

## Chemical Bonding

◆ There are basically two types of chemical bonds:

1. Covalent bonds—electrons are shared by more than one nucleus
2. Ionic bonds—electrostatic attraction between ions creates chemical bond

Hydrogen bonding and van der Waals' bonding are subsets of electrostatic bonding

## The Octet Rule

◆ Atoms want to have a filled valence shell—for the main group elements, this means having filled s and p orbitals. Hence the name “octet rule” because when the valence shell is filled, they have a total of eight valence electrons.

◆ We use “dot structures” to represent atoms and their electrons.

## Lewis Dot Structures

◆ Dots around the elemental symbol represent the valence electrons.

### Examples

Hydrogen ( $1s^1$ )      H·

Carbon ( $1s^2 2s^2 2p^2$ )      ·C·  
  ·

Chlorine ( $[\text{Ne}] 3s^2 3p^5$ )      :Cl·  
  ·

## Lewis Dot Structures

- ◆ None of the atoms in the previous example contained full valence shells.
- ◆ When creating bonds, atoms may share electrons in order to complete their valence shells.

## Lewis Dot Structures

### Examples

H<sub>2</sub> molecule:

H needs two e<sup>-</sup>'s to fill its valence shell.  
Each hydrogen atom shares its electron with the other in order to fill their valence shells.



## Lewis Dot Structures

### Examples

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

The result is a “covalent bond” in which two electrons are shared between nuclei and create a chemical bond in the process.

When two e<sup>-</sup>'s are shared, it makes a “single” bond.

## Lewis Dot Structures

### Examples

F<sub>2</sub> molecule:

F has seven valence e<sup>-</sup>'s, but wants eight e<sup>-</sup>'s to fill its valence shell.



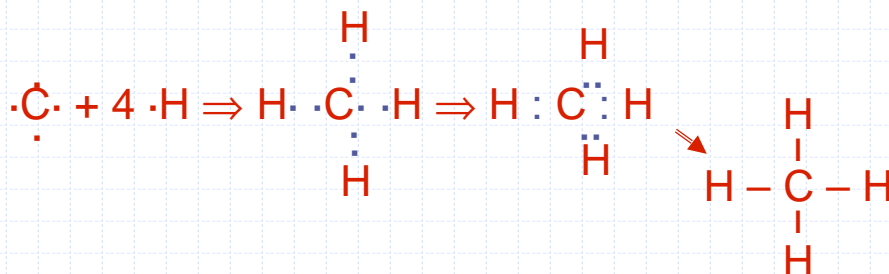
A line is often used to represent shared electrons.

## Lewis Dot Structures

### Examples

CH<sub>4</sub> molecule:

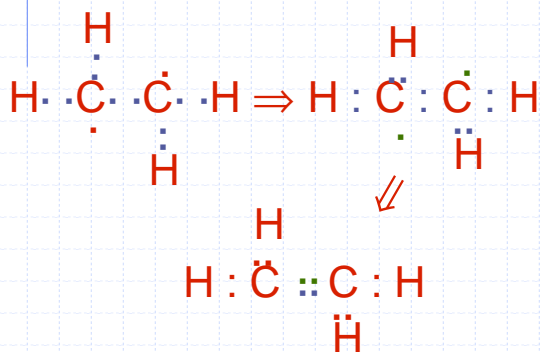
C has four valence e<sup>-</sup>'s; H has one valence e<sup>-</sup>.



## Lewis Dot Structures

### Examples

C<sub>2</sub>H<sub>4</sub> molecule:

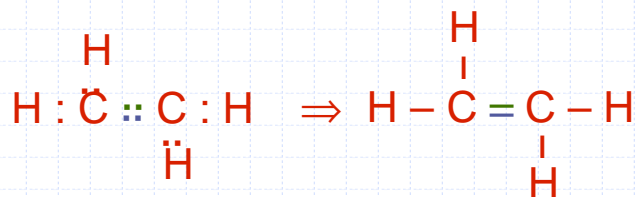


Is this complete—do all atoms have filled valence shells?

## Lewis Dot Structures

### Examples

C<sub>2</sub>H<sub>4</sub> molecule:

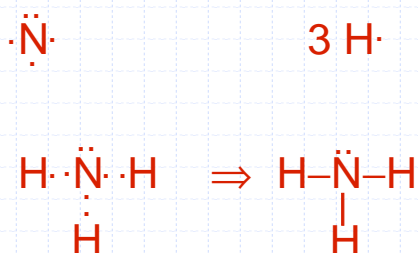


Sharing of four electrons between two nuclei results in a “double” bond.

