Chemistry 125 Second Examination Preliminary Answer Key

October 18, 2004

1. (6 minutes) **R** functions for H-like atomic orbitals use ρ (Greek *rho*) rather than r. The formula for ρ in terms of r is given at the right. .Use this formula as an aid to **explain** the relationship between the **energy** of an H-like atom and its **nuclear charge**.

$$\rho \equiv \frac{2Z}{na_o}r$$

The size of the (negative) energy of an H-like atom is proportional to Z^2. This is because of its two components, kinetic energy and potential energy, are each individually porportional to Z^2.

The average kinetic energy involves the second derivatives of R(r) with respect to r. Using ρ for r means that we want the second derivative of R(Zr). This second derivative is Z^2 times the second derivative of R(r) itself. Thus the kinetic energy is proportional to Z^2.

The average potential energy is proportional to two factors, each proportional to Z.

The first factor is that Coulombic energy at any given distance is proportional to the nuclear charge, Z.

The second factor is that the orbital is condensed because of the larger nuclear charge. This scaling of ρ shows that with an increase in Z, the wave function will have the same character for a smaller r as the original orbital had for a larger r. That is, the wave function is condensed by a factor proportional to Z.

[I apologize that this first question was so long, I had intended to ask about averagepotential energy only.]

2. (4 min) Name the **problem** one might address by replacing Z by an "effective" Z (**Z_{eff}**) in the atomic R function. [Just a name will do; no description necessary]

e-e Repulsion

Name a **better** (but still understandable) **theoretical technique** for addressing this problem. [Just a name will do; no description necessary]

Self-Consistent Field (SCF)

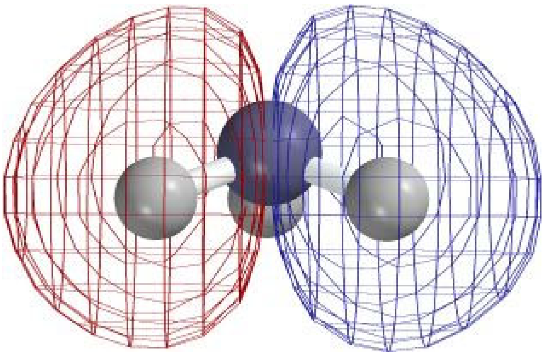
3. (6 min) Explain **in terms of the most important orbital mixing** why BH_3 and CH_3 form stable, covalently-bonded dimers (B_2H_6 and C_2H_6), but NH_3 does not give a covalently-bonded N_2H_6 dimer.

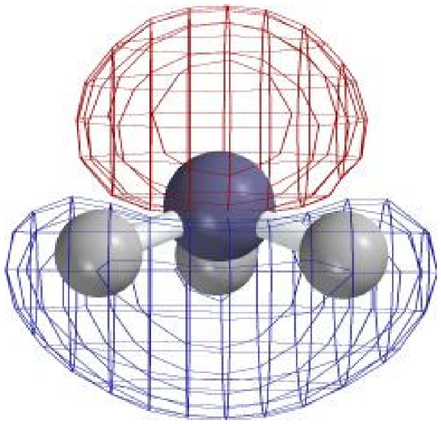
With an odd number of electrons, CH_3 has a SOMO. The mixing of SOMO with SOMO is always strongly favorable.

BH_3 has both an unusually high HOMO (the B-H sigma bond, high because B has a smaller nuclear charge than C, thus poor E-match) and an unusually low LUMO (the vacant 2p AO of B). These can mix to form a 3-center-2-electron "Y" bond (in fact two such bonds form).

NH_3 has an unusually high HOMO (the unshared $sp^{\sim 3}$ electron pair on N). The NH sigma* LUMO is indeed lower that CH sigma*, but it is an antibonding orbital. If a HOMO were to mix with this LUMO, the proton would be transferred to give NH_4^+ and NH_2^-, not a covalently bonded dimer.

4. Below are shown images of two molecular orbitals of NH_3 (drawn by the program *Spartan*). In each case the nets covering the two lobes were drawn with different colors.





A. (4 minutes) **Explain** the **shape and relative energy** of these two orbitals viewing them as **"united-atom"** orbitals of a Ne atom with a fragmented nucleus.

