A Crash Course on Molecular Orbital Theory
For Students of CHEM 332

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Introduction
Each semester in CHEM 332, we hold an out-of-class workshop at the beginning of the semester addressing concepts from CHEM 232 that students will need to know for the second semester of organic chemistry. In every workshop, without exception, we end up discussing the nuts and bolts of molecular orbital theory—and for good reason, as a solid understanding of MO theory will allow you to rapidly see and draw reasonable reaction mechanisms. MO theory should help you bridge the gap between structure and reactivity—the orbitals that define the structure of molecules are also the fundamental units that overlap and change as chemical reactions occur.

Let’s begin with a simple definition of an orbital. An orbital is a container inside of which electrons are likely to reside. Each orbital may contain up to two electrons. The container is defined by a closed surface that may contain some discontinuities. We call these discontinuities nodes, and they are not just outside of the orbital surface—electrons cannot possibly sit on them. The three 2p orbitals are pictured below. Notice the nodes at the origins, where the nuclei sit.

The 2p orbitals contain green and blue regions, which correspond to the two phases of the orbital. The phases correspond to positive and negative “values” of the orbital. Most importantly, as we’ll see shortly, the phase affects how orbitals overlap.

The 2p orbitals are examples of atomic orbitals (AOs), which house electrons associated with atoms. You should be familiar with the atomic orbitals from general chemistry—recall that the valence atomic orbitals of the organic elements (minus hydrogen) are the 2s and 2p levels. Electrons associated with molecules, on the other hand, reside in molecular orbitals (MOs). Although molecular orbitals are more complex than atomic orbitals, they are built from simple linear combinations of the atomic orbitals. Just mix pieces of different atomic orbitals together, and the result is a set of molecular orbitals! You should recognize pieces of the atomic orbitals (including
the hybrid atomic orbitals) in the molecular orbitals we’ll see in CHEM 332. The “magical” mathematics is unimportant, but the results of that math are, so the figure below sums up what you’ll need to know. The “Beyond Diatomic MOs” lesson will address the fundamentals of constructing and combining orbitals, so we’ll leave things here for the moment.

![Diagram of an orbital mixing machine]

**The Dirty Little Secret of Molecular Orbital Theory**

You may be surprised to learn that purely organic chemistry deals with only six classes of molecular orbitals. The “magical machine” is only able to generate a few unique molecular orbital shapes, reflected by the six classes described below. Just as the atomic orbitals of organic chemistry are limited to 1s, 2s and 2p, the molecular orbitals of organic chemistry are limited to these types: \( \sigma \), \( \pi \), \( n \), \( \sigma^* \), \( \pi^* \), and \( \alpha \). The first three classes are filled orbitals, meaning that they contain two electrons. The latter three are empty orbitals and lack electrons.

We draw Lewis structures to describe the electronic structure of molecules (i.e., where electrons are). However, where electrons are not in a molecule is also very important, as these regions represent places where electrons can go. Hence the importance of the empty molecular orbital—without it, electrons could never go anywhere! As a simple rule of thumb, for every filled bonding molecular orbital, there is a corresponding empty antibonding molecular orbital. Nothing comes free in life: stabilization must be accompanied by destabilization.

With a full understanding of the concepts of filled and empty molecular orbitals in hand, we’re ready to address the “dirty little secret” of molecular orbital theory:

**Bonds and lone pairs in Lewis structures reflect the localized molecular orbitals that organic chemists most commonly use (and that you’ll regularly use in CHEM 332).**

There are exceptions to this rule that we will address in CHEM 332, and they arise when resonance and conjugation become important (see the “Pi Delocalization & Color” lesson). However, take a few minutes to appreciate the power of this idea. This means that the lines and dots in a compound’s Lewis structure reveal to you its available molecular orbitals. Furthermore, because MOs are the fundamental units of chemical change in organic chemistry, the Lewis structure clues you in to how the compound reacts. Structure and reactivity are inexorably related!
Localized MOs in Organic Compounds

The figure below outlines the six kinds of molecular orbitals: their shapes (in blue), the Lewis structures to which they correspond (in black, underneath the orbitals in blue), and curved arrows showing their use as either electron sources or sinks.

