

## FOCUS QUESTION

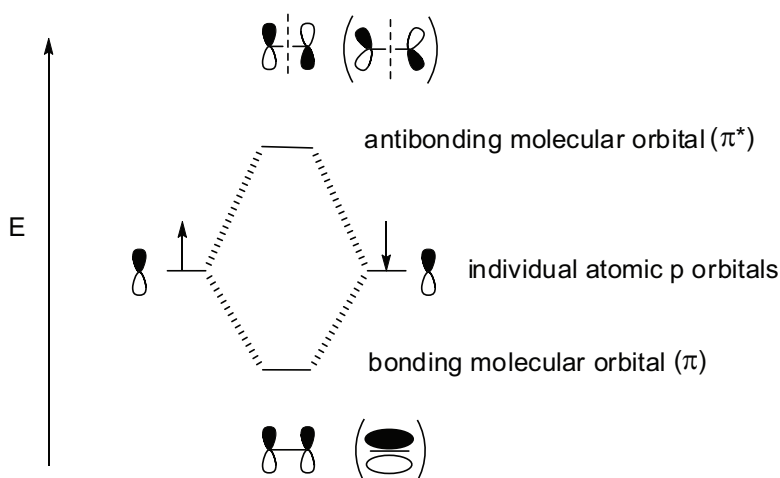
What can MO theory do for us that VSEPR theory cannot?

## MODEL 1

## Qualitative Molecular Orbital Theory

Molecular Orbital (MO) theory is a way to describe bonding in molecules that applies quantum mechanics to linear combinations of atomic orbitals. In this course we will use MO theory, in particular Hückel MO theory, to describe  $\pi$  systems in organic molecules. However, we will be working with only qualitative MO theory; we will leave the quantum mechanical computations to the physical chemists.

Below is an MO diagram of a  $\pi$  bond using two p orbitals. A nodal plane is a plane of zero electron density formed when orbitals of opposite phases overlap. It is indicated on the diagram below by a dashed line.



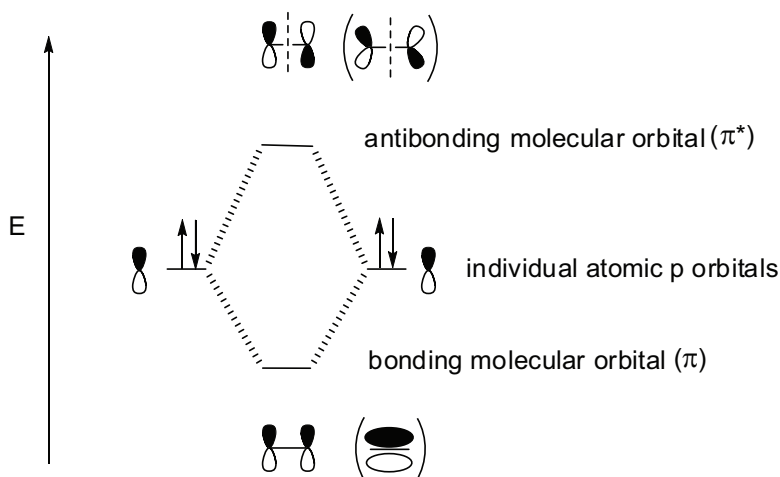
1. How many individual atomic orbitals are shown in Model 1?
2. How many electrons are present in each atomic orbital?
3. How do the energies of the bonding and antibonding MOs compare?
4. Another difference between the bonding MO and the antibonding MO is the presence of a nodal plane. Which MO contains this node?
5. How many electrons are in a  $\pi$  bond?
6. For this  $\pi$  bond, put the electrons in the appropriate molecular orbital(s) in Model 1. Explain why you chose this configuration.

7. From Model 1, does in-phase overlap (both the same color) or out-of-phase overlap (one of each color) have to be present for a bonding interaction?
8. Is an in-phase interaction between atomic orbitals favorable or unfavorable? Explain how you know this.
9. Is an out-of-phase interaction between atomic orbitals favorable or unfavorable? Explain how you know this.

### INFORMATION

The following are some rules for drawing MOs:

- a. The number of MOs must always equal the number of atomic orbitals used to create them;
  - b. When combining atomic orbitals, the antibonding orbital always goes up in energy slightly more than the bonding orbital goes down;
  - c. A node must be placed symmetrically within the molecule.
10. Using the following MO diagram, show what the electron configuration would be if each atomic orbital started with two electrons.



11. Using the information given previously, would the interaction that you showed in question 8 be favorable or unfavorable? Explain.

