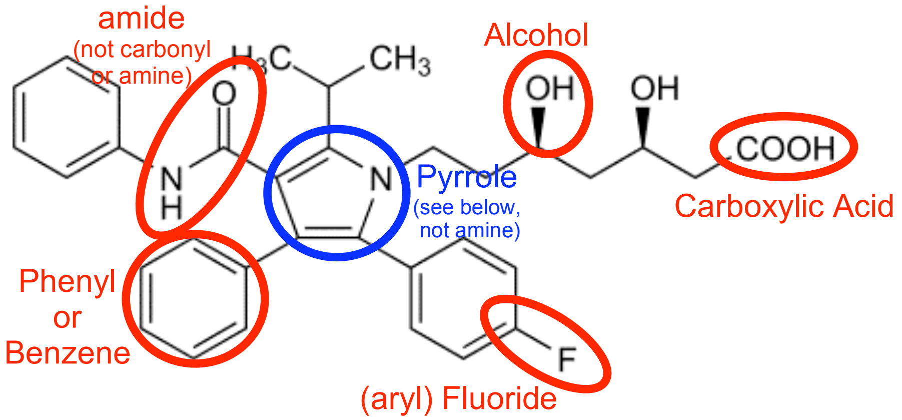
Chemistry 124 First Examination Answers **September 25, 2009**

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.

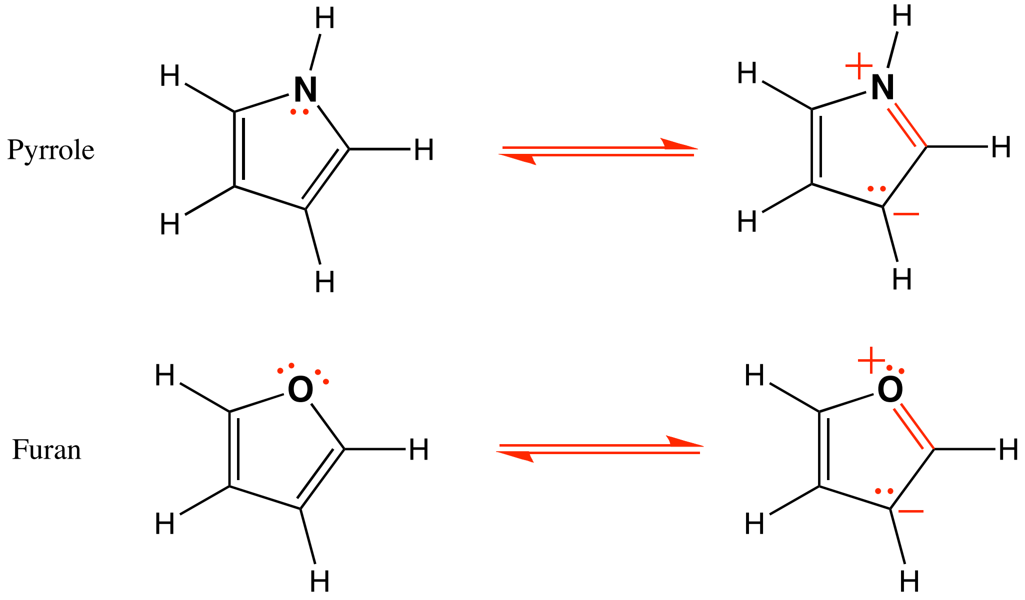
1. (5 min) Here is atorvastatin, the active ingredient of lipitor, the world's top selling drug (> $13 billion in 2008).



Circle five **(5) DIFFERENT** functional groups in atorvastatin and **NAME THEM.**

[As we will discuss soon, the C=O and the adjacent NH are ***NOT*** *a carbonyl and an amine, but an amide, which does not behave like normal C=O and NH. Smilarly, a pyrrole does not behave like a diene and an amine.]*

2. (5 min) The pentagonal ring containing nitrogen in the center of atorvastatin is called pyrrole. The analogue with O for N is called furan. **Add bonds / unshared pairs / formal charges** to complete the scheme below so it shows a pair of **resonance structures** for pyrrole and a pair for furan. Use a **proper symbol** to connect the members of each pair.



(most chemists would not write both : and the – sign on the anionic carbon)

Give a reason to anticipate greater resonance stabilization in one of these molecules than in the other.

In the charge-separated structures, it would be better to put the + charge on N than on O, that is, it would be easier for N to give up part of its electron pair than for O to do so, because of the smaller nuclear charge of N.

