

Week 2

Bonding Models

2.1 Bonding Models 1

- 9/10:
- Lecture 1 recap.
 - Aspects of mechanism.
 - Orbitals, energy surface, and kinetics.
 - Masha redraws Figure 1.6.
 - These are the three main pictures that we'll learn about.
 - Today, we'll focus on orbitals.
 - Today: Bonding models.
 - Reading: Anslyn and Dougherty (2006), Chapter 1!!
 - **Bonding:** How electrons are shared between nuclei.
 - This determines all of molecular structure and reactivity (which is the name of this class, and underpins all of organic chemistry!).
 - From bonding, there arise concepts such as nucleophilicity, electrophilicity, etc.
 - There are several levels of bonding theory / models that we'll talk about today.
 - Caveat: *All* of these models are no more than *approximations* of reality that are useful to us.
 - Lecture outline.
 1. Lewis structures.
 2. VSEPR.
 3. Valence Bond Theory (VBT).
 4. Molecular Orbital Theory.
 5. Qualitative Molecular Orbital Theory (QMOT).
 - Lewis structures.



Figure 2.1: Lewis dot structures.

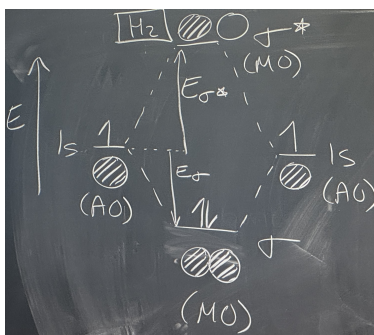
- Developed in 1916 by G. N. Lewis.
 - He was nominated 48 times, but never won the Nobel Prize because some people on the review committee didn't like his "interesting personality."
- In this model, we use dots to — on paper — indicate where electrons are in bonds.
- From these **Lewis dot structures**, people developed the "stick structures" that we still use today.
- Lewis structures are very useful in identifying the number of bonds and lone pairs.
- Valence Shell Electron Pair Repulsion (VSEPR).
 - Developed 1939-1957.
 - Key finding: Electrons in bonds repel each other, so you maximize the distance between bonds.
 - This let us go beyond Lewis structures into things like explaining tetrahedral carbon (and its 109.5° bond angles).
 - Issues develop when we try to rationalize other molecules.
 - For example, isobutane has 110.6° Me–C–Me bond angles. The VSEPR purists will cite "sterics."
 - As another example, NH_3 has 107° H–N–H bond angle. The VSEPR purists will cite "lone pair is big."
 - Really, these were just excuses by the VSEPR purists for a bad model, and what we really needed was a new model.
- Valence Bond Theory (VBT).
 - Developed by Linus Pauling, with his seminal paper in 1931.
 - For this work and some other stuff, he won the Nobel Prize in Chemistry in 1954.
 - To be historically accurate, Pauling built off the work of Heitler and London (1926).
 - However, Pauling was the person to both put everybody else's work all together and be visible enough to take the credit.
 - Additional takeaway from Pauling's biography: Don't make your whole life about your work. For example, Pauling was shunned by many of his colleagues after he got into nuclear proliferation, but now we say he was so brave. He even won the Nobel Peace Prize!
 - Takeaway on Pauling vs. Lewis: It pays to not be a jerk. Lewis died via cyanide poisoning (may have been an accident, but was probably suicide).
 - This is a quantum mechanical (QM) description of Lewis structures.
 - Central tenet: Each atom contributes 1 valence electron in a QM-derived atomic orbital (AO).
 - Shows that electrons are delocalized between atoms, and where two electrons overlap and localize is a chemical bond.
 - In other words, electrons are not restricted to tight orbitals.
 - Many concepts arise within VBT until the advent of MO theory.
- VBT was key for many conceptual innovations, such as **hybridization**, **electronegativity**, and **resonance**.
- **Hybridization**: The mixing of orbitals on the same atom to make new orbitals.
 - Specifically, we can take a linear combination of AO waveforms (or AOs).
 - More directional orbitals give you better overlap and therefore stronger bonds.
 - Example: A linear combination $s + p_y + p_x + p_z$ yields four sp^3 -hybridized orbitals. That's four orbitals with uneven lobes. We can draw all of these on top of each other, and from *there*, we get the tetrahedral carbon.

