



# CHEMISTRY 2500

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Topic #5: Bonding in Organic Molecules

Fall 2014

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# Molecular Orbital Theory Review

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- Molecular orbital theory is the most widely used model for bonding in molecules. A molecular orbital (MO) is similar to an atomic orbital (AO) in that it describes the probability of finding an electron in a given region. The difference is that a molecular orbital can be spread across multiple atoms within the same molecule.
  - Atomic orbitals are labelled  $1s$ ,  $2s$ ,  $2p$ ,  $3s$ ,  $3p$ ,  $3d$ , etc. where the letter ( $s$ ,  $p$ ,  $d$  or  $f$ ) indicates the orbital shape:
  - Molecular orbitals are labelled  $1\sigma$ ,  $2\sigma$ ,  $1\pi$ ,  $2\pi$ , etc. where the Greek letter ( $\sigma$  or  $\pi$ ) indicates the orbital symmetry:
  - Molecular orbitals are generated by combining atomic orbitals:



# Molecular Orbital Theory Review

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- We are usually only interested in the valence electrons of molecules and, therefore, the valence orbitals.
- To construct a valence molecular orbital diagram:
  - Ignore the core electrons
  - Total number of MOs = Total number of AOs
  - Only AOs of **similar energy** combine to make LCAO-MOs
  - Only AOs of **compatible symmetry** combine to make LCAO-MOs:
    - $\sigma$ -type AOs (no node along the bond axis) make  $\sigma$  MOs
    - $\pi$ -type AOs (with a node along the bond axis) make  $\pi$  MOs

e.g. valence MO diagram for H<sub>2</sub>



# Molecular Orbital Theory Review

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e.g. valence MO diagram for  $F_2$



# Molecular Orbital Theory Review

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- In summary, our approach to building valence MO diagrams is:
  - Identify the valence atomic orbitals from each atom and determine their energy levels (relative energy levels if no values given). Draw these on the edges of the MO diagram.
  - Sort the atomic orbitals by symmetry ( $\sigma$  vs.  $\pi$ ).
  - Within each group, sort the atomic orbitals into those with close enough energies to interact. 1 Ry ( $2.179 \times 10^{-18}$  J) is a good cut-off.
  - Combine compatible atomic orbitals to make an equal number of molecular orbitals with the same symmetry.
  - Predict approximate energy levels of the MOs. The “most bonding” one will be lower in energy than all the AOs from which it was made. The “most antibonding” one will be higher in energy than all the AOs from which it was made. The remaining MOs will have intermediate energies; increasing with number of nodes.
  - Complete the MO diagram by adding the MOs in the middle.
  - Fill in the electrons and identify the HOMO (Highest Occupied Molecular Orbital) and LUMO (Lowest Unoccupied Molecular Orbital).



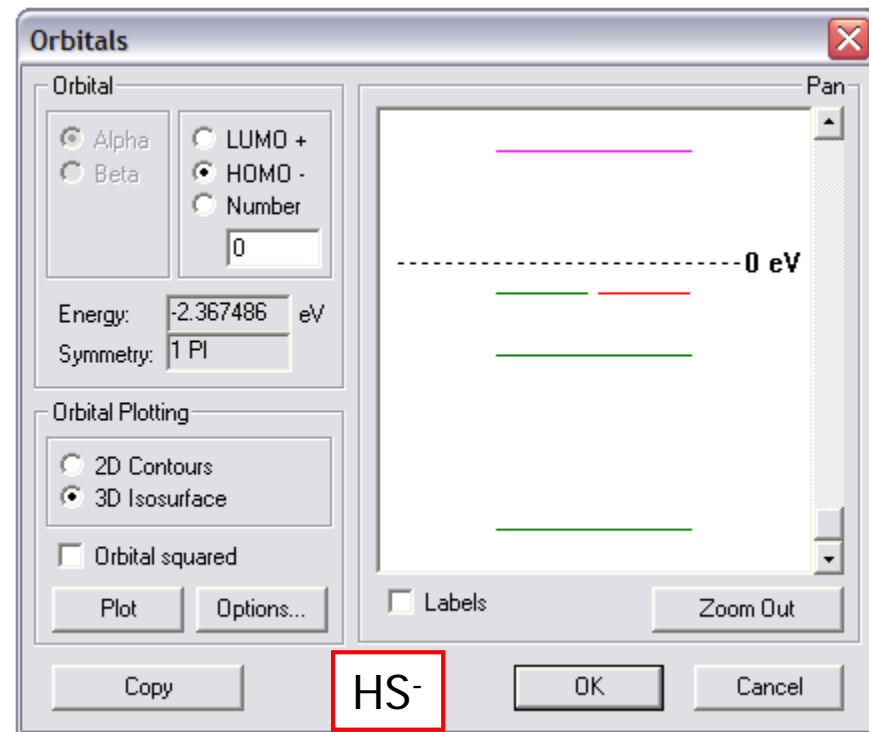
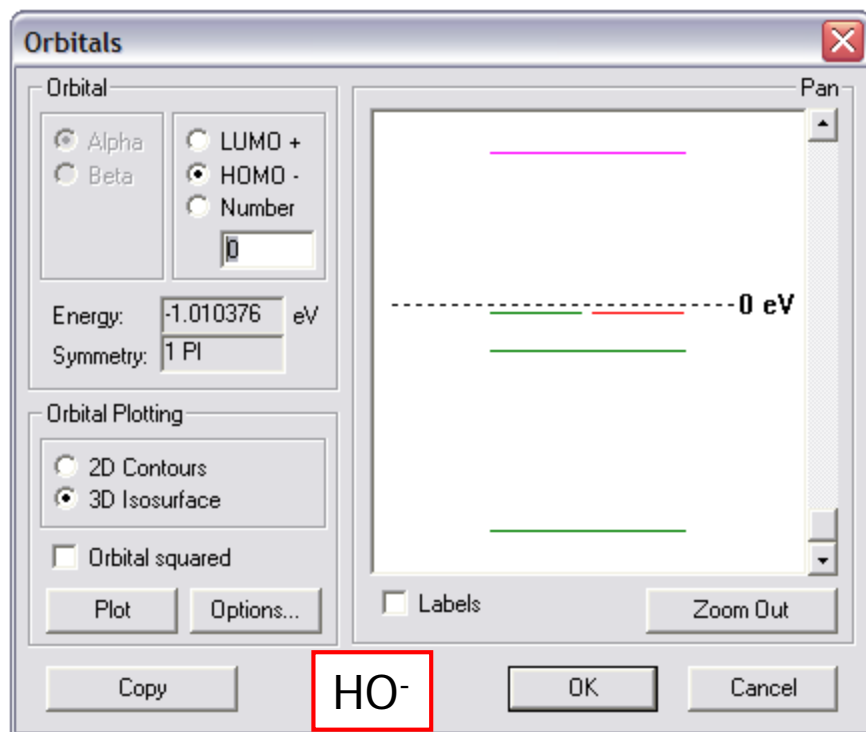
# Frontier Molecular Orbitals

