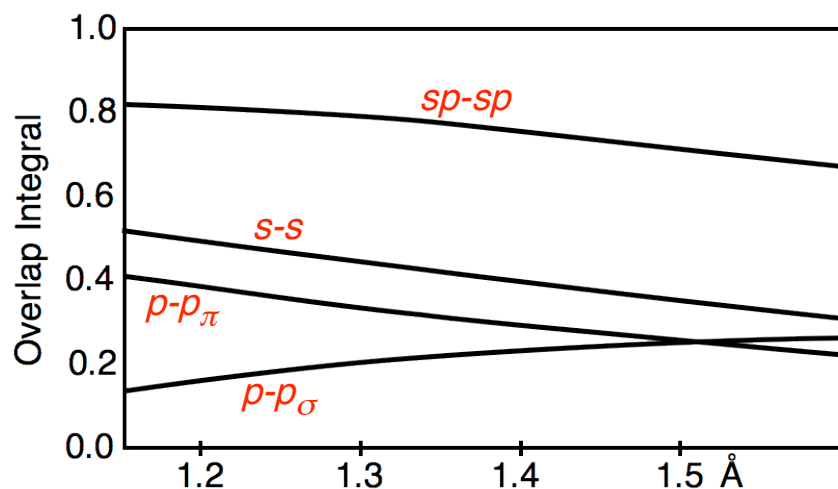


The exam budgets 50 minutes, but you may have 60 minutes to finish it. Good answers can fit in the space provided. Question values correspond to allotted time. Don't waste too much time on cheap questions.

**Read each question carefully to see what it asks for (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. (4 min) **Label** the *symmetric* atomic orbital pairs that would give the following **four** profiles for overlap integral versus C-C distance.



2. (4 min) **Explain** whether Correlation Energy should raise or lower a molecular energy calculated by the SCF procedure.

“Correlation Energy” is the name for the error that remains after a complete SCF molecular orbital calculation. SCF necessarily overestimates the energy, because the electrons are kept in fixed clouds and are unable to avoid one another by correlating their motion. Thus correction for correlation energy always lowers the energy calculated by SCF.

3. (2 min) Name two accurate **QUANTITATIVE** tools that would have been available to you, if you were a chemistry student in Yale’s Sheffield Scientific School in the class of 1901.

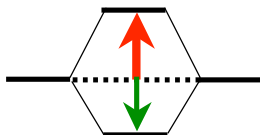
Burettes for titration

Analytical balances for precise weighing

4. (4 min) Assuming, perhaps unrealistically, that the atom-atom distances and overlap integrals are identical, **explain**, in terms of electron energies, which of the following bonds should be stronger. (A diagram would help.)

