

Queen's **CHEM 112A**

Fall 2024, Chapter 5 Notes



Table of Contents

Chapter 5. Bonding Theories

5.1. Valence Bond theory

5.1.1. Introduction to Valence Bond Theory

Theory

5.1.2. Example: Valence Bond Description of O₂ and N₂

5.1.3. Hybridization Theory

5.1.4. Example: Valence Bond Description of Acetone

5.1.5. Practice: Hybridization of Atoms in Methyldiazene

5.1.6. Practice: Bonding in Methyldiazene

5.1.7. Practice: Bonding in Methyldiazene Part 2

5.2. Molecular Orbital Theory

5.2.1. Molecular Orbital Theory Introduction

5.2.2. Bond Symmetry

5.2.3. Combining s type orbitals

5.2.4. Combining p type orbitals

5.2.5. How to Draw MO Diagrams for Homonuclear Diatomics

5.2.6. Example: Molecular Orbitals of Li₂

5.2.7. Example: Molecular Orbitals of HeH⁺

5.2.8. Practice: Diamagnetic Diatomics

5.2.9. Practice: MO Orbitals Problem

5.3. Delocalized Bonding in Extended π Systems

5.3.1. How to Draw MO's of Organic π Systems Theory

5.3.2. 1,3,5-hexatriene

5.3.3. The Chemical Origin of Colour

5.3.4. Chromophore Identification

5.3.5. Color Shift Question

5.3.6. Phenolphthalein

5.Q. Exam Questions & Practise

5. Bonding Theories

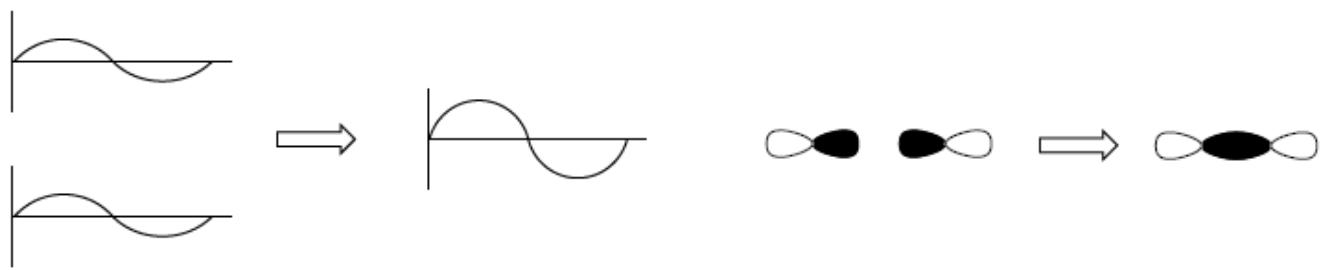
5.1 Valence Bond theory

5.1.1

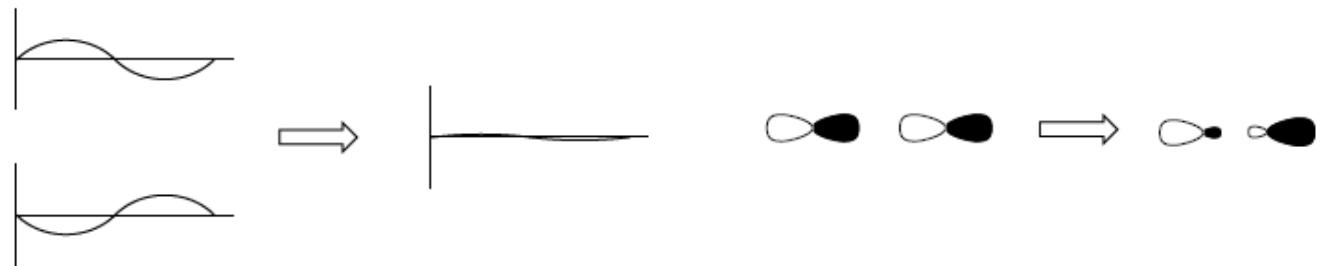
Introduction to Valence Bond Theory

- Valence bond theory (VBT) is another theory of bonding. It is a more advanced theory because it is based on the atomic orbitals obtained from quantum mechanics.
- While VSEPR theory provides an adequate theoretical basis for simple inorganic compounds with a central atom and some number of peripheral atoms it is not adequate to discuss more complex chemical systems
- In VBT a singly occupied atomic orbital overlaps with another singly occupied atomic orbital from the adjacent atom creating a bond. An example for O_2 is shown below.
- The basis of VBT is that overlapping atomic orbitals of the same phase produce bonds and if the phases are opposite they do not. This is similar to wave mechanics.

