Exam II, Chemistry 4610/5560, Fall 2002

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Student name: ______________________________

(1) Construct molecular orbital schemes to describe the bonding in the following diatomic species. Fill the electrons in the appropriate molecular orbitals and label the HOMO and LUMO.

(24 points)

a) B_2

c) NO

b) LiF

d) $[Co^{2+}]_2$

(2) For each of the molecules in Question 1, determine the following: (8 points)

a) bond order

B_2 :

LiF :

NO :

$[Co^{2+}]_2$:

b) spin multiplicity

B_2 :

LiF :

NO :

$[Co^{2+}]_2$:

(3) For each of the following pairs of atomic orbitals:

i. Determine whether a bonding molecular orbital may form as a result of their interaction.

ii. If so, sketch the orientation of the atomic orbital on each atom which will lead to the formation of the <u>bonding</u> molecular orbital (*<u>not</u> the antibonding orbital*). Use a suitable axis system in your drawing (always assume that the bonding axis is the *z*-axis).

iii. Identify whether the resulting bonding is a ? , ?, or ? orbital.

(12 points)

a) p_z, p_z

c) 1*s*, 5p_z

b) d_{xz}, p_x

d) d_{xy}, d_{xy}

(4) Construct a reasonable molecular orbital scheme to describe the bonding in a water, H_2O, molecule. Fill the electrons in the molecular orbitals and explain how does your diagram agree with the Lewis dot structure of water. (18 points)

(5) Determine the effect of the following processes on the strength of O-H bonds in water (i.e., determine whether each process leads to strengthening, weakening, or no change in the O-H bonds).

(6 points)

a) One-electron oxidation:

b) One-electron reduction:

c) Light absorption to form the lowest-energy exciton:

(6) Arrange the following and give a brief explanation:

(20 points)

a) Relative basicity among NH_3, PH_3, and SbH_3:

b) Relative acidity among aqueous solutions of Fe^{3+}, Cr^{2+}, and Sc^{+}:

c) Relative acidity among SnH_4, SbH_3, and TeH_2:

d) Relative solubility among LiCl, LiBr, and LiF:

e) Even though polynuclear aromatic compounds like naphthalene and pyrene are not known as bases, they do form an acid-base adducts with the trinuclear mercury compound $[Hg(C_6F_4)]_3$.

(7) Using the table attached in the next page: (12 points)
a) Explain the basicity order of NH_3, CH_3NH_2, $(CH_3)_2NH$, and $(CH_3)_3N$ in the gas phase.

b) Why does the order change in aqueous solutions of the same compounds?

c) Why does the order change when the same compounds act as Lewis bases with the Lewis acid $B(t\text{-}Bu)_3$?

Bonus question: AlF_3 becomes soluble in liquid HF if NaF is present. When BF_3 is added to the solution, AlF_3 precipitates. Explain by (a) writing the two chemical equations responsible for these observations, and (b) explaining why these equations occur in the forward instead of the reverse direction.

(6 points)