- We always like new models that agree with old models; this is called a **sanity check**.
- We can also calculate something called the **hybridization index**.
- **Hybridization index:** The number i in the following formula, expressed as a function of the experimentally determined bond angle θ . Denoted by i . Given by

$$1 + i \cos \theta = 0$$

- Example: NH_3 has a hybridization index of 3.4.
- Example: H_2O has a hybridization index of 4! That's why it has the tiny bond angle. The remaining s -character is localized on the oxygen, and that's why we say that oxygen is electron dense and nucleophilic.
 - Would this similarly predict that H_2O has longer bonds than NH_3 ??
- **Electronegativity:** The power of an atom to attract electrons to itself.
 - There are different scales for this. We probably used the **Pauling scale**, but there is also a **Mulliken scale**.
 - More electronegative atoms have lower energy orbitals.
 - This is summarized via the **inductive effect**.
- **Inductive effect:** The withdrawing of electron density through σ -bonds.
 - Example: ACN. We think about nitrogen having a partial negative charge and carbon having a partial positive charge. This results in a dipole.
 - Takeaway: Dipoles arise from electronegativity in VBT!
- **Resonance:** The superposition of several Lewis structures.
 - Example: Consider an α, β -unsaturated ketone. Its resonance structure is a zwitterionic intermediate, and a second resonance structure is a different zwitterion. We have three resonance forms, so that predicts more stable than something with less resonance structures. It also identifies our positive and negative reactive sites.
 - Resonance usually happens through π -networks, but it *can* happen through σ -networks.
 - Takeaway: Delocalization of electron density leads to stability.
 - Know your rules for drawing good resonance structures.
 - We only move bonds, not atoms (no nuclear motion).
 - Prefer to have the least separation of charge.
 - Put the more negative charge on the more electronegative atoms.
- Limitations of VBT.
 - Over time, some key experimental findings emerged that VBT couldn't explain. These results motivated people to develop a new model to explain these rare cases.
 - Nowadays, exceptions to VBT are not so rare.
 - Remember: If a model can't explain certain cases, it's not a useful model.
 - Maxim: Not predictive = not useful.
- Here's a list of the limitations of VBT.
 - Doesn't account for unusual stability/instability (e.g., aromaticity and antiaromaticity).
 - No antibonding orbitals (i.e., no explanation of interactions between molecules).
 - When a nucleophile attacks a ketone, the interaction is with the antibonding orbital of the ketone. Forming a new bond involves populating an antibonding orbital.
 - Thursday is all about aromaticity, and modern ways to conceptualize it.

- This leads to the mother of all bonding models, Molecular Orbital Theory.
 - Central tenet: Molecular orbitals (e.g., σ , σ^* , π , π^*) arise from linear combinations of atomic orbitals (in Orgo, this is s & p ; we won't consider d -orbital effects so much).
 - We consider the electronic structure of the whole molecule, not just atoms or bonds.
 - We focus on key molecular orbitals such as the HOMO and LUMO.
 - We also get **group orbitals**: Leads into QMOT, which is MOs for prototypical groups.
- MO theory leads to MO diagrams.

Figure 2.2: MO diagram for H_2 .

- Two atomic orbitals interact to fill two molecular orbitals.
- We fill the bonding orbital with all the electrons that come in (in this case, 2).
- The energy of stabilization is E_σ .
- The destabilization energy is E_{σ^*} .
- Read Anslyn and Dougherty (2006) for more rules.
- Notes.
 - $|E_{\sigma^*}| > |E_\sigma|$. Thus, if the antibonding orbitals get populated, the molecule breaks. This is because of nuclear repulsion.
 - The σ -bond is more stable than the $1s$ orbitals by themselves. This is why the H–H bond forms. This kind of analysis allows us to predict whether or not a bond will form.
- Question for us to consider: Why doesn't He–He form?
 - Because its antibonding MOs would be populated.
- Example MO diagram: Ethylene.

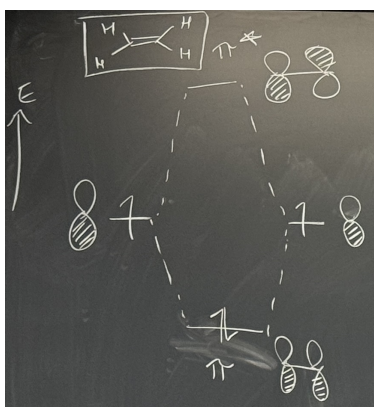


Figure 2.3: MO diagram for ethylene.

- Looking specifically at the π -bond formation.
- This is why we form a stable π -bond.
- Example MO diagram: Formaldehyde.

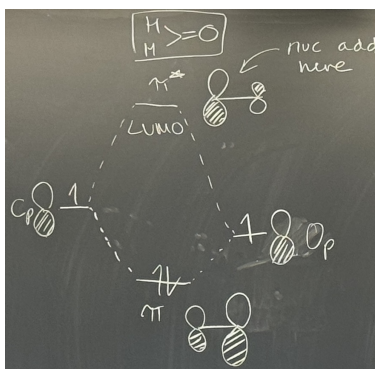


Figure 2.4: MO diagram for formaldehyde.

