Chemistry 125 First Examination Answer Key **September 29, 2006**

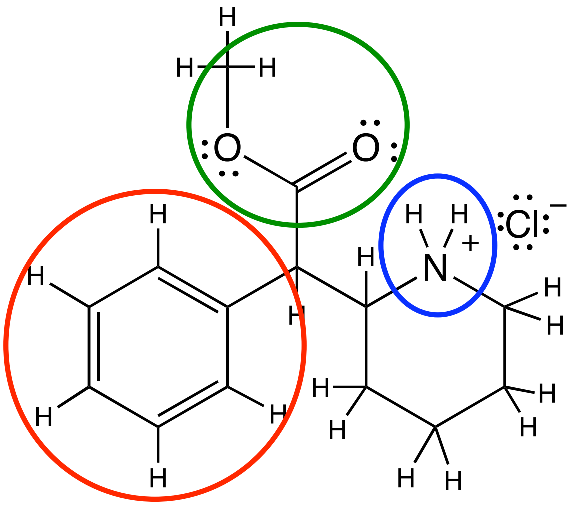
Read each question carefully to see what it asks for (bold face is used to help highlight questions).
Make sure you are answering the question, not just saying something vaguely relevant to its topic.

The class did well on this exam. The mean score was 71.5/100
One third of the scores were > 77, and two thirds were > 67.

Don't become overconfident if you did well, or depressed if you did badly. This exam counts for only 1/6 of the semester grade, so what you do from here on in is much more important that how you scored on this exam. On the other hand, remember that the course content is highly cumulative. If the exam reveals weaknesses, be sure you correct them soon, so that you catch up with your classmates and don't fall further behind.
The teaching staff is here to help you!

1. (5 minutes)

A) Complete this structure of methylphenidate (Ritalin) by adding **H atoms,** and the bonds that attach them, together with unshared electron pairs.



Note (at top) that lines are assumed to terminate with a carbon atom unless another atom is shown.
H-atoms complete unsatisfied valences.
Few people showed **all** unshared pairs (including Cl).

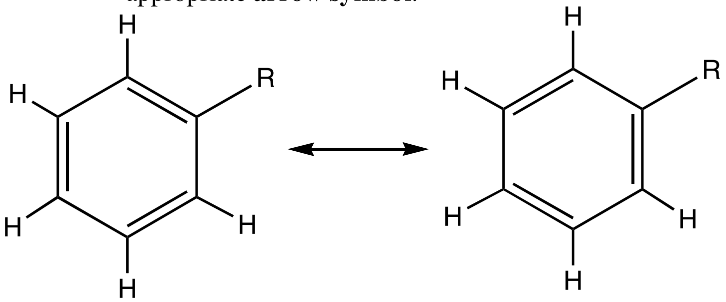
B) Circle and **name** each functional group in Ritalin.

Ester includes at least 2 oxygens and 2 carbons, to distinguish from carboxylic acid (neither alcohol or carbonyl – they)

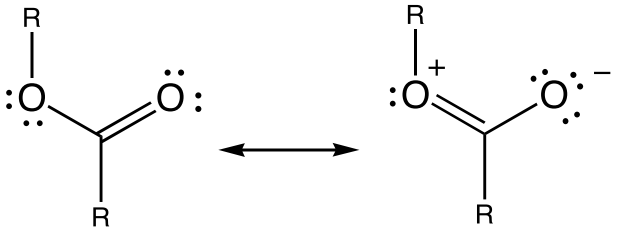
Aromatic Ring (or Benzene, or Phenyl)

Ammonium The N needs to be quadrivalent to have a + charge, thus add two H atoms.

2. (6 min) It would be appropriate to write two **"resonance structures"** for **one portion** of Ritalin. **Draw the two structures of this group** below using R to denote the remainder of the molecule, and connecting them with the appropriate **arrow symbol**.



OR



Need to write resonance structures, not equilibrium structures.

Explain the meaning of what you have drawn, being sure that your explanation includes the term "**double minimum**".

"Resonance", denoted by a double headed arrow, involves a single true structure (single minimum) denoted by two different bonding pictures. This is to be contrasted with "equilibrium", denoted by two anti-parallel arrows, where there are two different structures (different nuclear positions) in a double minimum potential.

3. (9 minutes) Give the **approximate distance** in appropriate units for each of the following and **explain how it was measured** near the year indicated in parentheses.

