Unit 2

Molecular Orbitals and Pericyclic Reactions

2.10 Molecular Orbital Theory - 1

9/27:
- See Georgia's notes on Canvas (also included below).

Lecture 10: MO Theory (1/2)

Exam Reflections
- You all did great
  "How did I do?"
    90-100 excellent
    80-90   good
    <80   adequate, reach out
- exams hand back in recitations
- these guidelines are exam specific
    ↳ first exam typically best
- You learned structure determination!
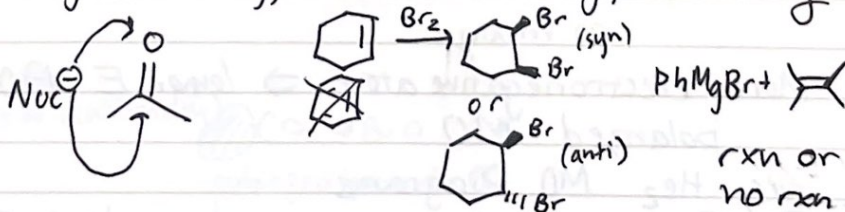
What's Next?
- how do you go from 2D structure to where are e⁻
  where do they react

Unit 2 Molecular Orbitals ¦ Pericyclic Reactions
- deeper look   at e⁻ movement
- new types of reactions, new class of mechanism
- use molecular orbitals (MO's) to predict reaction
  outcomes
    ↳ regioselectivity, diastereoselectivity, reactivity

- MO's provide insight into structure ¦ reactivity

Background/Review ¦ Study
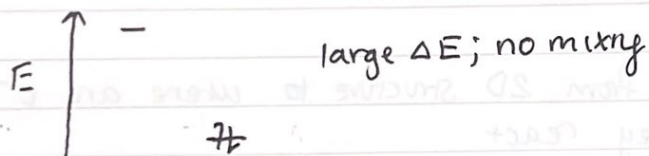- review gen chem (5.111/5.112) ¦ Orgo 1 (5.12)
- Clayden: ch. 4, 5, 6

Lecture 10 :: Cont

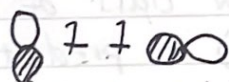- orbitals are wavefunctions that describe the ability to find an electron in space
  - ↳ they interact constructively & destructively

Rules:
1. # atomic orbitals (AOs) in = # MO's out
2. interacting orbitals must have similar energy
   - if large ΔE ; no mixing
   - if same E ; best mixing

$$E \uparrow \quad \overline{}$$

large ΔE; no mixing

$$\cancel{\text{#}}$$

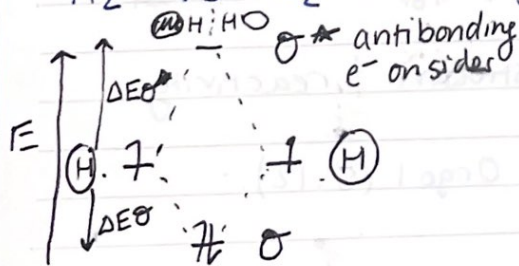3. interacting orbitals must overlap efficiently and have similar ~~energy~~ symmetry

   perpindicular orbitals
   - poor overlap
   - no mixing

4. More electronegative atom ⇒ lower E AO = more polarized MO

H₂ vs He₂ MO Diagrams

H;HO σ^* antibonding
e⁻ on sides

$E \uparrow$

$\Delta E\theta$

H $\cancel{\uparrow}$ $\uparrow$ H

$\Delta E\theta$

$\cancel{\text{#}}$ σ

HOH
bonding; e⁻ in middle

Note: $|\Delta E\theta^*| > |\Delta E\theta|$

antibonding is more destabilizing than the bonding is stabilizing

H_2 MO more stable than $2 \times$ H· AO

↳ why H₂ bond forms

Lecture 10 Continued

He₂ MO Diagram

E ↑
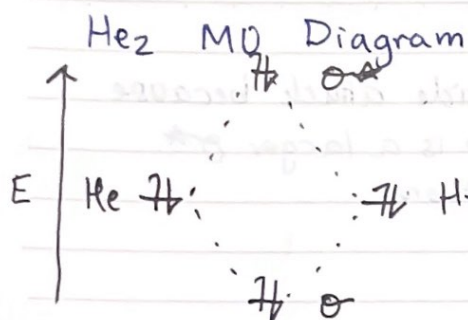
- antibonding MO filled!
- this is less stable than two individual H atoms
- forming He-He requires filling σ^* (which is more destabilizing) than

He ⇅ : :⇅ He

⇅ σ

- this is the MO explanation for the full octet rule

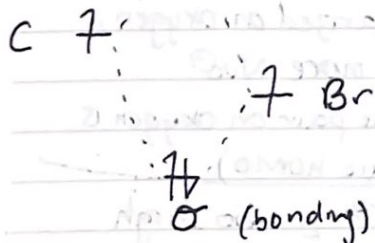## SN₂ MO Picture

MeΘ → Br ⟶ ΘSEt
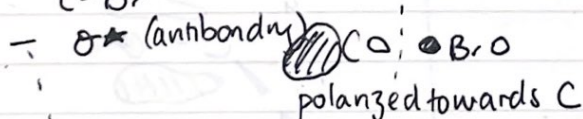
Me Br

Br, H
EtS Me

Why backside attack?
- identify HOMO & LUMO

HOMO highest occupied MO = nucleophile, filled orbitals, lone pair. π orbital, ΘSEt

LUMO lowest unoccupied MO = electrophile = empty orbitals = π* or σ^* orbital, cations, C of C-Br bond

MO of C-Br
- σ^* (antibonding) C○ ●Br○
polarized towards C

C ⇃

⇃ Br

⇅
σ (bonding)

●C ◯Br●
polarized towards Br

Lecture 10: Cont

backside attack because
there is a larger σ^*
lobe there

HOMO

meanwhile

     σ bond breaks because σ^* populated

our mechanistic arrows show this

$C=C$ vs $C=O$ MOs

π^*
LUMO
antibonding

π bonding

$C=O$

polarized
towards C;
more electrophilic

LUMO —

HOMO

polarized on oxygen,
more Nu$^\ominus$
(lone pair on oxygen is
true HOMO)
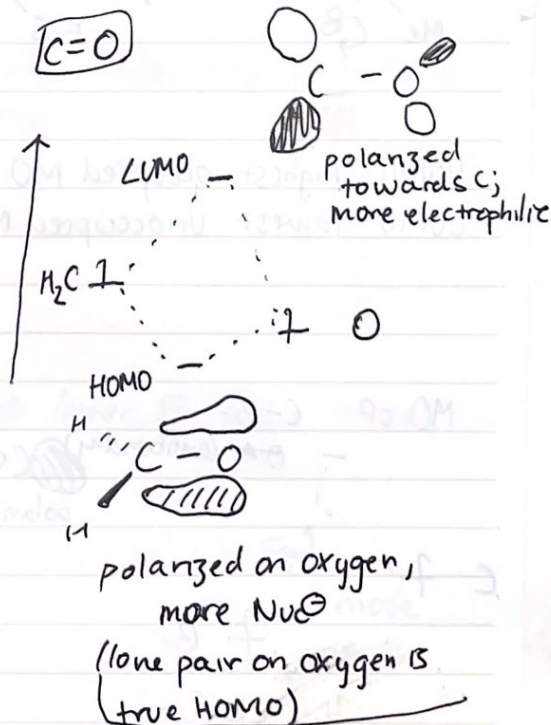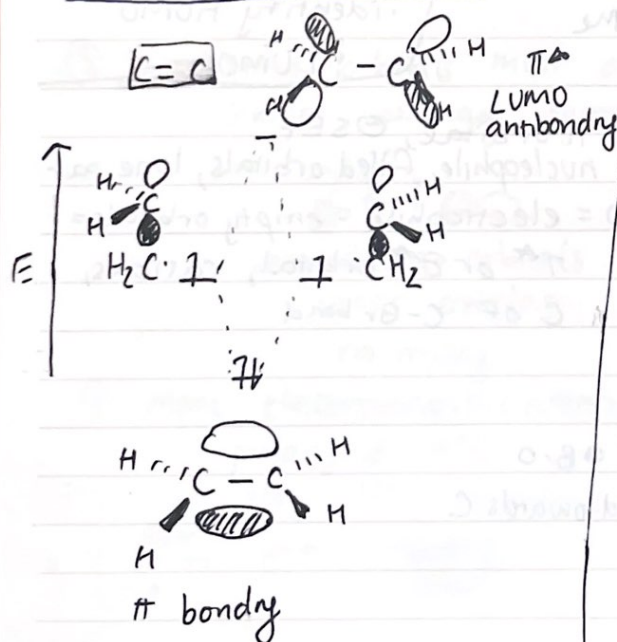
Consequences:
  $C=C$ less reactive towards Nuc b/c π^* E too high
  $C=C$ generally nucleophilic unless somehow polarized
      ex:

$C=O$ electrophilic on carbon

2.11 Molecular Orbital Theory - 2

9/30:   • Lecture 10 recap: What MO theory can explain.

(a) A regioselective reaction.   (b) A diasterioselective reaction.   (c) An unreactive mixture.

