

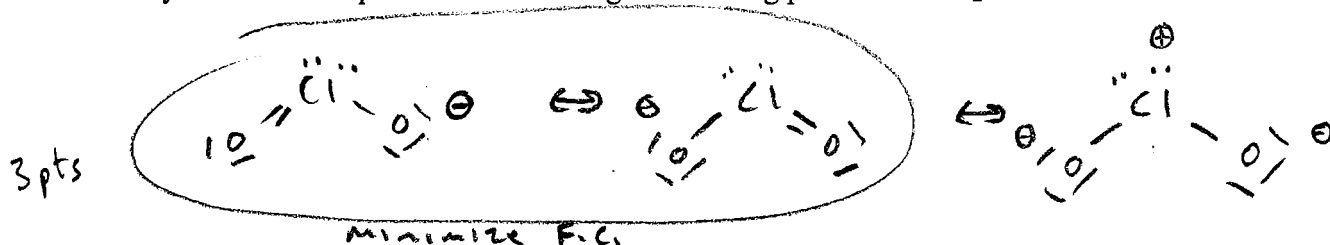
KEY

PART A. (30 points) BASIC QUESTIONS. Answer all THREE of the following questions. SHOW ALL YOUR WORK TO RECEIVE FULL CREDIT

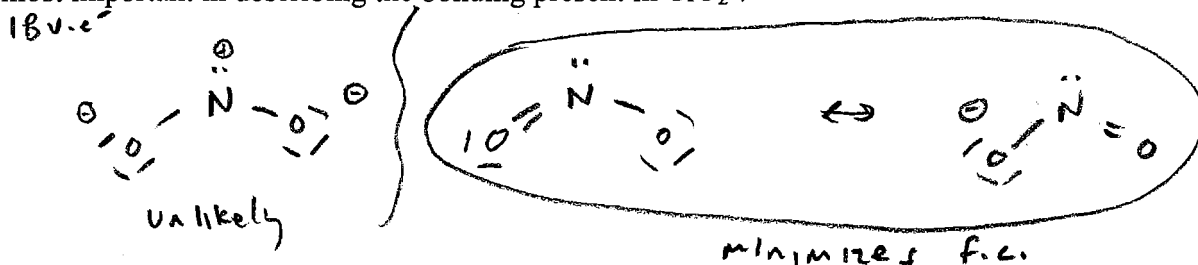
1. Consider the anions ClO_2^- and NO_2^- .

20ve

- a) Write out the Lewis structure of the anion ClO_2^- showing *all* resonance forms. Based on formal charge analysis, *circle* the resonance structure(s) that you expect is likely to be most important in describing the bonding present in ClO_2^- .



- b) Write out the Lewis structure of the anion NO_2^- showing *all* resonance forms. Based on formal charge analysis, *circle* the resonance structure(s) that you expect is likely to be most important in describing the bonding present in ClO_2^- .



