

Exercise 3.2

Molecular Orbital Energy Level Diagrams: Heteronuclear Diatomics

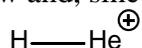
This exercise assumes that you are familiar with the “count and sort” algorithm described in Exercise 2.3 (which also contains a table of atomic orbital energies).

Molecular Orbital Energy Level Diagram for HHe^+

First, write electron configurations for hydrogen and helium: $1s^1$ for H and $1s^2$ for He

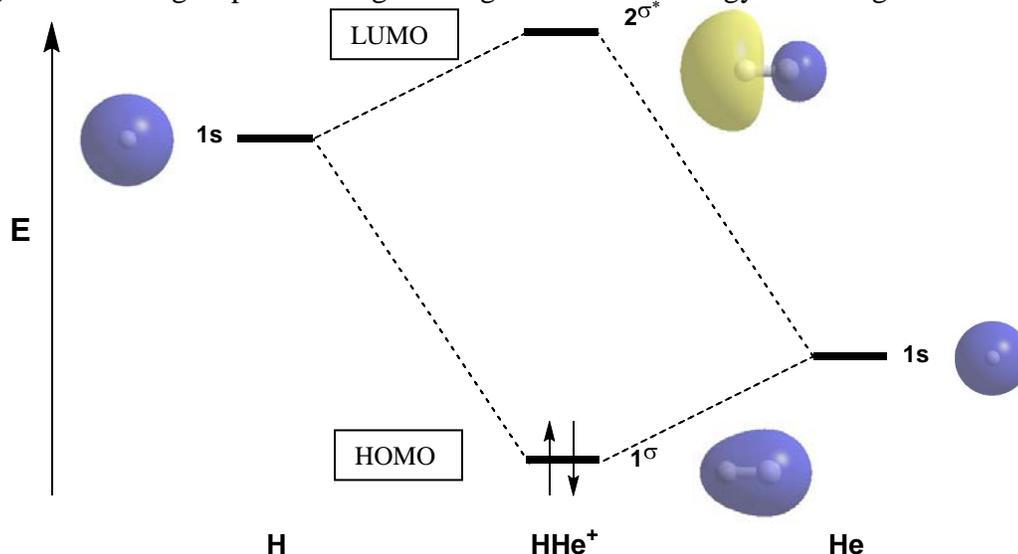
This tells us that the valence shell for each atom is $n = 1$, and that the only valence AOs are the $1s$ orbitals. It also tells us that HHe^+ has two valence electrons since HHe would have three valence electrons, and the $+$ charge means that one of those electrons has been lost. Because it isn't clear which atom lost the electron, we may choose not to show the electrons in the AOs.

A Lewis diagram for HHe^+ is shown below and, since there are only two atoms, it must be linear.



Both $1s$ orbitals have sigma symmetry, and their energies are within 1 Ry, so they interact.

Following the remaining steps of the algorithm gives this MO energy level diagram:



The bond order of HHe^+ is $\frac{2-0}{2} = \frac{2}{2} = 1$, matching the single bond shown on the Lewis diagram.

The polarization of 1σ and $2\sigma^*$ was introduced in Exercise 3.1. 1σ is much closer in energy to $1s(He)$ than it is to $1s(H)$, and it is therefore larger on the helium atom. Since this is the only MO containing electrons, this means that the $H - He$ bond is polar and that the electrons in that bond spend more time near the He nucleus than the H nucleus. As such, He does not bear the full positive charge shown on the Lewis diagram. By pulling electron density toward itself (and away from H), some of the positive charge is shifted onto H, making both atoms partially positive.

By contrast, $2\sigma^*$ is much closer in energy to $1s(H)$ than it is to $1s(He)$, and it is therefore larger on H. Since $2\sigma^*$ is the LUMO, this polarization tells us that electrons would be donated to H (the large end of the LUMO) rather than to He. Since the LUMO is antibonding, adding electrons to it will reduce the $H - He$ bond order. Putting this together, we can see that HHe^+ would act as an acid (that is so strong that it cannot coexist with anything remotely basic):

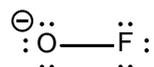


Molecular Orbital Energy Level Diagram for OF^-

First, write electron configurations for both atoms: $1s^2 2s^2 2p^4$ for O and $1s^2 2s^2 2p^5$ for F

This tells us that the valence shell for each atom is $n = 2$, and that the valence AOs are the $2s$ and $2p$ orbitals. It also tells us that OF^- has fourteen valence electrons since OF would have thirteen valence electrons, and the $-$ charge means that one more electron has been added. Because it isn't clear which atom gained the extra electron, we may choose not to show the electrons in the AOs.

A Lewis diagram for OF^- is shown below and, since there are only two atoms, it must be linear.