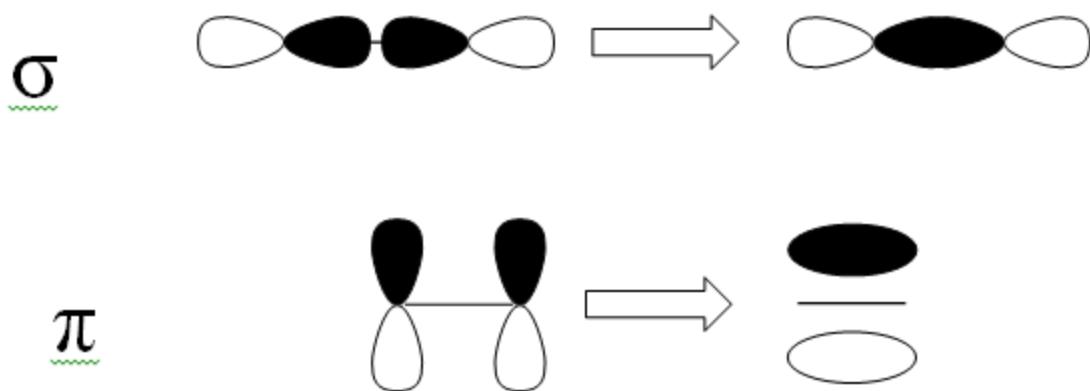
In Phase



Out of Phase

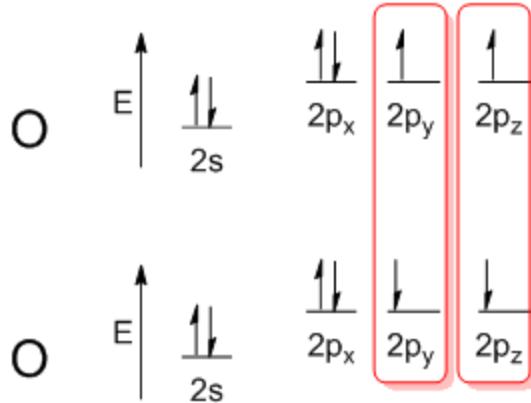


- There are two ways orbitals can overlap. Sigma type overlap, and pi type overlap. Sigma overlap is when the overlap occurs along the internuclear axis (between two nuclei) and pi overlap occurs above and below the internuclear axis.

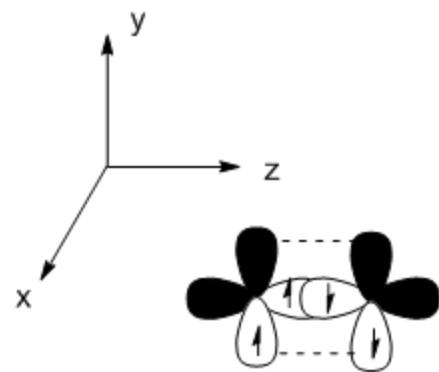


- Notation: We use the following notation to denote bonds $X(O_1-O_2)$ where X is the type of bonding (sigma or pi for this course), O_1 and O_2 are the types of orbitals involved.

- Shown below are the two types of diagrams you are responsible for being able to draw.



Valence Bond Diagram



Orbital Overlap Diagram

5.1.2

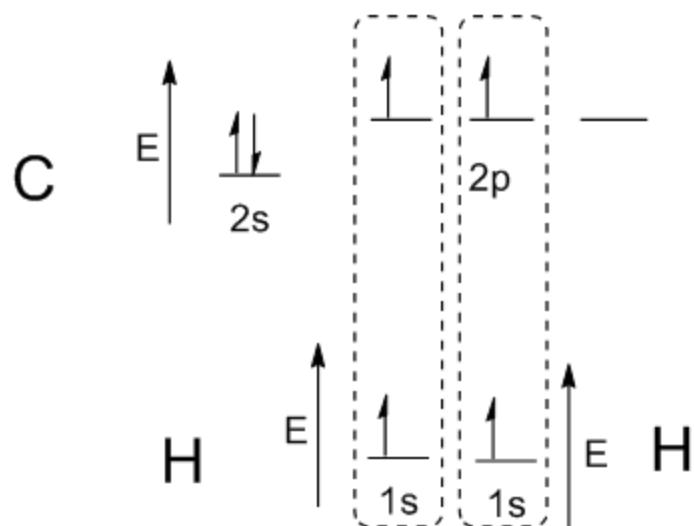
- 1) Describe the bonding in O_2 using appropriate notation, do not use hybridization theory for this problem. You may assume the internuclear axis is the z-axis.

- 2) Draw a Valence bond diagram and an Orbital Overlap Diagram for N_2 , just as we did for O_2 above using atomic orbitals.

Hybridization

Why do We Need Hybridization?

- VBT as described above is not sufficient to explain certain observations. For example it does not explain how carbon is bound to 4 hydrogen atoms in CH_4
- If we examine what the VBT diagrams would look like without hybridization we can quickly see that carbons ground state electron configuration only allows two bonds to be formed.

