Chemical Bonding

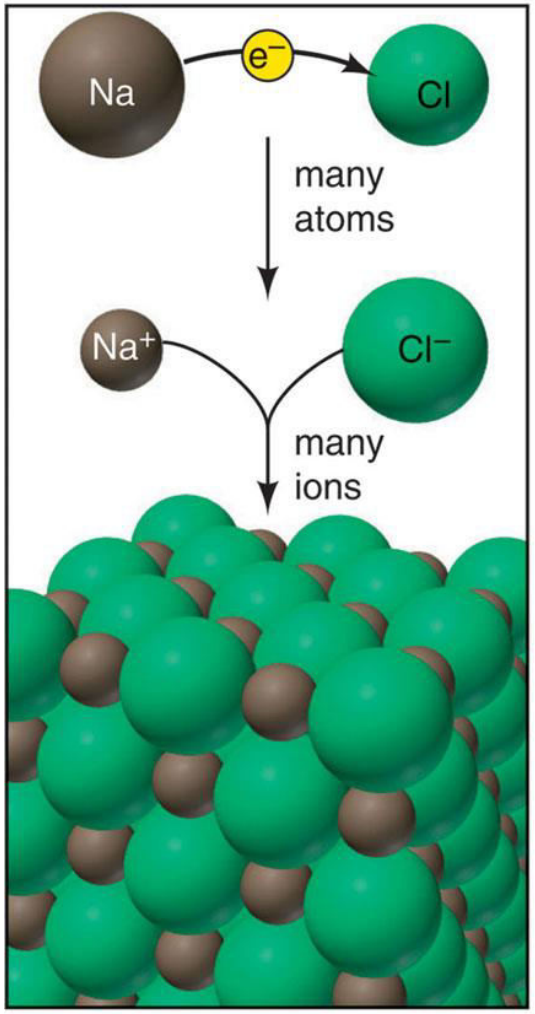
- Chemical bonds are strong electrostatic forces holding atoms or ions together, which are formed by the rearrangement (**transfer** or **sharing**) of outermost electrons

- Atoms tend to form chemical bonds in such a way as to achieve the electronic configurations of the nearest noble gases (**The Octet Rule**)

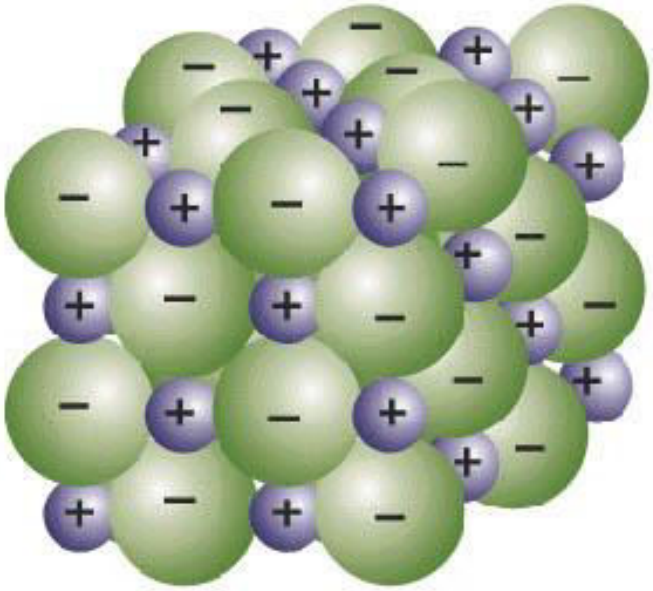
Types of Bonds

- Ionic
- Metallic
- Covalent

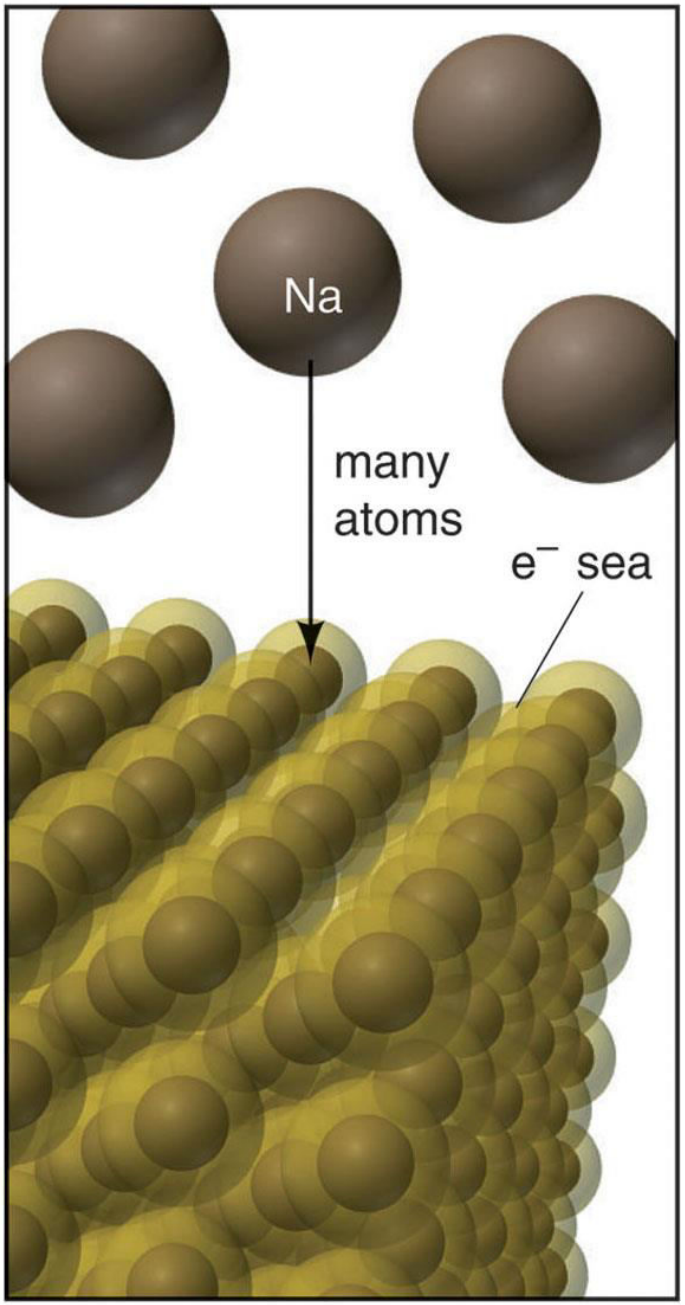
1. Ionic bond



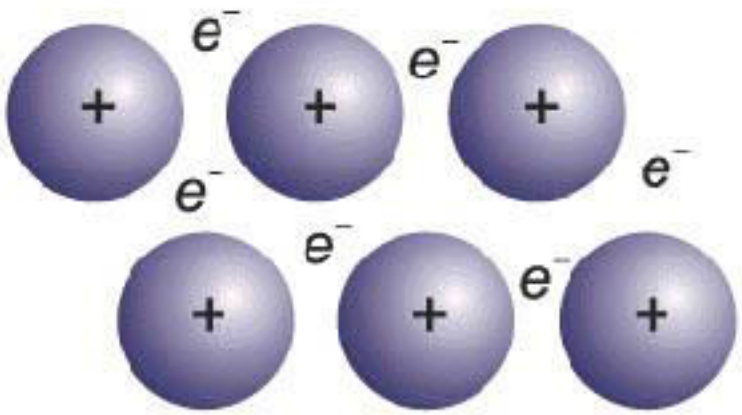
Electrostatic attraction between **positively** charged particles and **negatively** charged particles



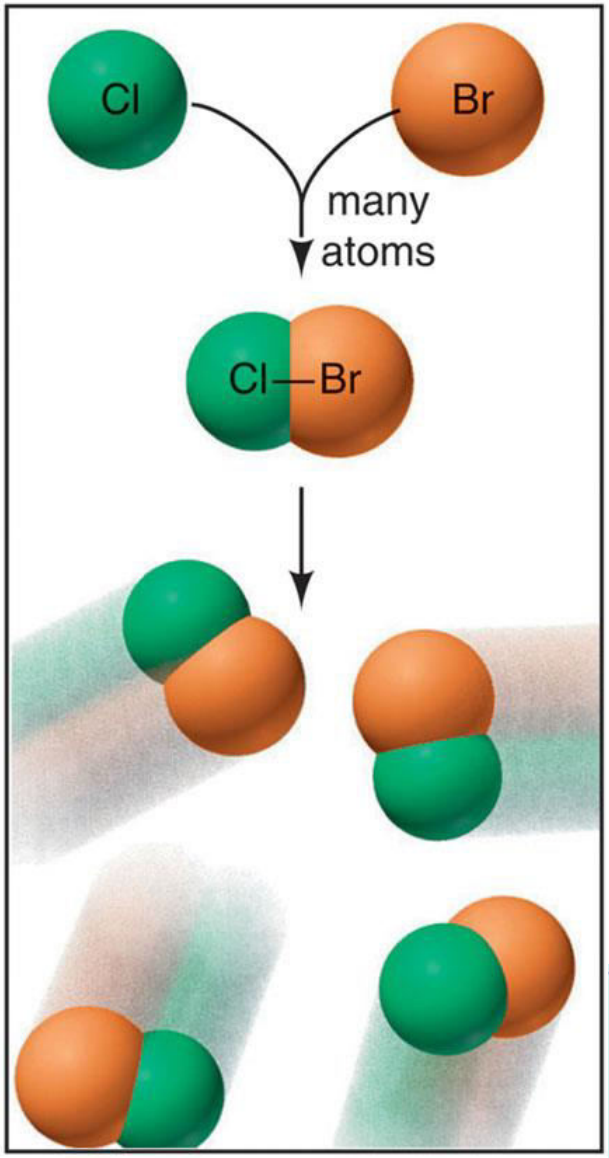
2. Metallic bond



- Formed by sharing of a large number of delocalized electrons
- Electrostatic attraction between **metallic cations** and **delocalized electrons** (electrons that have no fixed positions)

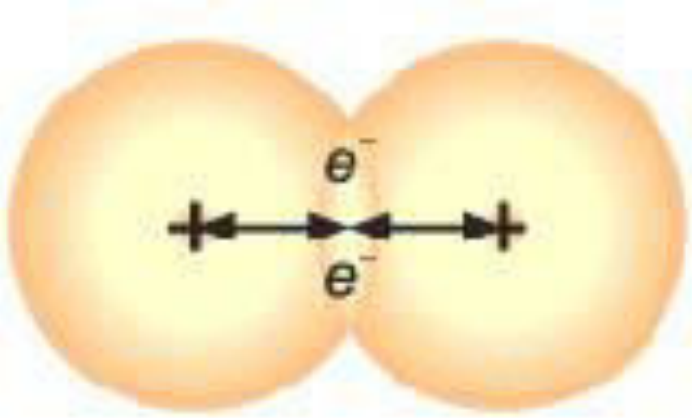


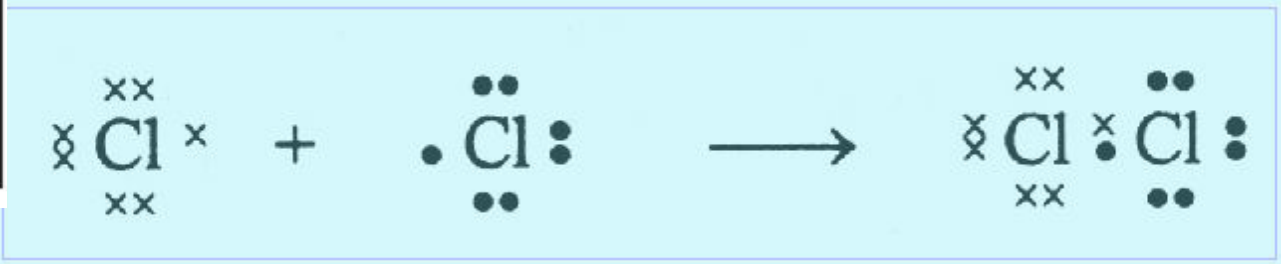
3. Covalent bond



Formed by sharing of electrons

Electrostatic attraction between nuclei and shared electrons

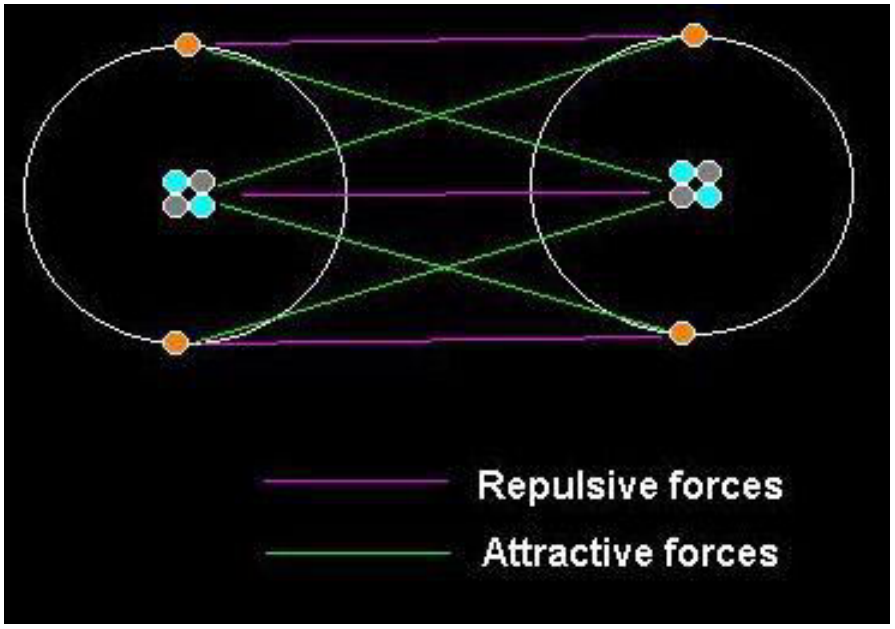




Bonds: Forces that <u>hold groups of atoms</u> together and make them function as a unit.

Bonding Forces:

- Electron – electron repulsive forces
- Nucleus – nucleus repulsive forces
- Electron – nucleus attractive forces



Electronegativity and Types of Chemical Bonds

Whether chemical bonding is Ionic or covalent depends on the electron-attracting ability of bonding atoms.

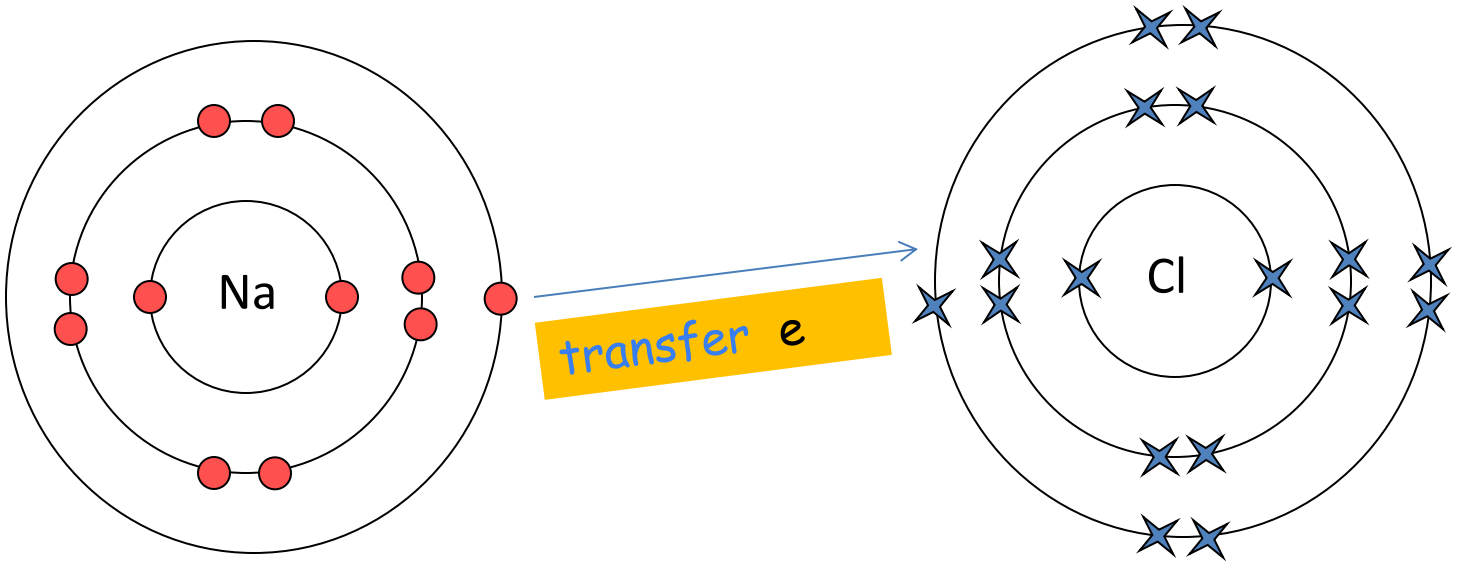
Ionic bonds are formed between atoms with great difference in their electron-attracting abilities

Covalent bonds are formed between atoms with small or no difference in their electron-attracting abilities.