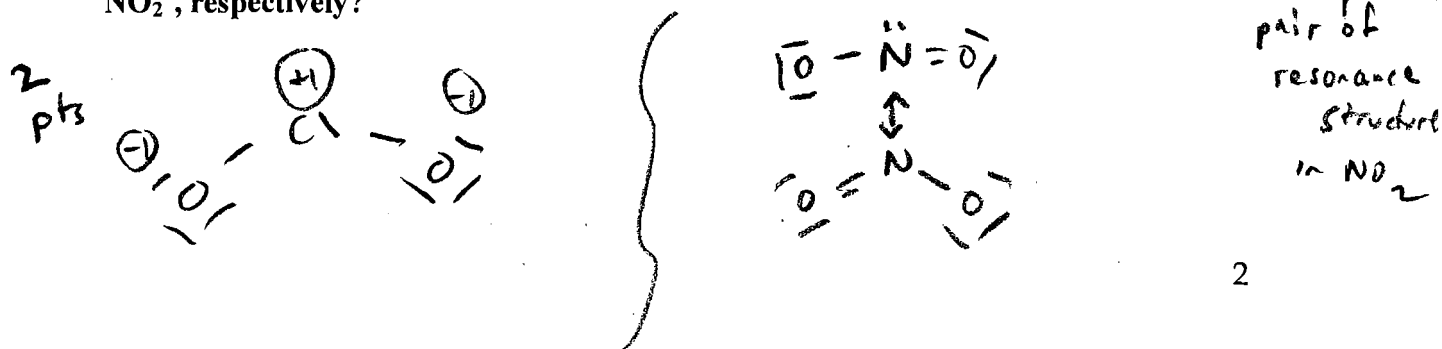
- c) Interestingly, WEBMO calculations show that the partial charge of Cl in ClO_2^- is actually +1, while that of each of oxygen atom is -1. In contrast, WEBMO calculations show that the partial charge of N in NO_2^- is +0.33, while that of each of oxygen atom is -0.66. Explain why the partial charge of Cl in ClO_2^- is likely greater than that of N in NO_2^- .

5 pts

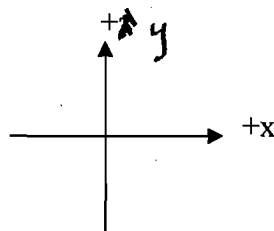
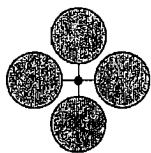
Although F.C. is minimized w/ multiple bonds between Cl-O (as shown in 1a) making the circled structures seem most likely, the ability of Cl to form π bonds (as compared to N in the analogous structure NO_2 shown in b) is unlikely due to its large size.

The "unique" ability of N to form multiple bonds makes $\text{O}=\ddot{\text{N}}=\text{O} \leftrightarrow$

- d) Based on your answer from part c), which resonance structure(s) do you now think is actually the most important in describing the bonding present in ClO_2^- and in NO_2^- , respectively?

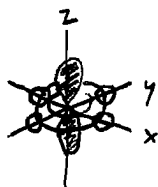


2. Consider the SALC shown below.



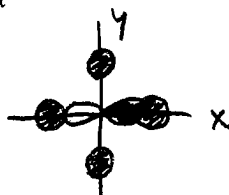
By drawing pictures, determine if the following atomic orbitals of an unidentified central atom have the correct symmetry to interact with (constructively or destructively) this SALC. If a particular orbital does not have the correct symmetry, write "non-bonding." (NB)

a) d_{z^2}



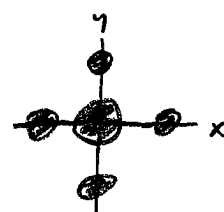
has correct symmetry

b) p_x



NB

c) s



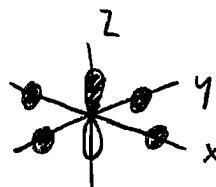
has correct symmetry

d) d_{yz}



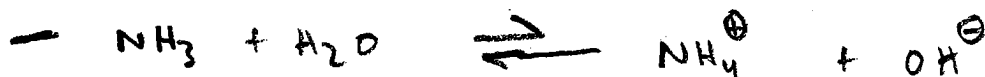
NB

e) p_z



NB

3. a) Solvents can change the acid-base behavior of solutes. Compare the acid-base properties of dimethylamine in water, acetic acid, and 2-butanone. Provide a complete, yet concise, explanation of how the solvent impacts the acid-base strength of this amine, showing acid-base equilibria, as appropriate.



