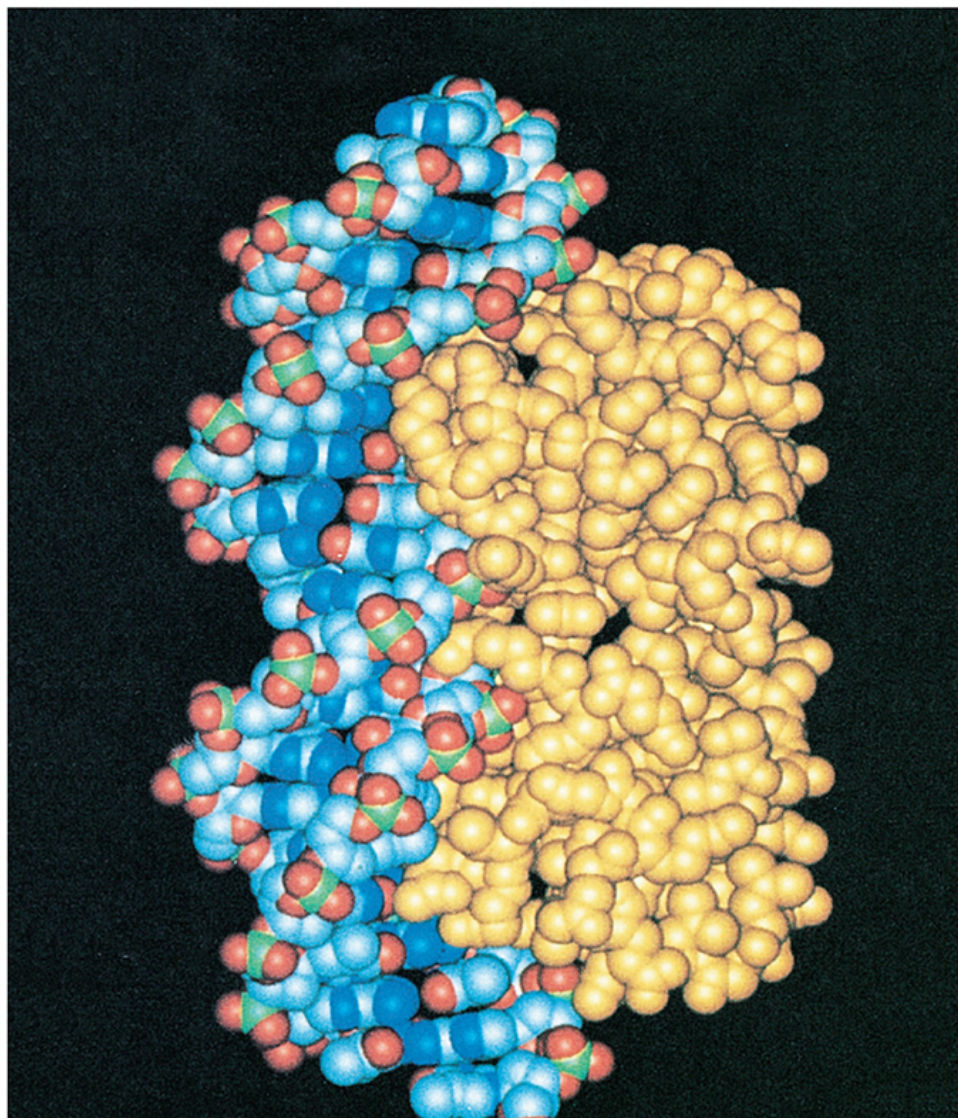


Chapter 10

Molecular Geometry and Hybridization of Atomic Orbitals

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Courtesy Aneel Aggarwal, Ph.D., and Stephen C. Harrison, Department of Biochemistry and Molecular Biology, Harvard University, from A.K. Aggarwal, et al., November 1988. Recognition of a DNA operator by the repressor of phage 434: A view at high resolution. *Science* 242, p. 899–907. ©1988 American Association for the Advancement of Science

Molecules and Magnetic Properties

- Draw Lewis structures for N_2 and O_2 . Are there any unpaired electrons?

- For a substance to be attracted to a magnet it must possess unpaired electrons.

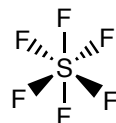
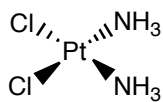
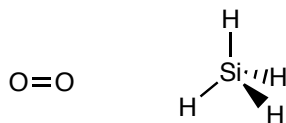
When Liquid N_2 or O_2 is poured between the poles of a magnet which of these will be attracted to the poles of the magnet.