Ion	s,p,d,f notation	Isoelectronic noble gas
Be^{2+}	Electronic Configuration	He
O^{2-}	[He] $2s^2,2p^6$ (2,8)	Ne
Sc^{3+}	[Ne] $3s^2,3p^6$ (2,8,8)	Ar
Br^-	[Ar] $3d^{10},4s^2,4p^6$ (2,8,18,8)	Kr
Ba^{2+}	[Kr] $4d^{10},5s^2,5p^6$ (2,8,18,18,8)	Xe
At^-	[Xe] $4f^{14},5d^{10},6s^2,6p^6$ (2,8,18,32,18,8)	Rn

Ionic bond (electrovalent bond)

- **Bonds that are formed by transfer of electrons from one element to the other.**
- **Each element (now an ion) will have a complete octet after the transfer of electrons.**

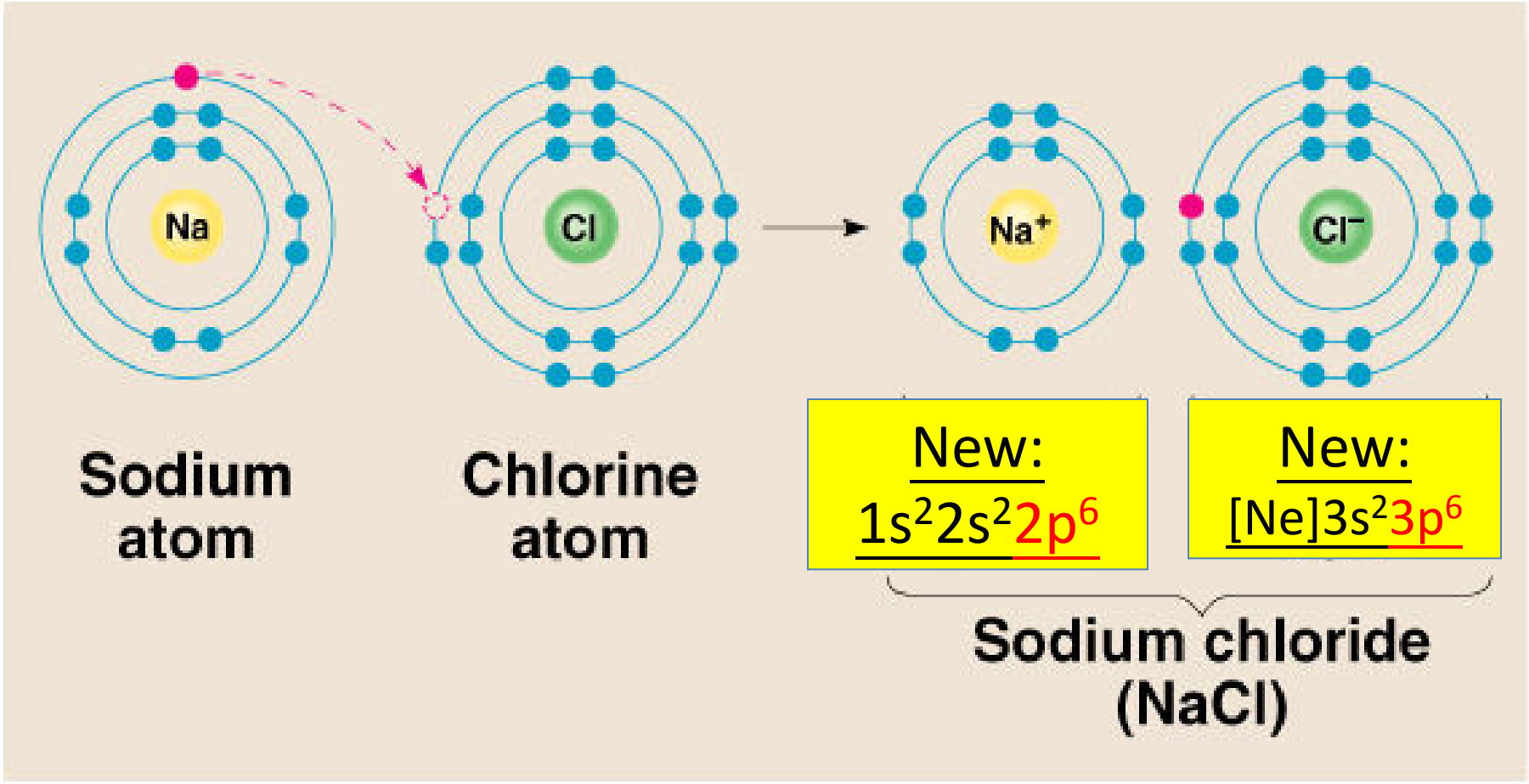


Sodium atom, **Na**

$1s^2 2s^2 2p^6 3s^1$

Chlorine atom, **Cl**

$1s^2 2s^2 2p^6 3s^2 3p^5$



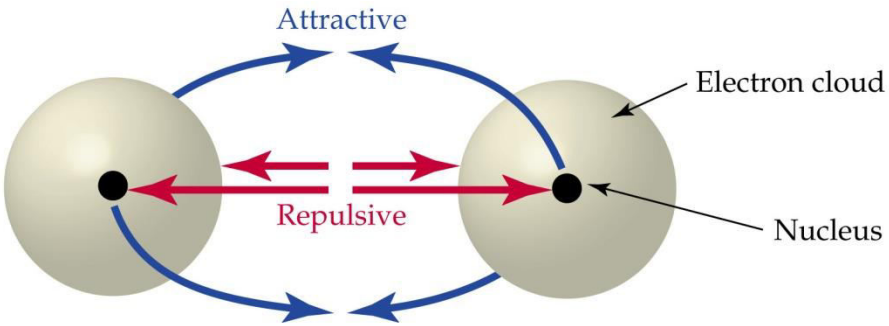
Ionic bond – electron from Na is transferred to Cl, this causes a charge imbalance in each atom. The **Na** becomes (**Na^+**) and the **Cl** becomes (**Cl^-**), charged particles or ions.

- Ionic Bonds with incomplete transfer of electrons have covalent character.
- Covalent Bonds with unequal sharing of electrons have ionic character.
- Ionic bonds and Covalent bonds are only extreme cases of a continuum
- In real situation, most chemical bonds are intermediate between ionic and covalent.

Covalent bond:

A covalent **H-H** bond is the net result of **attractive** and **repulsive** electrostatic forces. When bringing together two atoms that are initially very far apart.

Three types of interaction occur:



The nucleus - electron attractions (**blue arrows**) are greater than the nucleus-nucleus and electron-electron repulsions (**red arrows**), resulting in a **net attractive force** that holds the atoms together to form an H_2 molecule.

Theories that Explain Chemical Bonding

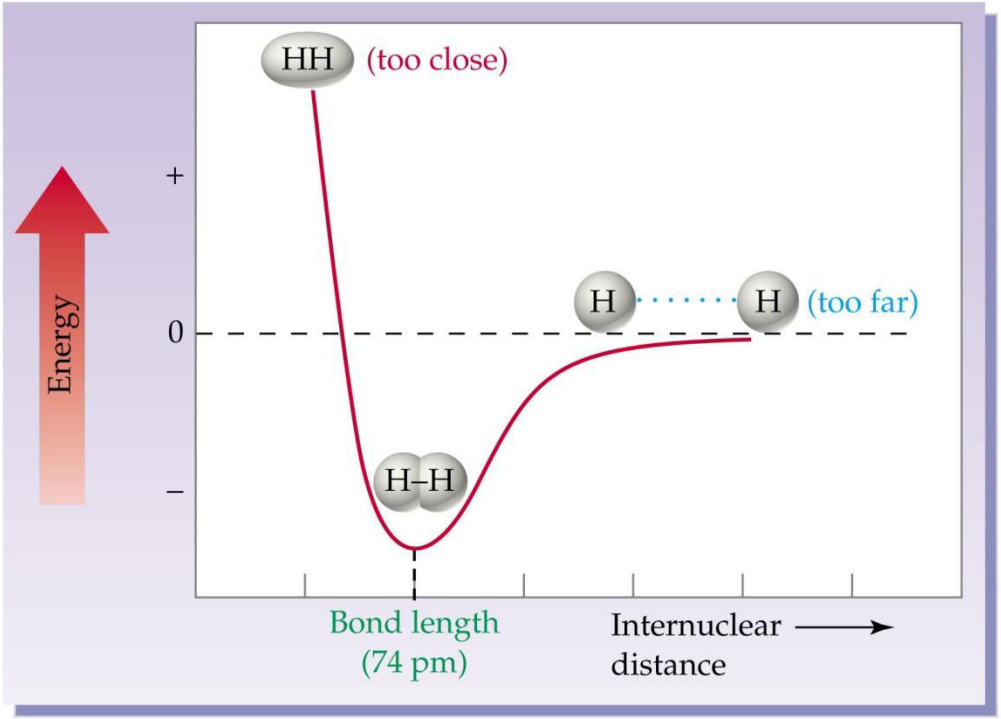
- Valence bonding theory
- Lewis Bonding theory
- Molecular Orbital theory

1. Valence-Bonding Theory

- If the atoms are **too far apart**, attractions are weak and **no bonding** occurs. A zero of energy when two H atoms are separated by great distances.
- A drop in potential energy (net attraction) as the two atoms approach each other.

- When the atoms are **optimally separated**, the energy is at a minimum. A minimum in potential energy at particular internuclear distance (74pm) corresponding to the **stable H_2** molecule.

- If the atoms are **too close**, strong **repulsions** occur. A increase in potential energy as the atoms approach more closely.



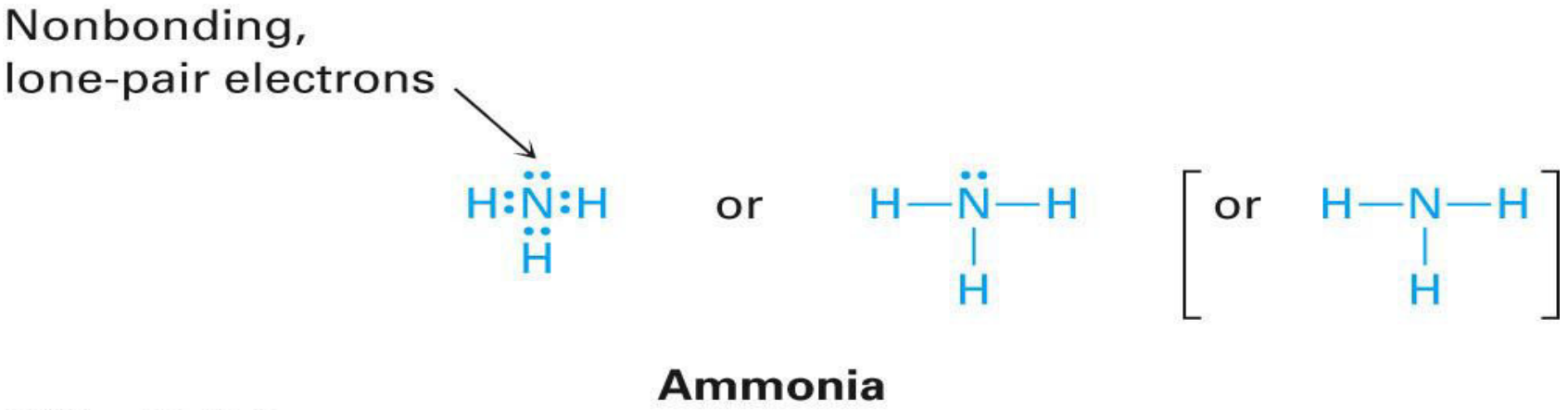
BOND LENGTH:
Distance between nuclei that leads to maximum stability

Non-bonding electrons

- Valence electrons not used in bonding are called **nonbonding electrons**, or **lone-pair electrons.**

  Nitrogen atom in ammonia (NH_3)

- Shares **six** valence electrons in **three** covalent bonds and **remaining two** valence electrons are nonbonding lone pair



Ammonia

Molecular Geometry

- Molecules are **three-dimensional** objects.
- the shape of a molecule often are described in relation to geometric figures.
- These geometric figures have characteristic "**corners**" that indicate the positions of the surrounding atoms with the central atom in the **center** of the figure.
- The geometric figures also have characteristic **angles** that we call **bond angles**.

Valence Shell Electron Pair Repulsion (VSEPR Model)

- It is used to **predict** the geometries of molecules formed.
- **Since electrons do not like each other, because of their negative charges, they orient themselves as far apart as possible, from each other.**
- **Postulate**: the structure around a given atom is determined principally by **minimizing** electron pair repulsion.
- The bonding and nonbonding pairs should be positioned **as far apart** as possible, **leading to molecules having specific shapes.**

Electron Pairs

Linear

Trigonal planar

Tetrahedral

Trigonal bipyramidal

Octahedral

Practice drawing these shapes below

Linear

TP

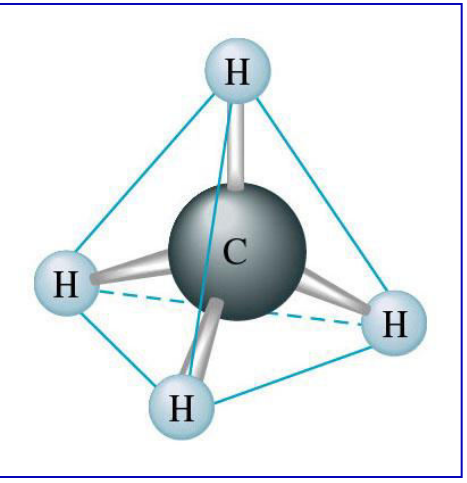
Tetrahedral

TBP

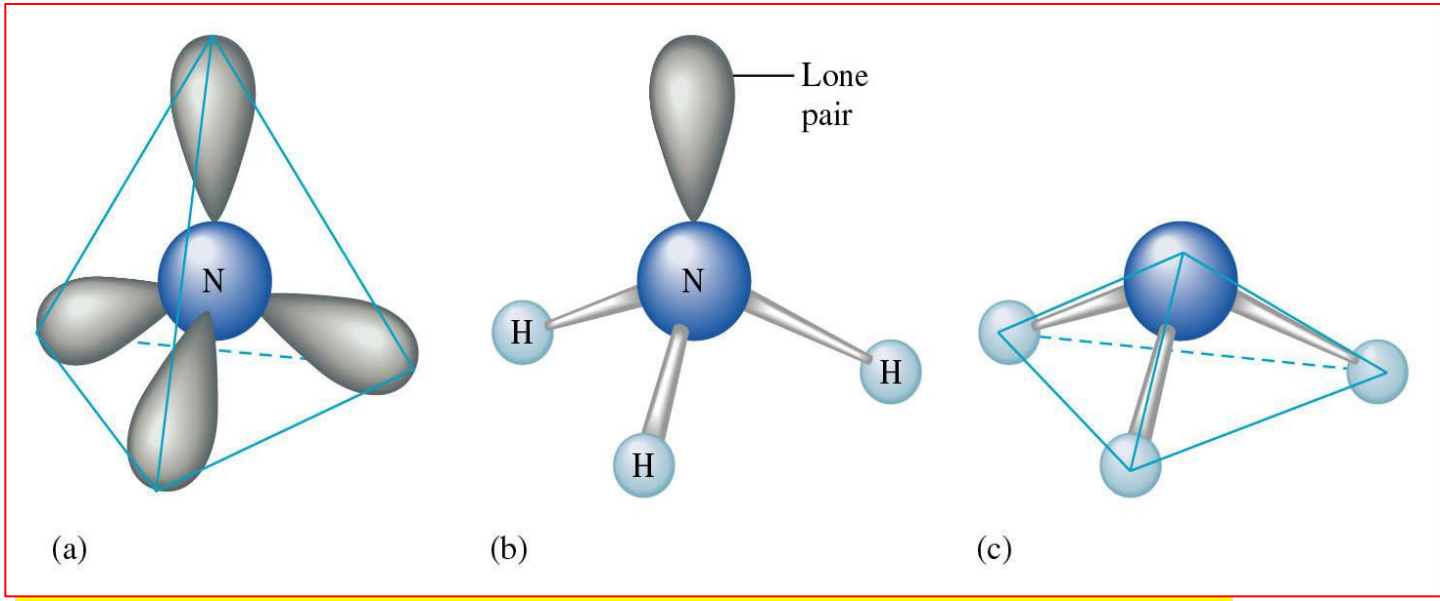
Octa

How to Predict a VSEPR Structure/Geometry

- Draw **Lewis structure**.
- Put pairs **as far apart** as possible.
- Determine **positions of atoms** from the way electron pairs are shared.
- Determine the name of molecular structure **from positions of the atoms** (NB: atoms, **NOT** the e^-)