— in acidic solvent...



on acid/base properties

— no effect in butanone (no solvent

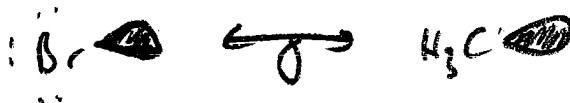
levelling)

weak base
(inside the H_2O window)

strong base
(complete dissociation)
(outside the H_2O window)

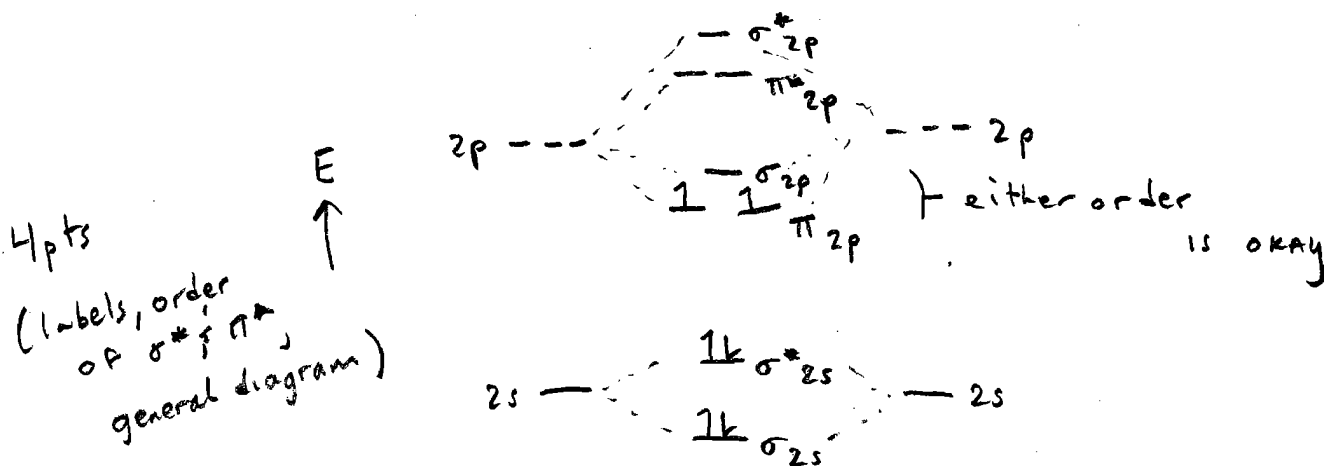
b) Provide an example of a molecular fragment that would be isolobal with a methyl group of dimethyl amine.

2 pts



Part B. (30 points) COMPETENCY QUESTIONS. Answer TWO of the following three questions in the space provided. SHOW YOUR WORK AND WRITE EXPLANATIONS IN COMPLETE SENTENCES, AS APPROPRIATE.

4. a) **Construct a molecular orbital diagram for a 2nd row diatomic molecule.** Include the valence orbitals only. Be sure to label each molecular orbital with its bond type, the atomic orbitals it was generated from, and whether it is bonding or antibonding (e.g. σ_{2s} , π_{2p}^*). Either ordering of the π_{2p} and σ_{2p} MOs is acceptable.



- b) **The molecule B₂ is only found in the gas phase.** Fill in the correct number of electrons in your diagram and calculate the bond order of B₂. Show your work.

1 pts B has 3ve \rightarrow B₂ has 6v.e.

2 pts B.O. = $\frac{1}{2} (4 - 2) = 1$

- c) **Experiments have shown that B₂ is paramagnetic.** What does this tell you about the ordering of your orbitals above? What does it tell you about the relative importance of *sp* mixing (configuration interaction) for B₂?

