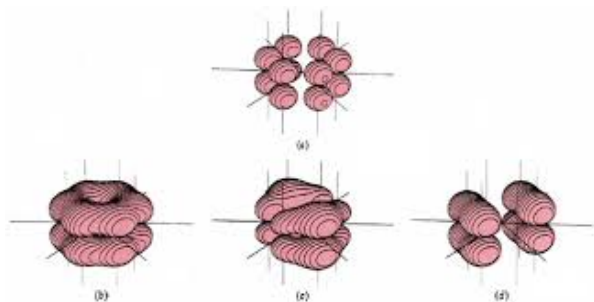


9.4 - 9.6 - Diatomic Molecules & Spectroscopy



MO Theory vs. Heteronuclear Diatomic Molecules

Thus far we have looked at molecular orbital theory from the perspective of identical elements bonding diatomically.

Realizing the enormous variety of elements, and their potential for pairing, we now look at heteronuclear diatomic molecules, those in which there are two different atoms.

The theory you have seen already is completely applicable as far as prediction bond order and magnetic qualities *if the atoms are similar in size*.

Molecular Model Examples

Draw a MO model for the following in order to predict the magnetism and bond orders of

- the NO^+ ion (called nitriloxonium ion), and the
- cyanide ion (CN^-).

1. NO^+ Answer

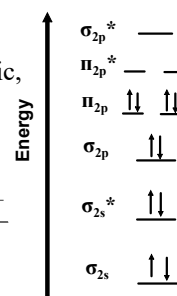
In the NO^+ ion, there are 10 valence electrons total, $5 + 6 - 1 = 10$, with a MO diagram of:

This is expected to be diamagnetic,

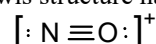
with a bond order of 3:

$$\text{Bond Order} = \frac{\text{bonding } e^- - \text{antibonding } e^-}{2}$$

$$\frac{8 - 2}{2} = 3$$



Indeed, the Lewis structure has three bonds:



2. CN^- Answer

The cyanide ion solves almost identically to the NO^+ ion: there are 10 valence electrons total, $4 + 5 + 1 = 10$, with a MO diagram of:

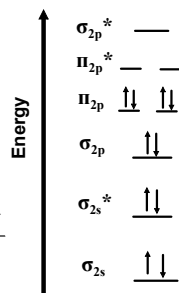
CN^- is diamagnetic,

with a bond order of 3:

$$\text{Bond Order} = \frac{\text{bonding } e^- - \text{antibonding } e^-}{2}$$

$$\frac{8 - 2}{2} = 3$$

The Lewis structure is: $[: \text{N} \equiv \text{C} :]^-$



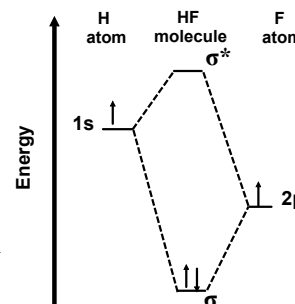
Energy Level Difference

When two atoms bind together with valence electrons from different energy levels, a new diagram must be produced.

Consider HF, wherein hydrogen's valence electron comes from the 1s sublevel, and fluorine's comes from a 2p sublevel.

Fluorine binds to its valence electrons more tightly than hydrogen, so the 2p energy level is shown lower down than 1s.

A sigma orbital is shown housing the electron pair because hydrogen has no p sublevels available.



Delocalization

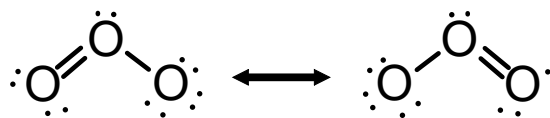
One of the main problems with the localized model is (oddly enough) the assumption that electrons are actually localized.

This problem comes up most significantly in molecules with Lewis structures having resonance. Because more than one structure is needed to show geometry, a more complete picture involves blending the simplicity of the localized electron model with the delocalization characteristic of the molecular orbital model.

Because resonance involves multiple possible locations of a double bond, we will look more closely at pi bonds, and p orbitals involved in bonding.

Delocalization Example

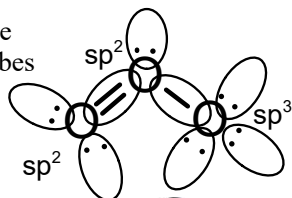
3. Consider ozone: O_3 . Make Lewis structures for ozone, complete with hybridization orbitals shown (meaning the regions of space where electrons would be expected to be found). To do this, determine the hybridization of each oxygen atom.



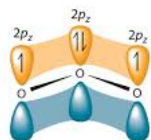
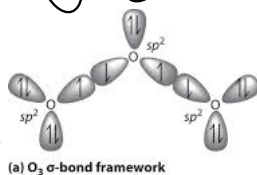
The central oxygen atom, and double bonded one are each sp^2 hybridized, while the loner is sp^3 .

Delocalization Answer

As such, the Lewis structure with overlaid hybridized lobes would look like this (but in 3-D):



To account for resonance, however, each terminal atom has sp^2 hybridization, and with a free p_z sublevel aligned perpendicularly to the plane of the molecule, a region of space forms in which the pi bond is equally possible. That region allows for freely delocalized movement of bonding electrons.



