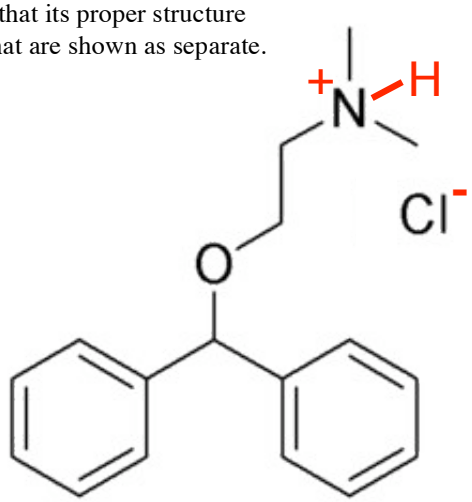
Chemistry 125 Second Examination Answer Key **October 22, 2007**

	Exam	Total
Mean Score :	73.2	149.0
1/3 of scores >	81	158
2/3 of scores >	69	143
A- / B+ border would be about		152
B- / C+ border would be about		103

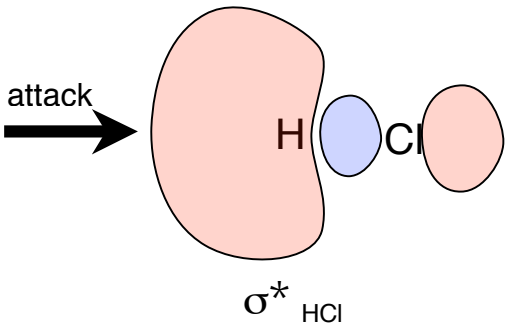
The exam budgets 50 minutes, but you may have 60 minutes to finish it. Good answers can fit in the space provided. Question values correspond to alloted time. Don't waste too much time on cheap questions.
Read each question carefully to see what it asks for (bold face is used to help highlight questions).
Make sure you are answering the question, not just saying something vaguely relevant to its topic.

1. In the last exam we encountered Benadryl (right) and considered the fact that its proper structure includes a "*pentavalent*" atom formed by reaction of the two molecules that are shown as separate.



A) (2 min) Scratch out the HCl and redraw its atoms to show a proper Lewis structure for benadryl with lines for bonds.

B) (5 min) **DRAW** a reasonable representation of the **SHAPE** of the orbital that makes the **HCl** molecule reactive showing **WHERE** it should be attacked; Give a descriptive **NAME** to the molecular orbital; and **EXPLAIN** in a few words and/or with a diagram **WHY** it is reactive.

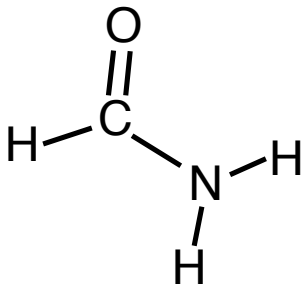


This σ* LUMO is unusually low, compared to $\sigma^*_{C\text{-}C}$ or $\sigma^*_{C\text{-}H}$, because of energy mismatch due to the high nuclear charge of the Cl atom

C) (4 min) **NAME TWO local orbitals** that make the **organic** (non-HCl) portion of the benadryl structure reactive. **Explain** why one should be more reactive than the other.

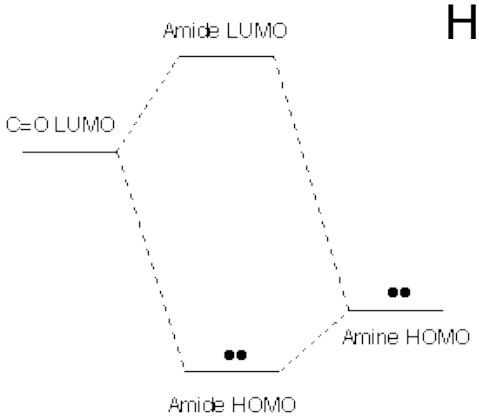
The organic portion of benadryl has two high HOMOs that are unshared pairs, on the O and N atoms. The pair on N is higher in energy because of its lower nuclear charge. (The pi molecular orbitals of the double bonds in the benzene rings are also a possibility, but they are more complicated because they overlap with one another, which will be discussed as "aromaticity" later in the course.)

2. A naïve student might guess properties (total energy, HOMO/LUMO energy, reactivity, geometric structure, polarity, rigidity, *etc*.) for formamide (the molecule shown) on the basis of its possessing a carbonyl group and an amine group. A more sophisticated student (you) would point out that this molecule must be considered an "amide" with its own characteristic properties.



