

Chem 344 2nd Hour Exam

Friday, Nov. 9, 2007, 2-3 PM

Closed book exam, only pencils and calculators permitted. No Computers. Put all of your work in the answer book. If you need graph paper there are sheets available. Explain how you get answers. If you can set up a problem but do not know how to do the integral, or are out of time, explain your method, don't just "give up". "Floating" answers without substantiation receive little credit. Possibly useful information is at the end of the exam. **Good Luck!!**

1. **(12 pts)** In the "old quantum mechanics" there were a number of "fixes" to classical theory to make it agree better with observation. The key element of some of these was a mixing of the classical concepts of waves and particles.

Answer only one (1) of the following, i.e. part a or b or c:

- Einstein explained the photoelectric effect by requiring light to have a particulate nature. Explain why this conclusion was necessary from the dependence of the electron emission on the light characteristics in his model.
- Davisson and Germer used electron diffraction to show that particles could have a wave nature. Explain how their experiment shows the particle has wave properties. (Hint: Recall the double slit experiment simulation shown by Dr. Wang.)
- DeBroglie brought the concept of waves and particles together. Explain how his theory unified these observations for light and for small high energy particles (show how it goes both ways).

Answer this one (part d):

- Typical x-ray diffraction studies of proteins use Cu-K α x-rays which have a wavelength of ~ 0.154 nm. If one wanted to measure crystals with smaller spacings, one would use shorter wavelengths. If you wished to get the same sort of resolution with an electron beam, you would excite it through a potential gradient (two plates at different voltages with the positive one having an exit hole to form the beam).
 - What would be the momentum of an electron to match the Cu-K α ?
 - What voltage would be required on the plates to get this beam?

2. **(10 pts)** We have discussed developing a means of using quantum mechanics through the assumption of postulates.
- If you have a set of H-atom wave functions and wish to evaluate what would be the measured value of the electric dipole moment in the $n=2, l=1, m=0$ state,
 - describe how you would get a value for the observed dipole moment?
[Dipole moment: $\mu = \sum_i q_i \mathbf{r}_i$, where q_i is the charge on particle i and \mathbf{r}_i is its position.]
 - which postulate (or formula and meaning) does this require?
 - How would this be different for evaluating the angular momentum? Why?

3. (20 pts) Use MO theory and the LCAO-MO method to explain the configuration and energy of the B_2 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!! You should be careful to get the right ordering, taking into account the appropriate separation of 2s and 2p orbitals)
 - 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 B_2^- and for B_2^+ . Give a brief reason to justify your answer.

Answer only one (1) of the following, part e or d:

- What is the term symbol $^{2S+1}\Lambda$ for the ground state of B_2 ?
 - Is your B_2 molecule diamagnetic or paramagnetic? Why?
4. (16 pts) Ionization potential is the voltage required to overcome the electron's binding energy and eject it from the atom or molecule into free space.
- What is the ionization potential for Be^{+3} , i.e. : $Be^{+3} \rightarrow Be^{+4}$?
 - For the second row in the periodic table, explain which elements would have the highest and lowest ionization potential and why.
 - We might expect the IP to increase or decrease steadily across a period, but in fact there are peaks and valleys between the highest and lowest (part b). In the second row, which elements have unusually high IPs and how do their electron configurations explain this pattern?

Answer only one (1) of the following, part c or d:

- Compare the expected ionization potentials of H, He, He^{+1} , Li, Li^{+2} , Be
 - Explain why the IP of O is lower than for N.
5. (15 pts) For only three (3) of the following 4 atoms or ions give:
- the ground state configurations (occupied orbitals) and
 - lowest energy term symbols: $^{2S+1}L_J$ (determined by Hund's rules):
- {Hint: it may help if you use rare gas configurations to represent inner filled orbitals, e.g. Mg: $[Ne]^{10}(3s)^2$ }
- S
 - Cu^{+2}
 - Al
 - Re^{+4}
6. (10 pts) For only two (2) of the following 3 cases: Give an expression for the potential energy and explain (briefly) the physical origin of the term for a single electron in a:
- single electron ion of atomic # Z.
 - six-electron diatomic molecule (e.g. Li_2)
 - bound to a surface with a linear restoring force that can be represented as $F = -k(\Delta x)$, $\Delta x = x - x_{eq}$

7. **(18 pts)** We looked at a particle in a box problem many times as an example system. One important technique was to solve it for multiple dimensions by reducing it to a simpler system of one dimensional problems. In this problem we solve a 2-dimensional problem for a particle (mass = m) in a box varying from $x = 0$ to N , and $y = 0$ to M , where $V = 0$ in the box and $V = \infty$ outside the box.
- Set up the Schroedinger equation for this problem.
 - Separate the equation into 1-dimensional problems.
 - Determine the solution. You may argue to it from the solution to a 1-D box.
 - Determine the energy levels for this problem
 - Describe what would happen if the size in the x direction doubled
 - Describe the consequences on the energy levels and wave functions if the box were square, i.e. $M = N$.
8. **(8 pts)** Consider the H-atom solution. It gives us shapes of orbitals that we can use for multielectron atoms and as input to developing molecular orbitals and descriptions of bonding. Sketch orbitals **for only two (2) of the following 3 functions**:
- angular dependence of: $R_{nl}Y_{lm}$, $n=3$, $l=2$, $m=0$
 - angular dependence of: $R_{nl}Y_{lm}$, $n=2$, $l=1$, $m=\pm 1$
 - radial function, R_{nl} , $n=3$, $l=0$