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- The reason why we are most interested in the valence molecular orbitals (and not the core molecular orbitals) is that they are the orbitals which will be involved in reactions. Reactions involve movement of electrons from one place to another – often from one molecule to another.
  - The electrons which can most easily be removed from a molecule are those in the **HOMO** (Highest Occupied Molecular Orbital).
  - The orbital which can most easily take electrons from another molecule is the **LUMO** (Lowest Unoccupied Molecular Orbital).
  - In the case of a radical (molecule with an odd number of electrons), the **SOMO** (Singly Occupied Molecular Orbital) fills both roles; however, this is a less common situation.
- The HOMO, LUMO (and SOMO) are collectively referred to as the **frontier molecular orbitals**. They are the most important orbitals from the perspective of predicting reactivity.

# Frontier Molecular Orbitals

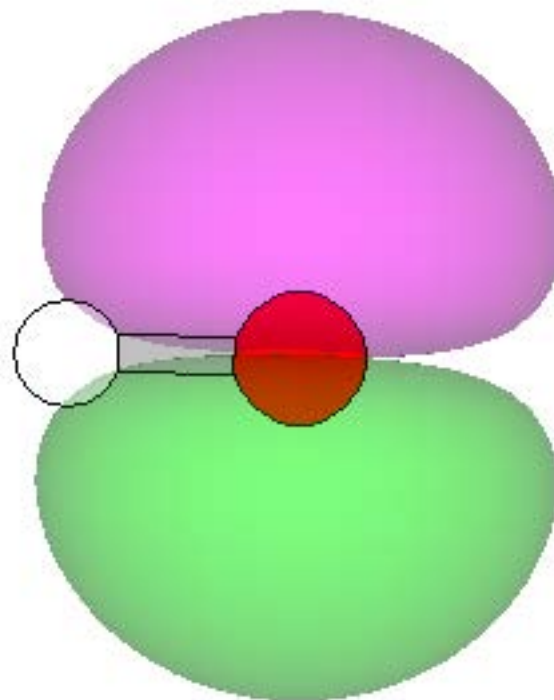
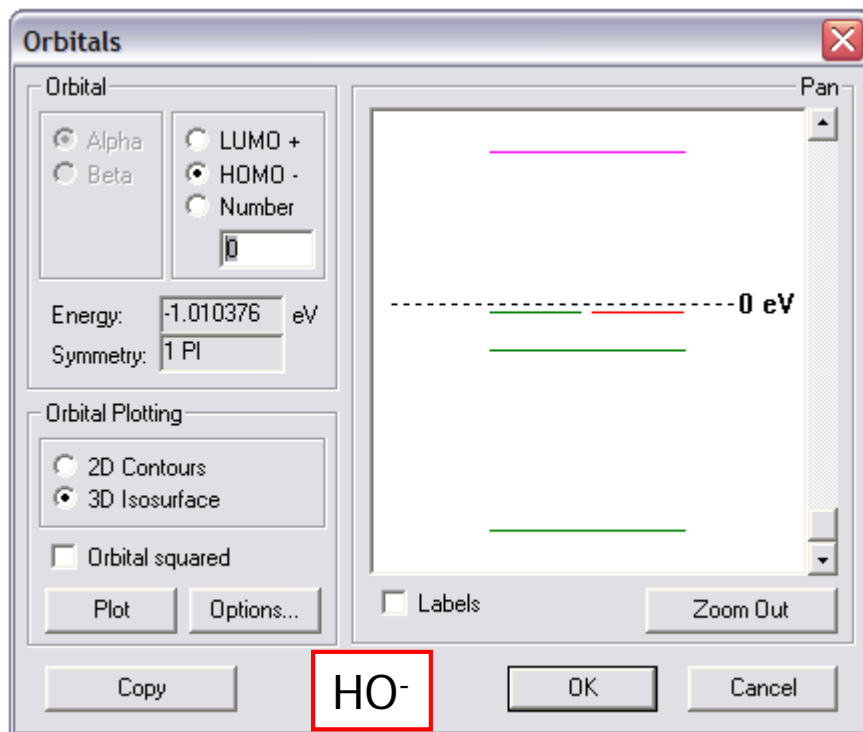
- Consider the ions HO<sup>-</sup> and HS<sup>-</sup>. Which is a stronger base?
- The MO diagrams below were generated using HyperChem. In each case, the HOMO is highlighted and its energy shown at the left. Which HOMO would be easier to remove electrons from?



