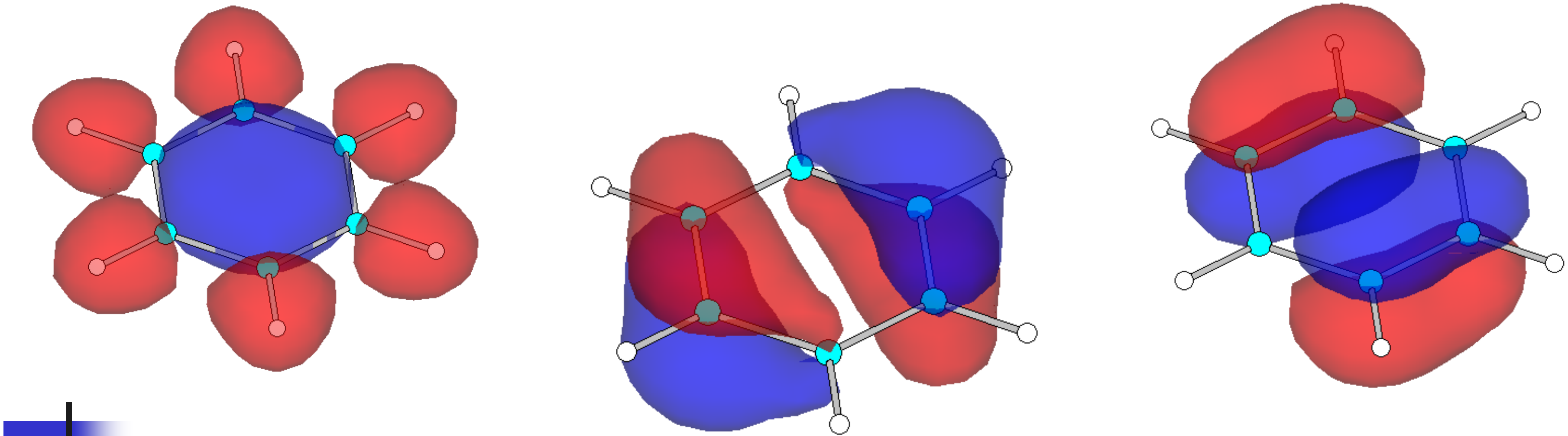


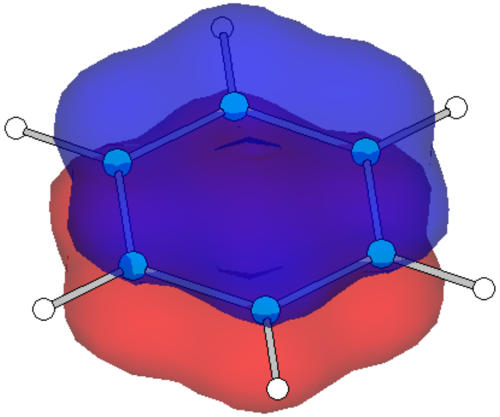
CHEMISTRY 2000

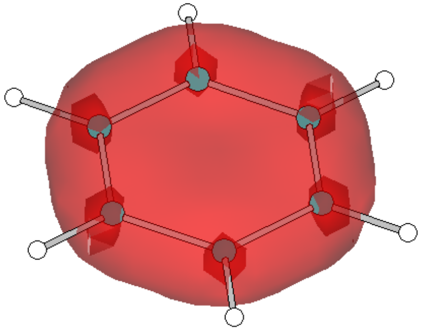
Topic #1: Bonding – What Holds Atoms Together?

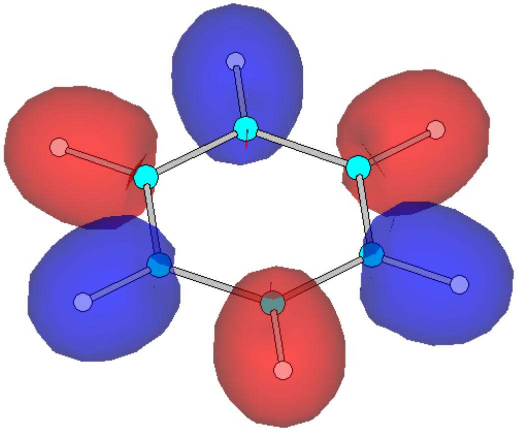
Fall 2020

Dr. Susan Findlay

See Exercises 4.1 to 4.6







Taking MO Theory Past the Diatomics

- Molecular orbital theory is valid for all molecules. Thus far, we've focused on the diatomics because it's only convenient to manually derive complete MO diagrams for molecules that are either very small or highly symmetric.
- It was easier for us to predict MOs for symmetric molecules (like O_2) than asymmetric molecules (like CO). For this reason, our studies of larger molecules will be confined to highly symmetric ones – like BeH_2, CO_2 and C_6H_6. Computers are used to predict MOs for less symmetric molecules ("computational chemistry").
- The principles used to predict MOs and MO diagrams for the diatomics are the same as those used for larger molecules.
  - Continue to look for valence atomic orbitals with:
    - COMPATIBLE SYMMETRY (σ vs. π)
    - COMPATIBLE ENERGY (as close as possible; no farther apart than ~ 1 Ry)
  - Make sure you make the same number of MOs as you had AOs!
  - Keep electron distribution in MOs symmetric if molecule is symmetric.

Molecular Orbitals for BeH_2

- BeH_2 is the simplest triatomic molecule. In the gas phase, it is linear (as we'd expect from the Lewis structure):

- The relative energies for the atomic orbitals of Be and H are:
  - 1*s* (Be) = -9.38 Ry
  - 2*s* (Be) = -0.61 Ry
  - 2*p* (Be) = +0.14 Ry
  - 1*s* (H) = -0.99 Ry

- Which valence atomic orbitals can combine to make σ MOs?