## Lewis Dot Structures

### Examples

NH<sub>3</sub> molecule:

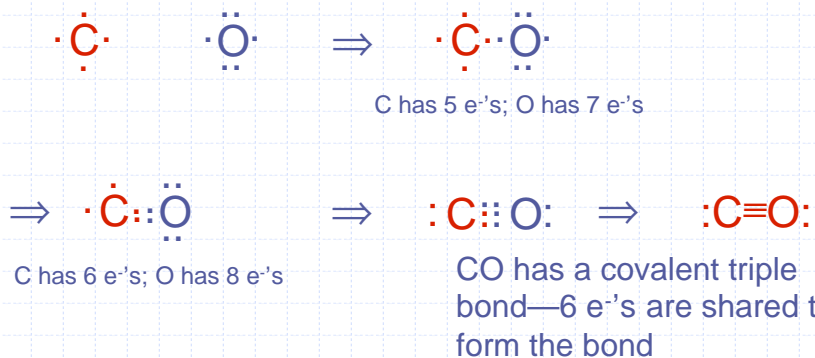


Not all electrons in a Lewis dot structure need to be part of a chemical bond—some electrons may be in the form of “lone pairs.”

## Lewis Dot Structures

### Examples

CO molecule:



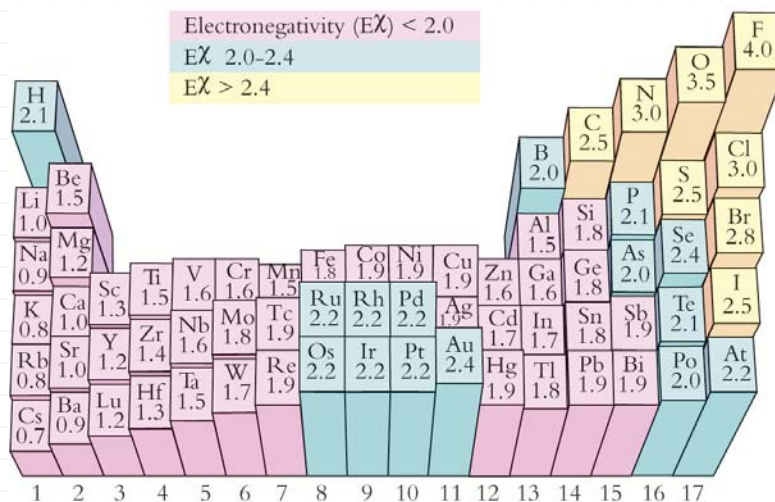
## Electronegativity and Bonding

- ◆ When nuclei share electrons to form a covalent chemical bond, the electrons are not necessarily shared equally—a shared electron may spend more time closer to one of the nuclei.
- ◆ The *electronegativity* of the nuclei determines how the electron is shared.
- ◆ Electronegativity is a measure of how strongly a “bound” electron participating in a chemical bond is attracted to a nucleus.

## Electronegativity and Bonding

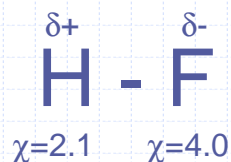
- ◆ Electronegativity is related to electron affinity and ionization energy.
- ◆ Electronegativity (denoted by the greek symbol  $\chi$ ) is highest for elements in the upper right hand side of the Periodic Table and increases from left to right and from bottom to top.

## Electronegativity and Bonding



## Polar Covalent Bonds

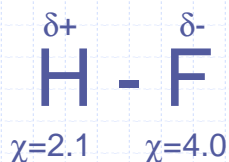
- ◆ When two elements with different electronegativities bond, the resulting covalent bond will be *polar*, *i.e.*, the shared electrons will spend more time closer to the nucleus with the higher  $\chi$ , so that end of the bond will be slightly more negative, and the other end will be slightly more positive.





## Polar Covalent Bonds

- ◆ The molecule has a polar bond meaning the electrical charge is not equally distributed between the nuclei involved in the chemical bond. The molecule also has a *dipole moment*—an uneven distribution of electrical charge.

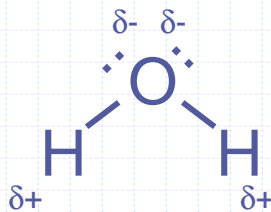


## Polar Covalent Bonds

### Other Examples

Water:  $\text{H}_2\text{O}$  is a bent molecule with two pairs of unshared e<sup>-</sup>s in p orbitals.