2 pts — π must be lower than σ to get unpaired e⁻

2 pts — mixing is important \rightarrow causes σ_{2p} to increase in E and move above π_{2p}

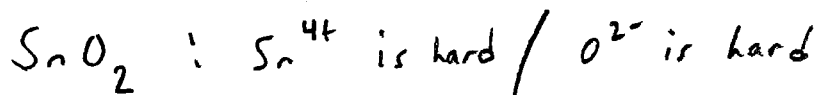
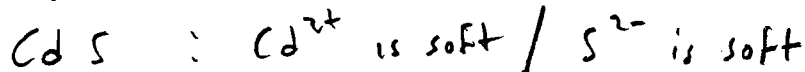
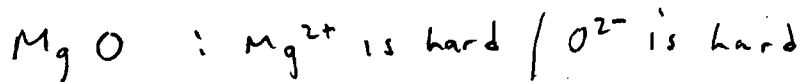
- d) **Predict which would have a shorter bond than B₂, B₂⁺, or B₂⁻? Explain.**

B.O. B₂ = 1

4 pts B.O. B₂⁺ = 0.5

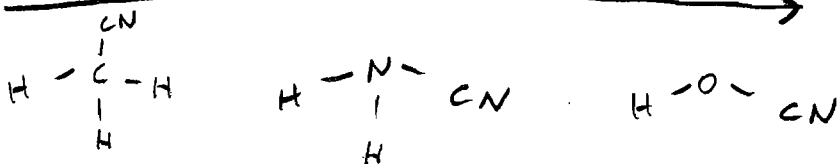
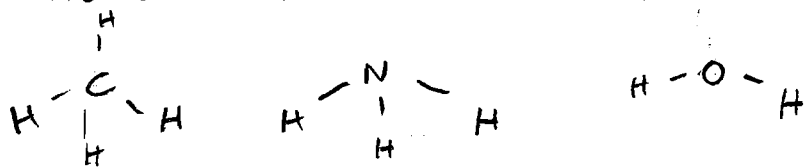
B.O. B₂⁻ = 1.5 \leftarrow shorter b/c B.O. is greater 4
(extra e⁻ goes into a bonding MO)

5. a) **Metal ions are often found in nature as oxide or sulfide ores.** For each of the three elements Mg, Cd, and Sn, predict the formula of one naturally occurring ore, and briefly explain your choice of ore composition using hard/soft acid/base theory.



- b) **The aqueous solution pK_a values of HOCN, H₂NCN, and CH₃CN are approximately 4, 10.5, and 20, respectively.** Explain the trend for these -CN derivatives of binary acids and describe how they compare with the trend observed for the corresponding H₂O, NH₃, and CH₄ parent molecules. Is -CN inductively donating or withdrawing in these examples?

- trend is the same as the parent molecules



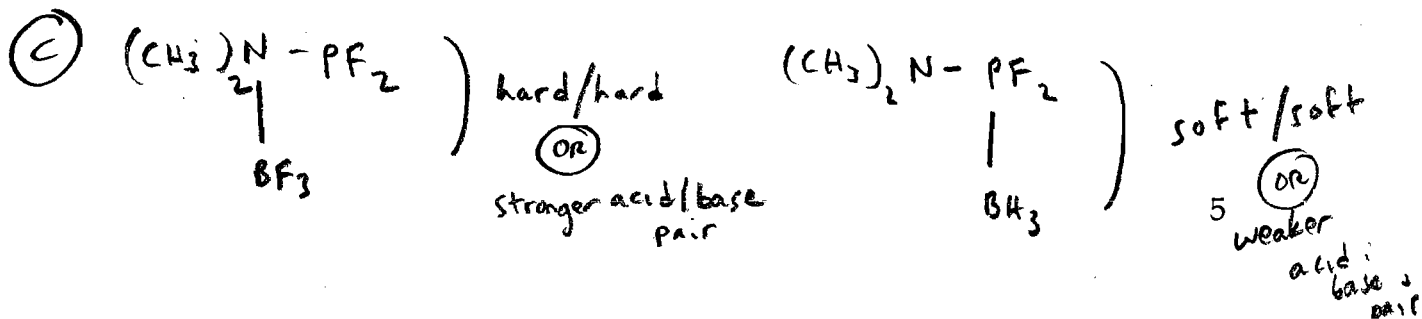
acidity increases left to right across periodic table