- Which valence atomic orbitals can combine to make π MOs?

- Which valence atomic orbitals will not combine at all (leaving them as either σ or π nonbonding MOs)?

Molecular Orbitals for BeH_2

- We are combining four σ-symmetric AOs to make four σ-MOs. To predict what these four MOs will look like, we use symmetry and an increasing number of nodes:

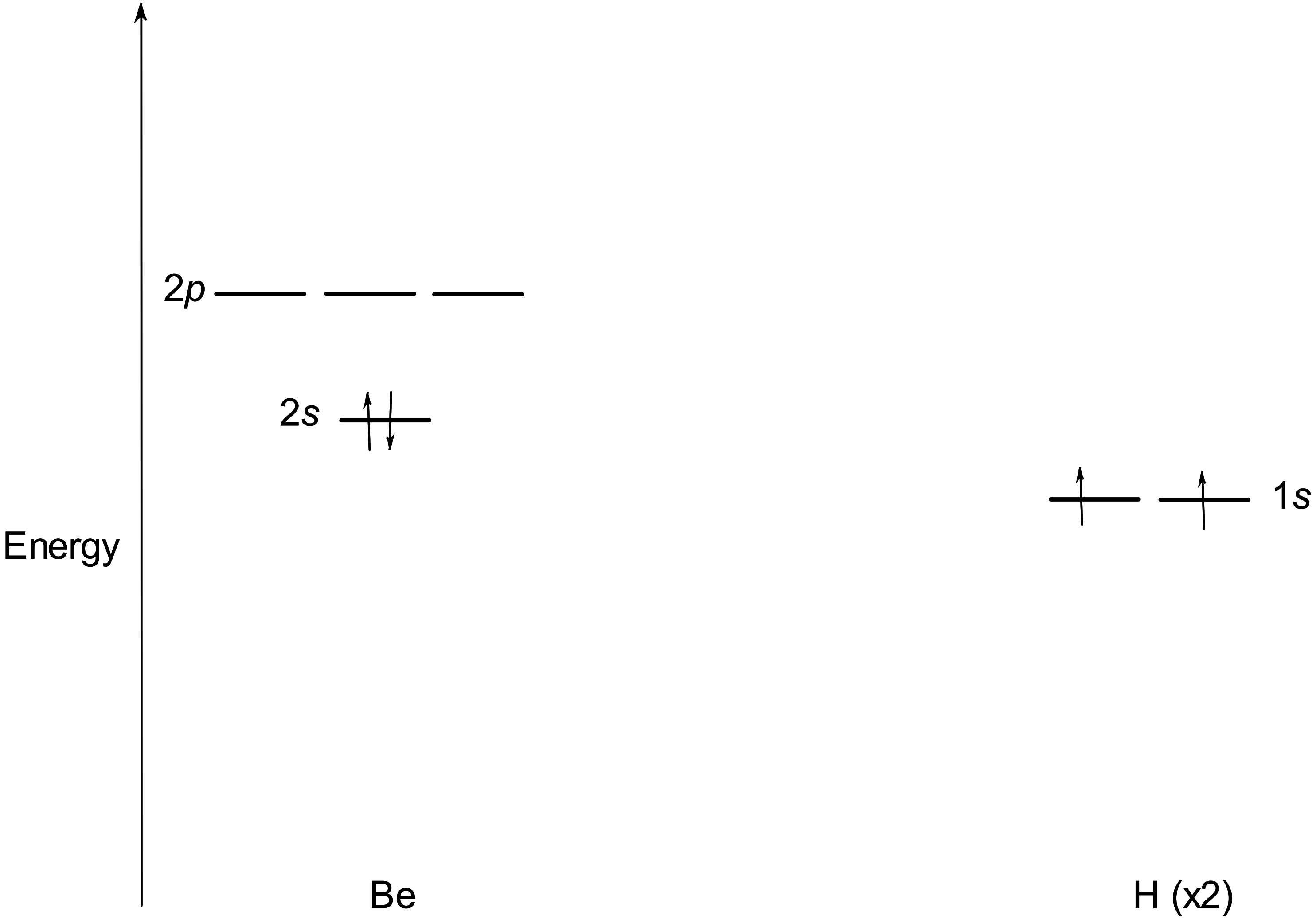
- The overall shape (i.e. shape of the lobes) for every MO in the set must share the symmetry of the overall molecule. If the molecule is nonpolar, none of the MOs should be "lopsided"!