Molecules

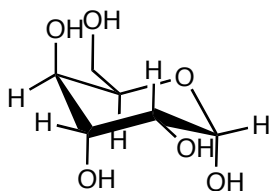
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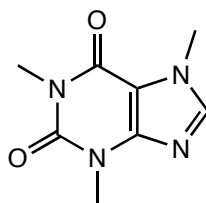
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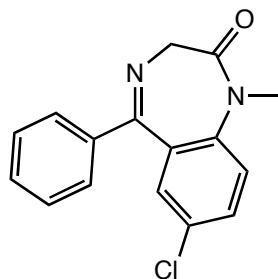
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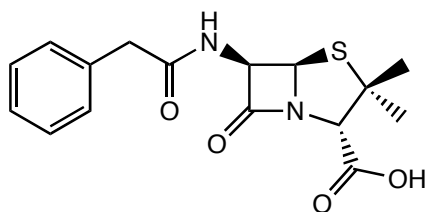
Glucose



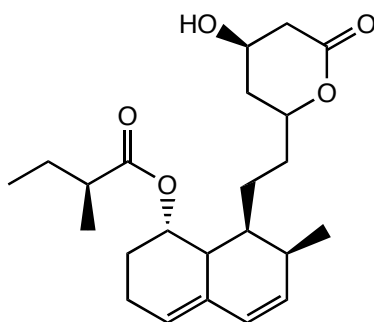
Caffeine



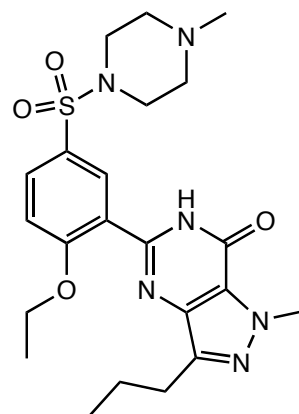
Diazepam (Valium™)



Penicillin



Lovastatin (Mevacor™)

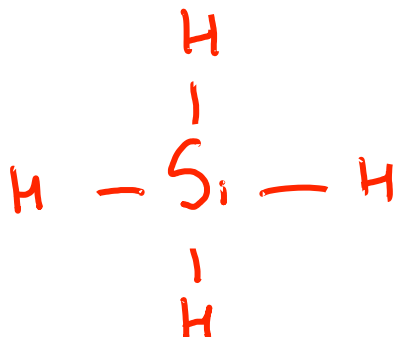


Sildenafil (Viagra™)

Molecular Geometry:

Using Valence-Shell Electron Pair Repulsion (VSEPR) model to determine the shape of a molecule

- Lets write the lewis structure of SiH_4



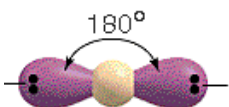
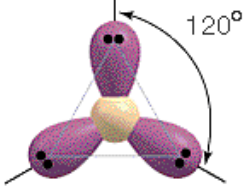
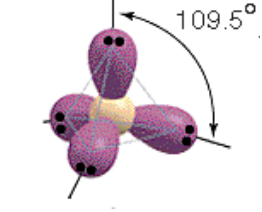
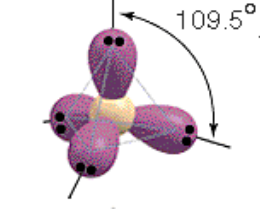
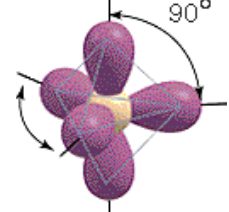
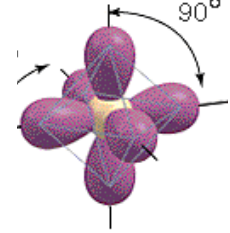
- What is taken into account by the Valence-Shell Electron Pair Repulsion (VSEPR) model to determine the geometry of a molecule?
- What count as electron pairs?

Molecular Geometry: No Lone Pairs

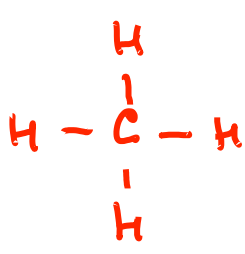
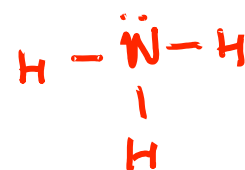

Guidelines for applying the VSEPR Model to predict molecular geometry

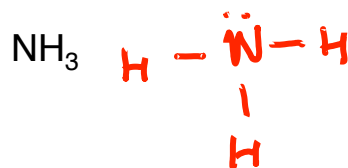
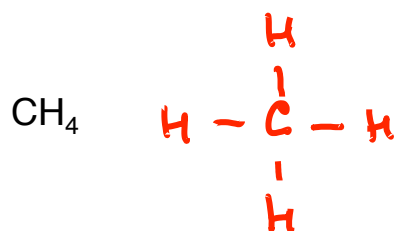
1. Determine the Lewis structure.
2. Determine the central atom and sum the electron pairs around it.
3. Determine the arrangement of the pairs that minimizes electron-pair repulsions. This type of geometry is called the **electron-pair geometry**.
4. Disregard the lone pair(s). Name the molecular geometry from the positions of the **atoms**. This is the **molecular geometry**.

