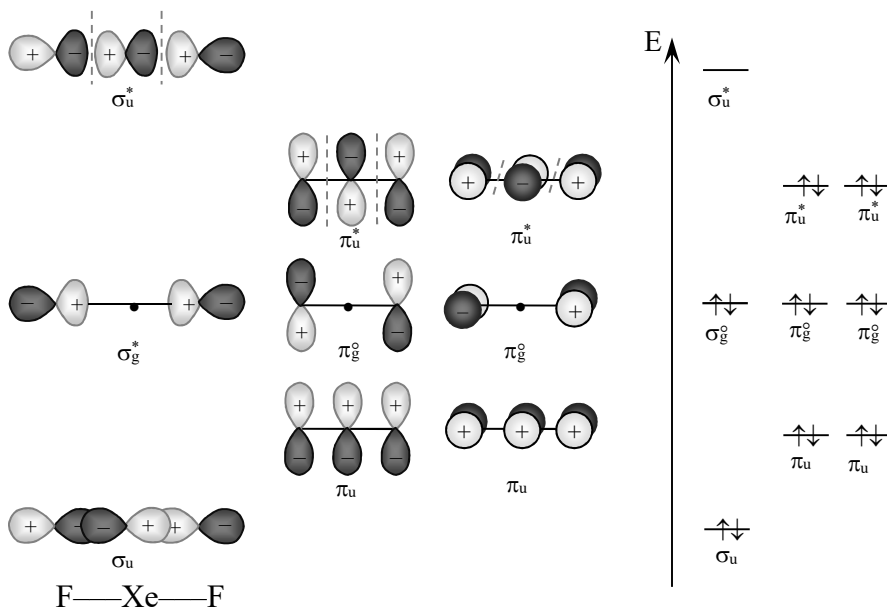


CH 342 Handin Homework 8

1. Sketch the qualitative molecular orbital diagram for XeF_2 . The molecule is linear and symmetric. Assume the valence 5s-orbitals of Xe are sufficiently lower in energy than the valence 5p-orbitals that the valence 5s-orbital of Xe and the 2s-orbitals of the F-atoms form an inner core set. In other words, combine just valence p-orbitals to give the MO diagram. Use the same reasoning that we used for linear BeH_2 and CO_2 . Characterize the molecular orbitals as σ or π , g or u. Characterize the molecular orbitals as overall bonding, non-bonding, or anti-bonding. Determine the electron filling and calculate the overall bond order. Characterize the bond order of each separate Xe–F bond. Halogens rarely form double bonds, especially as the atom radius increases. Does your MO diagram agree with this expectation? Determine the primary MOs that determine the bond order. Compare the general features of your MO diagram to the MO diagram for $[\text{F}–\text{H}–\text{F}]^-$, Figure 26.9.1; explain the stability of XeF_2 in terms of the pattern of MO formation. For example, compare the number of filled and empty bonding, non-bonding, and anti-bonding orbitals and the resulting bond orders between XeF_2 and $[\text{F}–\text{H}–\text{F}]^-$.

Answer: The plan is to combine the $5p_x$, $5p_y$, and $5p_z$ -orbitals on Xe and the $2p_x$, $2p_y$, and $2p_z$ -orbitals on both F-atoms to give 12 molecular orbitals that follow the symmetry of the molecule; that is, have the same character, bonding or anti-bonding, on either side of the central Xe-atom.

The XeF_2 is an electron excess molecule. You can think of the molecule as the complex between Xe and F_2 , both of which are closed shell. The s-orbitals on each atom give a completely filled, low energy, net non-bonding set of molecular orbitals: a bonding, non-bonding, and anti-bonding set: $\circ\circ\circ$, $\circ-\bullet$, and $\circ\bullet\circ$. As a consequence the s-orbitals do not contribute to the bonding and we omit these MOs from the diagram. Counting only p-electrons gives $6 + 2(5) = 16$ electrons. We align the nuclei along the x-axis. The p_x -orbitals on each atom give a σ -set of molecular orbitals: a bonding, non-bonding, and anti-bonding set: $\bullet\bullet\bullet\circ\bullet\bullet$, $\bullet\circ-\bullet\circ$, and $\bullet\bullet\bullet\circ\bullet\bullet$. The most bonding π_u -orbital results from the constructive all-in-phase overlap of the p_z -orbitals, $\bullet\bullet\bullet\bullet$. The most anti-bonding π_u^* -orbital results from alternating phases for the p_z orbitals, $\bullet\bullet\bullet\bullet$.



Flipping the phase of the outer orbital gives a π_g^o non-bonding orbital along the z-axis. The p_y -orbitals overlap to give a corresponding π bonding, non-bonding, and anti-bonding set, which is perpendicular to the p_z -set. The eight pairs of electrons fill through the π -anti-bonding orbitals.

