Chapter 5: Advanced Theories of Covalent Bonding

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1

Valence Bond Theory

According to **valence bond theory**, atoms share electrons when atomic orbitals overlap.

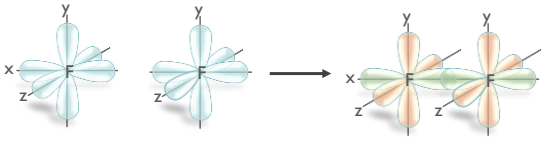
1) A bond forms when single occupied atomic orbitals on two atoms overlap.
2) The two electrons shared in the region of orbital overlap must be of opposite spin.
3) Formation of a bond results in a lower potential energy for the system.

The H–H bond in H_2 forms when the singly occupied 1s orbitals of the two H atoms overlap:

The F–F bond in F_2 forms when the singly occupied 2*p* orbitals of the two F atoms overlap:

$2s^2$ **$2p^5$**

Orbital Diagram for F



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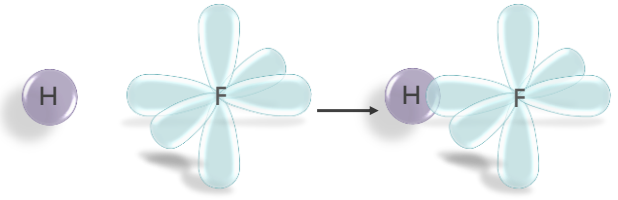
Valence Bond Theory

The H−F bond in HF forms when the singly occupied 1s orbital on the H atom overlaps with the single occupied *2p* orbital of the F atom:



Bond Lengths and Bond Energies of H_2, F_2, and HF		
	Bond Length (Å)	Bond Energy (kJ/mol)
H_2	0.74	436.4
F_2	1.42	150.6
HF	0.92	568.2

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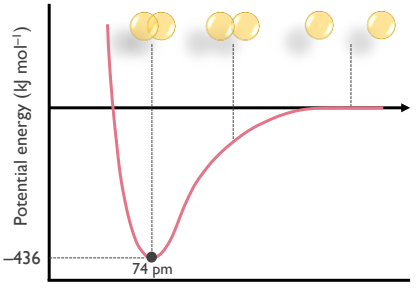
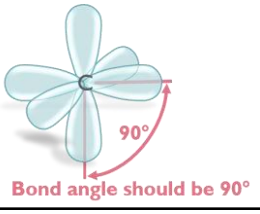
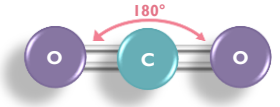
Valence Bond Theory

A covalent bond will form if the potential energy of the molecule is lower than the combined potential energies of the isolated atoms



Hybridization or mixing of atomic orbitals can account for observed bond angles in molecules that could not be described by the direct overlap of atomic orbitals.





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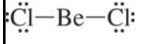
Hybridization of Atomic Orbitals

$BeCl_2$ Lewis theory and VSEPR theory predict Cl–Be–Cl bond angle of 180°



2 electron domains; Linear molecular geometry

A ground state beryllium atom can not form two bonds; there are no unpaired electrons.

An excited state configuration for Be has two unpaired electrons and can form to bonds.

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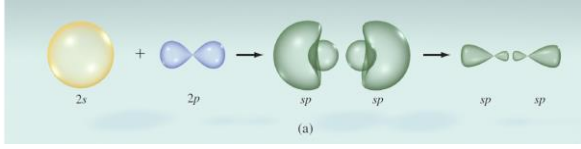
Hybridization of Atomic Orbitals

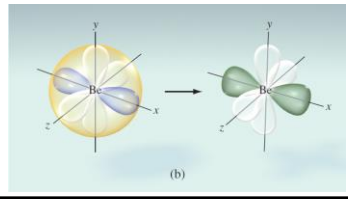
$BeCl_2$

Experimentally the bond in $BeCl_2$ bonds are identical in length and strength. Mixing of one *s* orbital and one *p* orbital to yield two *sp* orbitals.



