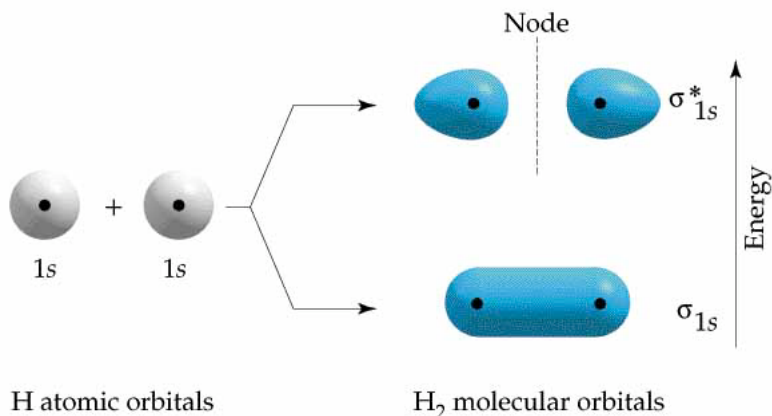


Molecular Orbitals: H₂ and He₂

- We originally showed that the overlap of atomic orbitals forms a single covalent bond. However, the mathematics of quantum mechanics requires that the number of orbitals must be conserved. Thus:

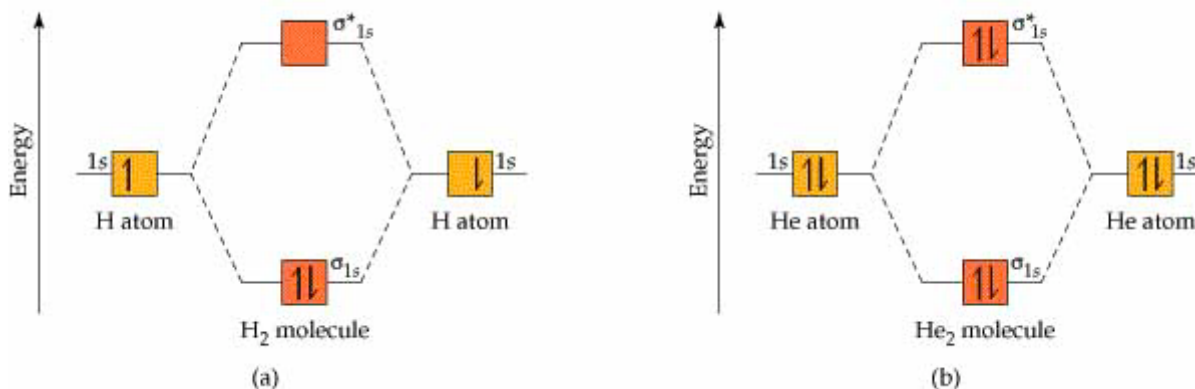
when **two** orbitals are combined, **two** new combinations must result.

How does this work in forming H₂?



- This molecular orbital treatment can explain why H₂ exists but He₂ does not. We can define the **bond order** of a species as:

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



Reading: Section 1.8

- Why do both *bonding* and *antibonding* orbitals form from the combination of atomic orbitals?

- What is an *antibonding* orbital, anyway?

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- Construct an MO diagram for the C–H σ -bond in methane (CH_4).

- Construct an MO diagram for the C–C σ -bond in ethane (C_2H_6).

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Forming π -bonds From “Leftover” p -Orbitals

