

Chemistry 125 First Examination Answer Key (preliminary)

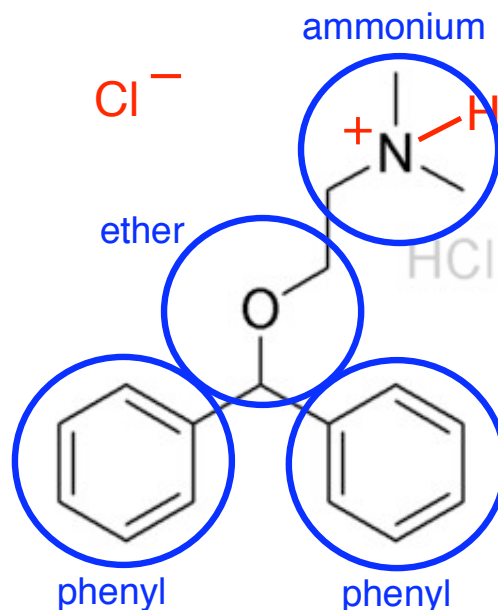
September 28, 2007 Mean Score 72.9 (1/3 > 79 ; 2/3 > 70)

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 allotted 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).
Make sure you are answering the question, not just saying something vaguely relevant to its topic.

1. The following structure is commonly drawn for the antihistamine Benadryl. This structure is misleading, because the HCl reacts with the organic molecule to form what used to be considered a “*pentavalent*” atom.

[George Rieveschl, the organic chemist who invented Benadryl at the age of 26 in the early 1940s, died the day before this exam. See [NYTimes obituary](#) Sept. 29, 2007.

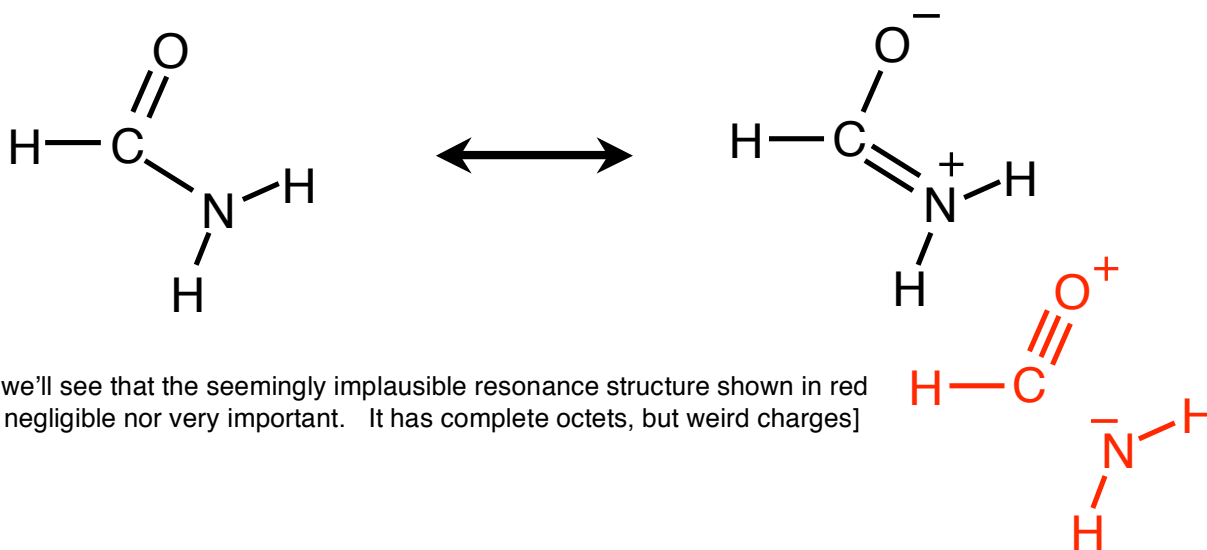


- A) (4 min) Scratch out the HCl and redraw its atoms to show a proper Lewis structure with lines for bonds. Write a few words to help explain the “*pentavalence*.”

The fourth bond from N to H, is formed by N's sharing its unshared pair of electrons with the proton from HCl. This gives the N a formal + charge, which causes it to attract chloride through an ionic bond. From the point of view of 19th Century chemists, before G. N. Lewis, this made normally trivalent N pentavalent.

- B) (3 min) **Circle** and **name** each **functional group** in your improved structure of Benadryl.

2. (4 min) Draw bond lines and necessary formal charges among the atoms below to show **the two most reasonable “resonance structures”** for formamide. Draw the proper **arrow symbol** between the two structures.



[Later on we'll see that the seemingly implausible resonance structure shown in red is neither negligible nor very important. It has complete octets, but weird charges]

3. (2.5 min) **Who** said "I cannot bear the Thought of being made Master of a Jewell I know not how to wear"? **What did he mean?**

Samuel Pepys wrote this in a letter to Isaac Newton to explain why he wanted to learn to make a calculation himself, rather than just accepting the answer from Newton. He wanted to be able to solve other related problems. He wanted to know why.

