Chemistry 125 First Examination Answer Key **September 26, 2003**

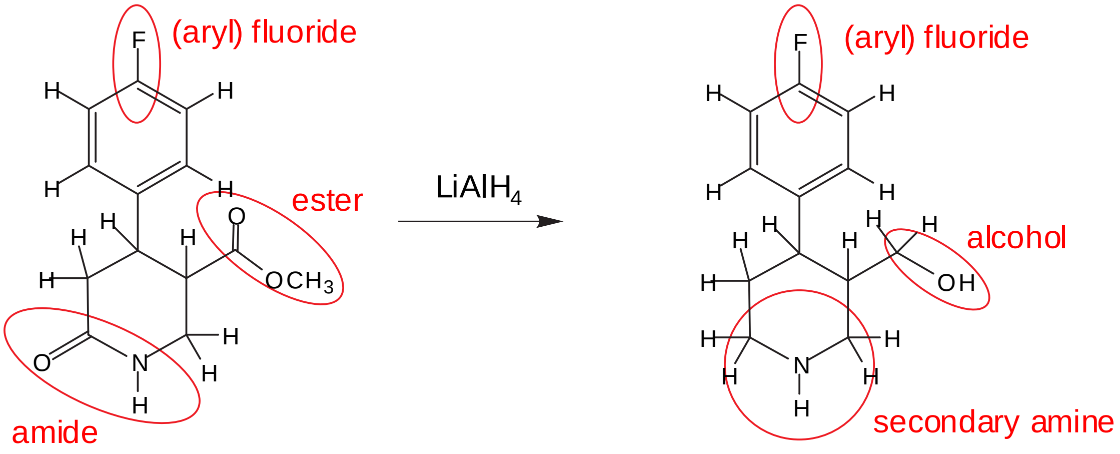
Exam Statistics:

Mean 74.8 (1/3 of the scores were greater than 82; 2/3 > 70)

A statistical oddity of this exam is that the mean on every question but one was within ±3% of 75% of the points allotted (twice the number of budgeted minutes). On question 4 the mean was 81%

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, and be sure to answer all of its parts.

1. (4 minutes) The following reaction occurs during the synthesis of paroxetine, the active ingredient of the antidepressant "Paxil". Within the two molecules shown in this reaction, **circle FOUR DIFFERENT functional groups that include atoms OTHER THAN CARBON AND HYDROGEN** and **give their names**. [Make sure the groups have different names. Remember that unlabelled junctions of lines are understood to be carbon atoms.]



Comments: 2 points for each of four identifications. Many answers labelled the flouride substituent on the benzene ring as an 'alkyl halide' when it is actually an 'aryl halide', because it is attached to a benzene ring. We'll see next semester that the characteristic reactivity of alkyl and aryl halides is quite different, so it is reasonable that they have different names as functional groups. Very often "ketone", "amine", and "ether" functional groups were identified within the amide or ester. This is definitely not correct, because none of the chemical behavior of the amide and ester are not at all like that of any of these simpler component groups. Resonance can be invoked to "explain" the difference, which we'll soon understand in molecular orbital terms. The aromatic group of a ring of six carbon atoms with alternating single and double bonds is indeed a functional group, but it was specifically excluded from being a proper answer by the insistence of the question that the group must include atoms other than C and H.

2. (8 min) The two images on the right are differently enlarged transmission electron micrographs of a newly available SPM tip called a “HI’RES probe.” Note the scale bars of 100 and 10 nanometers. The structure shown is made of tough, inert, electrically insulating carbon something like diamond. It is attached to a much larger piece of thin, flexible material (not shown) that is coated with aluminum.

A) Circle the kind(s) of SPM this tip might this tip be good for: [✓ **AFM**] **STM** **SNOM**

Won’t do for STM because it is electrically insulating (the Al coating is only on the triangular cantilever, which holds this tip to help it reflect the laser light.

Won’t do for SNOM because it is not appropriate for transmitting light (not an optical fiber)

B) Why might be this tip’s **advantage** over previously available tips?

The tip is remarkably fine. The radius of curvature at the tip is less than 1 nm, where normal AFM tips have radii of curvature more like 20 nm, or larger. Thus is should provide unusually high resolution (hence the name) for resolving strutures closer than 1 nm to one another. [Incidentally, the tip is also said not to oxidize. Addition of a layer of oxide to the tip would of course make it thicker and lower the resolution.]

C) Why might the **disadvantage** of this tip compared to previously available tips, at least for some samples? [Neglect its cost and possible fragility.]

To detect the surface contour in “contact mode” pressure on the tip must be able to bend the flexible material on which the tip is mounted. Even though this requires relatively little force, when the force is concentrated on such a very narrow tip, it has the ability to carve through any softish material. Thus this tip is probably better suited for high resolution study of very hard materials.

