

Chemistry 125 First Exam Answers

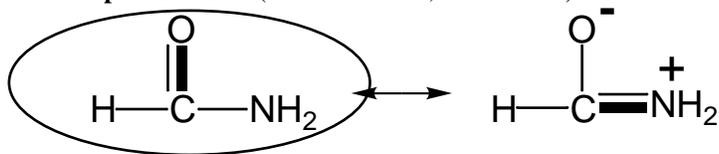
Average 74.2

September 26, 2001

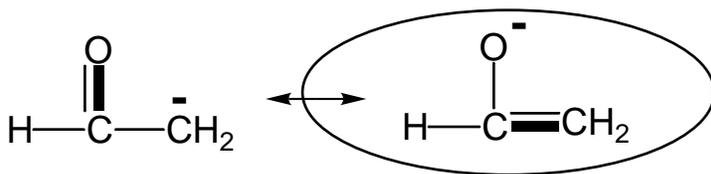
1/3 of scores > 84; 2/3 > 69

Answers in Helvetica Font ; Questions in Times

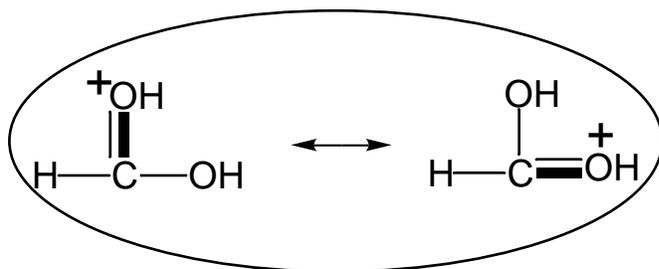
1. (4.5 minutes) **Complete** each structure below. Then in each pair of resonance structures **circle the more important one**. (In case of a tie, circle both.) Write a few words **explaining** your choices.



The **heavy lines** in each structure indicate the double bonds necessary to make reasonable resonance structures with complete octets.



In the first pair the left structure is better because there is no separation of charge.



In the second pair the right structure is better because the more electronegative atom (O) gets the negative charge.

In the third pair the structures are equivalent, because these formulae do not show actual geometry, only bonding. [The actual molecule is Y shaped rather than T shaped.]

2. (4.5 min) The ribosome is a pretty big structure containing some 300,000-400,000 atoms (including water molecules inside the ribosome and hydrogen atoms). Pretending that these atoms are packed in a cube, which of the values below gives a reasonable estimate for the **length of an edge** of the cube (**circle** one value):

15 atoms 70 atoms 500 atoms 1500 atoms 5000 atoms

70 cubed is about 350,000

Assuming that the distance between neighboring atoms is on average 1.5 bond distances, **circle** the approximate **length of an edge** of this ribosome box:

30 Å 16 nm 160 nm 0.75 μm 11 μm 0.3 mm

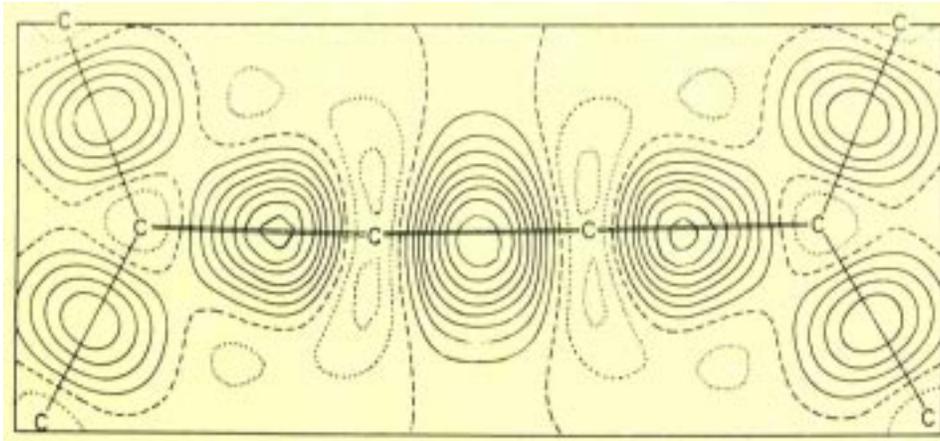
Bond distances are about 1.5Å. 1.5 bond distances is about 2.25Å. 2.25 X 70 is about 160Å = 16 nm.

