Chemistry 125 **September 27, 2002** First Examination Answers

1. (4 min) **Explain** which of the following techniques would be best for measuring the distance between two copper atoms about 5Å apart on a graphite surface: AFM, STM, high-powered optical microscopy.

AFM (atomic force microscopy) would be inadequate because the width of a typical tip (the radius of curvature at the tip) is four or more times as great as the spacing between the atoms.

High-powered **optical microscopy** would be inadequate because the light wavelength is about 100 times as great as the separation between the atoms. Thus there could be little difference in phase between the scattered waves from the two atoms, and the variation of intensity with scattering angle that comes from dephasing is the ultimate source of information about the existence of two scatterers.

STM (scanning tunneling microscopy) with a very narrow tip ending in a single atom could do a fine job, because the graphite and copper are electrically conductive and allow detecting near-contact between a single pair of atoms by the variation of electrical conductivity.

2. (8 min) **What is fundamentally wrong** with the idea of orbitals? How do the $\mathbf{Z_{eff}}$ and **SCF** methods attempt to circumvent this difficulty? What is "**correlation energy**"?

Orbitals are fundamentally wrong when they are used to express a many-electron wave function as a PRODUCT of one-electron wave functions (orbitals). Using the square of such a product wave funtion to predict the joint probability of each of the electrons being in a particular region could be correct only if the electrons are indepent of one another. But the **electrons are very much interdependent**, because they repel one another (and because the Pauli principle does not allow two electrons to be in the same place at the same time).

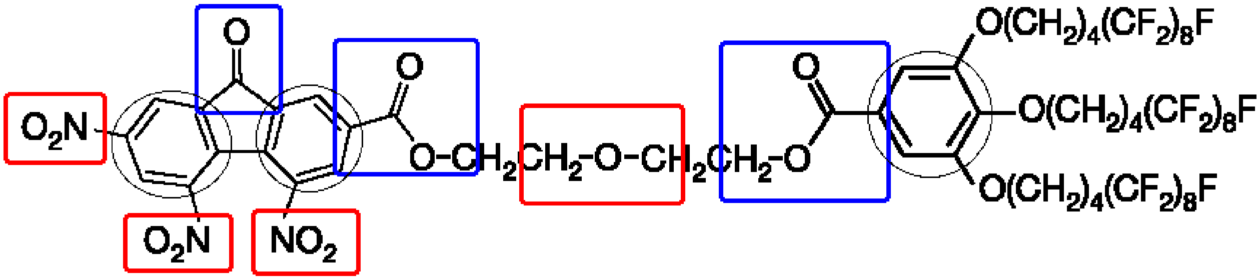
If one makes the "orbital approximation", it is important somehow to make allowance for the repulsions among the electrons.

The simplest way to do this is to use an *effective* nuclear charge ($\mathbf{Z_{eff}}$), where the nuclear charge used to write the wave function of one electron is reduced by contributions from the others.

A more sophisticated correction is to calculate the wave function for one electron using for the source of potential energy not only the fixed nuclei, but also fixed clouds of the other electrons. By cycling repeatedly among the in calculating improved functions one ultimately arrives at values that cease changing, which is called the self-consistent fiels, or **SCF**, limit.

Even at the SCF limit, there is residual error due to the failure to account for the distortion of the other electron clouds as the electron of present interest moves from place to place, that is, to the ability of the electrons to correlate their motion in order to keep apart. The resulting overestimate of energy is called "**correlation energy**".

3 . (4 minutes) In yesterday's issue of the journal *Nature* [vol. 419, p. 384] is a description of "helical dendrimers" that show promise as electronic materials. The formula below shows one of the molecules discussed. **Neglecting** the three $(CH_2)_4(CF_2)_8F$ groups on the far right, **circle FOUR DIFFERENT functional groups** in this molecule and **give their names**. Make sure the groups have different names.:



The functional groups are:

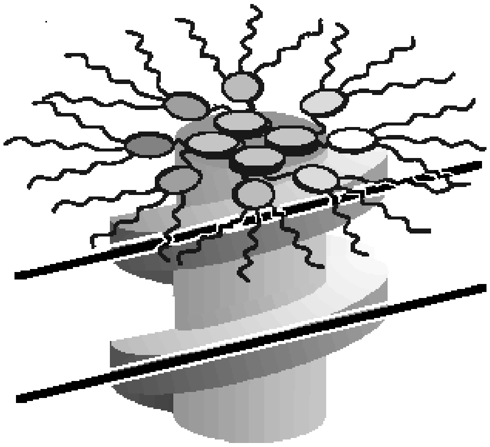
3 nitro groups in red boxes (use only one)
1 ether group in red box (3 others involve the ignored groups)
1 ketone in blue box on the left
2 ester groups in blue boxes (use only one)
3 aromatic rings in black circles

[Note that the ester group is NOT a ketone and an ether, but its own separate group. We'll see why soon. We'll also see why nitro groups are VERY different from amines. The book includes alkanes in the table of functional groups. They are not really functional, in fact they are the definition of non-functional, but if you were marked off for including an alkane in your list, you should request a little more credit.]

4. (6 min) The authors of the *Nature* paper suggests that molecules of the type shown in Question 3 pack together with the flat portion on the left (the part with all the NO_2s) stacked in the middle to form a cylinder and the "hairy" part on the right arranged as a helical wrapping around the cylinder, denoted by the spiral around their rough figure shown on the right

As evidence to support the stacking and the helical wrapping of this material they show a fiber's x-ray scattering pattern, six spots of which are shown below right.

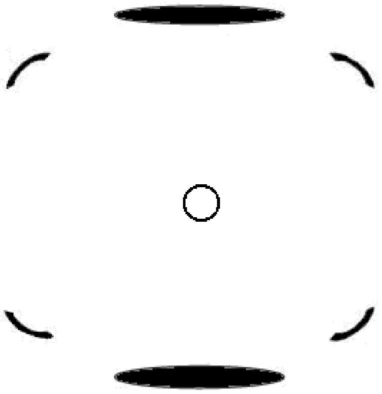
(The open circle in the middle shows where the undeflected x-ray beam would hit the film.)



Explain how the **six spots** support the existence of **stacking and helix**, and explain how the pattern shows the **spacing** of the stacking and the **pitch** (steepness) of the helix. **Is the pattern consistent** with the rough figure showing the packing?

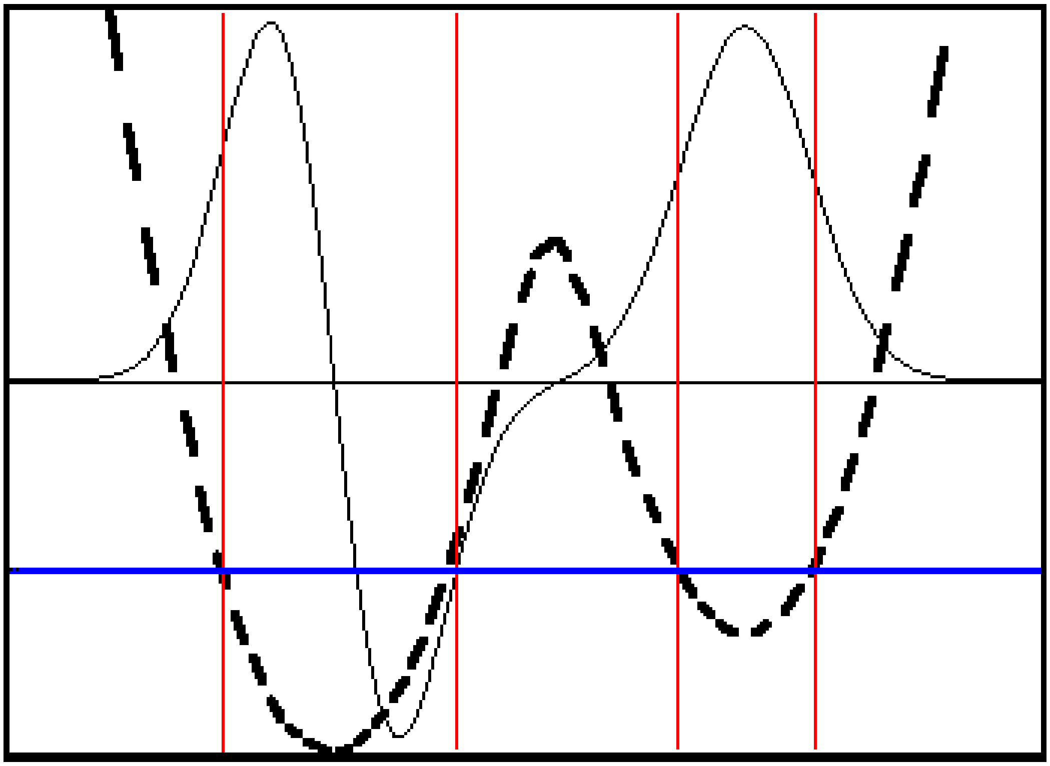
Stacking: The two large, dark spots at the top and bottom result from the stacking. The lie on a line perpendicular to the planes of high electron density, that is, along the axis of the cylindical core where the "aromatic" (benzene-like) groups are stacked. Their distance from the of the center of the x-ray photograph (that is, the angle of deflection of the "reflected" beam) is inversely related to the plane-to-plane spacing of the stacked groups, so that the waves scattered by successive planes wil be out of phase by exactly one wavelength. This is consistent with the rough figure.