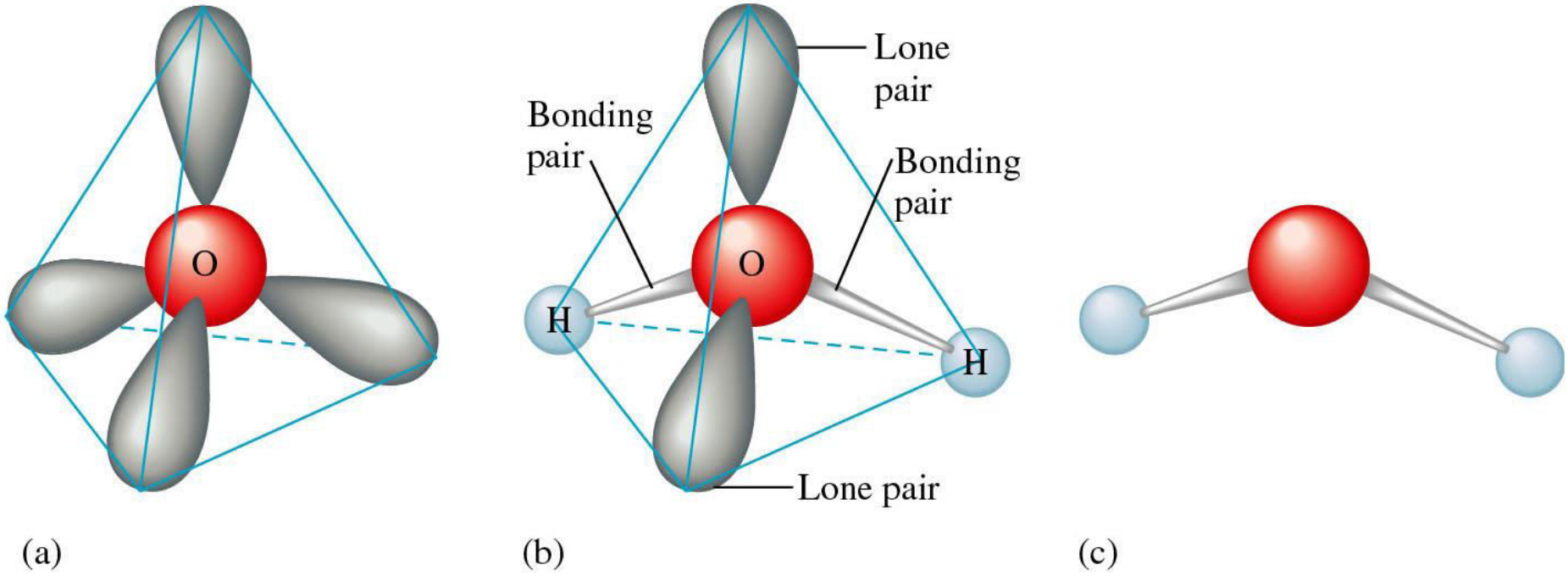


CH_4 -Td



NH_3 - Square Pyramid

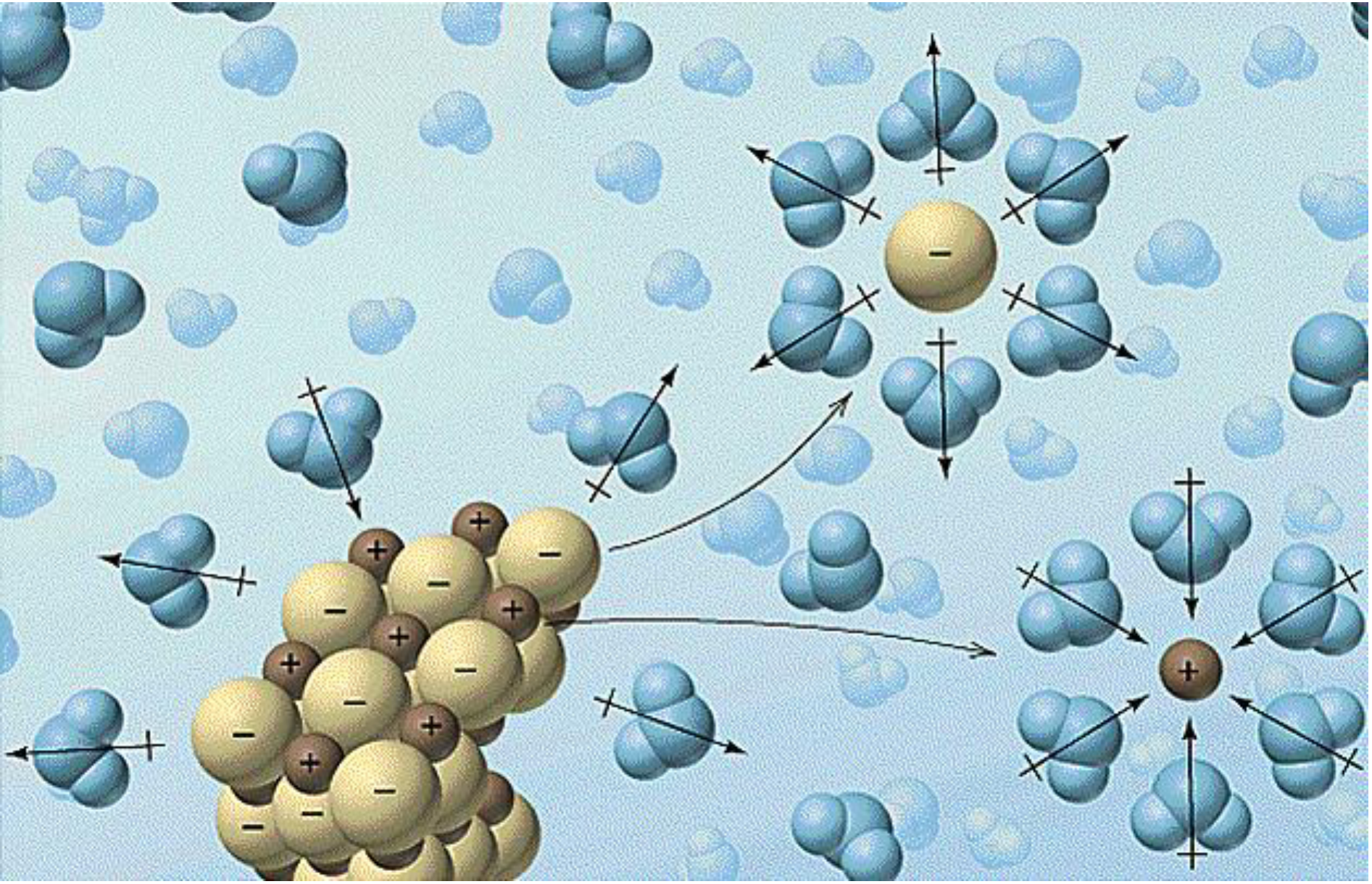
Geometry of H_2O - bent

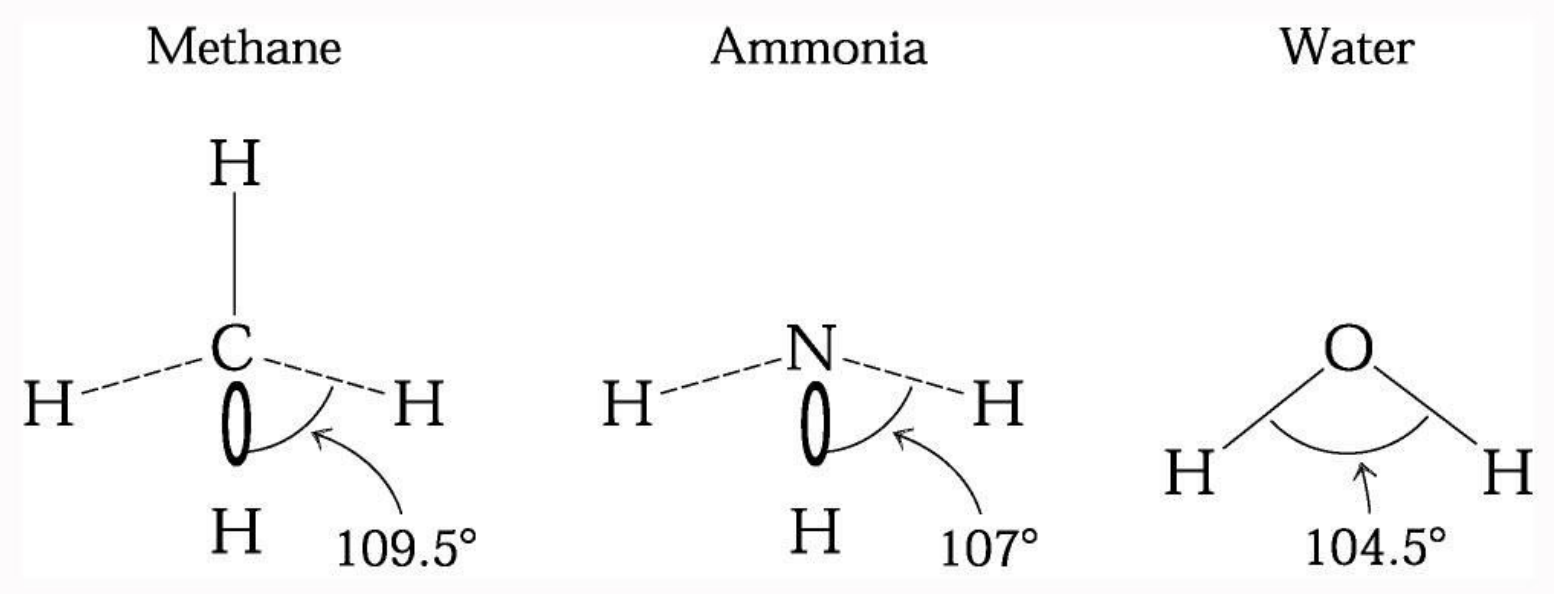


4 e^- pairs around central atom

Repulsion: Td

Atoms only: bent





- **Bonded electrons take up less space then un-bonded/unshared pairs of electrons.**
- The bonding pairs are increasingly **squeezed** together as the number of lone pairs increases.
- Repulsion strength:

Lp ⟷ Lp > Lp ⟷ Bp > Bp ⟷ Bp

Linear

EXAMPLE:

BeF_2

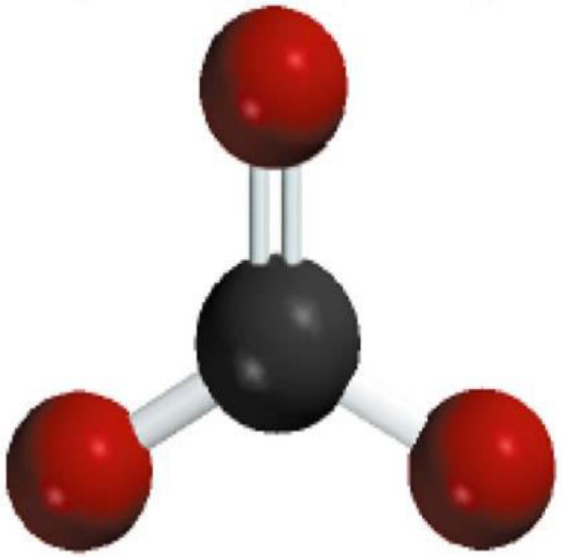
H — Be — H

- **Number of Bonds = 2**
- **Number of Shared Pairs of Electrons = 2**
- **Bond Angle = 180°**

Trigonal Planar

EXAMPLE:

BF_3

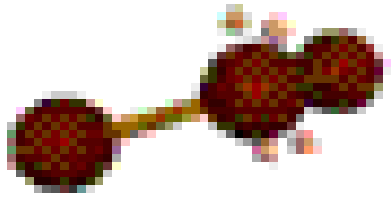


- **Number of Bonds = 3**
- **Number of Shared Pairs of Electrons = 3**
- **Number of Unshared Pairs of Electrons = 0**
- **Bond Angle = 120°**

Bent

EXAMPLE:

H_2O

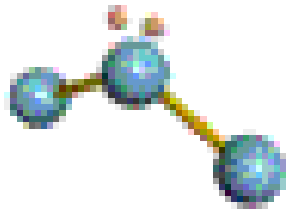


- Number of Shared Pairs of Electrons = 2 (bonds)
- Number of Unshared Pairs of Electrons = 2(lone pairs)
- Total # of e pairs = 4 (Td repulsion, but what is the geometry of the molecule?)
- Bond angle = < 109.5° (= 104.5°)

Bent

EXAMPLE:

O_3

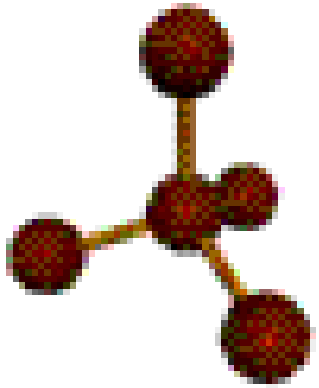


- **Number of Bonds = 2**
- **Number of Shared Pairs of Electrons = 2**
- **Number of Unshared Pairs of Electrons = 1**
- **Bond Angle = < 120°**

Tetrahedral

EXAMPLE:

CH_4

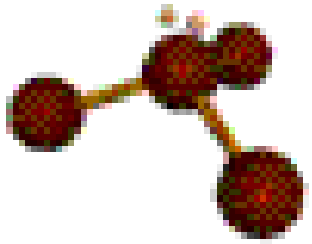


- Number of Bonds = 4
- Number of Shared Pairs of Electrons = 4
- Number of Unshared Pairs of Electrons = 0
- Bond Angle = 109.5° (perfect Td)

Trigonal Pyramidal

EXAMPLE:

NH_3

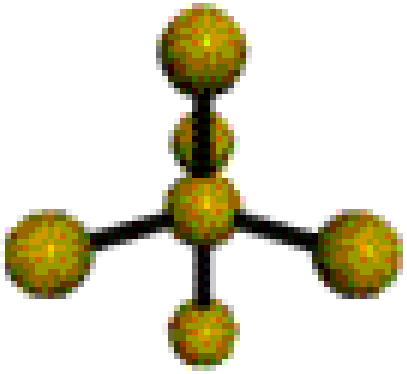


- **Number of Bonds = 3**
- **Number of Shared Pairs of Electrons = 4**
- **Number of Unshared Pairs of Electrons = 1**
- **Bond Angle = <109.5° (= 107°)**