The 2*s* orbital and one of the 2*p* orbitals on Be combine to form two *sp* hybrid orbitals.

Like any two electron domains, the hybrid orbitals on Be are 180° apart.



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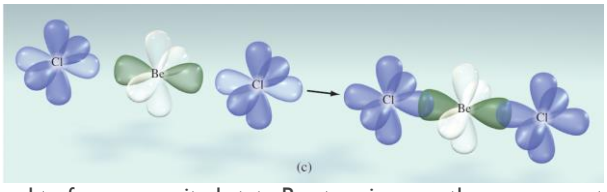
Hybridization of Atomic Orbitals

$BeCl_2$

The hybrid orbitals on Be each overlap with a singly occupied 3*p* orbital on a Cl atom.



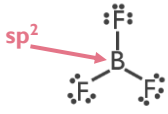
The energy required to form an excited state Be atom is more than compensated for by the energy given off when a bond forms.

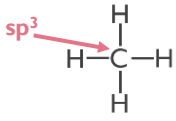
What is the hybridization of the central atom in BF_3 and CH_4?

Orbitals available in a single row on the Periodic Table:

1s; 3p; 5d; 7f

To find hybridization, use these orbitals to add up to the number of electron domains





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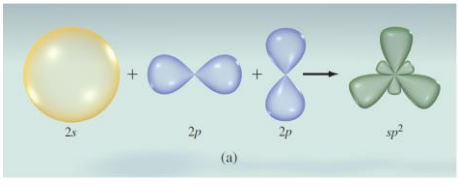
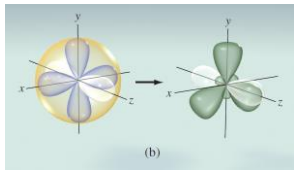
Hybridization of Atomic Orbitals

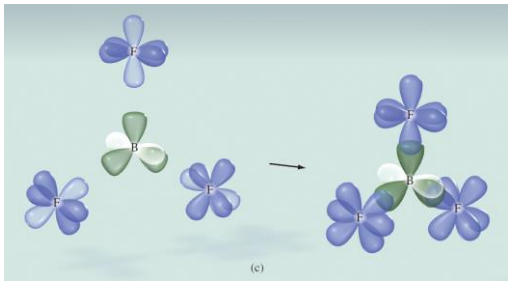
BF_3

Mixing of one *s* orbital and two *p* orbitals to yield three sp^2 orbitals.





Hybrid orbitals on boron overlap with 2*p* orbitals on fluorine.



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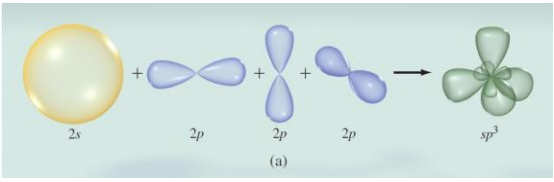
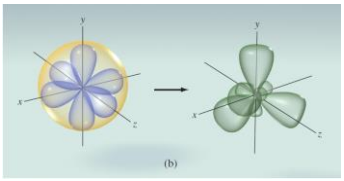
Hybridization of Atomic Orbitals

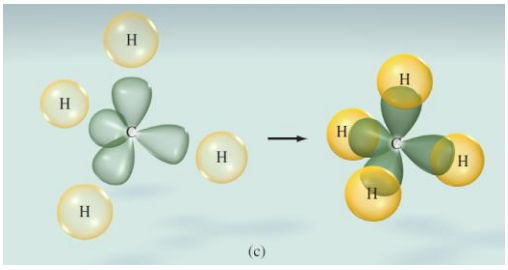
CH_4

Mixing of one *s* orbital and three *p* orbitals to yield four sp^3 orbitals





Hybrid orbitals on carbon overlap with 1*s* orbitals on hydrogen.