If a bunch of ribosomes were lying next to one another on a glass slide, would a high-powered **optical microscope** be able to see them as separate structures? **Explain** your thinking, being sure to mention how scattered light incorporates information on the distance between such particles.

NO. The shortest wave length for visible light is about 400 nm. This is nearly 30 times longer that the distance that needs to be resolved, so an optical microscope could not do the trick.

The way scattered light tells that it came from separate bodies (rather than from a single body) is by the variation of intensity as a function of scattering angle as a result of interference. If spacing between the bodies is much shorter than the wavelength of the light, their scattered waves are effectively in-phase for any scattering angle, and they look like a single body.

3. (16 minutes) Consider the following figure in which the four terminal C atoms are parts of benzene rings not shown.

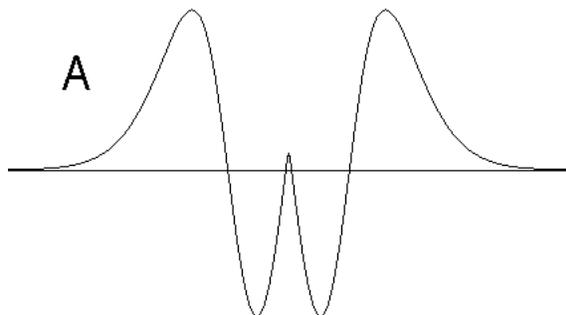


- A. Explain the procedure that was used to generate data plotted in this figure (mention both experiments and calculations).
- B. Explain exactly what the straight and curved lines show (and how dotted and solid curves differ).
- C. What qualitative and quantitative insight does one gain about the nature of carbon-carbon bonds from this figure?
- D. Explain a way in which this plot supports the Lewis theory of bonding and a way in which it refutes the theory.
- A. X-ray diffraction from a single crystal of the substance was used to create a map of the total electron density as a function of position within the sample. This map showed what was essentially atoms (spherically symmetrical distributions) at the location of the Cs in the picture above. From this map was subtracted the electron density that would be observed from a set of ideal non-interacting atoms (densities from quantum theory) located at the same positions to generate this “difference density plot”. This map is a planar section through the three-dimensional electron difference density map. The section is chosen to pass through the nuclei of the 8 atoms shown.
- B. The straight lines are symbols for single and double bonds, they don't mean anything physical. The solid curves are contours of successively higher difference density within this xy plane. (The contour level is fine - difference between successive lines is only $0.05 \text{ e}/\text{\AA}^3$.) The dotted curves show negative difference density contours, i.e. where the electrons shifted from to increase density in the regions bounded by solid curves. [Incidentally, the dashed curve is where the difference density is zero.]
- C. On forming a molecule, electron density shifts from the region near atomic nuclei to the region between nuclei. However the amount of electron density that shifts is very small (the maximum difference density is only about $0.5 \text{ e}/\text{\AA}^3$, and this holds only over a very small volume). The difference density in the double bonds is greater than in the single bonds (but not twice as great). Cross sections through the center of the C=C double bonds show ellipsoidal increase in electron density, whereas single bonds are roughly round in cross section. This is evident in this view from the fact that the central C=C difference density is higher top-to-bottom than that in the flanking C=C bonds.
- D. It supports the Lewis theory by showing that there is in fact sharing of electron density between adjacent bonded atoms [but not for the C-F bond, or O-O, or a number of others]. It refutes the theory by showing that the amount of electron density that is shared is very much less than two electrons. [Analogous plots show unshared pairs on appropriate atoms.]

4. (12 min) These four 1-dimensional wave functions look superficially similar, but they represent different potentials - **Coulombic**, **Harmonic Oscillator**, **Double Minimum**, and **Morse** (not necessarily in that order). **Label** each picture with the name of the appropriate potential, and for each **explain** what distinctive feature(s) proves your assignment.

