Chemistry 125 Second Examination Answers **October 20, 2003**

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.

If A and B are AOs on different atoms and we write the bonding orbital as $\Psi = \frac{<1}{\sqrt{2}}(A+B)$

Then its total electron probability is $\Psi^2 = \frac{<1}{2}(A^2+B^2)+(<1)AB$

The first part of this expression is just the sum of the AO probabilities, which is consistent with the x-ray observation that the total electron density looks mostly like a collection of atoms.

The last term is small . It builds up electron density only where BOTH A and B have significant values, that is, between the atoms. This is consistent with what one sees in electron-difference-density maps, where subtracting theoretical atomic density from the experimental density shows a slight increase of density between the nuclei.

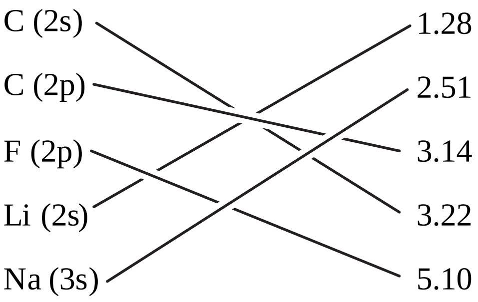
2. (6 minutes) The following (mixed-up) table shows values of Z_{eff} for a variety of atomic orbitals.

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

Li has only 3 protons altogether and the 1s electrons effectively shield most of their charge: obviously 1.28

F has 9 protons, 1s electrons effectively "remove" two of these charges, and partial screening somewhat reduces the effect of the remaining 7. Also F is well-known to be the most "electonegative" i.e. lowest energy electrons: 5.10

For C the 1s electrons reduce the +6 nuclear charge to +4 and mutual shielding of the valence electrons reduces the nuclear charge a bit more. 2s penetrates closer to the nucleus and "sees" a larger charge than 2p. Thus C (2s) is 3.22 and C (2p) is 3.14



Na has 11 protons, but the 10 1s, 2s, and 2p electrons do a good job shileding them from the 3s electron, which "sees" a nuclear charge of only 2.51.

[Website for Z_{eff} values: http://www.webelements.com/webelements/elements/text/C/effn.html]

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.

Z_{eff} is designed to take into account the electron-electron repulsion that is implicitly ignored in approximating a many-electron wave function as the product of one-electron wave functions (orbitals).

Since the nuclear charge Z is used to scale ($\rho \propto Zr$) the distance from the nucleus in the negative exponential term (e^(-ρ/2) of the atomic orbitals, decreasing Z to Z_{eff} expands the orbital (requires a larger r to cause a certain reduction in the value of the wave function).

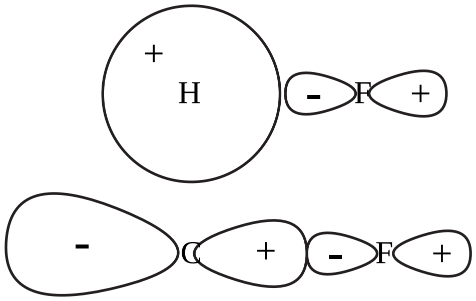
Z_{eff} can't quite do the trick because the other electrons do not sit at the nucleus they are both spread around and, more importantly, can move as the electron in question changes position, giving rise to the so-called "correlation energy" error.

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.

Atomic polarization can be understood to result from mixing p-orbitals with s-orbitals to build up electron density on one side of the nucleus and deplete it on the other side. The 1s orbitals of both He and Li are too far in energy from the 2s orbitals to mix easily (the lowest energy orbital looks mostly like 1s, whether or not an external electric field is applied). The 2s electron is much easier to mix with 2p, because it is much closer in energy. Furthermore 2s, with its radial node, is much more spread out, so a given amount of mixing with 2p causes a much larger electron shift. These two factors (energy match and position of overlap) are of comparable importance in causing the high polarizability of Li.

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**).

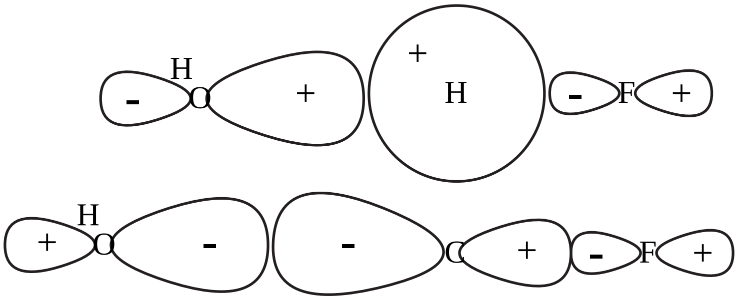


The two most important features of these schematic drawings are that there is a node between F and H (or C) and that the anti-bonding orbitals are larger on H (or C) than on F (because the occupied bonding orbital is larger on the lower energy F).