Molecular Orbitals for BeH_2

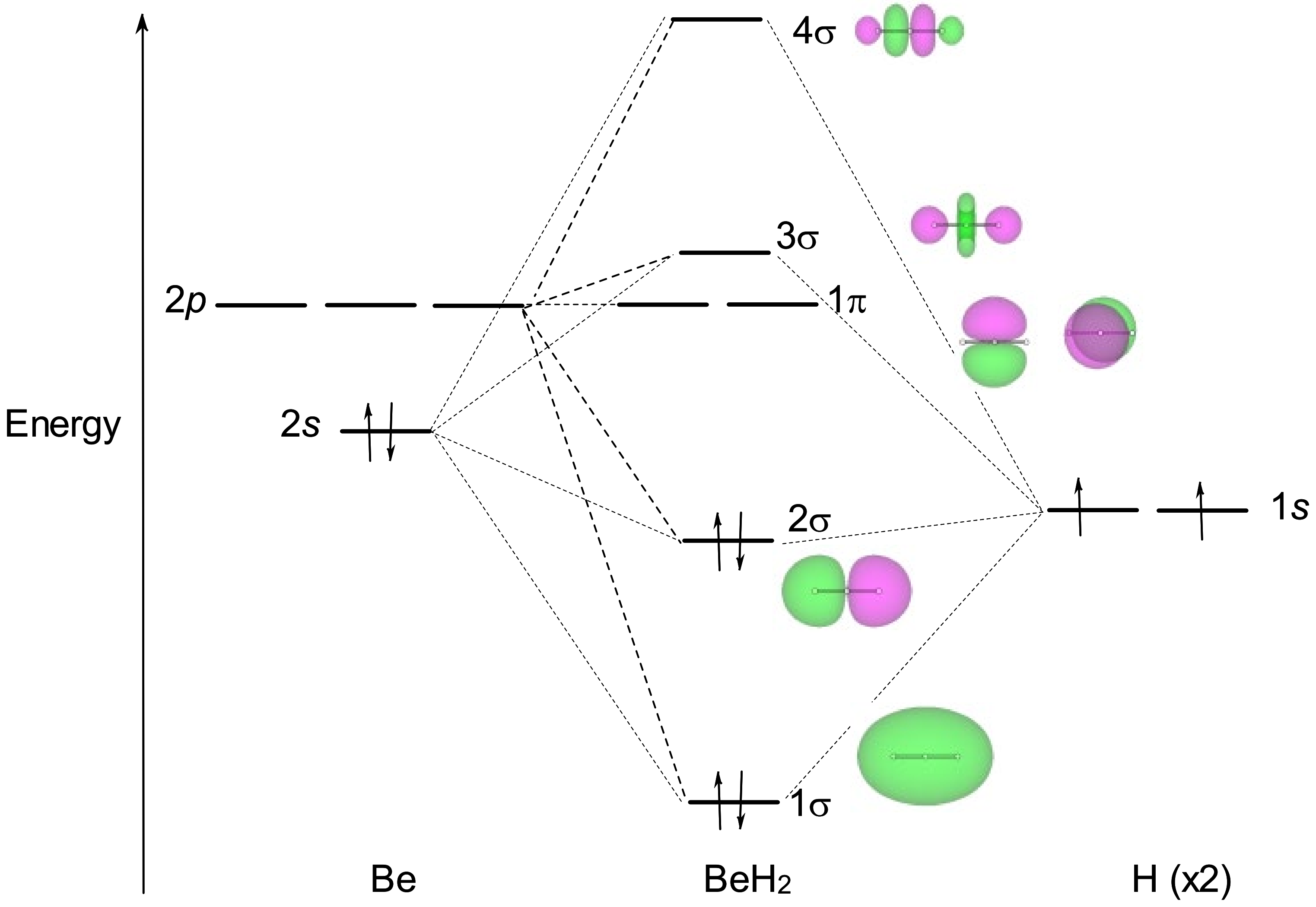
- To predict the energies of a set of MOs:
  - The lowest energy σ-MO is lower in energy than all AOs from which it's made.
  - The highest energy σ-MO to be higher in energy than all the AOs from which it's made.
  - Use these two MOs and the energies of the AOs that were used to build the set of MOs to estimate the energies of the middle MOs.

- As in the MO diagrams for diatomics, the MOs are tracked in the middle of the diagram with the AOs at the sides. Equivalent atoms (such as the Hs in BeH_2) are grouped at one side, making sure to include all their valence AOs (one 1*s* AO for each H).

Molecular Orbitals for BeH_2


Energy
2p
2s
1s
Be
H (x2)

Molecular Orbitals for BeH_2


4σ
3σ
2p
1π
Energy
2s
2σ
1s
1σ
Be
BeH2
H (x2)

Molecular Orbitals for BeH_2

- When you calculate bond order for bonds in polyatomic molecules, it’s essential to account for the number of “bonds” (atom-to-atom connections) over which the electrons are distributed.

- How many Be-H bonds share the bonding electrons in BeH_2?

- Compare the bond order predicted by the Lewis diagram for BeH_2 to the bond order calculated from the MO diagram.

Molecular Orbitals for BeH_2

- What is the **H**ighest **O**ccupied **M**olecular **O**rbital for BeH_2?

- What is the **L**owest **U**noccupied **M**olecular **O**rbital for BeH_2?

- Is BeH_2 more likely to react as a Lewis acid or a Lewis base? Use the energies of the HOMO and LUMO to justify your choice. Use the shape of the relevant MO to show the most likely reactive site in BeH_2.

Molecular Orbitals for CO_2

- CO_2 may not appear much more complicated than BeH_2 – both of them being linear triatomic molecules – but it has rather more valence orbitals to consider. As usual, we will divide the atomic orbitals by symmetry:

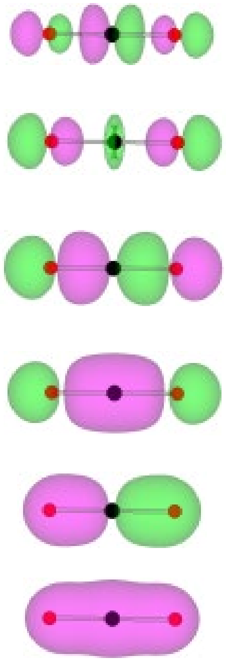
σ-symmetric **π-symmetric**

Valence Molecular Orbitals for CO_2

- The six π-symmetric AOs can be subdivided into two sets: the $2p_x$ AOs and the $2p_y$ AOs. Each of those sets can be combined to make three MOs.
- Use symmetry and nodes to predict the shapes of these MOs and their relative energies:

Valence Molecular Orbitals for CO_2

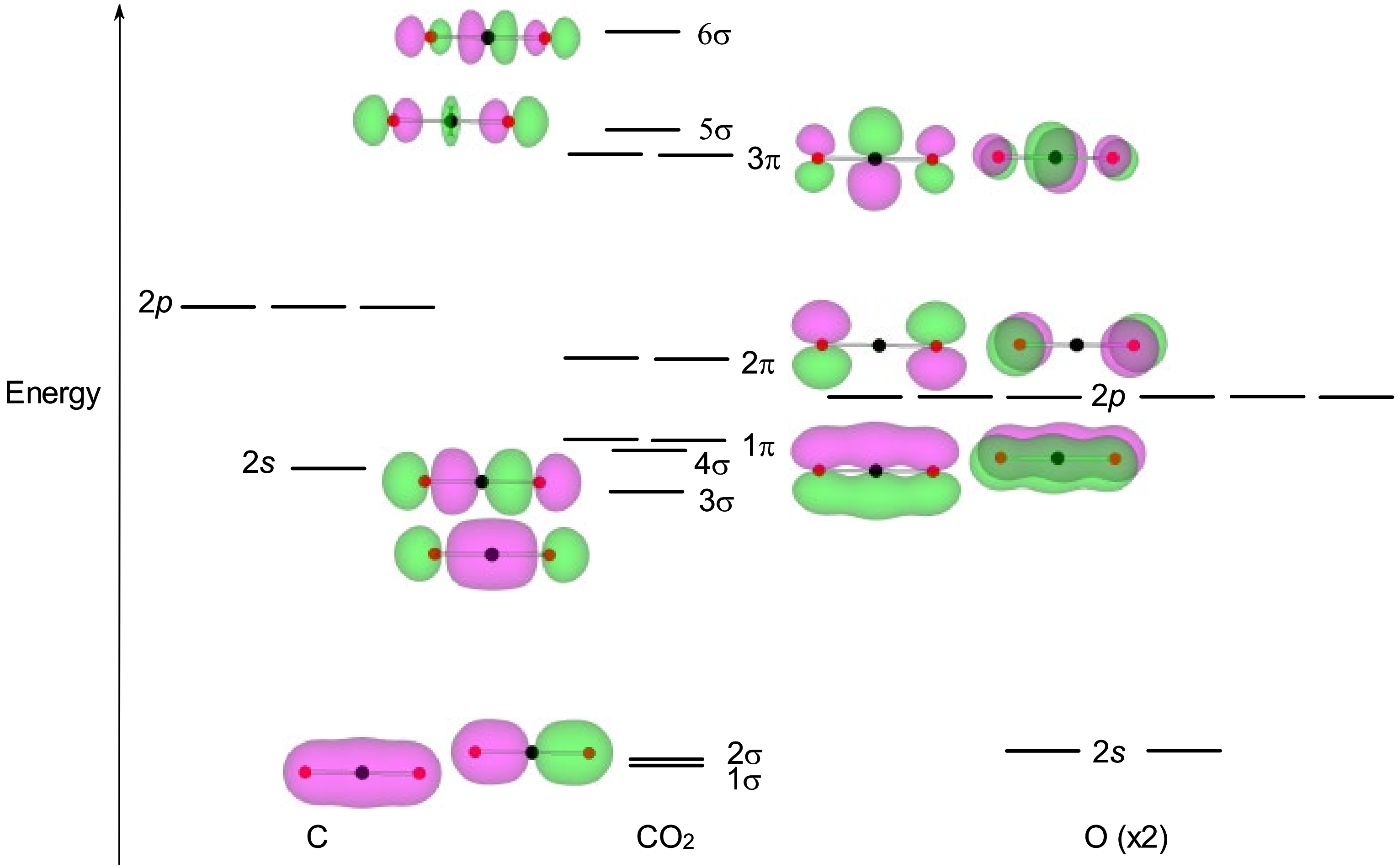
- The six σ-symmetric AOs can be treated as a group and combined to make six σ-symmetric MOs. Symmetry and nodes can be used to predict their shapes and relative energies:



- Find the perpendicular nodes in these MOs to convince yourself that they are in the correct order by energy. Can you work out which atomic orbitals each might have been made from?

Valence Molecular Orbitals for CO_2

- A computer shows us the relative energies of all these MOs:


6σ
5σ
3π
2p
Energy
2π
2p
1π
2s
4σ
3σ
2σ
1σ
2s
C
CO2
O (x2)

Valence Molecular Orbitals for CO_2

- Complete the MO diagram on the previous page:
    - Fill in the electrons.
    - To the best of your ability, label each MO as bonding, antibonding or nonbonding.
- Write the valence orbital occupancy for CO_2.
- Use the MO diagram to calculate the average C-O bond order. Compare it to the bond order predicted by the Lewis diagram.

Valence Molecular Orbitals for CO_2

- Use the **frontier molecular orbitals** (the HOMO and LUMO) to predict how CO_2 will react.
    - Identify the HOMO. When CO_2 acts as a Lewis base, which atom(s) donate the electron pair, and is bond order affected?
    - Identify the LUMO. When CO_2 acts as a Lewis acid, which atom(s) accept the electron pair, and is bond order affected?