4. (2.5 min) Why did J. J. Thomson propose that negative corpuscles (or electrons) were arranged **INSIDE** a cloud of positive charge density?

Earnshaw's Theorem showed that a set of particles interacting through inverse-square forces (like Coulomb's Law) could not have a stable structure for separated particles. By having the negative particles **inside** the positively charge cloud, it was possible to have structures (which he hoped would explain periodicity).

5. (3 minutes) Explain how a discovery by Chladni relates to the idea of "**degenerate**" orbital energies.

Chladni observed that vibrational modes with different patterns could give the same vibrational frequency (pitch). In the same way, wave functions for one-electron atoms with the same principal quantum number (n), but different combinations of nodal surfaces, can yield the same energy.

A key feature of this question was degeneracy (note the **bold face**), which some answers did not address.

[Note that Chladni was VERY far from knowing anything about electrons, since he died in 1827, and electrons weren't discovered until 1895. He did acoustics, but the waves that were involved, especially 3-dimensional ones, proved analogous to Schroedinger's wave functions of 1926.

It is interesting that there is no degeneracy in one dimension (only one way to get nodes, e.g. one point for one node), and less degeneracy in 2-dimensions (one circle or one line for one node), than in 3-dimensions (one sphere or any of *three* different planes for one node).]

6. (5 minutes) **How and Why** does one **hybridize** atomic orbitals? Explain using the **example** of an H-like atom in an electric field.

Hybrid orbitals are a **weighted sum of hydrogen-like orbitals for a single atom**. They are created to provide a simple approximation to the wave functions that would result from a potential that is more complicated than simple coulombic attraction to a single nucleus. (They have the advantage of preserving the virtues of the shape of the pure H-like orbitals in cases where attraction to the nucleus provides the most important part of the potential energy – especially when the orbitals being combined, or mixed, that is **added**, are degenerate, *i.e.* have the same principal quantum number.)

For example, when one imposes an electric field on an H atom, it will not move, because it has no overall charge, but it will distort with the nucleus shifting one way and the electron cloud shifting the opposite way. Adding a $2p$ function (which is positive on one side of the nucleus and negative on the other) to a $2s$ function (which has the same sign on both sides) gives a new function which is larger on one side than on the other. This the electron cloud is shifted off-center. (This extension is maximum for 50:50 mixing of $2p$ with $2s$.)

[A number of answers failed to address the second part of the question about the electric field.

I am sorry that so many people failed to see that a hybrid orbital results from simple addition of two normal H-like orbitals on the same atom. Perhaps the lecture was unclear; if so, it is a pity that no wiki was prepared on this topic to help clarify the situation.]

7. (4 minutes) Explain how the average potential energy of a hydrogen-like atom scales with the nuclear charge. That is, if the nuclear charge is doubled, **how much** does the average potential energy change, and **why**?

The average potential energy of a hydrogen-like atoms scales with the **square** of the nuclear charge. That is, doubling the nuclear charge will lower the average potential energy by a factor of four.

One factor of two in the energy come from the proportionality of coulombic energy at any particular distance to the nuclear charge ($V = Ze/r$, doubling Z doubles V for fixed r).

The other factor of two comes from shrinking the atom in proportion to the charge. (rho is proportional to Z times r, so doubling Z gives the same rho value for an r distance only half as great.)

8. (4 minutes) Which of the following techniques offers the **best** resolution (most detail), and which the **least**? **Explain**.

Scanning Tunneling Microscopy (intermediate – tip can sharpen to a single contact atom)

Atomic Force Microscopy LEAST – The tip used to probe the sample in AFM is about 20 nm wide. With such a great contact area it simultaneously touches hundred of molecules and cannot easily distinguish among them, though it can measure the average height with sub-Å resolution.

X-ray diffraction BEST - Using short-wavelength x-rays (and high-angle scattering) and averaging over an entire crystal gives positional accuracy to within 0.001Å.

9. (6 min) **How** is an electron **difference (or deformation) density** map prepared? Cite an **example** where it revealed “pathological” bonding. Be as **specific** as you can.

An electron difference density map is prepared by subtracting the electron density expected for undistorted, spherical atoms from the experimental electron density measured by x-ray diffraction (or by another method). Positions for the atoms to be subtracted are determined from the centers of electron density in the experimental map.

The weirdest example is the absence of difference density (usually associated with bonding) between atoms that participate in two three-membered rings of a polycyclic framework. Somewhat less weird are other bonds in the same three-membered rings, where the maximum of deformation density lies outside the ring from the line of centers between the bonded atoms (as if the bonds are bent).

