Part B: MO Explanation for Aromaticity
(How can we explain anti-aromaticity using molecular orbital theory?)

Model 3: Molecular Orbital Explanation for Hückel's Rule
- Rule of thumb: the MO diagram of a cyclic conjugated pi system always takes the shape of the ring involved, with one vertex pointing down. For example...

MO Diagram of Benzene (completed)
MO Diagrams of Other Cyclic Conjugated Pi Systems (electrons not filled in yet)

- Molecular orbitals on the same MO diagram with the same energy are called degenerate orbitals.
- Degenerate orbitals must all be half-filled before any one is filled. For example.

Valence Electron Orbital Occupation for a Oxygen Atom

CORRECT

NOT CORRECT

Critical Thinking Questions
9. How many pairs of degenerate molecular orbitals are there in the MO diagram of benzene? Label them.

10. Add the appropriate number of electrons to the three other MO diagrams in Model 3.

Information
The situation of an unpaired electron in an orbital is unfavorable. We will say that a species with an unpaired electron has "radical character", to remind us that, like other radicals, it will be very reactive.

a) According to the information above, label two compounds at the top of the page with the words "has radical character-very reactive."

b) Employing Hückel's Rule, label aromatic compounds at the top of the page with the words "aromatic-very stable."
11. The anion below, left, has two pi bonds, which contain four pi electrons. **Place four electrons in the MO diagram for this species**, shown below, right.

![MO Diagram](image)

\[ \pi^* \text{ (anti-bonding)} \]
\[ V.E. \]
\[ \pi \text{ (bonding)} \]

a) According to your MO diagram does this anion have radical character?

b) **NOW, assume the lone pair on this anion resides in a p orbital (instead of a sp³ orbital as you might expect). Add two more electrons to your MO diagram** to reflect that the lone pair electrons are part of the pi system.

**Information**
A lone pair will "choose" to reside in a p orbital if doing so makes the molecule aromatic.

c) Do you expect the lone pair on this anion to reside in a p orbital as we assumed in part b)? Explain your reasoning.

d) Is this cyclic anion aromatic?

12. For each column, check one or the other box. You will get the same answer no matter which cyclic MO diagram you use to figure out your answer. (MO diagrams for 6, 5, 4 and 3 member rings are shown on the previous page; 7,8,9 & 10 are shown below.)

<table>
<thead>
<tr>
<th># Of Electrons in the ( \pi ) System</th>
<th>2</th>
<th>4</th>
<th>6</th>
<th>8</th>
<th>10</th>
<th>12</th>
</tr>
</thead>
<tbody>
<tr>
<td>Has Radical Character According to MO</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Aromatic (according to Hückel's Rule)</td>
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</table>

**MO Diagrams for 7, 8, 9 and 10 Member Rings**

![MO Diagrams](image)

13. The first half of Hückel's Rule states that a cyclic conjugated pi system with \( 4n+2 \) electrons will be very stable. **The second half states that a cyclic conjugated pi system with \( 4n \) electrons (4,8,12, etc.) will be very unstable.** Explain the second part of Hückel's Rule.
Model 4: Anti-Aromatic Molecules
Cyclobutadiene can be isolated and studied at temperatures less than -200°C. At temperatures above -200°C it immediately reacts with itself to form other more stable products.

\[
\text{Cyclobutadiene (very very reactive)}
\]

If a pi system obeys all the rules for aromaticity, but has 4n electrons (where \( n = 1,2,3 \ldots \text{etc.} \)) then it is called anti-aromatic.

- Anti-aromatic molecules display an almost magical instability (due to radical character). Think of it as the evil twin of aromaticity.
- A molecule will "do" anything it can to avoid being anti-aromatic.

Critical Thinking Questions
14. List four things about cyclobutadiene that makes it anti-aromatic. (Hint: see CTQ 8.)

15. Cyclooctatetraene is quite stable at room temperature. However, close examination of the structure reveals that it is not planar.

\[
\text{Cyclooctatetraene in its Preferred Conformation}
\]

a) Speculate about why this molecule does not “want” to be planar.

b) Cyclooctatetraene is considered non-aromatic. This means it is neither aromatic nor anti-aromatic. Explain.

c) Give an example of another non-aromatic molecule. (Hint: most molecules fall into this category.)