Chemistry 125 Second Examination Answers **October 21, 2002**

Most of these answers supply more information than was minimally required.
[Material in square brackets and small type is supplemental.]

1. (6 min) **Explain** the following apparent paradoxes:

a) BH_3 is both an acid and a base

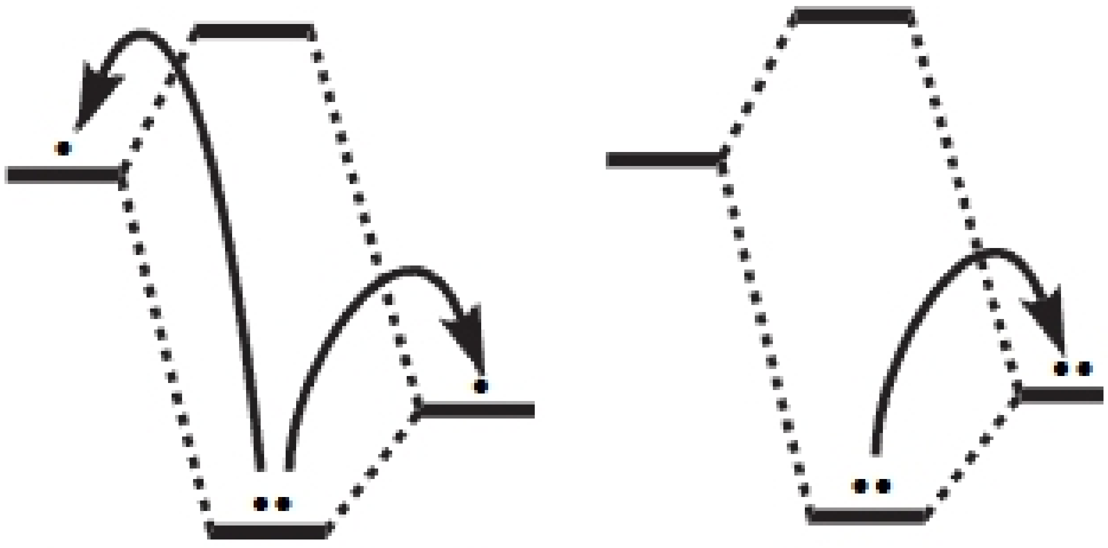
The most general definition of an acid is a species that possesses an unusually low LUMO, and of a base, a species that possesses an unusually high HOMO. BH_3 has an unusually low LUMO in 2p orbital of the boron atom, which is unusual because it has paired with another atomic orbital to shift to a higher energy. It has an unusually high HOMO in the B-H σ bond, which is unusual because of poor energy match between 1s of H and the sp^2 hybrid AO of boron (because of boron's low nuclear charge for a first row atom).

b) HF is properly called an acid even though its H-F bond is much stronger than a typical C-H bond

The statement of a paradox suggests thinking about Bronsted acidity, that is the dissociation of H-F to $H^+ + F^-$. The paradox involves how this dissociation can be easy when the bond is unusually strong (1/3 stronger than a C-H bond).

The explanation involves the difference between easy heterolysis to give ions, where the electron pair requires little energy to go into the lower AO of fluorine, and homolysis to give atoms, where one of the electrons must go to much higher-energy AO of hydrogen.

[Partial credit was given for a low LUMO definition of HF acidity, but this does not directly address the paradox.]



homolysis - hard

heterolysis - easy

2. (6 min) Cite and interpret **experimental** evidence relevant to the favored H-X-H bond angles in $\mathbf{BH_3}$ and $\mathbf{NH_3}$.
(**Don't** worry about the orbital explanation of why they have these angles.)