Is water a polar molecule?



$$\chi(\text{O}) = 3.5$$

$$\chi(\text{H}) = 2.1$$

## Polar Covalent Bonds

### Examples

Carbon monoxide: CO

Is CO a polar molecule?



$$\chi(\text{O}) = 3.5$$

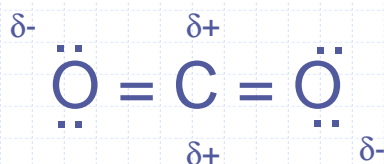
$$\chi(\text{C}) = 2.5$$

## Polar Covalent Bonds

### Examples

Carbon dioxide: CO<sub>2</sub> is a linear triatomic molecule.

Is CO<sub>2</sub> a polar molecule?



$$\chi(\text{O}) = 3.5$$

$$\chi(\text{C}) = 2.5$$

## Bond Lengths

- ◆ The bonding between atoms can have a significant effect on the bond distance between atoms.
- ◆ Multiple bonds between two atoms have shorter bond lengths compared to single bonds involving the same elements:

## Bond Lengths

### Examples

	average bond lengths			
single bond	C-C	154 pm	C-O	143 pm
double bond	C=C	133 pm	C=O	120 pm
triple bond	C≡C	120 pm	C≡O	113 pm

## Bond Energies

- ◆ The bond energy is the amount of energy it takes to pull two atoms apart and break the chemical bond.
- ◆ For some diatomic gas phase species, we know the bond energies exactly through measurement.

## Bond Energies

- ◆ For polyatomic molecules, we can calculate the average bond energy for a given type of bond by measuring bond energies in a wide variety of molecules containing that specific type of bond and averaging the results.
- ◆ Just as in bond lengths, the type of bonding has a dramatic effect on the bond energy in molecules.
- ◆ Multiple bonds are much harder to break than are single bonds.

## Bond Energies

Examples (see Table 8-2 for a more complete list)

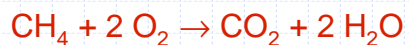
Average bond energy (kJ mol<sup>-1</sup>)

	<u>single bond</u>	<u>double bond</u>	<u>triple bond</u>
C-H	416		
C-C	356	598	813
C-O	336	750	1073
C-N	285	616	866
N-N	160	418	946
N-O	201	605	
C-S	272	575	

## Bond Energies

Example: Calculate the reaction enthalpy for the combustion of methane

Step 1—Write balanced chemical equation:



Step 2—Determine energy needed to break bonds:

$$4 \text{ C-H bonds: } 4 \times 416 \text{ kJ/mol} = 1664 \text{ kJ/mol}$$

$$2 \text{ O=O bonds: } 2 \times 498 \text{ kJ/mol} = \underline{996 \text{ kJ/mol}}$$

$$\text{total energy to break bonds} = 2660 \text{ kJ/mol}$$

## Bond Energies

Example: Calculate the reaction enthalpy for the combustion of methane

Step 3—Determine energy released in forming new bonds:

$$2 \text{ C=O bonds: } 2 \times -750 \text{ kJ/mol} = -1500 \text{ kJ/mol}$$

$$4 \text{ O-H bonds: } 4 \times -467 \text{ kJ/mol} = -1868 \text{ kJ/mol}$$

$$\text{total energy to form bonds} = -3368 \text{ kJ/mol}$$

Step 4—Determine enthalpy of reaction:

$$\begin{aligned} \Delta H_{\text{rxn}} &= E_{\text{break bonds}} + E_{\text{form bonds}} \\ &= 2660 \text{ kJ/mol} - 3368 \text{ kJ/mol} = -708 \text{ kJ/mol} \end{aligned}$$

$$\Delta H_{\text{rxn}} = -802 \text{ kJ/mol (literature value)}$$

## Reaction Energies

Example: combustion of acetylene



∞ Which bonds are broken?

$$4 \times \text{C-H} \quad 4 (415 \text{ kJ mol}^{-1}) = 1660 \text{ kJ mol}^{-1}$$

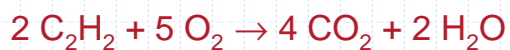
$$2 \times \text{C}\equiv\text{C} \quad 2 (835 \text{ kJ mol}^{-1}) = 1670 \text{ kJ mol}^{-1}$$

$$5 \times \text{O}=\text{O} \quad 5 (495 \text{ kJ mol}^{-1}) = 2475 \text{ kJ mol}^{-1}$$

$$\text{total energy needed} = 5805 \text{ kJ mol}^{-1}$$

## Reaction Energies

Example: combustion of acetylene



∞ Which bonds are formed?

$$8 \times \text{C}=\text{O} \quad 8 (800 \text{ kJ mol}^{-1}) = 6400 \text{ kJ mol}^{-1}$$

$$4 \times \text{O}-\text{H} \quad 4 (460 \text{ kJ mol}^{-1}) = 1840 \text{ kJ mol}^{-1}$$

