

Chemistry 125 First Examination Answers September 22, 2004

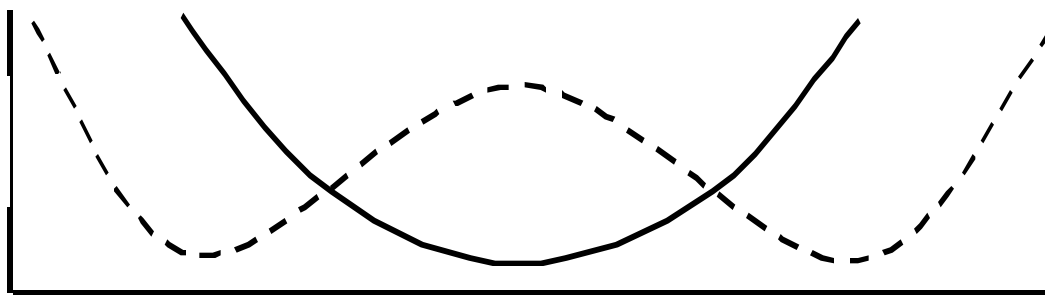
Statistics: average score 71.4 1/3 of scores >75 2/3 of scores >68

1. (7 minutes) **DRAW TWO** Lewis-Dot structures for a chain of 3 O atoms (ozone). Then **DRAW a graph** to **EXPLAIN** how the “single- vs. double-minimum” concept relates to the idea of resonance involving these structures.



[Note: These pictures may look identical, but they are not, because the oxygen atom on the right is double bonded in the left structure and singly bonded on the right. Be careful to show that triply bonded oxygen atoms bear a + charge, because its third bond is formed by sharing one of its unshared pairs. Actually the O-O-O bond angle is 117°, not 180° as suggested by these formulas. We'll discuss such things later.]

One can associate bond length with bond type (double shorter than single), so these two structures *might* denote different geometries. This is shown by the dashed curve below, which displays the change in potential energy as the central carbon moves from the left (left structure) to the right. On the other hand, the two structures might denote two different Lewis dot pictures of the **same** minimum energy structure with the central O atom precisely in the middle, giving the single-minimum potential energy curve shown as a solid line. *A priori* it is not obvious which view is correct, but, as in many such cases (*e.g.* benzene, carboxylate anions), experiment shows the single-minimum is correct, and from the Lewis point of view the two structures are said to be “resonance structures.”



2. (8 min) **State** Earnshaw’s Theorem: In a system of particles governed by inverse square forces [or $1/r$ energies], there can be no local minimum (or maximum) of energy in free space (away from particles).

Explain how J. J. Thomson’s “**plum-pudding**” atom conformed to the requirements of Earnshaw’s Theorem:

By placing his negative electrons (“corpuscles”) *INSIDE* a diffuse cloud of positive charge, Thomson could find positions that were local energy minima for positive charges. Thus a static structure with the electrons in these positions constituted a stable structure [if electrons were displaced a small distance they would “roll back” to the local energy minimum].

Explain how G. S. Lewis could advocate his “**octet**” structure for the atom, despite believing Earnshaw’s Theorem:

Lewis proposed that at the short distances corresponding to atomic dimensions, Coulomb’s Law no longer applied. Since the forces were not inverse square, Earnshaw’s Theorem did not apply. [What he actually wrote was, “this field is not a continuum but is strikingly discontinuous.”]

3. (15 minutes) What is the **simplest way** to measure of each of the following with reasonable accuracy?
(Name the **EXPERIMENTAL** method – you **don't** need to describe it - but if any **calculations** are required to interpret the results, **mention them very briefly**.)

- A) The approximate size of the molecules in olive oil [6 points]

Franklin's method of seeing how far a small known volume of the oil would spread on water. Note that the monolayer is too thin to be detected by interference colors of visible light (λ too big). Franklin observed the area by its ability to still ripples on the water. Division of the volume by the area gives the thickness of the layer, which we now know to be monomolecular. [Actually Franklin did not do this calculation, because he thought that the particles repelled one another, so there was no reason for him to think they were still in contact with one another in the monolayer.]

- B) The precise positions of numerous iron atoms on the surface of a small sheet of copper. [4 points]

Scanning Tunneling Microscopy (STM). No calculations are necessary. It is just necessary to know how far the probe tip has moved from one atom to the next. [It is VERY difficult to image single atoms by AFM.]