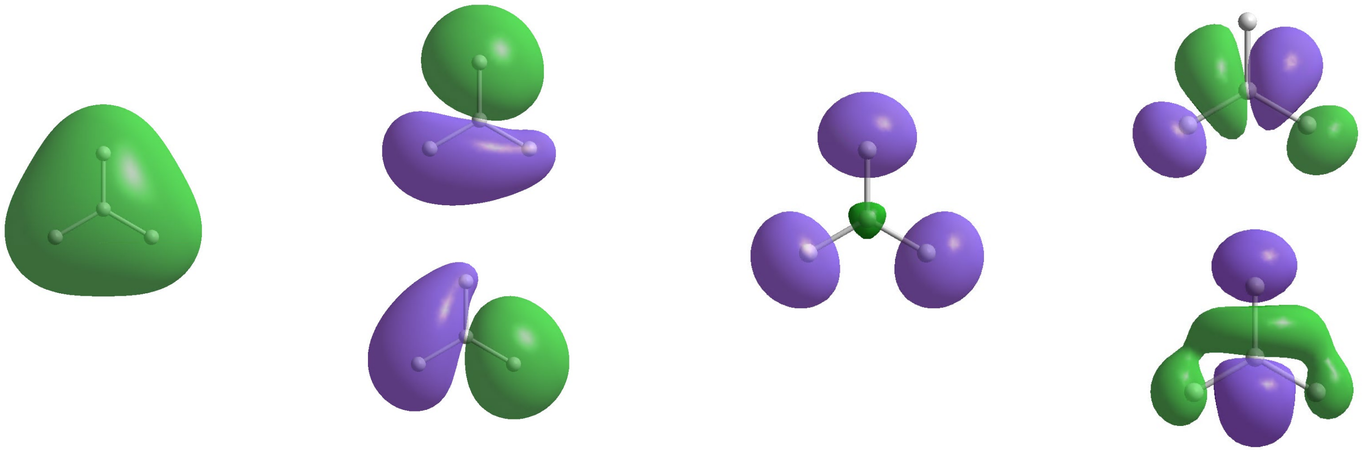
Valence Molecular Orbitals for CO_2

- What is the main difference between the picture of CO_2 provided by MO theory and the picture of CO_2 provided by the Lewis structure?

MO Theory and Delocalized π Electrons

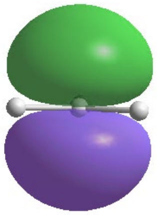
- Once we move beyond the linear triatomics, the σ-MOs quickly become relatively complicated and difficult to predict.

  e.g. the valence σ-MOs of BH_3:



- The π-MOs, on the other hand, are still relatively straightforward to predict.

  e.g. the valence π-MO of BH_3:



MO Theory and Delocalized π Electrons

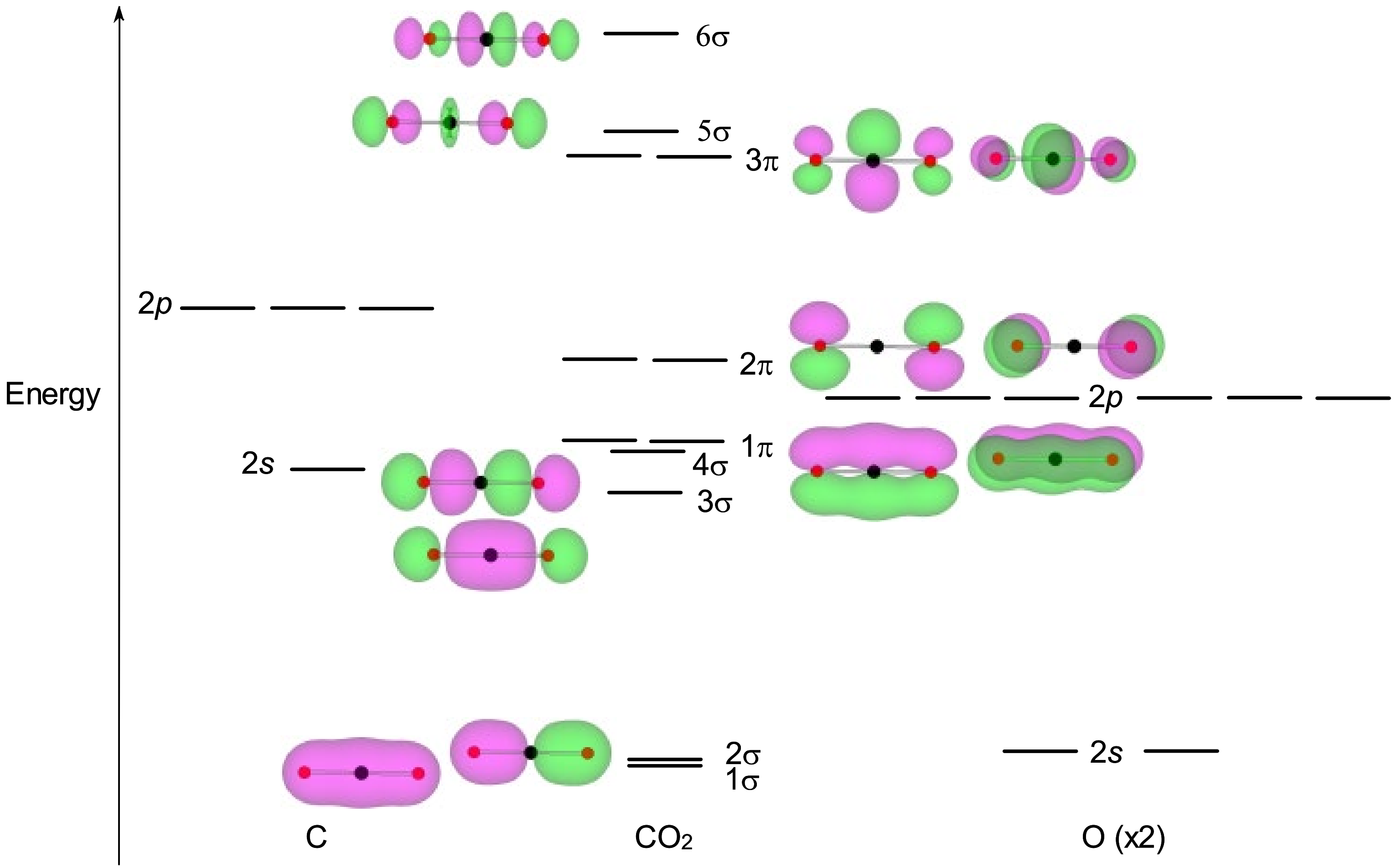
- Fortunately, the phenomenon of **sigma-pi separation** means that we've been discussing σ-MOs and π-MOs separately.

- You may have noticed that the HOMO and LUMO in molecules like CO_2 are often both π-MOs. For many molecules (especially organic ones), it can be quite helpful to focus on the π-MOs when talking about their properties or reactivity.