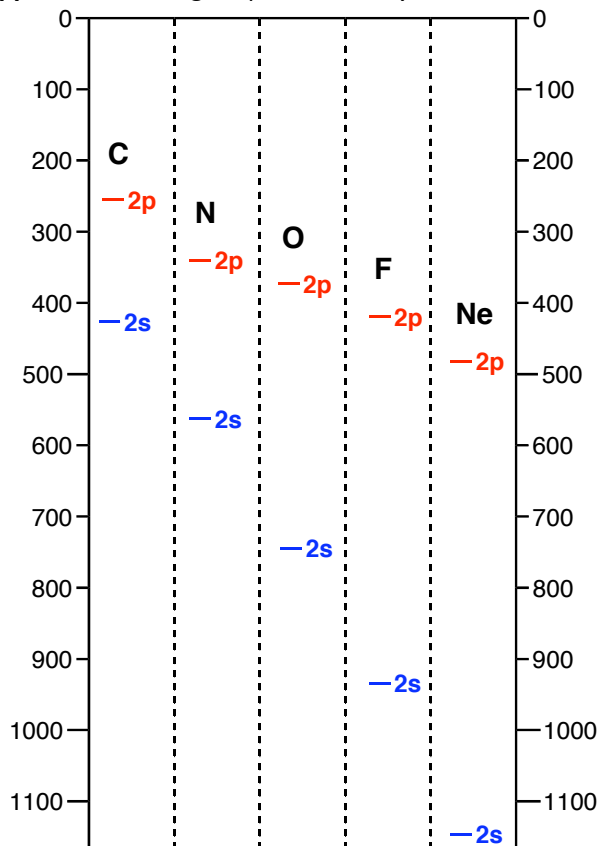
- Construct an MO diagram for the C=C π -bond in ethene ($\text{H}_2\text{C}=\text{CH}_2$).

Reading: Supplemental Handout, Section 2.2

Energies of Atomic Orbitals

- The following chart shows the approximate energies of orbitals in several of the second-period elements. Can we make any generalizations about the energies of orbitals based on these observations?

Approximate energies (in kcal mol⁻¹) of atomic orbitals



- How would the *charge* on an atom affect the energies of its orbitals?
- To summarize: What are the **three factors** that will lead to **lower orbital energies**? (You might call this the “*low-energy trifecta*” and you’ll see it again!)

Reading: Supplemental Handout, Section 2.2

Forming Molecular Orbitals from Atomic Orbitals with Different Energies

- Construct an MO diagram for the C–Cl σ -bond in methyl chloride (CH_3Cl):
- Construct an MO diagram for the C=O π -bond in formaldehyde ($\text{H}_2\text{C=O}$):
- What generalizations can we make about molecular orbitals that are constructed from two atomic orbitals with different energies?

Reading: Supplemental Handout, Section 2.2

Energies of Molecular Orbitals

- Most organic molecules contain carbon, hydrogen, and several more electronegative elements such as O, N, Cl, Br, etc. In general, the energies of the molecular orbitals in such a molecule will have the following pattern: (X represents an electronegative atom)
 - σ^* C–H
 - σ^* C–C
 - σ^* C–X

 - π^* C=C
 - π^* C=X

 - C nonbonding orbital
(lone pair OR carbocation)
 - X nonbonding orbital
(lone pair)

 - π C=C
 - π C=X

 - σ C–H
 - σ C–C
 - σ C–X
- Explain *why* the energies of the molecular orbitals follow the pattern above.

Reading: Supplemental Handout, Section 2.3

Energy-Level Diagrams for Simple Molecules

- Construct an approximate energy-level diagram for acetonitrile, CH_3CN , using the following steps:

Step 1. Draw a complete Lewis structure for the molecule, including all lone pairs.

Step 2. Make a list of all the molecular orbitals in the molecule. Count the orbitals to make sure that you haven't forgotten any! (How many molecular orbitals must there be?)

Steps 3&4. Arrange the molecular orbitals in order using the general order on the previous page.

Step 5. Fill the molecular orbitals with the correct number of electrons.

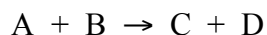
Step 6. Check your energy-level diagram:

- Does it have the correct number of orbitals?
- Does it have the correct number of electrons?
- Are all the bonding orbitals filled with electrons? (They should be!)
- Are all the antibonding orbitals vacant? (They should be!)
- Count the total number of filled bonding orbitals:
is that equal to the total number of bonds in the Lewis structure?

