Topic 2: Molecular Orbital Theory

Reading:

Ch. 1 of your sophomore organic chemistry textbook
I. Fleming  Molecular Orbitals and Organic Chemical Reactions, Ch. 2 & 3

Bradley, J. D.; Gerrans, G. C.
“Frontier molecular orbitals. A link between kinetics and bonding theory.”
The Need For Orbitals

Heisenberg said we can't specify the location of electrons
We need orbitals to describe where the pairs of electrons want to be
Orbital phases help us see how one electron avoids the other, even though they are in the same orbital

- There are three basic types of orbitals
  1. Atomic Orbitals
  2. Hybrid Atomic Orbitals
  3. Molecular Orbitals

Let's review them…
There are four types of atomic orbitals: \( s, p, d, f \)

We can rationalize everything in this class using combinations of \( s \) and \( p \) orbitals.

\( p \) orbitals are way higher in energy than \( s \) orbitals.

Electronegativity decreases orbital energy.

There's a spherical node inside the 2s orbital, but let's ignore it.
2. Hybrid Atomic Orbitals - Review

**Mixing Rule:** When you mix two orbitals, you get two orbitals.

*The reason you get two orbitals is because there are always two arbitrary phasing combinations.*

Three ways to mix one 2s and three 2p orbitals of 2nd row atoms to give non-bonding orbitals, \( n \).

**Note:** Electrons in higher energy orbitals are more reactive.

Atom **geometry correlates with hybridization** (VSEPR theory). If you could force ammonia to be planar, the lone pair would end up in a *super high energy* p orbital.
2. Hybrid Atomic Orbitals – Differences in Reactivity Based on p Character

Assess p character in molecular orbitals corresponding to every bond and every lone pair because it predicts the reactivity of the electrons.

The magnitude of the effect is less pronounced for oxygen, which is less reactive overall than nitrogen.

More p character = more basic and more nucleophilic

<table>
<thead>
<tr>
<th>Lone pair</th>
<th>p%</th>
<th>( pK_a' )</th>
<th>Relative Basicity</th>
</tr>
</thead>
<tbody>
<tr>
<td>C–( \equiv )N(_2)</td>
<td>sp(^3)</td>
<td>75</td>
<td>+10</td>
</tr>
<tr>
<td>C–( \equiv )NH</td>
<td>sp(^2)</td>
<td>67</td>
<td>~5</td>
</tr>
<tr>
<td>C–N=</td>
<td>sp</td>
<td>50</td>
<td>-10</td>
</tr>
</tbody>
</table>

100,000x more basic

1000x more basic
2. Quantitative Differences in Reactivity based on $p$ Character

More $p$ character in C-H sigma bonds correlates with lower Bond Dissociation Energies. (Compare only C-H bonds)

<table>
<thead>
<tr>
<th>C-H bond</th>
<th>$p$</th>
<th>$s$</th>
<th>C-H $BDE$</th>
<th>relative homolytic reactivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-CH$_2$—H</td>
<td>75</td>
<td>25</td>
<td>98 kcal/mol</td>
<td>1</td>
</tr>
<tr>
<td>C=CH—H</td>
<td>67</td>
<td>33</td>
<td>110</td>
<td>$10^{-9}$</td>
</tr>
<tr>
<td>C≡C—H</td>
<td>50</td>
<td>50</td>
<td>131</td>
<td>$10^{-24}$</td>
</tr>
</tbody>
</table>

**BIG Caution:** assign hybridization AFTER considering resonance. If you don’t consider resonance then you’re not really thinking about molecular orbitals.

BDE is defined as the energy required for homolysis in a hypothetical reaction:

$$R-H \rightarrow R^+ + \cdot H$$

which atom is most basic?
3. Molecular Orbitals – Six Types of “Frontier” Molecular Orbitals

Arrows start from filled orbitals and end on un-filled orbitals. There are six canonical classes of frontier molecular orbitals that are used for arrow pushing.

Commit these canonical orbitals, and their relative energies to memory.

Since there are only three types of filled FMOs and three types of unfilled FMOs, that means that there are only 3x3 = 9 types of non-concerted elementary chemical reactions. We'll spend the rest of this quarter talking about these nine types of interactions between filled and un-filled orbitals.

Note that unfilled molecular orbitals are always higher in energy than filled molecular orbitals. (Aufbau principle).
3. Molecular Orbitals - M.O. Interaction Diagrams

- Perturbation theory says that you get more orbital interaction energy, (I.E.) by mixing MOs that are closer in energy.

\[
\text{Orbital Interaction Energy} = \frac{\text{orbital overlap}}{E_{\text{filled}} - E_{\text{empty}}}
\]

- M.O. Interaction diagrams are used to graphically depict the energetic consequences that result from perturbation of molecular orbitals through pair-wise mixing.