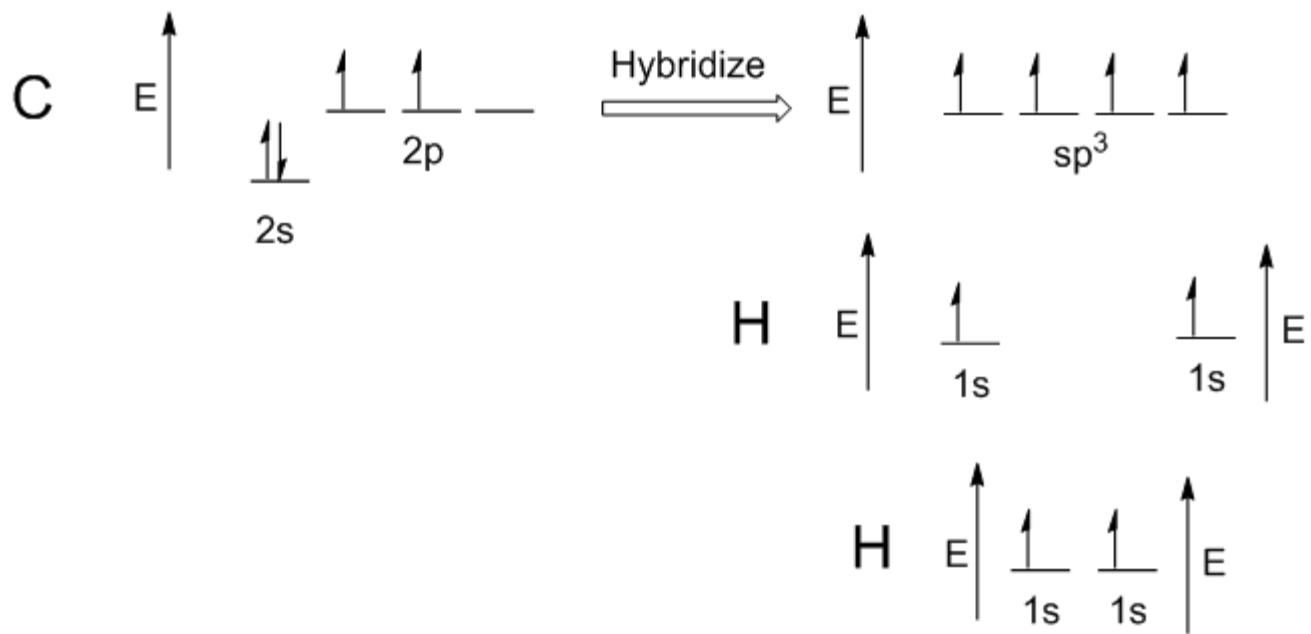


- However we know from experiment that the true form is CH_4 and all 4 C-H bonds are equal.
- To explain how this comes about using VBT we need to invoke hybridization

What is Hybridization?

- Hybridization is a theoretical tool we use to explain experimental observations
- When we hybridize orbitals, we are actually constructing linear combinations of atomic orbitals. The orbitals will constructively or destructively interfere
- Hybridization does not consume or create orbitals. Therefore if we hybridize one s-orbital and one p-orbital we create two hybrid orbitals.
- The names of the hybrid orbitals are based purely on which orbitals were combined to make the hybrid. They are named as follows. sp , sp^2 , sp^3 , sp^3d , sp^3d^2 .

- Now that we have introduced hybridization we can use it to explain the bonding of methane.
- If we hybridize the s-orbital and all the p-orbitals of carbon to form four new hybrid orbitals we end up with the following picture. From this picture it seems fairly obvious that carbon can now form four bonds to hydrogen



What do Hybrid Orbitals Look Like?

- All of the hybrid orbitals look very similar, shown in figure below. Although there are slight differences in their shape, for the purpose of this course they can all be drawn the same. The main thing you must remember is how many of each hybrid orbital there are and what directions they point in (it's the same as VSEPR)

Hybrid Orbitals

sp



sp²



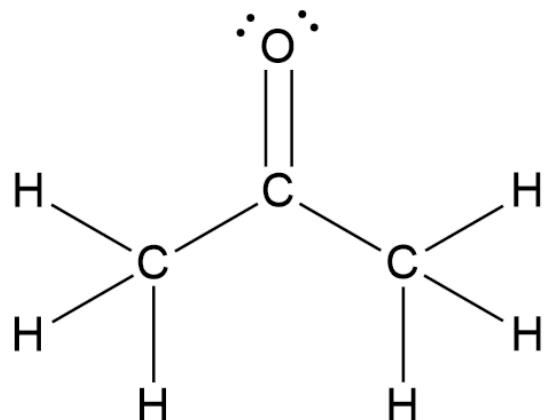
sp³



(This is an ugly tetrahedron)

5.1.4

Acetone C_3H_6O is shown below

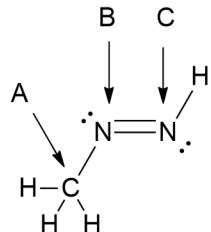


- a) What is the hybridization of each non-hydrogen atom?
- b) What type of bond is formed between the carbon atoms of acetone? Use valence bond theory nomenclature.

c) Draw a valence bond diagram and an orbital overlap diagram for the C=O bond in acetone.

5.1.5

The structure of methyldiazene is shown below. What is the hybridization of the atoms labelled A, B and C respectively?