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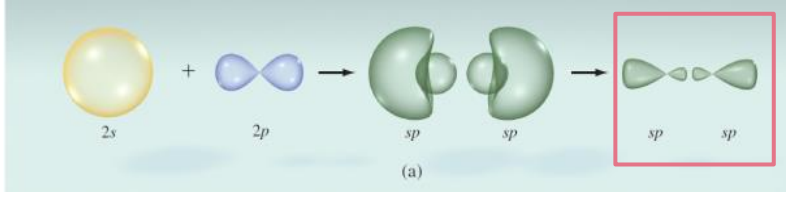
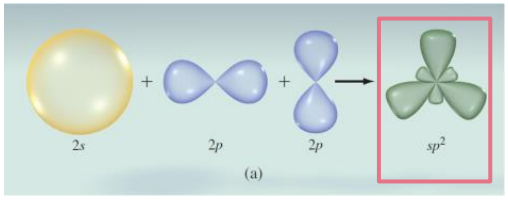
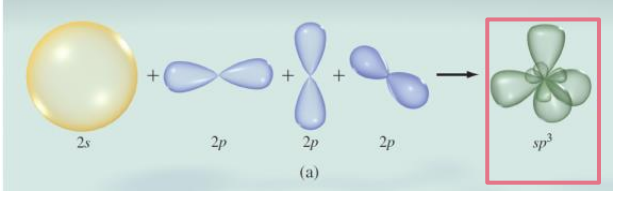
Hybridization of Atomic Orbitals







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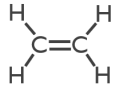
Hybridization in Molecules Containing Multiple Bonds

Valence bond theory and hybridization can be used to describe the bonding in molecules containing double and triple bonds.

ethylene (C_2H_4)



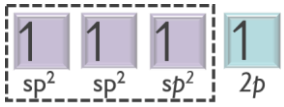
Each carbon has three electron domains:
2 single bonds
1 double bond
Expect sp^2 hybridization

Maximize unpaired electrons on carbon by promotion:

Hybridize the required number of atomic orbitals (one for each e⁻ domain on carbon)

One unhybridized atomic 2p orbital gives rise to multiple bonds

Three equivalent sp^2 hybrid orbitals explain three bonds around carbon



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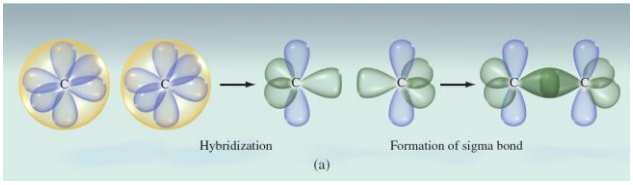
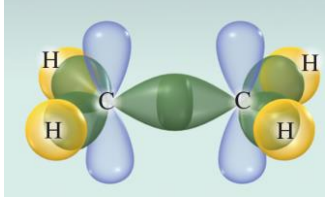
Hybridization in Molecules Containing Multiple Bonds

A **sigma (σ) bond** forms when sp^2 hybrid orbitals on the C atoms overlap. In a sigma bond, the shared electron density lies directly along the internuclear axis.



The ethylene molecule contains five sigma bonds:
- 1 between the two carbon atoms (sp^2 and sp^2 overlap)
- 4 between the C and H atoms (sp^2 and 1s overlap)



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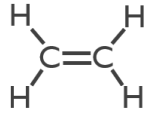
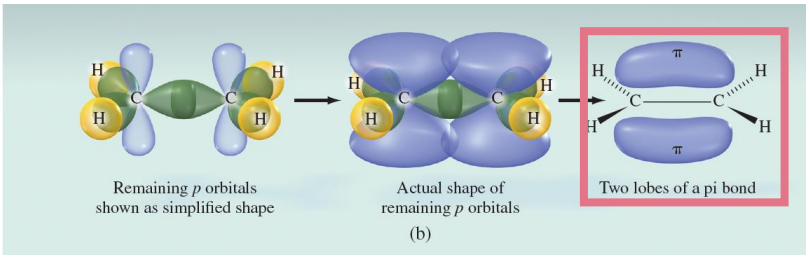
Hybridization in Molecules Containing Multiple Bonds

The remaining unhybridized p orbital is perpendicular to the plane in which the atoms of the molecule lie. The unhybridized p orbitals overlap in a sideways fashion to form a **pi (π) bond**.