- If you could predict which filled orbitals are higher in energy and which unfilled orbitals are lower in energy, then you could predict which reactions would be fast and which reactions would be slow. You’ll spend the rest of the quarter practicing those predictions.
3. Molecular Orbitals – **FRONTIER Molecular Orbitals**

When two reactants interact, every filled orbital in one reactant interacts with every filled orbital in the other reactant. We can quantify that with perturbation theory resulting in a mathematical equation with lots of terms.

\[
\text{Orbital Interaction Energy} = \sum_{r} \sum_{s} \frac{2(c_{ra}c_{sb}\delta_{ab})^2}{(E_s - E_r)} + \sum_{r} \sum_{s} \frac{2(c_{ra}c_{sb}\delta_{ab})^2}{(E_s - E_r)} = \sum_{\text{all MOs}} \frac{\text{orbital overlap}}{E_{\text{filled}} - E_{\text{empty}}}
\]

When two reactants interact, most of the orbital interactions are not energetically favorable. The summed energy from orbital interactions usually comes from a single interaction: between the highest occupied molecular orbital (HOMO) in one reactant, and the lowest unoccupied molecular orbital (LUMO) in the other reactant. The HOMO and LUMO are the **frontier orbitals**.
3. Molecular Orbitals - The Importance of Orbital Overlap

**Correct symmetry** is required for effective overlap. Graphically, like phases lead to constructive interactions, but unlike phases lead to destructive interactions.

**Bredt's Rule**: Bridgehead olefins are unstable

**p** orbitals overlap more effectively when they are closer together. Longer bonds are less stable and more nucleophilic.

\[
\text{p overlap} = \begin{array}{c}
  \text{C} = \text{C} \\
  1.46 \text{ Å}
\end{array} \quad \begin{array}{c}
  \text{C} \equiv \text{C} \\
  1.20 \text{ Å}
\end{array}
\]

Capon, R. J.; Barrow, R. A. J. Org. Chem. 1998, 63, 75-83
n Generally the reactivity of nucleophilic groups used for arrow pushing follows the order: l.p. > pi > sigma.

n Electronegativity plays an important role in determining nucleophilicity.

n You usually won’t have a problem identifying the most reactive pair of electrons in a molecule.

Based on MO energies calculated with B3LYP/6-31++G(d,p) versus the LUMO for \( \text{H}_3\text{CCH}=\text{O} \). Assumes equal orbital overlap.
Intrinsic Reactivity of Canonical MOs Used for Arrow-Pushing

How accurate are the intrinsic reactivities of the canonical MOs? **Maybe ±10^5 ???**

Lot’s of the lower energy FMOs will have similar reactivity, but usually, it won’t be difficult to identify the most reactive frontier orbital.

Remember that generally: l.p. > pi > sigma

Suggest a plausible arrow-pushing mechanism:

Gabriel, et al.  
*Chem. Ber.* **1890**, 2478
The Importance of Hybridization and p Character

More p character = more nucleophilic
Less p character = less nucleophilic

p orbitals overlap more effectively when they are closer together. Longer bonds are less stable and more nucleophilic

\[
\begin{align*}
N & \quad 10^2.1 \\
C\equiv C & \quad 10^{1.5} \\
C\equiv C & \quad 10^8 \\
N & \quad 10^2.9 \\
N & \quad 10^{-2.2} \\
C&\equiv N & \quad 10^{-2.2} \\
C\equiv N & \quad 10^{-2.9} \\
N & \quad 10^{-10} \\
C\equiv H & \quad 10^{-9.3} \\
C\equiv H & \quad 10^{-10.4} \\
C\equiv C & \quad 10^{-9.4} \\
\end{align*}
\]
Effect of Bond Length on the Energy of Frontier Orbitals

- Longer bonds are more nucleophilic.
- Longer bonds are easier to break.

That is why: $\text{AlH}_4^-$ is more nucleophilic than $\text{BH}_4^-$

That is why: $\text{S}_N2$ reactions with $\text{R—I}$ are faster than $\text{S}_N2$ reactions with $\text{R—Cl}$
n Pi conjugation raises the HOMO and lowers the LUMO

That is why:

conjugated

\[ \text{---} \rightarrow \text{---} \rightarrow \text{---} \]

non-conjugated

\[ \text{---} \rightarrow \text{---} \rightarrow \text{---} \]

n That is why:

\[ \text{---} \rightarrow \text{---} \rightarrow \text{---} \] faster than \[ \text{---} \rightarrow \text{---} \rightarrow \text{---} \]

\[ \text{---} \rightarrow \text{---} \rightarrow \text{---} \] faster than \[ \text{---} \rightarrow \text{---} \rightarrow \text{---} \]

even though \[ \text{---} \rightarrow \text{---} \rightarrow \text{---} \] more stable than \[ \text{---} \rightarrow \text{---} \rightarrow \text{---} \]
Summary of FMO Trends

Rate $\propto$ Coulombic + steric + $\frac{\text{overlap}}{\Delta E_{\text{MO}}}$

electrons in orbitals with more p character are way more reactive

Longer bonds are more nucleophilic
Longer bonds are easier to break (lower $\sigma^*$ orbitals)

Conjugation raises HOMO
Conjugation lowers LUMO