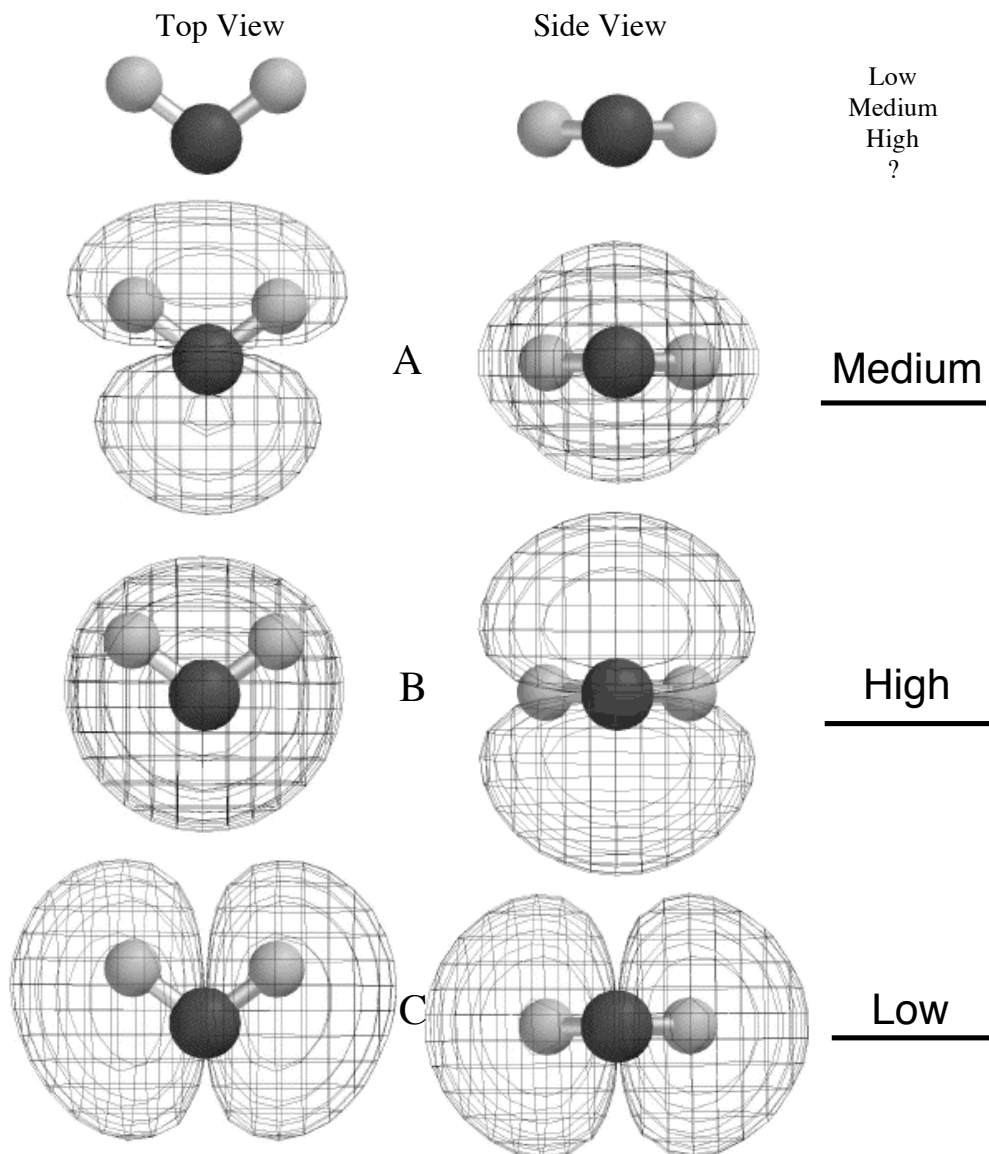
the 1-electron bond of  $\text{H}_2^+$

the 3-electron bond of  $\text{He}_2^+$



In either case there is perfect energy match, so if we assume identical overlap, the shifts of the electronic energy levels will be identical. In the two-electron case, one electron falls the same as in the one-electron case, but the **fall of the second electron** is more than offset by the **rise of the third**, because of the different normalization constants ( $<1/\sqrt{2}$  for the bonding orbital;  $>1/\sqrt{2}$  for the antibonding). Thus the 3-electron bond should be weaker. [Note that it is not trivial to predict the effect of change in electron repulsion on bonding, or the influence of small changes in bond distance and nuclear repulsion.]

5. (4 min) Use the idea of plum-pudding orbitals to rank these three one-node MOs of the water molecule (A,B,C) by their relative energy (**low, medium, high**). Each orbital is shown in both top and side view, as is the molecular skeleton in the first row. **Explain** your reasoning in a very few words. (You need not give names or signs)



From the “plum-pudding” perspective these are all  $2p$  orbitals with a single nodal “plane”, and they would have the same energy except for differences in the location of the proton “plums” relative to the lobes of high electron density.

They all have the C nucleus very near their node, but orbital C has the H nuclei very near the maximum electron density. It is thus the lowest in electronic energy. Orbital B is highest because all nuclei are on its nodal plane.

6. (6 min) Use **hybridization theory to explain** whether the F-C-F angles of the  $\bullet\text{CF}_3$  radical should be larger or smaller than the H-C-H angles of the  $\bullet\text{CH}_3$  radical. **Describe the experiment** that justifies your prediction.

