Physical Chemistry II
Problem Set 4
Due Friday, March 28, 2008 (at 4:00 p.m.)
Total Number of Points = 55

Note: The answers to most of these problems are in the back of the book. However, you must justify your answers to receive credit.

1. (6 points) Atkins and de Paula Exercise 10.18b. Note that, just like $\vec{L}$ and $\vec{S}$, $\vec{J}$ has $2J + 1$ possible values of M_J.

2. (4 points) Atkins and de Paula Exercise 10.19b.

3. (3 points) In class on March 12, we considered the most important lasing transition in the He-Ne laser:

   $$\text{Ne } (2p^5 5s^1) \longrightarrow \text{Ne } (2p^5 3p^1) + hc/\lambda \quad (\lambda = 632.8 \text{ nm})$$

   I asserted that *if* the Ne $(2p^5 3p^1)$ atom were in a ^{3}P state, the Ne $(2p^5 5s^1)$ atom would have to be in either a ^{3}D or a ^{3}S state. This statement is true, but somewhat misleading. Explain why it is impossible for a Ne $(2p^5 5s^1)$ atom to emit a photon and relax down to a ^{3}P state of Ne $(2p^5 3p^1)$.

4. (8 points) Atkins and de Paula Exercise 11.1b. You are also required to draw the molecular orbital energy level diagram (including the atomic orbitals the MO's are formed from) and predict the bond order for each species.

5. (12 points) Atkins and de Paula Exercise 11.3b. You are required to write out the ground-state electronic configuration for the neutral form of each species. (You are free to draw the energy level diagrams as well, but you are not required to.) Justify your answers by writing down the bond orders for the neutral, cationic, and anionic forms of each species.

6. (10 points) Consider an orbital given by $\Psi_1 = N(0.145A + 0.844B)$, where A and B are real, normalized, and mutually orthogonal. Find a linear combination of A and B that is both normalized and orthogonal to Ψ_1.

7. (12 points) Atkins and de Paula Problems 11.2 and 11.3. Note:
   - Plot S as a function of R with R in units of a_O. Do both plots on a common set of axes. Plot enough points to make the overall shapes of the functions clear.
   - Very briefly justify the form of your qualitative sketch for the 1s-2p overlap integral.
   - Using calculus to find the location of the maximum in the 1s-2p overlap integral is admirable, but challenging. (Just like in Experiment 2, you would need to find the zeroes of a cubic equation.) I recommend finding the maximum graphically. In any case, find the maximum location to <u>three</u> significant figures in units of a_O.
   - Turn in some justification for how you located the maximum in the 1s-2p overlap integral.