Organic reaction mechanisms are built from the six fundamental curved-arrow formalisms in the above figure. In CHEM 332, we describe each step of a reaction mechanism as a combination of one of the filled orbitals with one of the empty orbitals. For instance, an intramolecular \( \sigma \rightarrow a \) interaction looks like this:

Recent students of CHEM 232 may recognize this as the \([1,2R]\) elementary step. Try drawing the other elementary steps as combinations of the fundamental electron flows above.

<table>
<thead>
<tr>
<th>Elementary Step</th>
<th>Interaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>([1,2R]) 1,2-rearrangement(^1)</td>
<td>(\sigma \rightarrow a)</td>
</tr>
<tr>
<td>([D_E]) electrophile dissociation(^2)</td>
<td>(\sigma \rightarrow a)</td>
</tr>
</tbody>
</table>

\(^1\) Forms a new sigma bond.
\(^2\) Forms a new pi bond.
<table>
<thead>
<tr>
<th>Reaction Type</th>
<th>Orbital Change</th>
</tr>
</thead>
<tbody>
<tr>
<td>[A_E] electrophile association</td>
<td>$\pi \rightarrow a$</td>
</tr>
<tr>
<td>[A_N] nucleophile association</td>
<td>$n \rightarrow a$</td>
</tr>
<tr>
<td>[pt] proton transfer</td>
<td>$n \rightarrow \sigma^*_{X-H}$</td>
</tr>
<tr>
<td>[S_N2] bimol. nuc. substitution</td>
<td>$n \rightarrow \sigma^*_{X-LG}$</td>
</tr>
<tr>
<td>[E2] bimolecular elimination</td>
<td>$\sigma \rightarrow \sigma^*$</td>
</tr>
<tr>
<td>[E_B] beta elimination$^3$</td>
<td>$n \rightarrow \sigma^*$</td>
</tr>
<tr>
<td>[D_N] nucleophile dissociation</td>
<td>$n \rightarrow a$</td>
</tr>
<tr>
<td>[Ad_N] nuc. addition across a pi bond</td>
<td>$n \rightarrow \pi^*$</td>
</tr>
</tbody>
</table>

What does all of this have to do with molecular orbital theory? For each elementary step, the interacting orbitals must be able to access the proper orientation for in-phase, constructive overlap. For many steps (e.g., all intermolecular steps), drawing proper orbital overlap is just a simple matter of lining things up. Here’s an example of an [S_N2] step, with the interacting MOs perfectly aligned:

![Example MO alignment](image)

However, interesting cases arise when, although curved arrows make an elementary step seem possible, it is actually prohibited because of poor orbital overlap:

![Prohibited MO overlap](image)

Geometry is the concern here: the $\sigma$ and $\sigma^*$ orbitals cannot orient themselves so that they are overlapping efficiently. In other cases, the phases of the orbitals are the important

$^3$ Forms a pi bond.
factor (we will see this in the “Other Pericyclic Reactions” lesson in CHEM 332). Cases like the one above make it imperative to consider the overlapping molecular orbitals of elementary steps. Make sure that the curved arrows you’re drawing are not bogus from an MO perspective. And remember: the curved arrows you draw imply the molecular orbitals involved. Resist the urge to memorize, and use the figures above to systematize the molecular orbitals and elementary steps in your mind.

**Orbital Energy: Whittling Down Multiple Possibilities**

At this point, you should be able to identify the MOs within a molecule and predict, based on those, the elementary steps it may undergo. How can we distinguish between the elementary step possibilities, to identify the most likely reaction pathway? The key is to identify the molecular orbitals on the “frontier” — that is, the highest-energy filled MO and the lowest-energy unfilled MO (also known as the HOMO and LUMO, respectively). It is essential to understand the figure below.

