

Learning Objectives and Worksheet VIII

Chemistry 1B-AL Fall 2016

Lectures (13-14) Molecular Orbital Theory of Covalent Bonding

WE WILL BE COVERING CHAPTER 14 IN A DIFFERENT ORDER THAN THE TEXT: first we will cover the quantum mechanics of covalent bond formation (pp 676-688, lectures 15-16) in diatomics and then polyatomic bonding and structure (pp. 663-676 & 688-692; lectures 17-18)

Supplemental video: MIT opencourse on diatomic molecules molecular orbital theory:
http://videlectures.net/mit5111f05_ceyer_lec14/

Now that we understand, from a Lewis structure perspective, how molecules may be formed from atoms that are covalently bonded by electron pairs, we are ready to return to quantum mechanics to ask “what are the wavefunctions that describe the electrons in an electron-pair bond?” Again, exact numerical solutions of the Schrödinger equation give molecular properties that exactly match experimental values; and again, as in many-electron atoms, an ‘orbital approximation’ will provide an excellent picture of the quantum mechanics of covalent bond formation. To describe the electronic structure of molecules we will place electrons in “molecular orbitals” in a way similar to the Aufbau Principle for placing electrons in “atomic orbitals”.

I. Introduction to the quantum mechanics of the covalent bond

1. What are two properties of the hydrogen molecule, H_2 , that correspond to the concept that in H_2 an **electron pair bond** occurs between the two H atoms ?

2. In forming a molecular orbital, two atomic orbitals (i.e. the waves describing the orbitals) can interact in what two ways:
 - i.
 - ii.
3. Constructive interference of two atomic orbitals (a.o.'s) leads to a _____ molecular orbital that has a _____ energy that the constituent a.o.'s and a greater electron density _____ than the sum of the a.o. electron densities.

4. Destructive interference of two atomic orbitals (a.o.'s) leads to an _____ molecular orbital that has a _____ energy that the constituent a.o.'s and a lower electron density _____ than the sum of the a.o. electron densities.

II. Molecular orbitals for first and second row homonuclear diatomics

1. Bond order is defined as

$$\text{b.o.} = \frac{1}{2} [\text{no. of } \underline{\hspace{2cm}} - \text{no. of } \underline{\hspace{2cm}}],$$

giving a bond order of _____ for the 'single' electron-pair bond in the molecule H_2 .

2. Understand orbital energy diagram for m.o.'s constructed from two 1s a.o.'s. What would be the electronic configuration for the ground state of H_2^- ? _____

What is the bond order of H_2^- ? _____.

3. What two factors that dictate whether two atomic orbitals will interact to form molecular orbitals?

i.

ii.

4. If two atomic orbitals have a very small spatial overlap, there will be a _____ energy difference between the bonding and antibonding molecular orbitals formed from combinations of these a.o.'s.

5. Understand the orbital energy level diagrams for m.o.'s constructed from 1s and 2s a.o.'s. In Li_2 and Be_2 , note that the energy difference between the σ_{2s} and σ_{2s}^* m.o.'s greater than the energy difference between the σ_{1s} and σ_{1s}^* m.o.'s. Why is this?

6. Understand the orbitals resulting from interactions among the 2p a.o.'s on the two atoms in a diatomic molecule. Let us assume (as does the text) that the intermolecular axis is in the x-direction. In a homonuclear diatomic ($A-x-A'$) which are true and which are false (circle correct choice):

