

Chemistry 124 First Examination Answers September 26, 2008

Congratulations, you did unusually well on the exam.

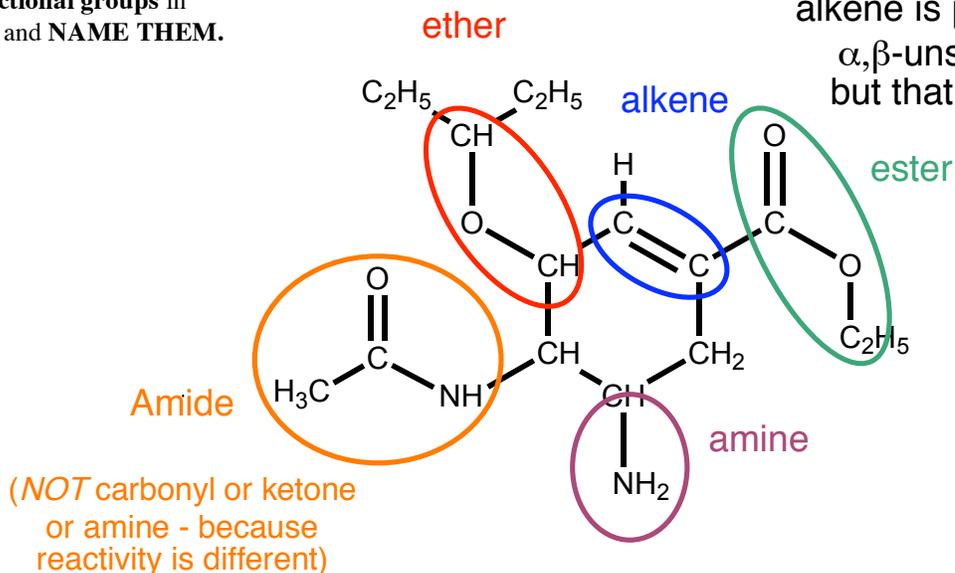
It appears that you have learned something!

Average Score = 80.0 1/3 of scores greater than 85; 2/3 greater than 76.

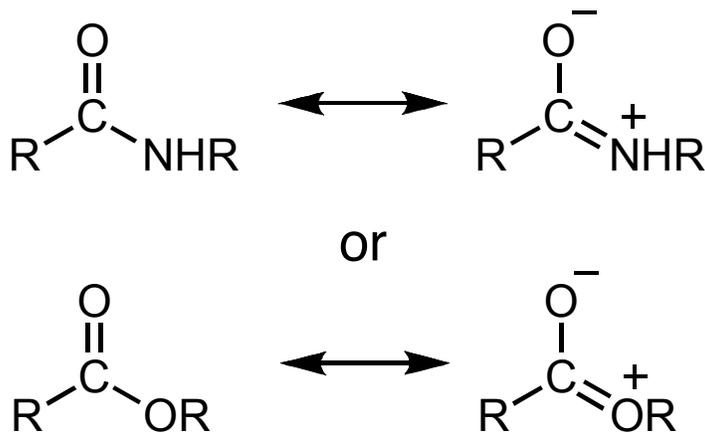
1. (5 min) A former Chem 125 student sent along a screen capture from last Monday's Season 3 premiere of *Heroes*. The character Hiro finds a paper in his father's safe containing chemical formulae, including one related to the structure of the antiviral *Tamiflu* shown below. Apparently Hiro says, "I knew I should've paid more attention in Chemistry class."

To help Hiro out **CIRCLE**
five functional groups in
Tamiflu and **NAME THEM**.

The ester with an adjacent
alkene is properly called an
 α,β -unsaturated ester,
but that will come later.



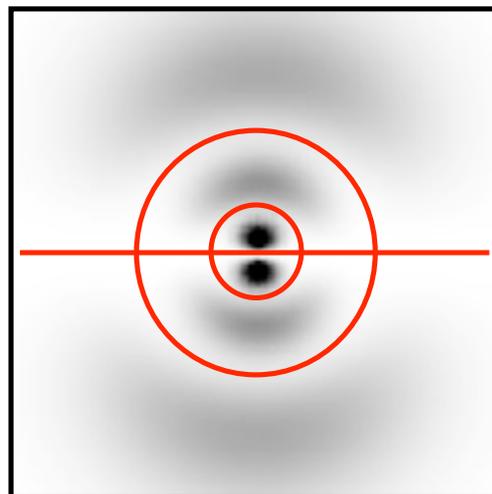
2. (3 min) Draw a pair of plausible resonance structures for a functional group that appears in Tamiflu. You may show only the functional group and use "R"s to denote other stuff. Use a proper arrow(s) to connect the pair.