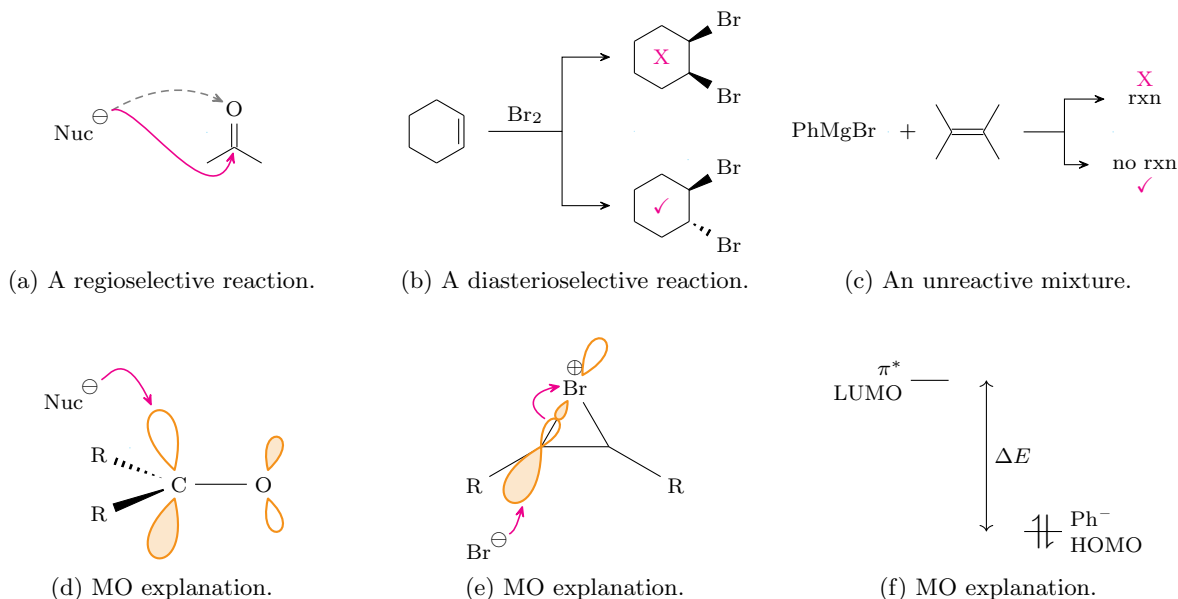(d) MO explanation.   (e) MO explanation.   (f) MO explanation.

Figure 2.1: MO theory explains these phenomena.

- Regioselectivity.
  - Consider a nucleophile adding into a carbonyl (Figure 2.1a).
    - Experimentally, we observe that the nucleophile attacks the carbon atom (magenta arrow) instead of the oxygen atom (grey dashed arrow).
  - To understand why, we must consider the carbonyl's molecular orbitals (Figure 2.1d).
    - Specifically, we must consider the carbonyl's LUMO, since this will be the MO that interacts with the nucleophile's HOMO. Here, the LUMO is the carbonyl's π^*-orbital.
    - The carbonyl's LUMO has big lobes on carbon and small lobes on oxygen; in other words, this LUMO is **polarized** toward carbon.
    - The difference in lobe size explains why the nucleophile attacks carbon instead of oxygen.
- Diastereoselectivity.
  - Consider the bromination of an alkene (Figure 2.1b).
    - Experimentally, we observe that the *anti* adduct is formed instead of the *syn* adduct.
  - To understand why, we consider the MOs of the bromonium ion intermediate (Figure 2.1e).
    - For the same reason as before, we must consider the bromonium ion's LUMO. Here, the LUMO is the C−Br σ^*-orbital.
    - The bromonium ion's LUMO has its largest lobe behind carbon.
    - Thus, this is the lobe that will be attacked by the Br$^-$ nucleophile. Such an attack is called a "backside attack" and induces the *anti* product.
- Reactivity.
  - Consider a Grignard reagent adding into an olefin (Figure 2.1c).
    - Experimentally, we observe no reaction here.
  - To understand why, we must consider the relative energies of the reacting MOs (Figure 2.1f).
    - Essentially, the alkene's LUMO (a π^*-orbital) is much higher in energy than the phenyl anion's HOMO. Thus, the ΔE gap is too big, i.e., there is a lack of energy symmetry.
    - Therefore, by Rule 3 from Lecture 10, no reaction occurs.

- Today: More MO theory.

- Lecture outline.
  - The Bürgi-Dunitz angle.
  - Hyperconjugation.
  - The anomeric effect.
  - Stereoelectronic effects and the rate of reaction.

- **Bürgi-Dunitz angle**: The angle at which nucleophiles typically add to carbonyls. *Given by* $107°$.
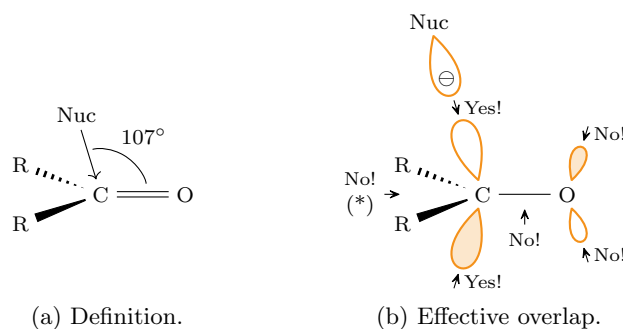

(a) Definition.   (b) Effective overlap.

Figure 2.2: Bürgi-Dunitz angle.

  - This is the angle between the new C–Nuc bond and the carbonyl's σ-plane (Figure 2.2a).
  - Nucleophiles attack at this angle because it's the location of the π^*-lobe on carbon (Figure 2.1d).
  - Let's elaborate a bit on Figure 2.1d now (Figure 2.2b).
    - Once again, consider the carbonyl π^*-orbital (its LUMO) and its "butterfly" lobes.
    - The nucleophile must approach the π^*-orbital with the right symmetry. This is why we see its HOMO's lobe approach the carbon atom's π^*-lobe dead-on at exactly the right angle.
      - This angle leads to efficient overlap, and hence an effective sharing of electron density.
      - This is an example of Rule 3 from Lecture 10.
    - Are there any other locations at which we can add into the carbonyl?
      - We can also add into the shaded carbon π^*-lobe on the other side of the σ-plane by reversing the shading of the nucleophile's lobe!
      - However, any other angle of attack will *not* work.
      - Note (*): A backside attack is good for interacting with the σ^*-orbital, but bad for interacting with the π^*-orbital that we need for carbonyl chemistry.

- **Hyperconjugation**: The mixing of filled and empty orbitals to stabilize a system.
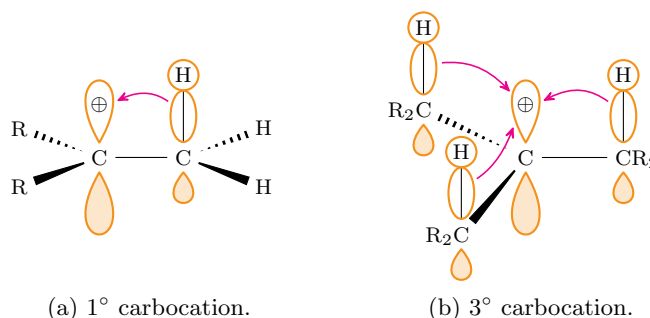
- Example (from 5.12): Stabilizing carbocations.

(a) 1° carbocation.   (b) 3° carbocation.

Figure 2.3: Hyperconjugation stabilizes carbocations.

- Consider a primary (1°) carbocation (Figure 2.3a).
    - In a carbocation, the positively charged carbon localizes its lack of electron density to an empty p-orbital.
    - However, adjacent to this empty p-orbital is a full σ-orbital, namely, the adjacent C−H bond. Moreover, this bond has the right *geometry* to donate into the empty p-orbital.
    - Thus, the σ-orbital of the C−H bond will donate electron density into the empty p-orbital, delocalizing both positive and negative charges and thereby stabilizing the system.
  - We denote hyperconjugation interactions using a special **notation**; the particular hyperconjugation in Figure 2.3 is denoted $\sigma_{\mathrm{CH}} \to p_{\mathrm{C}}$.[1]
  - In a tertiary (3°) carbocation, we get electron donation from *three* adjacent σ_{CH} orbitals.
    - These *three* stabilizing interactions explain why 3° carbocations are more stable than 1° ones!
    - Such effects are also why more substituted cations are more stable in general.

- **Hyperconjugation notation**: The concise method for denoting a certain hyperconjugative orbital interaction. *Given by*
$$\mathrm{orbital}_{\mathrm{atoms}} \to \mathrm{orbital}_{\mathrm{atoms}}$$

  - The arrow means "donates into."
    - Indeed, we always write the filled orbital first (before the arrow) and the empty orbital second (after the arrow).
  - Possible orbitals: $\sigma, \sigma^*, \pi, \pi^*, p, n$.
    - Note that n denotes a <u>n</u>onbonding lone pair.

- **Anomeric effect**: The tendency of heteroatom substituents adjacent to heteroatoms in cyclohexane derivatives to prefer the axial orientation.

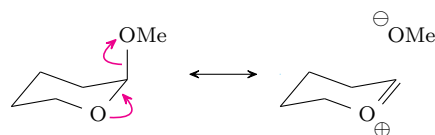- Let's break this rather complicated definition down through an example.
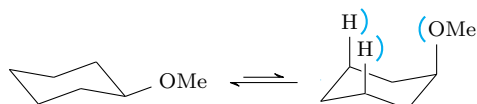
(a) Sterics win in methoxycyclohexane.
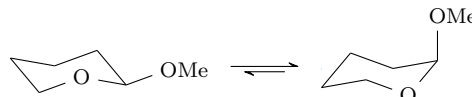
(b) Anomeric wins in 2-methoxytetrahydropyran.
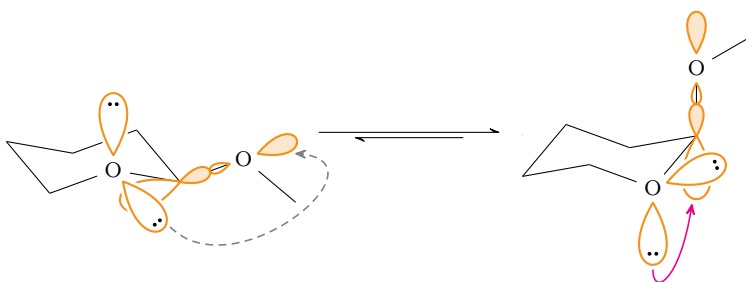
(c) MOs explain the anomeric effect.