Trigonal bipyramidal

EXAMPLE:

PCl_5

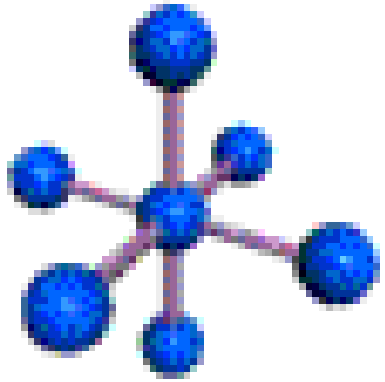


- **Number of Bonds = 5**
- **Number of Shared Pairs of Electrons = 5**
- **Number of Unshared Pairs of Electrons = 0**
- **Bond Angle = 120°/90°**

OCTAHEDRAL

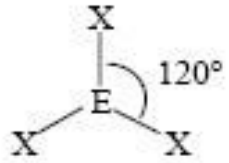
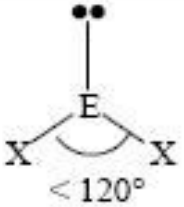
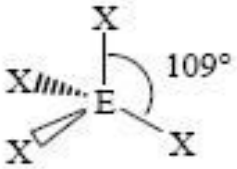
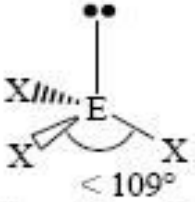
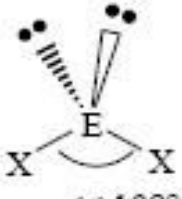
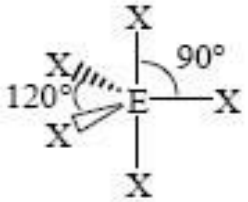
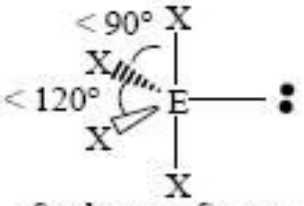
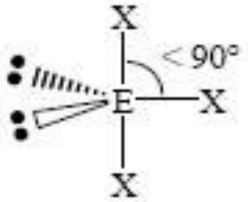
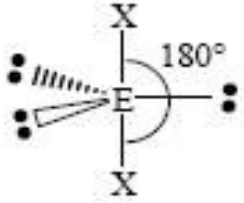
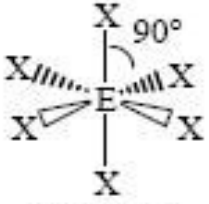
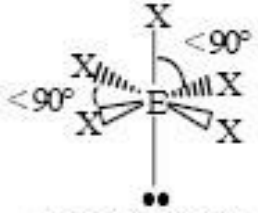
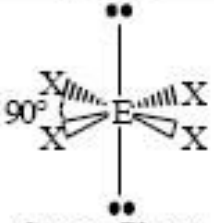
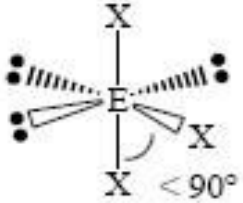
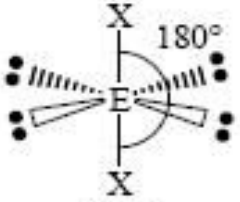
EXAMPLE:

SF_6



- **Number of Bonds = 6**
- **Number of Shared Pairs of Electrons = 6**
- **Number of Unshared Pairs of Electrons = 0**
- **Bond Angle = 90°**

VSEPR Geometries

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

2. Lewis Bonding theory

(Lewis Structures)

Rules for Writing Lewis Structures

Rules for Drawing Lewis Structures

1. *First **sum** the number of valence electrons from each atom*
2. *The **central atom** is usually written first in the formula*
3. ***Complete the octets** of atoms bonded to the central atom (remember that H can only have two electrons)*
4. *Place any **left over electrons** on the central atom, even if doing so it results in more than an octet*
5. *If there are not enough electrons to give the central atom an octet , **try multiple bonds** using e pairs from atoms bonding to central atoms.*

Write the Lewis structure of nitrogen trifluoride (NF_3).

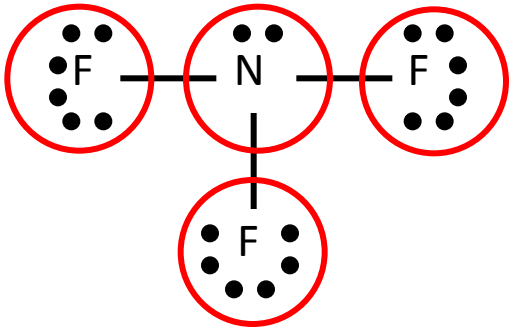
Step 1 – **N** is less electronegative than **F**, put N in center

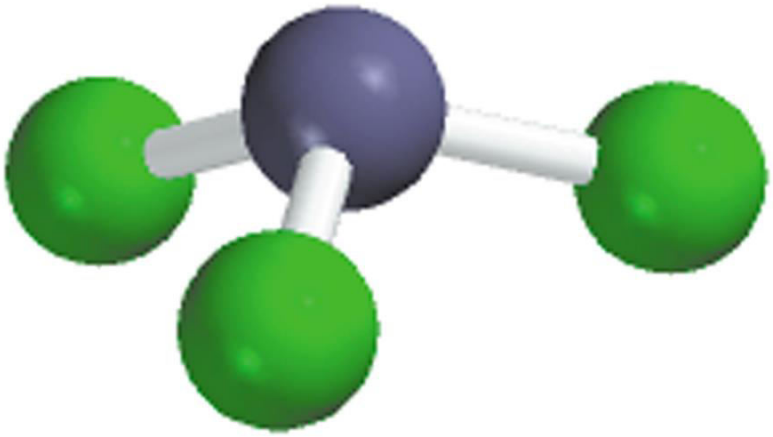
Step 2 – Count valence electrons **N** - **5** ($2s^2 2p^3$) and **F** - 7 ($2s^2 2p^5$)

5 + (3 x 7) = **26** valence electrons

Step 3 – **Draw single bonds** between N and F atoms.

Step 4 – Arrange remaining **20** electrons to complete octets





Write the Lewis structure of the carbonate ion (CO_3^{2-}).

Step **1** – **C** is less electronegative than **O**, put C in center

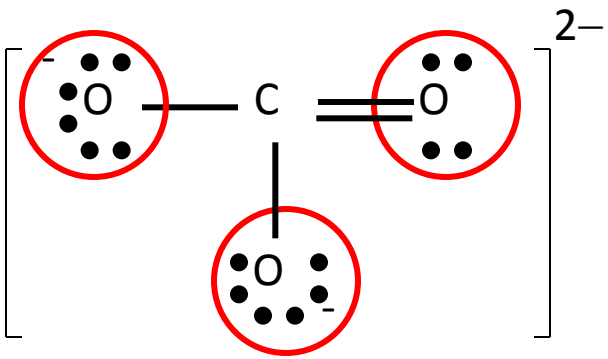
Step **2** – Count valence electrons **C** - **4** ($2s^2 2p^2$) and **O** - **6** ($2s^2 2p^4$)
-2 charge – $2e^-$

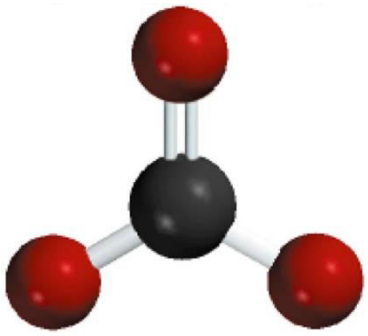
4 + (3 x 6) + 2 = **24 valence electrons**

Step **3** – Draw single bonds between **C** and **O** atoms

Step **4** - Arrange remaining **18** electrons to complete octets

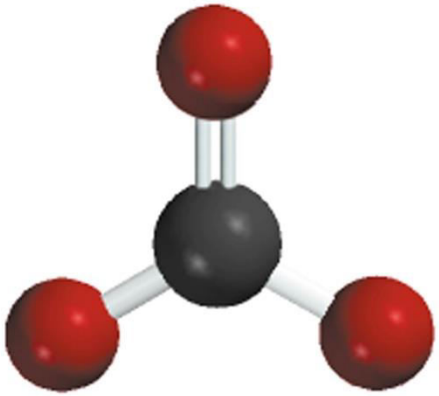
Step **5** – The central **C** has only **6** electrons. **Form a double bond**.

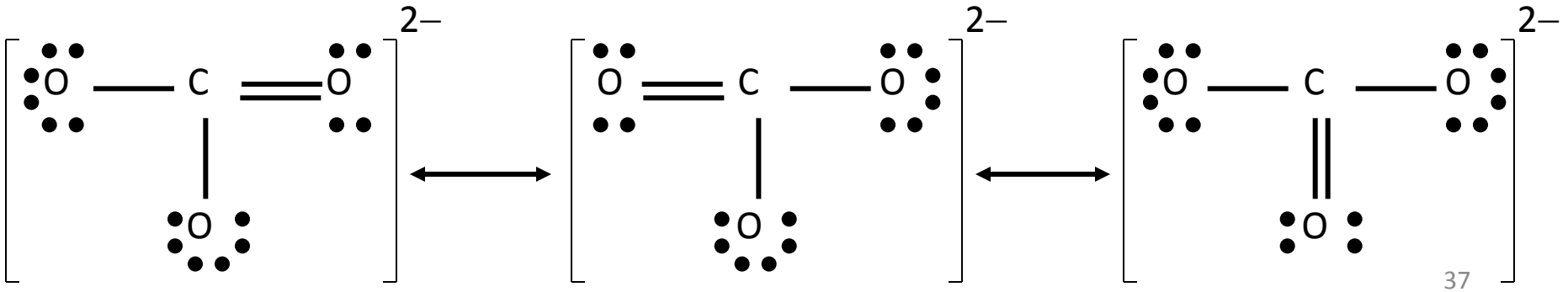




Resonance

- More than one valid Lewis structures can be written for a particular molecule
- The actual structure of the carbonate ion is an average of the **three** resonance structures



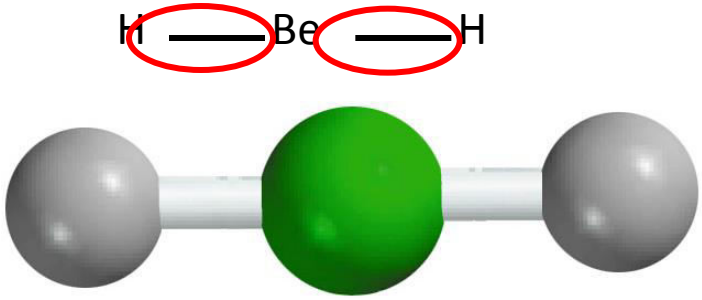


Exceptions/Violation to the Octet Rule

(a) The Incomplete Octet

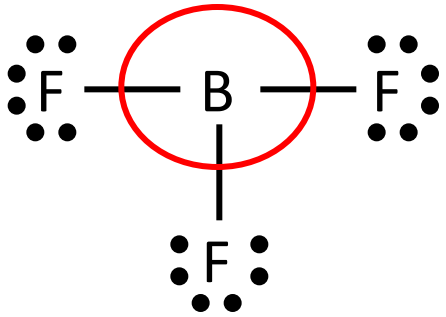
BeH_2

Be – 2e^-
2H – 2x1e^-
4e^-

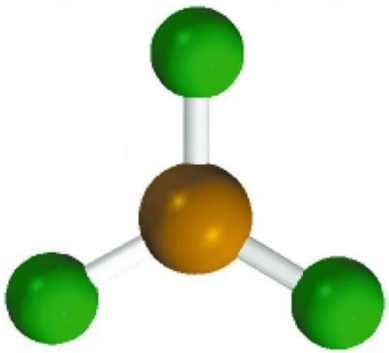


BF_3

B – 3e^-
3F – 3x7e^-
24e^-



3 single bonds (3x2) = 6
9 lone pairs (9x2) = 18
Total = 24

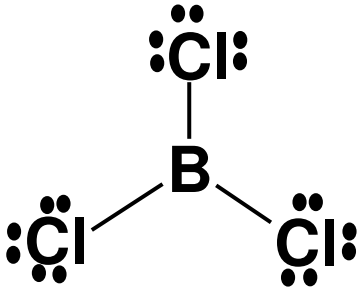


The B atom has a share in only 6 electrons (or 3 pairs).
B atom in many molecules is electron deficient.

Less than an Octet

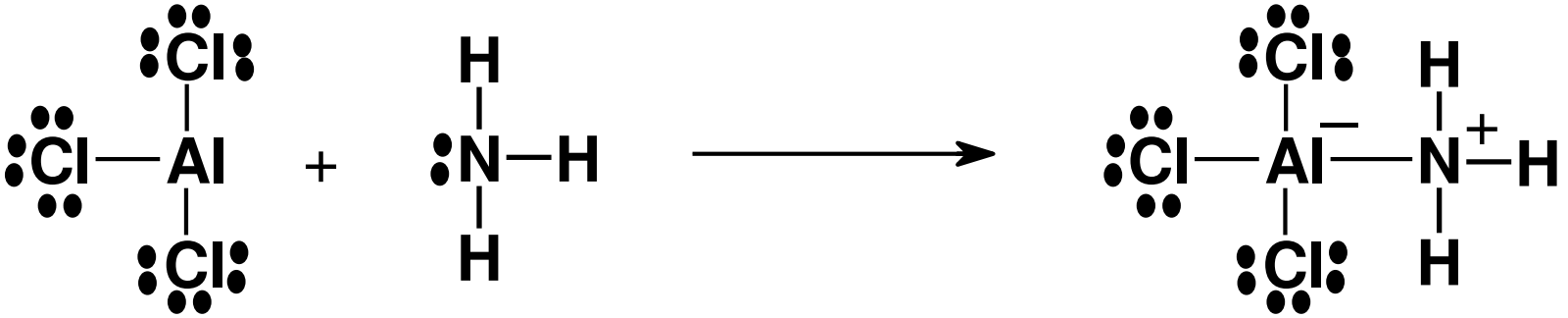
Includes Lewis acids such as halides of B, Al and compounds of Be

BCl_3



Group 3A atom only has six electrons around it

However, Lewis acids "accept" a pair of electrons readily from Lewis bases to establish a stable octet



Lewis acid **Lewis base** **salt**

Exceptions to the Octet Rule *cont.*

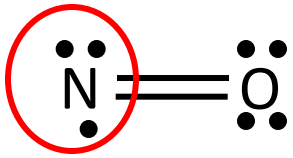
(b) Odd-Electron Molecules

NO

$N - 5e^-$

$O - 6e^-$

$11e^-$



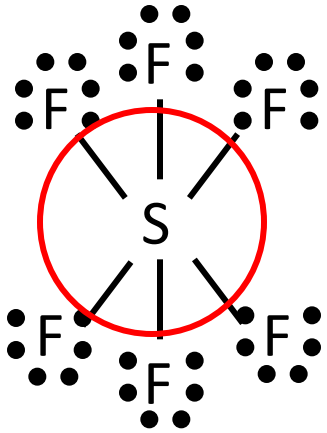
(c) The Expanded Octet (Central atom with principal quantum number n > 2)

