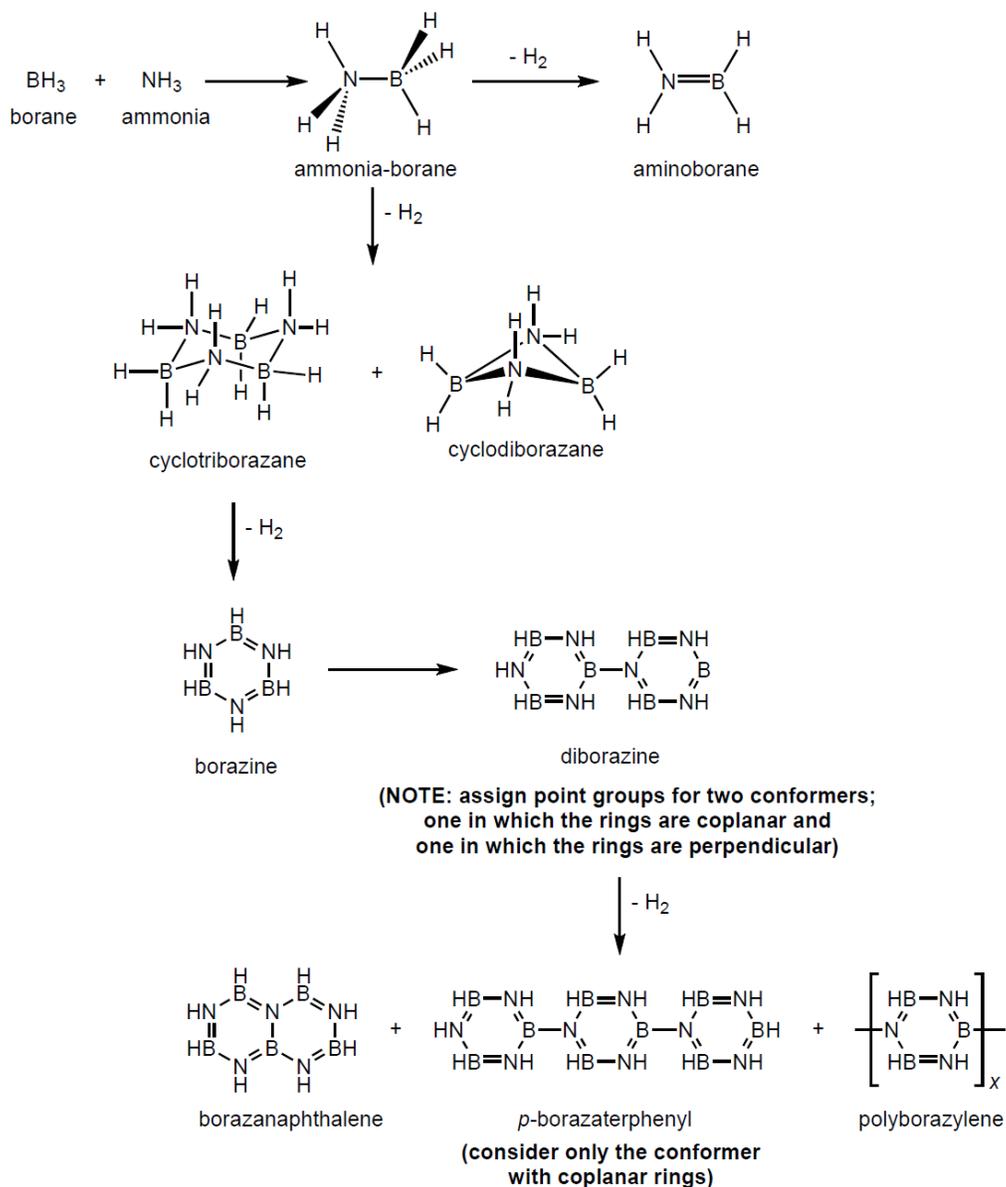**Recommended Reading:** 5.1 – 5.7, **15.2-15.11** (3rd/4th edition)