(d) Resonance explains the anomeric effect.

Figure 2.4: Anomeric effect.

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[1] This is pronounced "sigma C−H to p C donation" or (very explicitly) "sigma see aech to pee see donation."

- – In methoxycyclohexane, the methoxy group prefers to be equatorial to avoid 1,3-diaxial interactions (Figure 2.4a).
  - ■ This leads to a 70 : 30 distribution in favor of the equatorial conformer.
- – However, in 2-methoxytetrahydropyran, the methoxy group prefers to be *axial* due to the anomeric effect (Figure 2.4b).
  - ■ This *also* leads to a 70 : 30 distribution, but this time in favor of the axial conformer.
  - ■ Notice how this empirical observation reflects the definition of the anomeric effect: We have a heteroatom substituent (the methoxy group) adjacent to a heteroatom in cyclohexane (the oxygen in the six-membered ring), and it is preferring the axial orientation!
- – What causes the anomeric effect? Let's investigate the stabilization of the axial conformer further using molecular orbitals (Figure 2.4c).
  - ■ In 2-methoxytetrahydropyran's equatorial conformation, we get poor overlap between the oxygen lone pair's orbital and the C–OMe antibonding orbital. This poor overlap is due to the *gauche* orientation of said orbitals.
  - ■ In 2-methoxytetrahydropyran's axial conformation, we get really nice overlap between the oxygen lone pair and the σ^*-orbital of the C–OMe bond. This is because both orbitals have large lobes pointing axial down. Because of this favorable geometry, $n_O \rightarrow \sigma^*_{CO}$ hyperconjugation occurs.[2]
- – Another way of showing how the anomeric effect stabilizes the axial conformer is by using resonance diagrams (Figure 2.4d).
  - ■ Indeed, starting from the typical picture, we can push the lone pair into an O=C π-bond and formally break the C–OMe σ-bond.
  - ■ The result is called a **no-bond resonance form**.
  - ■ Something should feel off to you here, though.
    - ➢ When you learned to draw resonance structures, you learned that you can't break σ-bonds.
    - ➢ However, we are now telling you that sometimes, you *are* allowed to break σ-bonds. This is "next-level resonance structures."
  - ■ Note that 2-methoxytetrahydropyran doesn't go all the way to the no-bond resonance form, but said resonance form *is* a major contributor.
    - ➢ This also means that the no-bond resonance form affects the reactivity of the molecule.

- Both hyperconjugation and the anomeric effect fall under the broader category of **stereoelectronic effects**.

  - – Note that they are not the only examples of such effects, though.

- **Stereoelectronic effect**: An effect on structure or reactivity of a molecule caused by the spatial orientation of its orbitals.

  - – We've previously learned that everything in Orgo can be explained by steric and electronic effects, but stereoelectronic effects are like a secret third option!

- Let's now look at some more places where stereoelectronic effects crop up.

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[2]Note that there is no particular reason why overlap with a σ^*-orbital, in particular, is stabilizing. Rather, the point is that we have a filled orbital (the lone pair) adjacent to an empty orbital (which just happens to be a σ^* orbital), so hyperconjugation can occur to spread out the negative and positive charges. This delocalization — like any — is then inherently stabilizing.

- Example: Hyperconjugation in noncationic species.

(a) Ethane's conformers.

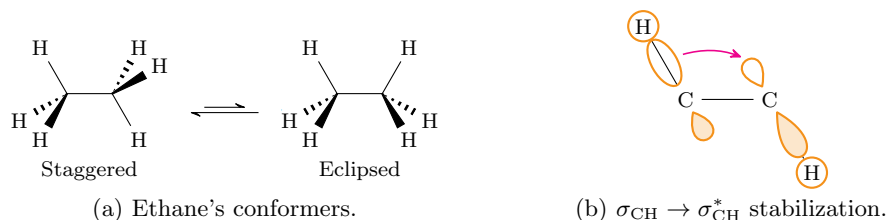

(b) $\sigma_{CH} \to \sigma_{CH}^*$ stabilization.

Figure 2.5: Hyperconjugation stabilizes staggered ethane.

  - We may have learned that ethane prefers the staggered conformer over the eclipsed conformer (Figure 2.5a) due to sterics.
    - This is not true!
    - We know this because H is really tiny.
  - In fact, this preference is due to hyperconjugation, a stereoelectronic effect (Figure 2.5b).
    - Staggered ethane is stabilized by electron donation from the σ-bond of one C−H bond into the adjacent, antiperiplanar C−H bond's σ^* orbital: $\sigma_{CH} \to \sigma_{CH}^*$.
    - This is a small interaction, but it occurs six times, once for each C−H σ-bond!
  - Takeaway: Electron delocalization is stabilizing, and more delocalization is more stabilizing.

- Example: Stereoelectronic stabilization can accelerate reactions.

(a) S_N1 without an adjacent heteroatom.

(b) S_N1 with an adjacent heteroatom.

(c) No heteroatom mechanism.

(d) Possible heteroatom-promoted mechanism.

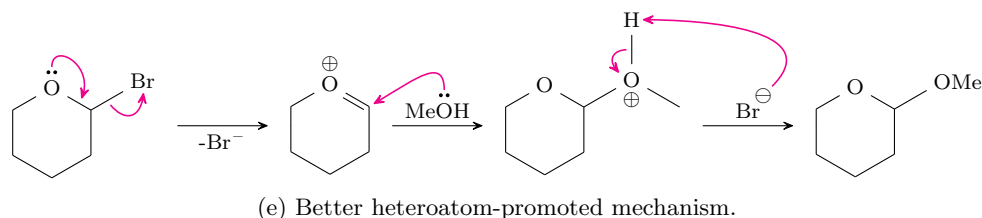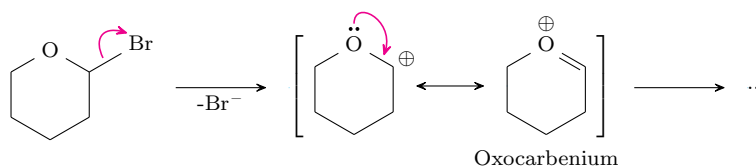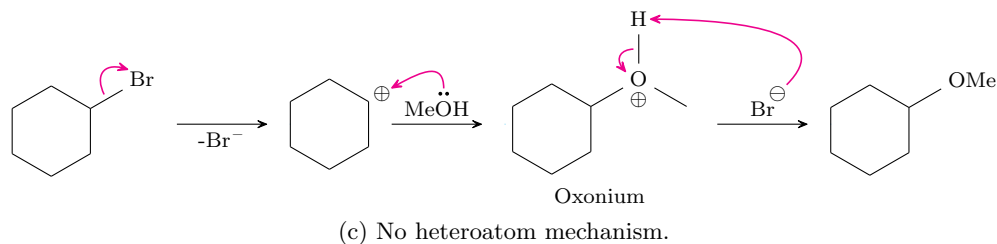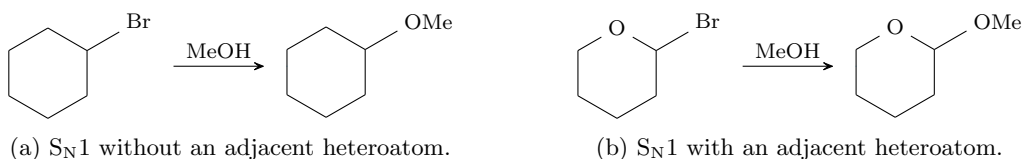(e) Better heteroatom-promoted mechanism.

Figure 2.6: Stereoelectronic effects accelerate reactions.

- Consider the S_N1 substitution of bromocyclohexane to methoxycyclohexane (Figure 2.6a), vs. the S_N1 substitution of 2-bromotetrahydropyran to 2-methoxytetrahydropyran (Figure 2.6b).
- Which of these substitutions occurs faster?
- To answer this question, let's look at the mechanism of each (Figures 2.6c-2.6d).
    - Note that in Figure 2.6c, either bromide or another equivalent of methanol can do the final deprotonation of the **oxonium** ion.[3]
    - Note that in Figure 2.6d, the fact that the **oxocarbenium** ion obeys the octet rule implies that it is the more stable resonance structure.
- In fact, the oxocarbenium ion is an example of oxygen stabilizing a carbocation through $n_O \rightarrow p_C$ hyperconjugation.
- This is one example of hyperconjugation in this reaction scheme, but there is another effect as well.
    - In the original 2-bromotetrahydropyran molecule, the oxygen lone pair will also hyperconjugate into the C−Br σ^*-orbital per the anomeric effect.
    - In other words, O mediates the departure of the leaving group through $n_O \rightarrow \sigma^*_{CBr}$ hyperconjugation.
- Thus, since both hyperconjugative stabilizing effects can (and do!) happen, it is better to say mechanistically that the arrow pushing in the first step happens simultaneously (Figure 2.6e).
    - Indeed, the rule in arrow pushing is "make a bond, break a bond," so that's what we do.
- We can now complete the mechanism for the heteroatom-promoted reaction (Figure 2.6e).
    - MeOH adds into the π^*-orbital of the oxocarbenium (at the Bürgi-Dunitz angle!), also kicking electrons up to the oxygen in a concerted step.
    - Then we get deprotonation again.
- Now that we've got both mechanisms, let's consider the energy surface in order to compare the rates of reaction.
    - Both reactions will have two-humped energy surfaces, befitting a mechanism with only one true catinoic intermediate.
    - However, in the energy surface for the heteroatom-promoted reaction, $n_O \rightarrow p_C$ hyperconjugation will stabilize the intermediate and $n_O \rightarrow \sigma^*_{CBr}$ will stabilize the transition state of the first step, lowering its activation energy!
    - Thus, the heteroatom-promoted S_N1 is faster!
- Takeaway: The overall reaction specifics depend on geometry and orbital overlap.

2.12 Pericyclics

10/2: - Lecture 11 recap.