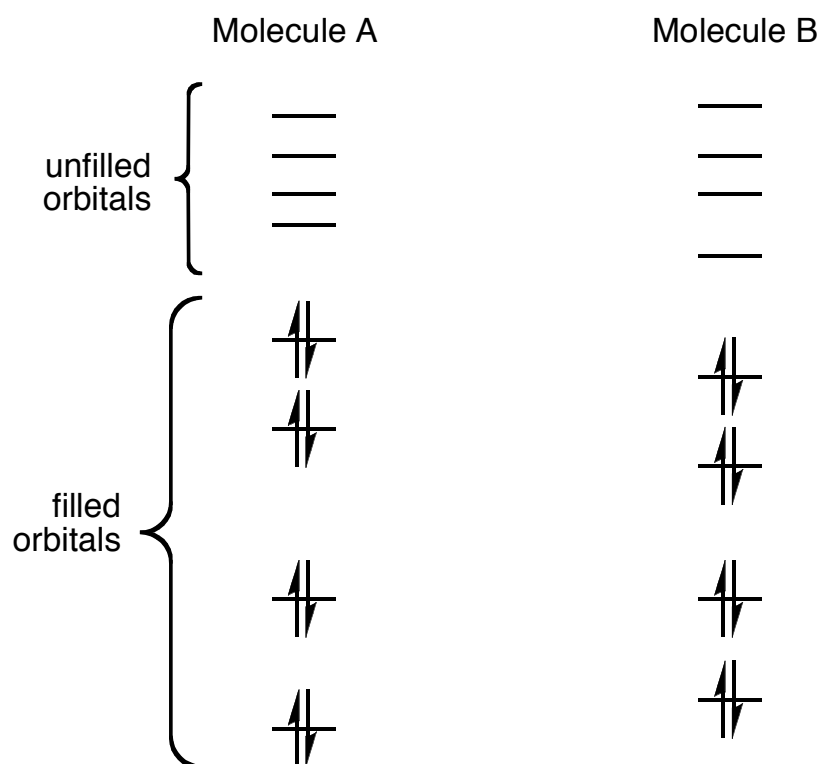
Reading: Supplemental Handout, Section 2.3

What Happens when Two Molecules React?

- Consider a general reaction between molecules A and B to yield products C and D:



- Each of the reacting species (A and B) has many molecular orbitals, filled and unfilled. What happens when these two molecules interact (when they come close together)?



- There are three basic types of interactions between the orbitals of A and the orbitals of B, depending on whether the orbitals are filled or unfilled. What can we say about these three types of interactions?

filled-filled

unfilled-unfilled

filled-unfilled

Reading: Supplemental Handout, Section 2.4

Frontier Orbitals: The Importance of the HOMO and LUMO

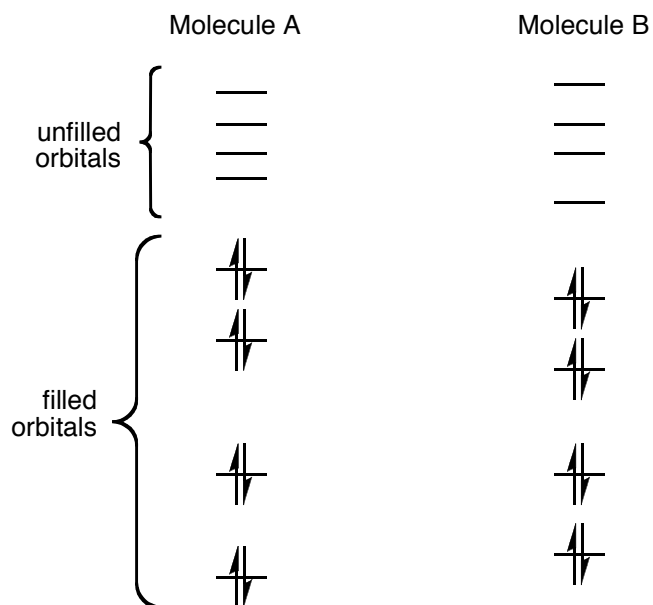
- It turns out that the interaction between orbitals that are *close in energy* is more important than the interaction between orbitals that are *far apart in energy*. Why is this the case?

