

Chemistry 1314 – Lecture Outline and Notes

Text: Chemistry – The Central Science, 10th edition, Brown, LeMay and Bursten

Chapter 9. Molecular Geometry and Bonding Theories

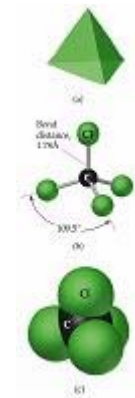
The Lewis diagram shows us the atoms and how they are bound, but it does not show us the overall shape because they are 2-dimensional.

Shape is important for function. For example, enzymes (very large molecules composed of C, N, O, and S that induce chemical reactions) are very selective to substrate (what they act on) shape. Also the sensors in our nose can distinguish many shapes of small molecules and thus signal and causes our brain to trigger the sensation of smell.

Molecular Shapes

What does CCl_4 (carbon tetrachloride) look like?

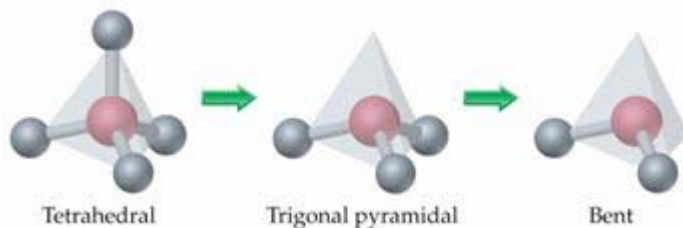
The Lewis structure shows us a carbon atom surrounded by 4 chlorine atoms, but it is a three-dimensional object.



It has a tetrahedral shape (a 4-sided object with equilateral triangles) with a Cl at each of the tetrahedral points.

Other molecular shapes:

The tetrahedral shape can also form the trigonal pyramidal and bent with successive remove of one of the peripheral atoms.

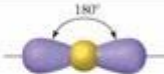
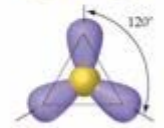
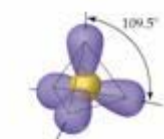
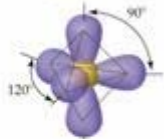
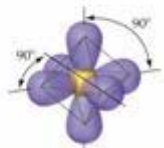


We will see that this trend also occurs for the other base forms.

The VSEPR Model

VSEPR = valence-shell electron pair repulsion theory. We use this with elements in the p area of the periodic table and help us to determine the electron arrangement (or **electron-domain geometry**) that can occur. The electron pairs try to get as far from each other as possible.

TABLE 9.1 Electron-Domain Geometries as a Function of the Number of Electron Domains

Number of Electron Domains	Arrangement of Electron Domains	Electron-Domain Geometry	Predicted Bond Angles
2		Linear	180°
3		Trigonal planar	120°
4		Tetrahedral	109.5°
5		Trigonal bipyramidal	120° 90°
6		Octahedral	90°

Just looking at the electronic configuration, we can obtain these shapes. They are the basis of how the atoms can be arranged in the **molecular geometry**.

TABLE 9.2 Electron-Domain Geometries and Molecular Shapes for Molecules with Two, Three, and Four Electron Domains Around the Central Atom















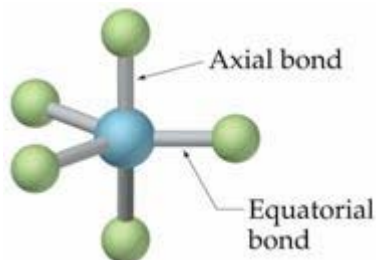
Number of Electron Domains	Electron-Domain Geometry	Bonding Domains	Nonbonding Domains	Molecular Geometry	Example
2	 Linear	2	0	 Linear	$\text{N} \equiv \text{C} \equiv \text{N}$
3	Trigonal planar	3	0	 Trigonal planar	BF_3
		2	1	 Bent	$[\text{NO}_2]^-$
4	Tetrahedral	4	0	 Tetrahedral	CH_4
		3	1	 Trigonal pyramidal	NH_3
		2	2	 Bent	H_2O

TABLE 9.3 Electron-Domain Geometries and Molecular Shapes for Molecules with Five and Six Electron Domains Around the Central Atom