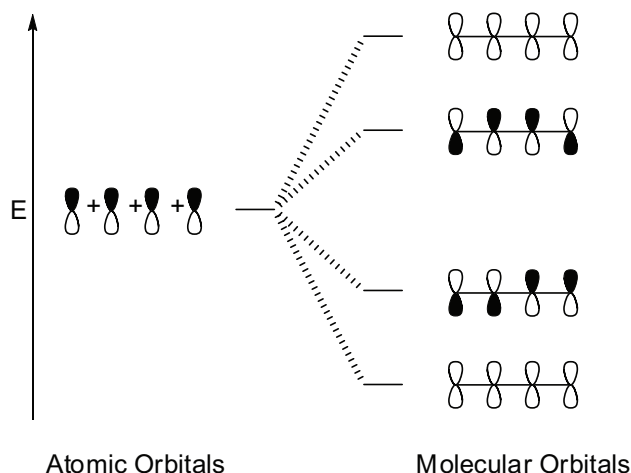
12. Draw the structure of 1,3-butadiene.

13. How many p atomic orbitals participate in the  $\pi$  system of 1,3-butadiene?

14. How many molecular orbitals does the  $\pi$  system of 1,3-butadiene contain?

## MODEL 2

### $\pi$ Molecular Orbitals of 1,3-Butadiene



15. The lobes of two of the MOs above have already been shaded in for you. Indicate on the diagram the location of any nodes present in these orbitals.

16. The lowest energy MO has zero nodes. Correctly shade in the lobes of this orbital.

17. The highest energy MO has nodes between all of the carbons. Correctly shade in the lobes of this orbital and indicate the nodal planes.

18. Is there a relationship between the number of nodes and the energy of the MO? If so, describe it.

19. How many electrons does the  $\pi$  system of 1,3-butadiene contain?

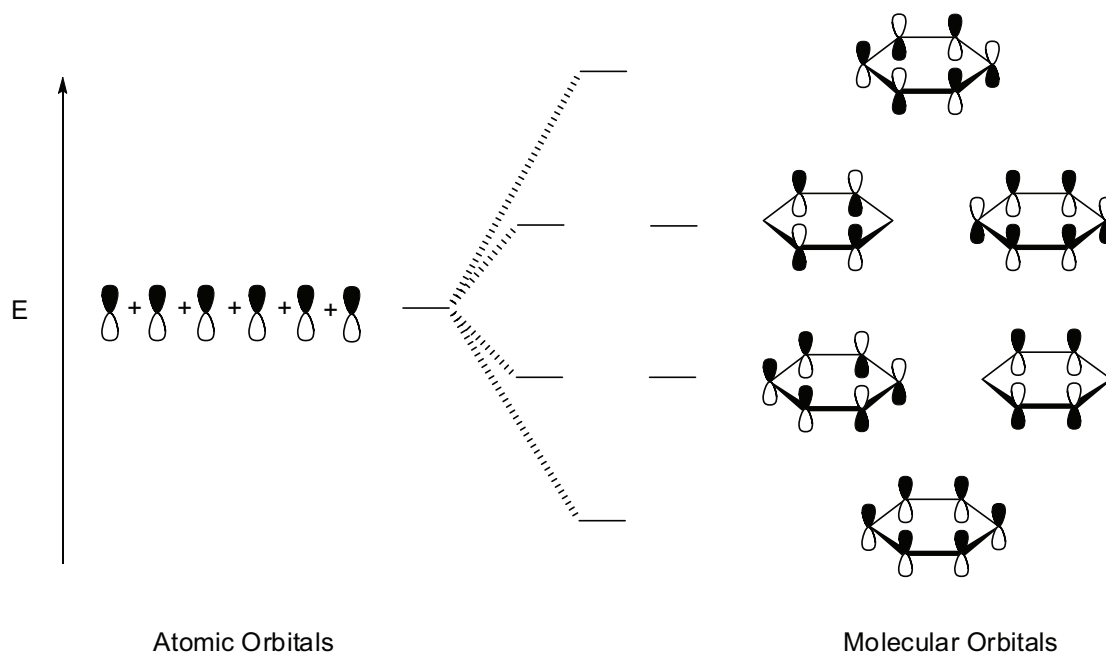
20. Fill each 1,3-butadiene MO with the appropriate number of electrons.

21. Are the  $\pi$  interactions in 1,3-butadiene favorable or unfavorable? Explain.

22. It has been experimentally determined that the C2-C3 bond of 1,3-butadiene has some double bond character. Explain this observation based on the MO diagram. Hint: Look at the phasing within the occupied MOs.