HyperChem gives energies in electron volts:  $1 \text{ eV} = 1.602 \times 10^{-19} \text{ J}$  ( $13.6 \text{ eV} = 1 \text{ Ry}$ )

# Frontier Molecular Orbitals

- Clicking on "Plot" lets us look at the shape of the molecular orbital of interest (the HOMO). This shows us where the electrons would come from in a reaction. Note that this MO looks an awful lot like a  $2p$  orbital (i.e. lone pair) on oxygen:

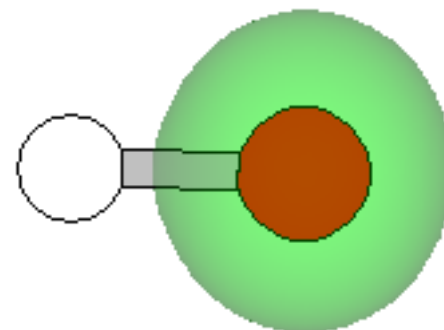


Convention has H in white and O in red. Usually, C is black (though HyperChem has it cyan), N is blue and chlorine is green. Other elements are generally your choice.



# Frontier Molecular Orbitals

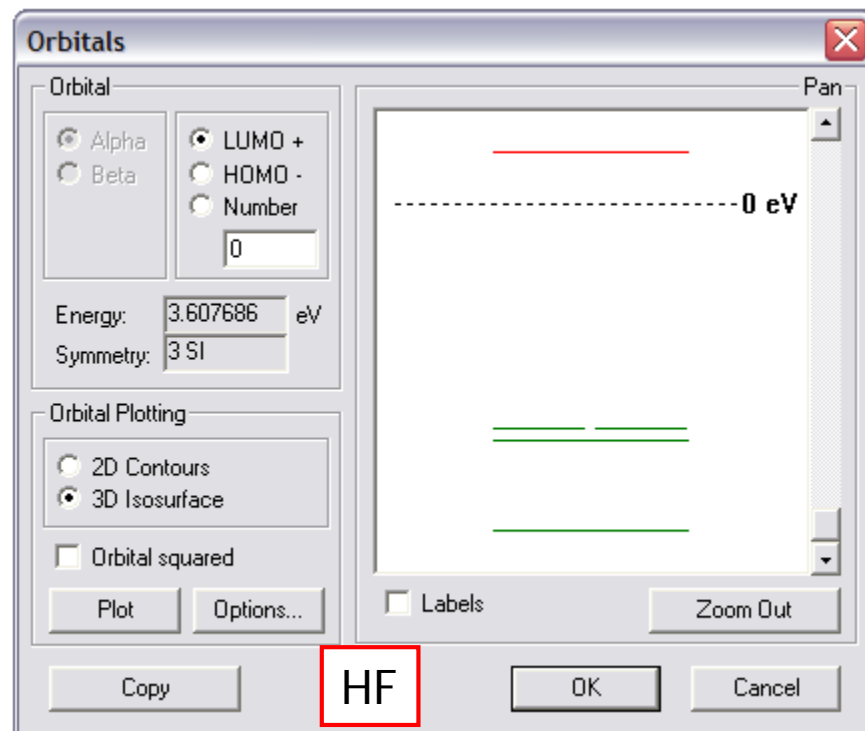
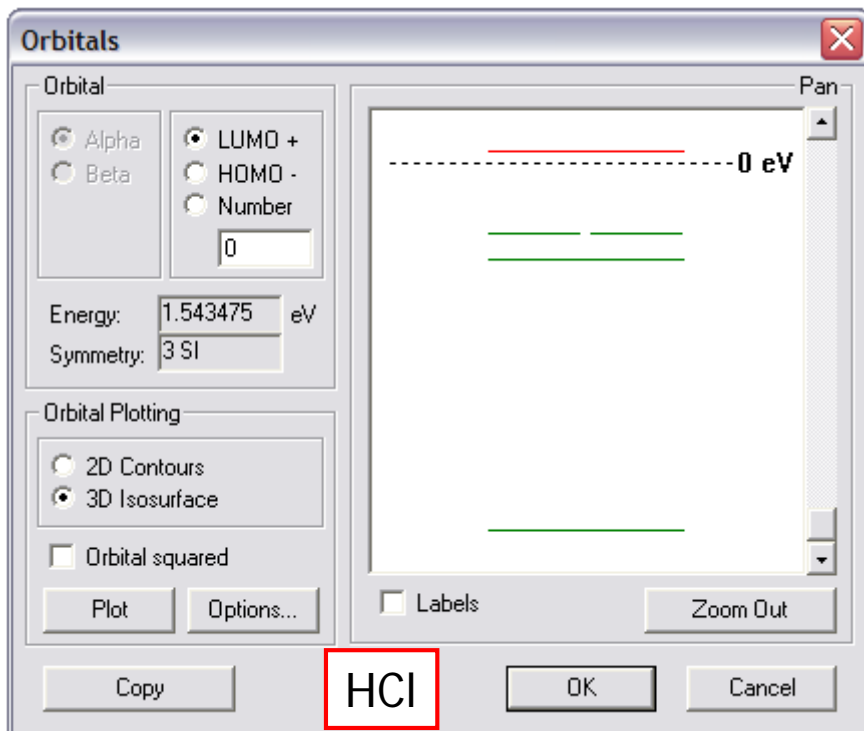
- HyperChem also lets us look at molecular properties like charge density. Unsurprisingly, the negative charge density in  $\text{HO}^-$  appears to be localized on the oxygen atom:



- You will learn how to use HyperChem in lab. Before generating any pictures, you'll have to Compute... Geometry Optimization (or Single Point in unusual cases). After that, MO diagrams can be found under Compute... Orbitals... while charge density maps can be found under Compute... Plot Molecular Properties.