This problem is discussed in detail in frames 15 and 16 of Lecture 14 and at the end of the  $\text{XH}_3$  web page. The idea is that because the electrons in the C-F bond spend more time on F than on C (because the F AO is lower in energy), the C finds it more profitable to use more than average low-energy  $s$ -character for the odd, unshared electron, which it has all to itself. Thus the bonding hybrids on C have less  $s$ -character, more  $p$ -character, and form sharper angles with one another. Thus the bond angles are smaller in  $\bullet\text{CF}_3$  than in  $\bullet\text{CH}_3$ .

The experimental evidence was from ESR, which measured a large splitting due to magnetic interaction between the  $^{13}\text{C}$  nucleus and an unpaired electron **on** the nucleus in an orbital with substantial  $s$ -character.

[NOTE: Doubling of the IR “umbrella” frequency doesn’t work here to demonstrate non-planarity, because F is so much heavier than H that wave functions in the double minimum potential for umbrella distortion are much narrower than for  $\text{NH}_3$  and do not overlap significantly, so tunnel splitting is negligible.]

IR did in fact confirm the ESR result (see *J. Chem. Phys.*, **48**, 2265-2271, 1968), but it did so by demonstrating the presence of an absorption due to symmetrical *stretching* of CF bonds which would have been absent for a planar structure. If you remind me we could talk about this in connection with IR next semester.]

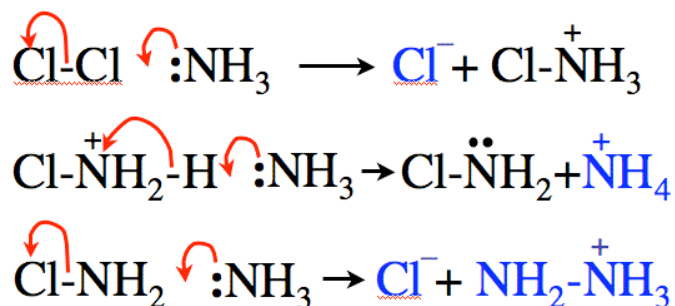
7. (5 min) How was the Bürgi-Dunitz angle for attack of N on C=O established **experimentally**?

This problem is discussed in detail in frame 13 of Lecture 17 and at the end of the “Where should  $R_2C=O$  be attacked?” web page. They compared the locations of the N, C, O atoms, and of the R atoms directly attached to C in a large number of crystal structures. In those structures in which the N was unusually close to the C, as if it were in the process of attacking the C=O LUMO, the N-C-O angle was about  $110^\circ$ .

[A number of answers were faulty because they did not mention that the experiments involved x-ray diffraction studies on many different crystals, in each of which the “reaction” was arrested at a different stage because of other groups in the molecules running into one another.]

8. (6 min) Use proper curved arrows to draw the 3 steps in a mechanistic scheme for conversion of  $NH_3$  to  $NH_2NH_3Cl$  by  $Cl_2$ .

This problem is discussed in detail in frame 5 of Lecture 17. It is important that curved arrows begin at the location of the relevant electron pair in the starting material and end where the pair is to be located in the product (on a lone pair, or between atoms to be bonded). Note that all the processes are “make & break”.



9. (6 min) According to “resonance” the properties of an amide are different from those expected for a molecule with simple carbonyl and amine groups. **Briefly explain three different ways** in which resonance influences the properties of protein polymers that contain multiple amide groups.

This problem is discussed in detail in frames 4 to 6 of Lecture 18 and on the [Intramolecular HOMO/LUMO mixing and "Resonance"](#) web page. The three important results of internal mixing of the unshared pair of N with the  $\pi^*_{C=O}$  are:

- Special stability and lack of reactivity (raised LUMO, lowered HOMO). This makes proteins chemically stable.
- Enforced planarity and inhibition of rotation about the N-C(=O) bond. This reduces flexibility in the protein chain and helps to stabilize structures like the  $\alpha$ -helix of Pauling (your chemical great-grandfather).
- $N^+ O^-$  polarity in a direction that caused favorable electrostatic interaction among neighbors in the  $\alpha$ -helix, making it more stable. This is often explained by saying that there is  $O \cdots H-N$  Hydrogen-bonding.