The AOs used are 1s on H and sp hybrids on C and F (mostly p on F) . Actually the sp hybrid on C points toward F, but its + lobe is reduced in size by overlapping with the F lobe of the opposite sign.

For more precise renditions of the orbitals see the web sites:
http://classes.yale.edu/chem125a/125/quantum/MOdiagrams/HForbs/HForbs.html and
http://classes.yale.edu/chem125a/125/quantum/MOdiagrams/CH3F/CH3Forbs.html

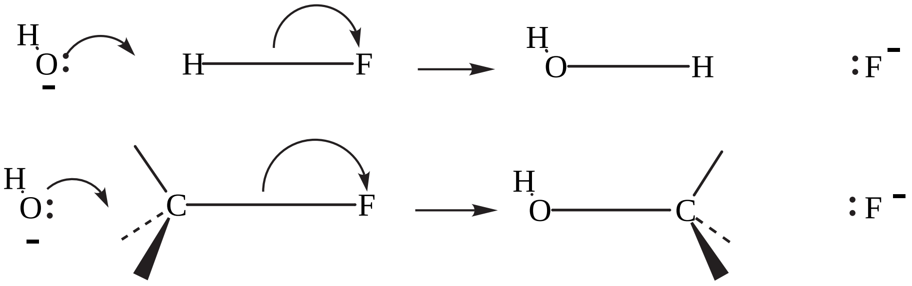
B. Referring to these pictures, explain how OH^- approaches each molecule. (Mention both **direction** of attack and influence of orbital mixing on the **bonding** between particular pairs of atoms.)



OH^- should approach from the left to optimize overlap with each LUMO (avoid mixing with LUMO lobes of the opposite sign). Incidentally, it is also good to avoid overlap of the OH^- HOMO with filled orbitals that are not shown, like those of the C-H single bonds of CH_3F, because such overlap give net repulsion.

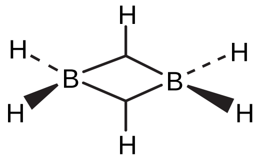
This HOMO/LUMO mixing creates bonding between O and H (or C) but anti-bonding between F and H (or C), where there is a node of the LUMO.

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

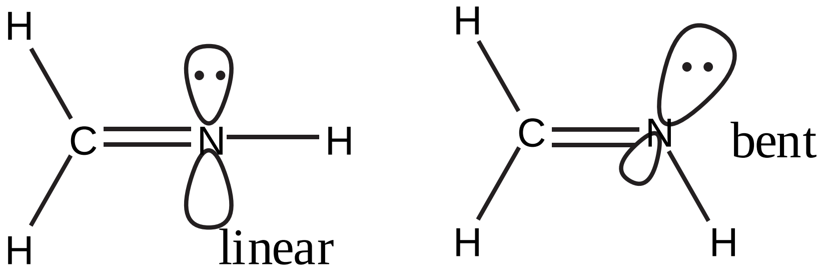


Note the importance of starting the curved arrows where the electron pairs start and ending them where they finish.

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.

The linear structure is favored by the stronger NH and σNC bonds formed with greater overlapping by the sp hybrids of linerar N than by the sp^2 hybrids of bent N.

The bent structure is favored by the lower energy of the unshared pair of electrons in the sp^2 orbital of bent N rather than in the p orbital of linerar N. The nitrogen orbital is fully responsible for both electrons in the unshared pair, but the bonding pairs reside partially on C or H, so the N is inclined to use s-character, which is in short supply, on the unshared pair orbital.

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

This problem seems analogous to deciding between the planar structure of XH_3, which is a single minimum potential, and the pyramidal structure, which is a double minimum. In that case NH_3 showed a splitting of the IR absorption for bending vibration (932 and 968/cm), because in the excited state there is a difference in energy due to overlapping of the one-node wave functions for the two bent structures (tunneling splitting).

The expected answer for this question is that, since the imine is bent, there should be an analogous splitting of the IR absorption for the C-N-H bending. This answer earned full credit.