3. (4 min) **DESCRIBE** the nodal pattern in this atomic orbital
AND CIRCLE its nickname: $1p$ $2p$ $3p$ $4p$ $5p$ $6p$

There are two spherical nodes (shown as circles) and one planar node (shown as a line).

Since there are three nodal surfaces, the principal quantum number, n , must be 4.



4. (4 min) **HOW** did J. J. Thomson propose to modify Coulomb's Law in 1923, and **WHY**?

He added a term ($-c/r$) that would change the sign of the electrostatic force for distances shorter than c (a distance on the order of atomic size).

He did this to allow the atom to have a minimum-energy structure despite the restrictions of Earnshaw's Theorem for inverse-square forces.

[Note that Thomson had ceased advocating his plum-pudding atom in 1909, when an experiment in the lab of his former star student, Ernest Rutherford, showed that the nucleus was miniscule compared to the size of the atom. Incidentally, Rutherford was a great friend of Bertram Boltwood, the Yale professor responsible for building Sterling Chemistry Lab, which explains why, although he was a physicist, he is the youngest member of the chemistry honor roll on the front of the building. Yale had tried to hire him as a professor about 1905, but he saw no point in coming to an institution where he would be expected to teach undergraduates!]

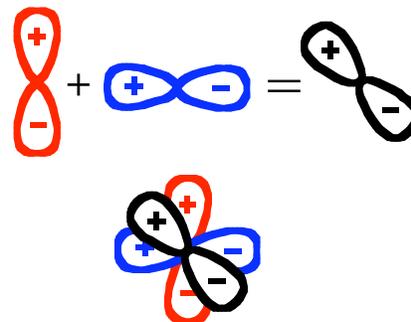
5. (3 minutes) What is remarkable about the electron difference density map of the $C=C=C=C$ group?

The cross sections of the double bonds are oval, and the major axis of the oval of the central double bond is perpendicular to that of the flanking double bonds (as if the bonds from the carbons are tetrahedrally oriented and the double bonds are bent).

6. (4 minutes) **Explain briefly** how combining perpendicular $2p$ orbitals generates a new $2p$ orbital.

(Pictures would help.)

One "combines" orbitals into a hybrid orbital by **adding** the values they assign at every point in space. The perpendicular $2p$ orbitals each assign positive and negative values on opposite sides of the **same** nucleus (clearer in the second drawing, which puts them on the same center). The positive (or negative) values reinforce one another in the top left (or bottom right) quadrant, but cancel one another in the top right and bottom left. This yields a new $2p$ orbital inclined between the original pair. This is easily seen mathematically: as well. Adding $x e^{-p/2}$ to $y e^{-p/2}$ gives $(x + y) e^{-p/2}$.



[A number of answers failed to notice the importance of signs in adding wave functions, or, worse, suggested that probability densities were being added. It is the orbitals (wave functions) not the densities (their uniformly positive squares) that are added. Otherwise there would be no destructive interference.]

7. (3 minutes) How does each of the following properties of the $2s$ state of an H-like atom scale with the nuclear charge Z ?
No explanation required, just give the dependence on Z .

$$\text{Radius of the spherical node} \propto 1/Z$$

$$\text{Maximum probability density} \propto Z^3$$

$$\text{Total energy} \propto Z^2$$

8. (4 minutes) Draw lines between the columns to choose the best experimental technique for studying each phenomenon.

No explanations required!

Techniques	Phenomena
Scanning Tunneling Microscopy	Dissolution of monomolecular layers from an organic crystal into a solvent
Atomic Force Microscopy	Shape of covalent bonds
SNOM	Location of rare fluorescent molecules on a microchip
X-ray crystallography	Location of atoms in a molecule deposited on graphite

9. (7.5 min) The second laser scattering during our in-class demonstration involved a mask with a large set of evenly-spaced **PAIRS** of vertical bars. **SKETCH** the resulting scattering pattern that appeared on the projection screen **AND MENTION** its relevance to Rosalind Franklin's x-ray pattern from a fiber of b-DNA.

