Chemistry 124   First Examination Answers   **September 24, 2010**

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 alloted 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. (4 min) Here is Rosiglitazone (Avandia), the diabetes drug whose withdrawal in Europe and the U.S. because of heart
risks was announced yesterday (and is the headline of today's *New York Times*).
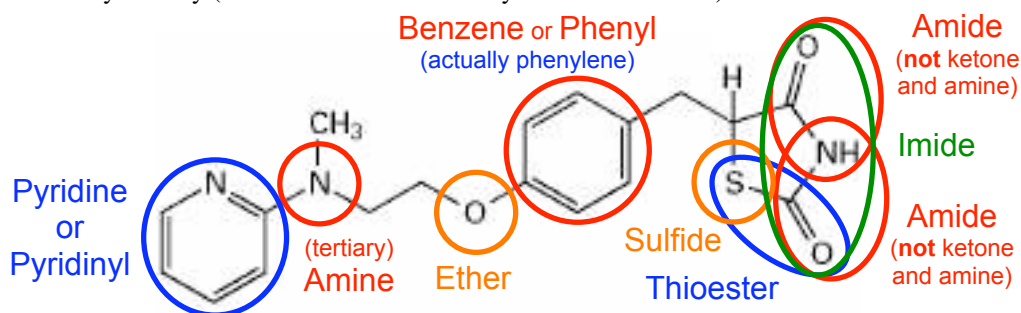
Circle four **(4) DIFFERENT** functional groups in Rosuvastatin and **NAME THEM.**

You should have known the red and orange functional groups.   The blue and green
ones will come in time. Methyl is a group, but not really functional, because it is not very
reactive. Note also that when a "heteroatom" with an unshared electron pair (like N, O, S) is
adjacent to a double bond they are considered a single group. Thus amide, **thioester**, and
imide are considered single groups and in fact the amine and the ether should join with their
adjacent "aromatic" rings. All the colored stuff on the right could be considered a single group,
thiazolidinedione, but most chemists would have to scratch their heads a bit to remember or
interpret this name. The basis for this grouping has to do with the resonance structures shown
below and will become clearer when we discuss molecular orbitals and conjugation.

2. On the left below is shown the "thiazolidinedione" ring from Rosiglitazone.
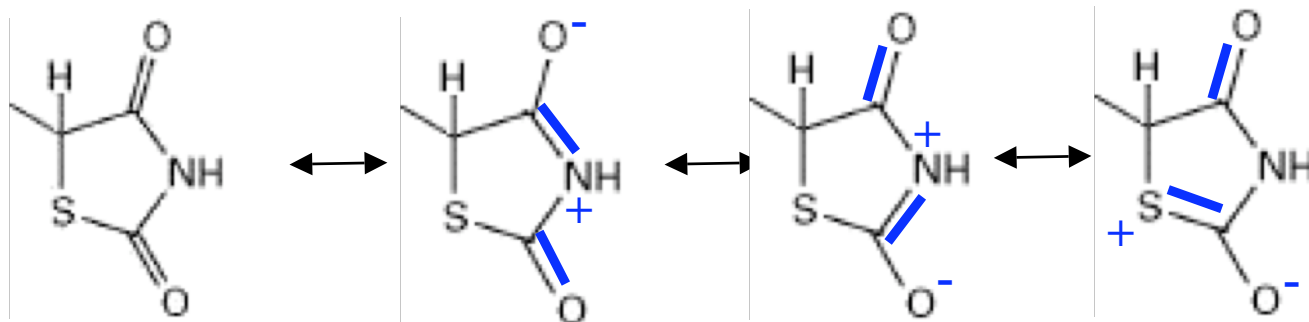
A. (4.5 min) **Complete the three structures on the right**
above to show reasonable resonance structures of the ring.