The infrared spectrum of BH_3 shows a single peak (at 1141/cm) [while CH_3 shows an analogous single peak at lower frequency (606/cm)]. Vibrations of this frequency are attributable to bending of the bonds to make the central atom move in and out of the plane of the triangle of attached hydrogen atoms [actually with the center of mass fixed, the hydrogens do most of the moving]. This is consistent with a parabola-shaped potential energy graph for the out-of-plane distortion with an energy minimum for the flat structure, because for such an "harmonic-oscillator" the allowed energy levels are equally spaced. [The lower frequency for CH_3 is consistent with the relatively easy distortion, where one electron, at least, profits from bending by gaining s character.]

By contrast the corresponding region of the NH_3 spectrum shows two closely spaced peaks (at 932 and 968/ cm). This results from the coupling between two local wavefunctions in a double-minimum potential. [The two lowest-energy local wavefunctions have little overlap, and combine to give sum and difference wave functions of essentially the same energy; the next local wavefunctions mix by tunnelling to give the states that differ by 36/cm.] Thus the minimum-energy structure of NH_3 is pyramidal (HNH = 107°), not planar like BH_3 (HBH = 120°.

[Note that electron spin resonance was used in discussing the difference between CH_3 and CF_3, not between NH_3 and BH_3. Only molecules with SOMOs can be studied by this technique, which measures magnetism of electrons in singly-occupied orbitals.]

3. (6 minutes), Name the **three factors** that could result in unusually high-energy HOMOs, and give an example for each. (Give three examples in all).

I. Presence in the molecule of occupied AOs that have not been mixed with other AOs and thus have not shifted in energy to the range of normal HOMOs. Typical examples are unshared pairs in NH_3 or HO^-. [It is true that the latter HOMO is especially high because of the negative charge, but we have not usually included this as a separate factor on a par with the "big 3". If you lost credit for this, you may ask for an adjustment of your grade.]

II. HOMOs formed between AOs that have poor overlap. For example the π orbital of $H_2C{=}CH_2$.

III. A HOMO formed by overlap between AOs at least one of which is much higher in energy that a valence shell orbital of C or H. An example would be the B-H σ orbital of BH_3.

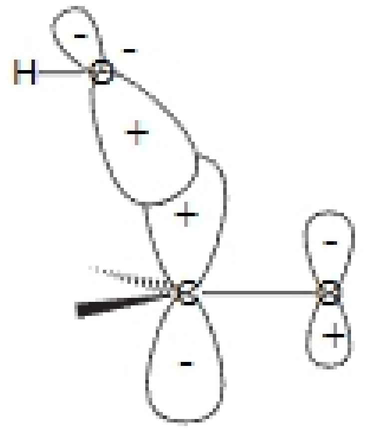
4. (8 min) Describe the attack of OH^- on a carbonyl group both from the point of view of **HOMO/LUMO** mixing and with a **curved arrow** diagram showing the bonding change.

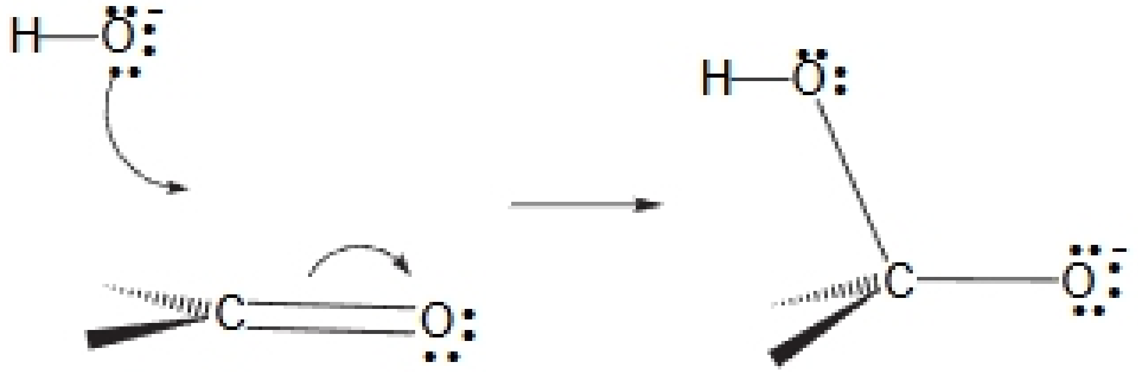
HOMO : unshared pair of OH^-. LUMO: π* of C=O (large on C)

Approach C from Bürgi-Dunitz angle for maximum net overlap.