A) the thickness of a layer that generates a visible color by reflection of incident light (~1700).

The distance is some hundreds of nanometers (depending on color), which we now know to be the wavelength of the light involved. It was measured the distance of a thin layer between a lens and a flat piece of glass by noting the diameter of a ring of the color of interest. Since the lens was portion of a sphere of known radius, it was possible to use trigonometry to reckon the distance between the lens and the flat. (note the year in which Newton made the measurement, which excludes Franklin and Bragg)

B) the diameter of the DNA double helix (~1950).

The deflection angle of the lateral spots (triangles in Rosalind Franklin's x-ray diffraction photograph) show that the spacing between the parallel planes of electron density corresponding to the sides of the cylinder is about 20Å (or 2 nm).

C) the length of an organic molecule about 20 bonds long (~1760).

A teaspoon (5 mL) of oil spreads to a layer 1 molecule thick on water, and the area it covers (half an acre) can be measured by its ability to still ripples on the surface. Dividing the volume by the area gave the thickness of about 25Å (or 2.5 nm).

4. (6 minutes) Explain **why** and **where** each of the following features appears in (different) one-dimensional wavefunctions that are solutions of the Schrödinger equation for the **Morse** potential.

A) exponential decay (e^{-x})

Exponential decay is the wave function corresponding to a CONSTANT NEGATIVE kinetic energy. This situation obtains at the far right of the Morse potential when the total energy is below the potential energy plateau (the particle is bound).

[Note that "exponential" is a very specific function, it does not just mean "curving down to meet the baseline asymptotically. It applies only after the potential energy curve has flattened out – certainly not on the left of the Morse curve, where the potential energy is rising rapidly. Incidentally, some answers sketched a "Morse" curve which flattened on both sides. This is not "Morse" behavior, where on the left the atom of interest collides with its bonded partner and the energy rises rapidly and without limit.]

B) sin(ax)

Sin(ax) corresponds to a CONSTANT POSITIVE kinetic energy. "a" determines the wavelength, which shortens for larger "a" in proportion to the square of the excess of total over potential energy. Again this obtains at the far right of the Morse curve, but when the total energy is greater than the potential plateau.

[Again note that "sin" is a specific function. The wiggles within the potential well are not truly sin behavior, because the kinetic energy, while positive, varies as the potential energy changes.]

5. (12 minutes) The C-H and C-F single bonds have fairly similar strengths, but in their lowest-energy states one of them vibrates with a much larger amplitude, that is, it covers a much wider range as it stretches and shrinks.

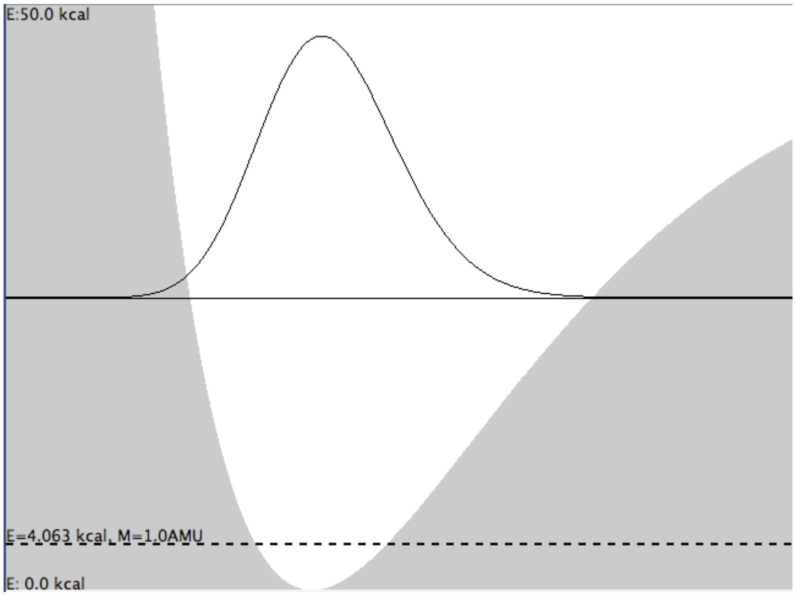
A) (3 min) **Write** the quantum-mechanical expression for **kinetic energy**

(or the multidimensional or multiparticle equivalent)

$$\boxed{-\frac{C}{m}\,\frac{\left[\text{Curvature of }\psi\right]}{\psi}}$$

Almost everyone got a perfect score on this section. Congratulations.