    - Hyperconjugation involves the delocalization of electrons, and hence is stabilizing.
        - This is a very common phenomenon, and it underlies most 5.12 reactions!
    - $\sigma_{CH} \rightarrow p_C$ hyperconjugation makes substituted cations more stable (see Figure 2.3).
    - $\sigma_{CH} \rightarrow \sigma^*_{CH}$ makes ethane more stable when staggered than eclipsed (see Figure 2.5b).
    - $n_O \rightarrow \sigma^*_{CX}$ stabilizes axially positioned heteroatom substituents with α-heteroatoms in cyclohexane derivatives, per the anomeric effect (see Figure 2.4c).

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[3]Note that — comparing the pK_a of protonated methanol to HBr — methanol is actually almost a million times more basic than bromide. As such, for every one time bromide does the final deprotonation, methanol will do it to almost a million other oxonium intermediates. However, it can still be useful to think of bromide as *formally* doing the final deprotonation so as to balance the reaction $C_6H_{11}Br + CH_3OH \longrightarrow C_6H_{11}OCH_3 + HBr$.

- Today: Pericyclic reactions.

  - They are cool because they couple MO theory to reactivity.
  - This is a whole new class of reactions, and we will spend the rest of Unit 2 talking about them.
  - Essentially, the rest of this unit looks like: "Here's a new reaction, and here's the MO picture underlying it."

- **Pericyclic** (reaction): A reaction characterized by a **concerted** movement of electrons in a **cyclic** transition state.

- **Concerted** (reaction): A reaction in which all electron movements happen at the same time, i.e., all bonds break and form in the same step.

  - There are no intermediates, and hence only a single "hump" in the energy diagram (Figure 2.7a).
  - Concerted reactions contrast with **stepwise** reactions.
  - Concerted reactions can be **synchronous** or **asynchronous**.
    - Essentially, we ask, "Is the transition state symmetric? Are all bonds breaking and forming to the same extent at the same time, or are some bonds breaking/forming first with others breaking/forming later?"
    - We touch on this concept to illustrate that even *concerted* reactions can have subtle differences between them.

- **Stepwise** (reaction): A reaction that *has* intermediates in its energy landscape.

  - There *are* intermediates, and hence multiple "humps" in the energy diagram (Figure 2.7b).

- To reiterate, concerted and stepwise reactions can be differentiated using their energy diagrams.

Rxn coord →   Rxn coord →
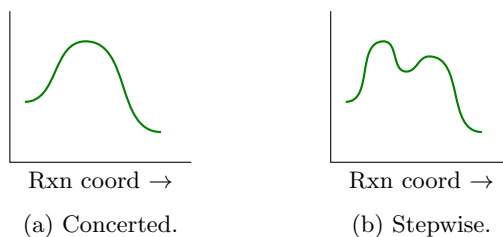
(a) Concerted.   (b) Stepwise.

Figure 2.7: Concerted vs. stepwise energy diagrams.

  - Example: S_N2 reactions are concerted, and S_N1 reactions are stepwise.

- **Synchronous** (concerted reaction): All bond-making and -breaking occurs to an equal extent in the transition state.

- **Asynchronous** (concerted reaction): All bond-making and -breaking does *not* occur to an equal extent in the transition state.

- **Cyclic** (transition state): A transition state in which all bonds that are being broken and made are connected in a ring.

  - Important implication: This is not as complicated as it sounds; rather, it just means that when you draw your electron arrows, you draw them in a ring.
  - See Figure 2.8 for an example.

- History of pericyclic reactions.
  - MO theory was developed *because* of pericyclic reactions.
    - Essentially, pericyclic reactions used to be called "no mechanism" reactions since everything happened in one step.
    - The extent to which organic chemists didn't understand how pericyclic reactions worked drove them to develop a theory that explained why they did.
  - Today, pericyclic reactions are credited with introducing quantum theory into organic chemistry.
    - Before pericyclic reactions, organic chemists thought that they could explain everything they needed to with Lewis structures and arrow pushing mechanisms.
    - However, after pericyclic reactions, it became clear to organic chemists that there *was* value in keeping track of where all the electrons are actually located in MOs and such.

- We'll now do an overview of the different classes of pericyclic reactions, i.e., what we have to look forward to over the next couple of weeks.
  - Types we'll discuss: **Cycloadditions**, **electrocyclizations**, and **sigmatropic rearrangements**.
  - Specifically, we've got one lecture on each of these topics coming up (and then a couple others).
  - As such, it's a good idea to get a general sense of these reactions now, but you don't need to think too much about them since you will get much more information in the coming days and weeks.

- **Cycloaddition**: A pericyclic reaction in which two separate π-systems react to convert two π-bonds into two σ-bonds.
  - Nomenclature: $[m+n]$, where m and n are the numbers of atoms in the two separate π-systems.
    - To reiterate: One of the π-systems has m atoms, and the other has n atoms.
  - Example: We may speak of a "[4+2] cycloaddition." This specific pericyclic reaction is also called the **Diels-Alder reaction**.
  - The reverse reaction of a cycloaddition is called a **cycloreversion**.

- **Diels-Alder reaction**: A $[4+2]$ cycloaddition.
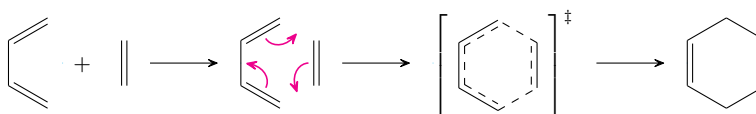

Figure 2.8: Diels-Alder reaction.

  - This is a really cool reaction — one of the most powerful in organic chemistry, in fact.
  - We'll spend the next two lectures talking about it!
  - Note that the magenta electron arrows in Figure 2.8 can go either counterclockwise *or* clockwise.
    - As long as they lead to the right product, you can draw either!

- **Cycloreversion**: A pericyclic reaction in which one system reacts to convert two σ-bonds back into two π-bonds in two separate π-systems.
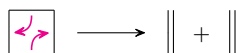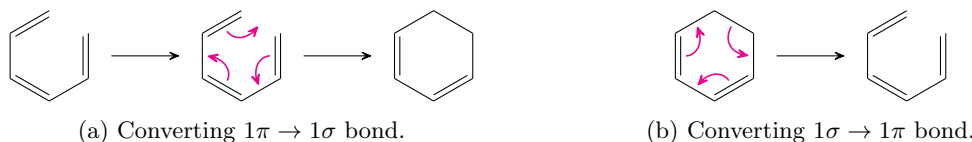

Figure 2.9: A cycloreversion.

  - Sometimes, we give cycloreversions special names.
  - Example: We can call the reaction in Figure 2.9 either a "4π cycloreversion" or a "retro-$[2+2]$."

- **Electrocyclization**: A pericyclic reaction in which one system reacts to convert one π-bond into one σ-bond, or vice versa.

(a) Converting $1\pi \to 1\sigma$ bond.   (b) Converting $1\sigma \to 1\pi$ bond.

Figure 2.10: A forward and reverse 6π electrocyclization.

  - Nomenclature: $m\pi$, where m is the number of electrons involved.
  - Always ring-opening or ring-closing.
  - Example: We may speak of a "6π electrocyclization" (Figure 2.10a).
    - Notice how we go from 5 σ- and 3 π-bonds to 6 σ- and 2 π-bonds in Figure 2.10a.
  - We can also go in reverse (Figure 2.10b).

- **Sigmatropic rearrangement**: A pericyclic reaction in which a σ-bond moves to the end of the π-system.
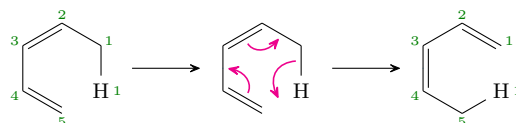

Figure 2.11: A $[1,5]$ sigmatropic rearrangement.

  - Nomenclature: $[m, n]$, where m and n are the "numbers" of the atoms to which the two ends of the σ-bond moves.
    - We'll dive into this nomenclature more in the lecture on sigmatropic rearrangements.
    - In particular, we will discuss a very specific way of "numbering" the atoms in our starting material and product!
  - Example: We may speak of a "$[1, 5]$ sigmatropic rearrangement" (Figure 2.11).
    - You can push the electron arrows either way, but Masha likes to start with the σ-bond and move that to the end of the π-system.
    - Observe that one end of the σ-bond (the side at the hydrogen) moved from atom 1 to atom 1, and the other end (the side at the carbon) moved from atom 1 to atom 5. This is related to the aforementioned "numbering."

- To reiterate from earlier, start familiarizing yourself with these types of reactions, but remember that we will go over these in more detail later in the course.

- Moving on, let's bring MOs back into the picture.

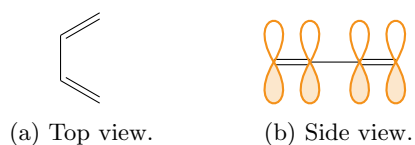(a) Top view.   (b) Side view.

Figure 2.12: Two views of buta-1,3-diene.

  - Observe that the reactants in Figures 2.8, 2.10, and 2.11 are all conjugated systems!
  - Thus, they have π-MOs. Let's consider the diene from Figure 2.8, in particular.
  - Looking at it from the side, we see that each π-bond is made up of two p-orbitals.

- We can mix the four p-AOs in Figure 2.12b to make MOs, but we have to do so according to the following rules.

  1. The number of MOs is equal to the number of atoms under consideration.
     - Example: A diene will have four MOs.
     - Example: An olefin will have two MOs.
  2. The lowest-energy MO has no **nodes**.
  3. For every increase in E, we add a node (in such a way that symmetry is maintained).

- **Node**: A change in sign of the orbital, at which there is no electron density.

- Example of nodes: Think of our π and π^* MOs.
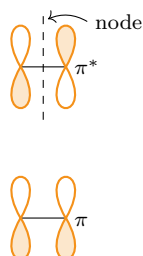
Figure 2.13: Nodes in π and π^* molecular orbitals.

