Chemistry 125   Second Examination Answers October 25, 2006

	Average	1/3 of scores >	2/3 of scores >	
This exam	82.2	89	78	**Congratulations!**
Sum of 2 exams	154.4	166	148	

1. (1 minute) Altogether about **how long** does it take at the APS source to mount a typical

enzyme crystal and collect the x-ray data necessary to determine its molecular structure?   __~15 min___

2. (4 min) Mention **TWO WAYS** in which the study of Chladni figures in acoustics is relevant to the subject of H-like wave functions.

They illustrate different geometrical forms of nodes (circles like atomic spheres, and linear like atomic planes).

They show that different combinations of nodes can give identical energies (vibration frequencies or pitches), like different AOs with the same principal quantum number *n.*

They were the physical problems that motivated the development of the mathematical techniques (differential equations) that are used to solve the Schrödinger equation for H-like atoms.

They provide a 2-dimensional bridge for understanding between 1-dimensional wavefunctions and 3-dimensional wavefunctions.

3. (2 min) Why are H-like wave functions formulated using ρ rather than *r* to measure distance?

So that the same functions may be used for atoms of different nuclear charge (which scales r to give ρ).

[Also so that the same $e^{-\rho/2}$ term occurs in the radial functions for all principal quantum number.]

4. (4 min) Explain why solving the quantum mechanical problem of the He atom with three charged particles is MUCH more complicated than solving the H atom with two, **AND NAME** (you need **not** describe) **TWO** methods that are used to address the complication.

The H-like atom is easy because the potential depends on only one variable (r), which means that the wavefunction may be written as a product of three functions of one variable each (using spherical polar coordinates). The potential energy of a system with two electrons and a nucleus depends on three variables (distances among all pairs including electron-electron repulsion), and true solutions may not be written as products (although that is what the orbital approximation attempts to do).   [It is true that more variables are involved in the three-particle case, but this would not be such a serious problem, if the solutions could be written as products of one variable as in the H-atom case.]

Electron repulsion is treated approximately by Z_{eff}, SCF, CI, and DFT methods.

5. (4 min) Give **TWO** reasons why it is sensible to formulate a molecular orbital as a weighted sum of atomic orbitals.

Because the shape of a molecular orbital should look much like the atomic orbitals in the vicinity of nuclei where the potential energy is dominated by the closest nucleus (this is confirmed both by electron densities revealed by x-ray diffraction and by the smallness of the change in energy due to bonding compared to the energy released when atoms are formed from nuclei and electrons).

Because squaring a weighted sum of AOs gives a total density that can be viewed as a weighted sum of two atomic densities distorted to shift some electron density into the internuclear region from regions that are more remote from the two nuclei, as shown by maps of electron difference densities from x-ray diffraction.
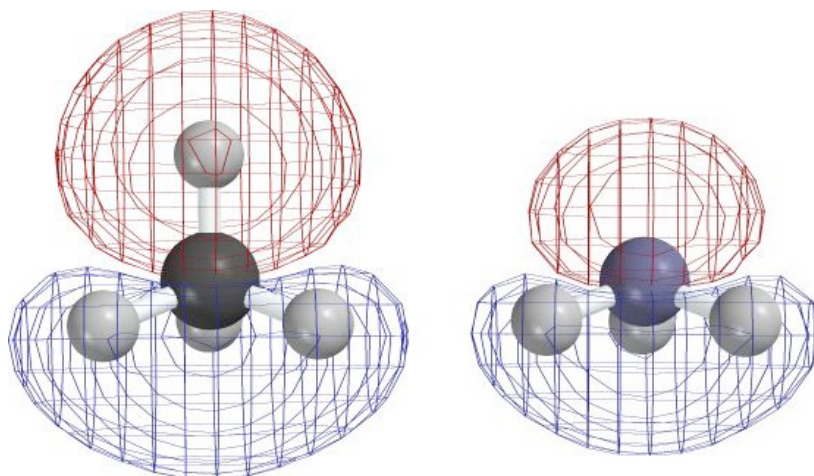
[I am sorry that some students focused exclusively on the word "weighted" and discuss only the asymmetry of MOs made from AOs of mismatched energy. I used "weighted sum of atomic orbitals" as a less jargon-ridden substitute for LCAO.]