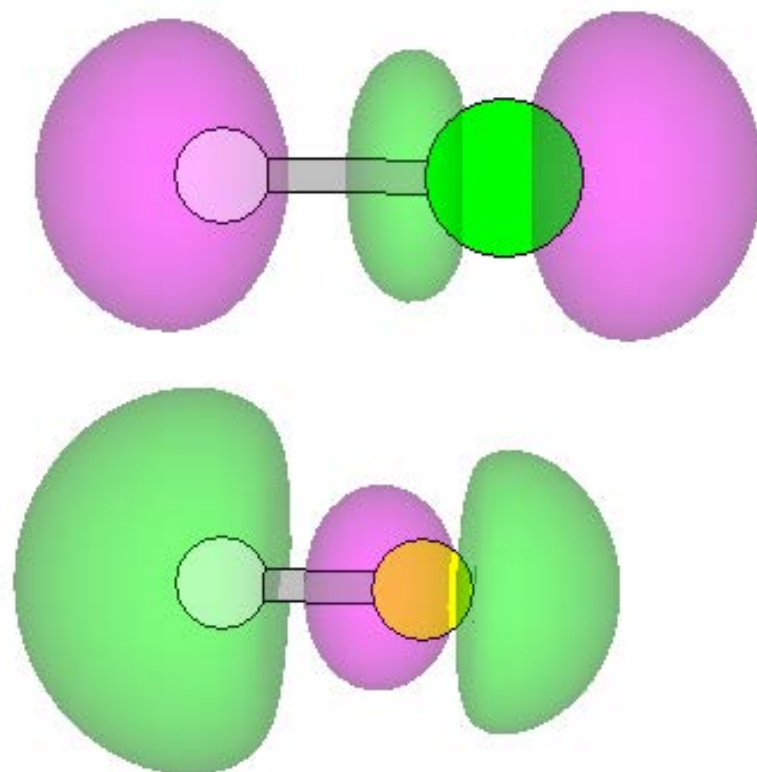
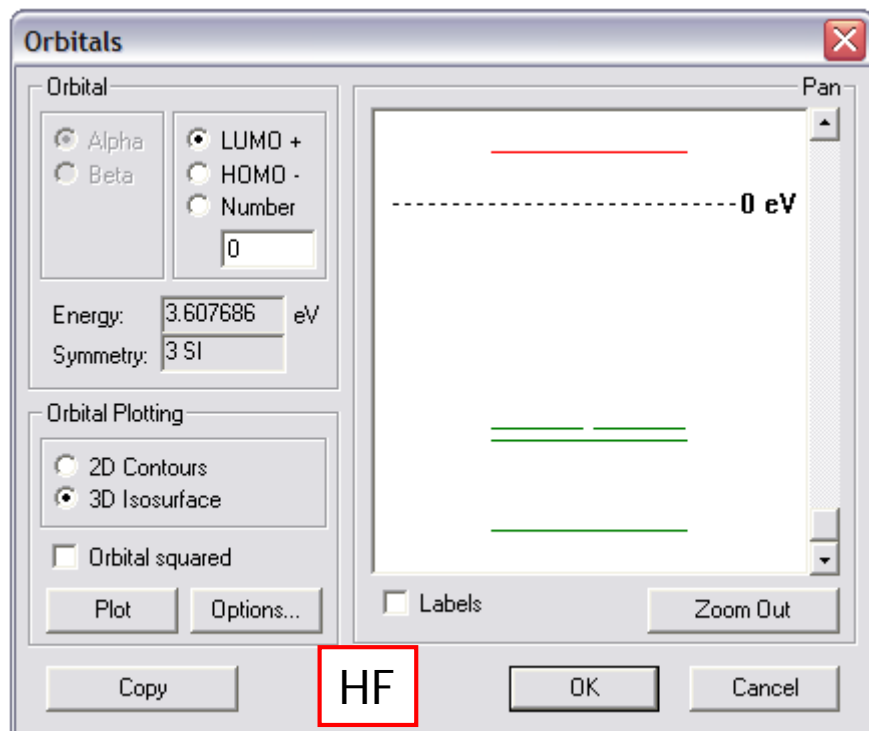
# Frontier Molecular Orbitals

- For molecules which are electron deficient and will receive electrons in a reaction, we look at the LUMO instead. Consider the molecules HCl and HF. Which is a stronger acid? Use the MO diagrams to justify your answer.



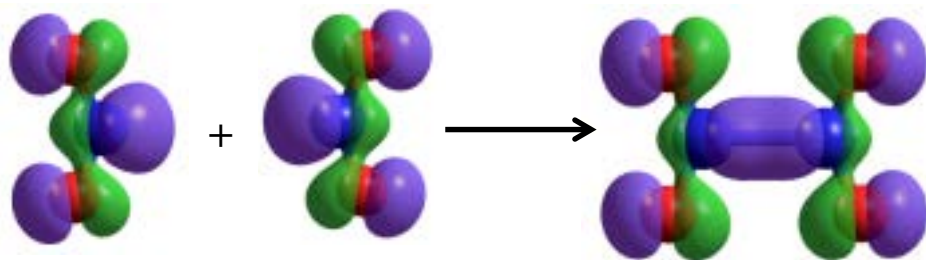
# Frontier Molecular Orbitals

- Note that the LUMOs both show antibonding character between the H and the halogen. Putting electron density into this orbital would therefore result in breaking the H-X bond (exactly what happens when a base deprotonates HF or HCl).



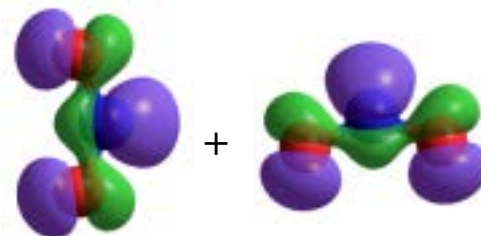
# Frontier Molecular Orbitals

- In order for two species to react, the molecules must collide in such a way that their frontier molecular orbitals are able to interact. This means that, in addition to predicting which species will be reactive, we can also use frontier molecular orbitals to predict the collision geometry required for the reaction to proceed.
- Consider the reaction of two molecules of  $\text{NO}_2$  to give  $\text{N}_2\text{O}_4$ . This is a radical reaction so each molecule reacts via its SOMO (contains one electron and can therefore accept one more):



react to give  $\text{N}_2\text{O}_4$  (HOMO shown)