Pictorial Guide to Molecular Orbitals

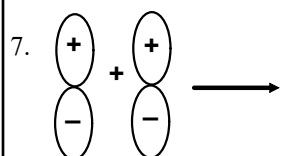
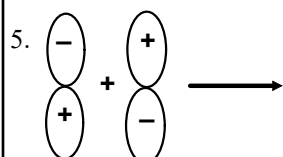
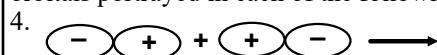
Often, one must identify bonding vs. antibonding orbitals in pictures.

Visually, if the signs of potentially overlapping lobes of hybridized orbitals are the same, it will form a bonding orbital.

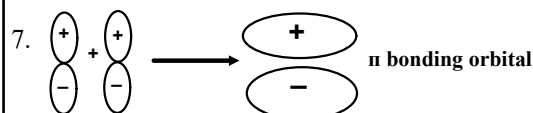
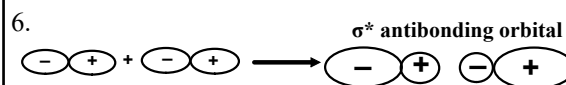
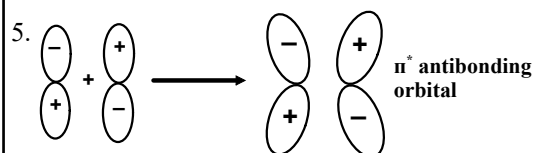
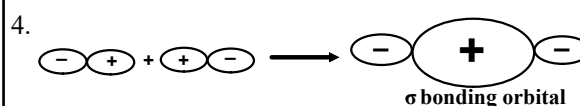
If the signs are opposite, it'll be antibonding.

Pictorial Orbitals Examples

Determine and sketch the types of molecular orbitals portrayed in each of the following:



Pictorial Orbitals Answers



Photoelectron Spectroscopy (PES)

Recall the photoelectric effect: electrons in metals can be ejected by shining light of the right frequency on a surface.

By gradually increasing the energy of light, it is possible to determine the binding energy of electrons in that metal.

Similarly, relative energies of electrons in individual atoms or molecules can be determined using PES.

Helium is often used to produce the high-energy photons, as its 58.4 nm wavelength photons have enough oomph to eject electrons from many common atoms or molecules.

PES Theory

To determine which electrons are being ejected from a sample, the following relation is used, which relates the binding energy of an ejected electron in the atom to the energy it is subjected to minus its kinetic energy upon release:

$$\text{Energy of } e^- = \text{energy}_{\text{photon}} - \text{kinetic energy of } e^-$$

Or:

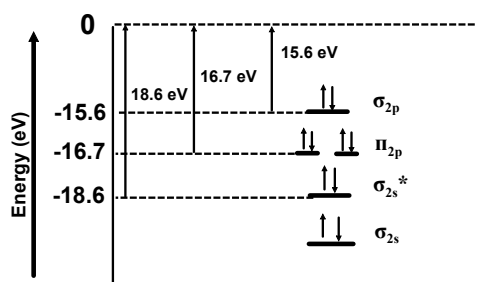
$$E_{\text{electron}} = h\nu - KE$$

While we won't go into any actual calculations, you must be able to interpret PES graphs armed with this theoretical knowledge.

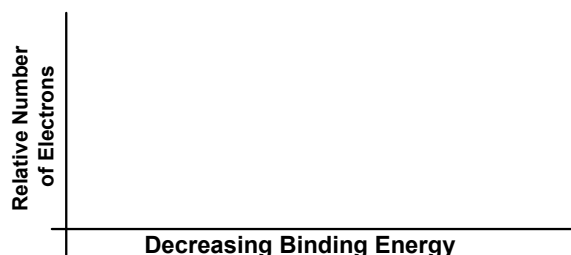
One detail is that PES graphs often show relative amounts of ejected electrons vs. decreasing binding energy.

PES Examples

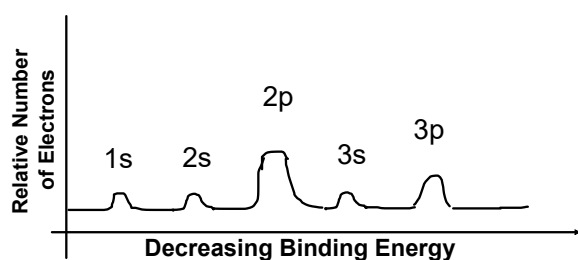
8. Reproduce this crude representation of diatomic nitrogen's electrons vs. energy levels. Note, in many molecules, N_2 included, the pi bonding orbitals are more tightly bound than are sigma, thus sigma appears *above* the pi bonding orbitals.

**PES Examples**

9. Draw a possible photoelectron spectroscopic graph for the element phosphorus. When making the graph, recognize and label which energy levels contain electrons, how many electrons there are in those levels, and that binding energy decreases as electrons are found in more distant energy levels.

**PES Graph Answer**

9. The electron configuration for phosphorus is: $1s^2 2s^2 2p^6 3s^2 3p^3$, and idealized PES graph would be:

**Homework**

9.4 - 9.6 Problems in your Booklet
Due: Next Class