One could also include a single-bonded
structure for carbonyl groups (C=O), but
showing only such structures shows limited skill.
   We appear to need considerably more practice with
Lewis dots on drawing proper resonance structure and
keeping account of charges and electron pairs.
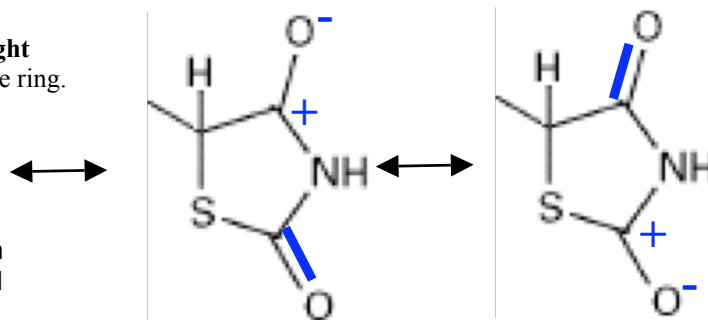
B. (2 min) Explain how the results of an **x-ray diffraction** study might help to decide whether the true structure of this ring in Rosiglitazone is one of the above, or whether it truly involves a resonance situation.

The most obvious way to distinguish among single, double, or intermediate (resonance) bonds is by the bond length. Since x-ray diffraction reveals the nuclear position (as the locus of maximum electron density) it allows determination of bond distance where single bonds are long, double bonds short, and resonant bonds in between. A much more complicated approach would be to integrate the electron density in a difference map or to examine the cross-section of bonds in such a map.

3. (4 min) How does one go about constructing an **electron difference (or deformation) density map**. (Mention the experiments and/or theories on which it depends.)

First one determines the atom locations and electron density distribution as accurately as possible by painstaking *x-ray diffraction experiments* at low temperature (to minimize blurring by molecular vibration). Then one subtracts from this experimental electron density map the density *calculated by quantum mechanics* for the corresponding set of independent spherical (or valence adapted) atoms. This difference or deformation map show where electron density has shifted to (and from) upon bonding.

4. (5 minutes) Cite **TWO different observations** from the electron difference density map of the following compound that would surprise a naïve chemist who thinks of bonds in organic molecules in terms of electron pairs shared between two nuclei.
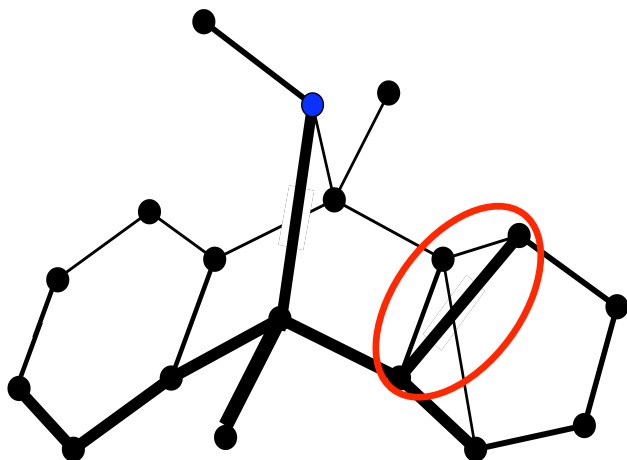
The bonds in the circled three-membered ring (and in the three-membered ring below it) are "pathological". There is no build-up of difference electron density in the region of the "single bond" that is common to these two rings, and the other two bonds are "bent". That is, their maximum concentration of electron difference density does not lie on the line joining the bonded carbon atoms.
A chemist who is sufficiently naïve might also be surprised that the amount of electron difference density in a single bond is only about 0.05 "Lewis" (0.1 electron), that the bonds in the aromatic ring are not different, or that H is hard to see.

5. (1 min) How much thinner than a hair was the oil slick that Benjamin Franklin measured on the pond on Clapham Common?

Circle one of the following fractions: 2/10   2/1000   2/100,000

[Hair has a diameter of ~100 μm. The thickness of the oil slick with which Franklin stilled waves was the length of a fat molecule, ~2 nm (or 20Å).]