The overall bond order is $(6 - 4)/2 = 1$. The bond order of each separate Xe-F bond is $1/2$. However, the net π -bond order is zero. There are as many π -bonding as π -anti-bonding electrons. XeF_2 follows the expectation that halogens don't π -bond. The reason is that since the halogens are in group seven, the seven valence electrons are usually sufficient to fill the π -bonding and π -anti-bonding orbitals, giving a net π -bond order of zero. The primary MOs that determine the bond order are the σ -orbitals, just as in $[\text{F-H-F}]^-$, Figure 26.9.1. The stability of XeF_2 is determined by the ability to put electrons in a non-bonding σ -orbital, which while not adding to the stability does not detract from the stability.

Note that we could have simply used Figure 26.6.9, but building the molecular orbitals from scratch using only p-orbitals is instructive. The σ_g^o in this model will not end up being degenerate with the π_g^o non-bonding orbitals in careful calculations. However, because of the low energy of the 5s-orbital compared to the 5p-orbital for Xe-atoms, the σ_g^o orbital will remain rather non-bonding in character, instead of the predominately anti-bonding character of $5\sigma_g^*$ in carbon dioxide or linear ozone.

2. Introduction: The HOMO for CH_4 at the HF/3-21G level from Spartan is given below:

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MO:                5
Eigenvalues: -0.54482
(ev)          -14.82540
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T2
 1 H1  S   0.15923
 2 H1  S'  0.14905
 3 C1  S1  0.00000
 4 C1  S   0.00000
 5 C1  PX  0.00000
 6 C1  PY  0.37446
 7 C1  PZ  0.00000
 8 C1  S'  0.00000
 9 C1  PX' 0.00000
10 C1  PY' 0.31001
11 C1  PZ' 0.00000
12 H2  S  -0.15923
13 H2  S' -0.14905
14 H3  S   0.15923
15 H3  S'  0.14905
16 H4  S  -0.15923
17 H4  S' -0.14905
```

The HOMO is MO 5 since there are 10 total electrons with two electrons per MO. MO 5 is one of a triply degenerate set that describe the C-H bonds. At the HF/3-21G level there are no polarization functions on either C or H. Since the Gaussian orbitals are at the 3-21G level, the valence shells are split into an inner and outer part:

$$\Psi_{\text{MO5}} = 0.1592 \Psi_{\text{H1,1s}}(\text{inner}) + 0.1490 \Psi_{\text{H1,1s}}(\text{outer}) + 0.3745 \Psi_{\text{C,2py}}(\text{inner}) + 0.3100 \Psi_{\text{C,2py}}(\text{outer}) - 0.1592 \Psi_{\text{H2,1s}}(\text{inner}) - 0.1490 \Psi_{\text{H2,1s}}(\text{outer}) + 0.1592 \Psi_{\text{H3,1s}}(\text{inner}) + 0.1490 \Psi_{\text{H3,1s}}(\text{outer}) - 0.1592 \Psi_{\text{H4,1s}}(\text{inner}) - 0.1490 \Psi_{\text{H4,1s}}(\text{outer})$$

Question: Write the HOMO of methanol at the HF/3-21G level in a similar fashion. Compare between methane and methanol the relative importance of the inner and outer portions of the split valence-shell orbitals on carbon. Do a geometry optimization and determine the MOs.

Answer: With 18 total electrons the HOMO is orbital 9:

```

MO:                9
Eigenvalues: -0.43452
(ev)          -11.82399
  A''
  1 C1  S1   0.00000
  2 C1   S   0.00000
  3 C1  PX   0.00000
  4 C1  PY   0.00000
  5 C1  PZ  -0.19378
  6 C1  S'   0.00000
  7 C1  PX'  0.00000
  8 C1  PY'  0.00000
  9 C1  PZ' -0.07308
10 H2   S    0.15280
11 H2  S'    0.20098
12 H3   S   -0.15280
13 H3  S'   -0.20098
14 H4   S    0.00000
15 H4  S'    0.00000
16 O1  S1    0.00000
17 O1   S    0.00000
18 O1  PX    0.00000
19 O1  PY    0.00000
20 O1  PZ    0.45907
21 O1  S'    0.00000
22 O1  PX'   0.00000
23 O1  PY'   0.00000
24 O1  PZ'   0.56440
25 H1   S    0.00000
26 H1  S'    0.00000

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The ratio of the outer to inner portions of the $2p_y(\text{C})$ in methane is: $0.3100/0.3745 = 0.828$

The ratio of the outer to inner portions of the $2p_z(\text{C})$ in methanol is: $0.0731/0.1938 = 0.377$

In other words, the bonding environment of the C-atom has a big effect on the shape of the $2p(\text{C})$ orbital. The inner portion of the orbital is more important methanol as compared to methane. STO type orbitals do not have this flexibility.

$$\Psi_{\text{MO9}} = 0.1938 \Psi_{\text{C},2p_y(\text{inner})} + 0.0731 \Psi_{\text{C},2p_y(\text{outer})} + 0.1528 \Psi_{\text{H}_2,1s(\text{inner})} + 0.2010 \Psi_{\text{H}_2,1s(\text{outer})} \\ - 0.1528 \Psi_{\text{H}_3,1s(\text{inner})} - 0.2010 \Psi_{\text{H}_3,1s(\text{outer})} + 0.4591 \Psi_{\text{O}_1,2p_z(\text{inner})} + 0.5644 \Psi_{\text{O}_1,2p_z(\text{outer})}$$