Total Electron Domains	Electron-Domain Geometry	Bonding Domains	Nonbonding Domains	Molecular Geometry	Example
5	Trigonal bipyramidal	5	0	 Trigonal bipyramidal	PCl_5
		4	1	 Seesaw	SF_6
		3	2	 T-shaped	ClF_3
6	Octahedral	2	3	 Linear	XeF_2
		6	0	 Octahedral	SF_6
		5	1	 Square pyramidal	BrF_5
4	2	 Square planar	XeF_4		

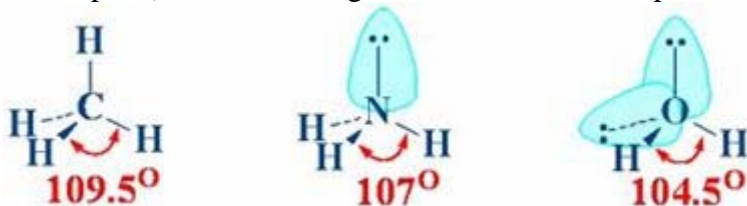
In the trigonal bipyramidal and octahedral shapes, the atoms (or lone pairs) at the poles are called the axial bonds and the ones around the center are the equatorial bonds.



The molecular shapes are based on the electron-domain geometry, but we only look at the atoms in place, so the trigonal planar electron-domain geometry can have molecular geometries of trigonal planar for a compound of AB_3 (such as BF_3) or bent for a compound of AB_2 that has a lone pair (as in NO_2^-).

We know that the angles between the electron pairs in the tetrahedral geometry are 109.5° apart. This is also true for CCl_4 or CH_4 where the C is surrounded by 4 identical atoms. But, will the angle increase or decrease if a lone pair appears in the trigonal pyramidal or bent forms (both derived from the tetrahedral shape)? The lone pairs are greedy with space and will compress the other atoms closer together.

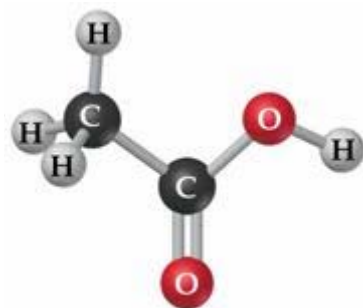
In CH_4 , the angles between the H-C-H angles are all 109.5° . In NH_3 (that has a trigonal pyramidal shape with one lone pair) the H-N-H angle is 107° , and in water H_2O (bent shape with 2 lone pairs) the H-O-H angle is 104.5° . The lone pairs are pushing the H atoms closer together.



Double bonds have a larger electronic-charge density than single bonds (4 electrons compared to 2) and will also take up more space than the single bonds.

Examples: Predict the electron-domain geometry and molecular geometry of (a) ClF_3 and (b) ICl_4^- .

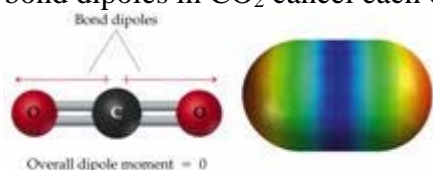
What do we do if we have a larger molecule? Lets look at acetic acid (CH_3COOH), it looks like:



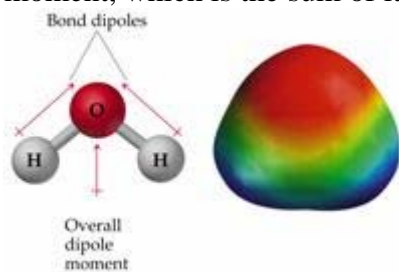
We look at each interior atom and determine the shape for each. The first C is tetrahedral, the second is trigonal planar, and the interior O is bent, but with a tetrahedral electron-domain geometry.