Helix: The four other spots show the beginning of the "X" on which spots from the scattering of a helix lie. The relevant successive planes of electron density (to which the branches of the "X" should be perpendicular) are more or less perpendicular to the plane of the figure above and intersect it approximately along the diagonal bars added to the figure. The angle of these bars show the pitch of the helix, and (as in the case of the stacking discussed above) their deflection from the direct x-ray beam is inversely related to the spacing between successive turns fo the helix.



There seems to be a problem with the schematic picture, because the pitch of the helix in the picture is much shallower than would be consistent with the branches of the "X" being perpendicular to the dark lines added to the figure. Furthermore the thickness of the stacked groups in the figure is much LESS that the spacing between successive turns of the helix, while the angle of deflection is slightly LESS, where it should be MUCH greater. Something seems fishy. Maybe the film wasn't flat, or the picture is overly schematic.

5.(9 minutes) The top frame shows a wave function Ψ (horizontal line is at 0). Ψ is a solution to the Schrödinger equation for a particle in one dimension with a certain potential energy as a function of position and a certain total energy. In the lower frame **sketch an appropriate potential energy** for this Ψ (the central horizontal line represents the total energy). You may wish to comment and/or use lines or arrows to show correspondence in position between the wave function and the potential energy function.



The heavy dashed line denotes the potential energy that generated the two-noded Ψ, and the horizontal solid blue line shows the total energy. The vertical red lines show where the light black Ψ has an inflection point (no curvature) and thus the kinetic energy is zero. Naturally this is where the total and potential energy lined intersect. Identifying these positions allows one to begin constructing the potential curve.

In the regions between the first and second red lines, and between the third and fourth, Ψ curves toward the Ψ = 0 baseline, and the potential energy must be below the total energy (kinetic energy positive). In the other three regions, the opposite is true.

The first maximum of has about the same amplitude as the second, but obviously greater curvature. The same is true of the minimum compared with the second maximum. Thus the kinetic energy must be much higher in the left well than the right one, and the potential energy correspondingly lower.

The potential energy thus must be an unsymmetrical double minimum.

[A common mistake was confusing nodes of Ψ, which have no special location, with inflection points, which denote positions of zero kinetic energy. A less serious mistake was failing to notice the greater curvature of Ψ in the region of the first well.]

6. (2 minutes) Could the wave function shown in question 5 be the lowest-energy solution for this Schrödinger equation. If not, **how many solutions of lower energy** should there be? Explain your thinking.

Since this wave function has two nodes, there should be two solutions on lower energy, one with one node and one with no nodes.

[A common mistake was counting crossings of the potential and kinetic energy as if they were nodes. Nodes are in the Ψ graph, not in the energy graph.]

7 . (5 min) **What factor** appears in **all** radial wave functions [R(ρ)] for one-electron atoms? **Why** is it reasonable that they should all contain this factor?.