- Because of the above observation, we can understand most of the reactivity of organic molecules by examining only a small number of orbitals, known as the **frontier orbitals**. These are:

HOMO (Highest Occupied Molecular Orbital)

LUMO (Lowest Unoccupied Molecular Orbital)

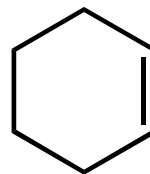
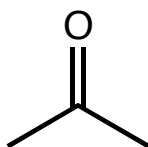
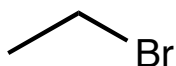
Show the interaction between the HOMO and the LUMO of molecules A and B. Why is this interaction the *single most important orbital interaction* for these species?



Reading: Supplemental Handout, Section 2.4

Finding the HOMO and LUMO

- Given the order of the energies of molecular orbitals of organic compounds, we can make some simple generalizations that will help us locate quickly the HOMO and LUMO for a given molecule. What are those generalizations? What should we look for?
 - σ^* C-H
 - σ^* C-C
 - σ^* C-X
 - π^* C=C
 - π^* C=X
 - C nonbonding orbital
(lone pair OR carbocation)
 - X nonbonding orbital
(lone pair)
 - π C=C
 - π C=X
 - σ C-H
 - σ C-C
 - σ C-X
- Using those guidelines, find the HOMO and LUMO for the following species:



Reading: Supplemental Handout, Section 2.4

The Shapes of Frontier Orbitals: Overlap Matters

- Draw “cartoon orbitals” to represent the shapes of the specified orbitals in the following molecules:

the HOMO of CH_3OH

the HOMO of ethylene ($\text{H}_2\text{C}=\text{CH}_2$)

the LUMO of the *tert*-butyl carbocation ($(\text{CH}_3)_3\text{C}^+$)

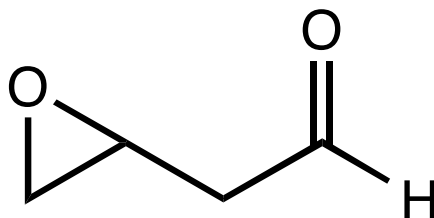
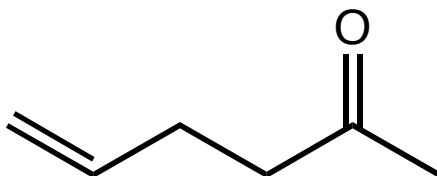
the LUMO of methyl bromide (CH_3Br)

the LUMO of formaldehyde ($\text{H}_2\text{C}=\text{O}$)

Reading: Supplemental Handout, Section 2.4

Molecules with Several Possible Frontier Orbitals

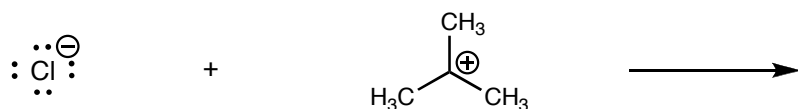
- Most organic molecules have *several* possible HOMO's and *several* possible LUMO's. Consider the following molecules. Why can't we simply specify a single HOMO or a single LUMO for these species? Identify all the possible HOMO's and LUMO's in these species.



Reading: Supplemental Handout, Section 2.4

Arrows: Non-Bonding HOMO + Non-Bonding LUMO

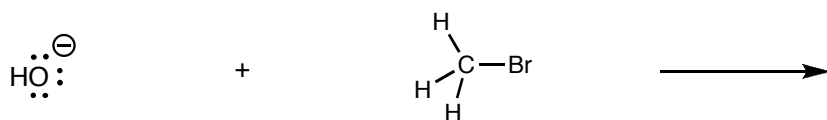
- For the following species:
 - 1) Identify the possible HOMO's and LUMO's
 - 2) Select the likely **nucleophile** and **electrophile** from these two species
 - 3) Show how these species will react using **curved arrows**
 - 4) Predict the immediate product of that reaction