  - The lower one has no nodes, because the phases are aligned left to right.
  - The upper one has 1 node, because the phases invert left to right.

- We are now ready to draw an MO diagram for the diene in Figure 2.12.
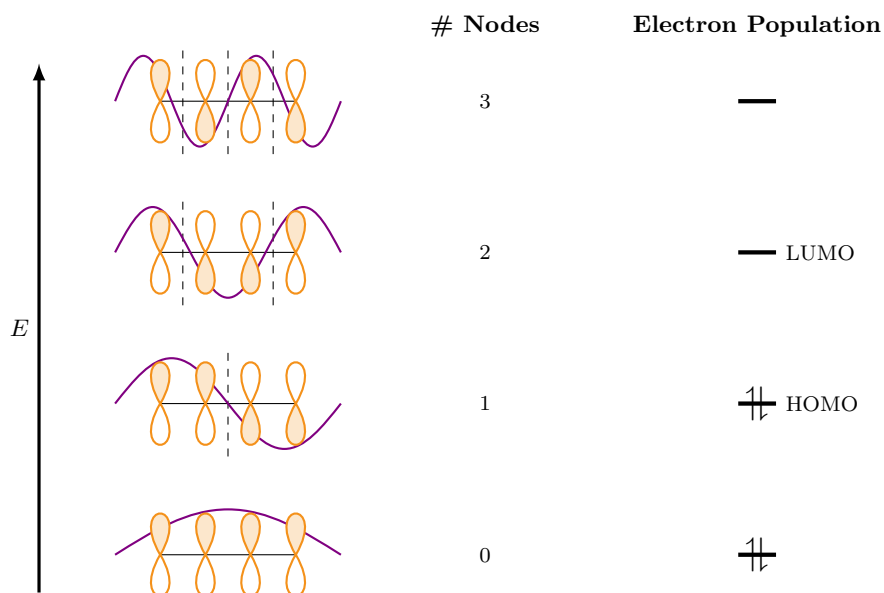
- Diene MOs.

Figure 2.14: Reactive molecular orbitals of a diene.

– Let's start with a rule-by-rule analysis.

    1. We have 4 atoms, so we draw lines for 4 MOs.

    2. The lowest energy MO in Figure 2.14 does indeed have no nodes.

      ■ Observe that Masha shades the top lobes first this time instead of the bottom lobes (as in Figure 2.13) because the shading is arbitrary. This comment is review, but the concept is important to remember!!

    3. For each increase in energy, we do indeed add one node.

      ■ For the second-lowest energy level, we draw our node symmetrically right in the middle.

        ➢ We go along shading the top (or bottom) lobes until we hit our node, and then we switch to shading the other side.

      ■ For the third-lowest energy level, we draw our nodes symmetrically as well.

      ■ For the highest energy level, we draw a node between every orbital and alternate shading.

        ➢ The highest energy level has the same alternating structure in the MOs of every conjugated π-system. For another example, see Figure 2.16.

– Note that we also draw (in purple) the **waveform** for every MO.

– Now let's populate our orbitals with electrons.

    ■ There are four π-electrons in a diene, so per Aufbau, Pauli, and Hund, we fill the bottom two energy levels of our diagram.

    ■ Filling electrons allows us to identify our HOMO and LUMO, which will be useful for justifying reactivity.

– Takeaway: You probably wouldn't just guess that the LUMO (or any other MO) of a diene looks the way it does, but you can derive it using the three rules and the method of Figure 2.14.

    ■ Then you can use the result of your derivation to make predictions about a diene's reactivity!

    ■ We'll cover such predictions next lecture.

• Why do the nodes have to be symmetric?

– Because quantum mechanics.

– Very simply, it has something to do with the waveform of each energy level, which you might notice mirrors the waveforms of the particle in a box.

– See the end of my notes for this lecture for more detail.

    ■ Note: All extra detail on this topic is beyond the scope of this class, and will never be tested nor appear on problem sets; it is purely to satisfy your curiosity.

• An interesting finding about pericyclic reactions: They can be started by either heat (Δ) or light ($h\nu$)!
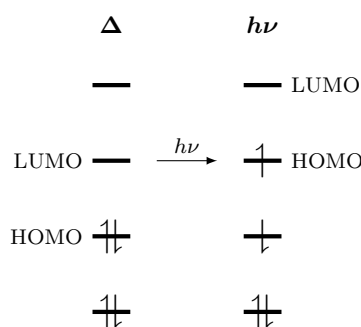

Figure 2.15: A diene's reactive orbitals in thermal vs. photochemical pericyclic reactions.

- When you think about it, heat and light are just different ways to add energy to our system so that the reaction goes.
- Indeed, pericyclic reactions are cool because you don't have to add a chemical reagent to make one go; rather, you just heat it up or shine light at it, and it reacts away!
- How do photochemical reactions work?
  - ■ When light is absorbed, one electron is excited from the HOMO to the LUMO, and none of the spins of *any* of the electrons change (Figure 2.15).
    - ➢ There's a lot more photophysics here that you can go into, but that's beyond the scope of this course.
  - ■ Such excitation is important because it gives us a new HOMO and a new LUMO.
    - ➢ These new reactive orbitals have important consequences that we'll discuss later, especially for the stereochemistry of the product.

• Let's now look at the MOs of one more conjugated system.
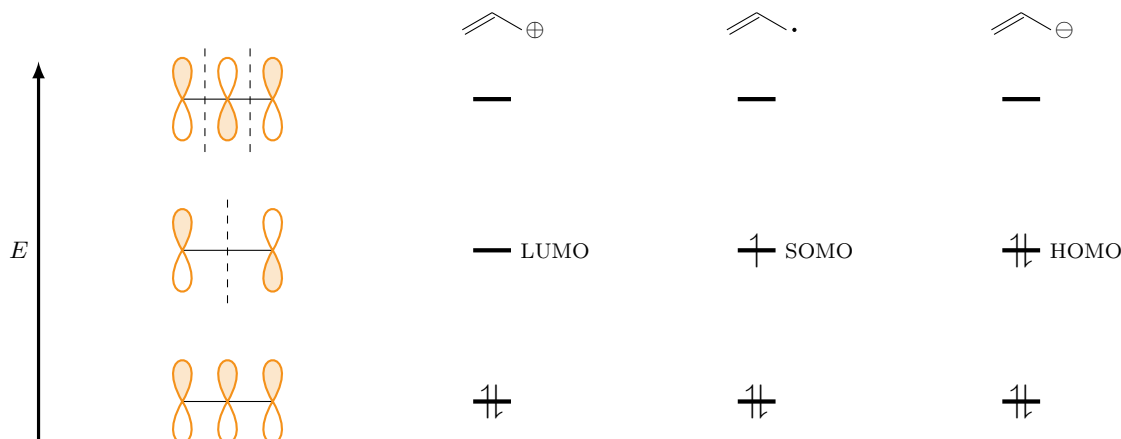
• Allyl MOs.

Figure 2.16: Reactive molecular orbitals of an allyl group.

- Let's do another rule-by-rule analysis.
  1. Three atoms going in means three MOs.
  2. Shade all the same phases in the bottom MO.
  3. Add nodes for the upper orbitals.
     - ■ Put your node right in the middle for the middle MO.
       - ➢ It has to be symmetric!
       - ➢ Every time you have an odd number of atoms, some *p*-orbital will get deleted like this.
     - ■ For the top MO, once again do everything alternating.
- Note that we have not yet specified whether this is an allyl cation, allyl radical, or allyl anion!
- We will have a different number of electrons for all three species (even though we have the same MOs), so let's fill electrons for each of these species.
  - ■ Allyl cation: Two electrons, so fill just the bottom MO.
    - ➢ Like any carbocation, the allyl cation will react as an electrophile.
    - ➢ If it reacts as an electrophile, it must react with its LUMO (which is the middle orbital).
  - ■ Allyl radical: Three electrons, so fill the bottom MO and start filling the middle MO.
    - ➢ Like any radical, the allyl radical reacts as a...well...radical.
    - ➢ If it reacts as a radical, it must react with its **SOMO** (also the middle orbital).

- ■ Allyl anion: Four electrons, so fill the bottom and middle MOs.
  - ➢ Like any carbanion, the allyl anion will react as a nucleophile.
  - ➢ If it reacts as a nucleophile, it must react with its HOMO (still the middle orbital!).
- – Interesting consequence of this filling: All three allyl species should only react with their middle-energy MO!
  - ■ This would predict that all allyl reactivity occurs at the termini of the allyl group, not the middle carbon, since all of the density of the middle orbital is at the termini and none of it is at the middle carbon.
  - ■ This prediction is experimentally confirmed!

- • **Singly occupied molecular orbital**: The molecular orbital in which an unpaired radical electron exists. *Also known as* **SOMO**.

- • An elaboration on why nodes must be placed symmetrically in the MOs of conjugated π-systems (see Figures 2.14 and 2.16 and the associated discussion).