10. (9 min) Using **all** of the following four molecules **SKETCH SIX (6) LOCALIZED “frontier” orbitals** that would account for significant reactivity, and **EXPLAIN** the energy that makes each of them special. (Show orbital signs.)

Unusually high  $\sigma_{\text{C-Li}}$  HOMO, big on C (small shift down from C hybrid AO because Li starts so high in energy – low nuclear charge)

Li-CH<sub>3</sub>

Unusually low unmixed  $2p$  AO on Li (high in energy for an AO, but unshifted, thus lower than  $\sigma_{\text{C-H}}^*$ )

Unusually low  $\pi_{\text{C=N}}^*$  LUMO, big on C (small shift up from  $2p_{\text{C}}$  AO because of poor p overlap and mismatch with lower-energy  $2p_{\text{N}}$  AO)

R<sub>2</sub>C=N-H

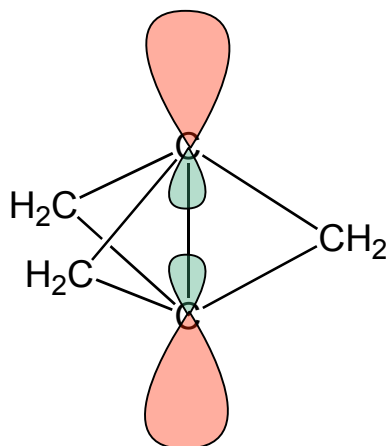
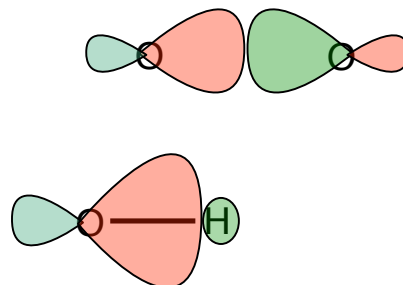
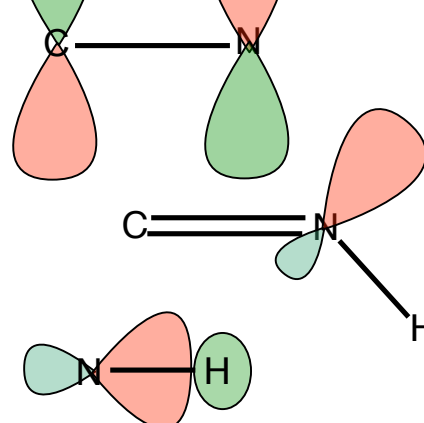
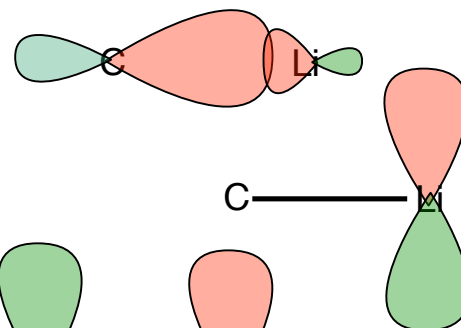
Unusually high unmixed  $sp$  hybrid AO unshared pair on N (lowish in energy for an AO, but unshifted, thus higher than  $\sigma_{\text{C-H}}$ )

[Note that  $\sigma_{\text{N-H}}^*$  is NOT so very unusual, despite poorish energy match. The pK<sub>a</sub> of NH<sub>3</sub> is 38, not a strong acid]

Unusually low  $\sigma_{\text{O-O}}^*$  LUMO (reasonable overlap, but  $2sp_{\text{O}}$  AO is pretty low because of largish nuclear charge)

R-O-O-R

[Note that  $\sigma_{\text{O-H}}^*$  is NOT so very unusual, despite poorish energy match. The pK<sub>a</sub> of H<sub>2</sub>O is 16, not a very strong acid, but better than NH<sub>3</sub>.]



Poor overlap of  $2sp_{\text{C}}$  hybrid AOs that point away from one another results in small shift of  $\sigma_{\text{C-C}}$  HOMO and  $\sigma_{\text{C-C}}^*$  LUMO from the AO energies, thus unusually high and low, respectively.