2015/2016 Ch 102 – Problem Set 3
**Due: Thursday, April 21 –** *Before Class*

Problem 1 (2 points)

a)   On-board storage of hydrogen is a major obstacle for the use of hydrogen as a clean-burning transportation fuel. Ammonia-borane is an appealing candidate for chemical hydrogen-storage applications. Amine-borane adducts can be readily synthesized from free amines and boranes. Thermal decomposition of ammonia-borane adducts yields hydrogen and a mixture of aminoborane and borazine products. Draw two resonance structures for aminoborane; given these structures, discuss the propensity to make oligomers.

cyclotriborazane   cyclodiborazane

borazine   diborazine

(NOTE: assign point groups for two conformers;
one in which the rings are coplanar and
one in which the rings are perpendicular)

borazanaphthalene   *p*-borazaterphenyl   polyborazylene

(consider only the conformer
with coplanar rings)

b)   Give the point group for cyclotriborazane, cyclodiborazane, diborazine, and *p*-borazaterphenyl (see notes under drawings). For polyborazylene, determine the 1-D space symmetry class (assume planar geometry); highlight unit cell and asymmetric unit. Also, determine the 2-D space group of the fully dehydrogenated $(BN)_x$ product (assume a graphene-like structure); highlight unit cell and asymmetric unit.

c) Using the equation below, calculate the hydrogen capacity (wt%) of ammonia-borane. Be sure to show how you arrived at your answer for full credit.

$$X \ H_3B{-}NH_3 \xrightarrow{\text{[cat]}} 3X \ H_2 + (BN)_X$$
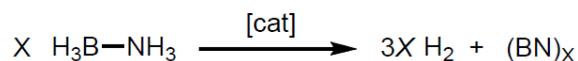
d) An alternative material for hydrogen storage is based on microporous metal-organic frameworks (MOFs). Metal-organic frameworks consist of metal ions or clusters connected through organic bridging ligands into extended one-, two-, or three-dimensional networks. The high surface area and porous nature of these new materials make them particularly promising candidates for high capacity (wt%) hydrogen storage materials. The crystal structures shown below are portions of metal organic frameworks that have been used for hydrogen storage. Assign point groups to each of the crystal structures as shown below and identify the number of different kinds of Mn atoms for each structure.
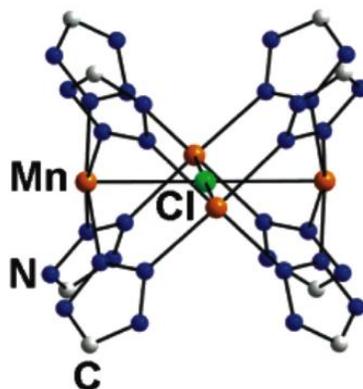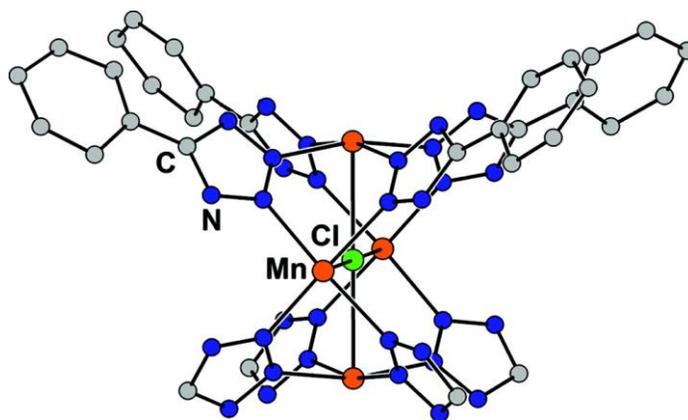
Problem 2 (2 points)

Part 1
Cyanate and fulminate are two anions with the same general formula $[CNO]^-$. There are three possible linear arrangements of these three atoms.

