Chem 344 2nd Hour Exam
Monday, Nov. 13, 2006, 2-3 PM

<u>Closed book exam</u>, only pencils and calculators permitted. <u>No Computers.</u> Put all of your work in the answer book. If you need graph paper there is a sheet in the exam packet. If you work out graphical values like slope and intercept on your calculator, you should fully explain your method, put in intermediate values and describe the result. "Floating" answers without substantiation receive little credit. Possibly useful information is at the end of the exam. ***Good Luck!!***

1. **(14 pts)** In the "old quantum mechanics" there were a number of "fixes" to classical theory to make it better agree with observation. Last year was the Einstein Centenary of several great discoveries. His 1905 explanation of the photoelectric effect in which light shining on a metal surface (in vacuum) ejects electrons with various kinetic energies was noted in his Nobel Prize.
   a. Explain what is observed and how Einstein explained it (i.e. how his formula works), what key development of Planck was used, note what particular new insight this formula/explanation developed about the behavior of quantum particles and/or light.

   Do only one (1) of parts b, c and d:

   b. If light of 450 nm wavelength shines on a Na metal surface and the ejected electrons are observed to have 1.5 eV of energy, what is the work function of the Na surface?
   c. If the goal were to create a larger electron current, what experimental parameter would be changed and why?
   d. What is the momentum of the electron ejected? Of the light hitting the surface?

Do only one (1) of #2 or #3 – (8 pts) :

2. Before Einstien's contribution, Planck explained the black body (bb) radiation effect.
   a. What was the important new (non-classical) idea introduced in this theory?
   b. Normal tungsten lights tend to have a yellow coloration (you will see this if you take photos indoors without a flash unit). If you want to make a light bulb better reflect the spectral distribution of the sun (peaking in the visible, eliminating the yellow tinge), how would you modify your light (using an analysis of the Plank bb result).?

3. If you excite many elements in a flame or an electric discharge, they give off light. Unlike the bb light, which has a continuous spectrum, atomic spectra are composed of sharp lines representing specific wavelengths.
   a. Explain the origin of these sharp lines.
   b. Bohr had a theory to explain the sharp lines of the H-atom. They come in several series, of which the Balmer series is in the visible. If the first two Balmer lines are: 656.28 nm (red) and 486.13 nm (blue-green), what is the next one?

4. **(14 pts)** Solving the Schroedinger Equation is central to answering quantum chemical questions:
   a. Write down a complete Hamiltonian operator for the diatomic molecule H-F. Be sure to indicate the correct limits of any summations you use to make your answer compact (which I recommend).
   b. Label each part with a brief explanation of its physical origin/meaning.

Do only one (1) of parts c and d:

   c. We usually do not care about where a molecule is in space or actually how fast it is moving. Describe (do not work it out) how you would use the Hamiltonian in (**a**) to make a Schroedinger equation for H-F and how you would simplify this equation to eliminate the motion of the molecule as a whole. (i.e. what transformation or assumptions would be needed—actually exactly soluble.)
   d. We are interested in the relative motion of the nuclei with respect to each other (vibration) but that is a topic of the next section of the course. How would you eliminate relative nuclear motion from the electronic motion to get an electronic Schroedinger equation useful for this part of the course (describe only, note the approximation used or give a representation for an approximate wavefunction that could be used).

5. **(12 pts)** For the following atoms or ions give the ground state configurations and term symbols: ${}^{2S+1}L_J$ {Hint: it may help if you use rare gas configurations to represent inner filled orbitals, e.g. Mg: $[Ne]^{10}(3s)^2$}
   a. P
   b. Ti^{+2}
   c. Co
   d. B

6. **(6 pts)** Filling atomic orbitals creates an electronic structure pattern that makes elements with similar configurations (but different principle quantum numbers) have similar chemistry which thus explains the shape of the Periodic Table.

Answer only one of the following, part a or b:

   a. Explain how the atomic radii vary across the 2nd and 4th rows of the periodic table. Give a reason for the trends.
   b. Explain how the ionization potentials vary across the second row. Note singularities, deviations from the overall trends. Explain.

7. **(22 pts)** Use MO theory and the LCAO-MO method to explain the configuration and energy of the BN diatomic molecule
   a. Give an orbital energy level diagram, indicate the relative energies of the n=2 AOs and the MOs they give rise to. (You may assume the 1s AOs give rise to non bonding MOs and skip them – warning do not miscount electrons!!)
   b. Fill the orbitals using the aufbau approach for the ground state. What is the bond order?

Answer only one of the following, part c or d:

   c. Is your BN molecule diamagnetic or paramagnetic? Why?
   d. Which end of the molecule (B or N) will have a higher electron density? Why?

Answer only one of the following, part e or f:

e. What is the term symbol $^{2S+1}\Lambda$ for the ground state and the first excited state of BN?
f. Predict it the bond length will increase or decrease for BN^- and BN^+. Give brief reason to justify your answer.

8. **(20 pts)** I guess there must be a particle in a box problem, and, if here, then I can put a harmonic oscillator one on the final. Normally for a box varying from 0 to L:

$$\psi_n(x)=(2/L)^{1/2}\sin(n\pi x/L) \text{ and } E_n= n^2h^2/8mL^2$$

a. If the box is shifted form x=0 → x=L to be centered on x=0 (i.e. now V=0 from x= -L/2 → x= L/2, and V=*oo* for |x|>L/2, *note: oo=infinity*) how will the solutions change form the usual ones. What will be the new wavefunctions and their energies? (Hint—you do not need to work this out if you can explain it. A drawing may help you.)
b. Evaluate $<p_x>$ and $<p_x^2>$ (expectation values of momentum) for n=2. (Hint—this is easy, no integrals, if you recognize some relationships)
c. Explain why $<p_x>^2$ =/ $<p_x^2>$ (not equal).

Answer only one of the following, part d or e:

d. Describe what would happen to both the wave functions and their energies if the walls at –L/2 and L/2 were reduced in height from V=*oo* to V=V_o (a constant value >0). Here a drawing might help make your point, you do not need to do any calculations or derivations.
e. Compare the number of nodes in n=3 for the particle in a box with n=3 for the H-atom (do not forget the extra dimension). Explain why the number of nodes should increase with energy.