ethylene (C_2H_4)





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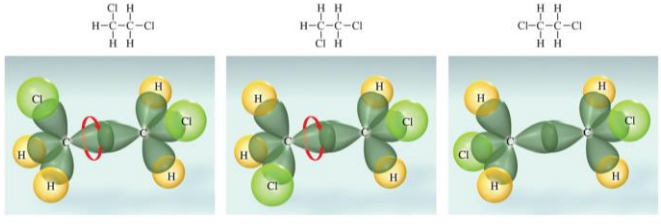
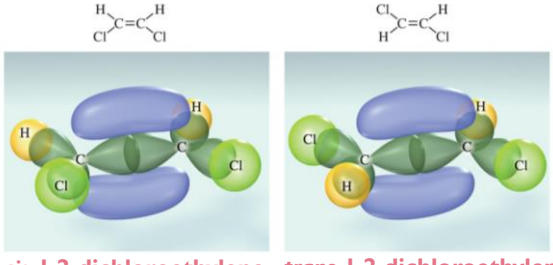
Hybridization in Molecules Containing Multiple Bonds

Sigma bonds exhibit free rotation around the bond axis.



All three Lewis structures represent the same molecule.

Pi bonds restrict free rotation around the bond axis.



There are two isomers of 1,2–dichloroethylene

***cis*-1,2-dichloroethylene** ***trans*-1,2-dichloroethylene**

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Hybridization in Molecules Containing Multiple Bonds

The acetylene molecule is linear with *sp* hybridized carbons.

H—C≡C—H
acetylene (C_2H_2)

Promotion of an electron maximizes the number of unpaired electrons:

3 sigma bonds:
1 between the two carbon atoms (*sp* and *sp*)
2 between the C and H atoms (*sp* and 1*s*)

2 pi bonds
2 between the two carbon atoms (2*p* and 2*p*)

The 2*s* orbital and one of the 2*p* orbitals then mix to form two *sp* hybrid orbitals:

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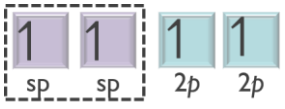
Hybridization in Molecules Containing Multiple Bonds

The acetylene molecule is linear with *sp* hybridized carbons.

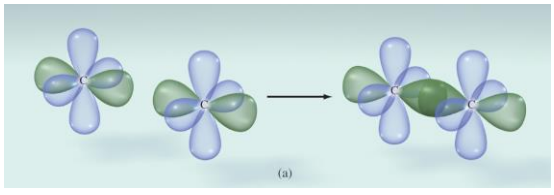
H—C≡C—H
acetylene (C_2H_2)

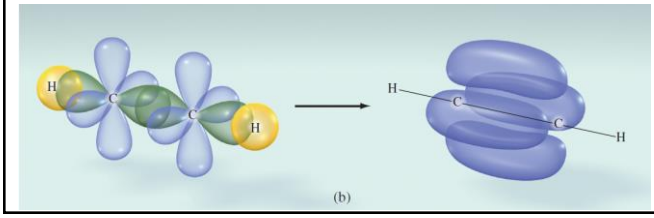
Two equivalent *sp* hybrid orbitals give rise to 2 sigma bonds



Two unhybridized atomic 2p orbitals gives rise to 2 pi bonds

3 sigma bonds:
1 between the two carbon atoms (*sp* and *sp*)
2 between the C and H atoms (*sp* and 1*s*)





2 pi bonds
2 between the two carbon atoms (2*p* and 2*p*)

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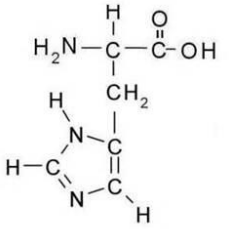
Practice

In addition to its use in aqueous solution as a preservative for laboratory specimens, formaldehyde gas is used as an antibacterial fumigant. Use hybridization to explain the bonding in formaldehyde (CH_2O).