SF_6

$S - 6e^-$

$6F - 42e^-$

$48e^-$

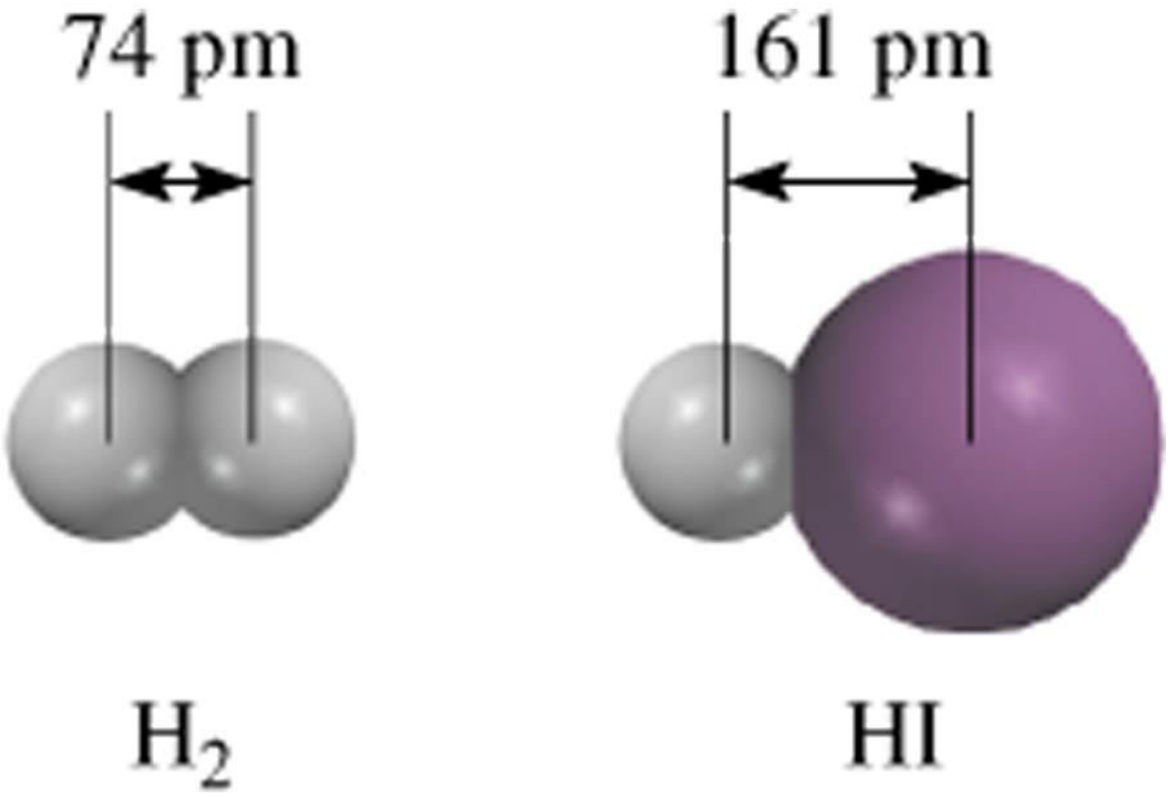


6 single bonds (6x2) = 12

18 lone pairs (18x2) = 36

Total = 48

Covalent Bond Lengths



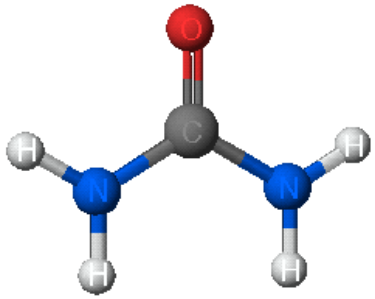
Bond Type	Bond Length (pm)
C-C	154
C=C	133
C≡C	120
C-N	143
C=N	138
C≡N	116

Bond Lengths: Triple bond < Double Bond < Single Bond

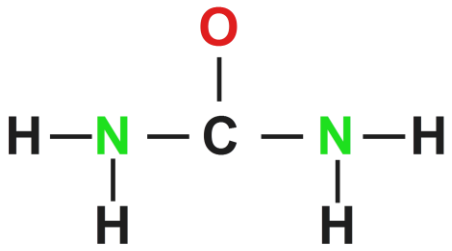
Bond Energies

Bond	Bond Energy	Bond	Bond Energy
C–C	347 kJ/mol	H–Cl	432 kJ/mol
C–O	358 kJ/mol	H–O	464 kJ/mol
C–H	413 kJ/mol	H–N	391 kJ/mol
C–N	286 kJ/mol	H–H	436 kJ/mol
C–Cl	346 kJ/mol	O=O	498 kJ/mol
Cl–Cl	243 kJ/mol	N≡N	945 kJ/mol

Urea $(NH_2)_2CO$

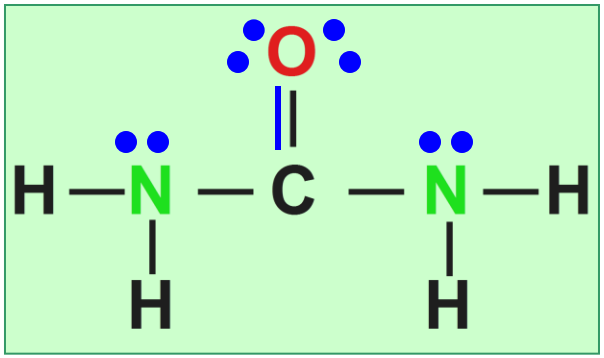


1. Number of valence electrons = 24 e-
2. Draw sigma bonds.



Leaves 24 - 14 = 10 e- pairs.

3. Complete C atom octet with double bond.
4. Place remaining electron pairs on oxygen and nitrogen atoms.



Draw the lewis structures of the following molecues/ ions and determine their geometry

- SF_4
- SO_2
- NO_3
- SCl_2
- SO_3^{2-}
- CO

Formal Atom Charges

- Atoms in molecules often bear a charge (+ or -).

- Formal charge = Valence ***e-***
  minus ½ (no. bond electrons)
  minus (no. of **LP** electrons)

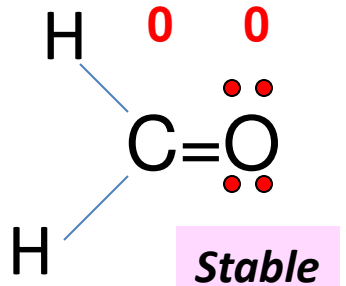
- The most important dominant resonance structure of a molecule is the one with formal charges as close to **0** as possible.

Formal Atom Charges

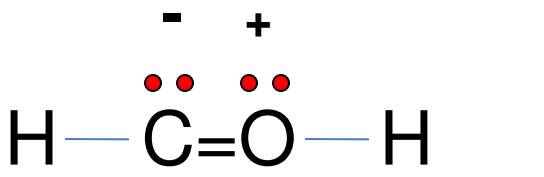
- For **neutral** molecules a Lewis structure <u>with no formal charge is preferable</u> to one in which f_c is present
- Lewis structures with **large** f_c (**+2**, **+3** or **-2**, **-3** etc) are less likely than those with small f_c (**-1**, **+1**)

- In choosing among Lewis structures having similar distribution of f_c the most stable is the one in which –ve f_c is on the most electronegative atom

Eg CH_2O

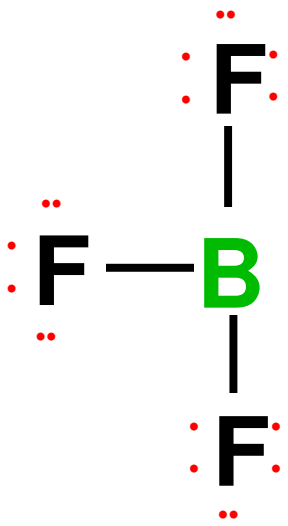


Stable



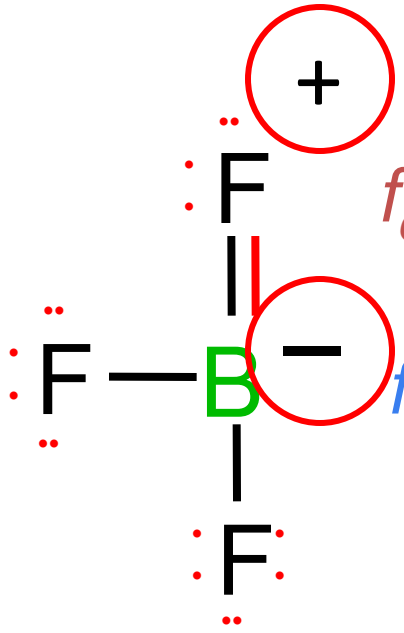
Unstable

Boron Trifluoride, BF_3



What if we form a **B—F** double bond to **satisfy** the **B** atom octet?

Boron Trifluoride, BF_3



$f_c = 7 - 2 - 4 = \mathbf{+1}$ **Fluorine**

$f_c = 3 - 4 - 0 = \mathbf{-1}$ **Boron**

- To have **+1** charge on **F**, with its very high electron affinity is not good. -ve charges best placed on atoms with high **EA**.
- Similarly **-1** charge on **B** is bad
- NOT important Lewis structure

3. The **M**olecular **O**rbital **T**heory

(**MOT**)

The Molecular Orbital Theory

- Lewis bonding- and valence bonding theories **do not always give satisfactory account for various properties of molecules**.

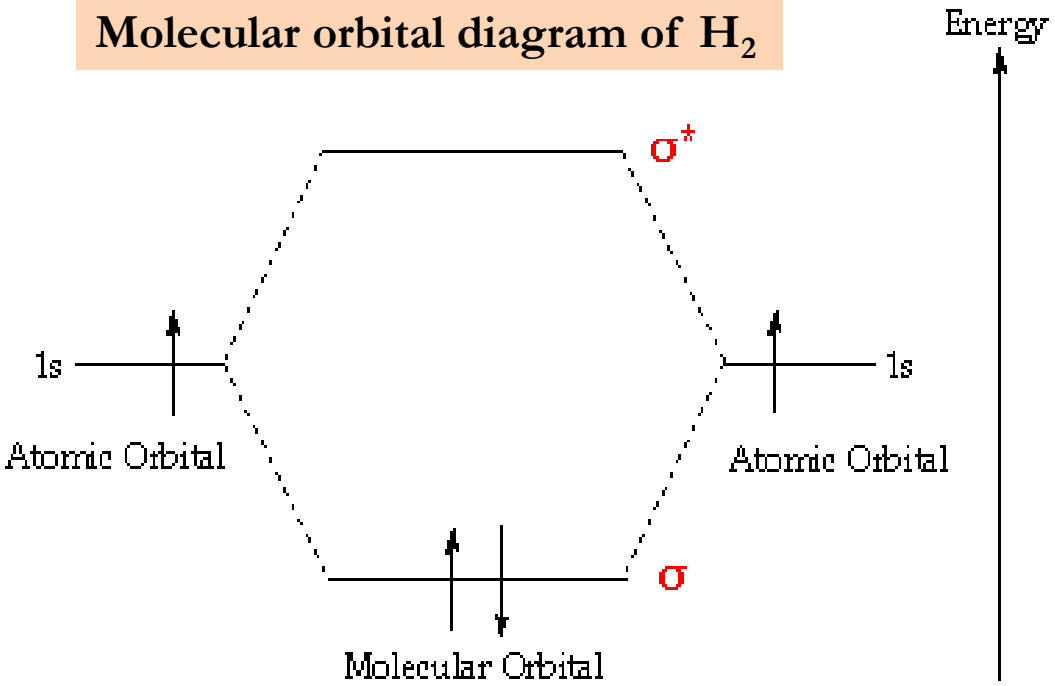
  - For example, the **Lewis** bondingand VB theory do not explain the fact that O_2 is **paramagnetic**.

- **MOT** is different from **VB** in that MOT;
  - **Considers the orbital of the whole molecules.**
  - **L**inear-**C**ombination-of-**A**tomic-**O**rbitals (**LCAO**) is usually used.

Atomic and Molecular Orbitals

- In atoms, electrons occupy **atomic orbitals**, but in molecules they occupy similar **molecular orbitals** which surround the molecule.
- The **two** 1s atomic orbitals combine to form **two** molecular orbitals, one **bonding** (σ) and one **antibonding** (σ^*).

Molecular orbital diagram of H_2



- One electron from each atom is being "**shared**" to form a covalent bond. This is an example of **orbital mixing**.

- **Electronic configuration** = σ_{1s}^{2}, for H_2 molecules

The gain in bonding orbital σ_{2p} (lower energy) is at the expense of the anti-bonding orbital σ_{2p}^{*} (higher energy)

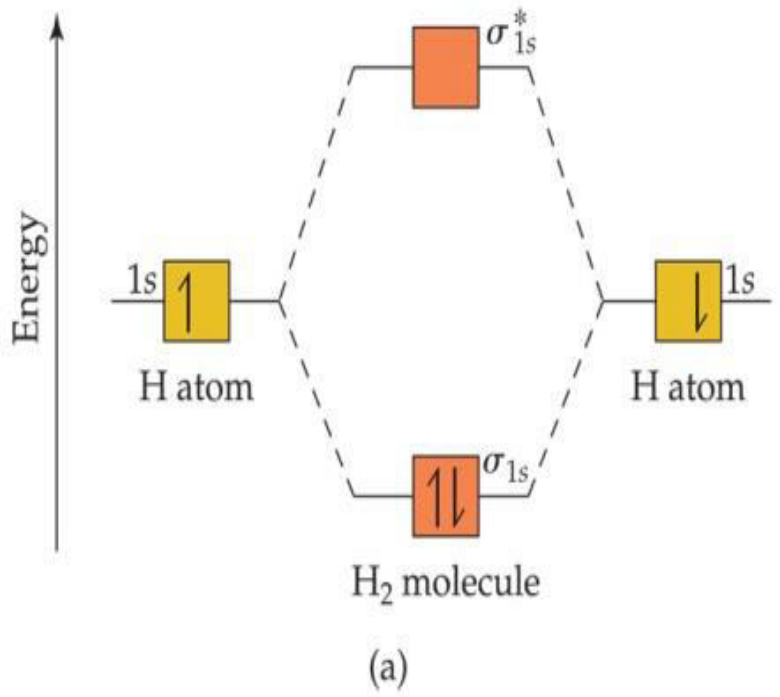
Bond Order

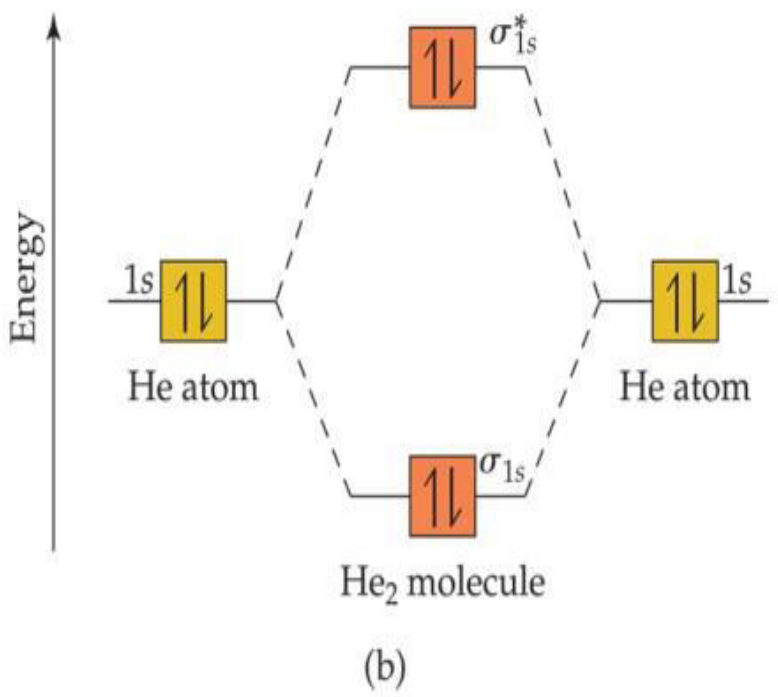
Electronic configuration = σ^2, for H_2 molecules

Stable species have **more electrons** in bonding orbital than antibonding.

$$\text{Bond Order} = \frac{\text{No. } e^- \text{ in bonding MOs - No. } e\text{- in antibonding MOs}}{2}$$

MO energy level diagrams: H_2 exists but He_2 does not





- **In H_2 <u>two</u> electrons are paired in the bonding σ MO, and the antibonding σ* MO is vacant.**
  - Bond order = 1
  - Configuration σ_{1s}^2

- In He_2 <u>four</u> electrons are paired, **two** in the bonding and **two** in the antibonding σ*
  - Bond order = 1
  - Configuration σ_{1s}^2 $\sigma^*_{1s}^2$

Electronic Configuration of H_2-type Molecules

Filling the **MOs** with electrons for the **H_2-type** molecule:

Molecule	***e-configuration***	**Bond order**	***Bond length***
H_2^+	1σ $(1\sigma^1)$	½	106 pm
H_2, He_2^{2+}	$1\sigma^2$	1	74, ~75
H_2^-, He_2^+	$1\sigma^2\, 1\sigma^*$	½	~106, 108
H_2^{2-}, He_2	$1\sigma^2\, 1\sigma^{*2}$	0	**not formed**

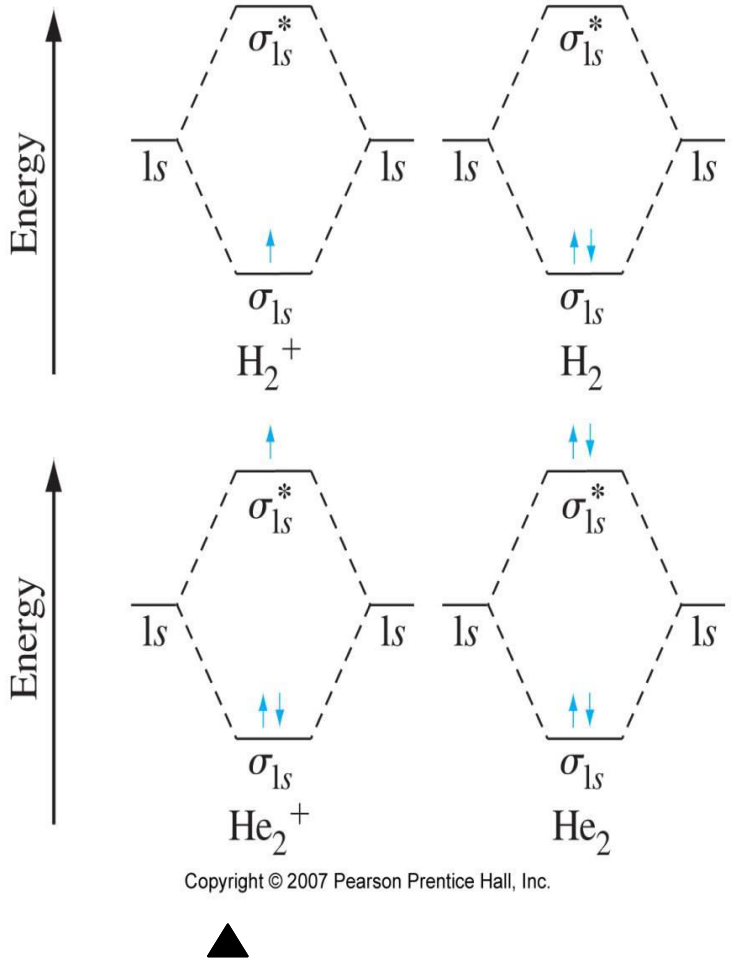
What is the relationships of **bond length** & **bond order** and **e-configurations**?

Bond Order vs. Bond Length & Energy

Species	Bond order	Bond length/pm	Bond energy/kJ mol^{-1}
H_2^+	$^1/_2$	105.2	256
H_2	1	74.1	432
H_2^-	$^1/_2$	–	100–200
He_2	0	297	0.1*
Li_2	1	267.3	101
Be_2	0	–	4
B_2	1	159	289
C_2	2	124.25	599
N_2	3	109.8	942
O_2	2	120.7	493
O_2^+	$2^1/_2$	111.6	643
O_2^-	$1^1/_2$	135	395
O_2^{2-}	1	149	–
F_2	1	141.2	155
Ne_2	0	310	0.2*

*Van der Waal forces.

Diatomic Molecules of the First–Period



$$BO = (e^-_{bond} - e^-_{antibond})/2$$

$BO_{H_2^+} = (1-0)/2 = ½$

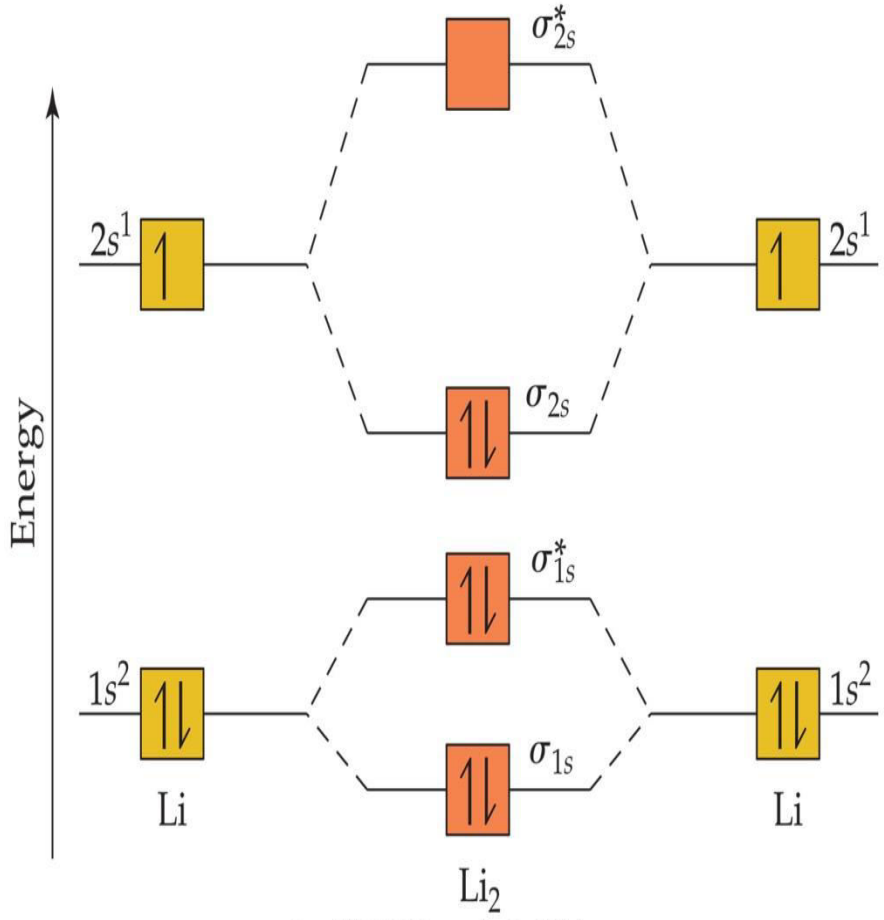
$BO_{H_2} = (2-0)/2 = 1$

$BO_{He_2^+} = (2-1)/2 = ½$

$BO_{He_2} = (2-2)/2 = 0$

- **Molecular orbital diagrams for the diatomic molecules and ions of the first-period elements**

Second Period elements



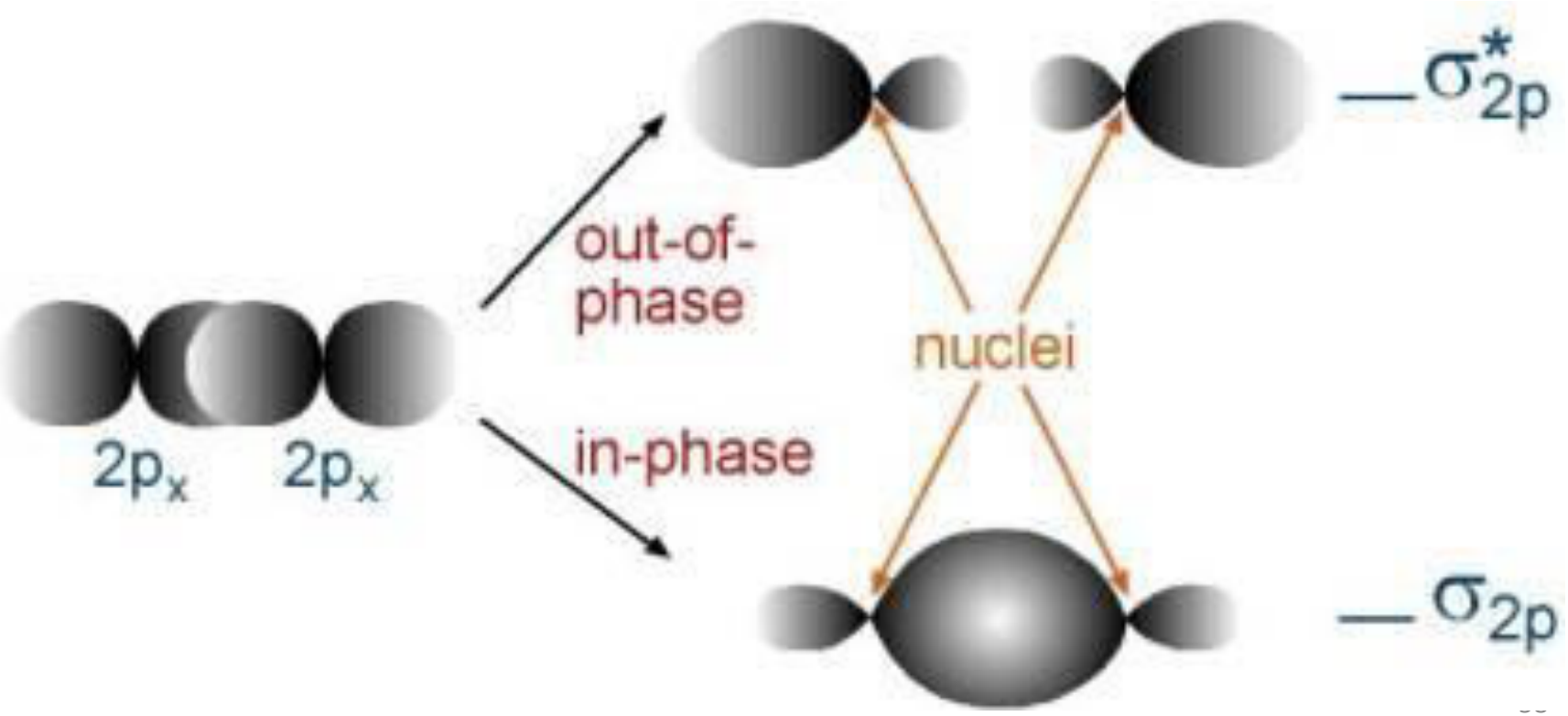
Molecular Orbitals

- Li_2 contains **6** electrons
- Bonding **σ** orbitals between **1s** and **2s**
- Antibonding **σ*** orbitals between **1s** and **2s**
- Occupied: σ_{1s}, σ^*_{1s} and σ_{2S}
- Bond order = 2 – 1 = **1**
- Does Be_2 exist?

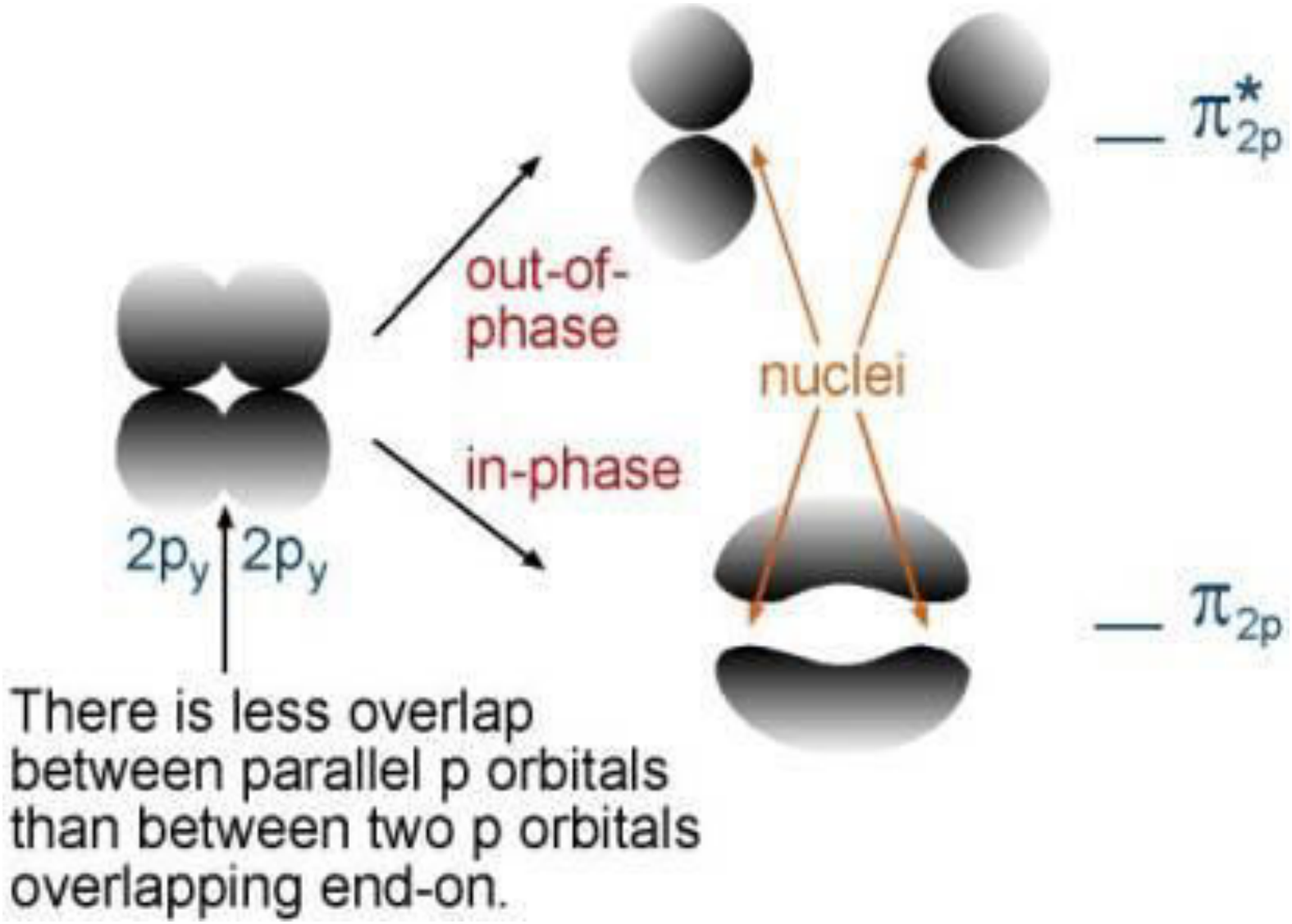
Sigma MOs Formed Using *p* AOs

Sigma MOs (σ_{2p} σ_{2p}^*) can be formed using *p* AOs, similar to **VB** theory.