D) Circle the feature(s) it might be able to reveal: [✓ **Individual Molecules**] **Individual Atoms** **Individual Bonds**

Normal “organic” atoms are too close together to be resolved by a tip with a radius of curvature of about 1 nm (= 10 Å or about 7 C-C single bond distances). Bonds are out of the question for AFM. This tip is sharp enough to resolve a number of typical molecules, however. (For specifications and an example of molecular resolution with the HI’RES probe see http://www.spmtips.com/hires/)

3. (6 minutes) Explain why the electrons used to make the transmission electron micrographs shown in the previous question had to be accelerated to a high kinetic energy. [Hint: mention **both** quantum mechanical kinetic energy **and** the advantage of x-ray diffraction over optical microscopy.]

To achieve resolution of an object in a normal (as opposed to scanned) microscope image, the wavelength of the light must not be significantly longer than the size of the feature to be resolved. This is why x-rays (with wave lengths of about 1Å) are suited for atomic resolution, whiile optical microscopes (with wavelengths >200 nm) are inadequate for this purpose.

With transmission electron microscopy one uses electrons (rather than photons) as the waves to be scattered. According to the Schrödinger formulation of kinetic energy, the wavelength has an inverse relationship to the kinetic energy of an electron in a region of constant potential. Thus high kinetic energy (or high voltage for acceleration) of the electrons is necessary to give wavelengths short enough to resolve small features.

[Note that tunneling is not a feature of this kind of imaging.]

4. (7 minutes) Choose **ONE** of the following quotes (**omit two of them**). Identify its **source** and **explain** its **relevance for Chem 125**. [If you choose Option A, you must identify and explain the pair of quotes.]

A) "I cannot bear the Thought of being made Master of a Jewell I know not how to wear." ***AND*** "Nullius in Verba"

B) "..if we use the electron as a test charge to determine the properties of the simplest possible electric field, namely the field about a hydrogen nucleus, we appear to find that this field is not a continuum but is strikingly discontinuous."

C) "the spherically-averaged fluorine atom in its four tetrahedral orbitals has got seven electrons in four orbitals, and therefore the spherically-averaged orbital pointing towards the carbon atom contains seven-fourths of an electron,"

Answers to this question were good and diverse (31 chose A; 19, B; 19, C)

A) The first quote is from a letter of Pepys (to Tollet, not to Newton, but with the same question he posed to Newton). Pepys wanted not only the authoritative answer to his question (about the odds of throwing at least a certain number of 6s with a certain number of dice) but even more to understand why the odds are what they are, so that he could confidently apply his knowledge to new situations. He had the courage to keep asking when he did not understand, which is a trait that is essential for students in Chem 125.

The second part of A (which some omitted) is the motto of the Royal Society which refers to a letter of Horace. The litteral translation is "In the Words of None" (not "Nothing in Words"). The idea is that a scientist is not bound to the assertions of any master or authority, but must be guided by the results of experiment. In Chem 125 students should ask "How do you know?"

B) In this quote from the final chapter of "Valence, the Structure of Atoms and Molecules" (1923) G.N. Lewis states that Coulomb's Law must break down at small distances, on the order of the size of atoms and molecules, so that the atom can have a static structure (the cubic or tetrahedral octet) despite the impossibility of a static structure for inverse square potentials (Earnshaw's Theorem).

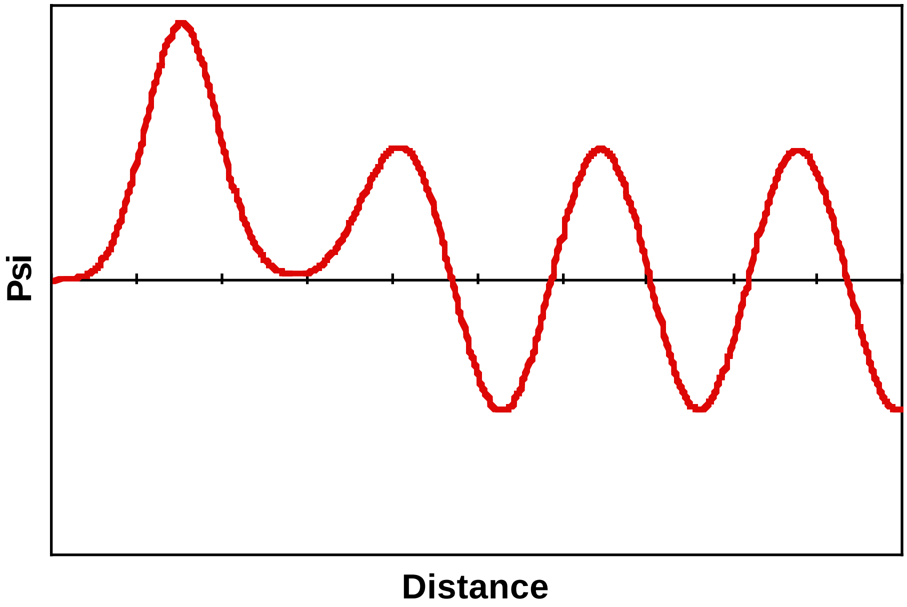
[Three years later Schrödinger discovered that Coulomb's Law was fine, but kinetic energy was weird.]

