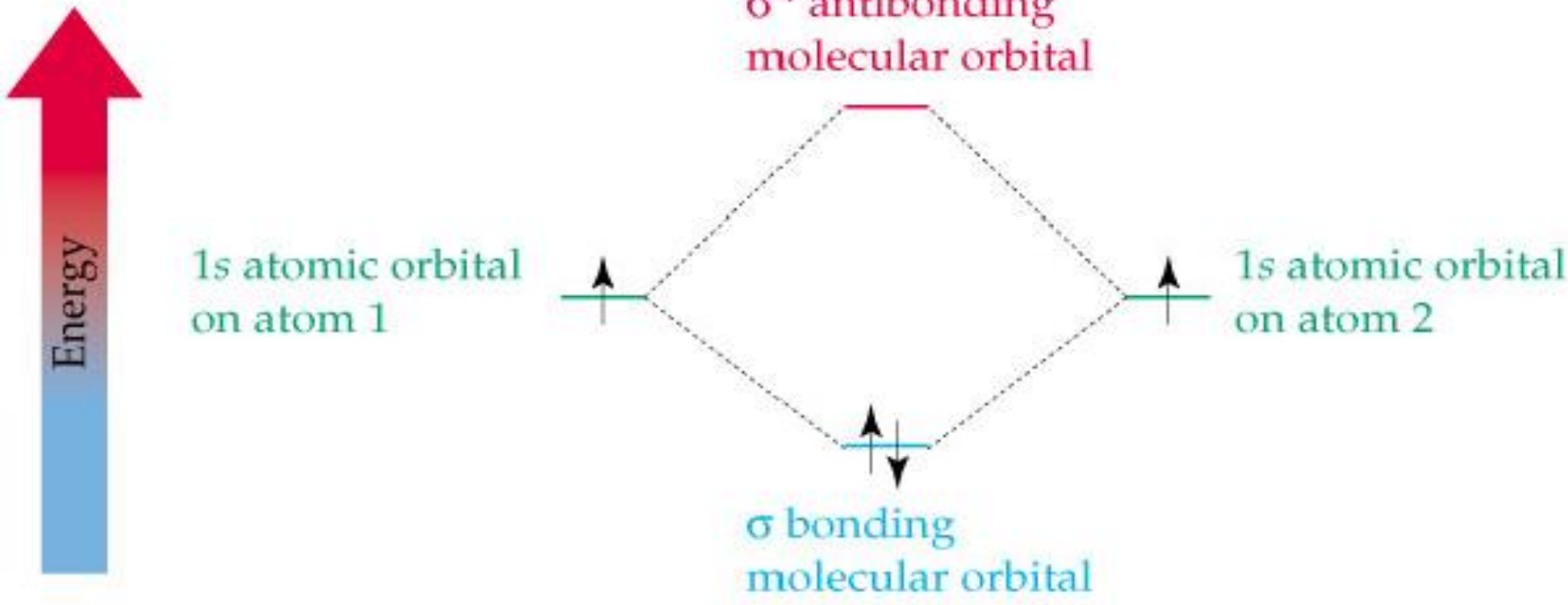
MOLECULAR ORBITAL THEORY

- The two electrons are placed in the lower-energy bonding molecular orbital with opposite spin.
- The ground-state molecular orbital electron configuration is $(\sigma_{1s})^2$.





MOLECULAR ORBITAL THEORY



MOLECULAR ORBITAL THEORY

Bond order—the number of bonds that exist between two atoms—can be calculated using the equation

$$\text{Bond order} = \frac{1}{2}\left(n_b - n_a\right)$$

n_b = number of electrons in bonding orbitals
n_a = number of electrons in antibonding orbitals

MOLECULAR ORBITAL THEORY

- For H_2 (two electrons), the molecular electron configuration is $(\sigma_{1s})^2$.
The bond order is ½(2 - 0) = 1.
- For H_2^+ (one electron), the molecular electron configuration is $(\sigma_{1s})^1$.
The bond order is ½(1 - 0) = ½.
- For He_2 (four electrons), the molecular electron configuration is $(\sigma_{1s})^2 (\sigma^*_{1s})^2$.
The bond order is ½(2 - 2) = 0. This means no bond forms.