Electron density builds up between C and C to make new bond.

Occupancy of C-O antibonding orbital reduces bonding between them.





5. (4 minutes) Describe atomic-orbital hybridization in the H_2 molecule. Explain what factors determine its extent.

The AOs in H_2 are mostly (96.7%) 1s, but they have nearly 3% 2p and 0.5% 2s character.

The dominant factor, which favors 1s, is to give a local electron distribution similar to that in the lowest-energy state of the H atom. Adding any other component gives the atom a much higher energy (higher principal quantum level). [This is why hybridization is so much easier in the case of carbon where 2p is mixing with 2s, both in the same principal quantum level.]

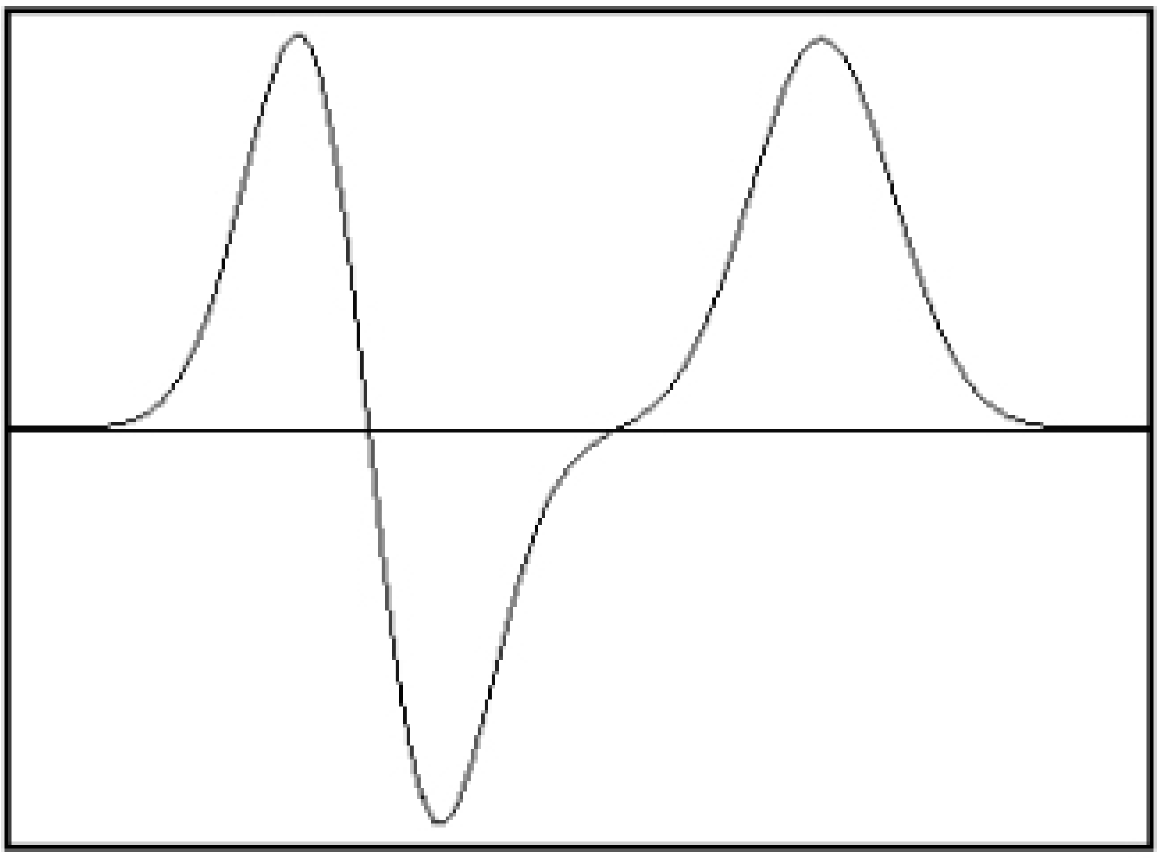
A secondary factor is to shift the atomic electron density toward the bonding region. Adding a small amount of 2p AO builds density on one side of the atom at the expense of the other side, without changing the average distance from the nucleus very much. This is why there is much more 2p than 2s character to the hybrid.