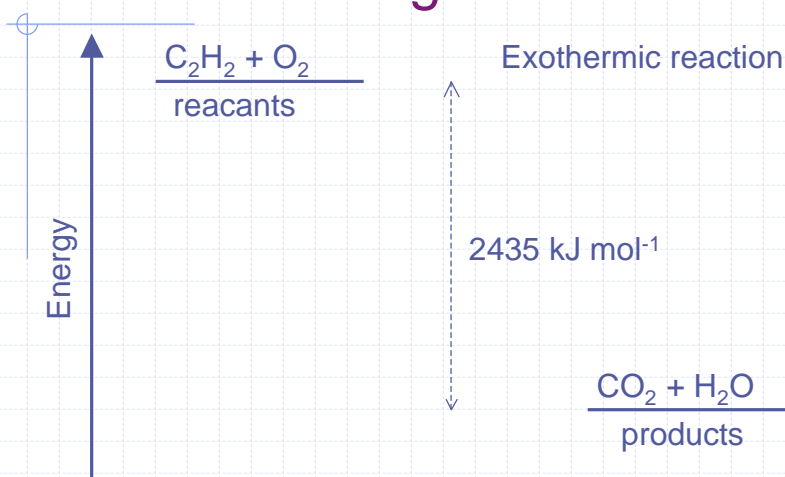
$$\text{total energy released} \quad = 8240 \text{ kJ mol}^{-1}$$

$$\Delta E_{\text{rxn}} = \Sigma \text{BE}_{\text{react}} - \Sigma \text{BE}_{\text{prod}}$$

$$= 5805 \text{ kJ mol}^{-1} - 8240 \text{ kJ mol}^{-1}$$

$$= -2435 \text{ kJ mol}^{-1} \text{ (-2512 kJ mol}^{-1} \text{ actual)}$$

## Reaction Energies



## Reaction Energies

Example:



∞ Which bonds are broken?

$$12 \times \text{O-H} \quad 12 (460 \text{ kJ mol}^{-1}) = 5520 \text{ kJ mol}^{-1}$$

$$2 \times \text{N}\equiv\text{N} \quad 2 (945 \text{ kJ mol}^{-1}) = 1890 \text{ kJ mol}^{-1}$$

$$\text{total energy needed} \quad = 7410 \text{ kJ mol}^{-1}$$

## Reaction Energies

Example:



∞ Which bonds are formed?

$$12 \times \text{N-H} \quad 12 (390 \text{ kJ mol}^{-1}) = 4680 \text{ kJ mol}^{-1}$$

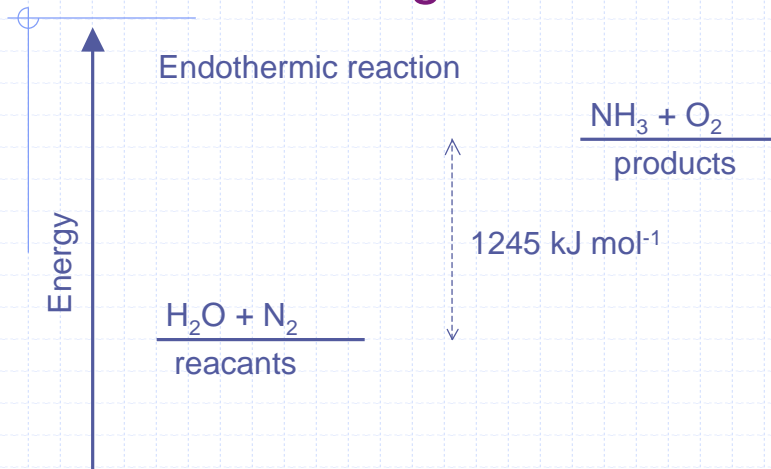
$$3 \times \text{O}=\text{O} \quad 3 (495 \text{ kJ mol}^{-1}) = 1485 \text{ kJ mol}^{-1}$$

$$\text{total energy released} \quad = 6165 \text{ kJ mol}^{-1}$$

$$\begin{aligned} \Delta E_{\text{rxn}} &= \Sigma \text{BE}_{\text{react}} - \Sigma \text{BE}_{\text{prod}} \\ &= 7410 \text{ kJ mol}^{-1} - 6165 \text{ kJ mol}^{-1} \\ &= 1245 \text{ kJ mol}^{-1} \text{ (1267 kJ mol}^{-1} \text{ actual)} \end{aligned}$$



## Reaction Energies



## Formal Charge of Atoms

The **formal charge** of an atom in a molecule is the charge the atom would have if all electrons were shared equally.

Rules:

1. All lone pair electrons are assigned to the atom to which they are associated.
2. Half of the bonding electrons are assigned to each atom comprising that bond.