- Determine the molecular geometry of BeCl_2 , CO_2 , BF_3 , CCl_4 , PF_5 , and SF_6

Molecule	Lewis Structure	Number of Electron Pairs	Arrangement of Electron Pairs	Electron-Pair/Molecular Geometry
BeCl_2	$\text{Cl}-\text{Be}-\text{Cl}$			
CO_2	$\text{O}=\text{C}=\text{O}$			
BF_3	$\begin{array}{c} \text{F}-\text{B}-\text{F} \\ \\ \text{F} \end{array}$			
CCl_4	$\begin{array}{c} \text{Cl} \\ \\ \text{Cl}-\text{C}-\text{Cl} \\ \\ \text{Cl} \end{array}$			
PF_5	$\begin{array}{c} \text{F} \\ \\ \text{F}-\text{P}-\text{F} \\ / \quad \backslash \\ \text{F} \quad \text{F} \end{array}$			
SF_6	$\begin{array}{c} \text{F} \\ \\ \text{F}-\text{S}-\text{F} \\ / \quad \backslash \\ \text{F} \quad \text{F} \\ \\ \text{F} \end{array}$			

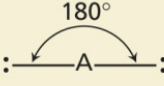
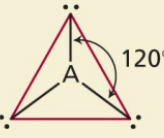
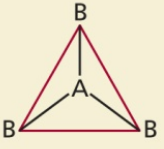
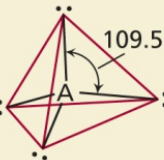
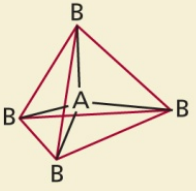
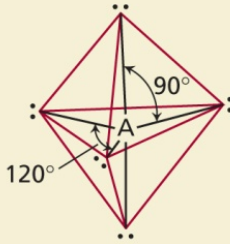
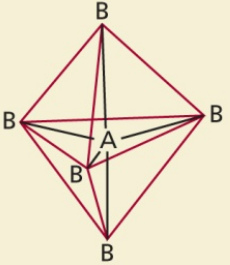
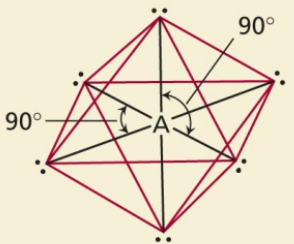
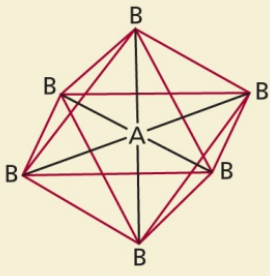
Molecular Shapes: Adding Lone Pairs

- Compare the molecular geometry of CH_4 (methane), NH_3 (ammonia), and H_2O (water)
- | Molecule | Lewis Structure | Number of Electron Pairs | Electron-Geometry | Molecular Geometry |
|----------------------|---|--------------------------|-------------------|--------------------|
| CH_4 |  | 4 | Tetrahedral | Tetrahedral |
| NH_3 |  | 4 | Tetrahedral | Trigonal Pyramidal |
| H_2O |  | 4 | Tetrahedral | Bent |



Note that the placement of the electron pairs determines the structure, but the name is based on the positions of the atoms. Therefore, it is incorrect to say that the NH_3 molecule is tetrahedral. It has a tetrahedral arrangement of electron

Table 10.1 Arrangement of Electron Pairs About a Central Atom (A) in a Molecule and Geometry of Some Simple Molecules and Ions in Which the Central Atom Has No Lone Pairs

Number of Electron Pairs	Arrangement of Electron Pairs*	Molecular Geometry*	Examples
2	 <p>Linear</p>	<p>B—A—B</p> <p>Linear</p>	BeCl ₂ , HgCl ₂
3	 <p>Trigonal planar</p>	 <p>Trigonal planar</p>	BF ₃
4	 <p>Tetrahedral</p>	 <p>Tetrahedral</p>	CH ₄ , NH ₄ ⁺
5	 <p>Trigonal bipyramidal</p>	 <p>Trigonal bipyramidal</p>	PCl ₅
6	 <p>Octahedral</p>	 <p>Octahedral</p>	SF ₆

Molecular Shapes: Adding Lone Pairs

- Predict molecular geometry of SF₄

There are 2 possibilities for placing the lone pair; which is the best geometry?

There 3 types of repulsive forces. The order of repulsive forces, from strongest to weakest is:

lone pair–lone pair > lone pair–bond pair > bond pair–bond pair

The closer together the electrons are forced, the stronger the repulsion between them.

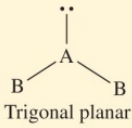
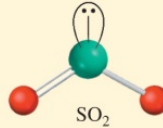
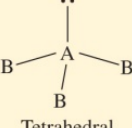
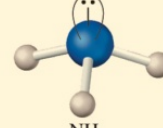
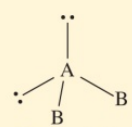
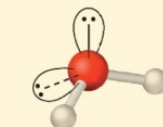
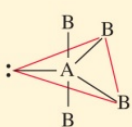

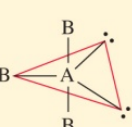

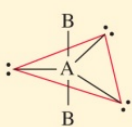
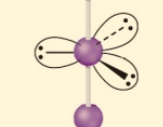
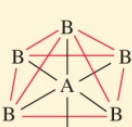