- Furthermore, the electrons which appear to "move" between resonance structures turn out to be electrons in π-MOs. MO theory demonstrates that those electrons are **delocalized**. When you look at the shapes of these π-MOs, you get a better picture of how those electrons are shared by multiple atoms.

MO Theory and Delocalized π Electrons

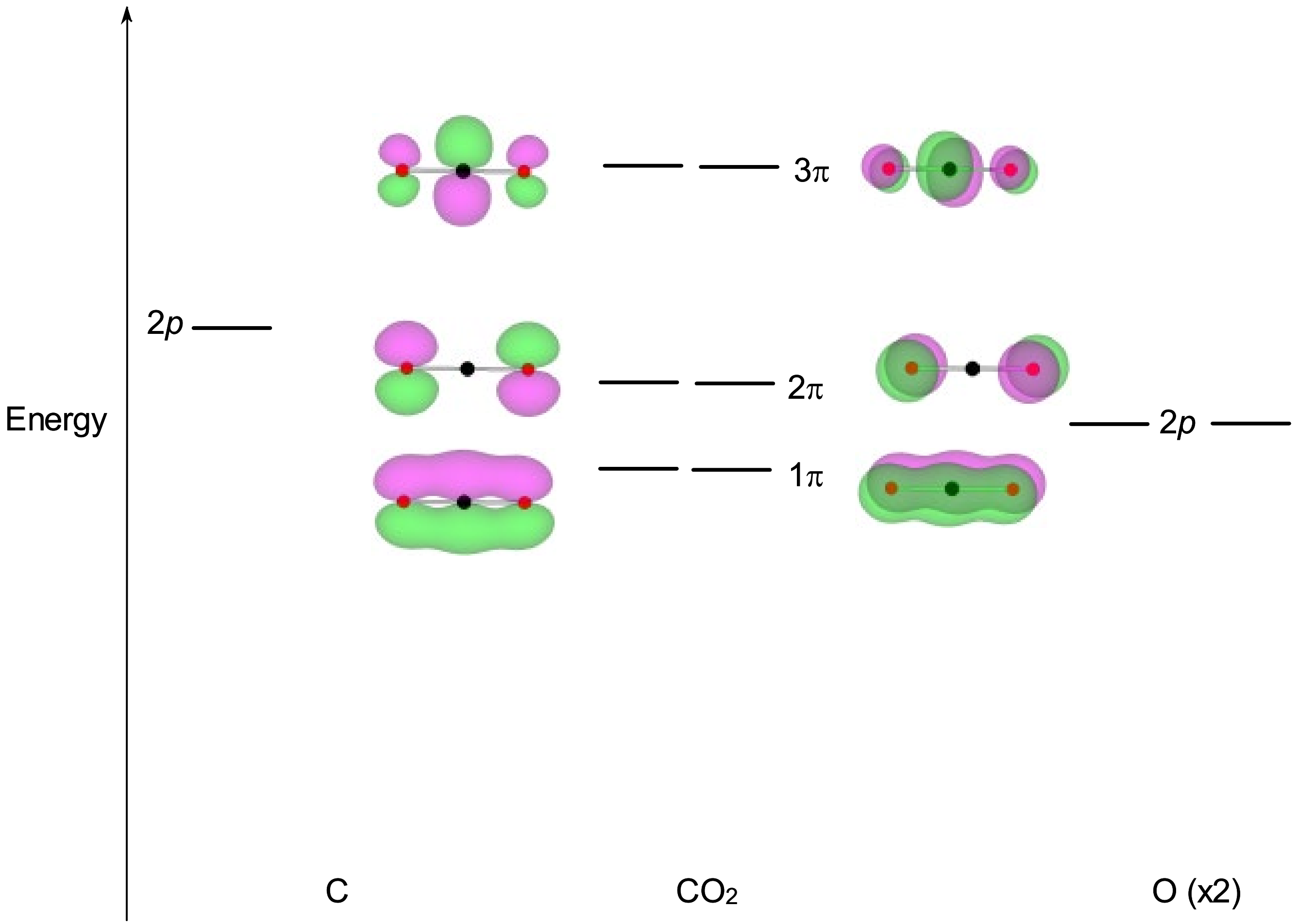
- Removing the σ MOs from our valence MO diagram for CO_2 …



6σ
5σ
3π
2p
Energy
2π
2p
1π
2s
4σ
3σ
2σ
1σ
2s
C
CO2
O (x2)

MO Theory and Delocalized π Electrons

- … leaves the valence π MO diagram for CO_2:


Energy
2p
3π
2π
1π
2p
C
CO₂
O (x2)

MO Theory and Delocalized π Electrons

- Important points to remember:
  - We are approximating that, for every bond (single, double or triple), there are two electrons in σ bonding MOs. This does not mean that there is a σ-MO focused on the bonding region. It may, for example, mean that there are three bonding σ-MOs holding together three different bonds *(as shown for BH_3 on page 17 – the three leftmost MOs are all σ-bonding, each containing 2 electrons)*
  - If an MO spans three or more atoms, the electrons in it are shared by more than one bond. e.g. a pair of pi bonding electrons in CO_2 provides a half bond order to *each* of the two C-O bonds.
  - When discussing bond order, only π bond order can be determined from a π-MO diagram. The total bond order will therefore be 1 more than the π bond order (since average σ bond order is 1).

$$\boxed{\text{Total bond order} = \pi \text{ bond order} + \sigma \text{ bond order}}$$

MO Theory and Delocalized π Electrons

- Recall that:
  - A π MO is bonding if its energy is lower than the average energy of the *p* orbitals in the pi system.
  - A π MO is nonbonding if its energy is the same as the average energy of the *p* orbitals in the pi system.
  - A π MO is antibonding if its energy is higher than the average energy of the *p* orbitals in the pi system.