3. (4 min) **Explain briefly** how measuring the abundance of the molecular masses M, M+2, and M+4 (by mass spectroscopy) can reveal that there are two chlorine atoms in a molecule.

Every Cl atom in a molecule has a 3/4 chance of being the Cl-35 isotope and a 1/4 chance of being the Cl-37 isotope. If there are two Cl atoms the chance of two Cl-35s (M) is 9/16; the chance of 1 Cl-35 and 1-Cl-37 (M+2) is 2 * 1/4 * 3/4 = 6/16; and the chance of two Cl-37s (M+4) is 1/16. Thus the abundance proportion is 9:6:1. Other numbers of Cl atoms in a molecule would generate different intensity patterns.

[From Problem 2 in the first problem set[

4. (5 minutes) Suppose your roommate understands x-ray diffraction but is a literal believer in shared-electron-pair bonds as drawn in typical Lewis dot structures. Cite a **specific experimental result** that you could use to convince your roommate to be more broadminded about the nature of bonds.

*[The word "**specific**" in the question is a red flag prompting you to cite some actual experiment (or calculation) on a real molecule, rather than speaking in generalities, which would be unlikely to convince your discriminating roommate anyway.]*

There are a number of possible examples:

3D electron density contours in Crowfoot's stack of plastic x-ray electron density contours of penicillin showed spherical atoms, not clustering of electron pairs.

Electron difference density maps ($Ph_2C=C=C=CPh_2$ by Leiserowitz and Berkovitch-Yellin, dicyano-tetrafluorobenzene by Dunitz, *et al.*) show only modest accumulation of electron density between bonded atoms, compared to what is expected for simply superimposed atoms.

The plot of integrated difference density *vs*. C-C bond length by Leiserowitz and Berkovitch-Yellin showed that such density amounted to only about 1/20 of a "Lewis".

The bonding region for the C-C bond shared by two three-membered rings in the work of Dunitz, Szeimies, *et al.* showed no accumulation of electron density at all.

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) (1.5 min) **Draw a horizontal line** showing the **TOTAL ENERGY** for ψ curve that **crosses zero** at the right.

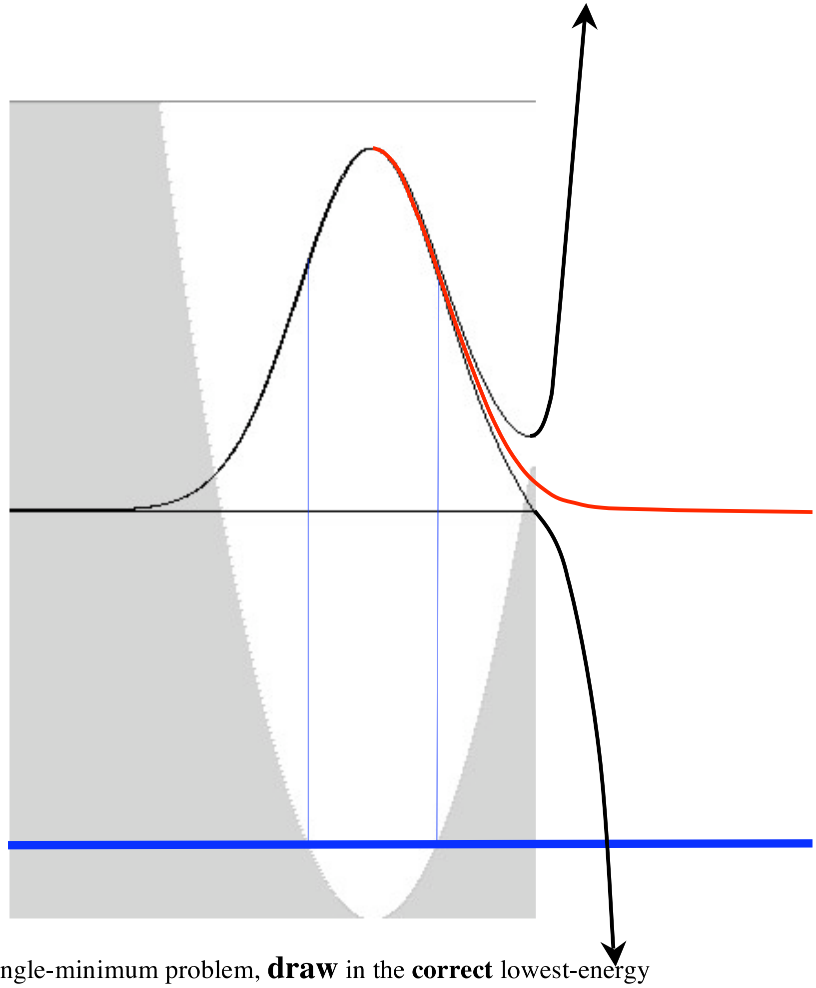
Be as accurate as you can.