The sum of these electrons is subtracted from the number of valence electrons to determine the formal charge

## Formal Charge of Atoms

Rules (con't.):

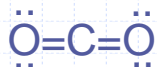
- The sum of formal charges for each atom in the molecule must equal the actual charge of the molecule: 0 for a neutral molecule; ionic charge for an ion.

Example: carbon monoxide

$:\text{C} \equiv \text{O}:$		<u>C</u>	<u>O</u>
Valence electrons	4	6	
Lone pair electrons	2	2	
$\frac{1}{2}$ shared electrons	3	3	
Formal charge	-1	+1	

## Formal Charge of Atoms

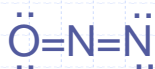
Example: carbon dioxide



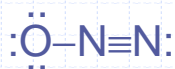
	<u>C</u>	<u>O</u>	<u>O</u>
Valence electrons	4	6	6
Lone pair electrons	0	4	4
$\frac{1}{2}$ shared electrons	4	2	2
Formal charge	0	0	0

## Formal Charge of Atoms

Example: Nitrous oxide, N<sub>2</sub>O



0 +1 -1  
structure #1



-1 +1 0  
structure #2

The formal charge can help predict which structure is preferred when multiple Lewis structure can be made:

- ∞ Smaller formal charges are preferred
- ∞ Negative formal charge should reside on more electronegative atoms
- ∞ Like charge should not be on adjacent atoms

## Molecular Orbitals

When atomic orbitals overlap to create a covalent bond, the result is the formation of *molecular orbitals*.

Molecular orbitals define the region of space most likely to contain bonding electrons—MO's are drawn as 90% electron density contours just as AO's are drawn 90% electron density contours in atoms.

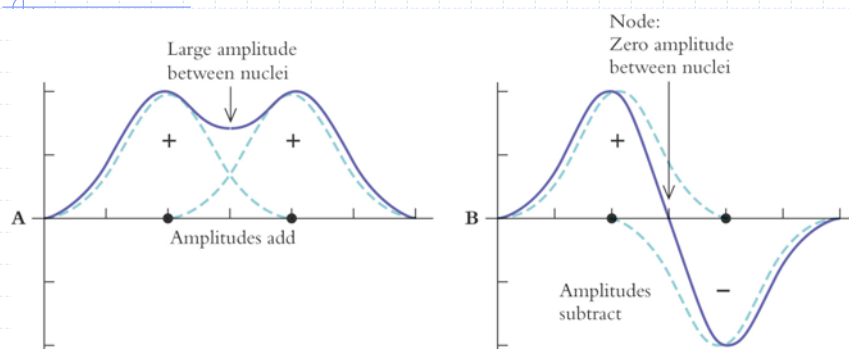
## Molecular Orbitals

Because electrons can be described as waves, when the AO's overlap, the waves may either constructively interfere or destructively interfere.

Constructive interference between the AO's results in a bonding MO—destructive interference between AO's results in an anti-bonding MO with a node along the internuclear axis.

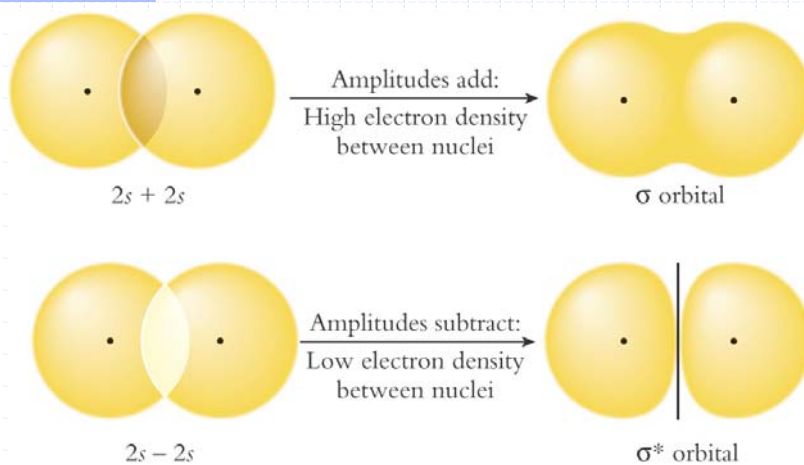
Anti-bonding orbitals are higher in energy than bonding orbitals.