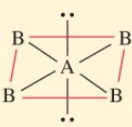
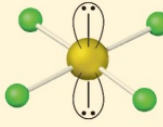
Therefore, the repulsion between two electron pairs is much more severe at an angle of 90° than at 120° or 180°, respectively.

lp-lp (90°)

lp-bp (90°)

bp-bp (90°)

Table 10.2 Geometry of Simple Molecules and Ions in Which the Central Atom Has One or More Lone Pairs

Class of molecule	Total number of electron pairs	Number of bonding pairs	Number of lone pairs	Arrangement of electron pairs*	Geometry	Examples
AB_2E	3	2	1	 <p>Trigonal planar</p>	Bent	 <p>SO_2</p>
AB_3E	4	3	1	 <p>Tetrahedral</p>	Trigonal pyramidal	 <p>NH_3</p>
AB_2E_2	4	2	2	 <p>Tetrahedral</p>	Bent	 <p>H_2O</p>
AB_4E	5	4	1	 <p>Trigonal bipyramidal</p>	Distorted tetrahedron (or seesaw)	 <p>SF_4</p>
AB_3E_2	5	3	2	 <p>Trigonal bipyramidal</p>	T-shaped	 <p>ClF_3</p>
AB_2E_3	5	2	3	 <p>Trigonal bipyramidal</p>	Linear	 <p>I_3^-</p>
AB_5E	6	5	1	 <p>Octahedral</p>	Square pyramidal	 <p>BrF_5</p>
AB_4E_2	6	4	2	 <p>Octahedral</p>	Square planar	 <p>XeF_4</p>

Deviations from Ideal Bond Angles

- How can we explain the following experimental observations?



H–C–H bond angle: 109.5°



H–N–H bond angle: 106.7°



H–O–H bond angle: 104.5°

Deviations from Ideal Bond Angles

- How can we explain the following experimental observations?

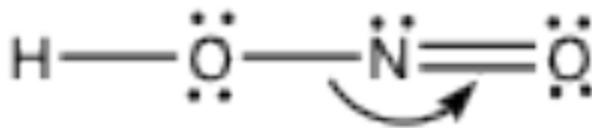


Cl–B–Cl bond angle: 120°



Cl–C–Cl bond angle: 111.8°

What is the approximate value of the ONO bond angle?

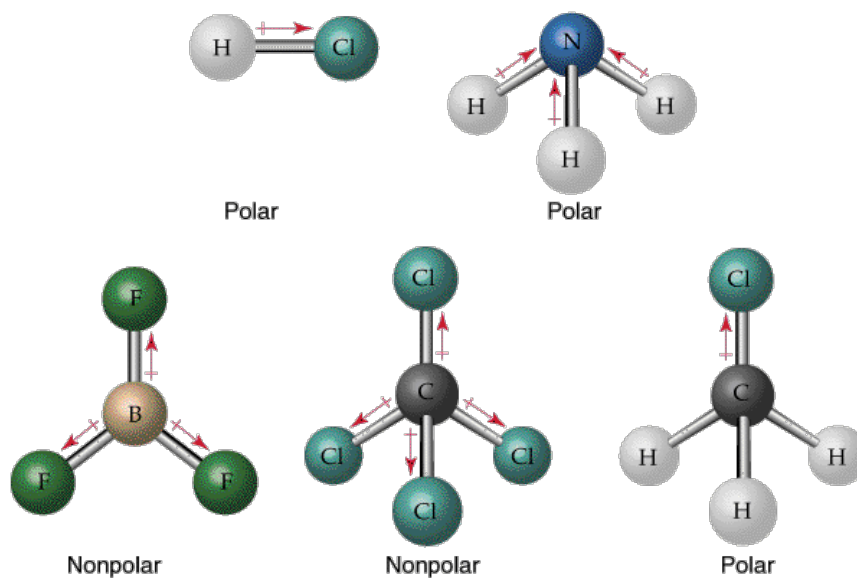


- 180 or slightly smaller
- 120 or slightly smaller
- 109.5 or slightly smaller

Polarity of Molecules

- Recall that bonds can be *polar* if there is a difference in electronegativity between the atoms in the bond. However, it is possible for a molecule with polar bonds to be *nonpolar*.

Let's look at other examples:

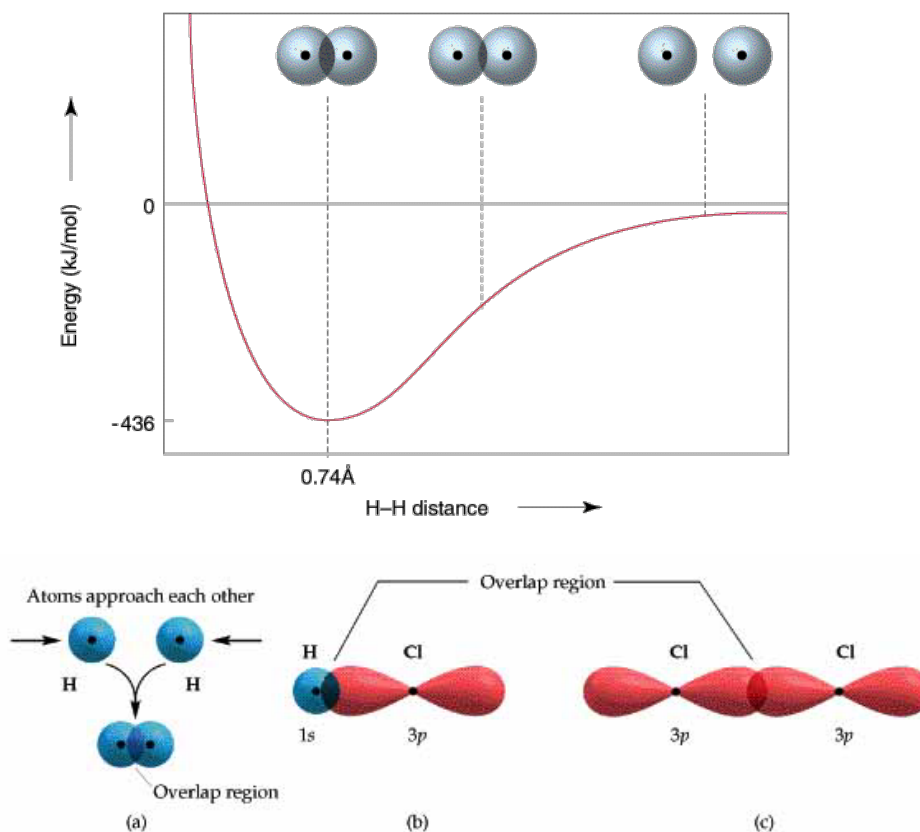


Valence Bond Theory

- Why do bonds form between atoms? How can we use atomic orbitals to explain bonding?
Let's look at the bonding in H_2 , HCl , and Cl_2 as examples.

What are the electron configurations of H and Cl?

How can these electron configurations be used to form bonds?



Looking at these pictures, can we understand why the bond lengths are:

H_2 0.74 Å

HCl 1.27 Å

Cl_2 1.99 Å

Hybridization: Why?

- How can we use atomic orbitals to account for the geometries of the molecules?
Consider the bonding in ammonia, NH_3 :

Draw the Lewis structure for ammonia:

How many bonds are being formed by nitrogen? What nitrogen orbitals are available?

Given those four orbitals, what geometry might we predict for ammonia?

What is the observed electron pair geometry of ammonia?

How can this be explained using hybridization?

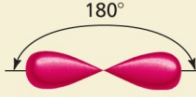
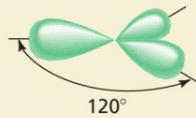
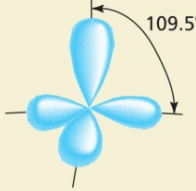
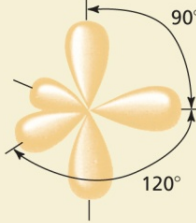
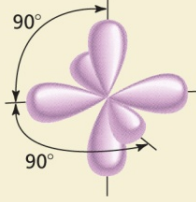
*Hybridization is a **convenient fiction**. It can be used to describe the bonding for most common geometries. Hybridization is not the reason but the way we can think about bonding between atoms.*

Hybridization: Quick and Dirty

- *A dirty secret:*

Hybridization is simply a code for electron-pair geometry. Let's take a look:

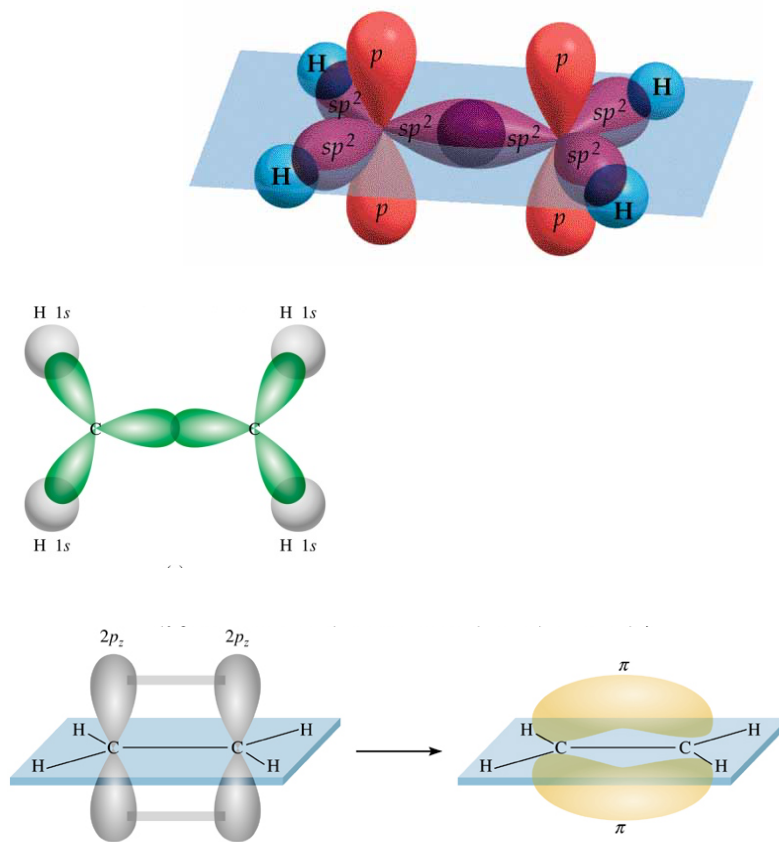
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Pure Atomic Orbitals of the Central Atom	Hybridization of the Central Atom	Number of Hybrid Orbitals	Shape of Hybrid Orbitals	Examples
s, p	sp	2	 <p>Linear</p>	BeCl_2
s, p, p	sp^2	3	 <p>Trigonal planar</p>	BF_3
s, p, p, p	sp^3	4	 <p>Tetrahedral</p>	$\text{CH}_4, \text{NH}_4^+$
s, p, p, p, d	sp^3d	5	 <p>Trigonal bipyramidal</p>	PCl_5
s, p, p, p, d, d	sp^3d^2	6	 <p>Octahedral</p>	SF_6