(Intersect PE curve below inflection points)

B) (1.5 min) Is the total energy for the other trial ψ (the curve that is higher at the right) **higher or lower** than that the energy you drew in A?

Explain your thinking.

The higher ψ does not make it to the baseline because it is less curved toward it in the region of positive kinetic energy, this means that it has a somewhat **lower** total energy than the ψ that crosses the baseline. [note that the question is backwards from the one asked in 2008]


Total Energy

C) (2.5 min) **Assuming** that this is a **Hooke's Law** single-minimum problem, **draw** in the **correct** lowest-energy ψ **function** (its curve, **NOT** its energy), and **extend all three** ψ **curves** to the right as far as possible.

D) (4.5 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".

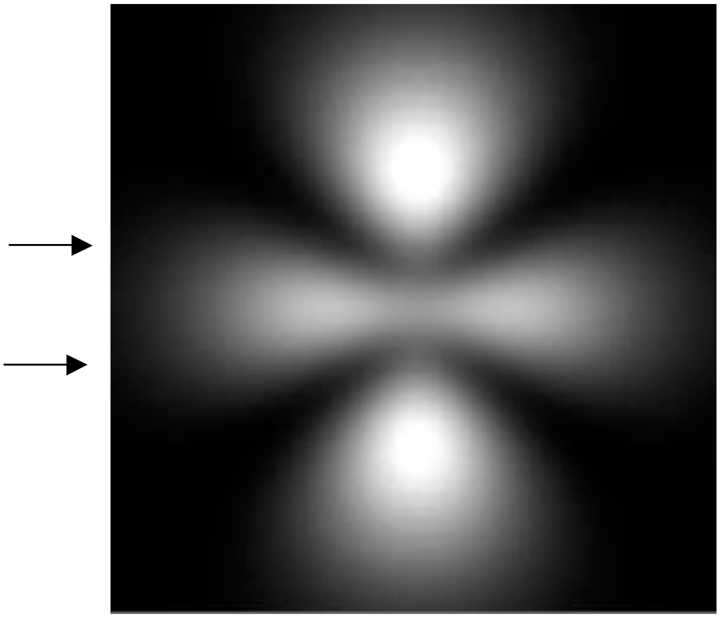
The upper curve has less curvature toward the baseline than the single-minimum red curve, and therefore less energy. So a particle described by this wave function of the double-minimum potential has lower total energy than it would have in the lowest-energy function of the single minimum. That means 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".

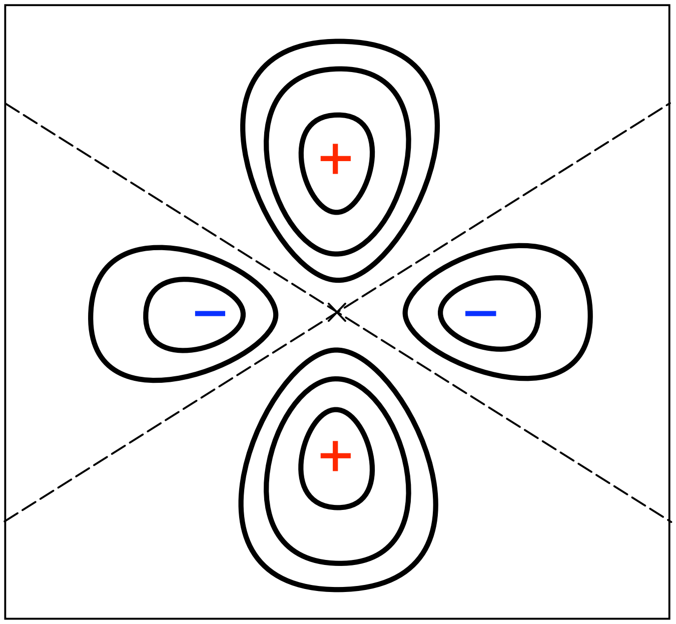
The lower curve has more curvature toward the baseline than the single-minimum red curve, and therefore more energy. By an analogous argument, this function can be said to be "antibonding".

[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.]*

6. The figure below displays the total 3-dimensional **electron density** of a hydrogen-like atomic orbital (from Atom-in-a Box).