What does this figure tell us? For reasons we’ll revisit in the “Orbital Interactions” lesson, the smaller the energy gap between a filled and an empty orbital, the more stabilizing their interaction. **Orbitals close in energy interact favorably with one another.** We might thus reason (correctly) that the most favorable interactions are \( n \rightarrow a \), \( n \rightarrow \pi^* \), \( \pi \rightarrow a \), and the like—interactions between orbitals on the pink-blue “frontier.” The molecules in question must possess these MOs in order for the interactions to occur, but using the above figure, we can make decisions about the most favorable orbital interactions between two molecules (or within a single molecule).

**Beyond A’s and B’s: the Effects of Charge and Atom Type**

Applying the six classes of MOs in a practical setting requires an understanding of the effects of charge and atom type (read: electronegativity) on the energy of molecular orbitals. For instance, we’re often interested in comparing the reactivity of two MOs in the same class. The fantastical molecule below contains two pi bonds. Which one is
more reactive as an electrophile? Say we treated this compound with a strong nucleophile, such as thiolate (–SH). Where will thiolate prefer to add, and why?

\[
\text{H}_3\text{C} \equiv \text{N} \equiv \text{O}
\]

Which pi bond is more reactive as an electron acceptor?

We need to make a decision here using the relative electronegativity of oxygen and nitrogen as the key factor. To start thinking in molecular orbital terms, you must forget about the products of thiolate addition and focus on differences in the MOs of the starting material.

Rather intuitively, more electronegative atoms are associated with lower energy orbitals. Another way of saying this is that more electronegative atoms are more electrophilic, or that they tend to be associated with more electrophilic unfilled orbitals. Remember that orbitals closer in energy tend to interact strongly. Using this idea, it makes sense that lower-energy unfilled orbitals are more reactive—not only are they more willing to accept electrons, but also they are closer in energy to the HOMOs of nucleophiles. Applying this concept to the example above, we would expect the pi bond associated with oxygen to be more electrophilic than the pi bond associated with nitrogen. You’ll need to make these kinds of decisions on a regular basis in CHEM 332!

\[
\text{H}_3\text{C} \equiv \text{N} \equiv \text{O}
\]

more electrophilic!

Employing a similar line of reasoning, we reach the conclusion that more electronegative atoms are associated with worse nucleophiles, because their filled orbitals are lower in energy and less reactive than filled orbitals associated with less electronegative atoms.

What about the effect of charge? Think of charges as electronegativity “boosters” or “restrictors.” Positive charge on an atom boosts its electronegativity over its neutral counterpart—positively charged atoms want electrons more badly than neutral atoms. Negative charge has the opposite effect, and lowers the electronegativity of the atom in
question vis-à-vis its neutral counterpart. Using the relationship between electronegativity and electron-accepting/-donating ability described above, we can reason about the effects of charge on electrophilicity/nucleophilicity. Work through the following imaginary examples on your own.

![Figure](image)

Which pi bond is more reactive as an electron acceptor?

Which oxygen atom is more reactive as an electron donor?

The figure below, a scale of electronegativity increasing from left to right, sums up our conclusions from this section.

![Conclusions](image)

**Conclusions**

What should you get from this document? You should understand…

- what an orbital is
- the classes of MOs used by organic chemists (and their associated curved arrows)
- how to narrow down mechanistic possibilities using orbital energy ideas
- the effects of atom type and charge on orbital energies

Organic chemists use these concepts to formulate reasonable reaction mechanisms. In CHEM 332, we will look at these ideas in more depth and apply them to a variety of contexts. I advise you to begin thinking about organic chemistry with orbital concepts.
now! Do not put off learning this material—although you may see your own way of thinking about things as adequate, we will generalize molecular orbital theory as the semester proceeds, and you will need to understand the basics to see where we’re going. Without a firm foundation based on what you already know, you may find yourself falling behind.