Another weird case is a C-F bond (or indeed any bond involving atoms with more than 4 valence electrons). In such cases subtracting a spherical atom gets rid of deformation density where the bond should be. (In such cases it is better to subtract atoms which are prepared for bonding by having single electrons in some quadrants and electron pairs in others.)

5. The diagram is *part* of an “Erwin Meets Goldilocks” plot with two trial wave functions for the potential energy, which is shown in gray.

A) (2 min) Draw a horizontal line showing the **TOTAL ENERGY** for the ψ curve that becomes horizontal at the right. Be as accurate as you can.

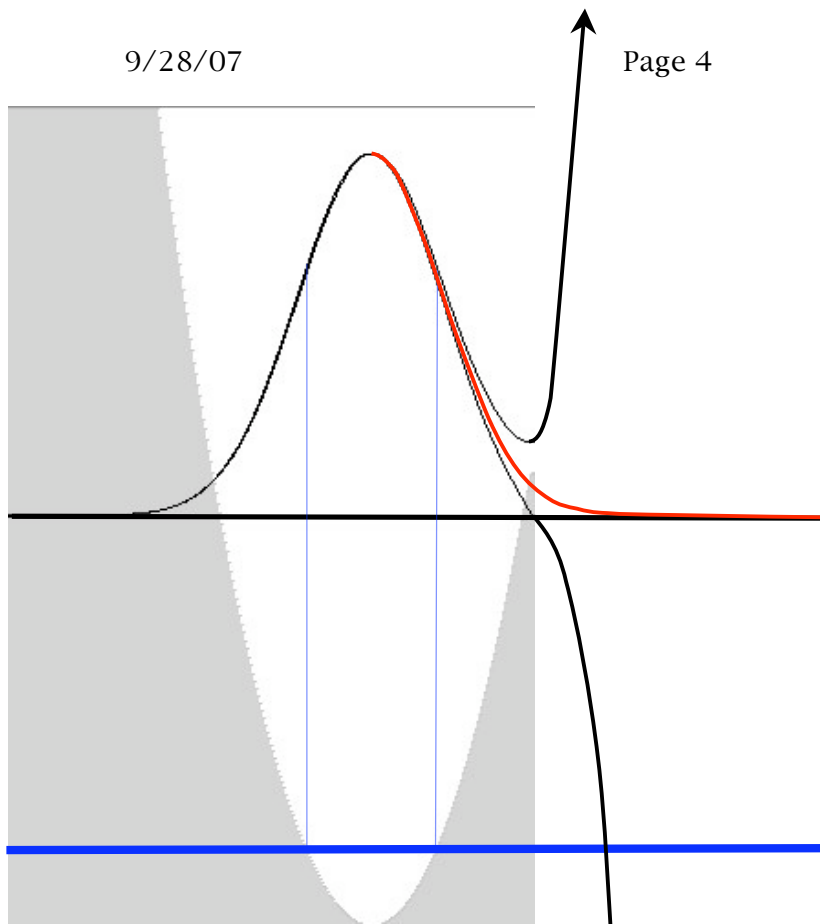
(Intersect PE curve below inflection points)

B) (2 min) Is the total energy for the other trial ψ (the one that has a value of 0 at the right) **higher or lower** than that the one you drew in A?

Explain your thinking.

The second trial ψ curves more strongly toward the baseline, this means that it has a somewhat higher total energy than the first.

Total Energy



C) (3 min) Assuming that this is a Hooke’s Law single-minimum problem, **draw** in the **correct lowest-energy ψ function** (NOT its energy), and **extend all three ψ curves** to the right edge of the page.

D) (5 min) Now assume that this potential is in fact the left half of a symmetric double minimum, and the original two ψ traces are part of **correct** solutions. **Explain** how one ψ may be considered “bonding”, and the other “antibonding”.

The upper curve has less curvature toward the baseline than the single-minimum red curve, and therefore less energy. So a particle described by this wave function of the double-minimum potential has lower total energy than it would have in the lowest-energy function of the single minimum. That means that the situation with the minima separated from one another, so that they behave independently and have the energy of the single-minimum situation, is of higher energy than the situation where they are close together. Since it requires energy to separate the minima, they can be said to be bound together, and the wavefunction can be considered “bonding”.

The lower curve has more curvature toward the baseline than the single-minimum red curve, and therefore more energy. By an analogous argument, this function can be said to be “antibonding”.

[Note that the question of “bonding” provides a great illustration of the importance of “**Compared to what?**” To see that there is a reason for bonding we need to **compare** the energy of the wave function for the **double minimum** to the energy for corresponding wave function for the **single minimum** (which is the same as when the two minima are very far apart). This shows that there is an energetic bias in favor of the minima being close together, that is, they are bonded with regard to the lowest-energy wave function. *Vice versa* for the higher-energy wave function of the double minimum.]