These MOs are analogous to 2p AOs of Ne, the first with a vertical, the second with an horizontal node. Electrons in the left orbital are lowered in energy by having hydrogen nuclei near the maximum in their density (in the middle of the two lobes). All nuclei in the right orbital are far from the locus of maximum electron density, so this "2p"-like orbital is higher in energy (in fact it is the unusually high HOMO of ammonia).

B . (4 minutes) **Describe** the MO on the **left** as a mixture of simpler orbitals, and **explain whether this orbital** should make the molecule especially reactive as an acid or base.

The MO on the left is a mixture of two C-H sigma bonds with little overlap between them. The energy of this combination is thus almost identical to the standard, non-reactive HOMO. This would be neither an acid nor a base.

5. (7 minutes) Explain why it makes sense, **in light of EXPERIMENTAL evidence**, to approximate a bonding orbital as a linear combinations of atomic orbitals. [Besure to mention the role of overlap.]

The relevant experimental evidence is difference electron density from x-ray diffraction, which shows more electron density between the bonded nuclei than would be expected from superposition of the isolated atoms.

If one writes the MO as $1/\sqrt{2}\ (A + B)$, the corresponding electron density is

$1/2\ (A^2 + B^2 + 2\ AB)$. For occupancy by two electrons the total electron density would be $A^2 + B^2 + 2\ AB$, where the superposition of the two atoms would give $A^2 + B^2$. The 2 AB difference density is large only between the two nuclei, where both AOs have a significant value, and increases the bonding density in this region, as observed experimentally.

(Of course the MO needs to be scaled down a bit for normalization, so that the bonding density represents a shift of density from the atoms to the bonding region, see next question.)

6. (7 minutes) Explain how the **normalizing constants** used in combining 1s AOs of a **pair of helium atoms** (to approximate the electron density in the lowest two MOs) result in net repulsion between the two atoms.

[Hint: it would help to write an expression for the total electron density.]

The density from the bonding electron pair would be $2 \times <1/2\ (A^2 + B^2 + 2AB)$

The density from the anti-bonding electron pair would be $2 \times >1/2\ (A^2 + B^2 - 2AB)$

When these are added to give the total density the > and < contributions tend to cancel for A^2 and B^2, but there is the –AB density depletion dominates in the overlap region. This means that the net effect is modest antibonding.

(Of course more accurate values of the normalizing constants show that this depletion of density appears on the atoms.)

7. (6 min) Explain briefly how the energies of wave functions for a double minimum potential are relevant to the **EXPERIMENTAL** demonstration that NH_3 is non-planar in its minimum-potential-energy geometry.

If NH_3 is non-planar in minimum-energy, the one-dimensional potential energy plot for out-of-plane distortion must have a symmetrical double minimum with a maximum for the planar geometry. This means that there will be mixing of wavefunctions centered in the left well with wavefunctions of exactly the same energy centered in the right well. This mixing will create pairs of overall wave functions, one with favorable (nodeless) combination of the equivalent "local" waves, one with an additional node. If the planar energy barrier is higher than the energy of these wavefunctions, there will be modest overlap and a smallish "tunneling" splitting of the energies. Thus while a single-well potential with a planar minimum would give roughly equally spaced energy levels, the double well would give pairs of closely-spaced energy. The infrared spectrum of NH_3 shows a pair of closely spaced absorptions (at 968 and 932 cm^{-1}), demonstrating the closely spaced levels of a double minimum potential (with an "inversion barrier" of about 3 kcal/mole).

8. (6 min) Mixing vacant orbitals:

A. Why may one often ignore the mixing of vacant orbitals?

Because there are no electrons in these orbitals, they are irrelevant to the actual energy and electron distribution of the molecule.

B. Why might one sometimes care about the **mixing** of two **vacant** orbitals (*e.g.* $\sigma^*_{C\text{-}H}$ and $\sigma^*_{C\text{-}F}$) of a single molecule?

One cares about the energy and structure of a vacant orbital when considering a process in which it will acquire electrons (e.g. as a result of HOMO/LUMO mixing or the absorption of light energy). In the case of ethyl fluoride the actual LUMO is a mixture of $\sigma^*_{C\text{-}H}$ with $\sigma^*_{C\text{-}F}$, so a high-energy HOMO (of hydroxide for example) can attack not only the backside of the C-F bond to give ethyl alcohol and fluoride ion by a substitution reaction, but also the H of the C-H bond to give the C=C bond of ethylene, water, and fluoride by an elimination reaction.