(a) (3 min) In the open box sketch **several contour levels** to show the wave function (Ψ) for this orbital on a **2-dimensional SLICE** that passes through the nucleus (×), drawing **dashed line(s)** to show any node(s).





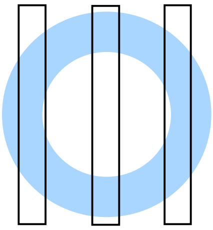
[Somehow the contour signs of Ψ must be indicated, as by + and – here.]

(b) (3 min) Give the **principal quantum number** for this atomic orbital: ***n*** **=** 3

and name the **shape of the node(s)** of the 3-dimensional orbital**:** Two Cones

(c) (6 min) **Explain** why, in the 3-dimensional view, the **horizontal** component of the density (the part between the upper and lower arrows) appears bulbous on the ends. **In addition explain** how this answer is related to why there are two spots revealing the double helix diameter on Rosalind Franklin's x-ray photo of b-DNA.

[*Hint*: It might help to draw a picture of the same component as viewed from the top.]



The "donut" between the arrows is axially symmetric about the vertical (approximately a torus), which one might think would look even from the side, but in fact the line of sight passes through much more electron density on the sides than through the middle, as shown on the right by the view from the top (along *z*, the $3d_{z2}$ symmetry axis).

This is exactly the same geometric factor that generates side-to-side scattering of x-rays by electron density on the surface of a cylinder, for example the electron-rich phosphorus and oxygen atoms from the backbone chain of Rosalind Franklin's b-DNA double helix. The same picture would apply, where the view is along the cylinder axis and blue denotes the locus of P and O atoms.

[This was an intentionally challenging question, and I was satisfied that the class average was as high as 5/12. Incidentally, the three rectangular boxes on the blue circle above are the same size, although the one in the middle looks narrower to me. I guess this is an optical illusion. It definitely holds less blue material.]

7. (4 minutes) All the radial wave functions $R_{n,l}(r)$ for hydrogen-like atoms share one common mathematical function, no matter what their principal quantum numbers. **Identify this function**, and explain briefly **why** it is **reasonable** for it to be there.

They all include the factor e^{-r}, where r is measured in some appropriate units.

This is reasonable because a negative exponential is the proper wave function in one dimension when there is constant negative kinetic energy, as there must be for a bound electron at substantial distances from an atomic nucleus (where the 1/r term in Coulombic potential ceases changing significantly).

[In 3D the math is a little more complicated (because of curvature with respect to other coordinates), with the fortunate result that e^{-r} is appropriate at all distances, not just long ones.]

8. (3 minutes) **Explain why** it is advantageous to have a scanning probe microscope with the sharpest possible tip, **AND draw a picture** the tip reported in the journal *Science* last month, **AND** give its effective **diameter** within a factor of 5.

A narrow tip is required to give high resolution, because a fat one cannot penetrate the space between molecules (or atoms) and thus cannot feel the grooves between them.

In an Auguse issue of *Science* there was a report of using a large gold atom on a metal-coated tip to pick up a single CO molecule by the C atom, so that only the O atom projected to feel the surface being probed.

The diameter of an oxygen atom is about 1.5Å (0.15nm). We did not discuss this value, but we did say that atoms are of the order of 1Å and simple organic molecules of the order of 10Å (1nm), and atoms are drawn approximately to scale in Frame 4 of Lecture 5 (where the experiment is presented).

[Full credit (2 points) was given for diameters between 0.2Å and 9Å (somewhat more generous than a factor of 5).]

9. (2 minutes) On the back of this page **sketch a potential energy curve** for which successive energy levels would become **MORE WIDELY spaced with increasing energy**.

We mentioned a number of times (and you found in the “Erwin” problem set) that the Hooke’s Law potential ($V = kx^2$) gives exactly even energy spacing, while a potential that broadens more rapidly with increasing energy (like the Morse potential or Coulomb’s Law) gives decreasing spacing with increasing energy (because the higher-energy waves can be longer than in Hooke’s parabola, and less curved).

By the same token, a potential that broadens less rapidly that kx^2 with increasing energy (for example kx^3), will confine the higher-energy waves more that the parabola, requiring more curvature and higher energy. This is the desired answer.

A number of students had the general idea, but proposed potentials with a maximum in the middle, or decreasing exponentials. Neither of these confines the particle, so there is no spacing at all (not quantized).

[I’m fully aware that this was a very challenging question, and I was not disappointed that the class average on it was 0.7/4.]