Chemistry 125 Second Examination Name _____

October 18, 2004

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).

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**.

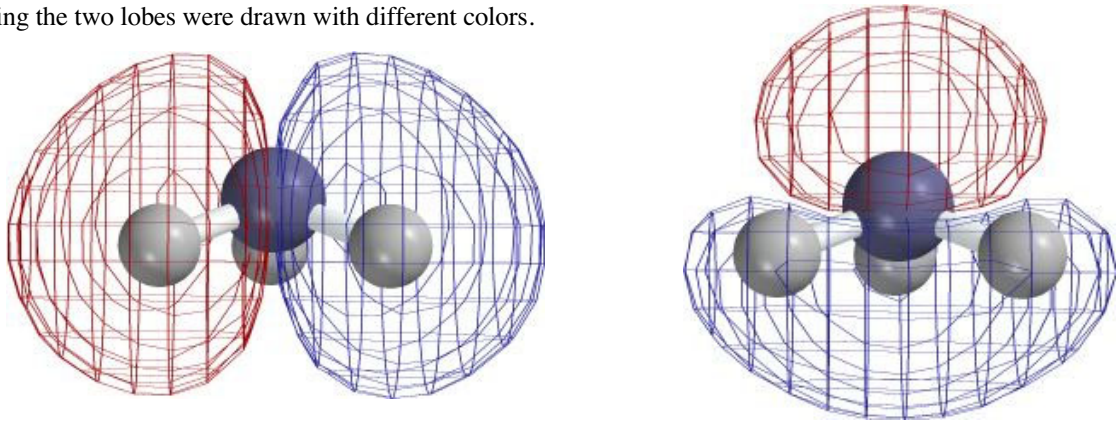
$$\rho \equiv \frac{2Z}{na_o} r$$

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

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

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.

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.

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.

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.]

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.]

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.

8. (6 min) Mixing vacant orbitals:

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

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?