Hybridization: Multiple Bonds

- Consider ethene (also called ethylene): C_2H_4 . Draw a Lewis structure, and use it to determine the geometry and hybridization of each of the carbon atoms.

How can we describe the double bond in terms of orbital overlap?









The Master Table of Bonding and Hybridization

- Let's fill out the following table of bonding and hybridization:

Number of Electron Domains	Electron-Pair Geometry	Hybridization	Number of σ bonds and lone pairs	Leftover p-orbitals

Justin's Super Complete Table Of Everything

The Complete Table of Hybridization and Geometry

Number of Electron Domains	Hybridization	Electron-Pair Geometry	Line, Dash, and Wedge Perspective Representation of the Electron-Pair Geometry	Number of Lone Pairs	Molecular Geometry	Bond Angles	Polar? (***)
2	sp (two sp hybrid orbitals) (2 unhybridized p orbitals are available for π bonding)	Linear	—A—	0	Linear	180°	No
3	sp ² (three sp ² hybrid orbitals) (1 unhybridized p orbital is available for π bonding)	Trigonal Planar	 or 	0	Trigonal Planar	120°	No
				1	Bent	< 120°	Yes
4	sp ³ (four sp ³ hybrid orbitals) (0 unhybridized p orbitals are leftover; no π bonding)	Tetrahedral		0	Tetrahedral	109.5°	No
				1	Trigonal Pyramidal	< 109.5°	Yes
				2	Bent	< 109.5°	Yes
5	sp ³ d (five sp ³ d hybrid orbitals) (0 unhybridized p orbitals are leftover; no π bonding)	Trigonal Bipyramidal	 Note: Contains Axial and Equatorial Positions. Lone pairs (if any) go in Equatorial Positions	0	Trigonal Bipyramidal	90° and 120°	No
				1	See-Saw	< 90° and < 120°	Yes
				2	T-Shaped	< 90°	Yes
				3	Linear	180°	No
6	sp ³ d ² (six sp ³ d ² hybrid orbitals) (0 unhybridized p orbitals are leftover; no π bonding)	Octahedral	 or 	0	Octahedral	90°	No
				1	Square Pyramidal	< 90°	Yes
				2	Square Planar	90°	No

Number of Electron Domains (or "Number of electron pairs") = (Number of Other Atoms Something is Bonded To) + (Number of Lone Pairs)

Hybrid orbitals are used to form σ bonds and to hold lone pairs of electrons.

Unhybridized p orbitals are used to form π bonds.

***Note: "**Polar?**" refers to a molecule in which all terminal atoms are the same. In general, if terminal atoms are different, the molecule will be polar.

Using The Master Table of Bonding and Hybridization

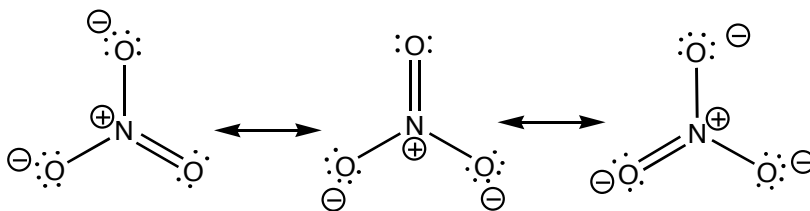
- Now let's use this table to describe the bonding in the following molecules:

HCN

CH₂O

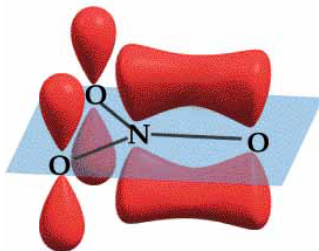
Delocalized π Bonding

- Here is the Lewis structure for the nitrate ion, NO_3^- .

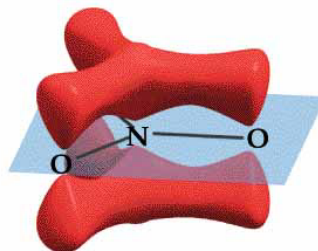


- Using the "Master Table", how can we describe the bonding in nitrate? Remember: the actual molecule must somehow be an "average" of the resonance structures.