FACTORS THAT DETERMINE ORBITAL INTERACTION

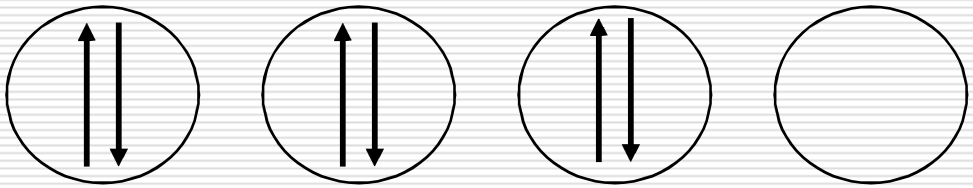
The strength of the interaction between two atomic orbitals to form molecular orbitals is determined by two factors:

- The energy difference between the interacting orbitals
- The magnitude of the overlap

For the interaction to be strong, the energies of the two orbitals must be approximately equal and the overlap must be large.

Second-Period Homonuclear Diatomic Molecules, Li_2

- In Li_2, the two 1*s* atomic orbitals combine to form two σ molecular orbitals: σ_{1s} and σ^*_{1s}.
- The two 2*s* atomic orbitals combine to form two σ molecular orbitals: σ_{2s} and σ^*_{2s}.
- Six electrons occupy the orbitals in order of increasing energy:



Second-Period Homonuclear Diatomic Molecules, Li_2

The molecular electron configuration is

$$(\sigma_{1s})^2(\sigma_{1s}^*)^2(\sigma_{2s})^2 \quad \text{or} \quad KK(\sigma_{2s})^2$$

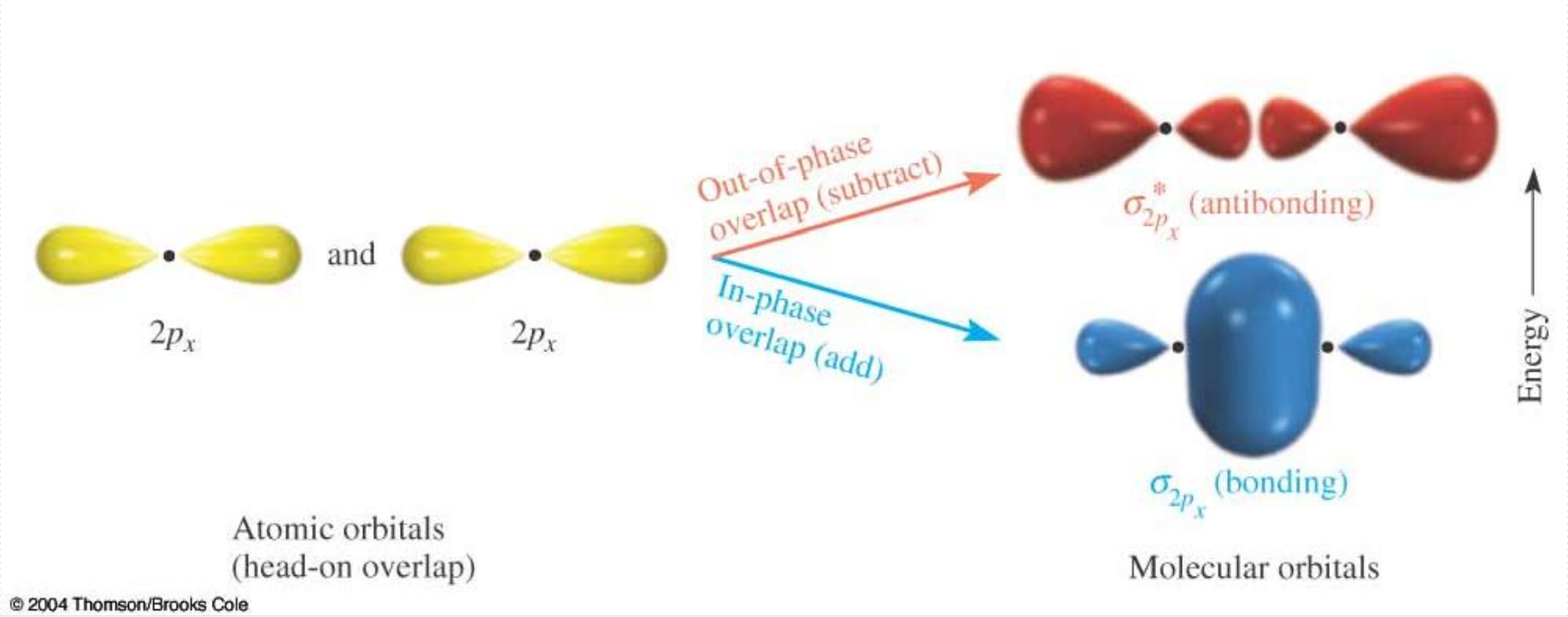
KK is the abbreviation for $(\sigma_{1s})^2(\sigma^*_{1s})^2$.