a) Draw the Lewis dot structure, complete with formal charges and any relevant resonance structures, for the anion with the arrangement $[CNO]^-$, and rank the resonance structures in order of importance.
b) Repeat part a) for the anion with the arrangement $[CON]^-$.
c) Repeat part a) for the anion with the arrangement $[OCN]^-$.
d) Salts of cyanate are stable and commercially available (e.g. potassium cyanate). Fulminate salts are known but they are unstable and therefore explosive. Salts of the third arrangement of atoms are unknown. Based on the Lewis structure you drew in parts a) – c), which do you think is which? Explain.
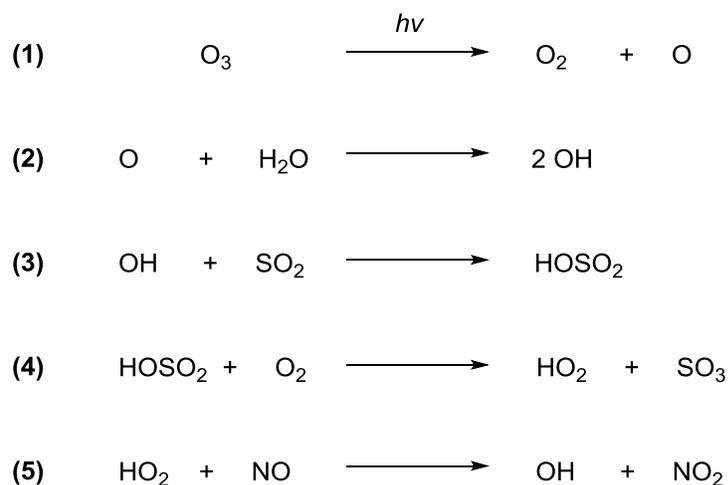
Part 2
For the following molecular formulas, draw appropriate Lewis dot structures (provide up to three most relevant resonance structures of molecules with delocalization, give a short explanation on which one is the best), use VSEPR theory to predict the molecular geometry (label expected values of bond angles based on this analysis, i.e. 180 °, ≤ 120 °, etc.), and provide the point group of the resulting molecule (draw it in a reasonable conformation and assume delocalization where appropriate).

a) $S_2O_4{}^{2-}$
b) $O_3SSO_2{}^{2-}$
c) O_3SNONO^{2-} (all oxygens terminal, one bridging nitrogen)
d) $N_5{}^+$ (single chain)

Problem 3 (2 points)

The octet rule predicts stable molecular species when atoms experience filled valence shells with paired electrons. Although compounds with unpaired electrons can be unstable, such radical species are involved in important processes. The hydroxyl radical ($\cdot$OH) plays a significant role in many atmospheric chemical reactions. One such process is the conversion of SO_2, which can be generated from anthropogenic activities such as the combustion of fossil fuels or natural sources such as volcanic plumes, to SO_3 and ultimately to H_2SO_4, contributing to acid rain. Shown below are a series of reactions involving the generation of hydroxyl radical and its catalytic role in the conversion of SO_2 to SO_3.

$$\text{(1)} \qquad O_3 \quad \xrightarrow{h\nu} \quad O_2 \quad + \quad O$$

$$\text{(2)} \qquad O \quad + \quad H_2O \quad \longrightarrow \quad 2\ OH$$

$$\text{(3)} \qquad OH \quad + \quad SO_2 \quad \longrightarrow \quad HOSO_2$$

$$\text{(4)} \qquad HOSO_2 \ + \quad O_2 \quad \longrightarrow \quad HO_2 \quad + \quad SO_3$$

$$\text{(5)} \qquad HO_2 \quad + \quad NO \quad \longrightarrow \quad OH \quad + \quad NO_2$$

a) For reactions **1-5**, draw correct Lewis dot structures for each compound, assigning formal charges and appropriate oxidation states for each atom. For SO_2, $HOSO_2$, and SO_3, draw at least one resonance structure displaying hypervalency and one in which hypervalency is avoided. *Note: reactions 1-5 are all balanced, conserving atoms and electrons.*

b) For each species, use VSEPR to predict the structure and assign bond angles (i.e. $>120°$); assign a point group for that molecule based on the prediction.

c) Determine which reagent in **1-5** is acting as an oxidant, as a reductant, or whether the reaction does not involve a redox process.

Problem 4 (2 points)

Part A
The bonding in LiF and HF were discussed in class. For this problem also consider HCl. Electronic structure calculations were performed with Gaussian, and the molecular orbitals of interest are depicted on page 5 vertically for the three species. Based on the atomic orbital contributions to the molecular orbitals, assign by visual inspection each MO diagram to LiF, HF, or HCl. (Hint: take into consideration the energies of the atomic orbitals involved) Clearly label which side corresponds to which atom (i.e. what are the identities of A and B for each case?). Briefly explain your assignments. For each horizontal set of three MOs also assign the axial symmetry using the A-B bond as the axis.