Reading: Supplemental Handout, Section 2.5

Arrows: Non-Bonding HOMO + Antibonding LUMO

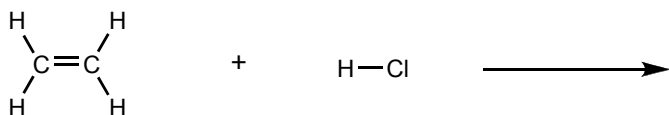
- For the following species:
 - 1) Identify the possible HOMO's and LUMO's
 - 2) Select the likely **nucleophile** and **electrophile** from these two species
 - 3) Show how these species will react using **curved arrows**
 - 4) Predict the immediate product of that reaction



Reading: Supplemental Handout, Section 2.5

Predicting Reactions Using Frontier Orbitals

- Here are two species you have **never seen before**. Using Frontier Molecular Orbital Theory (FMO Theory), *predict* the first step of the reaction between these two species. Draw the curved-arrow mechanism that shows how they react, and predict the immediate product of that reaction.



Reading: Supplemental Handout, Section 2.5

Brønsted-Lowry Acids and Bases

- One of the most useful theories of acidity and basicity is the **Brønsted-Lowry Theory**. In this theory, acids and bases are defined as follows:

A **Brønsted Acid** is a species that can **donate** a proton (H^+).

A **Brønsted Base** is a species that can **accept** a proton.

- Every Brønsted acid, therefore, must have a **conjugate base**. What are some examples of Brønsted acids? For each one, identify its conjugate base.

Brønsted Acid

Conjugate Base

- When a Brønsted acid reacts with a Brønsted base, a proton is transferred from the acid to the base. These reactions are called **proton-transfer reactions**. Give some examples of proton-transfer reactions using the above list of acids and bases.

Reading: Section 3.4

Strengths of Acids and Bases: K_a and pK_a

- All proton-transfer reactions are **reversible** (at least in principle). In general, though, one direction of the reaction will predominate over the other (that is, the proton transfer will tend to be unequal). For instance, consider the reaction between the ammonium ion and the hydroxide ion. Do you have a sense of whether this reaction proceeds mainly to the right or mainly to the left?
- Because so much chemistry takes place in water, we typically use water as a “standard reference” for the strengths of acids and bases. For any Brønsted acid HA, the reaction with water will reach some equilibrium:

The equilibrium constant of this reaction is $K_a =$

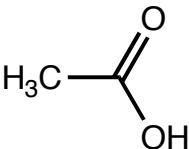
- * Just as “pH” means “the negative log of the H^+ concentration,” we use the term “pKa” to refer to “the negative log of the K_a ” How can we express that fact mathematically?
- Fill in the blanks: “A **strong** acid will have a _____ pKa”

“A **strong** base will have a *conjugate acid* with a _____ pKa”

Reading: Section 3.4

pKa Values for Common Acids

- Here are some important pKa values. You should **memorize these values**, at least to the nearest 5 pKa units:

Conjugate Acid	pKa	Conjugate Base
CH_4	48	
NH_3	35	
$\text{HC}\equiv\text{CH}$	24	
$\text{H}_3\text{C}-\text{OH}$	16	
H_2O	16	
NH_4^+	9	
HCN	9	
	5	
H_3O^+	-2	
HCl	-7	

- For each of the above acids, fill in the **conjugate base**.
- We typically define a **strong acid** as an acid that is at least as strong as H_3O^+ , and a **strong base** as a base that is at least as strong as OH^- . Identify the strong acids and strong bases in the above list.

Reading: Section 3.4

Using pKa Values to Predict Acid-Base Equilibria

- Consider, again, the reaction between the ammonium ion and the hydroxide ion. What will be the **predominant species** present in this system at equilibrium?

- Can you calculate the **equilibrium constant** for this reaction? How?

- What does the value of the equilibrium constant tell you about the concentrations of reactants and products at equilibrium?

Reading: Section 3.4