6. (4 min) Explain **why**, having formulated an MO as a SUM of atomic orbitals, it is relevant to be interested in a **PRODUCT** of atomic orbitals (the overlap integral). In your answer **mention** both **mathematics** and relevance to **experimental data**.

When the sum $1/\sqrt{2}\ (A+B)$ is squared to find the electron density, the cross term $(A*B)$ gives the change in density from a simple weighted sum of the atomic orbital densities, $1/2\ (A^2 + B^2)$. This product is the mathematical expression of the increase of electron density in the overlap region between the nuclei that is observed in difference density maps obtained from x-ray diffraction.

7. (4 min) CH_4 has the same number of protons and of electrons as does NH_3. The MOs illustrated for these species have very similar shapes - red lobe above, blue below. **Explain** briefly which of the two orbitals should be higher in energy.

The central heavy nucleus lies near the node of this **$2p_z$-like orbital**, in a region of very low electron density, while the hydrogen nuclei lie in regions of relatively high electron density. This is especially true of the top proton in the CH_4 orbital. In NH_3 this proton has been merged with the N nucleus and thus pulled away from the position where it can do the best job of stabilizing the electrons **of this orbital**. Thus it is not surprising that the energy of **the CH_4 orbital** (-0.546 a.u. according to an SCF calculation) **is considerably lower** than that of the NH_3 orbital (-0.424 a.u.). [1 a.u = 628 kcal/mole]
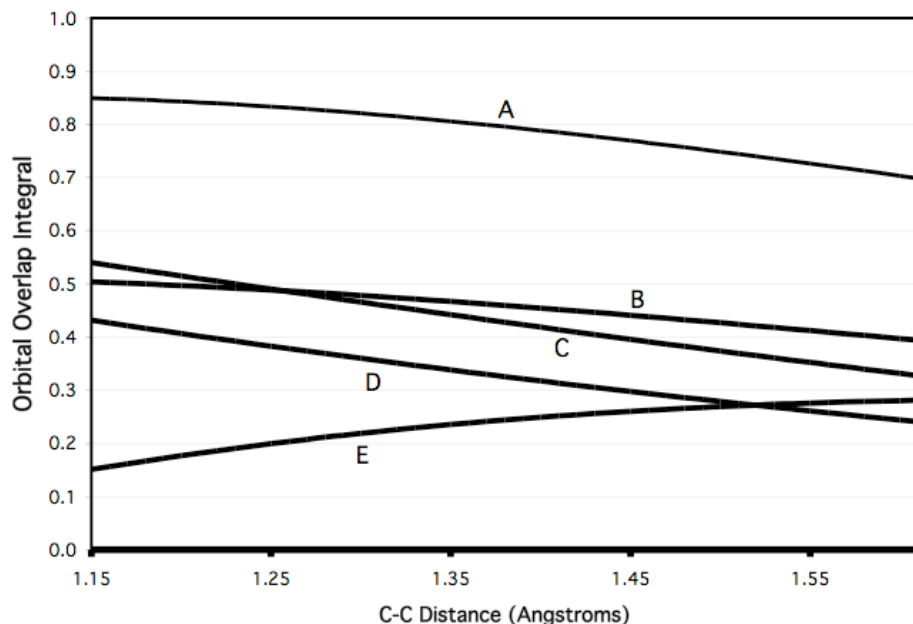

$$CH_4 \hspace{4cm} NH_3$$

[Of course the *1s* and *2s*-like orbital energies are much lower for NH_3, because of the extra proton has moved into the heavy atom nucleus, where these orbitals have very high electron density. For *1s* the NH_3 advantage is -15.5 *vs.* -11.2 a.u.; for *2s* its advantage is -1.15 *vs.* -0.95 a.u. Thus overall NH_3 is much more stable than CH_4 (-56.2 *vs.* -40.2 a.u.), **but** its HOMO is 0.12 a.u. = 77 kcal/mole higher in energy. Just stating that NH_3 is reactive because of its high HOMO was not a satisfactory answer if there was no explanation as to **why** it is high.]