- Looking at nodes can also help us categorize MOs. Check if an MO appears bonding or antibonding in each bonding region.
  - If there are more bonding interactions than antibonding interactions, the MO is net bonding.
  - If there are more antibonding interactions than bonding interactions, the MO is net antibonding.
  - If there are the same number of antibonding and bonding interactions, the MO is nonbonding.

Resonance and MO Theory: Ozone (O_3)

- One of the first molecules for which we drew resonance structures in CHEM 1000 was ozone:

- The molecular geometry of ozone is ________________________.

ALWAYS ***check whether a molecule is planar or linear. Linear molecules have 2 pi systems. Planar ones have 1!***

- Ozone has:
  - ____ π-symmetric valence AOs therefore ____ valence π-MOs.
  - ____ σ-symmetric valence AOs therefore ____ valence σ-MOs.

Resonance and MO Theory: Ozone (O_3)

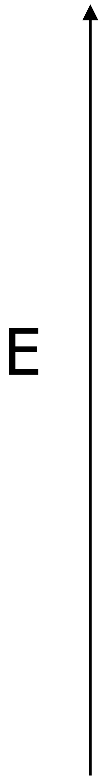
- To decide how many electrons go into π-MOs and how many go into σ-MOs, look at the Lewis diagram.
  - Each single bond corresponds to two electrons in σ-MOs
  - Each double bond corresponds to two electrons in σ-MOs and two electrons in π-MOs
  - Each triple bond corresponds to two electrons in σ-MOs, two electrons in one set of π-MOs (one pi system) and two electrons in another set of π-MOs (another pi system)
  - A lone pair on an atom **next to** a double/triple bond corresponds to two electrons in π-MOs
  - Any other lone pair corresponds to two electrons in σ-MOs

Notice that the lone pairs on atoms **next to** a double/triple bond are the ones which move between resonance structures!

- Ozone has:
  - _____ electrons in valence π-MOs.
  - _____ electrons in valence σ-MOs.

Resonance and MO Theory: Ozone (O_3)

- Use symmetry and nodes to work out what the π-MOs of ozone look like, ranking them from lowest to highest energy. Then, fill in the electrons to give a complete π-MO diagram.

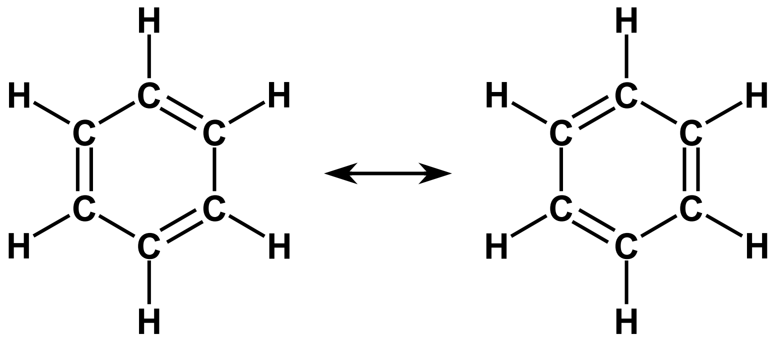


Resonance and MO Theory: Ozone (O_3)

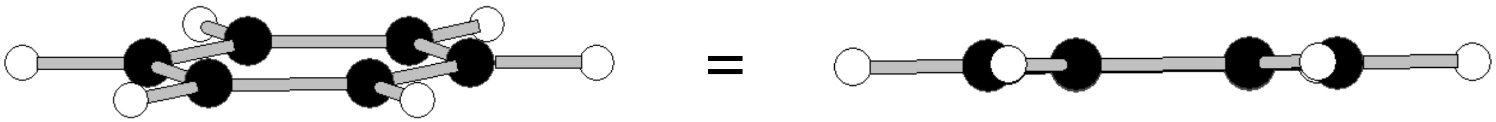
- How does your MO diagram for O_3 relate to the Lewis diagrams you drew for it? Consider both bond order and formal charges.

Resonance and MO Theory: Benzene (C_6H_6)

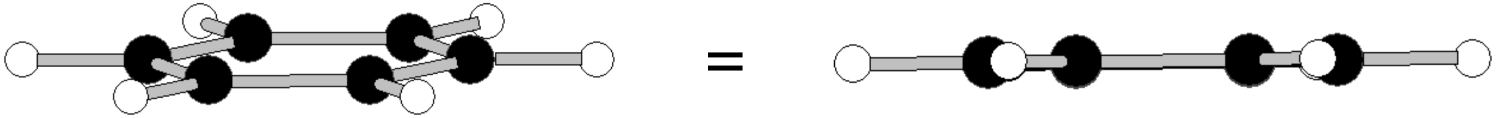
- The classic example of delocalized π electrons and MO theory is benzene. The Lewis structure of benzene is:



- If we assign molecular geometries to each carbon atom, we see that benzene is a planar molecule:



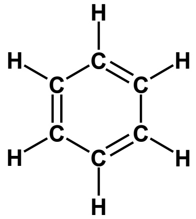
Resonance and MO Theory: Benzene (C_6H_6)

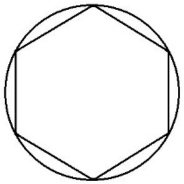


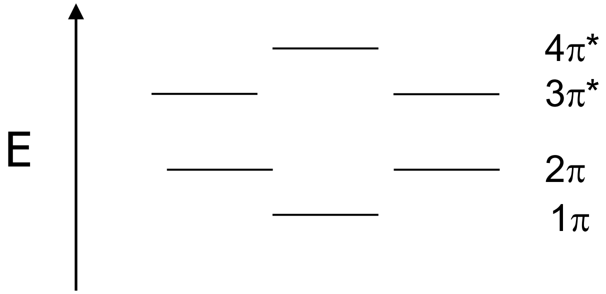
- Sorting the valence atomic orbitals by symmetry gives _____ σ-AOs and _____ π-AOs.
- Therefore, benzene will have _____ σ-MOs and _____ π-MOs.
- There are _____ electrons in σ-MOs and _____ electrons in π-MOs.