B) (9 min) In terms of your kinetic-energy expression above **explain**, by modifying the following C-H stretching figure, whether the lowest **energy** for C-F stretching should higher or lower than that for C-H, and whether is has a higher or lower vibrational **amplitude.**



This is precisely the problem treated in slides 9-14 of the Powerpoint of 9/27/06. See those slides for a correct answer with proper curves.

Note that one cannot simply say that because mass appears in the denominator of the kinetic energy formula, increasing the mass will lower the energy (although this happens to be true in this case). The reason this is erroneous is that increasing the mass will change the wavefunction for this total energy to an unsatisfactory one. In this case that new (erroneous) psi is too much curved toward the baseline, so that the total (thus the kinetic) energy must be lowered to return to a nodeless wave that approaches the baseline asymptotically on the right.

With a lower total energy, the classically allowed part of the well is narrower, that is, the inflection points of the new wave (where kinetic energy is zero) will be closer together for F than for the proton, so the vibrational amplitude (not the “amplitude” or height of the psi wave) is reduced.

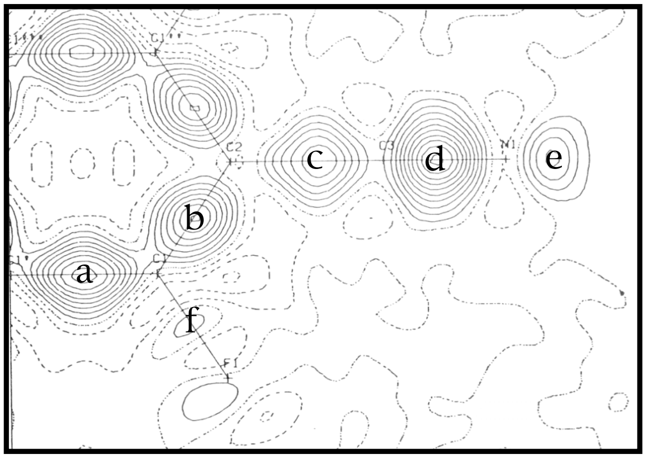
6. Tetrafluorodicyanobenzene

A) (3 min) Explain **how** and **why** the map below was generated using **experimental** and **theoretical** input.

The contour map was generated by subtracting (spherically symmetric) atomic electron densities, calculated by **quantum mechanics** for a set of free atoms then arranged as they would be in the tetrafluorodicyanobenzene molecule, from the true molecular electron density measured by careful **x-ray diffraction** from a crystal of this substance.

The densities are reckoned in the plane of the molecule's nuclei.

The purpose of the "density difference" map is to show how the electron density changes when the atoms interact to form bonds and lone pairs.



b) (9 min) Explain what is to be learned from each of the labeled sets of contours in the figure **(a-f)**, or from their cross-sections perpendicular to the plane of the page.

a and **b** are aromatic bonds. They are intermediate between single (c) and triple (d) bonds in electron density. Their cross section perpendicular to the page is oval (because of the presence of pi bonds, as we will see later). Note also that they are equivalent to their symmetry related counterparts in the top half of the ring, showing that there is no alternation between single and double bonds in the benzene ring.

[Note that cross-sections are planar figures; they can't be spherical. Be careful to distinguish the cross-section shown from the one **perpendicular** to this page.]

c is a C-C single bond, with less electron density (fewer contours) than the multiple bonds. Its cross-secton perpendicular to the page is round.

d is a CN triple bond, with much more electron density (more contours) than the single and aromatic bonds. Its cross-secton perpendicular to the page is (perhaps surprisingly, but be patient) also round.

The bonds in general show only about 1/20 of the amount of electron probability that would be "expected" between the nuclei for a Lewis bonding pair (or 1.5 or 3 pairs).

e is a lone pair of electrons on the N atom. [Note that this pair is "unbonded" and "unshared" but NOT "unpaired"]

f should be the bonding density for the C-F single bond. It is practically invisible because the spherically symmetric F atom that was subtracted from the experimental electron density is an inappropriate model, because if undistorted, it would seriously violate the Pauli Exclusion Principle by putting more that two electrons in the bonding region. Using an F atom model with a single electron in the region that will form the bond gives a more realistic picture of how C-F bonding arises (see discussion by J. D. Dunitz on the course website).