Molecular Shape and Molecular Polarity

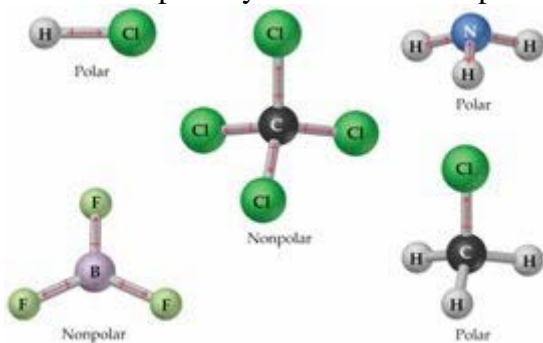
When there is a difference in electronegativity between two atoms, then the bond between them is polar. The dipole moment in a bond (the **bond dipole**) is directed toward the more electronegative atom. Bond dipoles are vectors meaning that they have both a magnitude and a direction. It is possible for a molecule to contain polar bonds, but not be polar. For example, the bond dipoles in CO_2 cancel each other because CO_2 is linear.



In water, the molecule is not linear and the bond dipoles do not cancel each other. Therefore, water is a polar molecule. Note that the two dipoles come together to give an overall dipole moment, which is the sum of its bond dipoles.



The overall polarity of a molecule depends on its molecular geometry.

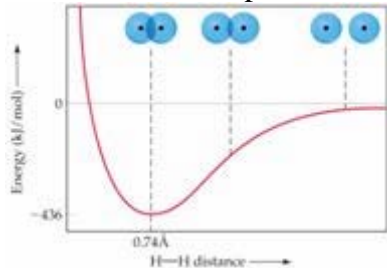


Example: Determine whether the following molecules are polar or nonpolar: (a) NF_3 ; (b) BCl_3 .

Covalent Bonding and Orbital Overlap

But why do covalent bonds occur? It is a concept based on the marriage of the Lewis structure and the idea of atomic orbitals called **valence-bond theory**. Bonds form when orbitals on atoms overlap and there will be two electrons of opposite spin in the orbital overlap.

The atoms approach each other and the energy goes down as they begin to overlap. When we reach the minimal point, this corresponds to the equilibrium bond distance.



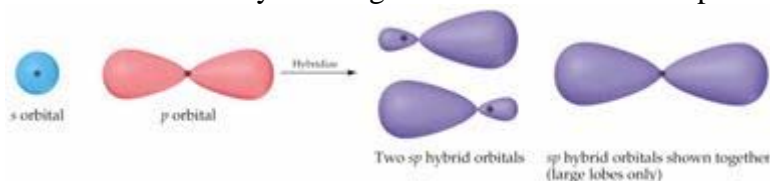
Hybrid Orbitals

Atomic orbitals can mix or **hybridize**, to get **hybrid orbitals**, in order to adopt an appropriate geometry for bonding. Hybridization is determined by the electron-domain geometry.

sp Hybrid Orbitals

Let's consider BeF_2 . We know from VSEPR theory that the F-Be-F angle is 180° , a linear molecule. But, how do we describe the bonding? The electronic configuration for F ($1s^2 2s^2 2p^5$) shows us we have an unpaired 2p orbital. So, this 2p electron can be paired with an unpaired electron of Be. But Be has the electronic configuration of $1s^2 2s^2$ with no unpaired electrons. If we promote an electron to the p orbital ($1s^2 2s^1 2p^1$), we would now have openings for 2 bonds to form. But, this electron promotion requires energy and the two Be-F bonds would not be identical because they would be formed from the overlap of different orbital types.

We can solve this by “mixing” the 2s and one of the 2p orbitals to generate 2 new orbitals:



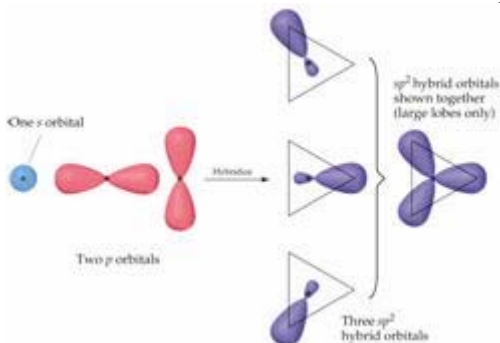
The new orbitals have 2 lobes, but with one larger than the other. The sp orbitals are energetically between the s and p orbitals that it is derived from. When combined, they are a linear molecule and the F atoms will interact with the bulbous ends.