C) This is a part of Jack Dunitz's explanation for the failure to observe bonding electron density between C and F in his experiment with tetrafluorodicyanobenzene. It is a problem of "Compared to what?" How should one treat the electron density of atoms for subtraction from the total electron density measured by x-ray diffraction in order to reveal the small shifts of electron density that arise during bonding?

The unbiased approach would seem to be to assume a spherical electron density for the atom. But in the case of atoms with more than four valence electrons this is problematic, because it puts more than 1 electron from this atom in the quadrant of space that will be involved in bonding with an electron from the neighboring atom. Since the true bonding "orbital" can contain a maximum of 2 electrons, subtracting more than two atomic electrons is a recipe for disaster in trying to visualize the bond. Better to start with an unsymmetrical F atom with only one valence electron in the region that will be used for bonding.

5. (10 minutes) The top frame shows a wave function Psi.
[The horizontal line is at Psi = 0)].

Psi is a solution to the Schrödinger equation for a particle in one dimension with a certain potential energy as a function of position and a certain total energy.



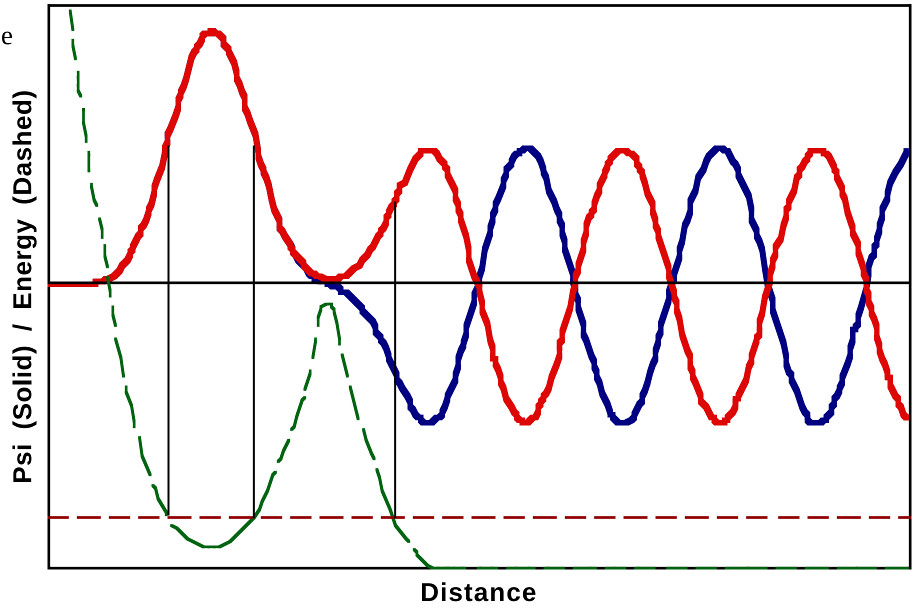
In this middle frame **sketch an appropriate potential energy** for the Psi shown above using the **same distance scale.**

[The central horizontal line represents the total energy.]
You may wish to comment and/or use lines or arrows to show correspondence in position between the wave function and the potential energy function.

The wave function in the top frame may be ***understood*** as the combination of two wave functions from simpler potential functions.

These **same two** component wave functions could be combined in a different way to give a very similar, but somewhat higher, total energy for the same complex potential energy function.

In the bottom frame **sketch what this different wave function, Psi(2), would look like.**



The dashed green line shows the **potential energy** (combination of harmonic oscillator and exponential decay potentials) and the dashed red line the **total energy** that generates the original red curve. The vertical black lines denote locations of zero kinetic energy which match inflection points of the Psi function(s). Note curvature away from the baseline in the forbidden regions of negative kinetic energy. The original red solution is the lowest psi of the sum of harmonic oscillator and “sine” wave for constant potential, while **the blue solution is their difference**, with very slightly higher energy giving an additional node.

Going from left to right with the potential energy function 12 points were assigned as follows: 2 points for the barrier on the left (if it went to a finite value and not to infinity - 1 point), 1 point for the first allowed region, 2 points for the forbidden region, 2 points for the constant potential going off to the right (1 point if the potential wentoff above Etot instead of below). 1 point for each inflection point correctly interpreted (and 0.5 for an inflection point recognized but not properly interpreted). Finally, 2 points for recognizing the first minimum should be higher than the eventual constant potential (similar curvature but higher amplitude compared to the sine wave means lower kinetic energy). Common wrong answers were the exponential function (typically scored at about 5/12) and the Morse potential (typically 6 or 7 of 12).