  - – Reminder: Everything from here, on, in these notes is beyond the scope of this class!
  - – The long-short.
    - ■ The waveforms in Figure 2.14 are *exactly* equal to their corresponding particle-in-a-box wave functions (according to some analyses of quantum mechanics).
      - ➢ This relationship can be rationalized intuitively because a conjugated π-system is like an extended, one-dimensional box in which a quantum particle (namely, an electron) lives.
    - ■ The implication is that the molecular orbitals of a conjugated π-system look *exactly* like the particle-in-a-box orbitals, including having nodes in the same places.
    - ■ This actually also means that the individual p-orbitals making up the MOs are different sizes!
      - ➢ For example, in the lowest energy MO in Figure 2.14, the two middle p-orbitals will be larger than the two terminal p-orbitals.
      - ➢ More relevantly, the HOMO and LUMO in Figure 2.14 will have larger terminal p-orbitals, which explains why dienes react at their ends and not in the middle; we have already seen an example of dienes reacting at their terminal carbons instead of their middle carbons in Figure 2.8.
  - – More detail.
    - ■ The exact sizes of each p-orbital in a given MO of a conjugated π-system can be calculated — by hand — using only linear algebra. This calculation is part of something called **Hückel theory**.
    - ■ You can learn about Hückel theory by taking a course in quantum mechanics, inorganic chemistry, or graduate physical organic chemistry.
  - – If you are interested in reading more about this now, look through the attached PDF. I'd recommend starting with the diagrams and sine/cosine functions on pages 6.6 and 6.7. Enjoy!
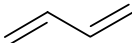
6   Hückel Theory

This theory was originally introduced to permit qualitative study of the π-electron systems in planar, conjugated hydrocarbon molecules (i.e. in "flat" hydrocarbon molecules which possess a mirror plane of symmetry containing all the carbon atoms, and in which the atoms of the carbon skeleton are linked by alternating double and single carbon-carbon bonds when the bonding is represented in a localised fashion). It is thus most appropriate for molecules such as benzene or butadiene, but the approach and concepts have wider applicability.

Basic Assumptions

1.   the atomic orbitals contributing to the π-bonding in a planar molecule (e.g. the so-called p_π orbitals in a molecule such as benzene) are antisymmetric with respect to reflection in the molecular plane; they are therefore of a different symmetry to the atomic orbitals contributing to the σ-bonding and may be treated independently.

s or p_σ
orbital

p_π orbital

Mirror plane (of molecule)
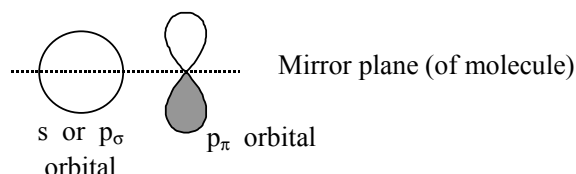
2.   the Coulomb integrals for all the carbon atoms are assumed to be identical.

   i.e. small differences in α-values due to the different chemical environment of C atoms in a molecule such as   are neglected.

3.   all resonance integrals between directly-bonded atoms are assumed to be the same; whilst those between atoms that are not directly bonded are neglected.

   i.e. $\int \phi_i \hat{H} \phi_j .d\tau$ $= \beta$: if atoms i and j are directly σ-bonded.

                                         $= 0$: if atoms i and j are non-bonded.

4.   all overlap integrals representing the overlap of atomic orbitals centred on different atoms are neglected.

   i.e. $\int \phi_i \phi_j .d\tau$ $= 0$: if $i \neq j$

   (note - if $i = j$ then $\int \phi_i \phi_j .d\tau$ $= 1$ since it is assumed that the atomic orbitals are normalized)

A Closer Look at the Secular Determinant

The basic form of the secular determinant for the bonding arising from the overlap of two orbitals (from 4.9) is reproduced below.

$$\begin{vmatrix} \alpha_1 - E & \beta_{12} \\ \beta_{12} & \alpha_2 - E \end{vmatrix}$$
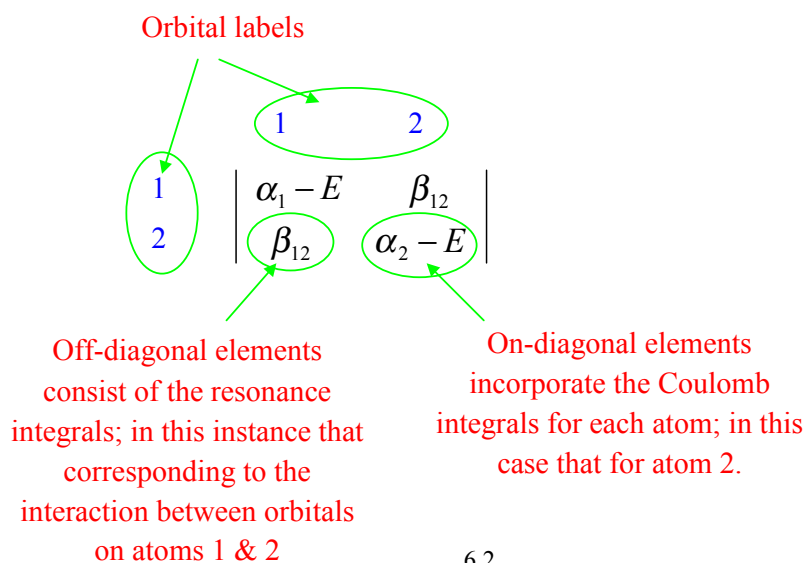
For three overlapping orbitals the approach outlined in Chapter 4 leads to a secular determinant of the form:

$$\begin{vmatrix} \alpha_1 - E & \beta_{12} & \beta_{13} \\ \beta_{12} & \alpha_2 - E & \beta_{23} \\ \beta_{13} & \beta_{23} & \alpha_3 - E \end{vmatrix}$$

From a comparison of the two secular determinants given above, it is becoming clear that all such secular determinants have a characteristic structure:

1. each row and column may be associated with one of the atomic orbitals; thus the first row and first column contain information about the nature of orbital 1 and its interactions with the other orbitals, the second row and second column contain information about the nature of orbital 2 and its interactions with the other orbitals.

2. The diagonal set of elements (comprised of those elements where row 1 intersects column 1, row 2 intersects column 2, ….. and so on) include the values of the relevant Coulomb integrals (α_1 , α_2 etc.).

3. The off-diagonal elements (comprised of those elements having different row numbers and column numbers) are equal to the relevant resonance integrals (e.g. β_{12} at the intersection of row 1 and column 2)
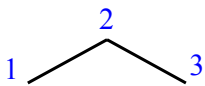
This structure is summarised below, where the rows and columns have been labelled with numbers identifying the associated atomic orbital:

Orbital labels

$$\begin{vmatrix} \alpha_1 - E & \beta_{12} \\ \beta_{12} & \alpha_2 - E \end{vmatrix}$$

Off-diagonal elements consist of the resonance integrals; in this instance that corresponding to the interaction between orbitals on atoms 1 & 2

On-diagonal elements incorporate the Coulomb integrals for each atom; in this case that for atom 2.

6.2

Linear Conjugated Hydrocarbons

C_3 Molecules (3-atom chain)

Secular Determinant / Equation

	1	2	3	
1	$\alpha - E$	β	0	
2	β	$\alpha - E$	β	$= 0$
3	0	β	$\alpha - E$	

$\Rightarrow$

$$\begin{vmatrix} x & 1 & 0 \\ 1 & x & 1 \\ 0 & 1 & x \end{vmatrix} = 0 \qquad \text{where} \quad x = \frac{(\alpha - E)}{\beta}$$

$\Rightarrow \qquad x(x.x - 1.1) - 1(1.x - 1.0) + 0(1.1 - x.0) = 0$

$\Rightarrow \qquad x^3 - x - x = 0$

$\Rightarrow \qquad x^3 - 2x = 0$

$\Rightarrow \qquad x(x^2 - 2) = 0$

$\Rightarrow \qquad x = 0 \qquad \underline{\text{or}} \qquad x = \pm\sqrt{2}$

i.e. $\qquad x = +\sqrt{2} \ , \ \ 0 \ , \ -\sqrt{2}$

Now $\qquad E = \alpha - x\beta$

So the energies of the molecular orbitals are:

$\qquad E = \alpha - \sqrt{2}.\beta \qquad$ - Highest Energy
$\qquad E = \alpha$
$\qquad E = \alpha + \sqrt{2}.\beta \qquad$ - Lowest Energy

The secular equations are:

$$c_1(\alpha - E) \quad + \quad c_2\beta \quad + \quad 0 \quad = \quad 0$$
$$c_1\beta \quad + \quad c_2(\alpha - E) \quad + \quad c_3\beta \quad = \quad 0$$
$$0 \quad + \quad c_2\beta \quad + \quad c_3(\alpha - E) \quad = \quad 0$$

or, in terms of x,

$$c_1 x \quad + \quad c_2 \quad + \quad 0 \quad = \quad 0 \qquad [1]$$
$$c_1 \quad + \quad c_2 x \quad + \quad c_3 \quad = \quad 0 \qquad [2]$$
$$0 \quad + \quad c_2 \quad + \quad c_3 x \quad = \quad 0 \qquad [3]$$

For $\underline{x = 0}$ (i.e. $E = \alpha$)
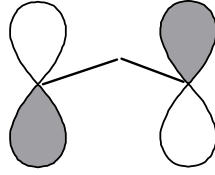
  [1] $\Rightarrow$ $c_2 = 0$

  [2] $\Rightarrow$ $c_1 + c_3 = 0$ $\Rightarrow$ $c_1 = -c_3$

If we now apply the normalisation condition ($\sum c_i^2 = 1$ - see Appendix 2)

   $\Rightarrow$ $|c_1| = |c_3| = \dfrac{1}{\sqrt{2}}$

i.e.

For $\underline{x = -\sqrt{2}}$ (i.e. $E = \alpha + \sqrt{2}.\beta$)

  [1] − [3] $\Rightarrow$ $c_1 - c_3 = 0$ $\Rightarrow$ $c_1 = c_3$

  [1] $\Rightarrow$ $-\sqrt{2}.c_1 + c_2 = 0$ $\Rightarrow$ $c_2 = \sqrt{2}.c_1$

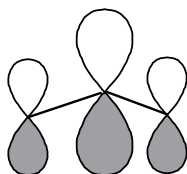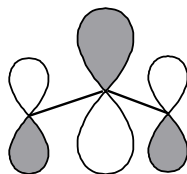If we now apply the normalisation condition ($\sum c_i^2 = 1$ - see Appendix 2)

   $\sum c_i^2 = c_1^2 + c_2^2 + c_3^2 = c_1^2 + (\sqrt{2}c_1)^2 + c_1^2 = 4c_1^2 = 1$

   $\Rightarrow$ $c_1^2 = \dfrac{1}{4}$

   $\Rightarrow$ $c_1 = c_3 = \dfrac{1}{2}$ ($= 0.500$)

   $\Rightarrow$ $c_2 = \sqrt{2}.\dfrac{1}{2} = \dfrac{1}{\sqrt{2}}$ ($= 0.707$)

i.e.

