1. (5 points each) Consider a proton ($p^+$) bound by the strong force to a nucleus ($L$ = 1.00 x $10^{-15}$ m), using the "particle in a box" model to describe the quantum mechanical behavior.

a) Calculate the energies (J) of the two lowest energy levels.

b) Calculate the wavelength (meters) of light emitted when $p^+$ makes a transition between the $n = 3$ and $n = 2$ levels. In what region of the spectrum does this emission occur?

c) Calculate the momentum of the photon emitted.

d) Calculate the probability of observing $p^+$ in the left 1/3 of the "box" for the $n = 3$ state. Compare this to the classical result.

$$\int \sin^2(bx)\, dx = \frac{x}{2} - \frac{1}{4b}\sin(2\,bx)$$

e) Are *sin* and *cos* functions equally acceptable as wavefunctions for this system? Explicitly support your answer.

f) Sketch the probability distribution for $p^{+}$ in the $n = 4$ state.

2. (3 points each) Order the following atoms according to <u>increase</u> in the stated property.

a) Atomic radius: Li, Na, C, O

smallest largest

b) Electron affinity: Li, F, C, Be

smallest largest

c) First ionization energy: He, C, N, Ne

smallest largest

d) Atomic radius: K, $F^{+}$, Rb, $Co^{25+}$, Br

smallest largest

e) Explain (with sketches) why the 4s orbital fills before the 3d.

3. (5+10+5+5+5+5 points) Consider the bonding in the ozone molecule ($O_3$).

a) Use VSEPR to determine the geometry (sketch) and hybridization.

b) Draw the correlation diagram for the pi molecular orbitals, showing the occupancy. Specify the number of sigma and pi bonds.

c) Sketch the shapes of the $\pi$ and $\pi$* molecular orbitals, labelling the axes and nodes.

d) Explain why the $\pi^*$ orbital is higher in energy than the $\pi$ orbital.

e) Why is a $\sigma(2s)$ orbital lower in energy than a $\sigma(2p)$ orbital in a homonuclear diatomic?

f) Sketch all the hybrid orbitals localized on the central oxygen.

4. (4+2+2+2 points) If an electron is removed from a fluorine molecule, an $F_2^+$ molecular ion forms.

a) Give the molecular electron configurations for $F_2$ and $F_2^+$.

b) Give the bond order of each species.

c) Predict which species should be paramagnetic.

d) Predict which species has the greater bond dissociation energy.

5. (5+5 points) NO reacts with $O_3$ to produce $NO_2$.

$NO + O_3 \rightarrow NO_2 + O_2$

Ozone has a peak absorption at 250nm and $NO_2$ at 400nm. Both absorption features are broad and they overlap. The absorption cross-section of $O_3$ peaks at 250nm where it is $1 \times 10^{-17}$ $cm^2$/molecules. The absorption is broad getting close to zero at about 350nm. For $NO_2$ at the absorption peaks at 400nm where the absorption cross-section is $6 \times 10^{-19}$ $cm^2$/molecules. The absorption cross-section drops to $6 \times 10^{-20}$ at 250nm. Absorption by NO begins at shorter wavelengths.

a) What product of pathlength and pressure do you require to have an absorbance by $NO_2$ of 0.4 at 400nm? by $O_3$ at 250nm? Recall $n/V = P/RT$ and note the difference between gas phase concentration units and liquid phase concentration units.

b) An unknown combination of NO and $O_3$ were mixed in a 20cm long cell and the reaction proceeds to the reactant limit. Describe a procedure for determining the initial concentrations of each compound?