CHEM-457 (S14)
Problem Set 3

1. Prepare a molecular orbital energy diagram for the cyanide ion (CN^-). Please be sure to label all atomic orbitals and molecular orbitals. Provide sketches to show how atomic orbitals interact to form MOs.

    a. Based on the MO diagram you prepared, what is the bond order of CN^-? What is the multiplicity of CN^-?

    b. Which molecular orbital of cyanide would you predict to interact most strongly with a proton in the acid-base reaction $CN^- + H^+ \rightarrow HCN$? Please explain your answer.

2. Build a molecular orbital diagram for the heterodiatomic ion $[Kr–Br]^+$ based on the valence shell *s* and *p* orbitals of each atom. Please be sure to label all atomic orbitals and molecular orbitals. Provide sketches to show how atomic orbitals interact to form MOs.

    a. Toward which atom would the HOMO be polarized? Please explain your answer

    b. Please predict the bond order of this molecule.

3. The first ionization energies of BF, CO and N_2 are 11.06 eV, 14.01 eV and 15.57 eV, respectively. Build MO diagrams for each of these diatoms and explain the increase in ionization energy for this isoelectronic series on the basis of atomic-orbital composition of the highest occupied molecular orbital.

4. Using the group theoretical approach we have developed in class, build MO diagrams for the CH_3^+ in D_{3h} symmetry (planar) and C_{3v} symmetry (pyramidal). Based on these two MO diagrams, which geometry would you expect to be preferred for CH_3^+? Please be sure to label all atomic orbitals and molecular orbitals. Provide sketches to show how atomic orbitals interact to form MOs.

5. Using the group theoretical approach we developed in lecture, build a MO diagram for ozone (O_3). Note: ozone belongs to the C_{2v} point group. Please be sure to label all atomic orbitals and molecular orbitals. Provide sketches to show how atomic orbitals interact to form MOs.

6. Consider the molecule silane (SiH_4).

   a. Using the group theoretical approach we developed in class, determine the MO diagram for this molecule in square planar geometry (D_{4h}).

   b. Using the group theoretical approach we developed in class, determine the MO diagram for this molecule in tetrahedral geometry (T_d).

   c. Based on the D_{4h} and T_d MO diagrams, which geometry of SiH4 is expected to be most stable?