For $x = +\sqrt{2}$ (i.e. $E = \alpha - \sqrt{2}.\beta$)

  [1] − [3] $\Rightarrow$ $c_1 - c_3 = 0$ $\Rightarrow$ $c_1 = c_3$

  [1] $\Rightarrow$ $\sqrt{2}.c_1 + c_2 = 0$ $\Rightarrow$ $c_2 = -\sqrt{2}.c_1$

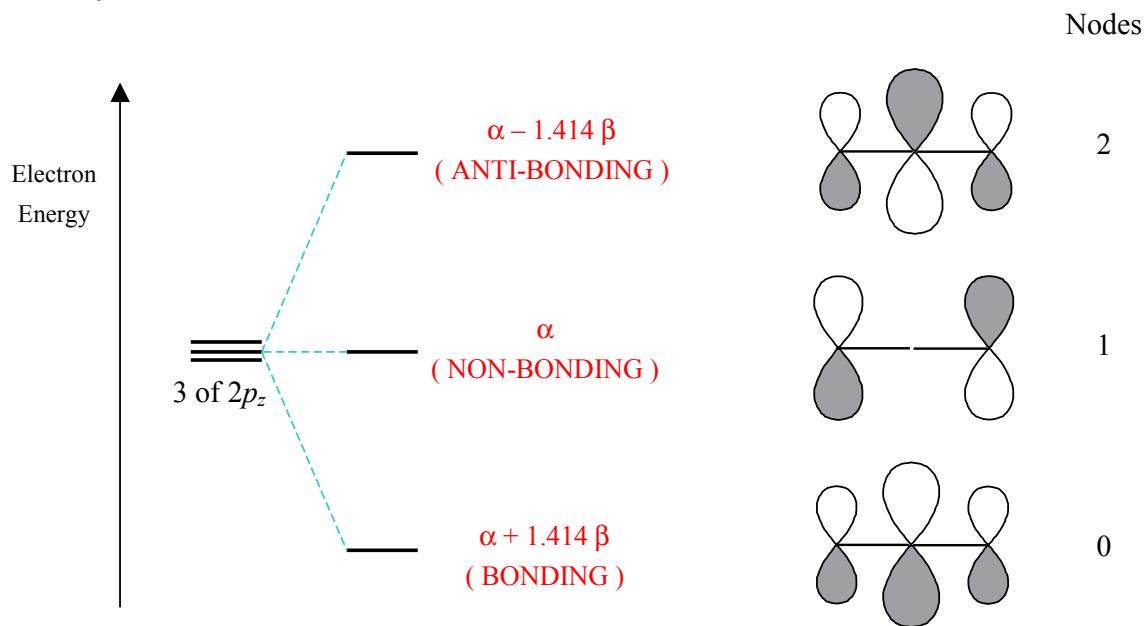If we now apply the normalisation condition ($\sum c_i^2 = 1$ - see Appendix 2)

  $\Rightarrow$ $c_1 = c_3 = \dfrac{1}{2}$ (= 0.500)

  $\Rightarrow$ $c_2 = \dfrac{-1}{\sqrt{2}}$ (= − 0.707)

i.e.

In summary,

Nodes

Electron
Energy

3 of $2p_z$

$\alpha - 1.414\,\beta$
(ANTI-BONDING)   2

α
(NON-BONDING)   1

$\alpha + 1.414\,\beta$
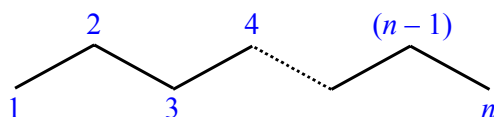(BONDING)   0

< *Lectures* - examples of bond order and charge distribution calculations for allylic species >

General Solution (n-atom chain ; e.g. $C_nH_{(n+2)}$ conjugated polyenes)

The secular determinant has the same basic form, whatever the chain length, as illustrated below:

	1	2	3			n
1	x	1	0	0	...	0
2	1	x	1			
3	0	1	x			
	0					
					x	1
n	0	...	...	...	1	x

$= 0$

Consequently the solutions also have the same basic form, whatever the chain length, and it can be demonstrated that:

<u>Orbital coefficients</u>:   are given by

$$c_s \propto \sin\left(\frac{\pi k s}{n+1}\right) \qquad\qquad [4]$$

where
- n -   total number of atoms in the conjugated chain
- s -   atom number   (i.e. 1, 2, ..., n)
- k -   quantum number, identifying the MO   (= 1, 2, ..., n)

and the constant of proportionality can be determined by applying the normalisation condition.

Example: consider the highest energy MO ($k = 3$) of the three carbon chain ($n = 3$).

$$\Rightarrow \qquad c_s \propto \sin\left(\frac{3\pi s}{4}\right)$$

i.e.

$$c_1 \propto \sin\left(\frac{3\pi}{4}\right) = \frac{1}{\sqrt{2}} \quad , \quad c_2 \propto \sin\left(\frac{6\pi}{4}\right) = -1 \quad , \quad c_3 \propto \sin\left(\frac{9\pi}{4}\right) = \frac{1}{\sqrt{2}}$$

These coefficients are <u>not</u> normalized - to achieve this we need to multiply them all by the same constant value, chosen to ensure that the new values of the coefficients satisfy the condition that $\sum c_i^2 = 1$.
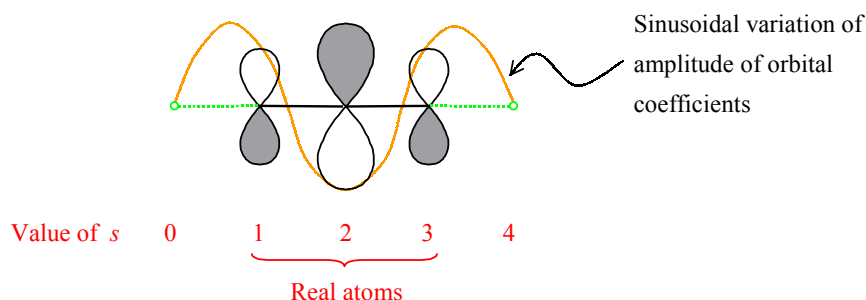
From the general expression for the coefficients given above it can be seen that the relative signs and sizes can also be visualised using the following trigonometric construction.

Procedure :

1. Draw the *n*-regularly spaced atoms (1, 2, ..., *n*) in a straight line and then add two imaginary atoms (labelled 0 and (*n* + 1)) at either end of the chain.

2. Sketch portions of sine waves between these two imaginary end atoms, ensuring that the imaginary end atoms correspond to nodes of the sine wave.

3. The lowest energy MO has no other nodes and corresponds to half a sine wave; the next MO has one additional node in the middle and corresponds to a complete sine wave; the next MO has two additional nodes .... and so on.

e.g. for the third MO (*k* = 3) of the three carbon chain (*n* = 3).

Sinusoidal variation of amplitude of orbital coefficients

Value of *s*   0   1   2   3   4

Real atoms

Orbital energies: are given by

$$E = \alpha + 2\beta \cos\left(\frac{\pi k}{n+1}\right)$$ [5]

where   *n* -   total number of atoms in the conjugated chain
               k -   quantum number, identifying the MO   (= 1, 2, ..., *n*)

Note that the cosine function varies only between the limiting values of −1 and +1.

i.e. $-1 \le \cos\left(\frac{\pi k}{n+1}\right) \le +1$

hence $(\alpha + 2\beta) \le E \le (\alpha - 2\beta)$

Consequently all molecular orbital energies must lie within an energy range of 4β, $\pm 2\beta$ of the original atomic orbital energy.

Recall also that for an *n*-atom chain, in which each atom contributes one atomic orbital to the conjugated π-system, there will be *n* overlapping atomic orbitals giving rise to *n* molecular orbitals.

Since all these MOs are confined to a fixed energy range, it follows that the average energy separation must decrease as n increases. This is illustrated below in an electron energy diagram which also shows the electron occupancy (for the neutral molecule) for the first three members of the series :
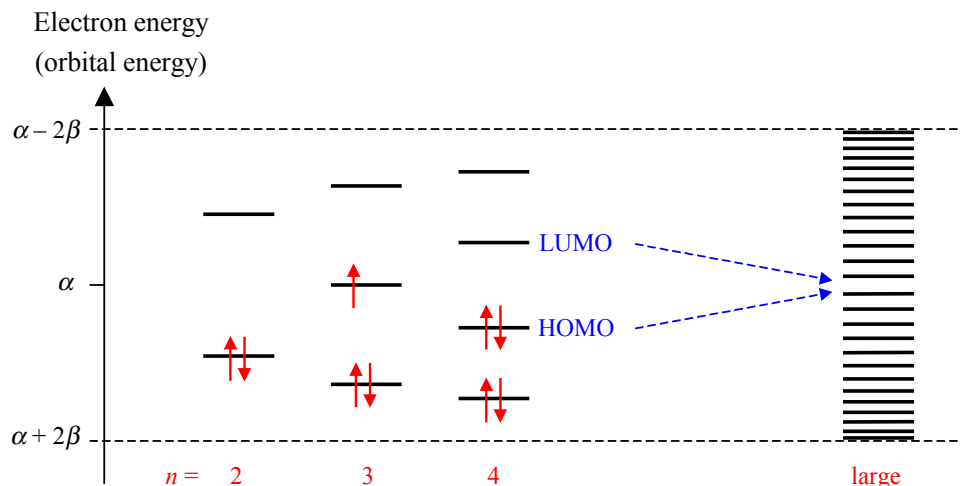
Note:

1. As n increases: the HOMO-LUMO separation decreases - consequently the photon energy required to excite an electron from the HOMO to LUMO also decreases.

    i.e. $h\nu = \Delta E = E_{HOMO} - E_{LUMO}$ decreases as n increases.