A: sp^3 B: sp C: sp

A: sp^3 B: sp C: sp^2

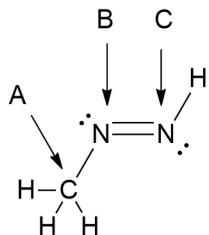
A: sp^3 B: sp^2 C: sp^2

A: sp^2 B: sp^2 C: sp^2

A: sp^3 B: sp^3 C: sp^3

5.1.6

The structure of methyldiazene is shown below. Which orbitals make up the σ bond between atoms A and B? In the options below the first orbital listed is from atoms A, and the second orbital listed is from atom B.



sp^3-sp^3

sp^2-sp^3

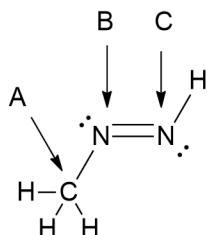
$2\text{p}-2\text{p}$

sp^3-2p

sp^3-sp^2

5.1.7

The structure of methyldiazene is shown below. Which orbitals make up the π bond between atoms B and C? In the options below the first orbital listed is from atoms B, and the second orbital listed is from atom C.



sp^3-sp^3

sp^2-sp^2

$2\text{p}-2\text{p}$

$\text{sp}^2-\text{2p}$

sp^3-sp^2

5.2 Molecular Orbital Theory

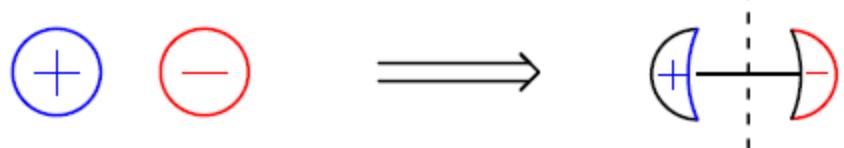
5.2.1

Introduction

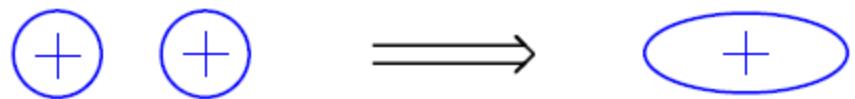
- Just as valence bond theory was introduced as a higher level of theory (as compared to VSEPR) molecular orbital theory (MO theory) is simply another even higher level of theory that was developed to explain some experimental observations.
- The basis of MO theory is similar to hybridization. This time though we will combine all the atomic orbitals from all the atoms and create new molecular orbitals from that
- It is very difficult to predict these MO's in general but you should know how to read and generate MO diagrams for diatomic molecules

- Another concept becomes important in MO theory and that is the idea of bonding and anti-bonding orbitals. Anti-bonding orbitals are orbitals in which there is a node between the two atoms in question as is shown below

Anti-Bonding



Bonding



- Once orbitals have been identified as bonding or anti-bonding we can discuss bond order. Bond order is a measure of bond strength. ie a triple bond would have a bond order of 3. To calculate the bond order from a MO diagram (we'll see this soon) you need to use the equation shown below.
- Bond order describes the degree of bonding between the two atoms and estimates the strength of the bond. The higher the bond order, the stronger the bond and therefore the shorter the bond.

$$\text{Bond Order} = \frac{(\text{number of bonding electrons}) - (\text{number of anti-bonding electrons})}{2}$$

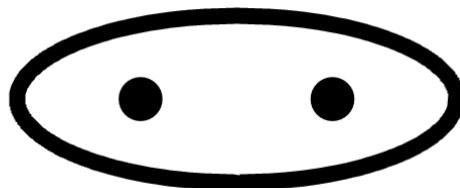
- If the bond order = 0, there is no bonding between the atoms and the molecule is unstable.

Types of orbital combinations

Symmetry

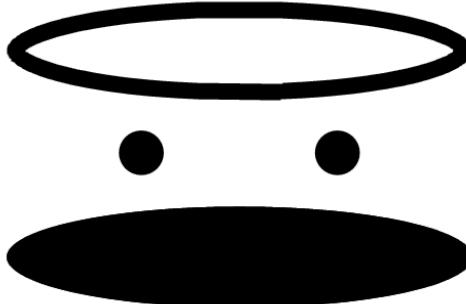
- Depending on the orientation of the atomic orbitals, there are two ways that s and p type orbitals can combine.
- An orbital which has electron density along the internuclear axis (typically z) is said to be a sigma orbital

σ



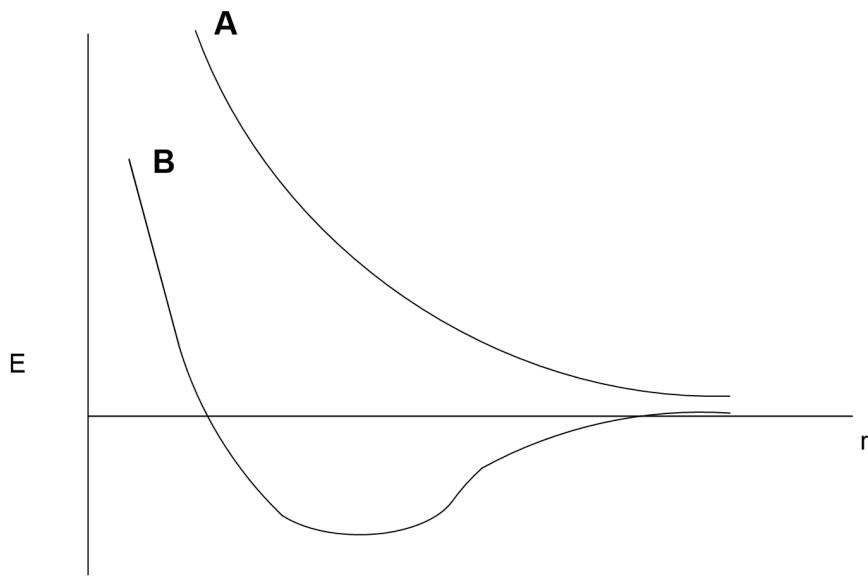
- An orbital which has a node through the internuclear axis is said to be a pi orbital

π



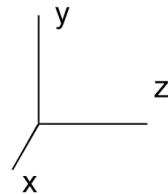
Potential Energy Surfaces

One curve is a bonding orbital, one curve is ant-bonding. Which is which?



