Chemistry 125 Second Examination Name ___________________

October 20, 2003

The exam budgets 50 minutes, but you may have 60 minutes to finish it. Good answers can fit in the space provided.
Question values correspond to allotted time; don't waste too much time on cheap questions.
Read each question carefully to see what it asks for, and be sure to answer all of its parts.

1. (5 min) Using **mathematical expressions** explain how writing the wave function of a bonding orbital as a sum of atomic orbitals is consistent with what one sees about bonds using x-ray diffraction.

2. (6 minutes) The following (mixed-up) table shows values of Z_{eff} for a variety of atomic orbitals.

C (2s)	1.28
C (2p)	2.51
F (2p)	3.14
Li (2s)	3.22
Na (3s)	5.10

A. **Draw lines** connecting each atomic orbital to the appropriate value of Z_{eff}.

B. Explain briefly three things about Z_{eff} : What **problem** it is designed to solve, how using it affects the **shape** of the AO, and why it is ultimately **inadequate** to the task.

3. (4 min) One might expect the lithium atom with its three electrons to be about half again as polarizable as the helium atom with its two electrons. In fact it is about 120 times more polarizable. Explain this dramatic difference.

4. (7 minutes) Consider the reactions of hydroxide with hydrofluoric acid and with methyl fluoride.

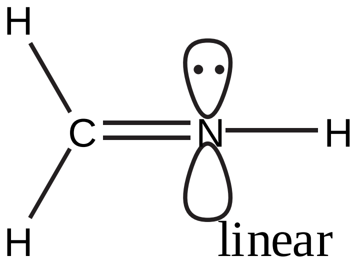
A. Draw the **shape** of the **LUMO** of **H-F** and that of **CH_3-F** (include **signs**).

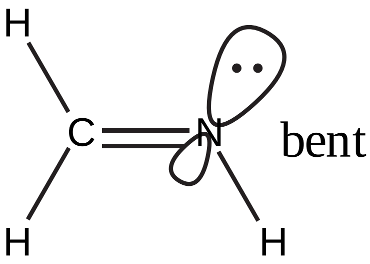
B. Referring to these pictures, explain how OH^- approaches each molecule. (Mention both **direction** of attack and influence of orbital mixing on the **bonding** between particular pairs of atoms.)

C. Use **curved arrows** and stick bonds to show electron-pair shifts in each reaction.

5. (3 minutes) Draw a specific example of a 3-center 2-electron bond .

6. (8 min) The “imine” functional group involves a carbon-nitrogen double bond. The “second” part of the double bond results from the overlapping between the 2p-orbitals of the carbon and nitrogen atoms that are perpendicular to the plane of the page.

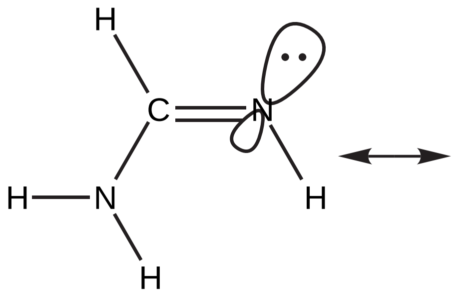




A. Discuss briefly in terms of the hybridization of nitrogen orbitals why the linear structure might be more stable than the bent structure **AND** why the bent strucure might be more stable than the linear structure.

B. In fact the bent structure is favored for the imine. Explain how you might confirm this fact using IR spectroscopy.

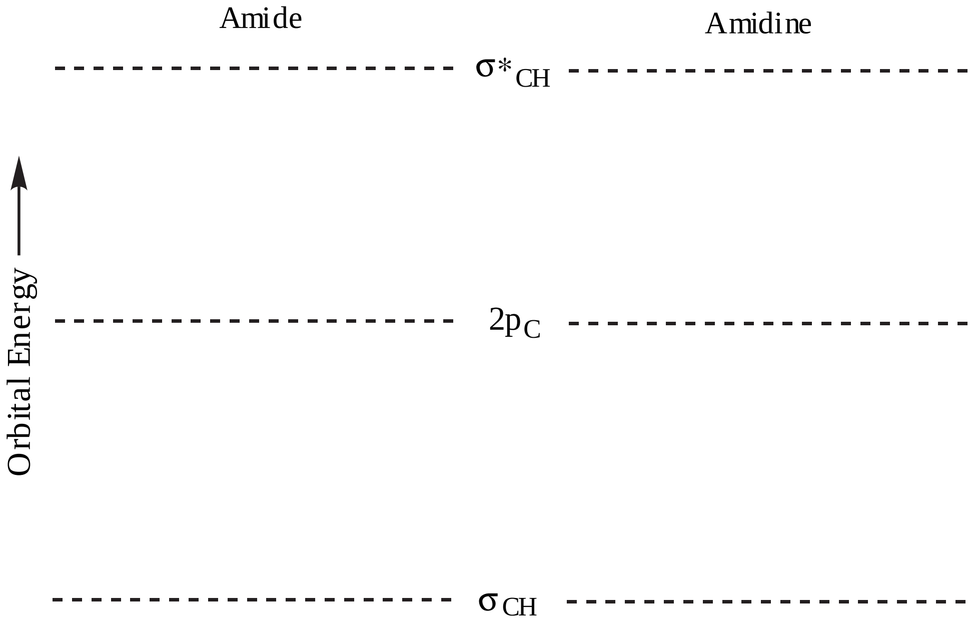
7. (9 min) The “amidine” functional group, shown below, is the imine analogue of an amide.



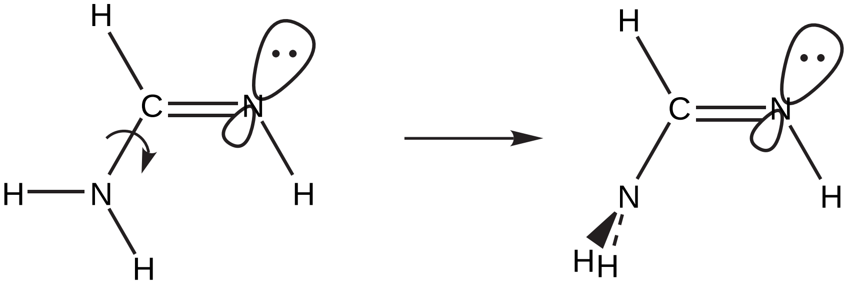
A. In the space to the right of the double arrow draw the most important alternative resonance structure for amidine.

B. Explain how the mixing of a localized “HOMO” with a localized “LUMO” in the amidine influences charge distribution and the bonding between specific pairs of atoms.

C. Should resonance stabilization due to orbital mixing be greater in an amide or in an amidine. Explain by showing the energies of the orbitals that mix and the energies of the resulting orbitals for each case. Use the following diagram which defines an orbital energy scale.



8. (5 min) Explain why twisting about the C-N single bond of an amidine (to make one H project toward the reader and the other away) should make one nitrogen atom more basic and the other less basic.



9. (3 min) [Note that this question has small credit. Don't waste too much time on it.]

The most strongly basic group of proteins is the guanidine group of the amino acid arginine (shown below). It is 300 times stronger as a base than a simple amine.

Why is guanidine such a strong base? That is, why is the protonated form of the guanidine group so unusually low in energycompared to the unprotonated form? [Consider both the hybridization of the nitrogen that becomes protonated and resonance stabilization from orbital mixing in the protonated form.]