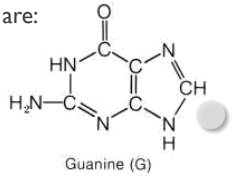
Determine hybridization around each atom in histidine and list the total number of sigma and pi bonds.



Histidine

The hybridization for carbons and nitrogens in guanine are:

A. All carbons sp^2/nitrogens both sp^2 and sp^3
B. Carbons both sp^2 and sp^3/ all nitrogens sp^2
C. All carbons sp^2/all nitrogens sp^2
D. Carbons both sp^2 and sp^3/ nitrogens both sp^2 and sp^3



Guanine (G)

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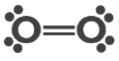
Molecular Orbital Theory

Lewis structures and valence bond theory fail to predict some important properties of molecules.

Paramagnetism is a result of a molecule's electron configuration. Species that contain one or more unpaired electrons are paramagnetic. Paramagnetic species are attracted to magnet fields.



The Lewis structure for O_2 shows no unpaired electrons.

O_2 exhibits paramagnetism.

Species that contain paired electrons are diamagnetic. **Diamagnetic** species are weakly repelled by magnetic fields.

The Lewis structure for N_2 shows no unpaired electrons.

N_2 exhibits diamagnetism.

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Molecular Orbital Theory

Another bonding theory is needed to describe the paramagnetism of O_2.

In **molecular orbital theory**, the atomic orbitals combine to form new orbitals that are the "property" of the entire molecule. The new orbitals are called **molecular orbitals**.

Molecular orbitals have characteristics like atomic and hybrid orbitals:

- specific shapes
- specific energies
- accommodate a maximum of 2 electrons each
- electron filling follows the Pauli exclusion principle
- the number of molecular orbitals obtained equals the number of orbitals combined

H_2 is the simplest homonuclear diatomic molecule.

Valence bond theory:

H_2 forms when from the overlap of the 1s orbitals.

Molecular orbital theory:

H_2 forms when the 1s orbitals combine to give molecular orbitals. Molecular orbitals result from the **constructive** and **destructive** combination of atomic orbitals.

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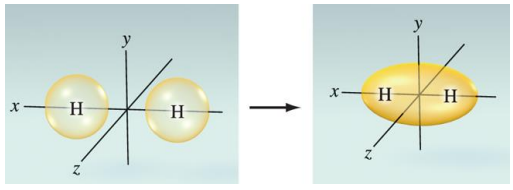
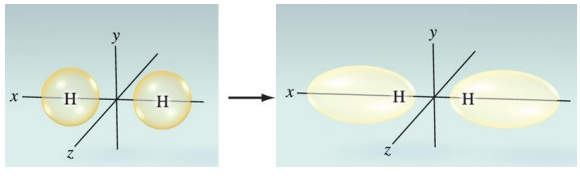
Bonding and Antibonding Molecular Orbitals

Constructive combination of the two 1s orbitals gives rise to a molecular orbital that lies along the internuclear axis **(bonding molecular orbital)**.
Constructive combination increases the electron density between the two nuclei.



Destructive combination of the two 1s orbitals gives rise to a molecular orbital that lies along the internuclear axis but does not lie between the two nuclei **(antibonding molecular orbital)** .
Electron density in this molecular orbital pulls the two nuclei in opposite directions.



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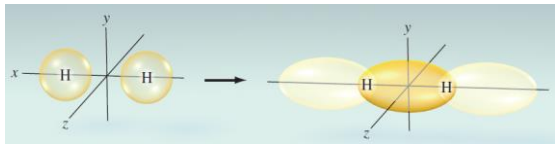
s orbitals combining to make Molecular Orbitals

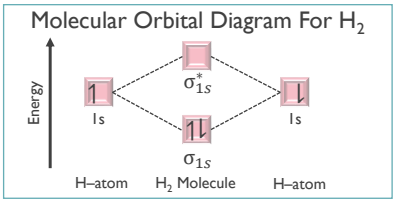
Molecular orbitals that lie along the internuclear axis are referred to as σ molecular orbitals.