5.2.3

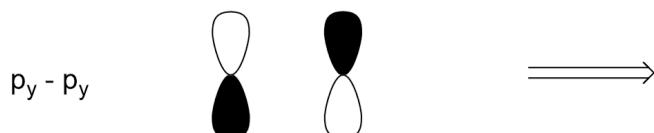
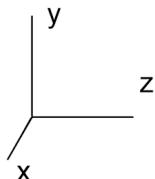
s-orbitals



- Notice how two s-orbitals can only form a sigma bonding (σ) or a sigma anti-bonding (σ^*) molecular orbital

5.2.4

p-orbitals



** Same types of combinations for $2p_x-2p_x$ **

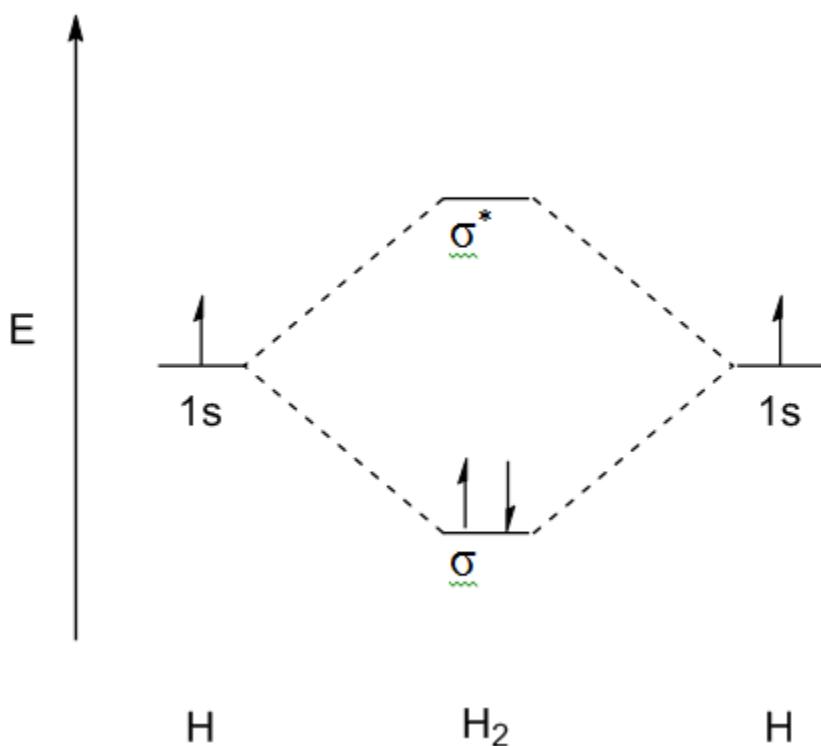
- Notice that combining p-orbitals of the same orientation (y,y or z,z or x,x) gives a bonding and anti-bonding pair just like s-orbitals. However, the p-orbitals can form π or σ orbitals depending on whether they lie on or perpendicular to the internuclear axis.

What would happen if we tried to combine a $2p_z$ with a $2p_y$?

Non-bonding interaction!

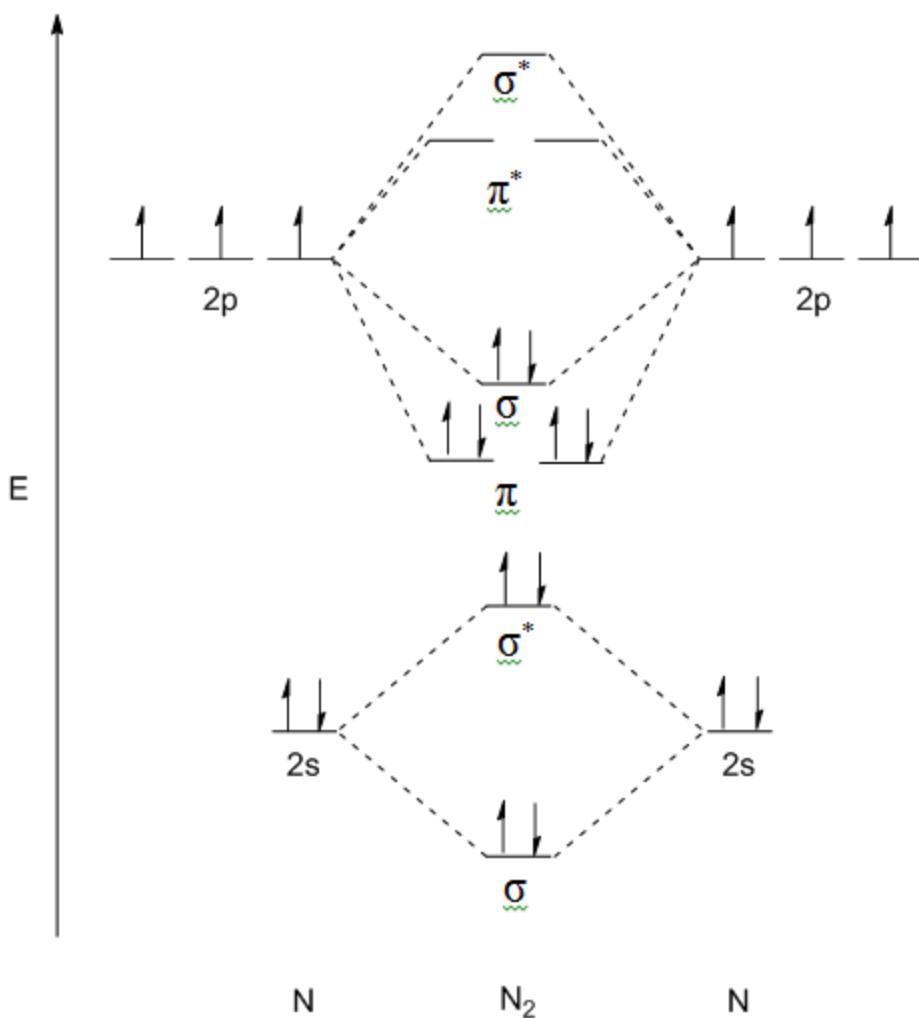
How to Draw MO Diagrams for Homonuclear Diatomics