Resonance and MO Theory: Benzene (C_6H_6)

- So, we know that benzene has _____ π-MOs containing _____ electrons. We also know that these π-MOs were made by combining six $2p_z$ orbitals on the six carbon atoms.
- Cyclic molecules tend to have degenerate π energy levels.
    - A "quick and dirty" trick to predict the relative energy levels for **cyclic** molecules is to draw a circle. Inside the circle, draw a polygon the same shape as your molecule. Make sure the tip of the polygon is at the bottom of the circle. The corners of the polygon are at the same height as the relative energy levels. If you draw a horizontal line across the middle of the circle (representing the energy of the *p* atomic orbitals), all orbitals below it are bonding and all orbitals below it are antibonding. This method (a **Frost circle**) is a huge oversimplification but it works.





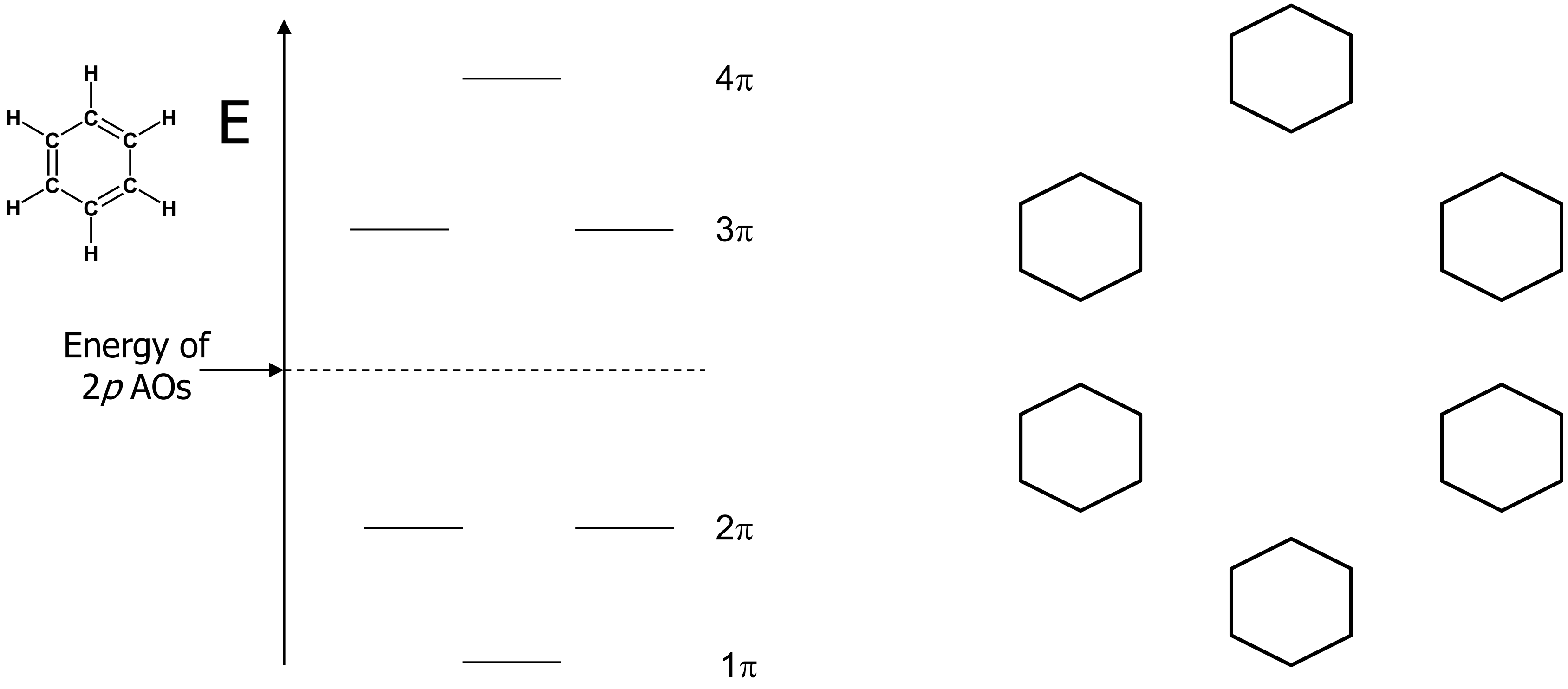


Resonance and MO Theory: Benzene (C_6H_6)

- We've worked out the energy levels, but what do the MOs look like? To answer that, we go back to our old standby method – symmetry and nodes!
    - The lowest energy π-MO (1π) has one nodal plane – the one cutting through the plane of the molecule. It has no nodes perpendicular to the plane of the molecule.
    - Every time you go up to the next energy level, add a node perpendicular to the plane of the molecule, keeping them as evenly spaced as possible. If there are two degenerate π-MOs, keep their nodes as askew as possible (perpendicular if possible, at a 45° angle as next choice, etc.)
    - The highest energy π-MO should be "as antibonding as possible" – i.e. nodes between every pair of neighbouring atoms

- Once you've determined the energy levels and the shapes of the π-MOs, the last step is to fill in the electrons. Recall that we have _____ π electrons to add to the π-MO diagram.

Resonance and MO Theory: Benzene (C_6H_6)



- This MO diagram confirms that benzene can’t be considered to have “three double bonds and three single bonds”. It really does have three bonds with bond order ______. *This has been proven experimentally: all six C-C bonds in benzene are 140 pm (whereas pure C-C bonds are 154 pm and pure C=C bonds are 134 pm).*