Therefore, we have hybridized one s and one p orbital to get two sp hybrid orbitals. We still have 2 unhybridized 2p orbitals remaining.

A linear arrangement of electron domains implies sp hybridization.

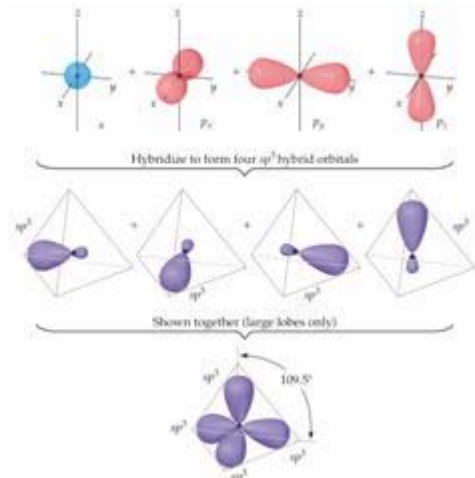
sp^2 and sp^3 hybridization

We can also mix an s orbital with two p orbitals to get the three sp^2 hybrid orbitals.



A trigonal planar arrangement of electron domains implies sp^2 hybridization.

We can also mix an s orbital with all three p orbitals to get the three sp^3 hybrid orbitals.



A tetrahedral arrangement of electron domains implies sp^3 hybridization.

Hybridization involving d orbitals

We can add a d orbital to the mix. This only occurs for elements with p orbitals in row 3 and beyond.

A trigonal bipyramidal arrangement of electron domains implies sp^3d hybridization.

An octahedral arrangement of electron domains implies sp^3d^2 hybridization.

We can use the following steps to determine the hybridization state of an atom:

1. Draw the Lewis structure of the molecule or ion.
2. Determine the electron-domain geometry using the VSEPR model.
3. Specify the hybridization based on the electron-domain configuration.

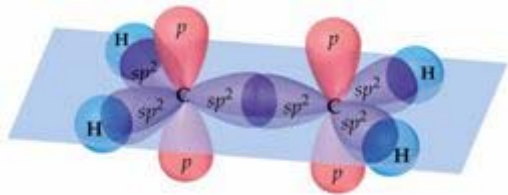
Example: Predict the electron-domain geometry and the hybridization of the central atom in (a) SO_3^{2-} and (b) SF_6 .

Multiple Bonds

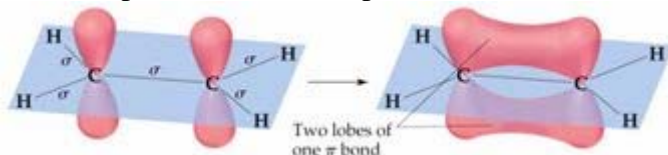
- σ -Bonds: electron density lies on the axis between the nuclei.
- All single bonds are σ -bonds.
- π -Bonds: electron density lies above and below the plane of the nuclei.
- A double bond consists of one σ -bond and one π -bond.
- A triple bond has one σ -bond and two π -bonds.
- Often, the p-orbitals involved in π -bonding come from unhybridized orbitals.
- π -bonds are usually weaker than σ -bonds.

Let's look at ethene (or ethylene), C_2H_4 . It has:

- one σ - and one π -bond;
- both C atoms sp^2 hybridized;
- both C atoms with trigonal planar electron pair and molecular geometries.

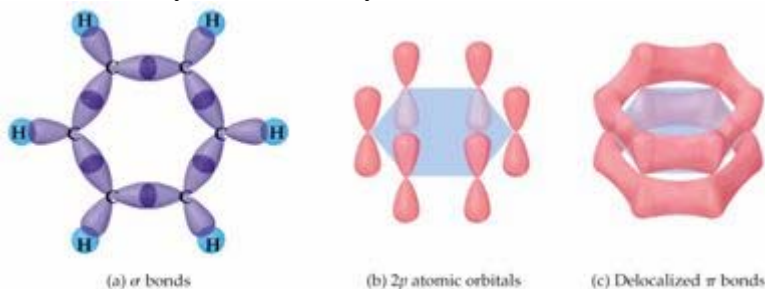


The lone p bonds can overlap to form a π -bond.