## Molecular Orbitals

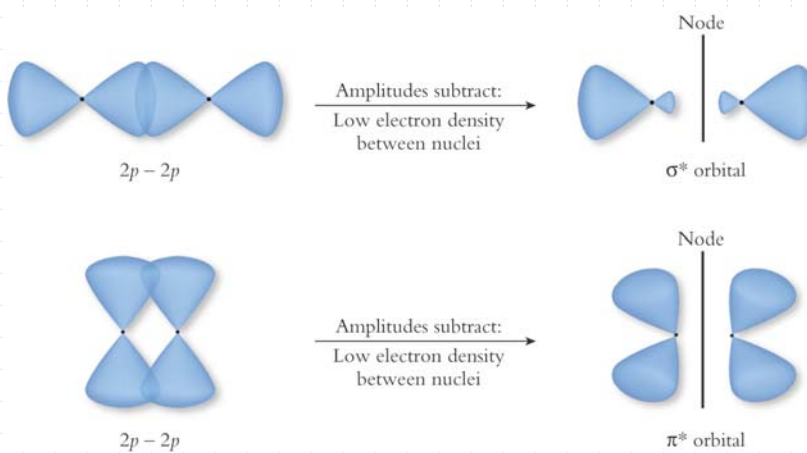


Overlap of s-type atomic orbitals to form either bonding or anti-bonding molecular orbitals. Anti-bonding orbitals are designated with an asterisk (\*).

## Molecular Orbitals

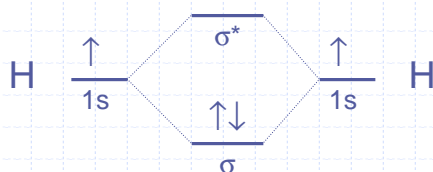


## Molecular Orbitals



## Molecular Orbitals

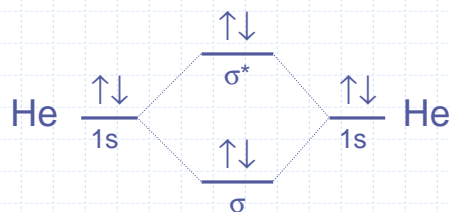
A molecular orbital diagram can be constructed from the atomic orbitals of the bonding elements.



The 1s e<sup>-</sup>'s of each H atom go into the lower energy  $\sigma$  MO resulting in the formation of a single  $\sigma$  bond.

Configuration:  $(\sigma)^2$

## Molecular Orbitals



The 1s e<sup>-</sup>'s of each He atom fill both the  $\sigma$  MO and the  $\sigma^*$  MO. The bonding effect of the  $\sigma$  MO is offset by the anti-bonding effect of the  $\sigma^*$  MO—no net bonding is observed.

Configuration:  $(\sigma)^2(\sigma^*)^2$

## Molecular Orbitals

Bond order is defined in the following way:

$$\text{bond order} \equiv \frac{1}{2} (\# \text{ e}^- \text{ s in bonding MO's}) - \frac{1}{2} (\# \text{ e}^- \text{ s in anti-bonding MO's})$$

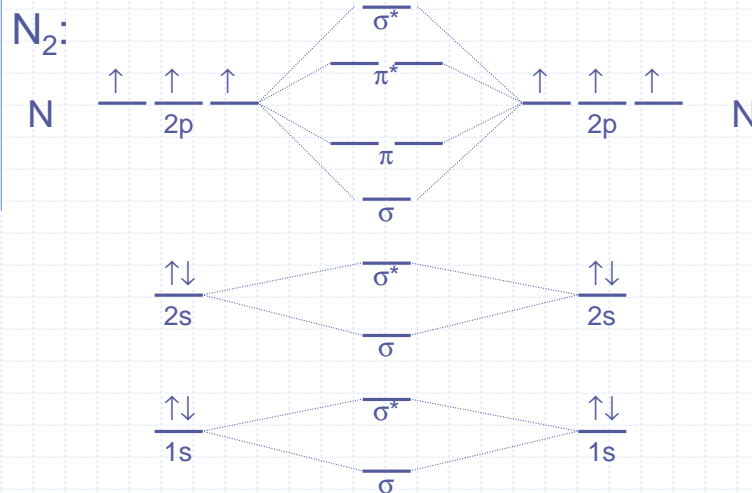
$$\text{H}_2: \text{ bond order} = \frac{1}{2} (2) - \frac{1}{2} (0) = 1$$

