Homework 9 Answer Key

November 19, 2014

1 Q 12.6

The molecular electrostatic potential maps for LiH and HF are shown here. Does the apparent size of the hydrogen atom tell you whether it is an electron acceptor or an electron donor in these molecules?

Yes, it does. The electrostatic potential is displayed on a total electron charge density contour. The excess electron charge around the H atom pushes the contour out and makes the H look bigger. In HF, electrons are withdrawn from the H, so that the contour is moved toward the H nucleus, making the H look smaller.

2 Q 12.17

Justify the Born-Oppenheimer approximation based on vibrational frequencies and the timescale for electron motion.

Atoms are much more massive than electrons. Therefore, the vibrational period (inverse frequency) of a molecule is significantly longer than the relaxation time needed for the much less massive electrons to adjust to the periodic changes in the nuclear positions. For this reason, the nuclear motion can be decoupled from the electron motion.

3 P 12.5

Calculate the bond order in each of the following species. Predict which of the two species in the following pairs has the higher vibrational frequency:

a. Li_2 or Li_2^+

Li_2: $(1\sigma_g)^2(1\sigma_u^*)^2(2\sigma_g)^2$
Bond Order $= \frac{4-2}{2} = 1$

Li_2^+: $(1\sigma_g)^2(1\sigma_u)^2(2\sigma_g)^1$
Bond Order $= \frac{3-2}{2} = 0.5$

b. C_2 or C_2^+

C_2: $(1\sigma_g)^2(1\sigma_u^*)^2(2\sigma_g)^2(2\sigma_u^*)^2(1\pi_u)^4$
Bond Order $= \frac{8-4}{2} = 2$

C_2^+: $(1\sigma_g)^2(1\sigma_u^*)^2(2\sigma_g)^2(2\sigma_u^*)^2(1\pi_u)^3$
Bond Order $= \frac{7-4}{2} = 1.5$

c. O_2 or O_2^+

O_2: $(1\sigma_g)^2(1\sigma_u^*)^2(2\sigma_g)^2(2\sigma_u^*)^2(3\sigma_g)^2(1\pi_u)^2(1\pi_u)^2(1\pi_g^*)^1(1\pi_g^*)^1$
Bond Order $= \frac{10-6}{2} = 2$

O_2^+: $(1\sigma_g)^2(1\sigma_u^*)^2(2\sigma_g)^2(2\sigma_u^*)^2(3\sigma_g)^2(1\pi_u)^2(1\pi_u)^2(1\pi_g^*)^1$
Bond Order $= \frac{10-5}{2} = 2.5$

d. F_2 or F_2^-

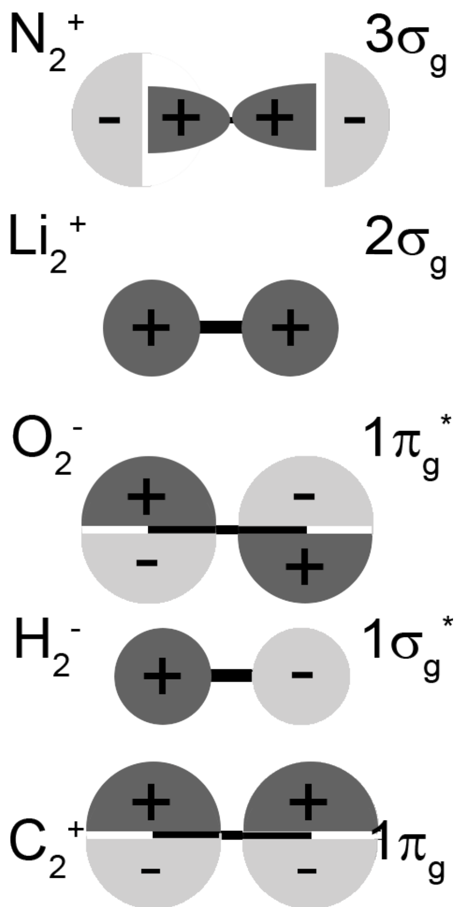
F_2: $(1\sigma_g)^2(1\sigma_u^*)^2(2\sigma_g)^2(2\sigma_u^*)^2(3\sigma_g)^2(1\pi_u)^2(1\pi_u)^2(1\pi_g^*)^2(1\pi_g^*)^2$
Bond Order $= \frac{10-8}{2} = 1$

F_2^-: $(1\sigma_g)^2(1\sigma_u^*)^2(2\sigma_g)^2(2\sigma_u^*)^2(3\sigma_g)^2(1\pi_u)^2(1\pi_u)^2(1\pi_g^*)^2(1\pi_g^*)^2(3\sigma_u^*)^1$
Bond Order $= \frac{10-9}{2} = 0.5$

The species with the higher bond order will have the higher vibrational frequency, so the answers are Li_2, C_2, O_2^+, and F_2

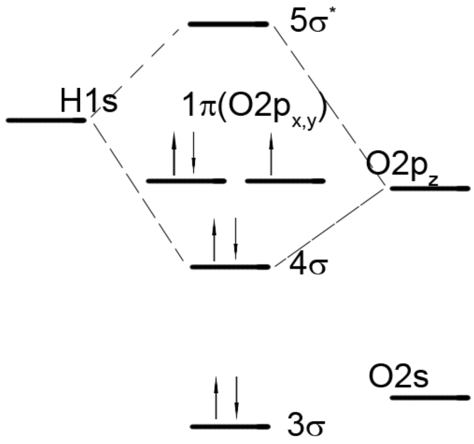
4 P 12.6

Make a sketch of the highest occupied molecular orbital (HOMO) for the following species:



5 P 12.19

Sketch the molecular orbital energy diagram for the radical OH based on what you know about the corresponding diagram for HF. How will the diagrams differ? Characterize the Homo and LUMO as antibonding, bonding, or nonbonding.



The diagrams differ in the relative energies of the AOs involved and in that there are nonbonding valence electrons on the OH radical, whereas there are none on HF. The HOMO is the 1 π, which is a nonbonding MO. The LUMO is the $5\pi^*$, which is an antibonding MO.