Examples:
σ_{1s} bonding molecular orbital from the combination of two 1*s* orbitals
σ^*_{1s} antibonding molecular orbital from the combination of two 1*s* orbitals.



Molecular orbitals have specific energies. Electrons in bonding molecular orbitals stabilize the molecule and are LOWER in energy than the isolated atomic orbitals.

Electrons in antibonding molecular orbitals destabilize the molecule and are HIGHER in energy than the isolated atomic orbitals.

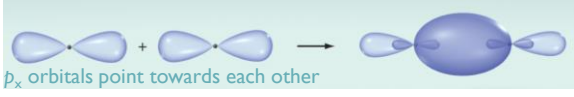


The * distinguishes an antibonding molecular orbital from a bonding orbital.

p Molecular Orbitals

p atomic orbitals also form molecular orbitals by both constructive and destructive combination. The orientations of p_x, p_y, and p_z give rise to two different types of molecular orbitals:

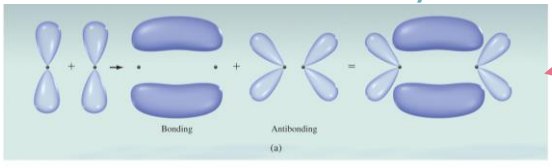
σ molecular orbitals – electron density along the internuclear axis



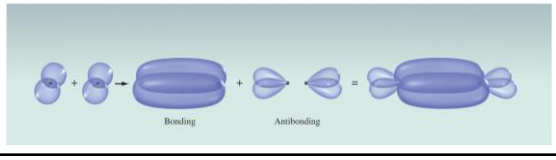
bonding and antibonding σ molecular orbitals

p atomic orbitals also form molecular orbitals by both constructive and destructive combination.

π molecular orbitals – electron density above and below the internuclear axis



bonding and antibonding σ molecular orbitals

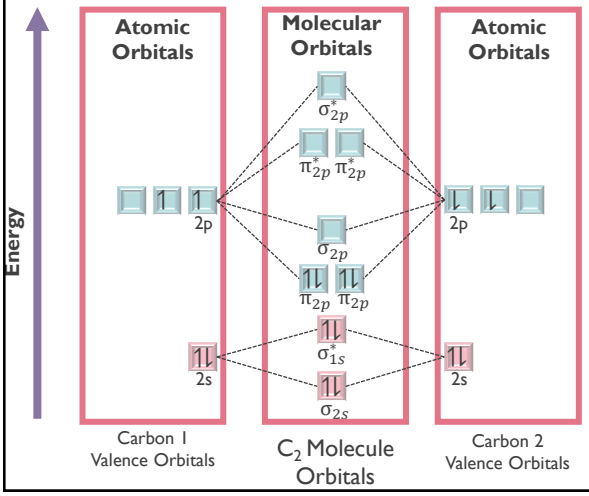


Molecular Orbital Diagrams

Filling molecular orbital diagrams follows the same rules as the filling of atomic orbitals.

- Lower energy orbitals fill first.
- Each orbital can accommodate a maximum of two electrons with opposite spin.
- Hund's rule is obeyed.

Let's look at two carbon atoms forming C_2 : Carbon has 4 Ve^-



When making molecular orbitals, *s* orbitals only interact with *s* orbitals. *p* orbitals only interact with *p* orbitals

Molecular orbitals resulting from the combination of *p* atomic orbitals are higher than those resulting from the combination of *s* atomic orbitals.

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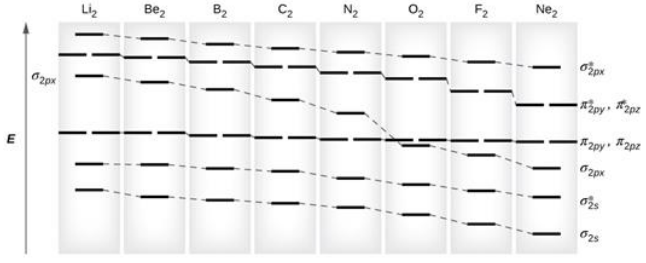
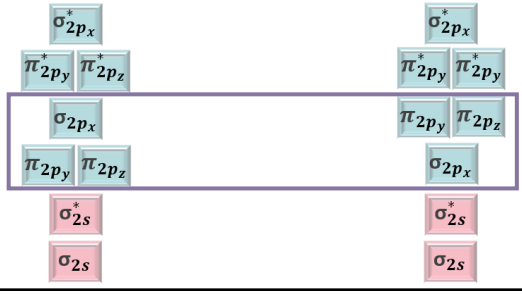
π Molecular Orbitals