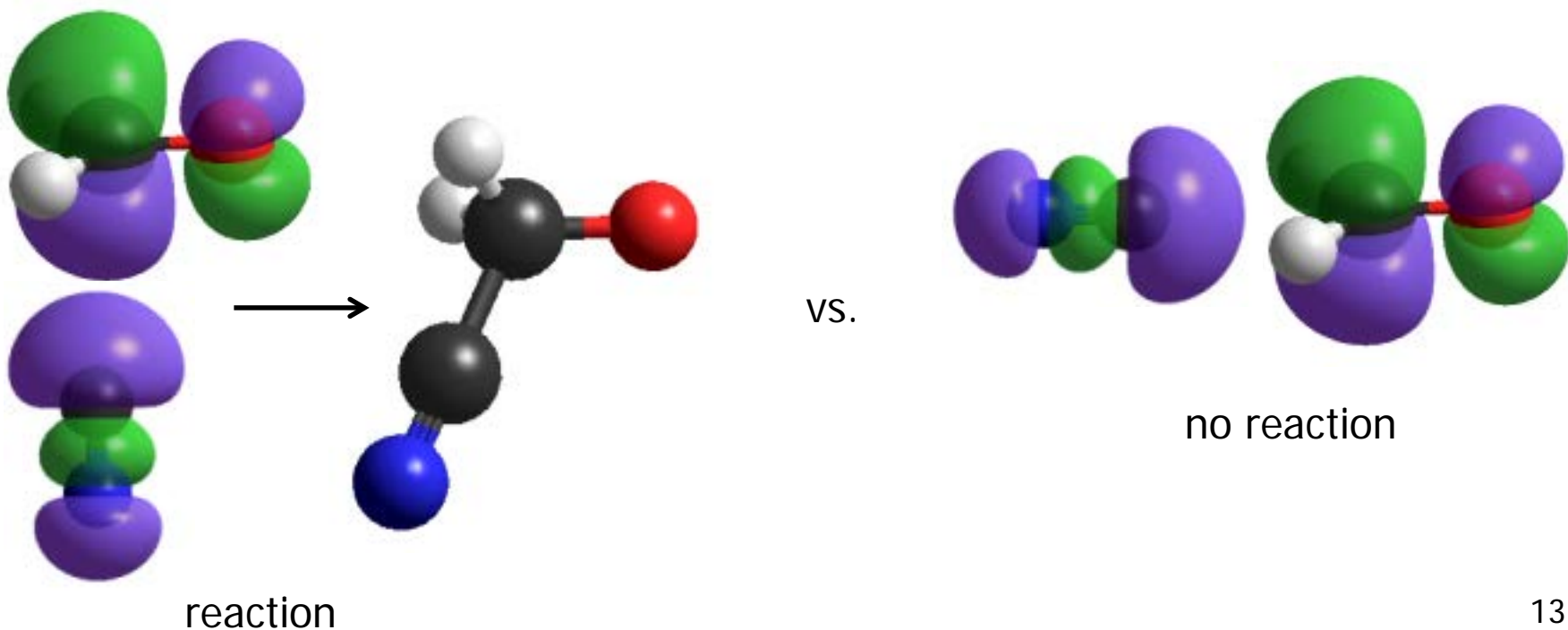
vs.



no reaction

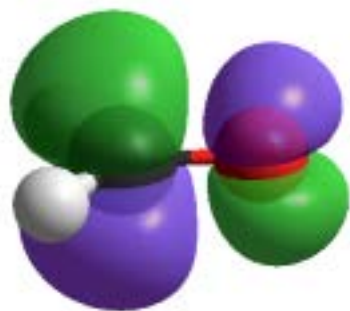
# Frontier Molecular Orbitals

- Consider the reaction between the cyanide ion ( $\text{CN}^-$ ) and methanal. The cyanide is the electron donor so it reacts via its HOMO. The methanal is the electron acceptor so it reacts via its LUMO. Therefore, for a collision to be successful, the HOMO of cyanide and the LUMO of methanal must have positive overlap where the new bond will form:



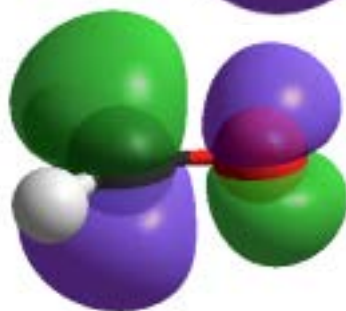
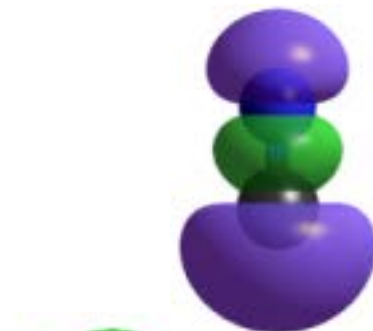
# Frontier Molecular Orbitals

- The collision must also give the best orbital overlap so look to have the largest lobe(s) on the electron donor's HOMO overlapping the largest lobe(s) on the electron acceptor's LUMO.



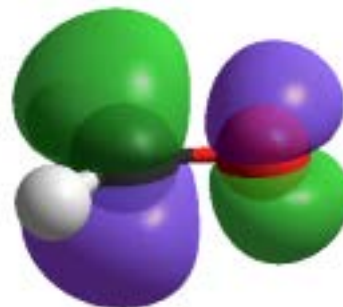
reaction

vs.