- C) The amount of electron density that is *actually* involved in forming a carbon-carbon bond. [8 points]

Very accurate determination of total electron density by X-ray diffraction (preferably at low temperature to minimize atomic vibration). Bonding electron density is then visualized by subtracting from this total electron density the density that would be predicted from overlapping UNDISTORTED atoms (atomic densities calculated by quantum mechanics). The resulting difference (or deformation) density maps show where electron density has built up to form bonds (or lone pairs). Integrating over a bonding region yields the amount of electron density involved in the bond.

- E) The arrangement of numerous fluorescent-molecule impurities within a thin layer of organic molecules. [4 points]

Scanning Near-Field Optical Microscopy (SNOM). As in STM, not special calculations are involved. [Note that AFM would have a difficult time distinguishing the impurity molecule from its surroundings by "feel", and that x-ray would not be useful because the sample is not crystalline, and even if it were, the impurities may not be arranged on a lattice. One needs a technique that can detect them singly, like their light emission. An optical microscope would not provide nearly as good spatial resolution as SNOM, where one knows the position of the optical fiber tip quite precisely at the time light emission from the illuminated molecule is detected.]

- F) The offset between the two helices of a DNA double helix [8 points]

X-ray diffraction (of an oriented fiber) as in Rosalind Franklin's diffraction pattern of b-DNA. For a given x-ray wavelength, the angular deflection of spots along the "x" pattern (denoting a helix) tells the distance between successive turns of a single helix. The sequence of intensities along a branch of the "x" pattern shows neither the steady decrease expected for a single helix, nor the alternation of absence and presence of spots, expected for evenly spaced double helix, but rather the weak-strong-strong-very weak-strong sequence expected for an offset double helix with major and minor grooves. [The actual offset may be determined by matching the intensities to expectations generated mathematically (or by the "wave machine" demonstrated in class) and using Bragg's law to analyze the spacing of dots.]

4. A respected text of molecular spectroscopy uses this figure to describe vibration of the H-Cl molecule (during which the H atom moves, but the Cl atom stays put, because it is so massive).

The vertical axis is labeled "Energy".

You may ignore the units (which are not kcal/mole).

- A. (1 minute) In the **box** below the graph **label** the **horizontal axis** appropriately, and **identify** its **units** (which run from -0.2 to $+0.2$).
- B. (4 min) Three types of figures appear on the graph. **Explain** below what **each TYPE of feature** is intended to show. [Hint: one type of figure shows two **different** things.]

(1) a **parabola** (labeled $1/2 ks^2$)

Shows the potential energy resulting from stretching (or compressing) the Cl-H bond.

(2) **three horizontal straight lines**,

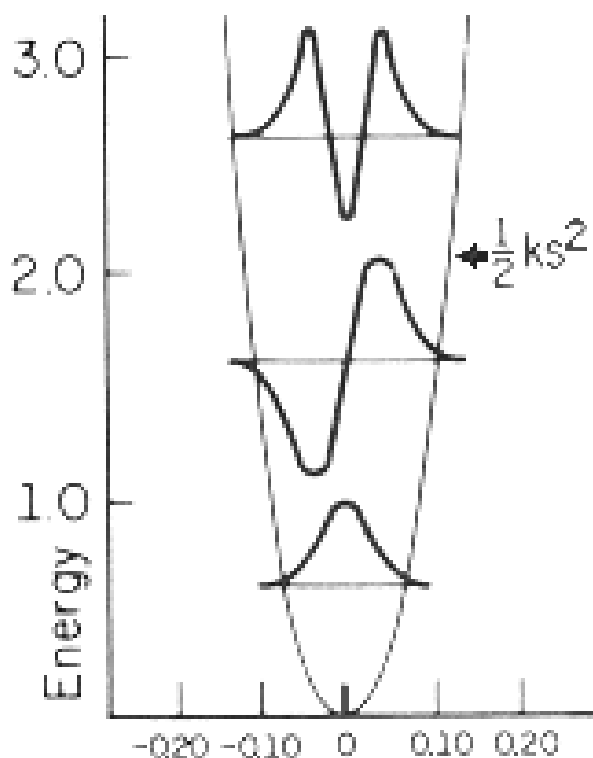
The horizontal lines show both the total energy of three satisfactory solutions of the Schrödinger Equation for this system AND zero of the vertical scale for the corresponding Psi plots (see below)

(3) **three curvy lines**

These are the three Psi functions that solve the Schrödinger Equation for this system with the total energies shows by the horizontal lines (which also show zero for the corresponding Psi function).

- C. (2 min) **Comment** on the **relative heights** of the three horizontal lines

For the parabolic ("harmonic oscillator") potential, the allowed energies are equally spaced with the lowest energy lying above the 0 of total energy by $1/2$ of the line-to-line spacing.