For the triple bond (as in ethyne (or acetylene), C_2H_2), two separate p orbital pairs overlap to form 2 π -bonds.

The double bond in ethylene and the triple bond in acetylene are localized between the two atoms that form the bond. In the case of benzene, C_6H_6 , the π -bonds are delocalized, which mean that they are essentially distributed over all the carbon atoms.



Molecular Orbitals

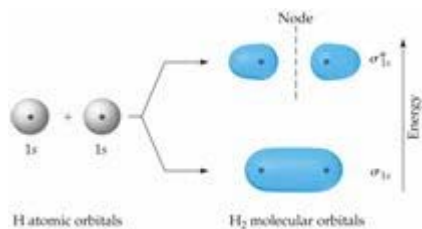
Some aspects of bonding are better explained by **molecular orbital theory**.

Just as we used wave functions to describe atomic orbitals (AO), we can use wave functions to discuss molecular orbitals (MO).

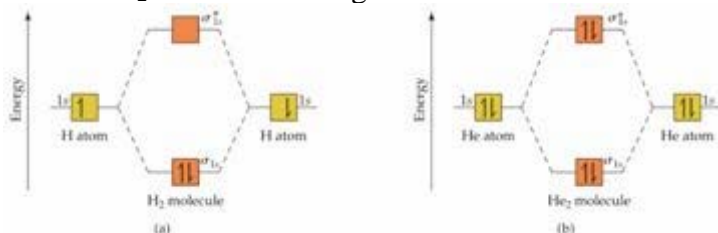
- Molecular orbitals:
 - each contain a maximum of two electrons;
 - have definite energies;
 - can be visualized with contour diagrams;
 - are associated with an entire molecule.

Let's look first at the hydrogen molecule, H_2 .

- When two AOs overlap, two MOs form.
- Therefore, $1s (H) + 1s (H)$ must result in two MOs for H_2 :
 - one has electron density between nuclei (bonding MO);
 - one has little electron density between nuclei (antibonding MO).
- MOs resulting from s orbitals are σ MOs.
- σ (bonding) MO is lower energy than σ^* (antibonding) MO.
- σ (bonding) MO is also lower in energy than the individual $1s$ orbitals.



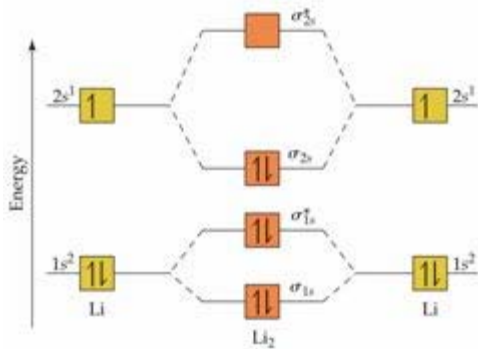
- Energy level diagram or MO diagram shows the energies and electrons in an orbital.
- The total number of electrons in all atoms is placed in the MOs starting from lowest energy (σ_{1s}) and ending when you run out of electrons.
 - Note that electrons in MOs have opposite spins.
- H₂ has two bonding electrons.
- He₂ has two bonding electrons and two antibonding electrons.



- We define Bond Order = $\frac{1}{2}$ (bonding electrons – antibonding electrons)
 - Bond order = 1 for single bond.
 - Bond order = 2 for double bond.
 - Bond order = 3 for triple bond.
 - Fractional bond orders are possible.
- For H₂
 - Bond Order = $\frac{1}{2}(2 - 0) = 1$
 - Therefore, H₂ has a single bond.
- For He₂
 - Bond Order = $\frac{1}{2}(2 - 2) = 0$
 - Therefore He₂ is not a stable molecule