The bond order is ½(4 - 2) = 1.

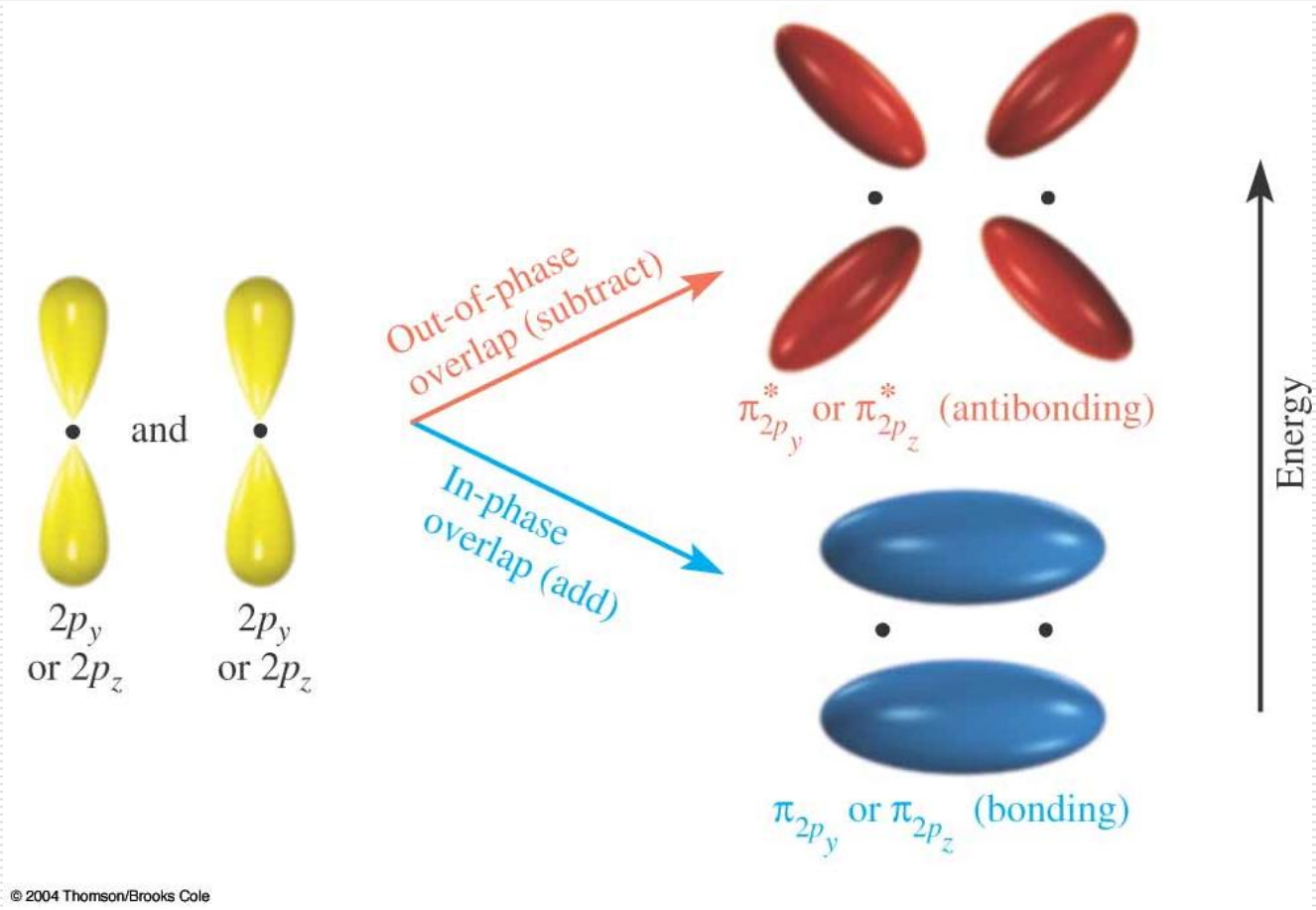
MOLECULAR ORBITAL THEORY

- Molecular orbitals formed by the overlap of atomic *p* orbitals are of two types.
- When two *p* orbitals overlap end-to-end, two σ molecular orbitals form: σ_{2p} and σ^*_{2p}.
- When two *p* orbitals overlap sideways, two π molecular orbitals form: π_{2p} and π^*_{2p}. Because two *p* orbitals on each atom overlap with two *p* orbitals on another atom, *a total of four molecular orbitals form*: two bonding and two antibonding.