### MODEL 3

#### $\pi$ Molecular Orbital Diagram of Benzene



23. Draw out the structure of benzene including resonance structures.

24. Is the benzene you drew in the plane of the paper or perpendicular to the plane of the paper?

25. Is the benzene in Model 3 in the plane of the paper or perpendicular to the plane of the paper?

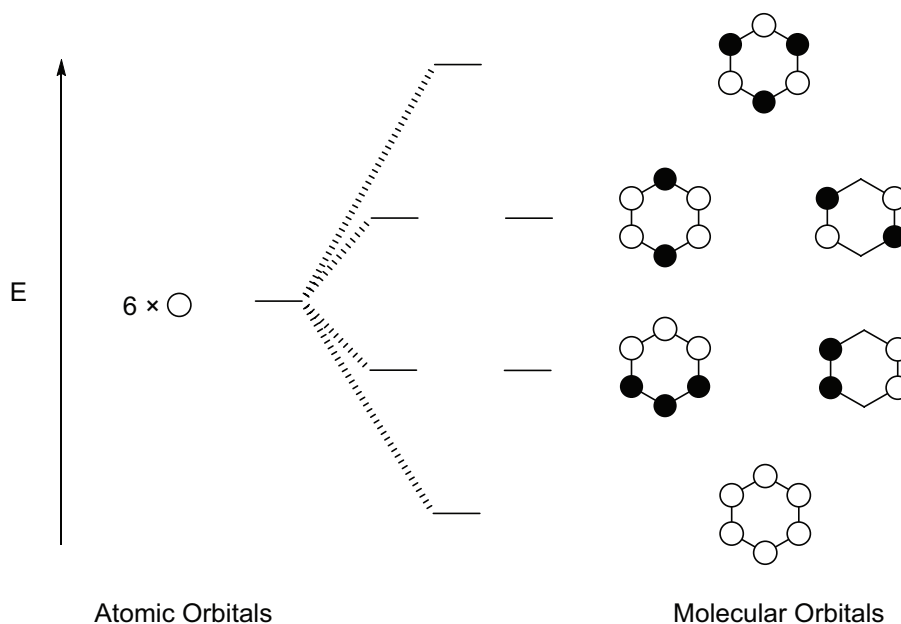
26. Place the  $\pi$  electrons in the appropriate MOs in Model 3.

27. Is the interaction of atomic orbitals in Model 3 favorable or unfavorable? Explain.

## MODEL 4

### A Different Perspective of the MOs of Benzene

Sometimes it is easier to draw molecular orbitals from a different perspective.



28. In Model 4, is the benzene ring drawn in the plane of the paper or in a plane perpendicular to the plane of the paper?

29. What part of the orbitals does this perspective not allow us to see?

30. Although we can only see one lobe of the orbitals, we know from that what the phase of the other lobe is. How?

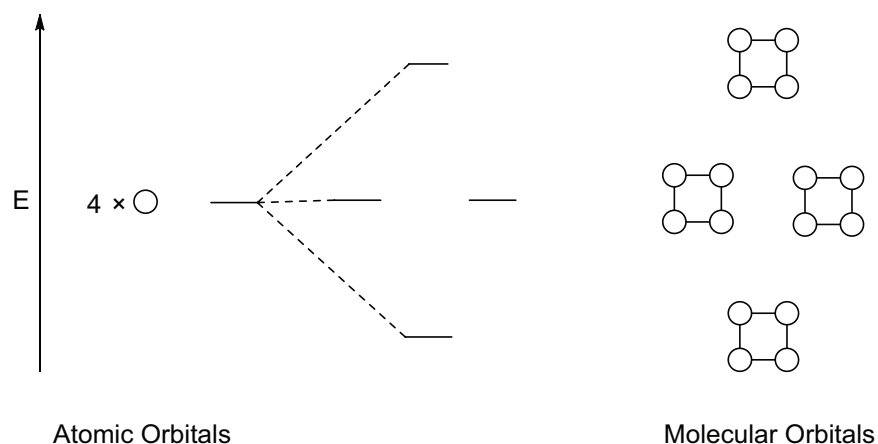
31. Indicate all nodal planes present in the MOs in Model 4. Do not count the node within each p orbital.

32. Place the  $\pi$  electrons in the appropriate MOs.

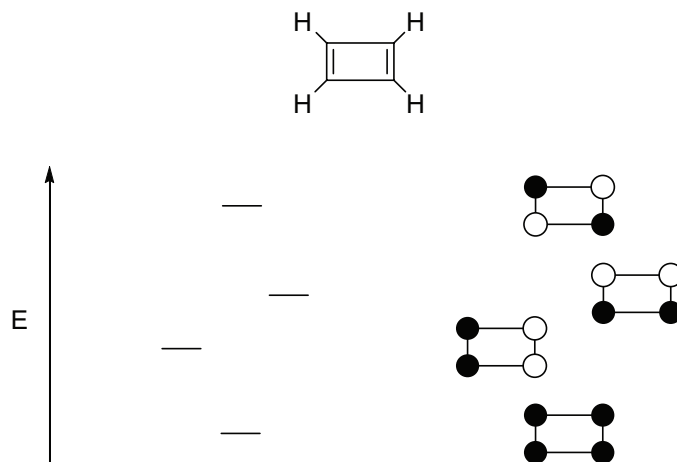
33. As you know, all of the bond lengths in benzene are equal. Explain this finding using the MO diagram.  
Hint: Look at the phasing within the occupied MOs.