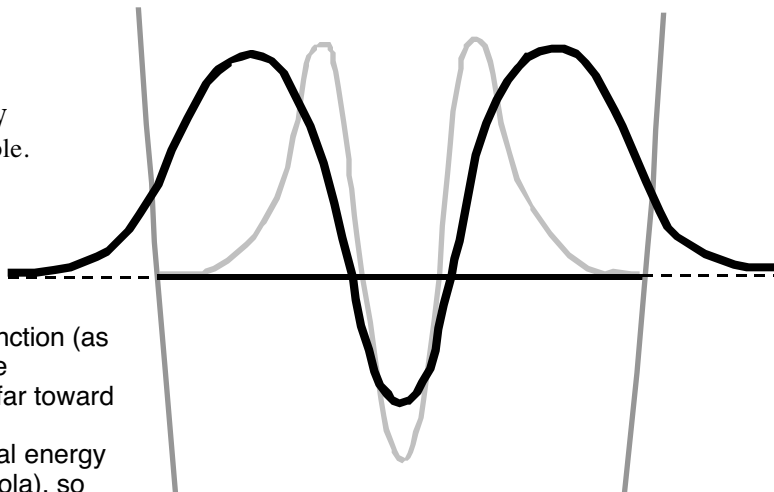


Displacement of the H atom from its position in the unstretched Cl-H bond (\AA)

(Question 4 continued)

- D.** (6 min) The curvy lines in the figure above were apparently drawn by hand - and none too carefully! The figure to the right reproduces a detail including parabola, horizontal line and curvy line. **REDRAW this curvy line** to make it as accurate as you are able.

Then **EXPLAIN** why the original was faulty, and how your adjustment fixes it.



The most serious error in the original wave function (as in the others in the original figure) is that it puts the inflection points, where the tails begin, **WAY** too far toward the center of the plot. They should come at the displacements where potential energy equals total energy (intersections of the horizontal line with the parabola), so that the kinetic energy and the curvature are zero. The corrected curve has inflections at the proper locations.

A corollary of this error is that the wave functions disappear at the parabola, rather than extending substantially into the “forbidden” regions of negative kinetic energy. The original curves show wave functions that are restricted to the classical allowed portion of space, rather than quantum mechanical wave functions.

[Incidentally, the reason physical chemists are prone to make such an error, or fail to notice it when a draftsman makes it, is that they hurt their intuition by spending too much time talking about the unrealistic “particle-in-a-box” potential, where the potential energy rises abruptly without limit on either side of a flat bottomed valley.]

A less important error involves the two maxima of the original (which correspond to positions of smaller kinetic energy, because they are away from the minimum of the parabola) have a ratio of curvature to amplitude of Ψ that is quite similar to that at the minimum of the original, whose position corresponds to greater kinetic energy, and thus should show a larger ratio. Here we have decreased the amplitude and increased the curvature of the central minimum to emphasize this difference. [Since the curve was drawn by hand, it is still not precisely correct.]

- E.** (5 min) “*Ut tensio sic vis*” (“As the extension so the force”)

Robert Hooke 17th Century

Who first wrote this statement and **in what century**?

Explain how the statement relates to the parabola in the figure on the previous page, **AND explain** whether one could use the **lines-of-force** concept to describe the direction and intensity of such a force in 3-dimensional space.

The slope (first derivative) of a potential energy curve shows the force experienced by a body at that position. If the energy is $0.5 \times k \times r^2$, then the force must be $k \times r$, that is the force is proportional to the displacement (or “extension”). This is of course Hooke’s Law.

To represent the magnitude of force by the number of lines of force in three dimensions, the force must be proportional to $1/r^2$, because the area of a sphere that cuts all the lines of force emanating from a single point increases in proportion to r^2 , and the number of lines of force must be independent of r . Since Hooke’s force is proportional to r rather than to $1/r^2$, it cannot be represented by a lines-of-force diagram.

- 5.** (2 min) **Why** did Berkovitch-Yellin and Leiserowitz choose a “cumulene” with **three C=C double bonds in a row** for their precise x-ray investigation of bonding density?

They wanted to show that bonding electron density, as shown in electron difference density maps, was experimentally significant and did in fact represent bonding. Chemists had long thought of C=C double bonds as extending in a particular direction from the straight line joining the two carbons (namely, the direction of the axis of the p-orbitals involved in the double bonds, or the direction of bending of the “bent” single bonds that constitute a double bond). Since this direction should change by 90° between successive double bonds sharing a common carbon, finding that the oval bond cross sections were rotated by the same 90° demonstrated the realism of this experimental technique.