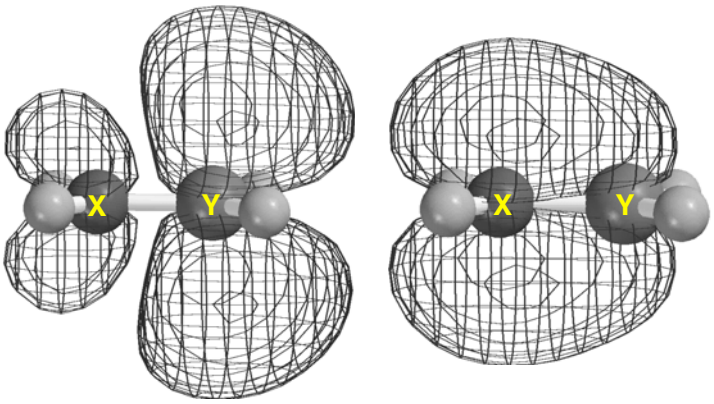
Chemistry 125 Second Examination Name _____

October 17, 2005

The exam budgets 50 minutes, but you may have 60 minutes to finish it. Good answers can fit in the space provided.

1. These two diagrams illustrate the HOMO and LUMO of an uncharged molecule H_2XYH_2, where the four lighter balls are H, and the two darker balls are X and Y, atoms from the second row of the periodic table.
(Relative wavefunction signs should be obvious.)



A) (2 min) Under **each** diagram write the orbital's name (HOMO or LUMO). **AND** name the single **H-like** "united-atom" orbital to which it is "plum-pudding" analogous.

B) (3 min) **Identify** the atoms **X** and **Y** as specific second row elements, **AND** explain the shapes of these orbitals.

C) (2 min) **Draw two** reasonable resonance structures for H_2XYH_2 (relabel X and Y as in your answer to **B**)

D) (1.5 min) On the figure at the top **draw an arrow to show the direction** from which you would expect hydroxide to attack the LUMO **AND** write a few words to **explain** your choice of direction .

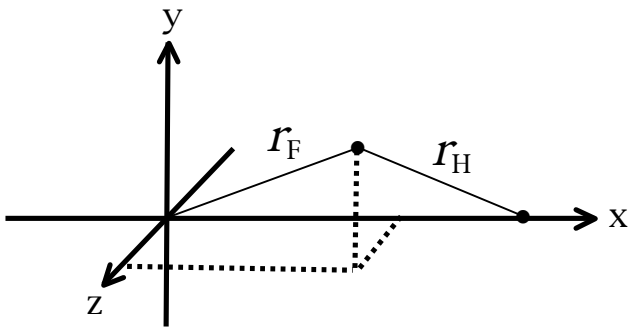
E) (3.5 min) Draw structures with **curved arrows** to explain how attack by hydroxide would influence the **XY distance**.

2. (3.5 min) Mention **two ways** Chladni figures are relevant to quantum mechanics.

3. (4 minutes) Briefly explain the relationship between SCF calculations and correlation energy.

4. (6 minutes) **Draw** an orbital-mixing energy diagram to explain how BH_2-CH=CH_2 might differ in **reactivity** from BH_2-CH_2-CH_3.

5. Consider the coordinate system shown, where a typical point at (x,y,z) is at a distance r_F from the origin and at a distance r_H from a fixed point on the x axis.



a) (9.5 min) Explain why one might be interested in the value of the following function:

$$xe^{-(k_1 r_F + k_2 r_H)}$$

That is, where would it appear in a quantum mechanical calculation, and what would be its significance?

[Remember: $e^{-(k_1 r_F + k_2 r_H)} = e^{-k_1 r_F} e^{-k_2 r_H}$]

b) (3 min) In the formula above, what might make k_1 different from k_2?

6. (12 minutes) In the infrared spectrum of interstellar clouds there is a band at **903.39 cm^{-1}** which astronomers have recently assigned to the out-of-plane bending vibration of the ion **NH_3^+** (ammonia which has lost one electron).

Reasoning from what you know of XH_3 molecules, **explain** whether NH_3^+ at its lowest potential energy should be **planar or pyramidal AND** rationalize the **903 cm^{-1}** frequency.