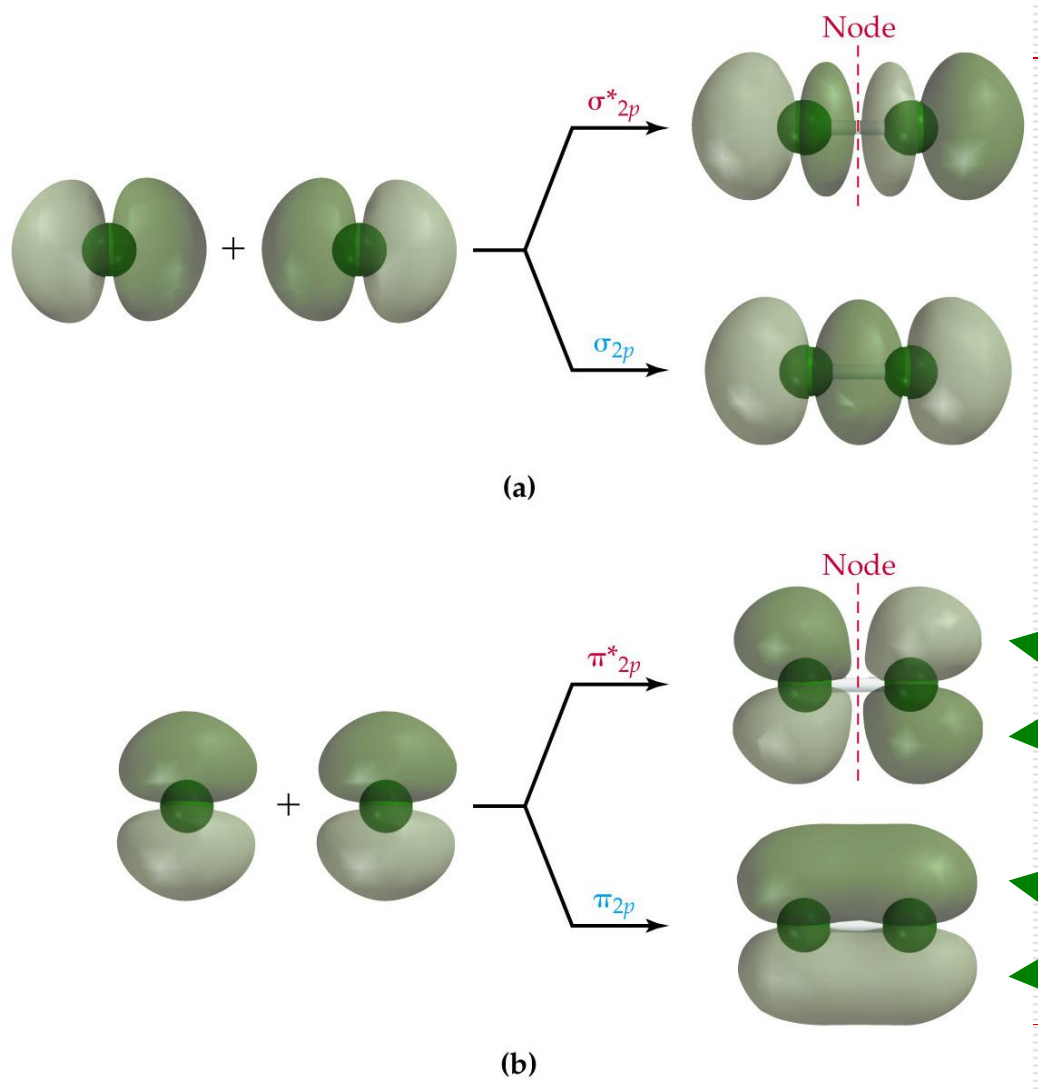
Head-on p overlap gives σ orbitals



Side-by-side p overlap gives π orbitals



Formation of Molecular Orbitals from p atomic orbitals

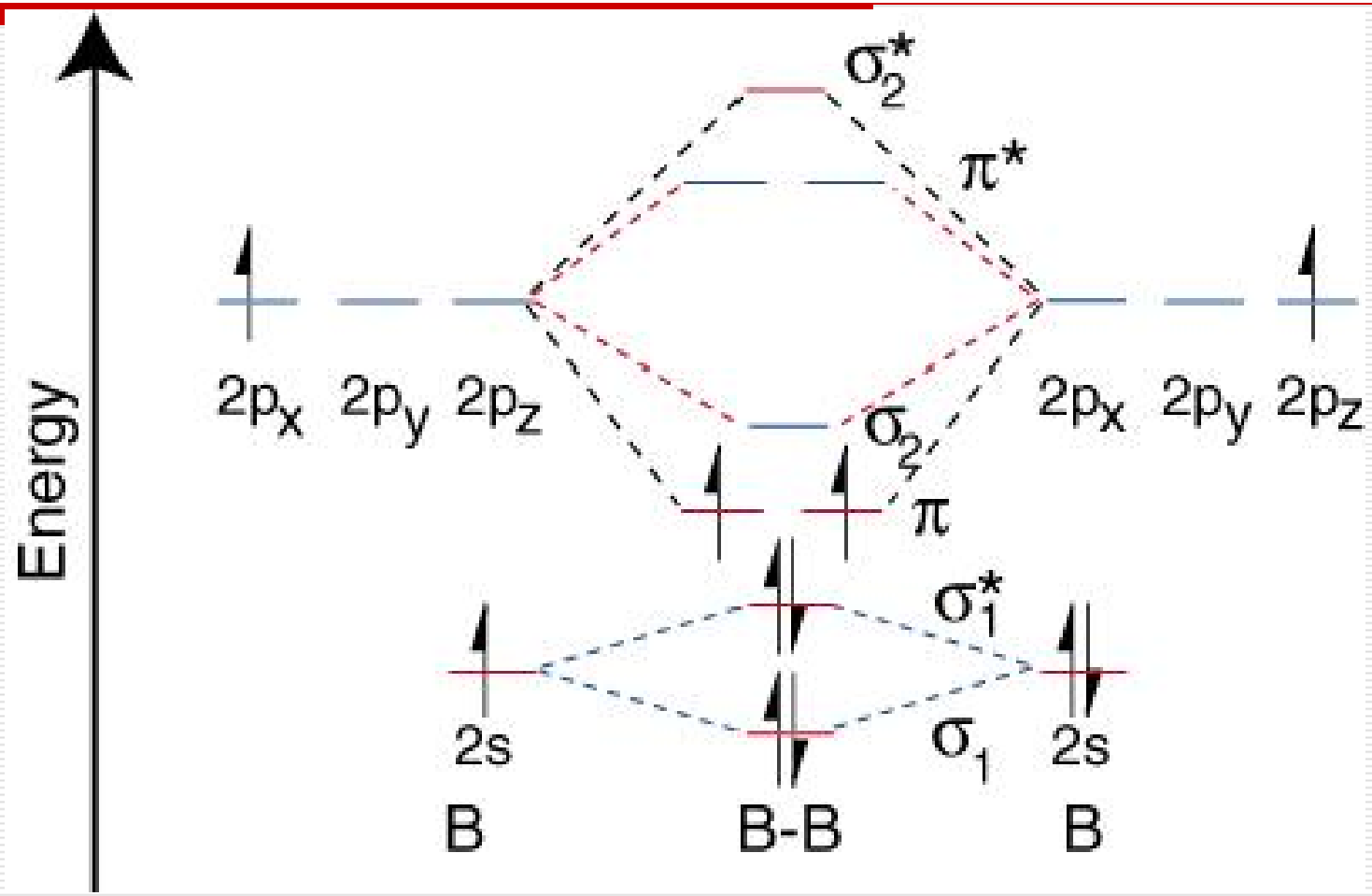


ORDER OF INCREASING ENERGY OF MOLECULAR ORBITALS

$\sigma_{1s} < \sigma^*_{1s} < \sigma_{2s} < \sigma^*_{2s} < \pi_{2p} < \sigma_{2P} < \pi^*_{2p} < \sigma^*_{2P}$

2 ORBITALS EACH

The molecular orbital diagram of the B_2 molecule.