6. (9 minutes) This one-dimensional wave function (from the first hour exam) is in some ways analogous to an interesting molecular orbital of HF.

a) Name the MO of HF.

b) Explain the analogy.

c) Explain how you would adjust the **potential-energy graph** that gave this wave function in order to make the wave function a better analogue of the MO of HF.



a) Analogous to the σ* MO of HF.

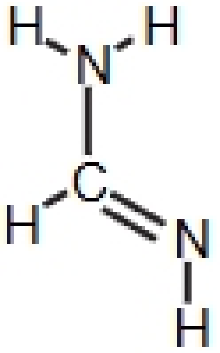
b) This orbital is the unfavorable (antibonding) combination between a function with no nodes ($1s_H$) on the right and a function with a single node ($2p_F$) on the left.

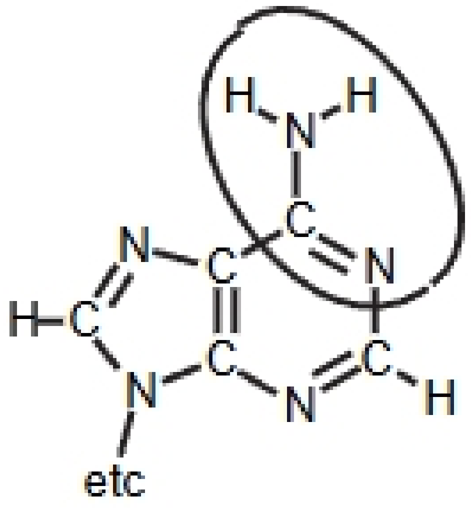
c) The orbital shown is, if anything, a little larger on the left than on the right. In HF the σ* MO should be larger on H than on F, because the favorable σ MO was larger on F than on H, $2p_F$ being lower in energy than $1s_H$. To make this one dimensional analogue more apt, one should lower the energy of the well on the left so that this unfavorable combination would be much larger on the right.

7. (10 min) Consider the group $H_2N\text{-}CH{=}NH$ (which could be a model for the circled portion of the adenine bases of DNA).

Explain why the three bonds to the top nitrogen of this group might prefer all to lie in the same plane, that is, **why the N might be flat** rather than pyramidal like a normal amine.

Incorporate the following concepts in your answer: atomic orbital energy, orbital hybridization, hybrid-orbital overlap, MO energy, resonance stabilization, curved arrows





Normally the nitrogen of an amine is pyramidal so that the unshared pair of N, for which N is the sole "support" can have some lower-energy s character.

In this case, however, the unshared-pair orbital can overlap with the $\pi^*_{C=N}$ "LUMO" next door, which is especially low in energy because it includes a 2p AO on N (with higher nuclear charge), and is large on C, where overlap can occur.

This interaction influences hybridization of the "amine" nitrogen in two ways: 1) By removing electron density from the N atom, it reduces the drive for using s-character in the N hybrid orbital that housed the formerly unshared pair. and 2) it is possible to increase the overlap involved in this stabilization by using a pure p orbital on the amine nitrogen. [Note that its s orbital is orthogonal to the $\pi^*_{C=N}$ "LUMO".]

Thus the amine N can minimize total energy by using sp2 hybrids to make its single bonds and a pure p orbital to hold the "unshared pair", which is now stabilized by theadjacent π* orbital.