- since the pK_a for the derivatives are smaller than the parents

- c) **The molecule (CH₃)₂N-PF₂ has two basic atoms, P and N.** One is bound to B in a complex with BH₃; the other to B in a complex with BF₃. Decide which is bound to which and explain how you determined your choice.

the -CN compounds are stronger acids (i.e. higher K_a°) for loss of H⁺

→ ∞ - CN must be electron withdrawing

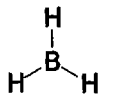


pta : 6pts
 ptb : 10pts
 ptc : 4pts

Part C. (20 points) MASTERY QUESTION. Answer the following question in the space provided. SHOW ALL YOUR WORK TO RECEIVE FULL CREDIT.

7. Develop a molecular orbital diagram for the trigonal planar molecule BH₃.

	D _{3h}	E	2C ₃	3C ₂	σ _h	2S ₃	3σ _v		
	A ₁ '	+1	+1	+1	+1	+1	+1		x ² +y ² , z ²
	A ₂ '	+1	+1	-1	+1	+1	-1	R _z	
	E'	+2	-1	0	+2	-1	0	(x,y)	(x ² -y ² , xy)
	A ₁ "	+1	+1	+1	-1	-1	-1		
	A ₂ "	+1	+1	-1	-1	-1	+1	z	
	E"	+2	-1	0	-2	+1	0	(R _x , R _y)	(xz, yz)



6 v.e.

a) Using the group theoretical approach to bonding, find the irreducible representations of the symmetry adapted linear combinations (SALCs) of H orbitals that will form sigma bonds with the orbitals of Br.

	D _{3h}	E	2C ₃	3C ₂	σ _h	2S ₃	3σ _v
Γ _{unmoved} = Γ _S		3	0	1	3	0	1

1pt

3pts

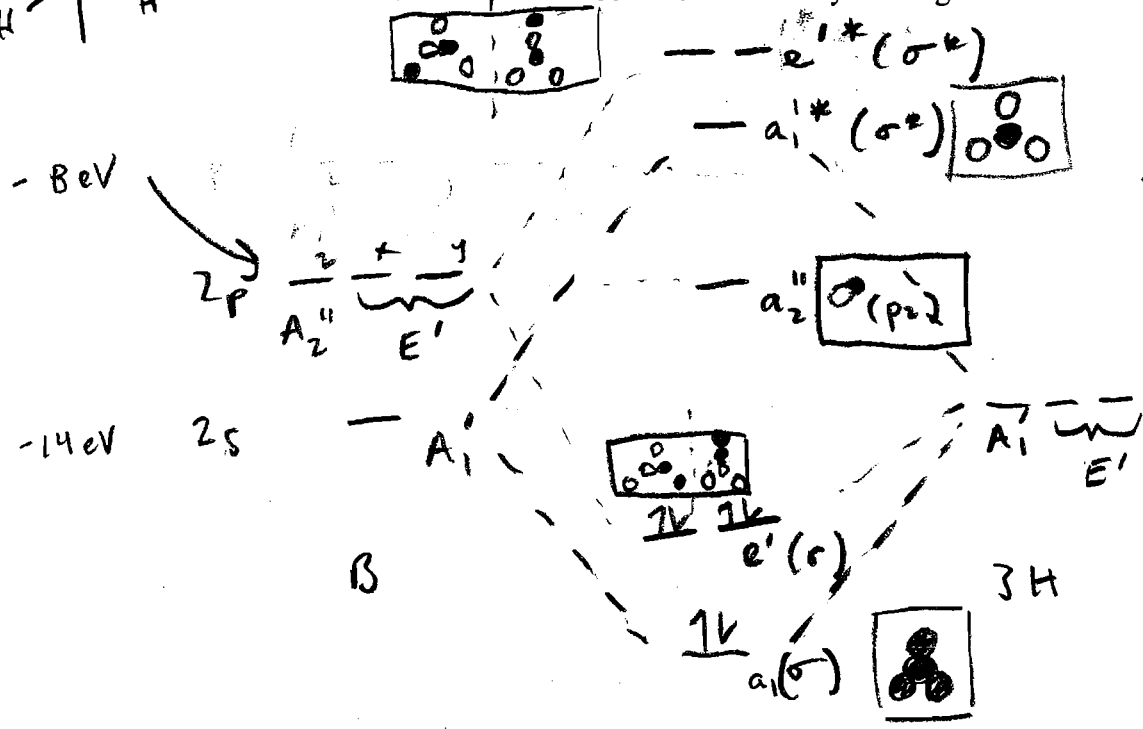
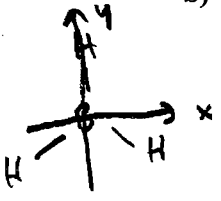
Γ_S = A₁' + E'

