# Chemistry 125   Second Examination Answers
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.

OH⁻

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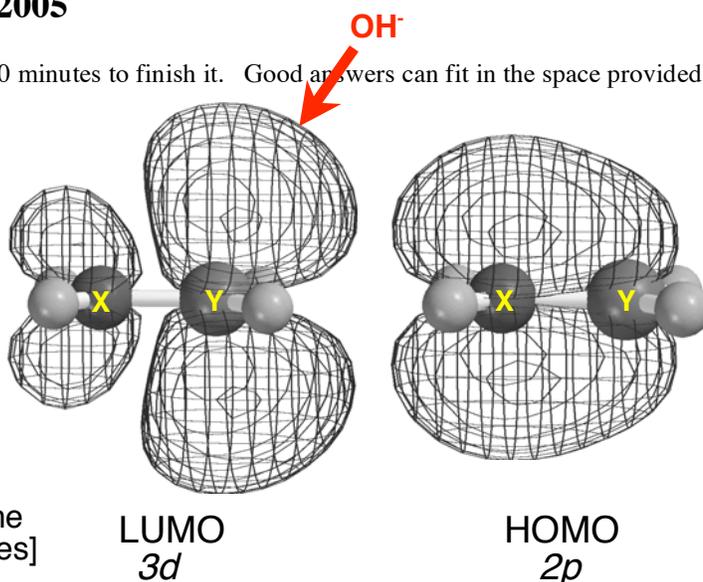
A) (2 min) Under **each** diagram write the orbital's name (HOMO or LUMO). **AND** name the single **H-like** "united-atom" orbital to which it is "plum-pudding" analogous.

[N.B. these are π* and π *MO*s, but the question asks for analogous AO types]

LUMO   HOMO
3d   2p

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

X and Y obviously have different nuclear charge to give unsymmetrical π/π * MOs. X must have the higher nuclear charge, since it dominates in the more favorable π HOMO, which has one node, rather than two. Since the molecule is uncharged, the X and Y must be **N** and **B**, respectively.

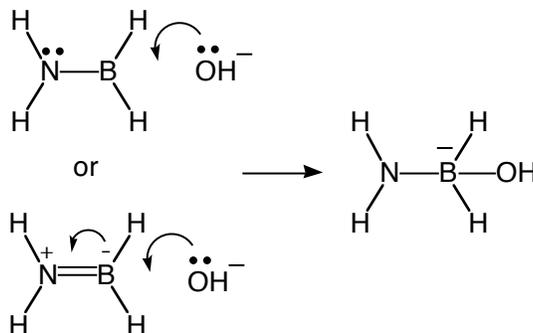**C)** (2 min) **Draw two** reasonable resonance structures for H_2XYH_2 (relabel X and Y as in your answer to **B**)

[N.B. tetravalent N is positive; tetravalent B, negative]
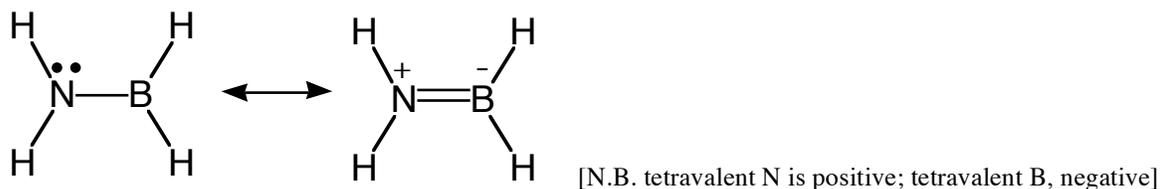
D) (1.5 min) On the figure at the top **draw an arrow to show the direction** from which you would expect hydroxide to attack the LUMO **AND** write a few words to **explain** your choice of direction .

To maximize overlap the HOMO of OH⁻ approaches the large lobe of the LUMO from a direction as far as possible from the LUMO's nodes.

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.

1) They illustrate the concept of different nodes (linear and circular in 2D).

2) Increasing numbers of nodes give increasing frequency (energy).

3) They illustrate degeneracy (same frequency for different combinations of nodes).