The gain in bonding orbital (σ_{2p} ,**lower in energy**) is at the expense of the anti-bonding orbital (σ_{2p}^* ,**higher in energy**)



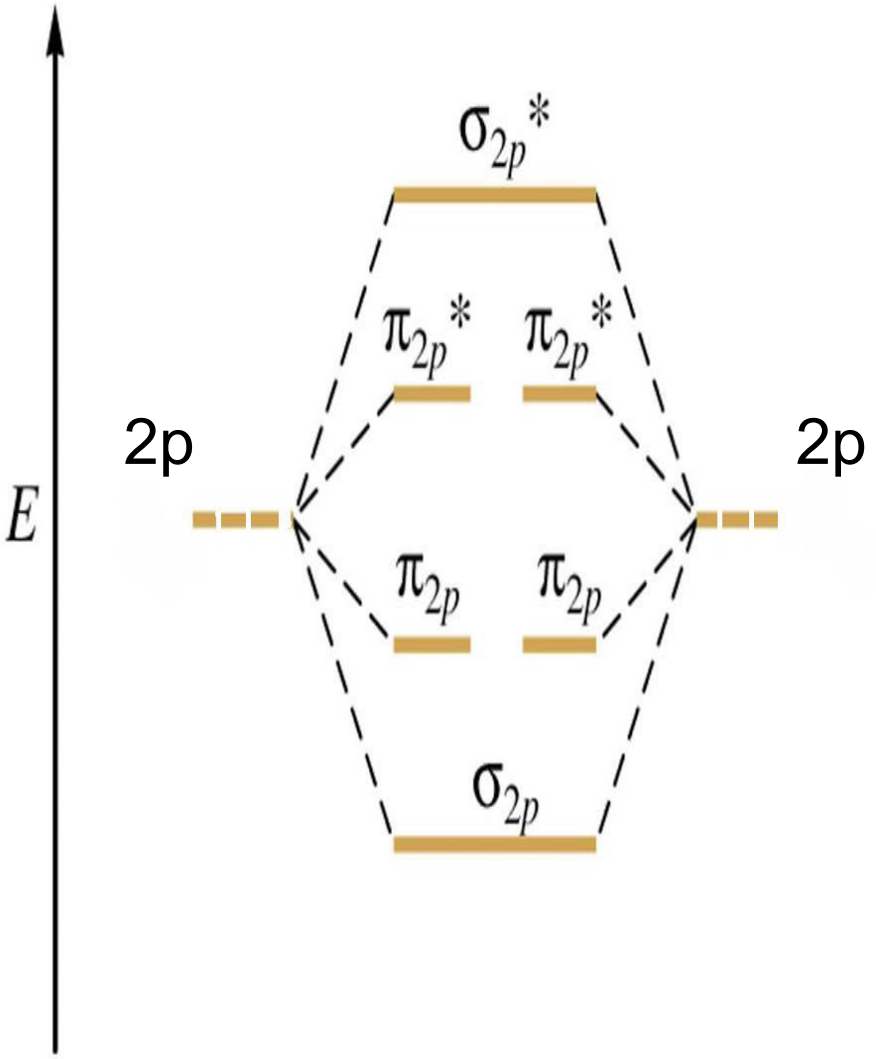
Pi (π) MOs from *p* AOs



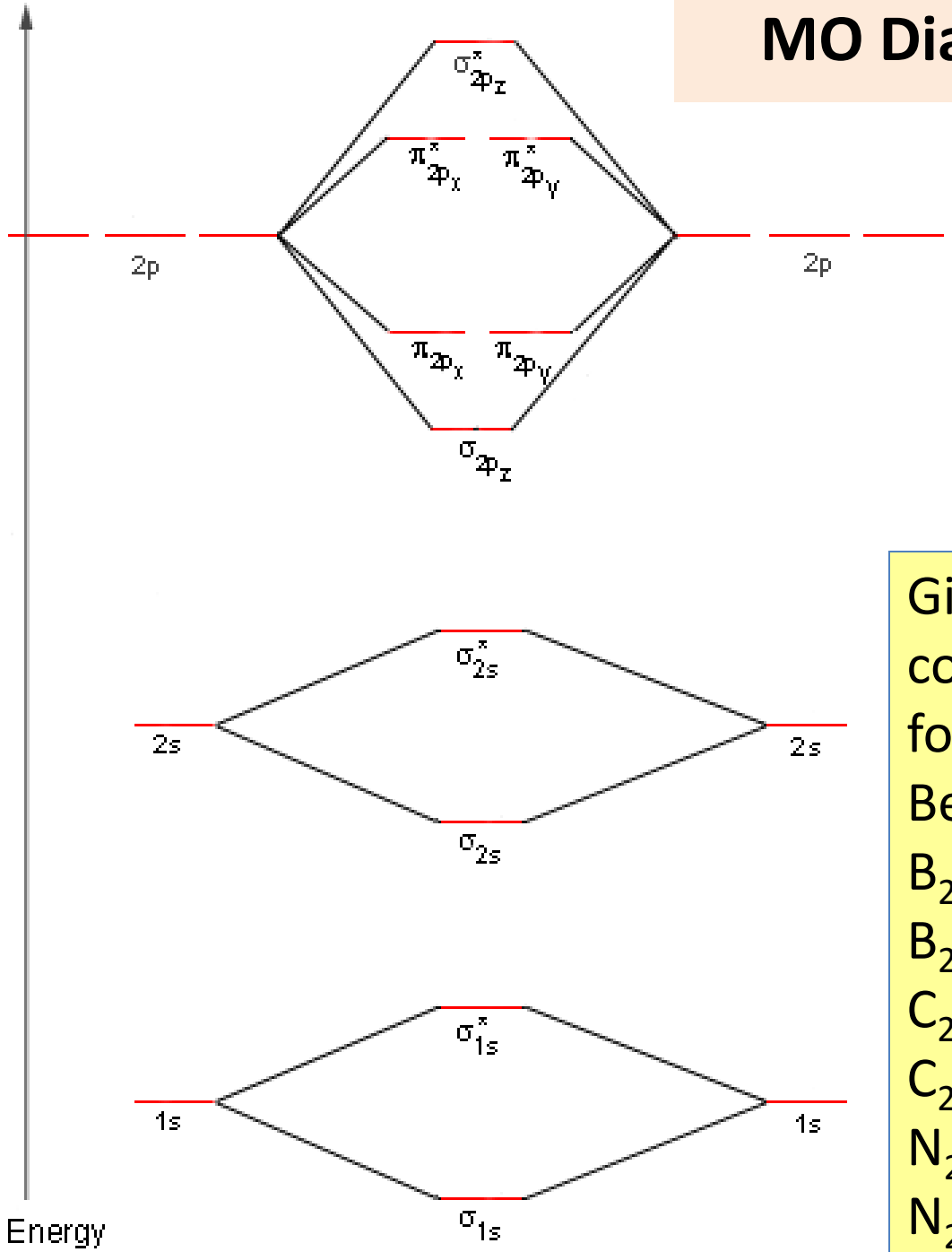
There is less overlap between parallel p orbitals than between two p orbitals overlapping end-on.

Molecular Orbitals formed from 2p atomic orbitals

- ✓ This is a molecular orbital energy level diagram for the ***p*** orbitals.
- ✓ Note that the **σ** bonding orbital is lowest in energy due to the greater overlap end-on-end.



MO Diagrams for O_2 and F_2



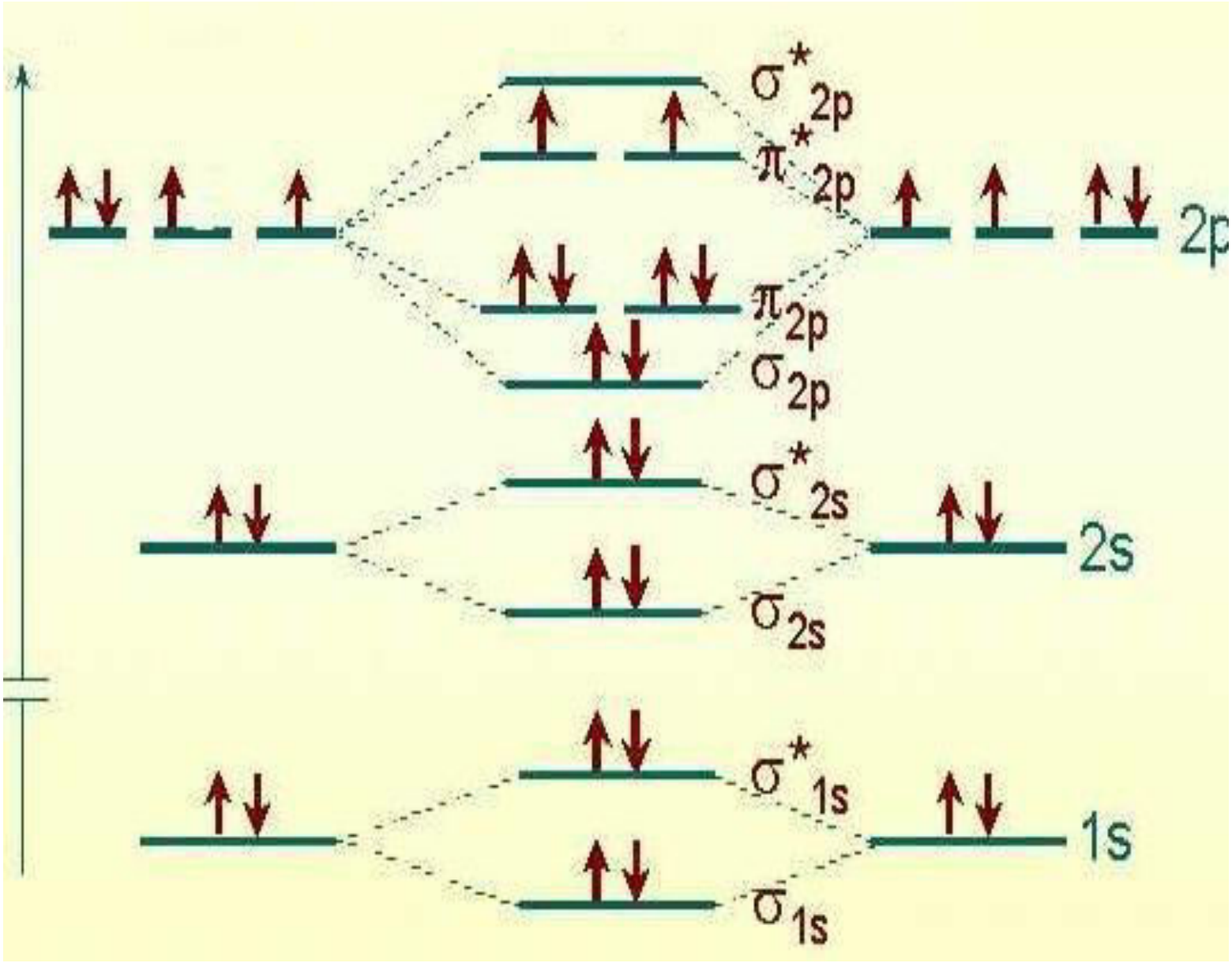
A full diagram of the energy level of molecular orbitals of O_2 and F_2 is as shown.

The relative (approximate) height of these energies

Give electronic configurations for Be_2^+, Be_2^-, B_2^+, B_2, B_2^-, C_2^+, C_2, C_2^-, N_2^+, N_2, N_2^-.

Write the electronic configurations for O_2, O_2^-, F_2, F_2^- & Ne_2.

MO Diagram for O_2



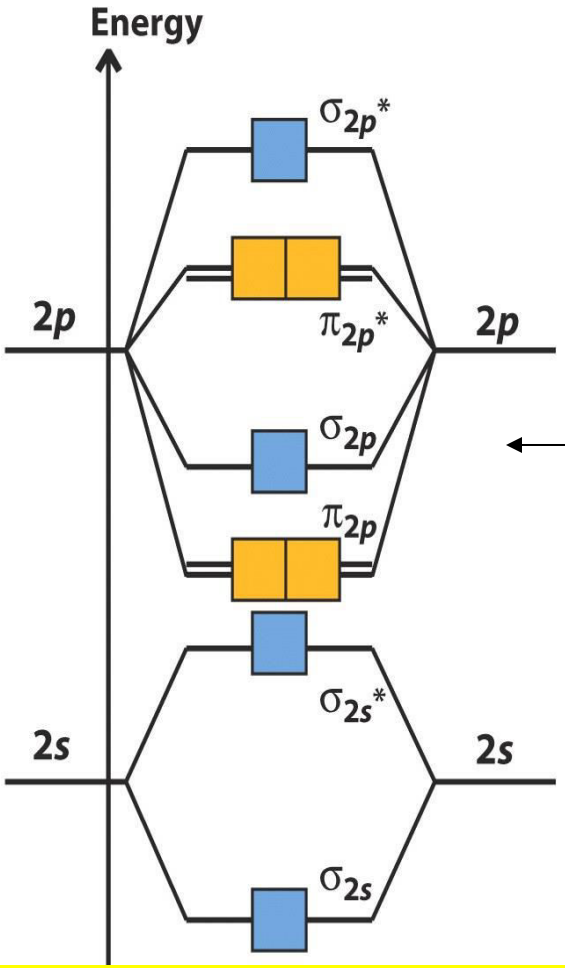
MO Diagrams for C_2

- Two possible **MO** diagrams can be illustrated for the **C_2** molecule.
- The presentation of MOs here is similar to that used in drawing orbital diagrams for atoms.
- Experimentally, that the C_2 molecule (**4** valence electrons contributed by each C atom for a total of **8**) is know to be diamagnetic.
- Which of the MO diagrams accounts for this diamagnetism?

Orbital energies for the ^{3}Li - ^{10}Ne

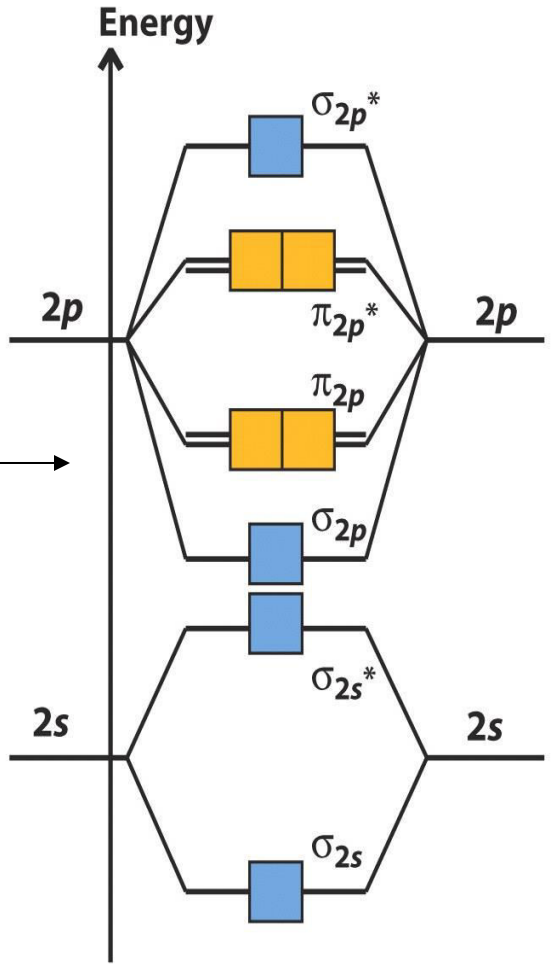
NB: (1) The energy of the π_{2p} and σ_{2p} orbitals switch energy places between **N** and **O**; (2) The electron configuration for any isoelectronic valences is the same

Li, Be, B, C, N



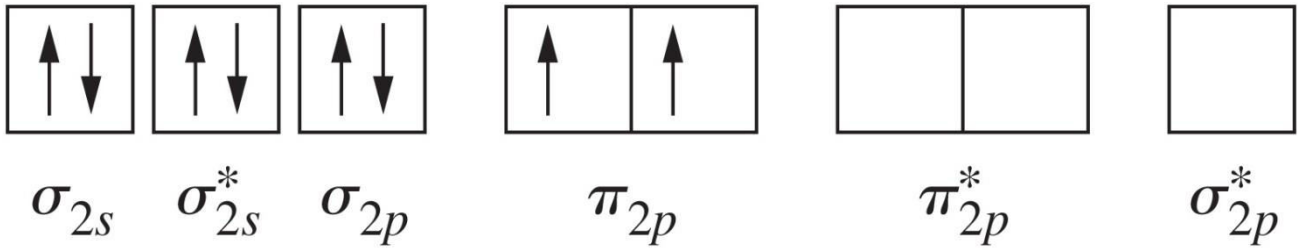
Switch

O, F, Ne

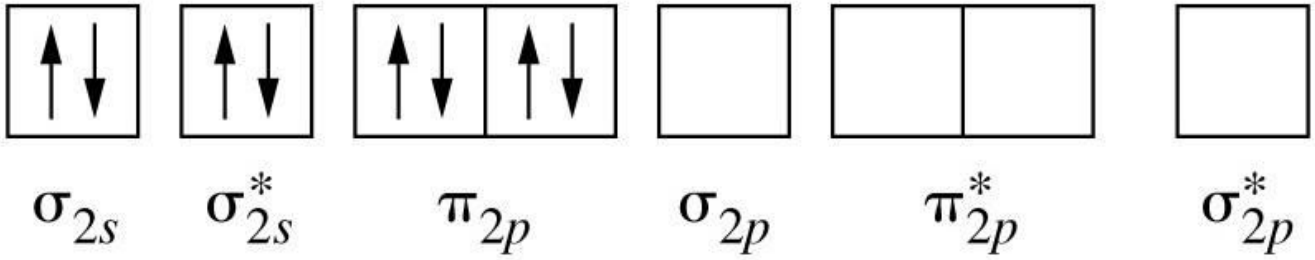


A more realistic energy level diagram for Be – N, involving ***sp*** mixing

Experiment shows C_2 to be **diamagnetic**, supporting a modified energy-level diagram