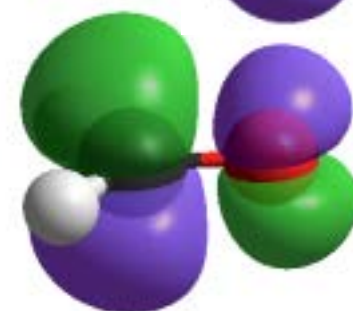
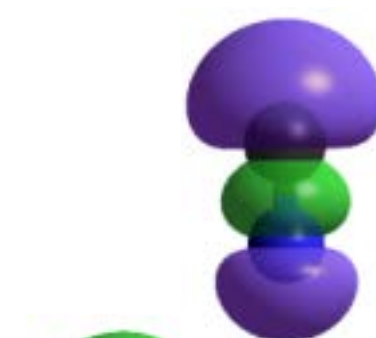
no reaction

vs.



no reaction

vs.



no reaction

Remember that, while relative phase is important, absolute phase is arbitrary. You could switch all the green with all the purple in any of the orbitals pictured



# Frontier Molecular Orbitals

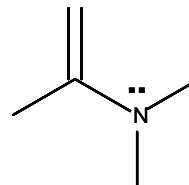
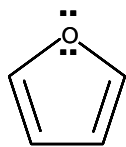
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- Recall that we identified functional groups by looking for heteroatoms (which often have lone pairs) and  $\pi$  bonds.
- Also, recall the usual energy ranking for MOs (high to low):
  - sigma antibonding ( $\sigma^*$ )
  - pi antibonding ( $\pi^*$ )
  - nonbonding (lone pairs; can be  $\sigma$  or  $\pi$ )
  - pi bonding ( $\pi$ )
  - sigma bonding ( $\sigma$ )
- In molecules containing  $\pi$  bonds, the frontier orbitals tend to have  $\pi$  symmetry. In these molecules, the filled  $\sigma$  MOs tend to have much lower energy than the HOMO while the empty  $\sigma^*$  MOs tend to have much higher energy than the LUMO. As such, we often draw simplified MO diagrams that just show the  $\pi$ -symmetric MOs.

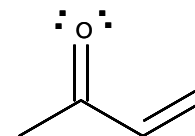
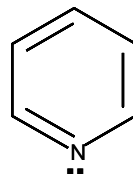
**THIS DOES NOT MEAN WE SHOULD FORGET LONE PAIRS!!!  
NOT EVEN THE ONES IN  $\sigma$ -SYMMETRIC MOs.**

# Pi Molecular Orbital Diagrams

- A  $\pi$ -MO diagram is a simplified MO diagram that is missing the  $\sigma$ -MOs for clarity. To generate one, after you sort the AOs by symmetry, discard the  $\sigma$ -AOs and only consider the  $\pi$ -AOs.
- You will need to be careful to include the correct number of electrons. Include two electrons for every pi bond on your Lewis structure and two electrons for every lone pair involved in the pi system.
  - A lone pair is involved in the pi system if the atom with the lone pair is bonded to at least one **other** atom which has a pi bond in the pi system. Only one lone pair per atom can be part of the same pi system.



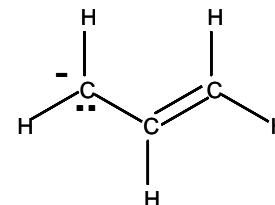
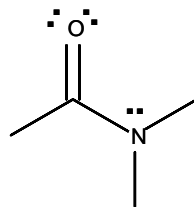
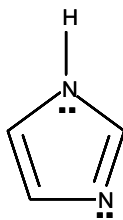
- A lone pair is **not** involved in the pi system if the atom has a pi bond in the pi system.





# Pi Molecular Orbital Diagrams

- Identify how many electrons there are in the pi system for each molecule below, and circle any lone pairs which are part of the pi system.



You may find it helpful to draw resonance structures and see which lone pairs (if any) "move" between reasonable (or, at least, not horrible) resonance structures.



# Pi Molecular Orbital Diagrams

- According to molecular orbital (MO) theory<sup>\*</sup>, all  $\pi$ -symmetric orbitals in a  $\pi$ -system combine to give a set of  $\pi$ -MOs in which:
  - The number of  $\pi$ -MOs is equal to the number of  $p$  orbitals which combined to make them.
  - In a linear  $\pi$ -system, # energy levels = #  $\pi$ -MOs.
  - In a cyclic  $\pi$ -system, use a Frost circle (polygon-in-a-circle trick) to predict energy levels; the polygon should always point down. *Note: while benzene has a cyclic  $\pi$ -system, 1,3-cyclohexadiene does not!*
  - The number of delocalized  $\pi$ -electrons is equal to 2 electrons per double bond + 2 electrons per **lone pair that is part of the  $\pi$ -system**. *We are primarily interested in the HOMO and LUMO of any given  $\pi$ -system, so make sure you count your electrons carefully to correctly identify the HOMO and LUMO!*

<sup>\*</sup> Sorrell implies that MOs can be made from hybridized orbitals. This is a case of mixing two different (and largely incompatible) bonding theories and drives the physical chemists nuts! ☺  
The  $\sigma$  (and  $\sigma^*$ ) MOs of any nonlinear molecule are not trivial to predict and do **not** resemble what you'd predict using hybridization and VB theory. Fortunately, we rarely need to know what they look like – and, if we do, we just ask HyperChem!  
All we need to know is how the energies of the  $\sigma$ - and  $\pi$ -MOs generally compare:  $\sigma$ ,  $\pi$ , nonbonding,  $\pi^*$ ,  $\sigma^*$



# Pi Molecular Orbital Diagrams

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- The shape of each MO can be predicted using symmetry and nodes:
  - The lowest energy  $\pi$ -MO has all  $p$  orbitals aligned in phase, giving no nodes perpendicular to the plane of the  $\pi$ -system.
  - The next  $\pi$ -MO will have one node perpendicular to the plane of the  $\pi$ -system, the next  $\pi$ -MO will have two such nodes, etc.
  - The highest energy  $\pi$ -MO will have every  $p$  orbital out-of-phase with the  $p$  orbitals on both neighbouring atoms.
  - As long as the  $\pi$ -system is symmetric, every MO will be either **symmetric** or **antisymmetric**.

e.g. ethene



# Pi Molecular Orbital Diagrams

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e.g. 1,3-butadiene



# Pi Molecular Orbital Diagrams

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e.g. allyl system (compare allyl cation, allyl radical and allyl anion)



# Pi Molecular Orbital Diagrams

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e.g. benzene



# Aromaticity

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- Given that we consider  $\pi$  bonds to be reactive sites, benzene rings are much less reactive than you might think. This is due to the **resonance energy** of benzene – a lowering of energy due to delocalization of the  $\pi$  electrons.
- A **resonance energy** is the difference between the energy of a molecule and a hypothetical equivalent in which all  $\pi$  bonds are isolated. So, for benzene, we compare it to the hypothetical “1,3,5-cyclohexatriene”.
- Since 1,3,5-cyclohexatriene doesn't actually exist, we can't measure its energy directly. We can, however, assume that if the three  $\pi$  bonds were isolated, each would behave in essentially the same way as the  $\pi$  bond in cyclohexene.