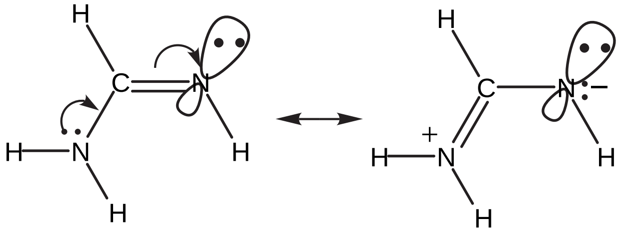
In truth, although this approach MIGHT work, it does not, because the H atom must move much further to go back and forth in this case than in the case of ammonia. This means that the wells in the double minimum are further apart, the overlap is much less, and the splitting is too small to observe by IR.

A different kind of analysis of the IR spectrum (or different kinds of spectroscopy – microwave or nmr) can demonstrate the bending at N in the imine.

[For references see *Journal of Chemical Physics*, **83**, 2078-2090 (1985) and *Journal of Molecular Spectroscopy*, **216**, 508-514 (2002)]

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.

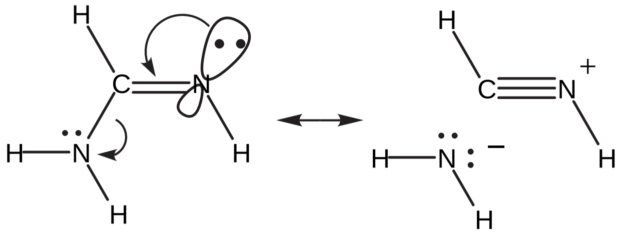


Note the charges of the N atoms on the resonance structure. They should not be partial charges (δ), which refers to the overall true charge distribution inferred from both structures considered together.

It is worth remembering that when N forms four bonds in a resonance structure it must bear a positive charge, because the fourth bond was formed by sharing its electron pair with another atom. (Same for trivalent oxygen.)

Note also that the initial unshared pair of electrons on the right N is not involved in this resonance. The negative charge comes from a second unshared pair on this N atom (which "originated" in the double bond).

[Some answers wanted to use the unshared pair on the right nitrogen to form a new bond in a resonance structure. This is possible as shown, but it is much less important, because the only vacant orbital with which this unshared pair overlaps is a relatively high LUMO, σ^* of CH (the unshared pair is orthogonal to π^* of the C=N group). Note the + tetravalent N again.]



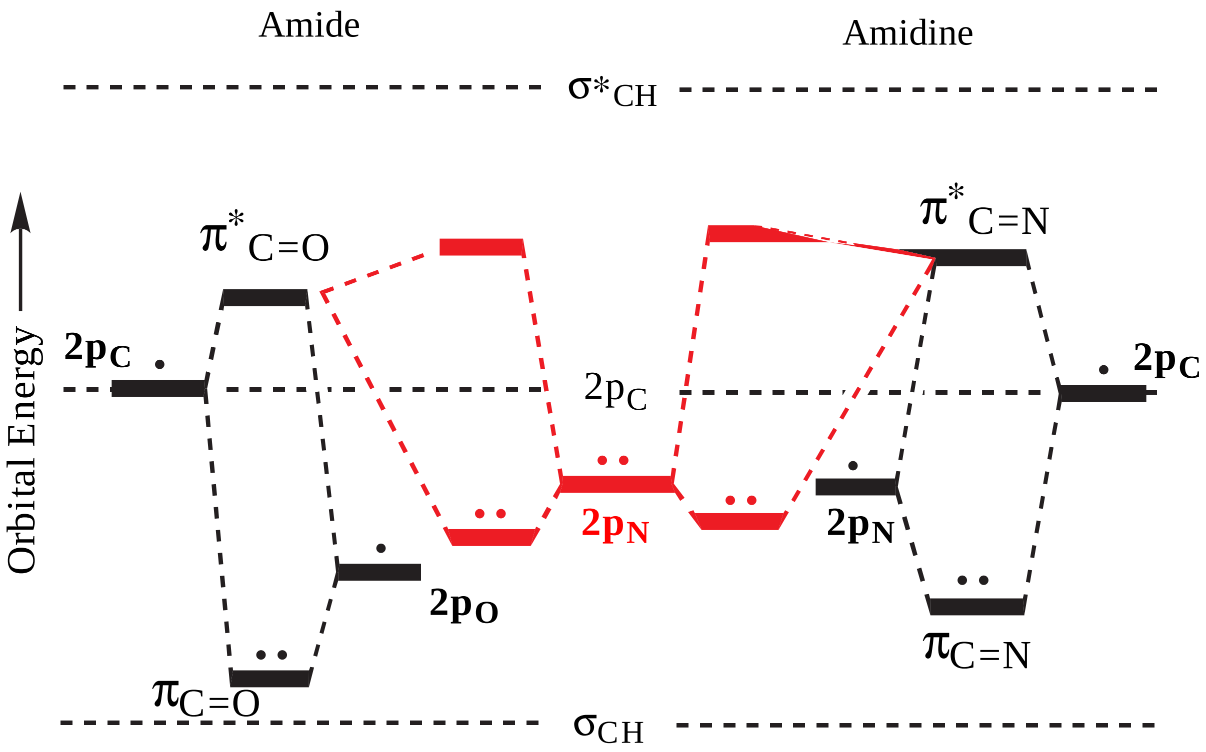
B. Explain how the mixing of a localized “HOMO” with a localized “LUMO” in the amidine influences charge distribution and the bonding between specific pairs of atoms.