- We mix a C_p AO and a (lower energy) O_p AO.
- These orbitals interact less well than those in ethylene due to their difference in energy.
- We benefit from constructive phasing, but the lobes are much bigger on oxygen.
- In the antibonding orbital, the lobes are much bigger on carbon.
- Principles revealed by this MO diagram.
 - Closer energy AOs give stronger mixing, resulting in lower energy MOs. Lower energy MOs are more stabilizing.
 - More electronegative atoms have lower energy atomic orbitals.
 - The π -orbital is asymmetric because its energetically more similar to O_p than C_p .
 - In other words, it's going to look more like the O_p orbital.
 - One more way of stating this is that the coefficient of oxygen in the LCAO is bigger.
- We know that the LUMO (frontier orbital) interacts with nucleophiles. The lobe of the LUMO is bigger on carbon, hence why we react there.
- Qualitative MO theory (QMOT).
 - All about forming group orbitals for common functional groups or motifs.
 - Essentially, we may not need to calculate MOs for the whole molecule to find out how every carbonyl reacts; we can trust that carbonyl group orbitals are decently conserved.
 - There are a bunch of rules for how to form a QMOT diagram.
 - See Table 1.7 in Anslyn and Dougherty (2006) for building QMOT diagrams.
 - This is the basis of **Walsh diagrams**.
 - We can build group MOs from linear combinations of s & p AOs.
- **Walsh diagram**: A representation of an MO diagram as a function of geometric distortions.
 - This matters because geometry affects orbital overlap, which can be destabilizing or stabilizing.

- Example QMOT diagram: CH_3 .

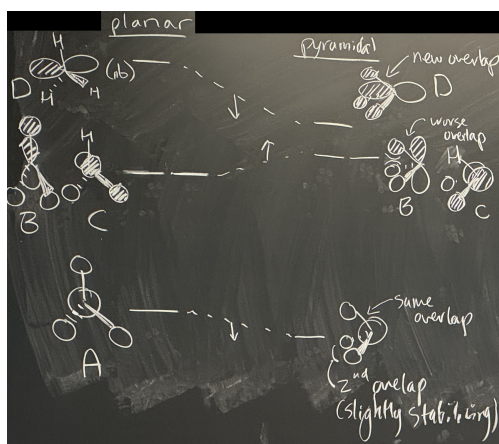
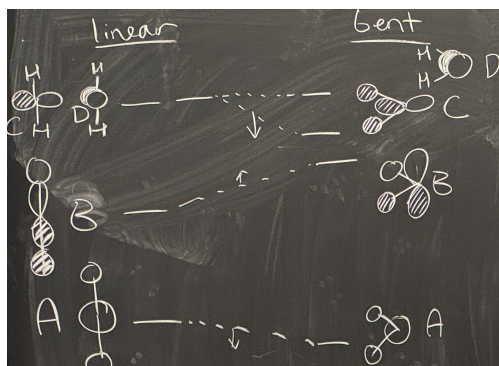


Figure 2.5: QMOT diagram for CH_3 .

- Key question: What geometry of CH_3 is favorable?
- Masha defines axes.
- Undetermined yet if this is a radical, cation, or anion. We'll get there!
- We look at a planar set of orbitals first.
 - A. All phases in sync, all s orbitals.
 - B. Phases align top to bottom with the p_x orbital of carbon.
 - C. Phases align in and out of the board with the p_y orbital of carbon.
 - D. Nonbonding; just the p_z orbital.
- There are also **E**, **F**, and **G** orbitals that are energetically above these, but we won't draw them for now (because we won't fill them with electrons in the carbocation, carbanion, or carbon radical).
 - The **E**, **F**, and **G** orbitals will have the opposite phasing of the lower orbitals!
- We now draw an analogous, pyramidal set of orbitals.
 - A. Overlap is *slightly* more favorable because we have a secondary orbital interaction between the hydrogens now. The C–H overlap stays the same.
 - B. Worse overlap. We're losing a **primary** interaction instead of gaining a **secondary** one, so the energy of **B** actually goes up *more* than **A** went down. We also get some destabilizing secondary interaction between the H orbitals.
 - C. Just like **B**, we get worse primary overlap, and new interfering secondary overlap.
 - D. Gets stabilized the *most* significantly! This is because we've taken something with no bonding interactions and *created* bonding interactions between the p -orbital and the hydrogens.
- Relationship between QMOT and Walsh diagrams: A Walsh diagram is a QMOT diagram with everything connected.
- Now how do we fill electrons?
 - Consider the CH_3^+ cation: We have 6 electrons, so we populate the planar orbitals because it's more stable overall.
 - Consider the CH_3^- anion: We have 8 electrons, so we populate the pyramidal orbitals because *they're* more stable overall.
- This rigorous prediction of conformation is the benefit of this model.
- We can also use this model for other isostructural molecules.