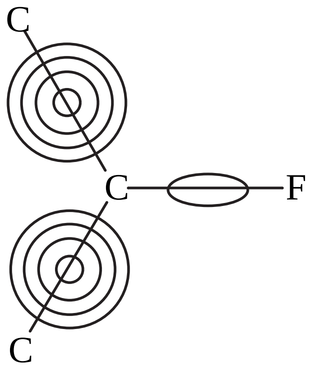
$\mathbf{exp}^{\mathbf{-r}}$ appears in all radial wave functions. This is reasonable because the potential energy (proportional to –1/r) becomes effectively constant at long distance, so that a bound electron (possessing less energy than would be required to escape from the atom) will in this region have a constant negative kinetic energy. The wavefunction that gives a constant negative kinetic energy is an exponential. [There are some subtleties because the atom is 3-dimensional, but this is the essential reason.]

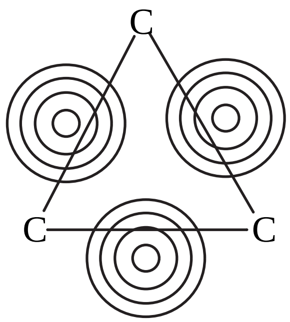
About 7 points were awarded for identifying the correct function, but providing a less convincing, or an unconvincing, reason, such as that the wave function must go to zero, or be largest near the nucleus (which is true only for *s* orbitals).

Some people earned 3 points for identifying r (or ρ) or Z as the persistent factor. Indeed they do occur, but the reason is much more complex. For example the, multiplicative Z just makes the wave function bigger by the same factor everywhere. It is included for purposes of normalization, not for adjusting the shape of the orbital.

8 . (12 minutes) For **ONE** of the following two cases **draw** a schematic **x-ray difference density** plot, **explain** how it would be generated experimentally, **and** use it to **discuss** the curious nature of the bonding:

The C-F bond from a benzene ring **OR** The C-C bonds in a ring of three bonded carbons.





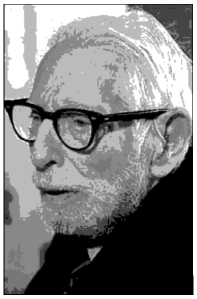
[These plots are schematic and do not include the more diffuse contours for negative difference density. Experimenal plots are shown on the course web page.]

Difference density plots are contour plots generated by subtracting spherically symmetric atomic electron densities (calculated quantum mechanically and positioned from x-ray results) from experimental total electron density maps generated by x-ray crystallography.

[Note incidentally that both of these groups are part of larger molecules that give good crystals. In particular a ring of three carbons would not only be a gas, it would also be so reactive that it could never exist in a crystal – as you will soon understand – so a structure with three double bonds is out of the question]

The curiosity in the C-F bond is that there is so little build-up of electron density in the bond. The reason is that the atomic model is spherically averaged, which puts 7/4 of a fluorine electron in the general region where the bond is to be formed. In fact only one electron from the fluorine will be used in forming the actual bond. In this sense to much atomic electron density is subtracted from the bonding region, and it is remarkable that any increase in density at all is observed. Subtracting fluorine atomic density for a distorted atom containing only one electron in the region to be used for bonding would have shown a substantial increase in difference density in the C-F bond. [See Dunitz interview on web page]

The curiosity in the three-membered ring (cyclopropane) is that the maximum concentration of difference density from the bonding does not occur on the line of centers of the bonded C atoms. The bonds are bent. [We will soon be discussing the quantum mechanical rational for such bent bonding, and independent evidence that such bonds are bent.]



9 . (Extra Credit) As a university science student, what is the most important trait you should have in common with Joseph Nathan Kane, who died last Sunday at the age of 103? [See obituary in today’s New York Times]

Kane was passionate about facts, and in particular:

> "At school, I would ask, **`How do you know?'** " he told an interviewer from Current Biography. "And that was usually at the end of the discussion."
>
> Late in life, he told a reporter for The Associated Press, "I'm stupid enough not to believe anything until I see the proof."

[Incidentally, Kane also “cared passionately about giving credit where credit was due.”]

What a great set of traits for a scientist !

[I was delighted by how well the class did on this extra-credit question when presumable none of you had actually seen the obituary notice in the morning paper. It made me feel as though I’d succeeded in teaching you something important. Perfect answers earned 2 points.]