With respect to the 8 points for drawing the blue wave function above 3 points were assigned to the first (Harmonic Oscillator-like) part, 3 points to the area around the inflection point, and 2 points to the sine wave.

Common wrong answers were: the 2nd HO solution plus the sine wave (5/8 points), the same function except for the forbidden region dipping down below the axis to generate new nodes (3 or 4 points), the same function but the sine wave has a different wavelength (5/8 points). Some people got 0.5 or 1 point off for not matching up the sine wave well enough with the first psi. However, some explained that it should look like the first one, only inverted; explanations such as these got full points. Also, people with wrong answers who explained that their solution had more curvature and/or more nodes and thus had a higher KE, higher Etot, got an extra 0.5 or 1 point.

6. (3 minutes) **Explain** whether the energy of the wave functions for Question 5 is quantized. That is, whether there are other satisfactory wave functions for this system with all possible values of the total energy near the energies of these two states, or whether only very specific energies are allowed.

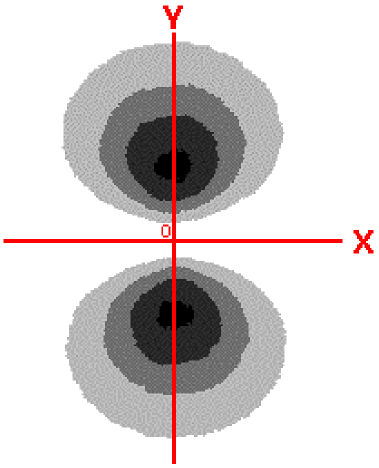
The system is not quantized because there is not an ongoing region of negative kinetic energy on the right. The system is not bounded on both sides so the curve does not need to become asymptotic to the psi = zero baseline on both ends. .

2 of the 6 points were given for just saying it's not quantized. 3 points for saying it's because it's not bounded on both sides. 1 point for explaining what that means in terms of negative KE, or psi having to get asymptotic to the baseline in the forbidden region. Some people had a very correct explanation but did not state whether the example in Q5 was indeed quantized or not, while others said it was "partially" quantized, or "quantized at one end". These people got 4 points for a good explanation, but 0-1.5 points for their answer depending on whether they seemed to know what the answer from Q5 was and simply didn't say it explicitly, or whether it seemed like they were hedging their bets by saying two things instead of one.

7. (6 minutes) **(A) Draw and label axes** and an **origin** for this plot.

(B) explain the meaning of the different **shades** of color.

(C) write the **mathematical expression** for the function that is being plotted.



A) The origin (o) of the axis system is the nucleus of the atom. Note that this plot shows a slice through a three dimensional 2p orbital, so there are **only two spatial coordinates**

B) Increasing darkness codes increasing electron probability density contours.

C) Psi = const * y * $e^{-rho/2}$ is a $2p_y$ orbital, but this plot makes no +/- distinction between the contours above and below the origin, so it must be showing the probability density, Psi squared

const * y^2 * e^{-rho}

8. (6 min) **Explain** how Rosalind Franklin's x-ray "photograph" of the b-form of DNA would have looked different if the two intertwined helices been evenly spaced, rather than being offset to give a major and a minor groove?

A single helix generates rows of equally spaced spots along the branches of an X. [You were not asked to explain how the angle of the X relates to the pitch of the helix, nor expected to state that there is a smooth decrease in intensity as one goes to higher diffraction angles.]

A double helix with even spacing would cause every other spot due to the single helix to disappear because for angles where waves scattered from the successive turns of a single helix differ in phase by an odd number of wave lengths, the intervening turn from the other helix will be exactly out of phase and thus will cancel. When successive turns of a single helix differ by an even number of wavelengths, the intervening turn will also be in-phase and scattering will be very strong.

The offset from even spacing in DNA causes the intensity sequence to be weak, strong, strong, weak, strong. With even spacing it would be absent, strong, absent, strong, etc.

Of the 12 points, 8 points were assigned for saying that the spots would not vary in intensity (or that they would vary smoothly, getting weaker as they went out, which is a more complete answer), and 4 points for recognizing that they would be spaced 2x as far apart on the film because alternate points would involve full adding, and full cancellation. Some people said that there would be constructive, then destructive interference, but in the absence of a picture or some other description of Franklin's observation 2/4 points were awarded for the spacing explanation. Those who said there would be strong-weak pattern rather than strong-none got 2/4 as well.

Afew people overthought this question and surmised what would happen to the pitch of the helix. If they said the angle of the X would change, 2 points were deducted, but if they qualified that by saying IF the pitch were changed by there being no major/minor grooves, then the change in angle would happen, of course no points were deducted.