- Examples.
 - NH_3 : 8 electrons, pyramidal.
 - BH_3 : 6 electrons, planar.
 - $\cdot\text{CH}_3$: 7 electrons, *slightly* planar.
 - But this is a special case only for $\cdot\text{CH}_3$; any other radical is pyramidal.
- **Primary** (orbital interaction): An interaction between orbitals on adjacent atoms in a molecule.
- **Secondary** (orbital interaction): An interaction between orbitals on atoms that are separated by one other atom in a molecule.
- What is quantitative about QMOT?
 - There is a lot more depth in Anslyn and Dougherty (2006). You can calculate the actual potential energy surface and figure out these conformations exactly.
- Example QMOT diagram: CH_2 .

Figure 2.6: QMOT diagram for CH_2 .

- Two geometries: Linear and bent.
- Linear.
 - A. Linear chain of s -orbitals with matching phases.
 - B. Linear chain of matching phases orbitals, with p_x on carbon.
 - C. One of the other p -orbitals, with no phasing.
 - D. The last remaining p -orbital, again with no phasing.
- Bent.
 - A. Goes down slightly. We kept primary, and added secondary.
 - B. Losing primary overlap and gaining a destabilizing secondary interaction; higher E like before.
 - C. Adding *significant* constructive interference. Biggest effect again!
 - D. Staying the same; no bonding interactions to begin or end with. We don't consider secondary interactions when there's no density at all there.
- Example species.
 - H_2O : 8 electrons, bent.
 - Note that this model predicts that H_2O has nondegenerate lone pairs, which has been experimentally verified!
 - Bulk water acts as if it has degenerate lone pairs. We can read Anslyn and Dougherty (2006) about this, but otherwise, it's outside the scope of the class.

- CH_2 (a **carbene**): 6 electrons, a mix of linear and bent!
 - We'll return to carbenes in a few weeks.
 - We'll define **triplet** (2 electrons in different orbitals) and **singlet** (2 electrons in same orbital) carbenes later.
 - Triplet is 136° , and singlet is 105° , so the triplet is more linear and the singlet is more bent! The triplet has reactivity more characteristic of the linear orbital picture, and the singlet has reactivity more characteristic of the bent orbital picture.
 - The triplet is more favored by 9 kcal/mol
- Example QMOT diagram: Formaldehyde.

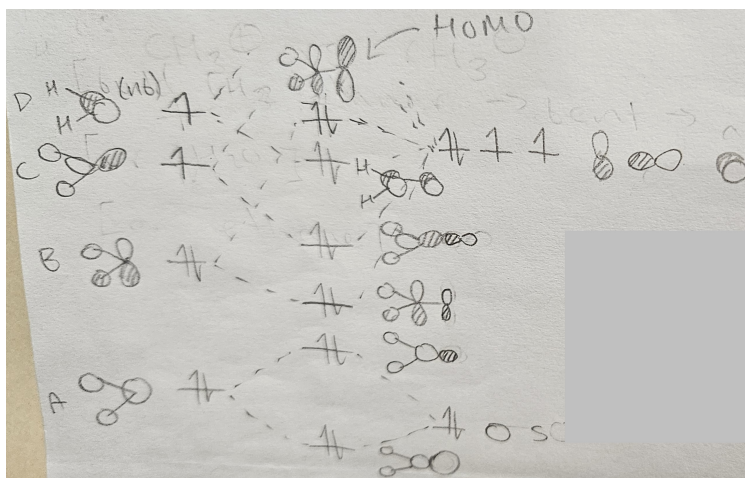


Figure 2.7: QMOT diagram for formaldehyde.

- The HOMO has a larger coefficient on O; this explains why protonation occurs on O and not C!
- Key takeaway: QMOT diagrams and MO diagrams both make the same predictions about the electronic structure and reactivity of formaldehyde (sanity check).
 - Example: They both predict that carbonyls are nucleophilic on oxygen.
 - Example: Orbital mixing is stronger when orbitals are of similar energy.
 - Example: Orbital coefficients are larger on an atom when the MO is closer in energy to the AO that originates with that atom.
 - Example: Orbitals are lower in energy on more electronegative atoms.
 - Etc.