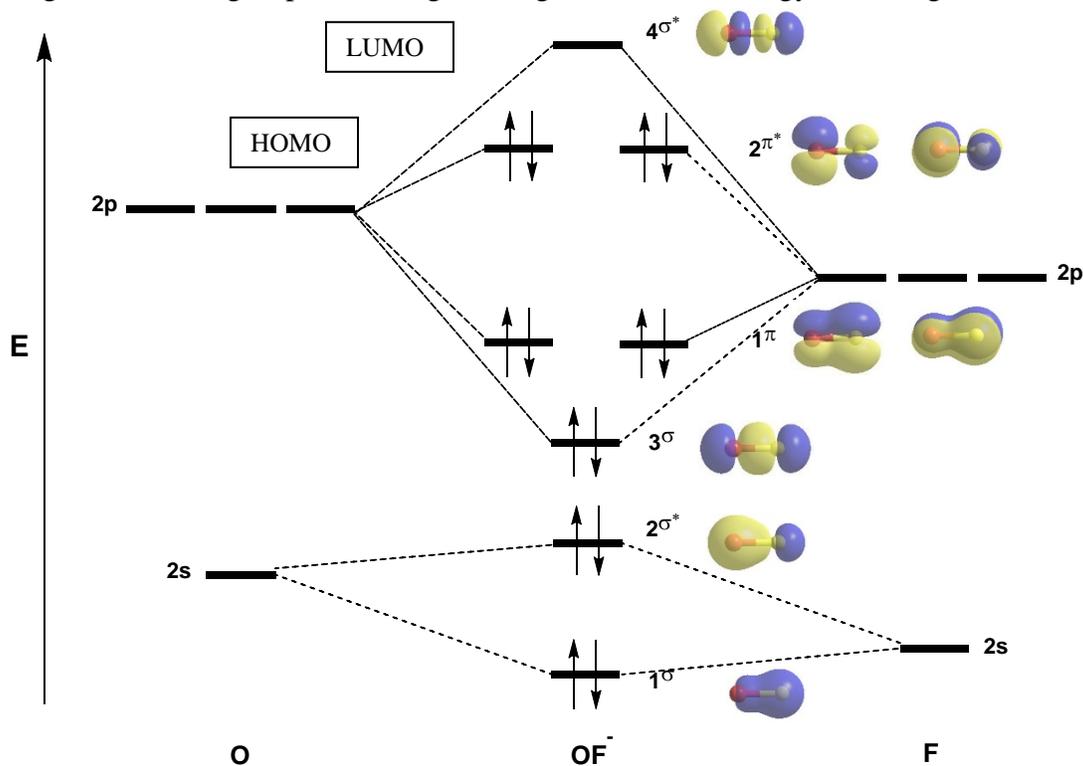


Grouping the valence AOs by symmetry and energy gives:

- two pi-symmetric $2p_x$ orbitals, one from each atom,
- two pi-symmetric $2p_y$ orbitals, one from each atom,
- two sigma-symmetric $2s$ orbitals, one from each atom, and
- two sigma-symmetric $2p_z$ orbitals, one from each atom.

Each group makes two MOs, one bonding and one antibonding.

Following the remaining steps of the algorithm gives this MO energy level diagram:



The bond order of OF^- is $\frac{8-6}{2} = \frac{2}{2} = 1$, matching the single bond shown on the Lewis diagram.

Since OF^- is an anion, it is more likely to act as an electron pair donor than an electron pair acceptor. We are therefore more likely to be interested in the HOMO than the LUMO. We can see that the $2\pi^*$ orbitals are much closer in energy to $2p(O)$ than they are to $2p(F)$, and they are therefore polarized to be larger on O. As such, if OF^- acts as an electron pair donor, it will donate electrons from O (not from F):



1.

(a) Construct a molecular orbital energy level diagram for LiH .

Include pictures of the orbitals on your diagram.

The energy of the $1s(H)$ orbital is -1.00 Ry; the energy of the $2s(Li)$ orbital is -0.40 Ry. You do not need to include the $2p(Li)$ orbitals.

(b) Calculate the bond order for LiH . Does it match the bond order from your Lewis diagram?

(c) LiH is polar. Which end of the $Li - H$ bond would you expect to be the negative end? Do your molecular orbitals support this prediction? Explain why or why not.

(d) If LiH reacted as an electron pair acceptor in a reaction, to which atom would the other species donate the electrons? Use the molecular orbitals to justify your answer. What would happen to the $Li - H$ bond order in this reaction?

2.

- (a) Construct a molecular orbital energy level diagram for OH^- .
Include pictures of the orbitals on your diagram.

The energy of the $1s(H)$ orbital is -1.00 Ry; the energy of the $2s(O)$ orbital is -2.38 Ry; the energy of the $2p(O)$ orbitals is -1.17 Ry.

- (b) Calculate the bond order for OH^- . Does it match the bond order from your Lewis diagram?

- (c) Label the HOMO and LUMO on your molecular orbital energy level diagram. Is OH^- more likely to react as an electron pair donor or acceptor? Will it react with its HOMO or its LUMO? Toward which atom is the reactive MO polarized? What does this allow us to conclude about the reactivity of OH^- ?

3.

- (a) Construct a molecular orbital energy level diagram for NO^+ .
Include pictures of the orbitals on your diagram.

The energy of the $2s(N)$ orbital is -1.88 Ry; the energy of the $2p(N)$ orbitals is -0.95 Ry; the energy of the $2s(O)$ orbital is -2.38 Ry; the energy of the $2p(O)$ orbitals is -1.17 Ry.

- (b) Label the HOMO and LUMO on your molecular orbital energy level diagram. Is NO^+ more likely to react as an electron pair donor or acceptor? Will it react with its HOMO or its LUMO? Toward which atom is the reactive MO polarized? What does this allow us to conclude about the reactivity of NO^+ ?