

Chem 344 2nd Hour Exam  
Friday, Nov. 14, 2008, 2-3 PM

Closed book exam, only pencils and calculators permitted. No Computers. Put all of your work in the answer book. *You may have one sheet of paper, 8.5"x11" with anything written on it, nothing more allowed.* If you compute things 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. **(16 pts)** In the "old quantum mechanics" there were a number of "fixes" to classical theory to make it better agree with observation. Planck's explanation of black body radiation was a key discovery that moved thinking away from classical models and resulted in his Nobel Prize.
  - a. Explain what is observed for blackbody radiators (sketch some spectra, take care to get the right intensity distribution, and show its temperature variation).
  - b. Briefly explain what important new (non-classical) idea Planck introduced in his theory to explain this shape and temperature dependence of the distribution.

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

- c. Briefly explain the problem classical models had particularly in the UV part of the spectrum.
- d. If you take photos indoors, without a flash unit, they tend to have a yellow coloration, but with a flash they look like they were taken outdoors. Briefly explain based on the Planck black body equation.

**Do only one (1) of #2, #3 or #4 – (8 pts) :**

2. These questions relate to the photo-electric effect:
  - a. If light of 350 nm wavelength shines on a Na metal surface and the ejected electrons have 1.5 eV of energy, what is the electron energy for 800 nm light?
  - b. What is the momentum of the electron ejected in both cases?
3. Bohr had a theory to explain the sharp lines of the H-atom in a flame or discharge,
  - a. The Lyman series is in the UV, Balmer is in the visible and Paschen is in the near IR. Explain why are they in different spectral regions, which is the highest energy and what parameter/constant differs between them.
  - b. If the fourth Lyman line occurs at 95.0 nm (vacuum UV), where is the first one (longest wavelength transition in the series)? What is its energy? [*watch units!*]
4. Chicago street lights are yellow in color and suburban ones are bluish but both use similar power. Please explain this observation using "old quantum mechanics" concepts and observations.

5. **(18 pts)** We have developed our formulations of quantum mechanics means of using five assumptions we called postulates.
- What properties must a wavefunction have according to the first postulate?
  - Suppose a hydrogen atom (ion) protonates the retinal Schiff base in rhodopsin, and its motion in this weak bond is described by an anharmonic oscillator. If you approximate the wavefunction for its lowest energy state by the  $v = 0$  harmonic oscillator solution, how would you determine the proton position?
  - If the Sc atom has one electron in the  $3dz^2$  orbital, determine its angular momentum about the z-axis and the magnitude (not direction) of its total orbital angular momentum? [Angular momentum:  $\mathbf{L} = \mathbf{r} \times \mathbf{p}$ , where  $\mathbf{r}$  is position and  $\mathbf{p}$  is momentum of a particle  $i$ .]
6. **(20 pts)** Solving the Schroedinger Equation is central to answering quantum chemical questions:
- Write down a complete Hamiltonian operator for the diatomic molecule B-H. Be sure to indicate the correct limits of any summations you use to make your answer compact (which I recommend).
  - Label each part with a brief explanation of its physical origin/meaning.
- Do only one (1) of parts c and d:**
- This is a multi-electron problem, yet we wish to solve it as though it were a single electron problem. Which terms in the Hamiltonian make the single electron model fail (or, in practice, require an approximation) and why?
  - Suggest a possible form of an LCAO-MO type solution to this problem (i.e. the minimum functions you would use and how they would combine).
7. **(6 pts) Do one of the following:**
- What is the variation principle and briefly describe how does it leads to improved solutions to the Hamiltonian (Schroedinger Equation) problem?
  - Describe what how the Hartree-Fock (H-F) approximation is typically used to make the MO approach work for multi-electron systems? Describe what is approximated in the SCF method and how.
8. **(12 pts)** For **three (3) only** of 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:  $[\text{Ne}]^{10}(3s)^2$ }
- Si
  - $\text{Mn}^{+2}$
  - Cr
  - $\text{W}^{+2}$
  - O

9. **(20 pts)** Use MO theory and the LCAO-MO method to explain the configuration and energy of the BN diatomic molecule
- 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!!*)
  - Fill the orbitals using the *aufbau* approach for the ground state. What is the bond order?
  - Predict if the bond length will increase or decrease for  $\text{BN}^-$  and  $\text{BN}^+$ . Give brief reason to justify your answer.

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

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