of times for A₁' : 1/12 (1*3*1 + 0 + 1*1*1 + 1*3*1 + 0 + 1*1*1) = 1
 " E' : 1/12 (2*3*1 + 0 + 0 + 2*3*1 + 0 + 0) = 1

b) Using the SALCs that you generated above, construct a MO diagram for BH₃.

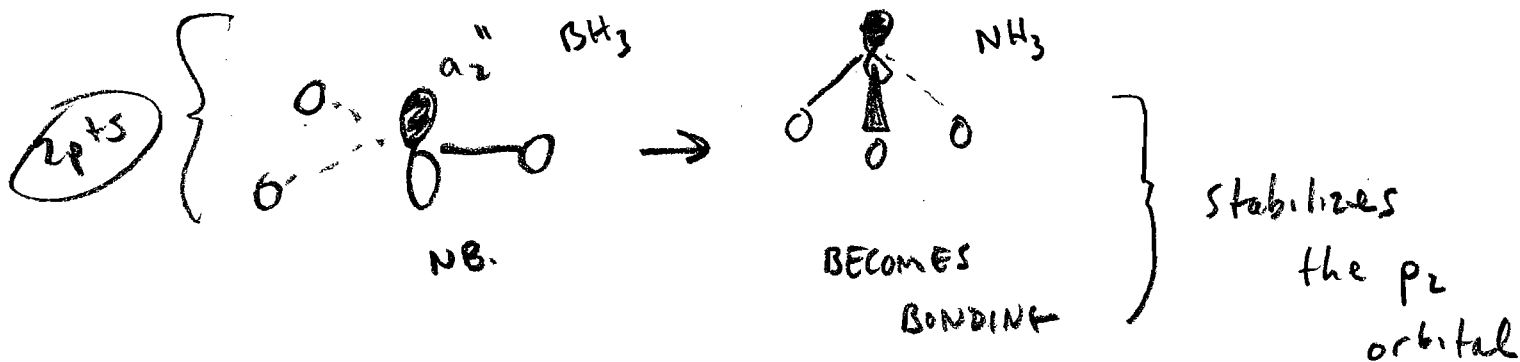
1. Label all molecular orbitals correctly (use lowercase letters for the MOs.)
2. Sketch what each MO looks like by showing the overlap of the appropriate atomic orbitals on boron with the SALCs generated from the H atoms.
3. Place the correct number of electrons in your diagram.

2pts



relative energy = 1pt
 symmetry = 1-pts
 type/order = 4pts
 electrons = 1pt
 pictures 3pts

c) BH_3 is planar, whereas NH_3 is pyramidal. Using pictures, predict what would happen to the a_2'' molecular orbital as the geometry changes from planar to pyramidal. How does this contribute to / alter the bonding in NH_3 compared to BH_3 ? Also, how does the role of this key frontier molecular orbital differ when comparing the reactivity of NH_3 with BH_3 ?



- 2pts
- In BH_3 p_z is empty (Lewis acid) LUMO
 - in NH_3 p_z is "full" (Lewis base) HOMO