6. (4 min) **Explain** which form of scanning probe microscopy yields **higher resolution**: STM or SNOM.

Resolution is limited by the size of the probe. In scanning tunneling microscopy the probe can be a single atom (a few tenths of a nm). In scanning near-field optical microscopy the light beam used to scan the sample is very many nm wide (~100), so the resolution is something like 1000 times worse.

7. (1.5 min) What feature(s) of an x-ray scattering diagram characterize(s) the spacing of the repeating "unit cells"?
(no explanation required)

The location of the diffracted spots (*i.e.* the angle at which rays are scattered).

(1.5 min) What feature(s) characterize(s) the molecular electron density distribution *within* the "unit cell"?
(no explanation required)

The intensity of the scattered rays.

8. (2.5 min) Since **electrons behave like waves**, and unlike for x-rays, there exist (electrostatic) lenses that can refocus scattered electron waves, it is possible to construct an electron microscope. **In terms of quantum mechanical wave functions**, explain why it is necessary to operate an electron microscopy at very high voltage (high electron kinetic energy) in order to obtain resolution of separate atoms within molecules.

As in the case of x-ray diffraction, high-resolution requires a short wavelength for the waves being scattered. We know from studying sine (or cosine) as the wave of a free electron that the wavelength is inversely proportional to the square root of the electron's kinetic energy. Thus accelerating electrons with high voltage is required to give them wavelengths able to resolve atoms in molecules.
[Electrons accelerated by 10 kV have a wavelength of about 0.1Å. For material particles like electrons, the energy is not inversely proportional to the wavelength, as it is for photons, but rathe inversely to the *square* of the wavelength, as we derived from Schrödinger's Equation.)
[Note that what is being described here is not scanning tunneling microscopy (STM), where one "feels" the surface, but rather electron microscopy (TEM, which we did not discuss), where, as for light, lenses are used to construct a magnified image of the sample.]

9.   All radial wave functions $R_{n,l}(r)$ for hydrogen-like atoms share one constant factor and one mathematical function.

A. (3 min) Write the **constant** factor **and** the mathematical **function**.

Constant Factor: $(Z/a_o)^{3/2}$ Mathematical Function: $\exp(-\rho/2)$

B. (4 min) Choose **ONE** of these (the factor **OR** the function) and **explain** why it is reasonable that all $R_{n,l}(r)$ share it.

$(Z/a_o)^{3/2}$ when squared is of course $Z^3/a_o{}^3$, that is some number (the cube of the atomic number) per unit volume (a_o, the Bohr radius, is a distance on the atomic scale). So these are the proper units for probability density.

More important, Z^3 is the proper normalizing factor to increase the probability density as increasing nuclear charge contracts the probability density toward the nucleus. Decreasing a linear dimension by a factor of Z (see the formula relating ρ to r) decreases the volume of the function by a factor of Z^3, so multiplying the Ψ^2 by Z^3 keeps the total probability constant (at unity).

$\exp(-\rho/2)$ When using the *Jeopardy* approach we saw that this wavefunction gives a constant negative kinetic energy. When an electron is far from the nucleus, its potential energy according to Coulomb's 1/r law is essentially constant, because 1/r is about 0, when r is great. This means that if the electron's total energy is below 0 (so that it is bound to the nucleus), its wavefuction will look like exp(-r).

There are of course subtleties involved because the atomic wavefunction is three dimensional, but still this interpretation is fundamentally correct.

A number of answers pointed out only that decreasing probability exponentially keeps the total probability finite, but one could imagine that other functional forms, like 1/r^n, would accomplish this. What is key for atoms is the constancy of potential energy at great distance from the nucleus.