Molecular Orbitals for Li₂ and Be₂

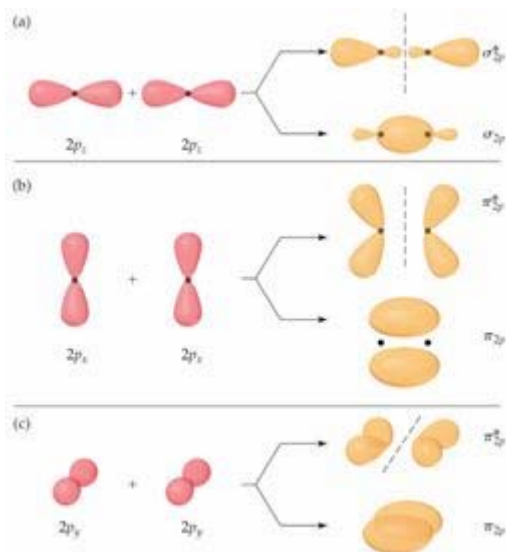
- We look at homonuclear diatomic molecules (e.g. Li₂, Be₂, B₂ etc.).
- AOs combine according to the following rules:
 - The number of MOs = number of AOs;
 - AOs of similar energy combine;
 - As overlap increases, the energy of the MO decreases;
- Pauli: each MO has at most two electrons;
- Hund: for degenerate orbitals, each MO is first occupied by one electron before pairing.
- Each 1s orbital combines with another 1s orbital to give one σ_{1s} and one σ^*_{1s} orbital, both of which are occupied (since Li and Be have 1s² electron configurations).
- Each 2s orbital combines with another 2s orbital, two give one σ_{2s} and one σ^*_{2s} orbital.
- The energies of the 1s and 2s orbitals are sufficiently different so that there is no cross-mixing of orbitals (i.e. we do not get 1s + 2s).



- There are a total of 6 electrons in Li_2 :
 - 2 electrons in σ_{1s} ;
 - 2 electrons in σ^*_{1s} ;
 - 2 electrons in σ_{2s} ; and
 - 0 electrons in σ^*_{2s} .
- Since the $1s$ AOs are completely filled, the σ_{1s} and σ^*_{1s} are filled. We generally ignore core electrons in MO diagrams.
- Li_2 molecules are observed in the vapor phase
- There are a total of 8 electrons in Be_2 :
 - 2 electrons in σ_{1s} ;
 - 2 electrons in σ^*_{1s} ;
 - 2 electrons in σ_{2s} ; and
 - 2 electrons in σ^*_{2s} .
$$\text{Bond Order} = \frac{1}{2}(4 - 4) = 0$$
- Since the bond order is zero, Be_2 does not exist.

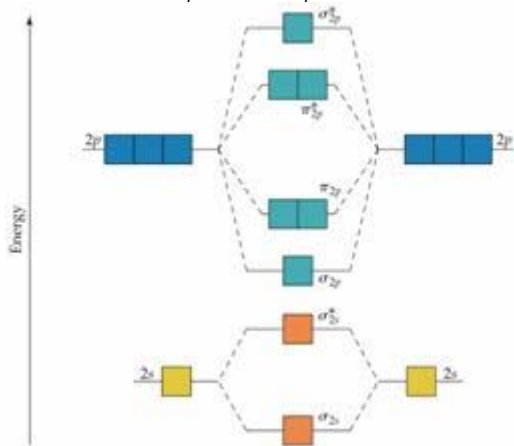
Molecular Orbitals from 2p Atomic Orbitals

- There are two ways in which two p orbitals overlap:
 - end-on so that the resulting MO has electron density on the axis between nuclei (i.e. σ type orbital);
 - sideways so that the resulting MO has electron density above and below the axis between nuclei (i.e. π type orbital).
- The six p -orbitals (two sets of 3) must give rise to 6 MOs:
 - σ , σ^* , π , π^* , π , and π^* .
 - Therefore there is a maximum of 2 π bonds that can come from p -orbitals.
- The relative energies of these six orbitals can change.



Electronic Configurations for B_2 through Ne_2

- $2s$ Orbitals are lower in energy than $2p$ orbitals so σ_{2s} orbitals are lower in energy than σ_{2p} orbitals.
- There is greater overlap between $2p_z$ orbitals (they point directly towards one another) so the σ_{2p} is MO in lower in energy than the π_{2p} orbitals.
- There is greater overlap between $2p_z$ orbitals so the σ^*_{2p} in MO is higher in energy than the π^*_{2p} orbitals.
- The π_{2p} and π^*_{2p} orbitals are doubly degenerate.