Mixing the unshared pair of the “lower”, single-bonded, nitrogen with the $\pi^*_{C=N}$ LUMO shifts negative charge from the single-bonded nitrogen toward the double-bonded nitrogen (as show by the most important charge-separated resonance structure, the less important one at the bottom of the previous page shifts electron density in the opposite direction).

The HOMO/LUMO mixing increases bonding between the single-bonded N and the C (partial double bond) and decreases bonding between the double-bonded N and the C (by creating anti-bonding).

Note that there is no mixing between the “in-plane” unshared-pair orbital on the double-bonded nitrogen atom and the $\pi^*_{C=N}$ LUMO, which is perpendicular to the plane of the page. Because these orbitals are orthogonal, this unshared pair is irrelevant to resonance (except as shown at the end of the answer for part A).

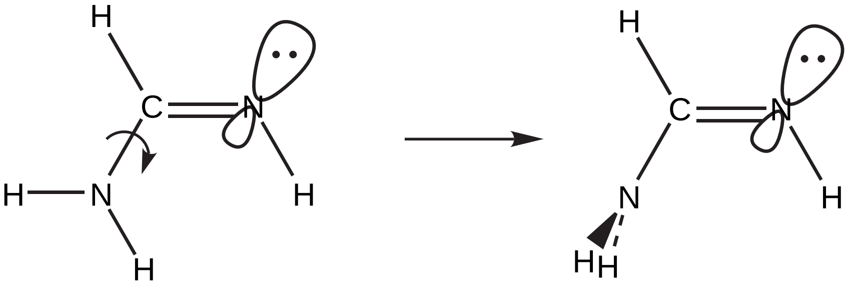
C. Should resonance stabilization due to orbital mixing be greater in an amide or in an amidine. Explain by showing the energies of the orbitals that mix and the energies of the resulting orbitals for each case. Use the following diagram which defines an orbital energy scale.



Because of poorer energy match between $2p_O$ and $2p_C$ (left) than between $2p_N$ and $2p_C$ (right), the $\pi^*_{C=O}$ LUMO of the amide is lower in energy than the $\pi^*_{C=N}$ LUMO of the amidine.

Thus there is better energy match for the mixing, shown in red, between the $2p_N$ unshared pair of the single-bonded nitrogen with the amide LUMO than with the amidine LUMO, and the amide has the larger resonance stabilization.

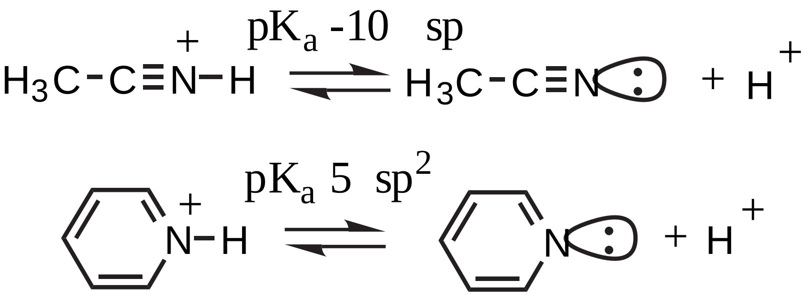
8. (5 min) Explain why twisting about the C-N single bond of an amidine (to make one H project toward the reader and the other away) should make one nitrogen atom more basic and the other less basic.