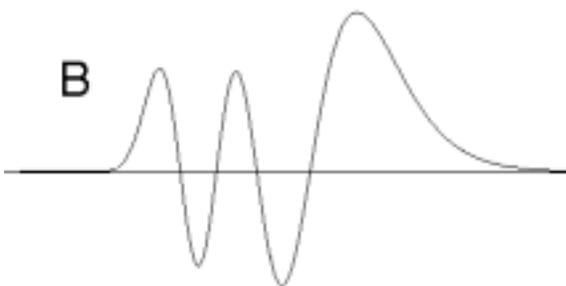
As a class you did very well on this question. Congratulations.

A few people forgot to explain, which was disastrous



Coulombic Potential

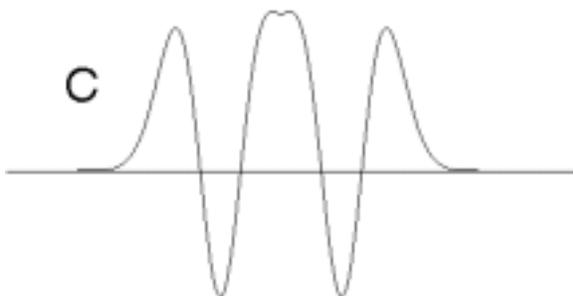
At the center the curvature toward the baseline is very sharp, especially compared to the amplitude. So the positive kinetic energy is VERY high. This happens near the center ($r = 0$) for a coulombic $1/r$ potential. [also the outer peaks are very broad, showing a long range of low positive kinetic energy, which again is consistent with a coulombic potential.]



Morse Potential

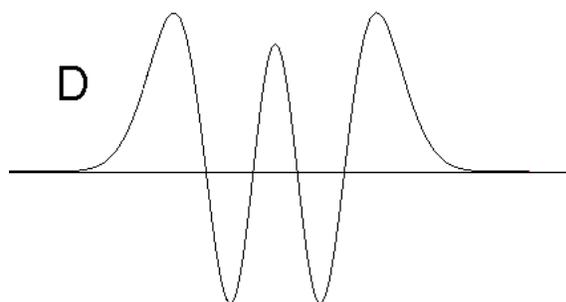
The unsymmetrical wave function indicates an unsymmetrical potential. The only unsymmetrical potential in the list above is the Morse potential.

[Furthermore the large peak on the right with relatively little curvature toward the baseline indicates an extended range of low positive kinetic energy consistent with the "tailing off" of the Morse potential as the bond breaks.]



Double Minimum Potential

The central peak has a dimple indicating a small range of curvature away from the baseline, that is of negative kinetic energy. In this region the potential energy must be greater than the total energy, whereas the flanking regions have positive kinetic energy, that is potential energy lower than the total energy. Thus there must be a maximum of potential energy between two minima.



Harmonic Oscillator

The central three peaks (one positive, two negative) have similar absolute values of curvature divided by amplitude denoting similar values of positive kinetic energy. The outer peaks have less curvature and greater amplitude denoting lower positive kinetic energy. Thus the potential is high on the sides and relatively flat in the middle, as expected for a parabola.

5. (3 min) Write the formula of the wave function for the electron

in a 2s hydrogen atom. [You may omit all multiplicative constants.]