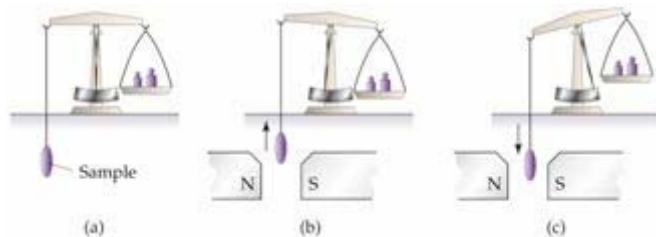


- As the atomic number decreases, it becomes more likely that a $2s$ orbital on one atom can interact with the $2p$ orbital on the other.
 - As the $2s$ - $2p$ interaction increases, the σ_{2s} MO lowers in energy and the σ_{2p} orbital increases in energy.
- For B_2 , C_2 and N_2 the σ_{2p} orbital is higher in energy than the π_{2p} .
- For O_2 , F_2 and Ne_2 the σ_{2p} orbital is lower in energy than the π_{2p} .
- Once the relative orbital energies are known, we add the required number of electrons to the MOs, taking into account Pauli's exclusion principle and Hund's rule.
 - As bond order increases, bond length decreases.
 - As bond order increases, bond energy increases.

	Large 2s-2p interaction			Small 2s-2p interaction		
	B ₂	C ₂	N ₂	O ₂	F ₂	Ne ₂
σ_{2s}^*	\square	\square	\square	\square	\square	\square
π_{2p}^*	\square	\square	\square	$\uparrow \uparrow$	$\uparrow \downarrow$	$\uparrow \downarrow$
σ_{2p}^*	\square	\square	\square	$\uparrow \downarrow$	$\uparrow \downarrow$	$\uparrow \downarrow$
π_{2p}	$\uparrow \uparrow$	$\uparrow \downarrow$	$\uparrow \downarrow$	$\uparrow \downarrow$	$\uparrow \downarrow$	$\uparrow \downarrow$
σ_{2s}	$\uparrow \downarrow$	$\uparrow \downarrow$	$\uparrow \downarrow$	$\uparrow \downarrow$	$\uparrow \downarrow$	$\uparrow \downarrow$
σ_{2p}	$\uparrow \downarrow$	$\uparrow \downarrow$	$\uparrow \downarrow$	$\uparrow \downarrow$	$\uparrow \downarrow$	$\uparrow \downarrow$
Bond order	1	2	3	2	1	0
Bond enthalpy (kJ/mol)	200	420	940	495	155	—
Bond length (Å)	1.79	1.31	1.10	1.21	1.43	—
Magnetic behavior	Paramagnetic	Diamagnetic	Diamagnetic	Paramagnetic	Diamagnetic	—

Electronic Configurations and Molecular Properties

- Two types of magnetic behavior:
 - paramagnetism** (unpaired electrons in molecule): strong attraction between magnetic field and molecule;
 - diamagnetism** (no unpaired electrons in molecule): weak repulsion between magnetic field and molecule.
- Magnetic behavior is detected by determining the mass of a sample in the presence and absence of magnetic field:
 - large increase in mass indicates paramagnetism (c of figure),
 - small decrease in mass indicates diamagnetism (b of figure).



- Experimentally O₂ is paramagnetic.
- The Lewis structure for O₂ shows no unpaired electrons.
- The MO diagram for O₂ shows 2 unpaired electrons in the π^*_{2p} orbital.
- Experimentally, O₂ has a short bond length (1.21 Å) and high bond dissociation energy (495 kJ/mol). This suggests a double bond.
- The MO diagram for O₂ predicts both paramagnetism and the double bond (bond order = 2).

Heteronuclear Diatomic Molecules

A heteronuclear diatomic molecule contains two different atoms, such as NO.

We can draw a MO energy diagram and look at the NO molecule. It will look similar to that above for O₂, but the energies of the 2s and 2p orbitals start at slightly different energy levels.