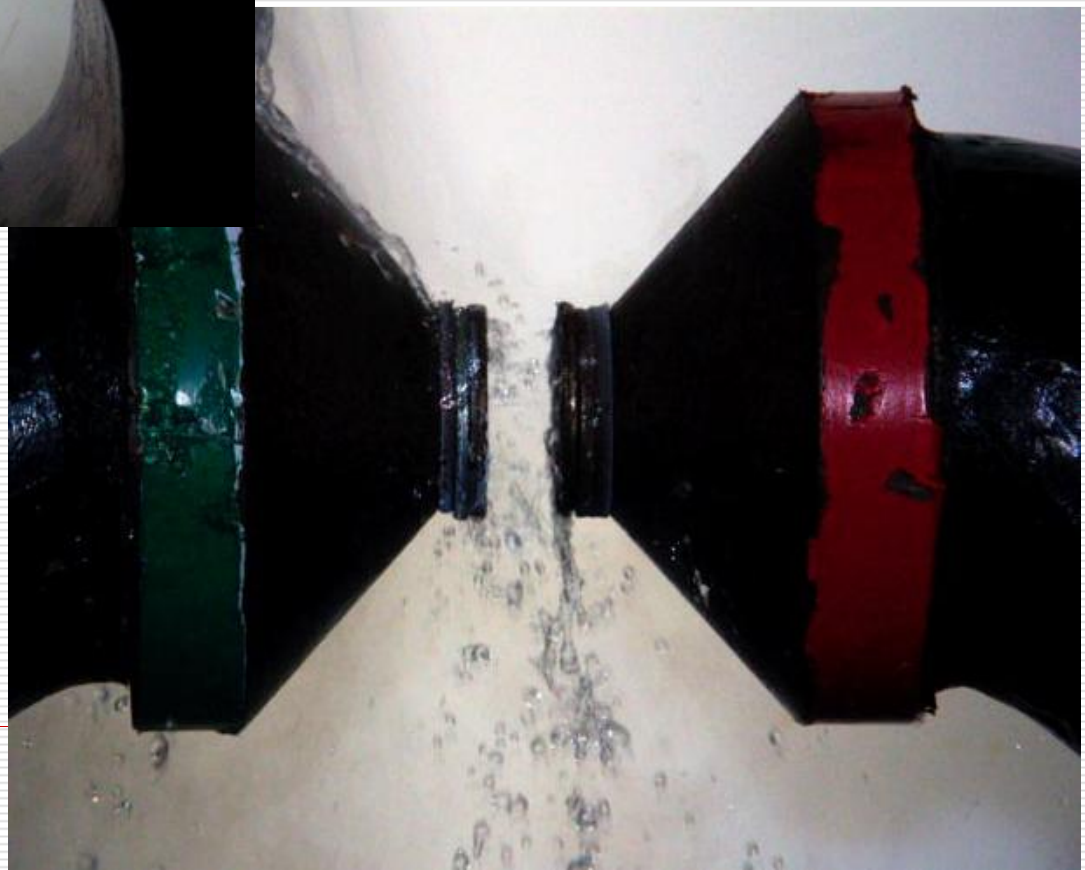
MAGNETIC CHARACTER OF MOLECULES

Paramagnetic **have unpaired electrons and are attracted to magnetic field**