Part B
The first ionization energies of BF and N_2 are 11.06 eV and 15.57 eV respectively.

a) Draw a molecular orbital diagram for each molecule using the concept of axial symmetry (take into account the energy of the valence atomic orbitals). Fill in the appropriate number of electrons and identify the symmetry of each orbital (σ or π) and label it as bonding, nonbonding (nb) or antibonding (*).
b) Label the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO).

c) Explain the difference in ionization energy for these isoelectronic species based on the atomic orbital character of the highest occupied molecular orbital.

d) Images of several molecular orbitals of BF and N_2, calculated with Gaussian, are depicted on page 6. Based on the atomic orbital contributions to the molecular orbitals, assign by visual inspection each MO diagram to BF or N_2. What are the identities of A and B for each case? Explain.

e) Based on the MO diagrams and atomic orbital contributions, which species do you expect to bind better to BH_3? Which one would you expect to have a stronger interaction with a molecule displaying a filled orbital of π symmetry of appropriate energy.

Note: Gaussian output files for these calculations are available on the course website. Visualization using the software is encouraged for this problem.

For Problem 4, Part A:

i) **A— B**

ii) **A— B**

iii) **A— B**

LUMO*

HOMO*
(degenerate set of two molecular orbitals)
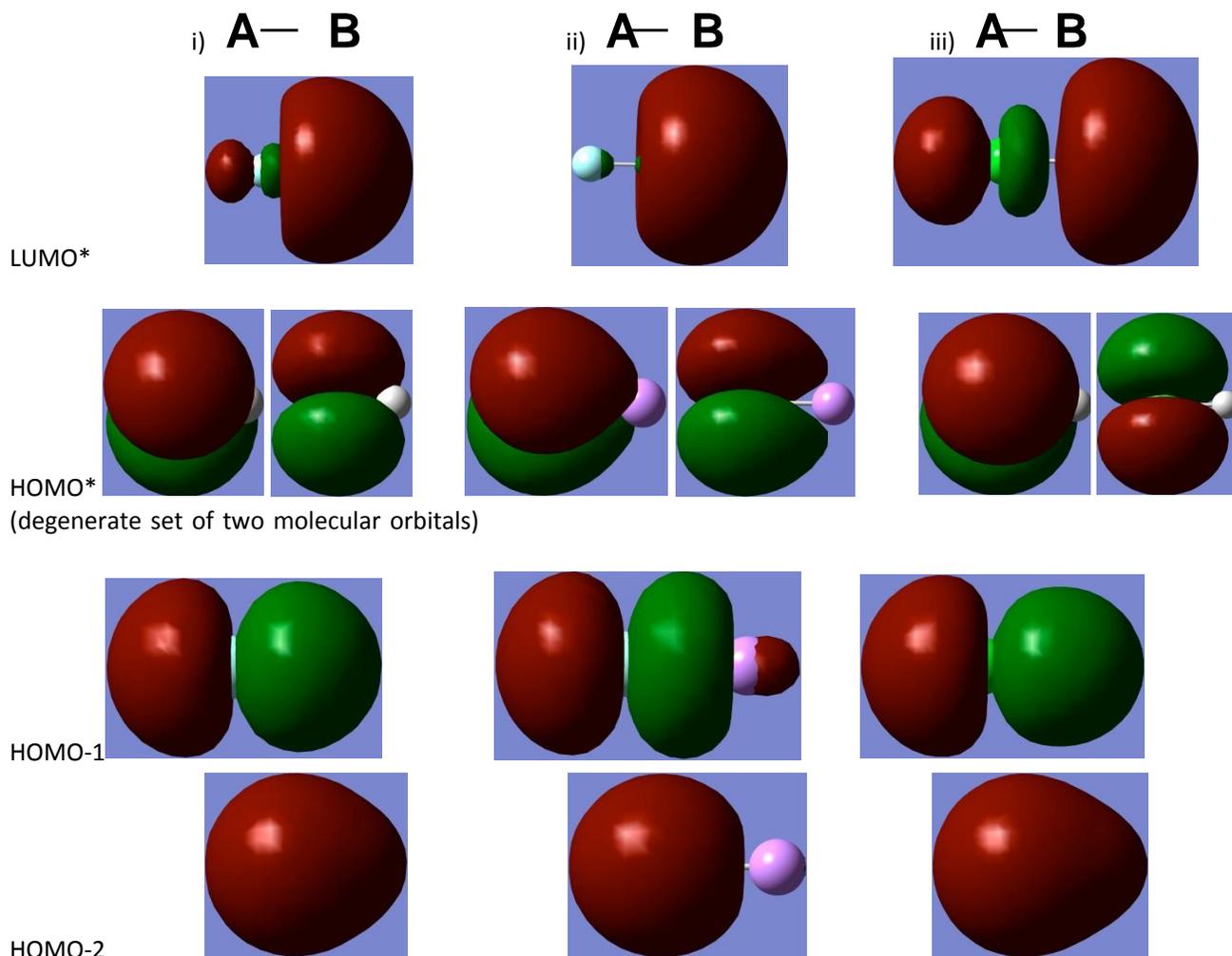
HOMO-1