- i. The six 2p a.o.'s (3 on A, 3 on A') interact to form six m.o.'s **T F**
- ii. Among the six 2p a.o.'s, the $2p_x$ on A will only interact with the $2p_x$ on A' to form σ_{2p_x} and $\sigma^*_{2p_x}$ m.o.'s. **T F**
- iii. The $2p_y$ a.o. on A and the $2p_x$ a.o. on A' will not interact to form m.o.'s since these atomic orbitals have very different energies. **T F**
- iv. In the 'simple' picture (little 2s-2p mixing as in O_2 and F_2), the π_{2p_y} m.o. will have a lower energy than the σ_{2p_x} m.o., since the side-on interaction of $2p_y \leftrightarrow 2p_y$ a.o.'s is greater than the end-on interaction of $2p_x \leftrightarrow 2p_x$ a.o.'s on A and A'. **T F**
- v. Of the six m.o.'s formed by the 2p a.o.'s, the $\sigma^*_{2p_x}$ will, in general, have the highest energy due to the greatest destructive interference between $2p_x \leftrightarrow 2p_x$ a.o.'s on A and A'. **T F**
- vi. In homonuclear diatomics a 2s a.o. on A and a $2p_x$ a.o. on A' will never interact in forming m.o.'s since there is no possibility of net constructive or destructive interference between these a.o.'s. **T F**
- vii. In homonuclear diatomics a 2s a.o. on A and a $2p_y$ a.o. on A' will never interact in forming m.o.'s since there is no possibility of net constructive or destructive interference between these a.o.'s. **T F**

7. Understand basis of orbital designations:

- i. A π_{2p_y} m.o. has the π designation because the orbital changes _____ for equivalent positions on one side of the molecule and the other relative to a plane that includes the internuclear axis.
- ii. The σ^*_{2s} m.o. has the _____ sign for all points on a circle that is centered on the internuclear axis and is contained in a plane perpendicular to this axis.
- iii. The σ^*_{2s} m.o. has a _____ plane halfway between the two atoms of a homonuclear diatomic molecule since it is an _____ orbital.

III. Electronic Configurations and molecular properties of homonuclear diatomic molecules

study via many
HW #6 problems

I COMMAND MY HOMEWORK
TO DO ITSELF!
No HOMEWORK, BE DONE!



HW#6: 46, 47,
48, S13

1. Understand the molecular orbital energy diagrams in the two instances
 - i. simple (applies to O_2 and F_2)
 - ii. modified (by significant 2s-2p mixing; applies to B_2, C_2, N_2)
2. Be able to write electronic configurations for these molecules and identify ground, excited, and not allowed ('impossible') electronic states.
3. Be able to evaluate number of unpaired electrons and bond order from electronic configuration.
4. Be able to relate configurations to molecular properties

e.g.

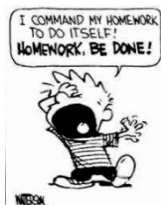
 - i. A molecule with no unpaired electrons will be _____.
 - ii. The higher the bond order, the _____ the bond energy and the _____ the bond length.
 - iii. The excited state of O_2 ($\sigma^2_{1s} \sigma^{*2}_{1s} \sigma^2_{2s} \sigma^{*2}_{2s} \sigma^2_{2p} \pi^3_{2p} \pi^{3*}_{2p}$) will have a _____ bond length than the ground state of O_2 .

IV. Third row homonuclear molecules

1. Inner shell m.o.'s from 1s, 2s, 2p orbitals are tightly bound 'atomic-like' inner shells
2. Valence orbital m.o.'s composed of 3s and 3p a.o.'s similar to those from 2s and 2p in diatomics from second row and their relative energies follow the same considerations.
3. For third row diatomics you would be instructed, if needed, whether the simple or s-p mixing energy ordering is applicable to a specific example.

V. Heteronuclear diatomic molecules

1. The same rules for forming m.o.'s from a.o.'s on different atoms still hold (similar energy and net interference) but:
 - i. pairs of a.o.'s on different atoms no longer have the same energies, e.g.
 - in B-F, the 2p on F will have a _____ energy than the 2p on B
 - in H-F, the 1s on H has an energy similar to the _____ atomic orbital on F
 - in N-O, the 2p on N will have a _____ energy than the 2p on O



HW#6: 49

- ii. a.o.s no longer make equal contributions to the m.o.'s
 - a. when a.o.'s of unequal energy interact to form bonding and antibonding m.o.'s, the higher energy a.o. makes a greater contribution to the _____ m.o. and the lower energy a.o. makes a greater contribution to the _____ m.o.
 - b. in a heteronuclear bond the unequal contributions from the a.o.'s on the two atoms and the resulting uneven distribution of electrons leads to a _____ bond