    For conjugated carbon atom chains the photon energy changes from the UV (for small n) to the visible (large n). Consequently, molecules with extended conjugated systems are coloured.

2. As $n \rightarrow \infty$: the separation between any two energy levels decreases towards zero and the energy levels (although still discrete in principle) effectively merge to give a continuous *band* of energy levels. The width of this band is 4β and is therefore determined by the effectiveness of overlap of the individual atomic orbitals and hence the strength of interaction and the magnitude of the resonance integral β. The system approaches the *metallic state* - that is to say that electrical conduction can readily occur (since the HOMO-LUMO separation is essentially zero) and all wavelengths of visible light are readily absorbed.

Cyclic Conjugated Hydrocarbons

General Solution (n-atom ring ; C_nH_n , cyclic conjugated hydrocarbons)
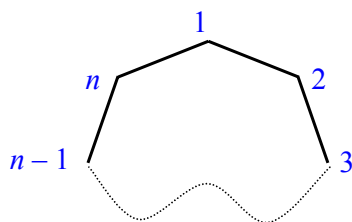
The secular determinant has the same basic form, whatever the ring size, as illustrated below:

	1	2	3			n
1	x	1	0	0	...	1
2	1	x	1			
3	0	1	x			
	0					
					x	1
n	1	...	...	...	1	x

$= 0$

Consequently the solutions also have the same basic form, whatever the ring size, and it can be demonstrated that the:

Orbital energies: are given by

$$E = \alpha + 2\beta \cos\left(\frac{2\pi k}{n}\right) \qquad\qquad [6]$$

where n - total number of atoms in the conjugated ring system
k - quantum number, identifying the MO $(= 0, 1, 2, ..., n–1)$

but, given the periodic and "even" (symmetrical about $\theta = 0$) nature of the cosine function, this permitted range of k-values may also be written in the form

$$k = 0, \pm1, \pm2, ..., \left(\frac{n}{2}\right) \qquad\qquad \text{for even } n .$$

$$k = 0, \pm1, \pm2, ..., \pm\left(\frac{n-1}{2}\right) \qquad\qquad \text{for odd } n .$$

Note that the cosine function varies only between the limiting values of -1 and $+1$, and because the cosine function is an even function, the energy depends only on $|k|$.

i.e. $\qquad -1 \le \cos\left(\dfrac{2\pi k}{n}\right) \le +1$

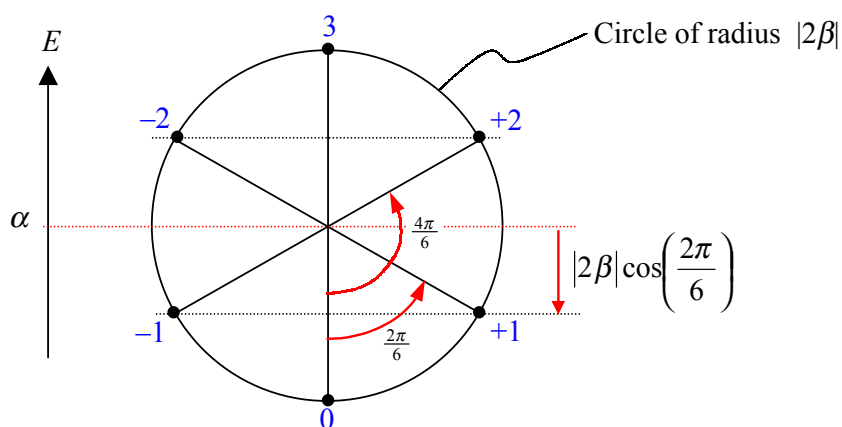hence $\qquad (\alpha + 2\beta) \le E \le (\alpha - 2\beta)$

It is possible to represent equation [6] as a geometrical construction, and this is illustrated below.

Consider $\underline{n = 6}$ (e.g. C_6H_6 - benzene) ; then the expression for E is

$$E = \alpha + 2\beta \cos\left(\dfrac{2\pi k}{6}\right)$$

where

$\qquad k = 0, \pm 1, \pm 2, \ 3 \qquad$ (since n is even).

Whilst the above diagram highlights the relationship between the geometrical construction and the equation for E, it also suggests that the energies of the orbitals may also be obtained using a simpler construction - namely by drawing the corresponding regular polyhedron (i.e. a hexagon for $n = 6$) inscribed inside the circle with one apex coincident with the bottom of the circle.
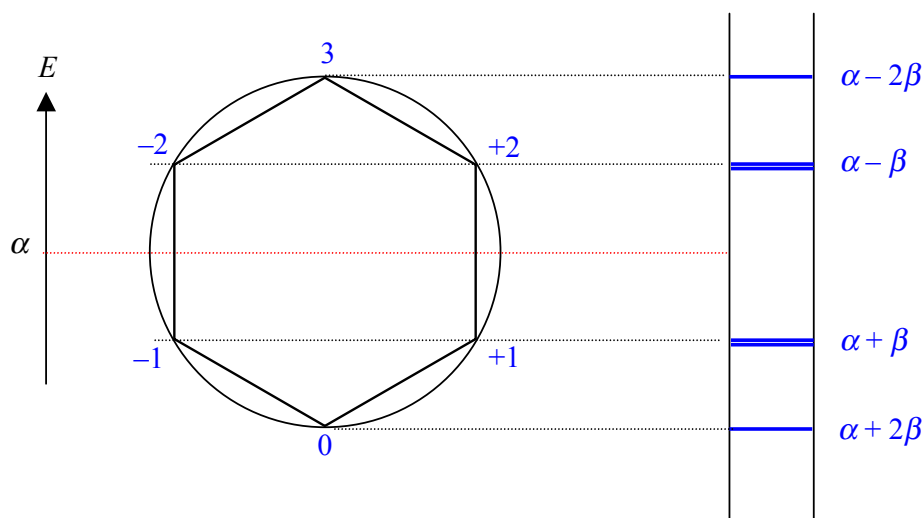
< *Lecture* - other examples, e.g. $n = 3$, $n = 5$ >

<u>Note</u> : for these cyclic conjugated systems

1. The lowest-energy MO is always non-degenerate
2. The highest-energy MO may be non-degenerate (if n is even) or degenerate (if n is odd).
3. All the remaining solutions form pairs of degenerate MOs

One consequence of this arrangement of the MOs is that only specific numbers of electrons can be accommodated if a stable molecule is to result - this is embodied in the ….

Hückel Rule

A stable, closed-shell conjugated cyclic structure is obtained for (4N + 2) electrons.

i.e. stable structures are obtained for 2, 6, 10, …. electrons.

< *Lecture* - examples of stable cyclic systems >
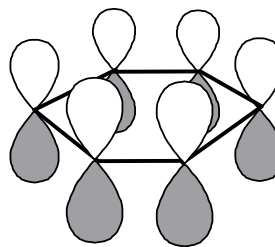
What are the Wavefunctions ?

The wavefunctions are generally complex (i.e. contain imaginary parts), the exceptions being the non-degenerate solution(s).

- The MO of lowest energy ($k = 0$) is always non-degenerate (irrespective of whether n is even or odd) and has the same coefficient for each and every contributing atomic orbital - there are therefore no angular nodes in the wavefunction.

  e.g. for $n = 6$
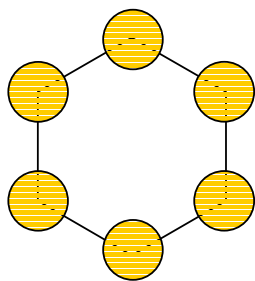
| Top view | Side view |

The molecular plane is a nodal plane for all the π-MOs , but for this particular MO there are no angular nodal planes in the wavefunction and all the interactions between orbitals on adjacent atoms are of a bonding nature.

- The highest-energy MO of even n systems is also non-degenerate.

  The magnitude of the coefficient is the same for each and every contributing atomic orbital but the sign changes between adjacent atoms.

  e.g. for $n = 6$
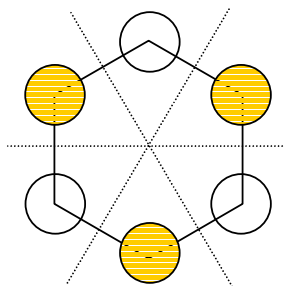
  In this case there are three angular nodal planes as marked (---) on the diagram - the wavefunction thus changes sign between each pair of atoms and all the interactions between orbitals on adjacent atoms are of an anti-bonding nature.

- The remaining degenerate pairs of solutions are complex wavefunctions but it is possible to generate completely real linear combinations of these which are still solutions of the Schrödinger equation with the same energies (in the same way that the p_x and p_y atomic orbitals may be constructed from the p_+ and p_- atomic orbitals).
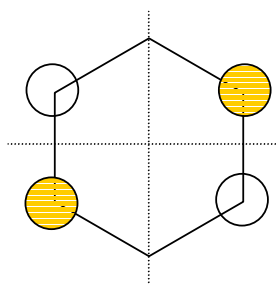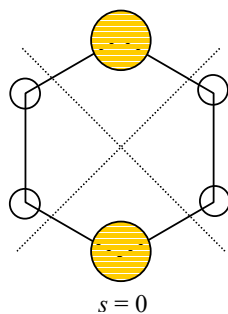
  The coefficients for the real functions are:

$$\psi_{k+} \propto \sum_s \left(\cos\left(\frac{2\pi ks}{n} \right) \right) \phi_s$$

$$\psi_{k-} \propto \sum_s \left(\sin\left(\frac{2\pi ks}{n} \right) \right) \phi_s$$

  e.g. for $n = 6$

$k = \pm 2$

$s = 0$

$k = \pm 1$

$s = 0$