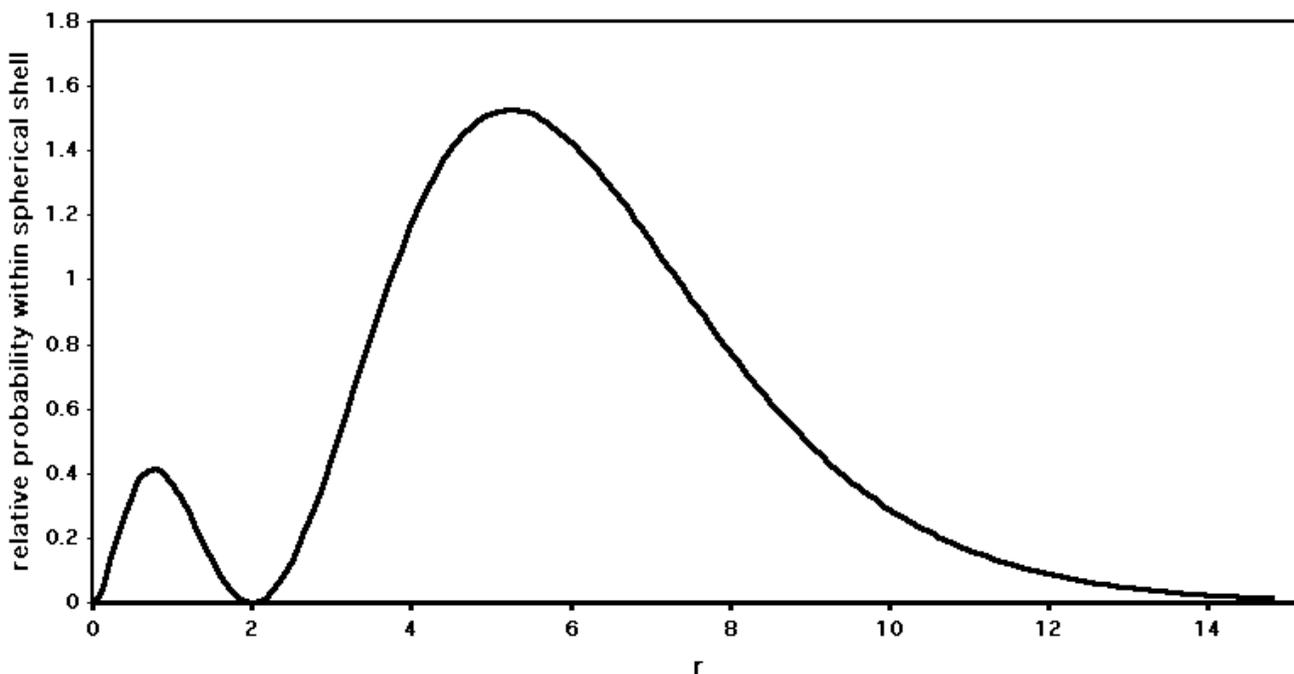
$$\Psi = (2-r)e^{-r/2}$$

[Although I had said $(2-r)e^{-r}$, I was wrong. It could either be the above or $(1-r)e^{-r}$.]

6. (4 min) **Explain** what function would you plot to make a graph of the **relative** probabilities of finding a 2s electron at various distances from the nucleus. **Sketch** a rough graph of the function.

The probability density is given by Ψ^2 . But one must multiply by r^2 to correct for the fact that the area corresponding to a certain r is proportional to r^2 (surface of a sphere is $4/3 \pi r^2$). Since we're only interested in relative probabilities we can forget multiplicative constants. Thus what we want to plot is $r^2 \cdot (4-4r+r^2) \cdot e^{-r}$

This function will start at 0 for $r = 0$ (because of r^2), increase for a time, then decrease to become 0 when $r = 2$ (because $4-4r+r^2 = 0$), then increase again until the decrease in e^{-r} makes it approach zero asymptotically. So there is a radial node between two maxima.



7. (2 min) Why should one believe that the Schrödinger equation gives a correct picture of the hydrogen atom composed of an electron and a nucleus, and that the clairvoyant picture of the hydrogen atom composed of 18 anu is incorrect?

HOW DO YOU KNOW? (remember Faraday and Feinman!)

Correct answers must mention **SPECIFIC FACTS** not just theories. Since this was one of the points emphasized during the course so far, we demanded facts, not assertions, in the answer.

Many different experiments have given results consistent with the Schrödinger equation, and nothing but the imaginations of Bishop Leadbeater and Mrs. Besant have given results consistent with the clairvoyant picture. No one has been able to repeat their clairvoyant "observations".

To be fair, we should say that not much of the direct evidence to support Schrödinger has been shown to you yet. Mostly you have had to rely on my assertions (which you shouldn't be satisfied with). But we have seen some real independent evidence, which you should cite as supporting the chemist's viewpoint. Theory should not count as independent evidence, only experimental observation consistent with the theoretical predictions.