# Aromaticity

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- So, we compare the amount of energy released when benzene is hydrogenated to cyclohexane with the amount of energy that is released when three molecules of cyclohexene are hydrogenated to cyclohexane:

This gives a resonance energy for benzene of 35.9 kcal/mol. The increased stability comes from  $\pi$  electron delocalization.



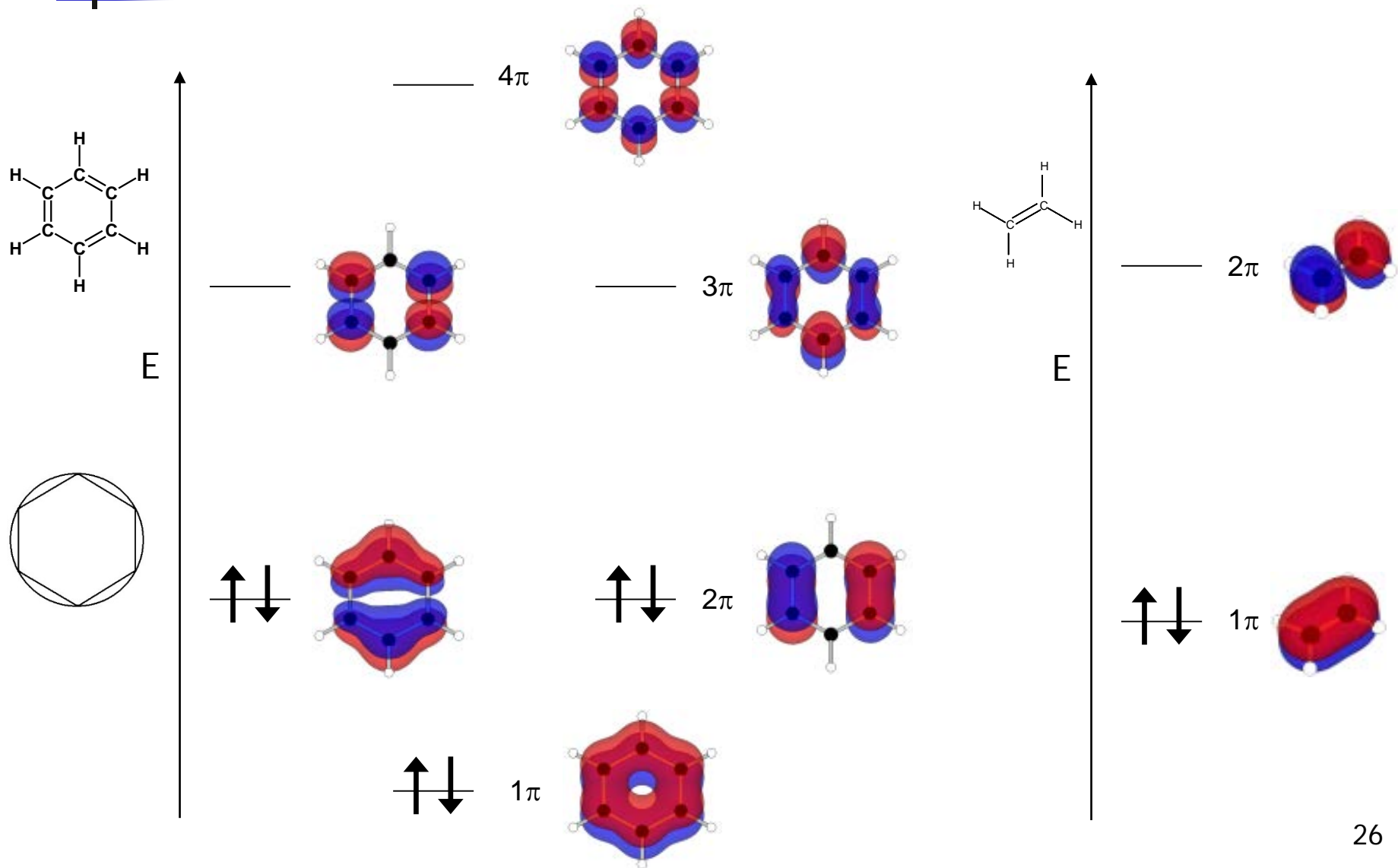


# Aromaticity

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- Benzene belongs to a class of molecules which all have large resonance energies. These **aromatic** molecules are therefore all quite stable and share certain characteristics.
- To be aromatic, a molecule must:
  - be cyclic (or contain a ring)
  - have an atomic  $p$  orbital perpendicular to the ring on every atom in the ring, creating a cyclic  $\pi$  system
  - be planar enough that the  $p$  orbitals can combine to make the cyclic  $\pi$  system
  - have  $4n+2$   $\pi$  electrons in the cyclic  $\pi$  system (**Hückel's rule**)
- Benzene is thus **aromatic**. It has  $4(1) + 2 = 6$   $\pi$  electrons in a planar cyclic  $\pi$  system. Note that all of the electrons in its  $\pi$ -MO diagram were paired and in bonding MOs. Also, the average energy of the  $\pi$ -electrons was lower in benzene than in ethene (or any other isolated  $\pi$  bond; see next page).