• • • • **X** • • • • •

The pattern is a row of evenly spaced dots of modulated intensity fading smoothly from X, which marks the position of the undeflected "direct" beam). The even spacing of dots is inversely related to the spacing between successive pairs (like the "peg board" through which scattering is viewed), the modulation derives from interference between the members of each pair of lines (like the smooth intensity variation within the "snowflake" derived from a hexagon of scattering dots).

The repetitive diagonal planes which dominate the electron density on a helix give rise to a row of dots on one branch of the X-pattern from b-DNA scattering. The existence of an unevenly offset second helix to give major and minor grooves creates the modulation of intensity. The set of diagonal planes for b-DNA in fact constitutes a regularly spaced set of **pairs** of planes, analogous to the set of paired "jail bars".

10. 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.

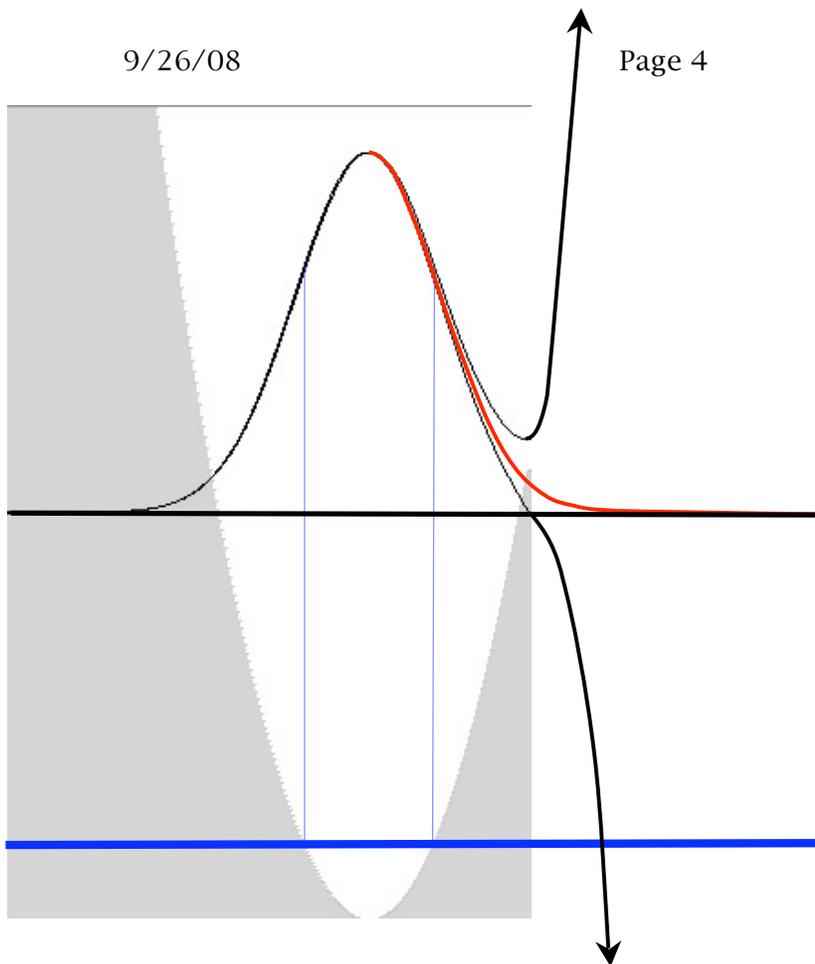
(Intersect PE curve below inflection points)

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 crosses the baseline because it curves more strongly toward it in the region of positive kinetic energy, 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 as far as possible.

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.]

11. (0.5 min only – cheap, don't waste time until you've finished the previous questions)

A class member created the following cartoon.

Briefly explain its relevance to our approach to quantum mechanics.



Obviously Goldilocks as a bound electron discarding energies that are too high or too low in her search for a quantized energy that is just right as in *Erwin Meets Goldilocks*.
(Thanks to Yoonjoo Lee)

Prophetically, Katharine Seelye's preview of the first Presidential debate in the *New York Times* on the morning of the exam included the observation, "Both will be adjusting their internal thermostats. Mr. Obama can be too cool, Mr. McCain too hot. Look for both to seek their inner Goldilocks."