4) They were explained using the same kind of mathematics subsequently used to solve Schrödinger's equation for 1-electron atoms.

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

SCF calculations attempt to treat e-e repulsion in many-electron systems by holding all electrons but one in fixed average clouds for purposes of calculate the potential in which the one electron moves. This is erroneous because the other electrons can shift dynamically to avoid close approach to the electron in question. Thus SCF must overestimate e-e repulsion. This error is called "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.

BH_2-CH_2-CH_3 BH_2-CH=CH_2

$\sigma*_{C\text{-}C}$ ——

raised LUMO —— $\pi*_{C=C}$

—— B   B ——

lowered HOMO

$\pi_{C=C}$

$\sigma_{C\text{-}C}$ ——

In the ethyl (CH_2CH_3) case on the left there is little mixing between the unusually low LUMO on B and the σ HOMO because of poor E-match. In the vinyl ($CH=CH_2$) case on the right there is substantial mixing with the π HOMO, so that both LUMO and HOMO become less reactive. This is a case of important resonance stabilization. [Note the analogy with the relatively unreactive amide group.]

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.

Consider t

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

The function in question is a PRODUCT of $xe^{-k_1 r_F}$ and $e^{-k_2 r_H}$. The first is a *2p_x* orbital
centered at the origin (F). The second is a *1s* orbital centered on the fixed point to the right
(H).

Such a product arises in the "2AB" cross-term from squaring the LCAO molecular orbital
($2p_{xF}$ + $1s_H$), the σ bond of the HF molecule. This is the "overlap" function that gives rise to
increased electron density between nuclei resulting in bonding.

[Product functions also occur in two- (or many-) electron wave function, but this function
is of only *x,y,z*, the coordinates of a single electron. Thus it is an LCAO overlap
function, not a two-electron function.]

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

These constants determine how rapidly the exponentials decay upon moving away from
the nuclei. The constant for F should be greater than that for H, because the higher nuclear
charge holds the electrons closer to the nucleus.

[In fact, k_1 should be 9/2 × k_2, 9 for the 9-fold greater nuclear charge, but divided
by 2 because of the increased principal quantum number for *2p vs 1s*. This is the
scaling of ρ *vs r*].
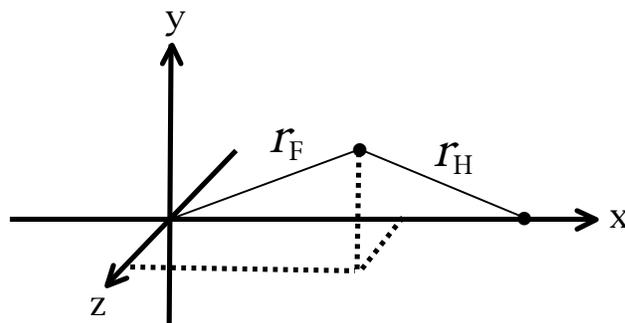
6. (12 minutes) In the infrared spectrum of interstellar clouds there is a band at **903.39 cm^{-1}** which astronomers have recently assigned to the out-of-plane bending vibration of the ion **NH$_3^+$** (ammonia which has lost one electron).

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.

NH$_3^+$ has the same number of valence electrons as CH$_3$, so the argument that three N-H bonds will be strongest with sp^2 hybridization, while the central atom with four singly occupied orbitals doesn't care ("whatever") about hybridization would seem to be the same predicting a single minimum potential for out-of-plane bending.

There is a difference, however, which I didn't really expect anyone to see.

The extra proton in the N nucleus causes the N-H bonding electron pairs to be held closer to the N than to the H nucleus. Thus from the point of view of the N atom, there is more than one electron in each bonding AO, but only one electron in the unshared orbital. [This reverses the effect that makes NH$_3$ pyramidal because there is one electron in each bonding AO, but two electrons in the unshared AO.]

This means that NH$_3^+$ has more reason to be flat, and more resistance to bending, than does CH$_3$. Since the vibration of CH$_3$ comes at 606 cm^{-1}, one expects a higher vibration frequency (903 cm^{-1}) in the ammonia cation case.