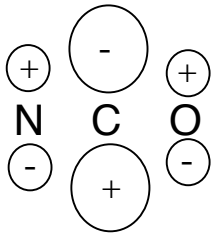
A) (3 min) **Explain in terms of molecular orbitals** (NOT resonance) why an amide is different in **energy** from expectations based on a "carbonyl amine".

The unshared electron pair of the "amine" nitrogen is stabilized by mixing with the unusually low pi* orbital of the "carbonyl" group.



B) (4 min) **Draw** a reasonable representation of the actual **LUMO** of an amide (a few words may help explain your drawing).

The LUMO will be mostly the pi* orbital of the carbonyl group (large p orbital on C, small p orbital on O, opposite signs) mixed unfavorably with a smaller amount of the p orbital of the N atom.



C) (4.5 min) Cite **three characteristic properties of the amide group** that are important for "polypeptides" or proteins (which contain many amide groups).

The three protein-relevant characteristic properties of the amide group (frames 5-7 of Lecture 18) are:

(1) Rigid planarity of the six atoms shown above, which makes the polypeptide chain less floppy.

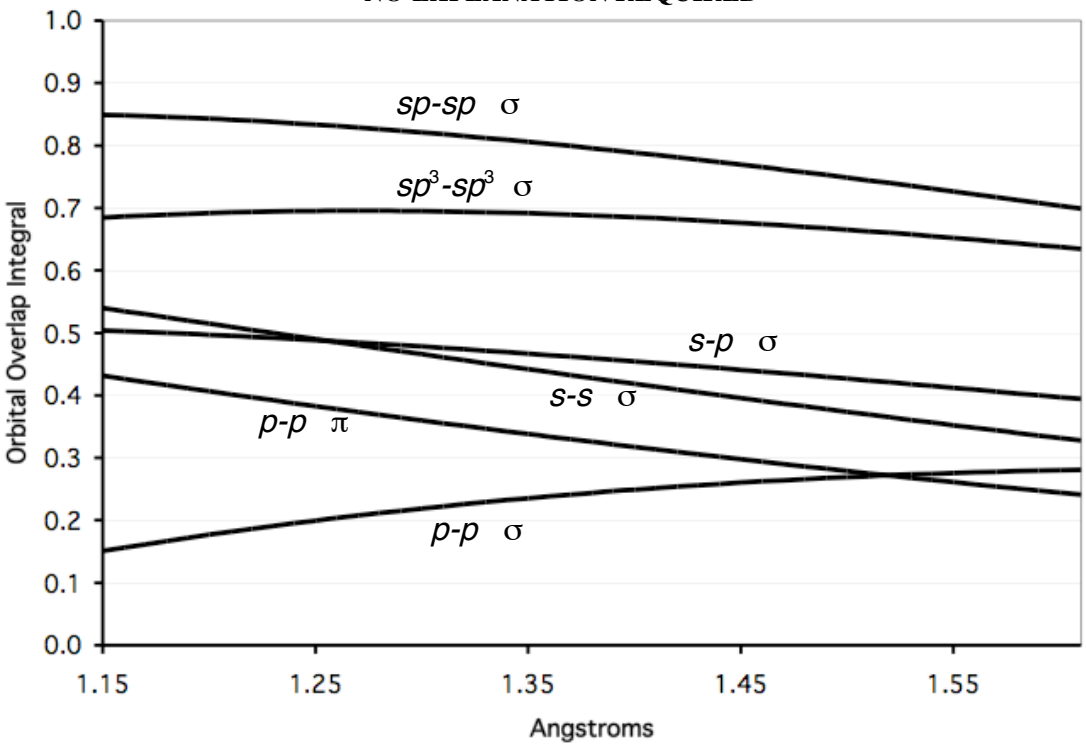
(2) Relatively unreactive (HOMO lowered compared to N:, LUMO raised compared to C=O)

(3) Dipole moment rotated about 90°, which assists H-bonding in alpha-helix of polypeptide.

3. (4.5 min) The following plot shows the **overlap integral** between valence-level atomic orbitals (**pure or hybrid**) of two carbon atoms over internuclear distances characteristic of single, double, and triple bonds.

Clearly LABEL each of the six curves with the **names of the AOs** involved (and as **sigma or pi**).