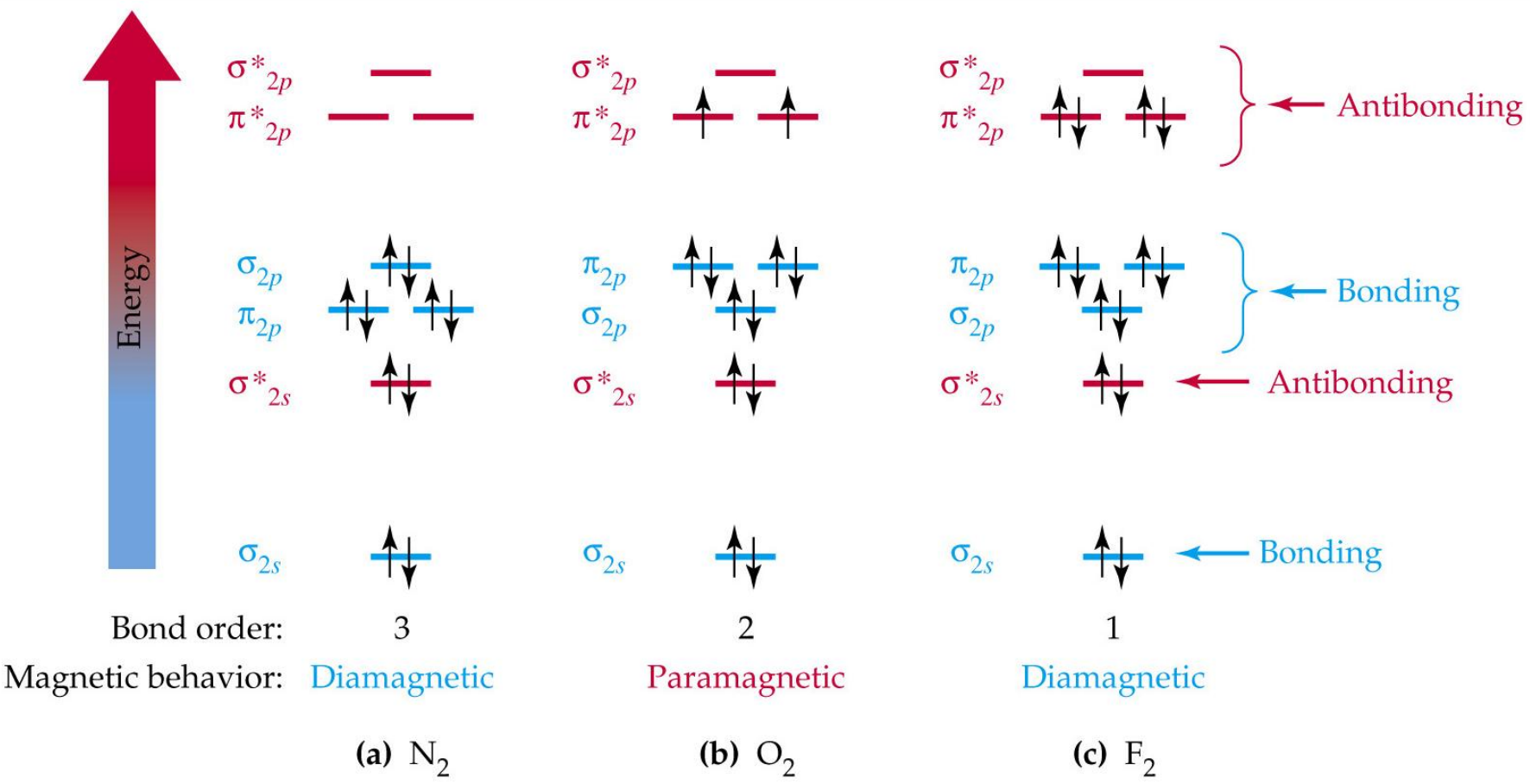
Diamagnetic **weakly repelled by magnetic field since all electrons are spin-paired**