- As an example the MO diagram for the simplest homodiatom, hydrogen, is shown below



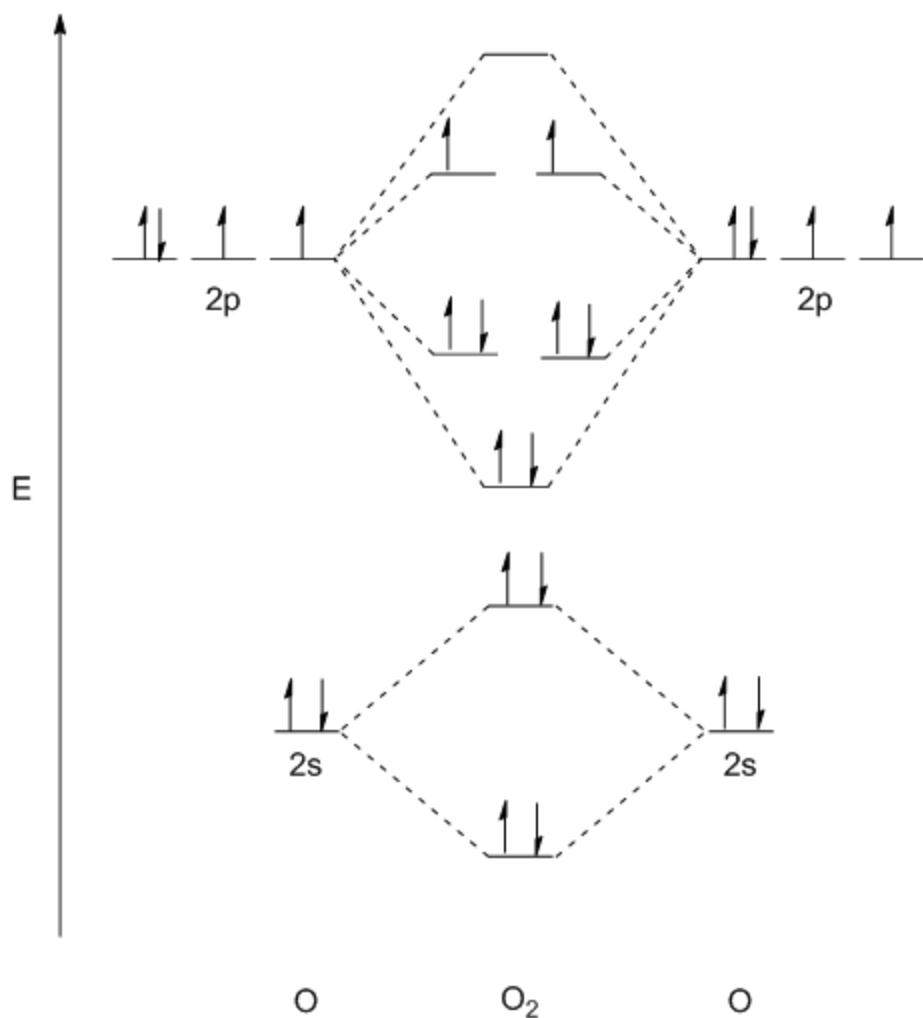
- Note: Now the atoms and the homodiatom are all on the same energy axis.
- Hydrogen has one electron so each side of the diagram is filled with one electron
- H_2 has two electrons so the middle column of orbitals is filled with two electrons.

- Filling the orbitals follows the same three rules that we talked about in chapter 2.
- The MO picture for H_2 is fairly simple because we only have one orbital on each atom. When we move to the second row of the periodic table we have to consider the p orbitals.



- Both the π and π^* orbitals are comprised of two degenerate pi orbitals.