8. (5 min) Give **plausible identifications** for the five pairs of pure or hybrid atomic orbitals of carbon atoms whose overlap integrals at various distances are shown by curves A-E below.   In every case but one the two AOs are identical.   (Feel free to give brief explanations if you want to be eligible for partial credit despite having made a mistake)

[limit at d=0]

A ___sp-sp___ 0

B ___s-p___ 0

C ___s-s___ 1

D __p-p (π)__ 1

E __p-p (σ)__ -1

9. (3 min) Why are valence orbitals so much more important in making bonds than core orbitals are?

     Primarily because core orbitals are so close to the nucleus that they have very poor overlap with orbitals on other atoms. (They also have poor energy match with valence orbitals of other atoms.)

10. (5 min) Why is HOMO/LUMO interaction between two molecules so much more important for reaction than interaction among any other pair of orbitals?

     UMO-UMO overlap is irrelevant because they contain no electrons; thus their energy is hypothetical.

     OMO-OMO overlap is mostly irrelevant because both of the new MOs are occupied by two electrons, so their energy shifts cancel (slightly unfavorable when normalization is taken into account).

     Most OMO-UMO overlap is irrelevant because there is poor energy match, and thus negligible mixing.'

     Highest occupied and lowest vacant orbitals have the best energy match, and thus give maximum mixing and energy shift of partially filled orbitals (assuming reasonable overlap).
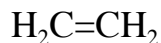
     (Actually SOMO-SOMO interaction is very important in the rare cases where there are such orbitals – that is, when reaction has not already occurred.)

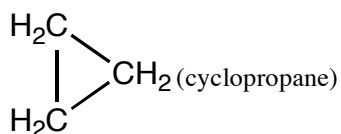**11.** (7 min) Explain in terms of orbital energies what makes each of the following 3 molecules reactive:

BH_3

> Unusually low LUMO: unmixed *2p* AO of B atom
>
> Unusually high HOMO: σ_{B-H} because of poor energy match between H *1s* and B sp^2 (low nuclear charge)

$H_2C{=}CH_2$

> Unusually high HOMO: π_{C-C} because of poor π overlap between C *2p* orbitals, which start out higher than *sp*-hybrid AOs

$H_2C \diagdown$
$\quad\quad\diagup CH_2$ (cyclopropane)
$H_2C \diagup$

> Unusually high HOMO (and unusually low LUMO) because of poor overlap in bent bonds between sp^n bonds that cannot point toward one another, since the smallest possible angle between *p*, or *sp*-hybrid AOs on the same carbon is 90°, while the C-C-C angle is 60°.

12.   (7 min) **Explain** how **spectroscopic** evidence (**not** x-ray) can be used to show that NH_3 is pyramidal at its minimum of potential energy.

> The out-of-plane (umbrella) bending of NH_3 appears as two peaks at very similar frequency (932 and 968 cm^{-1}). This is expected for a double-minimum potential because of the smallish overlap, and thus modest splitting, between excited vibrational wavefunctions in the two wells separated by a planar maximum of potential energy. [A single minimum would have more widely spaced energy levels – as in the Hooke's Law potential, where the energies are odd multiples of the lowest (zero-point) energy.]
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> Note that Electron Paramagnetic Resonance evidence is irrelevant for NH_3, because it requires the magnetism of a molecule with an odd number of electrons (or at least unpaired electrons).