HOMO-2

*LOMO = lowest unoccupied molecular orbital

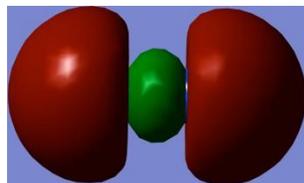*HOMO = highest occupied molecular orbital

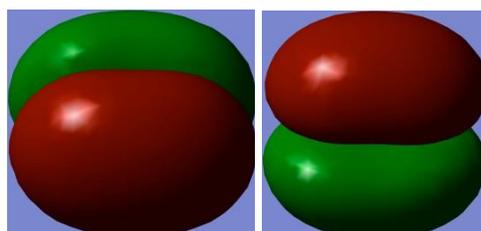For Problem 4, Part B:

i) **A— B**
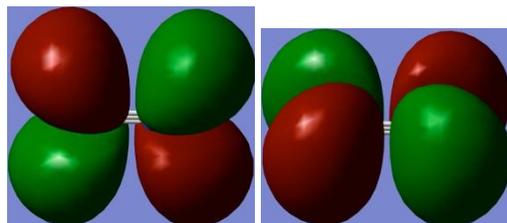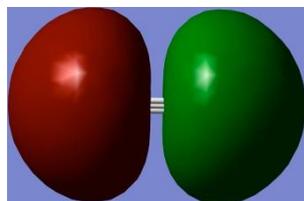
ii) **A— B**

LUMO
(degenerate set of two molecular orbitals)

HOMO

HOMO-1
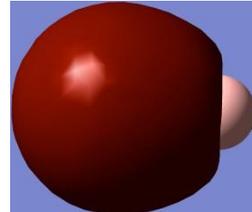(degenerate set of two molecular orbitals)
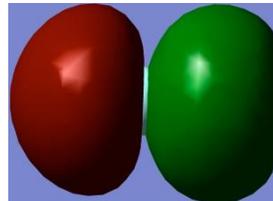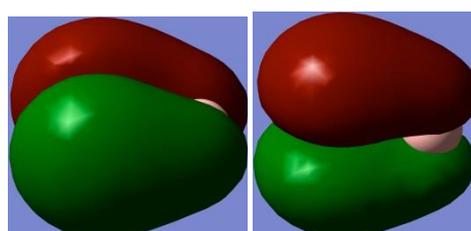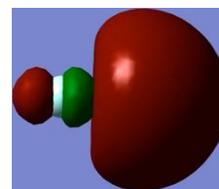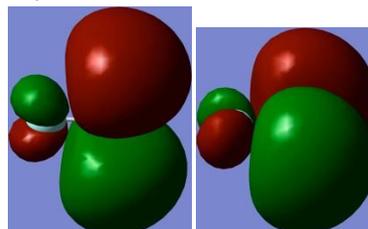
HOMO-2

HOMO-3

Problem 5 (2 points)

Pick a topic of interest from the recommended reading in bold. Prepare two power point slides including relevant descriptive chemistry (background on synthesis, applications, reactivity, properties, trend, etc, as applicable), some concepts presented in class (oxidation states, Lewis dot structures, symmetry, etc) and some application of the provided software (for example, highlight symmetry elements / operations). Turn in a printout of the slides with your problem set, and email the TAs the slides in pdf format by 12:00 noon on the due date.