- This orbital diagram is the same for all homodiatomic molecules of the second row from Li to N.
- When we move to the right of nitrogen along the second row there is a small change to the MO picture. The σ_{2p} switches places with the π_{2p} as shown in figure 8.4 below.
- The reason for this is complex but a partial explanation is obtained by noting that the 2s-2p orbital gap in oxygen is larger (due to electronegativity) and so less 2s-2p “mixing” is observed.



-
- O_2 is a good example of why we need MO theory. MO theory predicts that O_2 is paramagnetic whereas VBT does not.

5.2.6

Draw the full MO for Li_2

5.2.7

Draw the MO for HeH⁺

5.2.8

Which of the following diatomic molecules are paramagnetic? Use MO theory in your analysis.

- i. O_2
- ii. N_2
- iii. O_2^{2+}
- iv. He_2^+
- v. N_2^+

i, ii

ii, iii

iii, iv, v

i, iv, v

All are paramagnetic

5.2.9

Choose the statement below about MO theory which is **INCORRECT**.

A π MO can NOT be formed with an s orbital

Li_2 would have a bond order of 1

A σ orbital can be formed between s orbitals or between p orbitals

O_2 is paramagnetic because it has unpaired electrons in a σ^* orbital

N_2 has a bond order of three when analyzed by MO theory

5.3

Delocalized Bonding in Extended π Systems

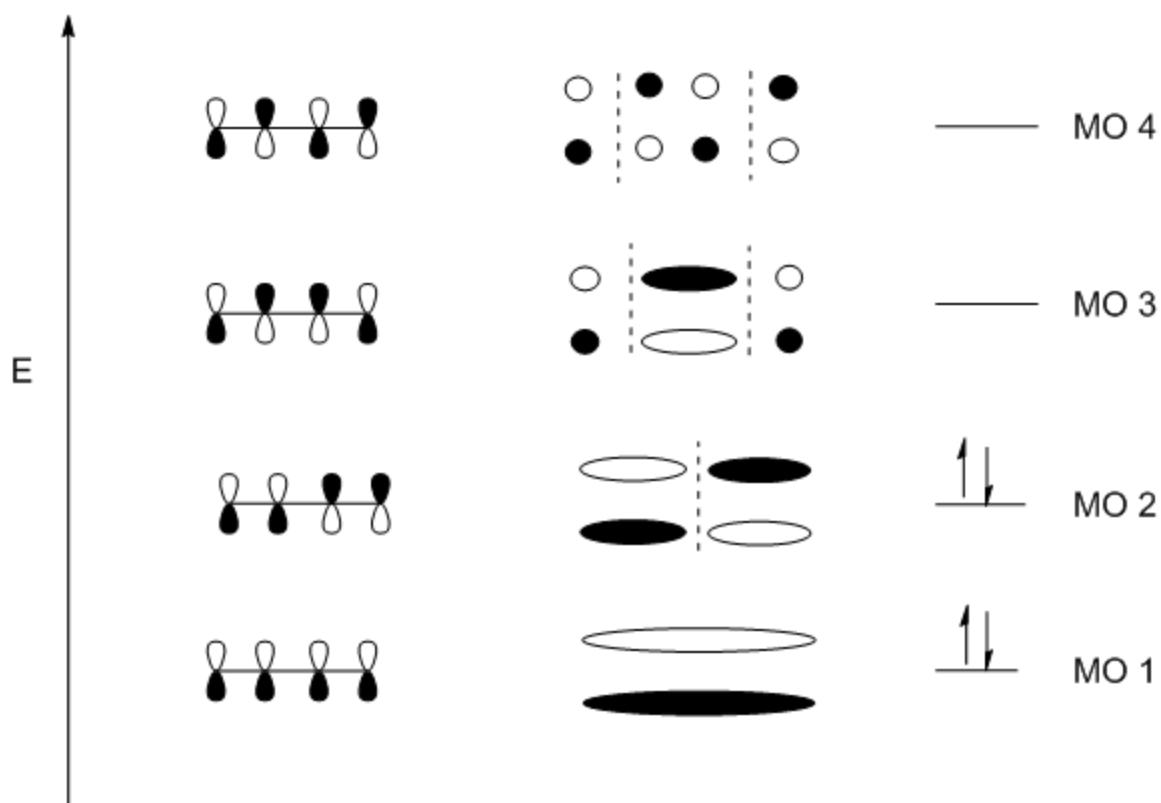
5.3.1

How to Draw MO's of Organic π Systems

- The second type of MO diagram you are responsible for is organic π systems
- Remember from VBT that hybrid orbitals are used for the lone pairs and σ bonds. The π network is composed of the remaining p-orbitals
- If we imagine a chain of sp^2 hybridized carbon each having one p orbital we can draw the following picture



- Now if you consider that all the p-orbitals (shown above) can be phased in one of two ways (black up or black down) then we have a number of possibilities shown below
- Notice that the MO's shown below are arranged on the energy axis based on how many nodes are present
- We used 4 p orbitals to construct our MO's and we obtained 4 MO's