10. Here is a one-dimensional wavefunction that solves the Schrödinger Equation for a certain particle mass and potential energy function. The dashed line shows $\Psi = 0$.
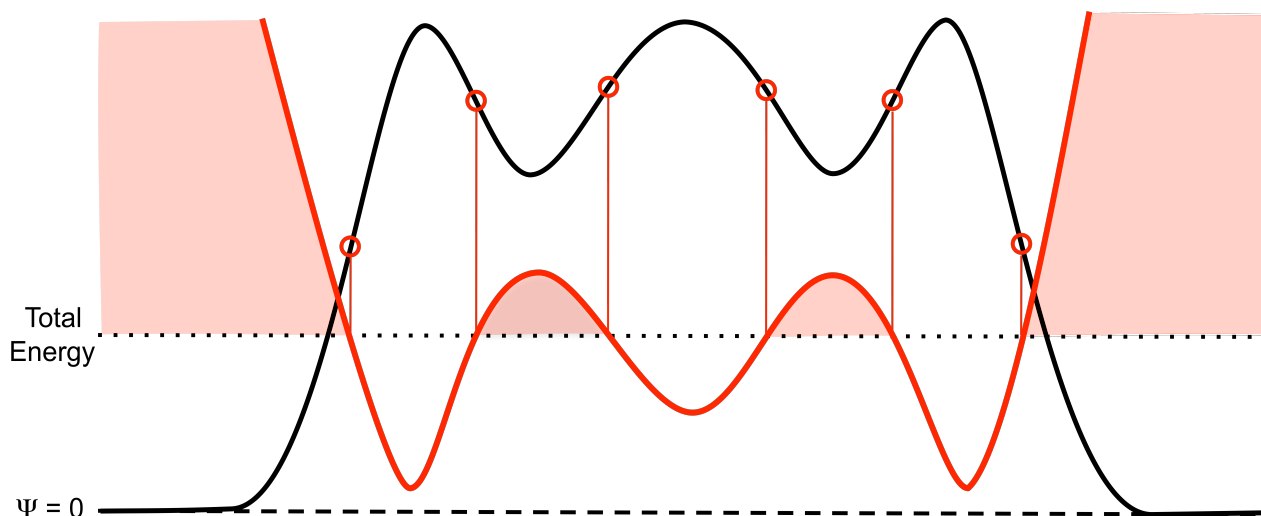
A. (6 min) **Draw** over the Ψ graph above another graph showing the **POTENTIAL ENERGY** for which this Ψ is a solution. Use the **dotted line** to denote the **Total Energy**, and be as accurate and complete as you can. A few words or extra marks might help show what you are trying to draw.

Red circles mark inflection points and correspond to positions where the potential energy = total energy (because the curvature and kinetic energy = 0). Note that the curvature at the top of the central peak is only about half of that of the flanking peaks, although they have the same amplitude. Thus the kinetic energy in the center of the triple well potential must be about half of that at the bottom of the flanking wells.

Regions of negative kinetic energy are denoted by red shading. Note that it is hard to know how the potential is shaped in the wings, where the amplitude is negligible.

B. (2 min) *EXPLAIN* **how many** wavefunctions that solve this problem would have energies **lower** than this one **and** how many would have energies **higher** than this one.

Since this function has no nodes, there can be no satisfactory functions with lower energy (and lower curvature toward the baseline). [Several students confused inflection points with nodes (or counted maxima). Nodes are where Ψ changes sign.]

There are an infinite number of higher-energy solutions with more nodes, whether the potential energy keeps rising in the wings (so that the energies are quantized) or plateaus (so that continuous values of energy become allowed above the dissociation limit).

C. (4 min) Describe how this wave function would change its shape as the **mass** of the particle is **increased**.

Increasing the mass while holding the total energy constant would require increasing the curvature (to keep the kinetic energy constant). Of course this would no longer give a solution in this quantized situation, where the potential rises at both extremes, so as to confine the particle. To retain the no-node solution one would need to lower the increased curvature a bit, thus lowering the kinetic energy and the total energy. So the overall wave function would contract and the peaks become sharper. Note the likelihood that, with a lower total energy, the kinetic energy would remain negative throughout the central region, so that the no-node wavefunction for a heavier particle would show only two humps.