## MODEL 5

### $\pi$ Molecular Orbital Diagram of Cyclobutadiene



34. In Model 5, is the cyclobutadiene ring drawn in the plane of the paper or in a plane perpendicular to the plane of the paper?
35. In Model 5, shade in the appropriate orbital lobes for cyclobutadiene. Remember that the lowest energy orbital has all bonding interactions (no nodes) and the highest energy orbital has all antibonding interactions (nodes between each bonded pair of carbons).
36. Place the  $\pi$  electrons in the appropriate MOs.
37. Is the above interaction of atomic orbitals favorable or unfavorable? Explain.
38. Based on the MO diagram above, is cyclobutadiene a stable molecule? Explain.

**MODEL 6****MO Diagram of Rectangular Cyclobutadiene**

29. What is the difference between the MO diagram of square cyclobutadiene and that of rectangular cyclobutadiene?

40. From the orbital phasing, explain why the two middle orbitals have different energies.

41. In Model 6, put the  $\pi$  electrons in the correct orbitals.

42. From the MO diagrams in Model 5 and Model 6, explain why cyclobutadiene is rectangular instead of square.

**SUMMARY**

43. Describe how to determine relative bond lengths within a compound based on the phasing of the MOs within the MO diagram.

44. Give an MO explanation for why benzene's C-C bonds are all the same length while cyclobutadiene has alternating bond lengths.

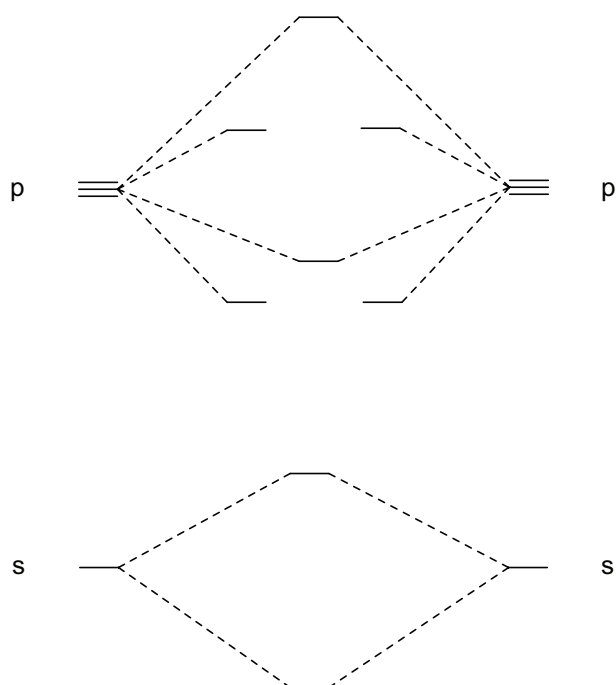
## EXERCISES

Review of VSEPR Theory for  $N_2$  and  $O_2$ 

1. For each bond and lone pair in Model 2, label in what type of orbital it is using VSEPR theory. (i.e.  $sp^3$ , p, etc.)
2. How many lone pairs does  $N_2$  have?
3. How many unpaired electrons does  $N_2$  have?
4. How many lone pairs does  $O_2$  have?
5. How many unpaired electrons does  $O_2$  have?
6. Using your general knowledge of chemistry, which is less reactive,  $N_2$  or  $O_2$ ? Explain your reasoning.
7. Can VSEPR theory account for this difference in reactivity? If so, how?

Molecular Orbital Theory Applied to  $N_2$  and  $O_2$ 

8. How many valence electrons does  $N_2$  have? Include all of the valence electrons, not just the  $\pi$  electrons.
9. How many valence electrons does  $O_2$  have? Include all of the valence electrons, not just the  $\pi$  electrons.
10. Put electrons in the appropriate orbitals in the MO diagrams below. Since the MOs diagrams below include both s and p orbitals, you must include all of the valence electrons.
11. Can the difference in reactivities between  $N_2$  and  $O_2$  be explained by MO theory? If so, how?

Molecular Orbital Diagram for  $N_2$ Molecular Orbital Diagram for  $O_2$ 