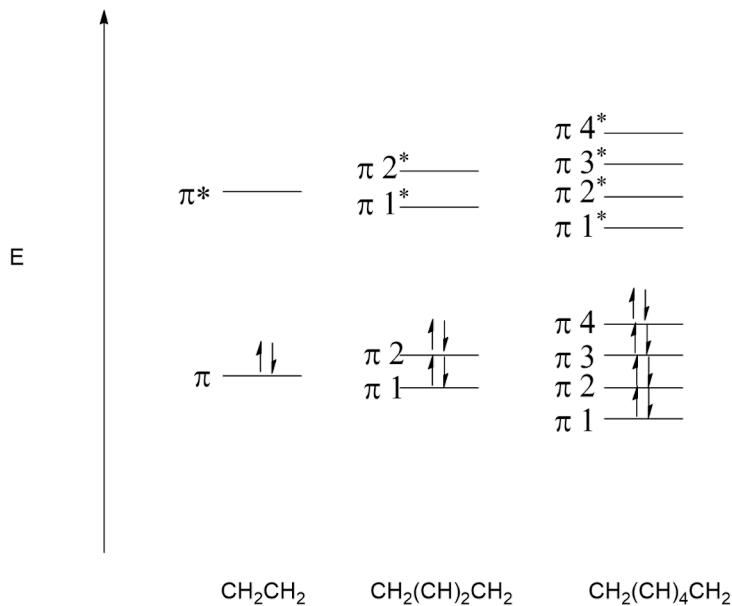
5.3.2

Draw an MO diagram for 1,3,5-hexatriene ($\text{CH}_2\text{CHCHCHCHCH}_2$), label all MO's and designate each one bonding or antibonding. Include a label for the HOMO and LUMO.

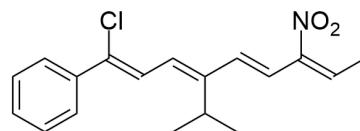
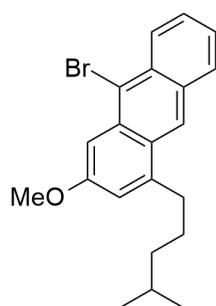
5.3.3

The Chemical Origin of Colour

- As the number of atoms in the conjugated system increases the number distance between the MO's decreases. By changing the length of the conjugated system, and the atoms that comprise we can tune the HOMO-LUMO gap and therefore change the color of light (wavelength) absorbed or emitted from electronic transition

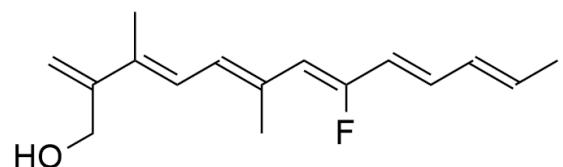
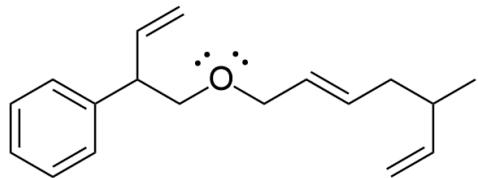
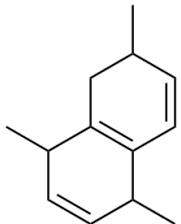


- Molecules with large conjugated pi systems are called chromophore, examples are shown below.



5.3.4

Which of the following molecules would you expect to be the most highly colored.



5.3.5

An organic molecule with a n=16 conjugated system absorbs blue light. If we wanted the organic molecule to absorb green light would we choose a molecule with a longer or shorter conjugated system? Explain.

We would choose a shorter conjugated system because that would lead to fewer π MO's and a smaller HOMO LUMO gap

We would choose a longer conjugated system because that would lead to more π MO's and a smaller HOMO LUMO gap

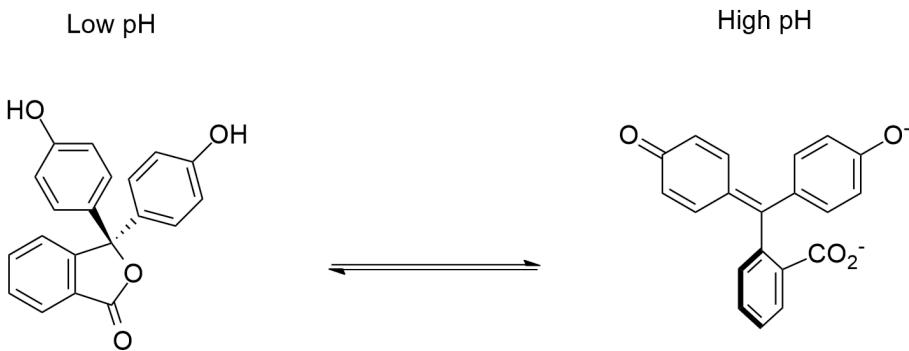
We would choose a shorter conjugated system because that would lead to fewer π MO's and a larger HOMO LUMO gap

We would choose a longer conjugated system because that would lead to more π MO's and a larger HOMO LUMO gap

Changing the length of the conjugated system will not change the color of the molecule

5.3.6

Phenolphthalein is used as an indicator in acid base titrations because it is halochromic, it changes color based on pH. Shown below are the two forms of phenolphthalein at low pH and high pH. One of the forms is colorless and one is bright purple. Which one is colored? Explain your answer.



The low pH form because it has more rings

The high pH form because it has fewer rings

The low pH form because it has a larger conjugated system

The high pH form because it has a larger conjugated system

Can't tell from the structures provided