Liquid O_2 is attracted to the strong magnetic field so it sticks

Liquid N_2 is not attracted to the strong magnetic field so doesn't stick



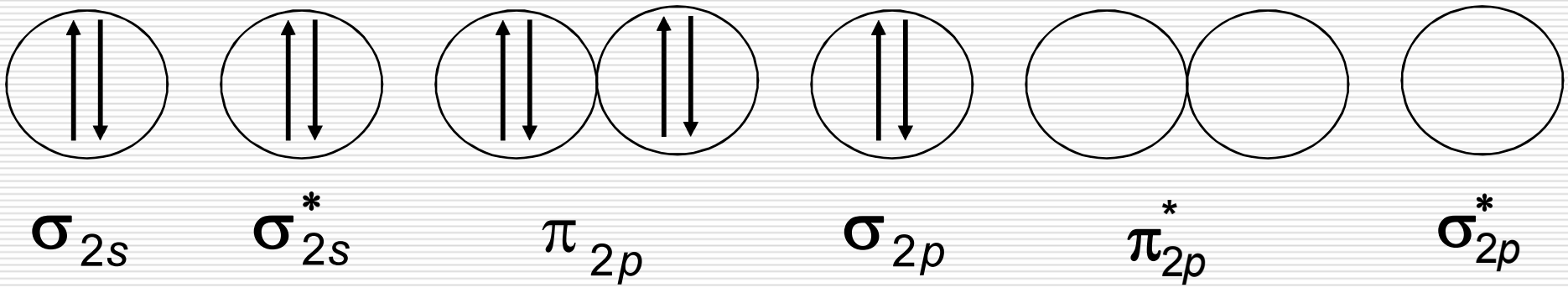
BOND ORDER AND MAGNETIC BEHAVIOR OF HOMONUCLEAR DIATOMIC MOLECULES, N_2, O_2, F_2



EXAMPLE, NO^+

- Give the molecular orbital diagram and the molecular electron configuration of the NO^+ nitrosonium ion.
- Is the molecular substance diamagnetic or paramagnetic?
- What is the order of the bond in NO^+?

NO^+ has 14 electrons. The KK shell holds 4 electrons, leaving 10 electrons for bonding.



The molecular electron configuration is

$$KK(\sigma_{2s})^2(\sigma^*_{2s})^2(\pi_{2p})^4(\sigma_{2p})^2$$

The bond order is ½(8 - 2) = 3.

The ion is diamagnetic.

THE END

http://mathcentral.uregina.ca/QQ/database/QQ.09.00/nishi1.html