This arrangement of orbitals is found in Li_2, B_2, C_2 and N_2.

This arrangement of orbitals is found in O_2, F_2, and Ne_2



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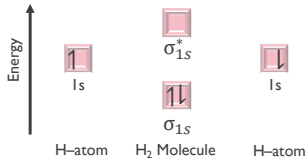
Bond Order

The **bond order** indicates how stable a molecule is. The higher the bond order, the more stable a molecule is.

$$\text{bond order} = \frac{\text{No. of e}^- \text{ in bonding orbitals} - \text{No. of e}^- \text{ in antibonding orbitals}}{2}$$

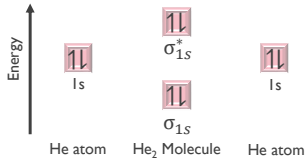
Find the bond order for the H_2 molecule:

$$\text{bond order} = \frac{2-0}{2} = 1$$



Find the bond order for the He_2 molecule:

$$\text{bond order} = \frac{2-2}{2} = 0$$



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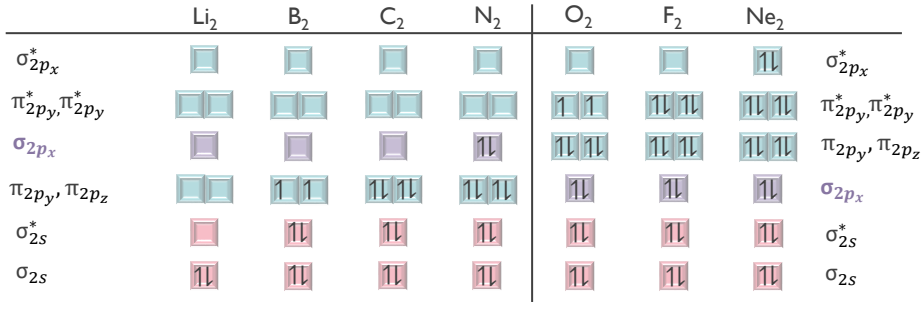
Molecular Orbitals of Homonuclear Diatomic Molecules



	Li_2	B_2	C_2	N_2	O_2	F_2	Ne_2
Bond Order	1	1	2	3	2	1	0
Bond Length (pm)	267	159	131	110	121	142	–
Bond Enthalpy (kJ/mol)	104.6	288.7	627.6	941.4	498.7	156.9	–
Magnetic Properties	Diamagnetic	Paramagnetic	Diamagnetic	Diamagnetic	Paramagnetic	Diamagnetic	–
Sigma Bonds	1	0	0	1	1	1	0
Pi Bonds	0	1	2	2	1	0	0

Remember that for O_2 and F_2, σ_{2p_x} is lower in energy than π_{2p_y} and π_{2p_z}

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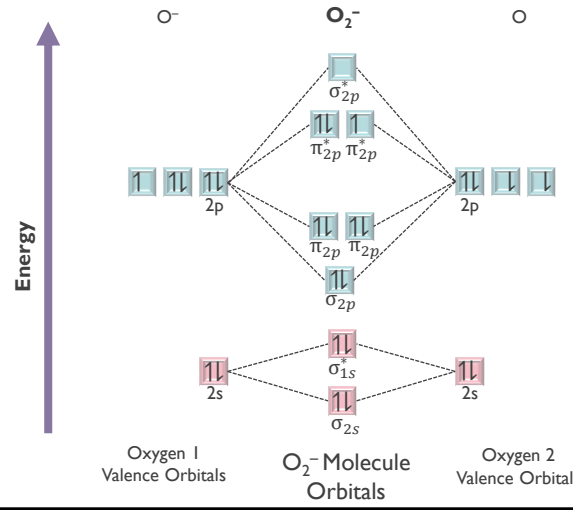
Practice

The superoxide ion (O_2^-) has been implicated in several degenerative conditions, including aging and Alzheimer's disease. Using molecular orbital theory, determine whether (O_2^-) is paramagnetic or diamagnetic, and then calculate its bond order.