- Nitrate is a classic example of delocalized p-bonding. How do the pictures below represent localized and delocalized p-bonding?



(a)



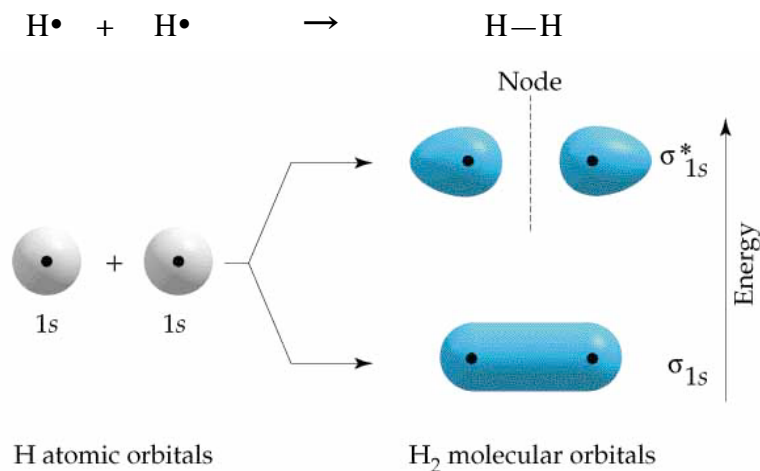
(b)

Molecular Orbital Theory

MO theory pictures electrons as being distributed among a set of molecular orbitals of discrete energies.

Electron density distribution

Imagine making H_2 from combining 2H atoms



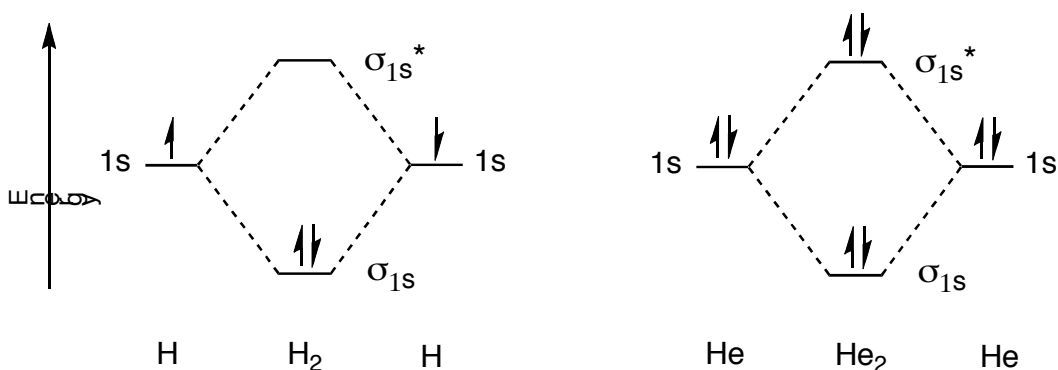
When two atomic orbitals are combined, two new molecular orbitals are created: bonding and antibonding

Bonding will result if the molecule has lower energy than the separated atoms.

Molecular Orbitals: H₂ and He₂

How to construct a molecular orbital (MO) energy level diagram

1. Write electron configurations for the valence electrons of the atoms involved.
 2. Create Molecular Orbitals(MOs) by combining the valence Atomic Orbitals (AOs). The number of MOs created will equal the number of AOs from the atom. Use dashed lines to indicate which AOs were combined to create a MO.
 3. Fill these MOs with the valence electrons.
 4. The filling of electrons in both AOs and MOs proceeds from low to high energies. Each orbital can accommodate up to two electrons with opposite spins. The number of electrons in the MOs is equal to the sum of all the electrons on the bonding atoms.
 5. Label the MOs to indicate their symmetries (σ or π), characters (bonding or antibonding) and atomic orbitals used to create the MOs.
- This molecular orbital treatment can explain why H₂ exists but He₂ does not.

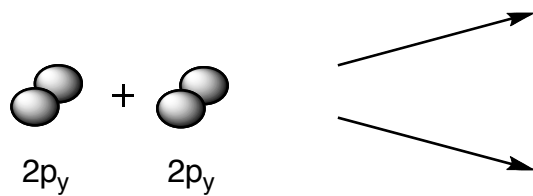
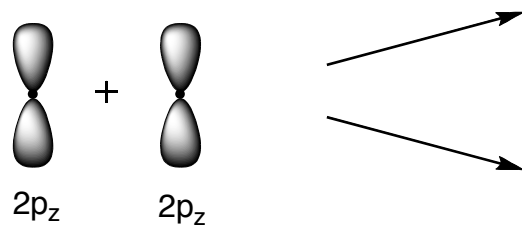
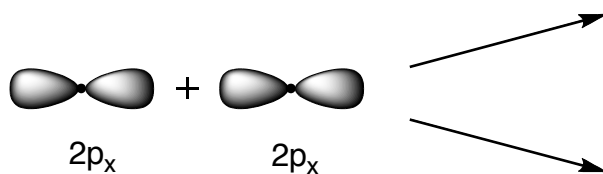