The total electron density of Rubofusarin showed spheres of electron density smoothly increasing toward the center of atoms with none of the fine structure reported by the clairvoyants. Moreover, when atomic densities calculated by the Schrödinger equation were subtracted from the x-ray total density, almost everything cancelled (except for small deformation density), showing how well the experimental atoms in

various molecules (such as tetrafluorophthalodinitrile) matched the Schrödinger calculation. For evidence specifically on the H atom, we showed the density for Hs on the benzene rings of the “tetraphenylbutatriene” molecule (also the subject of Question 3 above).

[AFM and STM don't have the resolution that would be necessary to disprove the existence of the tiny anu.]

8. (4 min) **ANSWER A OR B (NOT BOTH)** Hard question for small credit, finish your other answers first.

A. Why would it be difficult to devise a version of “Erwin meets Goldilocks” to handle more than one dimension?
or

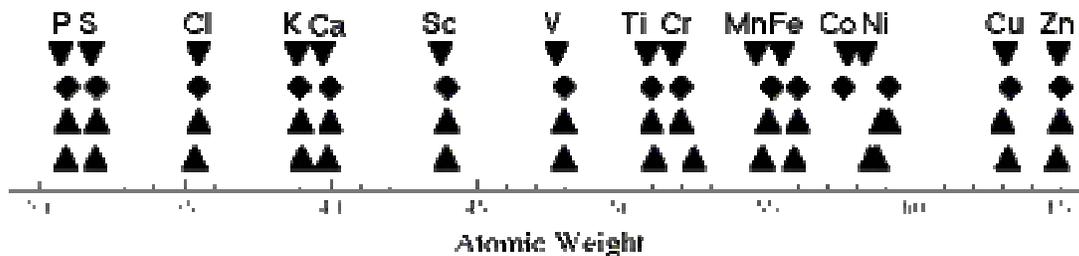
B. Explain how data in the following figure were used to show that at least some of the “clairvoyants” were intentionally cheating rather than being innocently self-deceived by their 1895-1907 “observations.”

Top triangles: 1905 Chemists' atomic wts.

Diamonds: number of Occult Anu / 18.

Bottom triangles: Meyer (1884) experimental values

Middle triangles: Meyer text (1884) rounded to integers



A. The program is able to test trial energies by using Schrödinger's formula for the kinetic energy to go from the difference between total and potential energy and the amplitude of ψ to reckon the curvature of ψ and thus to draw a trial wave function. The problem in more than one dimension is that the difference between total and potential energy gives only the total kinetic energy, which is a sum of curvature terms (actually curvature over ψ , and mass as well, when there are several particles), and there is no way of knowing how much curvature is to be associated with each individual dimension. Therefore it is not possible to trace out the wave function in two dimensions à la *Erwin meets Goldilocks*.

It is true, as some answers said, that it is harder to plot in four dimensions (x, y, z, Ψ) than in 2, but it is easily possible with a computer (for an example see *Atom in a Box*).

B. What makes this question hard is trying to show that even though Leadbeater and Besant were obviously wrong, and must have been aiming to agree with an earlier, incorrect chemical table, they were not innocently self-deluded.

Having chemical data like that in the 1884 text available, they could have made a large number of “observations” of their fanciful atoms and then decided that only the ones near authentic chemical atomic weights were correct. They could even have decided which element they were observing on the basis of the number of anu being 18 times some known atomic weight. Perhaps they would recall that something about the erroneous observations was a little fuzzy or indistinct. Honest scientists make this kind of mistake in good faith all the time picking data to fit a preconceived notion.

This excuse will not work, however. Even if they made 60 “observations” within the range of the graph shown above (35 AMU, or $18 \times 35 = 630$), and reported only the best 15 of them, the chance of making exact hits on 10 of these is only 1 in 10,000,000,000,000.

Still it has been argued that they may have subconsciously tailored their observations to fit atomic weights that they had previously happened to memorize. The complexity of the structures they reported makes subconscious tailoring implausible. At least some of them consciously cheated.