H<sub>2</sub> has a single bond

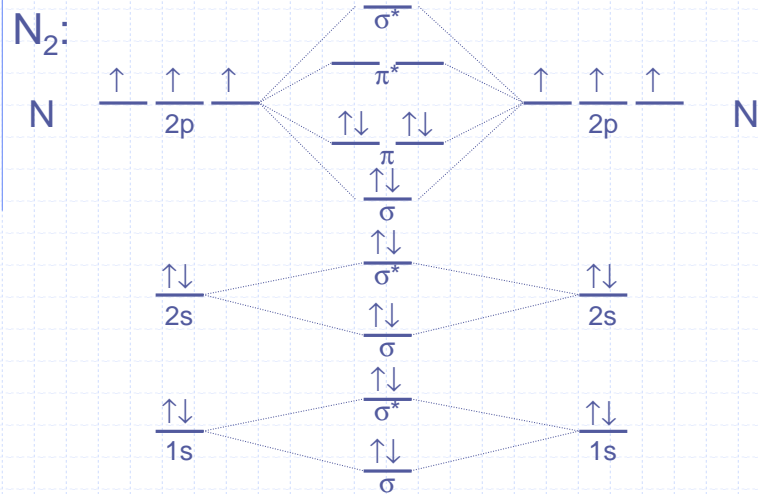
$$\text{He}_2: \text{ bond order} = \frac{1}{2} (2) - \frac{1}{2} (2) = 0$$

He<sub>2</sub> has no bond  $\Rightarrow$  compound does not form

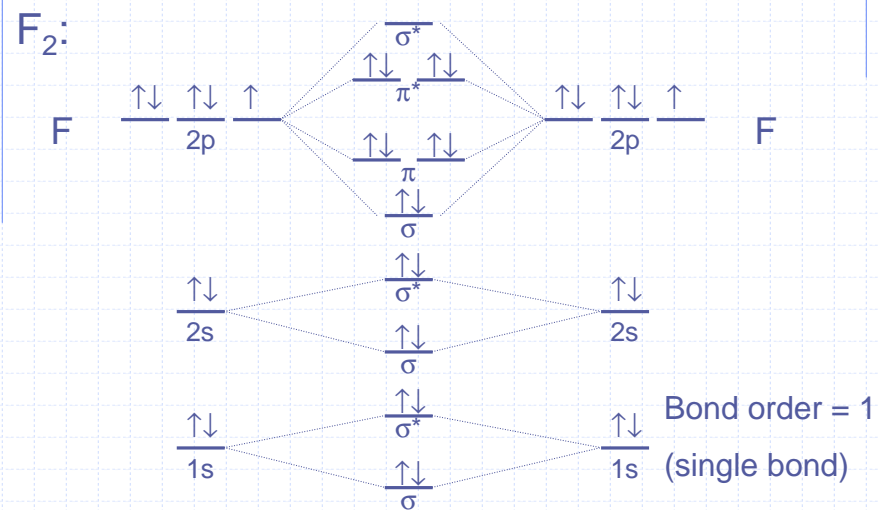
## Molecular Orbitals



## Molecular Orbitals



## Molecular Orbitals





## Problems with Valence Bond Theory and Lewis Dot Structures

Valence Bond Theory (including Lewis structures and hybrid orbital theories) does an excellent job at explaining the bonding in many chemical systems.

It fails miserably in describing delocalized bonding systems and some very simple molecules like  $O_2$ .

## Problems with Valence Bond Theory and Lewis Dot Structures

Molecular oxygen,  $O_2$

Properties

$O_2$  has a double bond

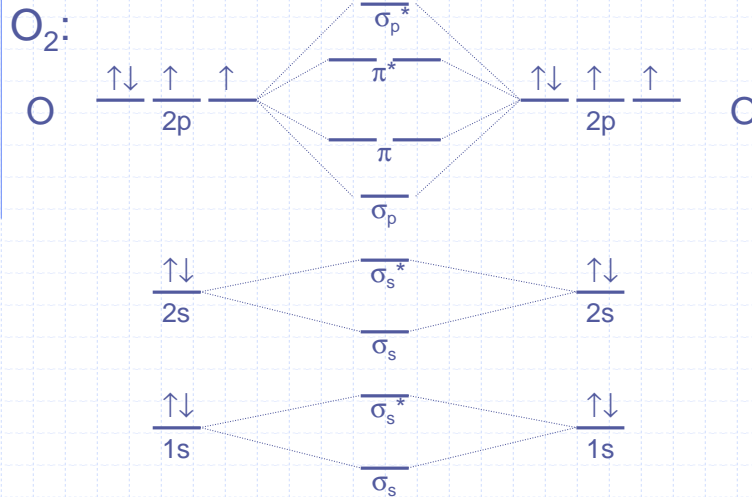
$O_2$  is paramagnetic (has two unpaired electrons)

Predicted Lewis structure:

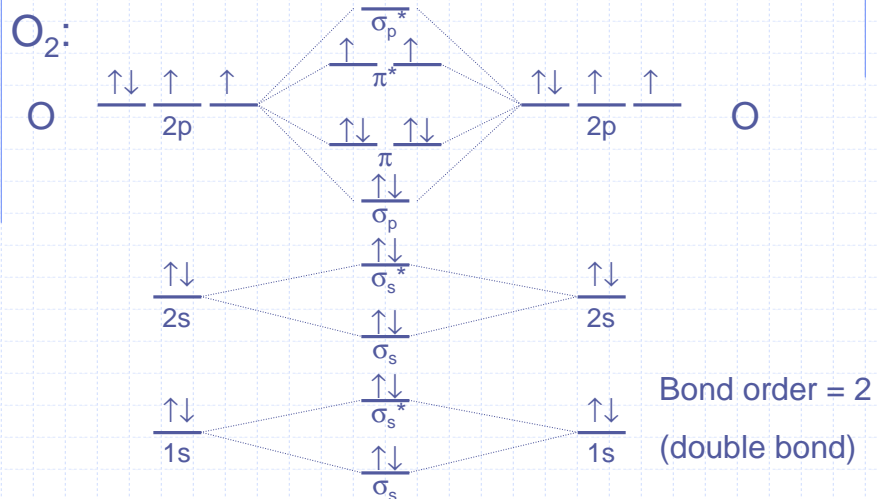


The Lewis structure correctly predicts a double bond, but there are no unpaired electrons.

# Molecular Orbitals

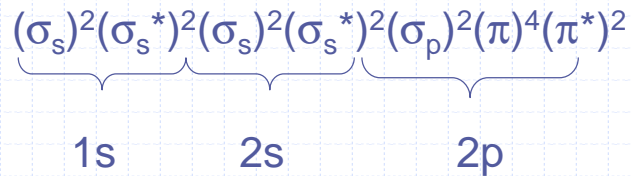


# Molecular Orbitals



## MO Description of Molecular Oxygen

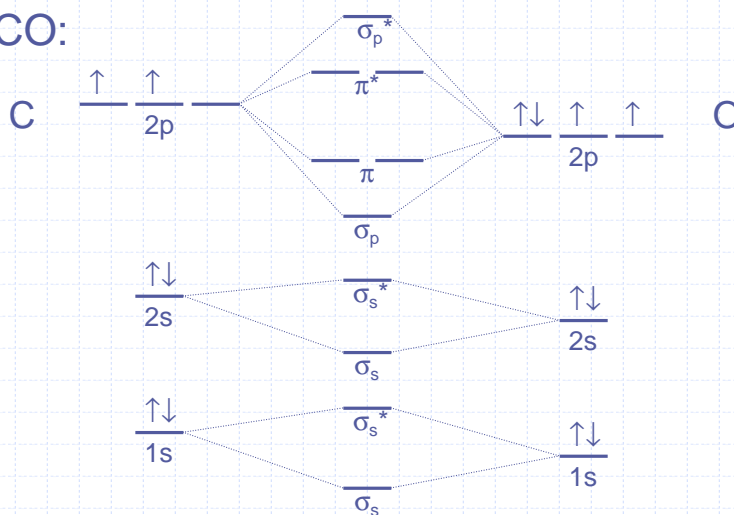
Electron configuration of  $O_2$  is:



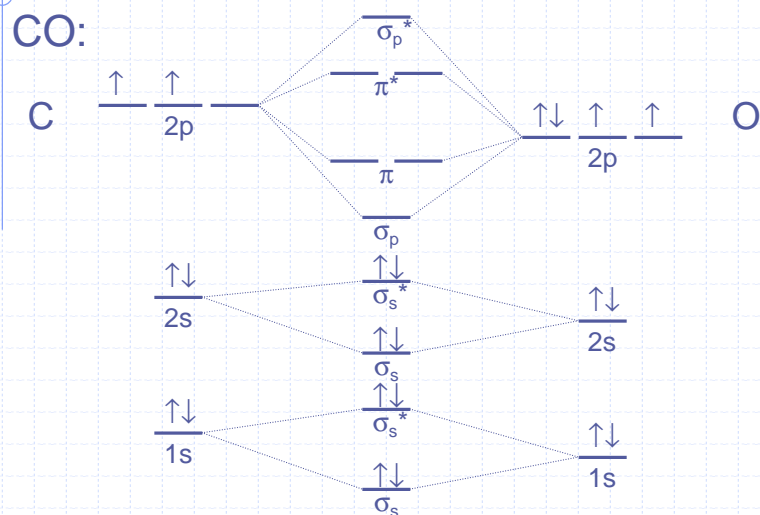
MO theory correctly predicts that  $O_2$  has a double bond (bond order = 2) and that  $O_2$  is paramagnetic.

## Molecular Orbital Diagram for Heteronuclear Diatomic Molecule

CO:



## Molecular Orbital Diagram for Heteronuclear Diatomic Molecule



## Molecular Orbital Diagram for Heteronuclear Diatomic Molecule