- Bond order is used to evaluate the stabilities of these species: If the number of bonding electrons is greater than the number of antibonding electrons in a given molecule, the molecule is predicted to be stable.

$$\text{Bond order} = \frac{1}{2} (\text{electrons in bonding orbitals} - \text{electrons in antibonding orbitals})$$

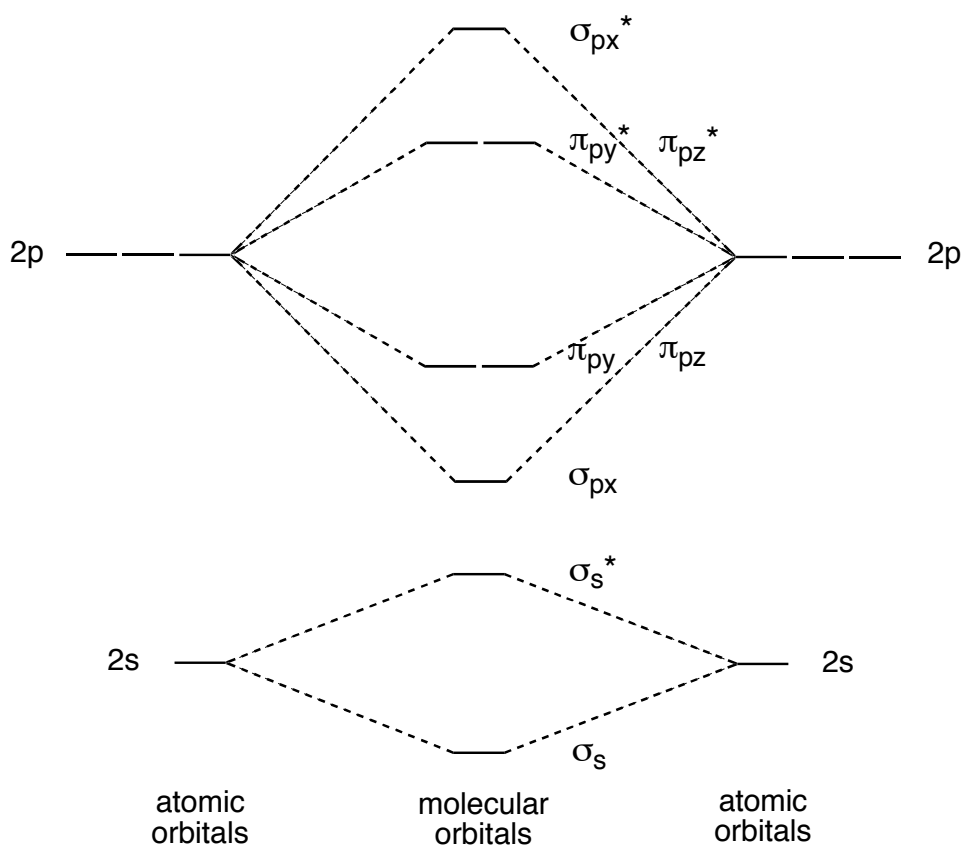
σ and π Molecular Orbitals

- If we use p-orbitals, we have more options for how to combine them. Note that these are analogous to the sigma (σ) and pi (π) bonds we saw earlier, except that now we have corresponding antibonding orbitals (which are required because of the rule of conservation of orbitals).



Molecular Orbitals: Second-Period Elements

- General MO energy diagram for the second-period homonuclear diatomic molecules. The diagram assumes no interaction between the 2s and the 2p atomic orbitals.



Molecular Orbitals: O₂, F₂, and Ne₂

- Now, all we need to do is fill the orbitals! Let's start with O₂:





































- What can we learn from the MO diagram?

Molecular Orbitals: B₂, C₂, and N₂

- For reasons that are beyond the scope of this course, the MO energies for B, C, and N are slightly different. What changes?

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TABLE 10.5 Properties of Homonuclear Diatomic Molecules of the Second-Period Elements*

	Li ₂	B ₂	C ₂	N ₂	O ₂	F ₂	
$\sigma_{2p_x}^*$							$\sigma_{2p_x}^*$
$\pi_{2p_y}^*, \pi_{2p_z}^*$							$\pi_{2p_y}^*, \pi_{2p_z}^*$
σ_{2p_x}							π_{2p_y}, π_{2p_z}
π_{2p_y}, π_{2p_z}							σ_{2p_x}
σ_{2s}^*							σ_{2s}^*
σ_{2s}							σ_{2s}
Bond order	1	1	2	3	2	1	
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	

For simplicity the σ_{1s} and σ_{1s}^ orbitals are omitted. These two orbitals hold a total of four electrons. Remember that for O₂ and F₂, σ_{2p_x} is lower in energy than π_{2p_y} and π_{2p_z} .

Molecular Orbitals of Heteronuclear Molecules

- Heteronuclear diatomic molecules (like NO) are exactly the same. Let's construct the MO diagram for NO, which has the same order of orbital energies as O₂:

- How does this relate to the Lewis structure for NO?