# Benzene is Aromatic





# Aromaticity

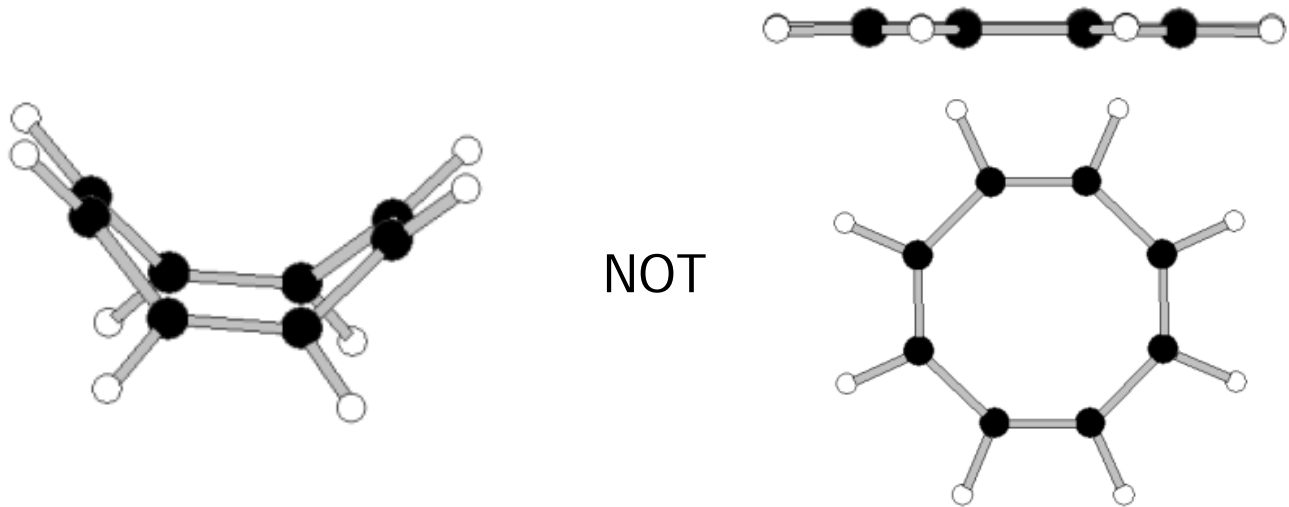
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- In a few cases, it is possible that delocalization of  $\pi$  electrons will destabilize a molecule. When this happens, the molecule is known as **antiaromatic**. The  $\pi$ -MO diagram for an antiaromatic molecule will be characterized by unpaired electrons, electrons in antibonding MOs and/or the average energy of the  $\pi$ -electrons being higher than in ethene
- To be antiaromatic, a molecule must meet all the criteria for aromaticity **except** that it will have  $4n$   $\pi$  electrons in the planar cyclic  $\pi$  system instead of  $4n+2$ .
- **Any** tetrahedral atom in the ring breaks up the cyclic  $\pi$  system, making the molecule neither aromatic nor antiaromatic.

# Aromaticity

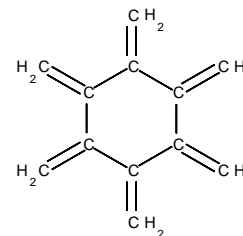
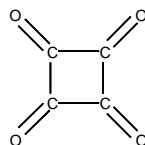
- Since an antiaromatic compound is actually *less* stable than a nonaromatic compound, molecules that we would predict to be antiaromatic based on electron count usually violate the “be planar” criterion for aromaticity/antiaromaticity and behave as though they have isolated double bonds.

e.g. 1,3,5,7-cyclooctatetraene looks like:

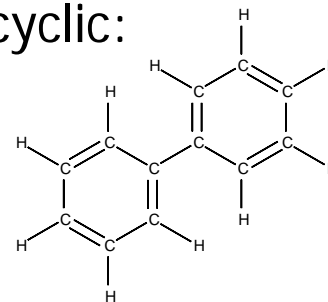
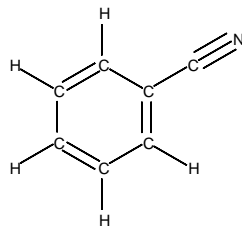


# Aromaticity

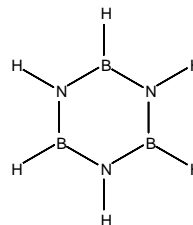
- Note that molecules with  $\pi$  systems extending out of the ring are not considered to be aromatic:



UNLESS the  $\pi$  system can be broken into two smaller  $\pi$  systems, one (or more) of which is cyclic:



- Remember that  $\pi$  systems can involve trigonal planar heteroatoms too! The electrons for the  $\pi$  system can come from lone pairs...





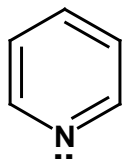
# Aromaticity

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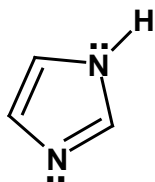
- Consider the cyclopropenyl cation and anion. Sketch a  $\pi$ -MO diagram for each and conclude if either is aromatic or antiaromatic.

# Aromaticity

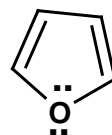
- Which of the following molecules/ions would you predict to be aromatic? Which are antiaromatic when forced to be planar? Which are nonaromatic?



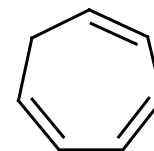
pyridine



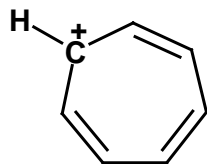
imidazole



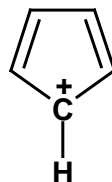
furan



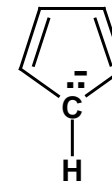
1,3,5-cycloheptatriene



tropylium cation

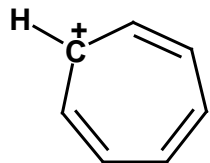


cyclopentadienyl cation



cyclopentadienyl anion

# Aromaticity



tropylium cation

- Consider the tropylium cation. Draw all valid resonance structures of this cation. Describe how the tropylium cation would look in “real life” (the average picture). How does this help to justify the stability of this ion?