In the planar amidine on the left the unshared-pair of the single-bonded nitrogen atom is lowered in energy and made less basic by mixing with the C=N LUMO. In the 90° twisted amidine the overlap between these two orbitals is destroyed (they are made orthogonal) so there is no mixing and the unshared pair is not lowered in energy. Thus twisting increases the basicity of the single-bonded nitrogen.

It might appear that, since the unshared pair of the C=N nitrogen atom is orthogonal to the pi system, its energy, and therefore its basicity, should be unaffected by twisting about the single C-N bond. However, in the planar form the unshared pair on the single-bonded nitrogen atom is mixed with $\pi^*_{C=N}$ shifting extra electron density toward the double-bonded nitrogen atom. Repulsion from this extra π electron density raises the energy of the unshared pair, even though it has no overlap with the π orbitals. In the planar form the unshared pair of the double-bonded nitrogen is unusually high in energy, while in the twisted form its energy is lower. Thus twisting decreases the basicity of the double-bonded nitrogen.

[Related Information: At first glance one would think the unshared pair in a typical imine, with sp^2 hybridization, should have the same basicity as the unshared pair in pyridine, which also has sp^2 hybridization. Basicity can be measured by the pK_a of the related protonated form (lower numbers mean the proton is held less tightly). The pK_a of protonated pyridine is 5, much less that that of a protonated alkylamine, ~10, as expected for the sp^2 *vs* sp^3 hybridization.



The pK_a of the protonated imine in the visual pigment rhodopsin, however, is ~16, that is, the basicity is about 10^{10} higher than that of protonated pyridine. This is handy because it is important that rhodopsin be protonated in order that absorption of light can deprotonate it to trigger the visual response, but what gives with the crazy pK_a for this special imide?

The structure of rhodopsin has recently been determined, and it appears that there is a carboxylate anion very near the imine in question. This negative charge in the environment makes this a much more favorable site for protonation, as in this question where the extra negative charge near the C=N nitrogen in the untwisted structure makes the unshared pair more basic.]

[Reference on rhodopsin structure: http://www.thp.uni-duisburg.de/Paper/minoru/Thr94_com.pdf]

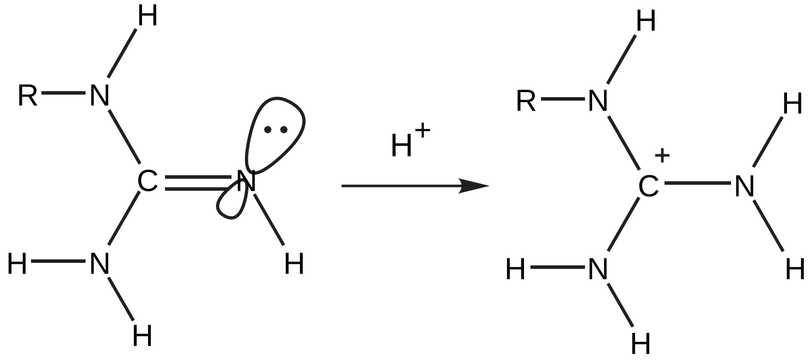
9. (3 min) [Note that this question has small credit. Don't waste too much time on it.]

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.]

As discussed above, the sp^2 hybridization of the unshared pair should make the imine nitrogen a weak base, rather than a strong base. This weakening effect on the base must be offset by a dramatic strengthening effect.

Obviously the strengthening must come from the presents of the two additional nitrogen atoms in guanidine. Their influence can be understood in two ways:



In the starting guanidine, the unshared pairs of both additional nitrogens can mix with the C=N LUMO, putting an especially high dose of electron density onto the third nitrogen, more than in the amidine. Repulsion by this electron density raised the energy of the sp^2 unshared pair and makes the group more basic. (Note again that this effect does not require overlap between the unshared pair and the pi system, which is good, because there is none.)

The second point of view has to do with the relative stability of the protonated and unprotonated structures. Although the two unshared pairs on the singly-bonded nitrogen atoms are indeed stabilized by the C=N LUMO in the unprotonated form, they are very much more strongly stabilized by the same LUMO in the protonated form, because protonation lowers the energy of the LUMO (not by mixing with it, but by creating postive charge in the neighborhood, just as adding an extra proton to the N nucleus, converting it to an O nucleus would do, and here there is no extra electron to contend with, as there would be with the oxygen of a real C=O group). The $C=NH_2^+$ group has a VERY low LUMO, this is depicted in the structure on the right above by writing it as C^+. This extra measure of stability helps draw the equilibrium to the right, that is it makes guanidine a very strongly basic group (the pK_a of the protonated form is 13).