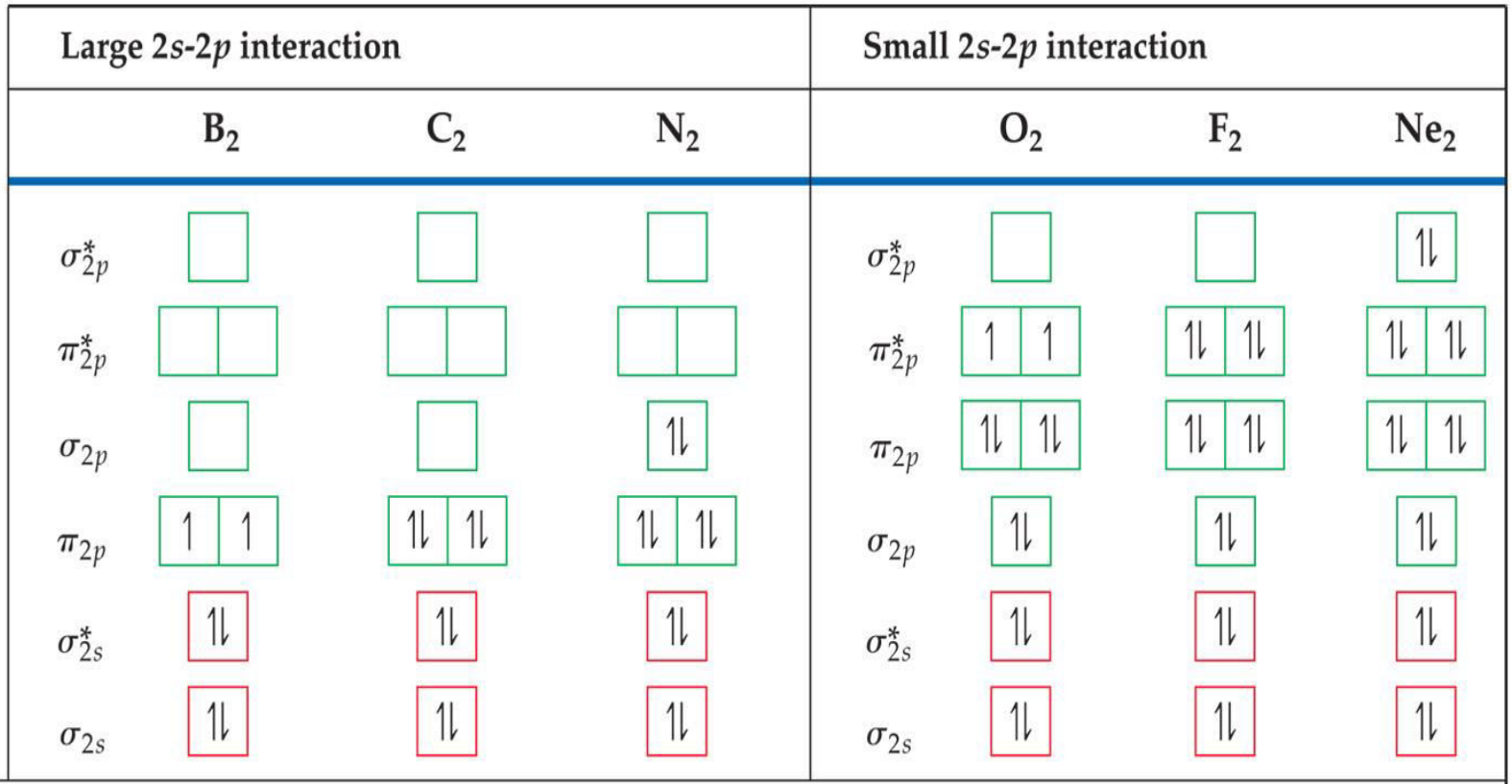


▲ Expected MO Diagram for C_2 (PARAMAGNETIC)



▲ Modified MO Diagram for C_2 (DIAMAGNETIC)

Correlate magnetic properties with MO diagram



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

Due to close energy levels of **2*s*** and **2*p***, the MO energy level diagram for **Be_2** to **N_2** differs from those of **O_2** to **Ne_2**.

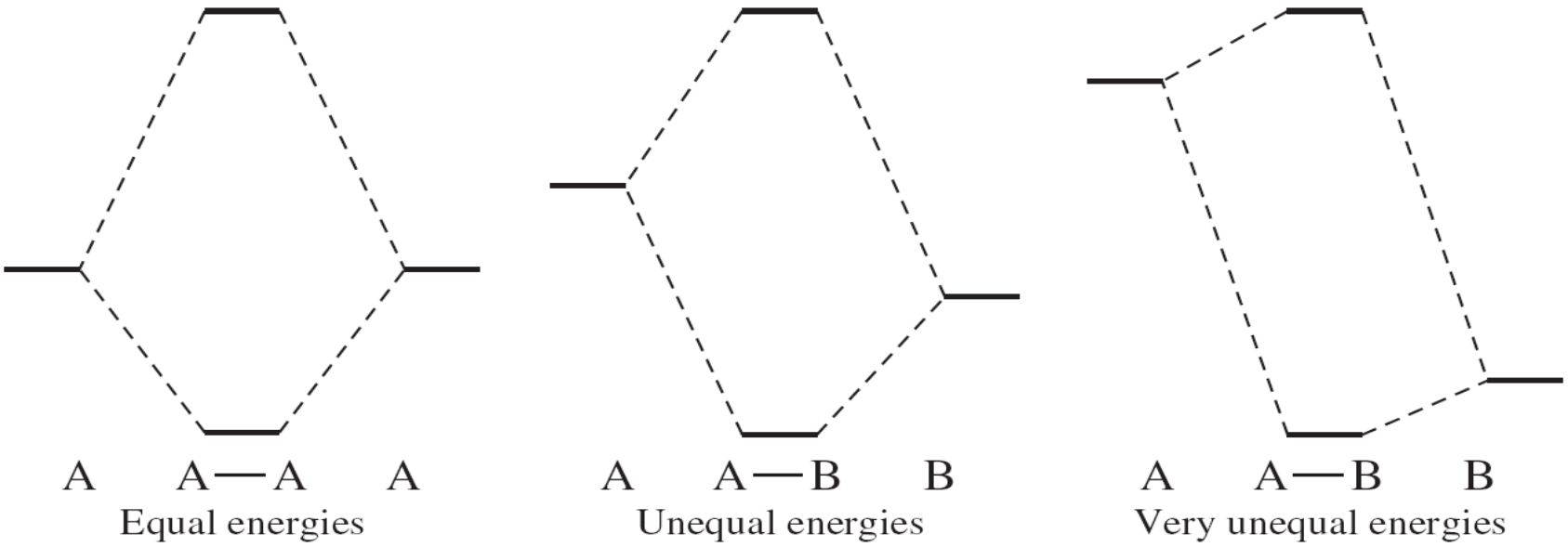
Give electronic configurations for:

Be_2^+,
B_2^+,
B_2^-,
C_2,
N_2^+,
N_2^-.

Be_2^-,
B_2,
C_2^+,
C_2^-,
N_2,

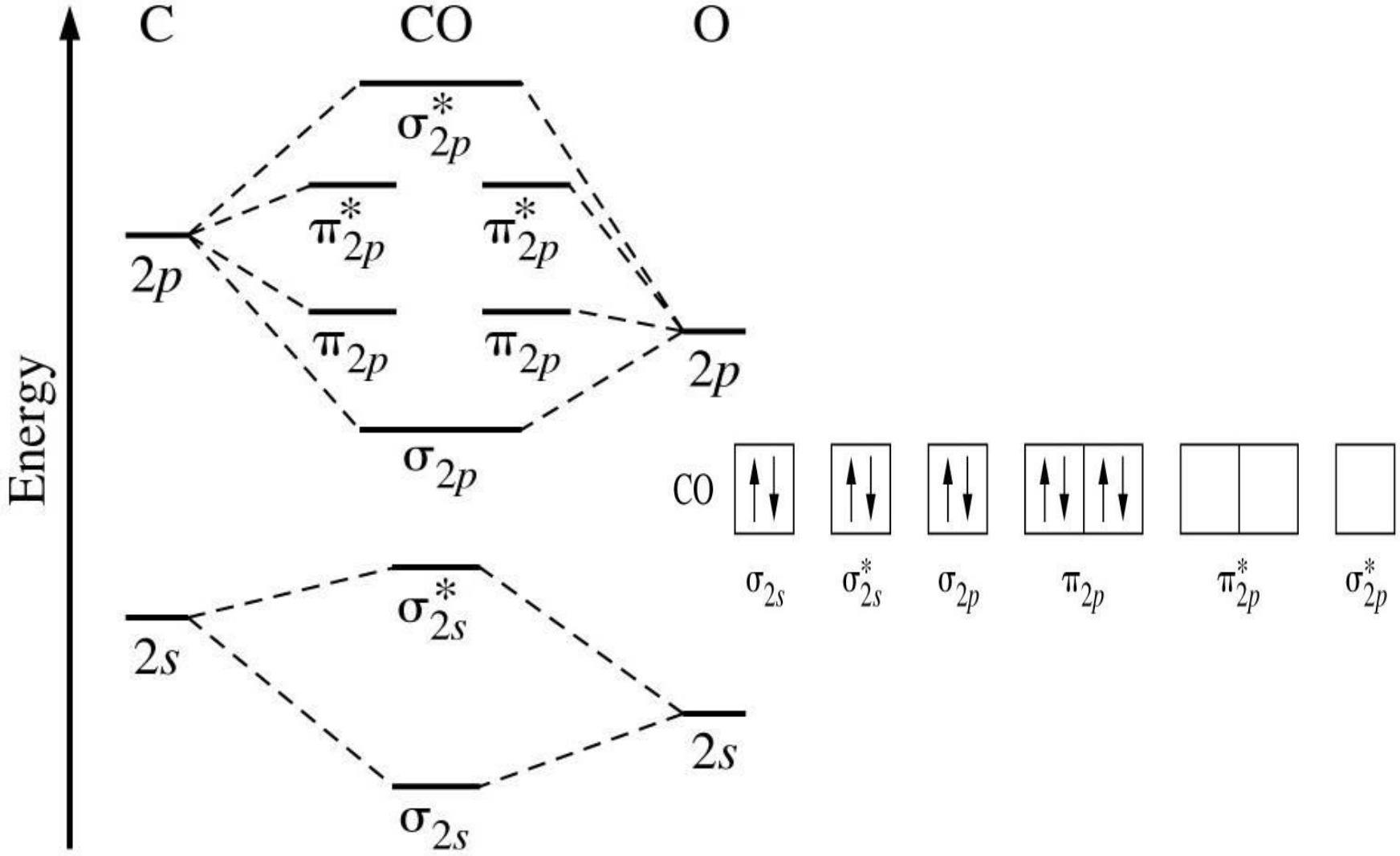
Heteronuclear Diatomics….

- **The energy level diagram is not symmetrical.**
- **The bonding MOs are closer to the atomic orbitals which are lower in energy.**
- **The antibonding MOs are closer to those higher in energy.**

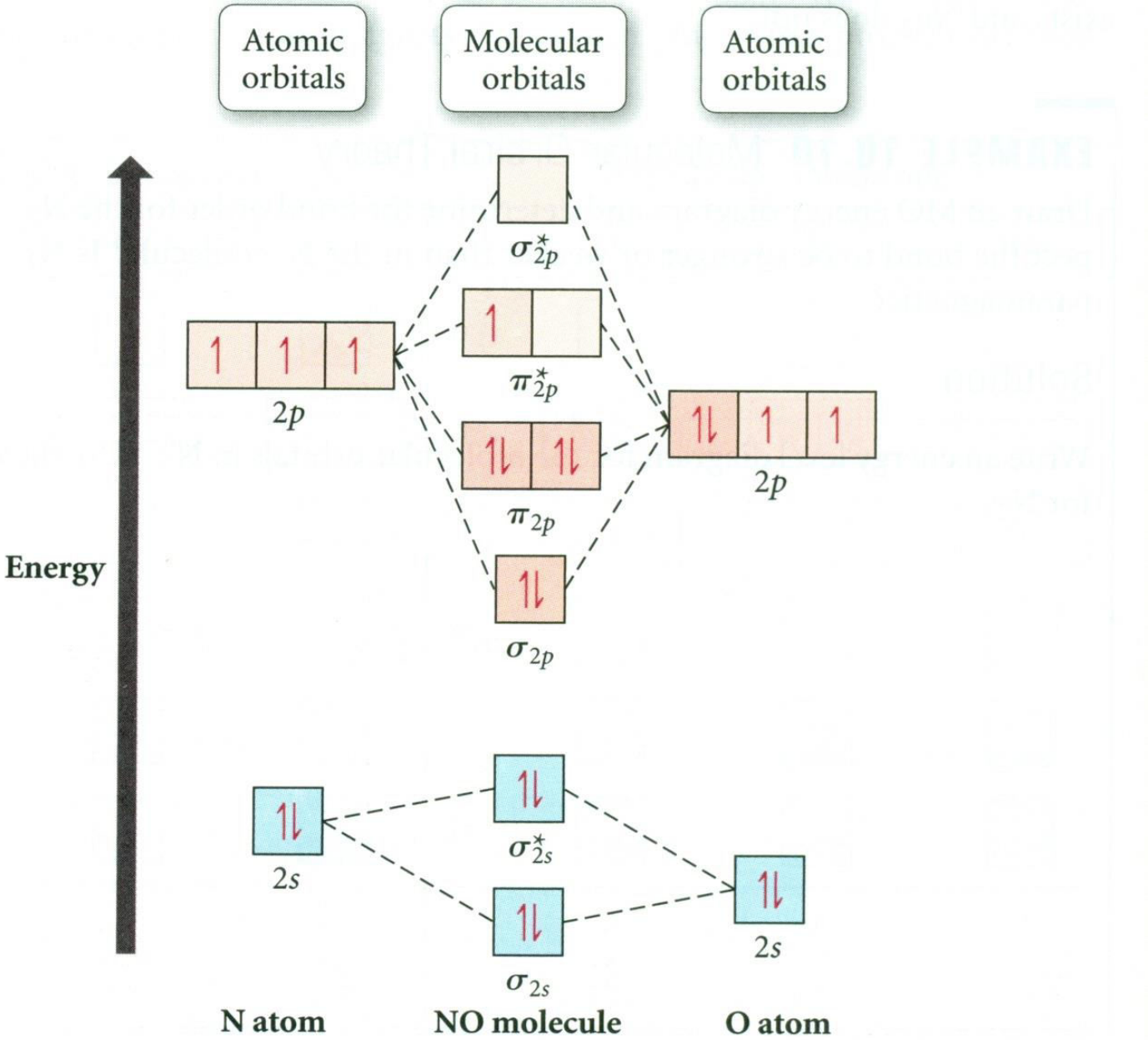


Energy match and Molecular orbital formation

CO


C
CO
O
Energy
σ^*_{2p}
π^*_{2p}
π^*_{2p}
2p
π_{2p}
π_{2p}
2p
σ_{2p}
σ^*_{2s}
2s
2s
σ_{2s}
CO
σ_{2s}
σ^*_{2s}
σ_{2p}
π_{2p}
π^*_{2p}
σ^*_{2p}

NO


Atomic orbitals
Molecular orbitals
Atomic orbitals
Energy
σ^*_{2p}
π^*_{2p}
π_{2p}
σ_{2p}
2p
2p
σ^*_{2s}
σ_{2s}
2s
2s
N atom
NO molecule
O atom

Molecular Orbital Diagrams

1. The electrons fill the molecular orbitals of molecules like electrons fill atomic orbitals in atoms
2. Electrons preferentially occupy molecular orbitals that are lower in energy.
3. Molecular orbitals may be empty, or contain one or two electrons.
4. If two electrons occupy the same molecular orbital, they must be spin paired.
5. When occupying degenerate molecular orbitals, electrons occupy separate orbitals with parallel spins before pairing (Hund's Rule.) .