NO EXPLANATION REQUIRED



(one aid to identifying the overlap is whether it approaches 1, 0, or -1 at 0 Å)

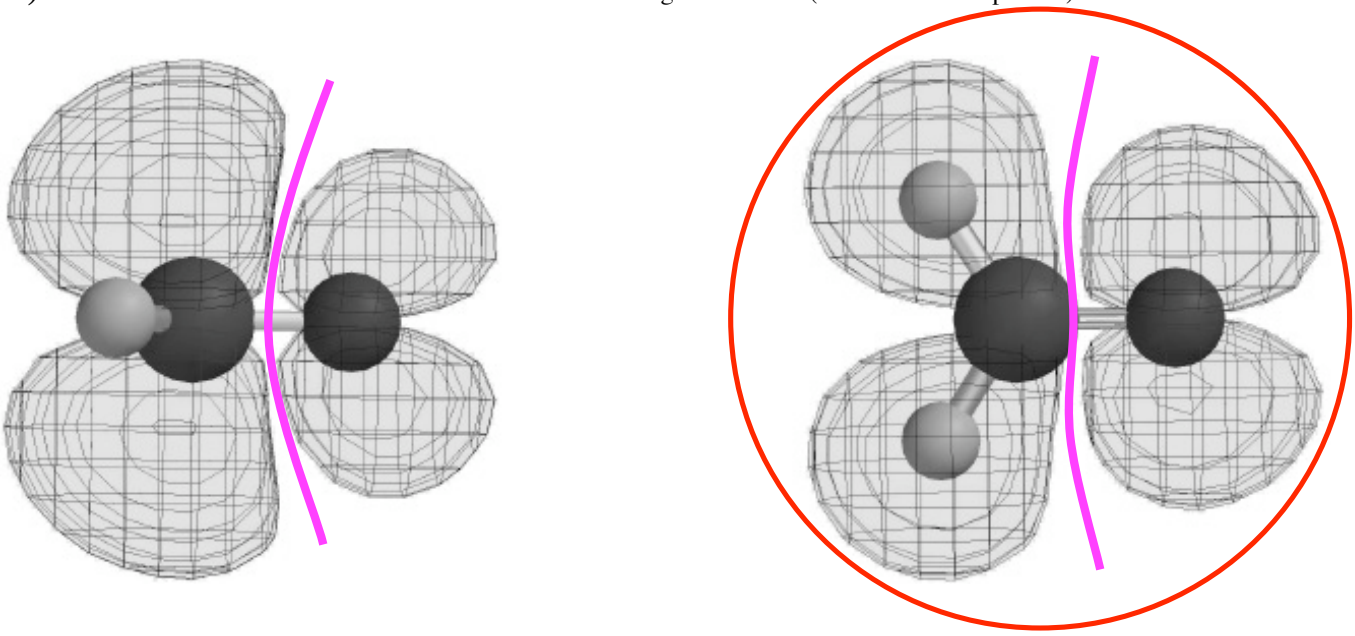
4. (4 min) **Explain** how the following question could be considered a **trick**: "Which bond is stronger H-H or H-F?"

H-H is stronger when breaking heterolytically (to two ions), which is one reason that H-F is called an acid; but H-F is stronger (by 136 to 104 kcal/mole) when breaking homolytically to two atoms, because one of the two electrons must go way up to the H atom from the low energy sigma bonding orbital that is mostly on F.

5. (4 minutes) Here are **TWO** MOs of $H_2C{=}O$. Each has two nodes and is analogous to a *3d* atomic orbital.

A) **CIRCLE** the MO that is **LOWER** in energy, and **EXPLAIN** your choice **in terms of "plum-pudding" orbitals.**

B) In **EACH** MO draw the node that would affect the strength of a bond (one line in each picture).



[Note that the horizontal nodes are atomic orbital, not antibonding, nodes.]

6. (4 min) Why are atoms to the left of carbon in the periodic table more prone to participate in 3-center-2-electron bonds than elements to the right of carbon?

Two Reasons:

(1) They have vacant valence-level orbitals that can mix with high-energy bonding orbitals between other atoms.

(2) Because they have relatively low nuclear charges, the bonding orbitals in which they participate tend to be unusually high in energy.

7. Trimethylamine, $(CH_3)_3N$, can be "oxidized" by hydrogen peroxide, HOOH, to give trimethylamineoxide, $(CH_3)_3NO$ in a process that involves **two reactions**.

A) (6 min) **Identify** the unusually high **HOMO** and the unusually low **LUMO** that are likely to be involved in the **first reaction** between $(CH_3)_3N$ and HOOH, **stating why** their energies are unusual.

High HOMO : unshared pair on N, unusually high because it is an unmixed AO

Low LUMO : σ^* of O-O, unusually low because of the relatively high nuclear charge of O (*vs.* C or H)

B) (5 min) Draw the two reactions using **curved arrows** to show the electron-pair shifts involved. (Show the molecules **properly oriented** to attack one another.)