Oxygen has 6 valence electrons, and we have two oxygens. Also we have one negative charge.

6+6+1=13 e^- to work with

$$\text{B. O.} = \frac{(8-5)}{2} = 1.5$$

Paramagnetic

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Bonding Theories and Descriptions of Molecules with Delocalized Bonding

Lewis Theory

Strength:

qualitative prediction of bond strength and bond length

Weakness:

two-dimensional model, real molecules are three dimensional

fails to explain *why* bonds form

Valence–Shell Electron–Pair Repulsion Model

Strength:

predict the shape of many molecules and polyatomic ions

Weakness:

fails to explain why bonds form (based on Lewis theory)

Valence Bond Theory

Strength:

covalent bonds form when atomic orbitals overlap

Weakness:

fails to explain the bonding in many molecules

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Bonding Theories and Descriptions of Molecules with Delocalized Bonding

Hybridization of Atomic Orbitals

Strength:

an *extension* of valence bond theory. Using hybrid orbitals it is possible to explain the bonding and geometry of more molecules

Weakness:

fails to predict some important properties, such as magnetism

Molecular Orbital Theory

Strength:

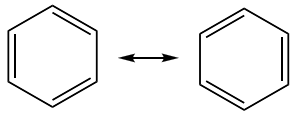
accurately predict the magnetic and other properties of molecules

Weakness:

complex

Some molecules are best described using a combination of models. Benzene, C_6H_6, is represented with two resonance structures:

The π bonds in benzene are **delocalized** – spread out over the entire molecule.



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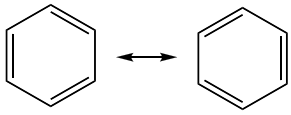
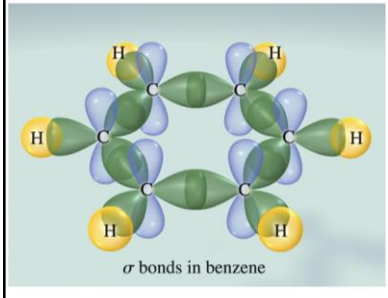
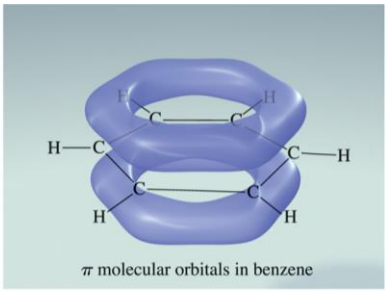
Bonding Theories and Descriptions of Molecules with Delocalized Bonding

The π bonds in benzene are **delocalized** – spread out over the entire molecule.







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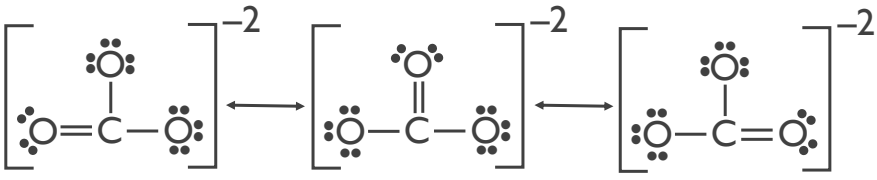
More Resonance Examples

It takes three resonance structures to represent the carbonate ion CO_3^{2-}:



None of the three, though, is a completely accurate description. As with benzene, the bonds that are shown in the Lewis structure as one double and two single are three equivalent bonds. Use a combination of valence bond theory and molecular orbital theory to explain the bonding in CO_3^{2-}.