C455A - Homework 8 -- Due **Tues Nov 28** at 5PM in Professor Ginger's Mailbox

Text Problems:

10.12 – Quantum numbers for terms

10.23 - Hund's rules for ground states of H through F

Additional Problems

1) Find the possible terms for the $1s^2 2s^2 2p^3$ configuration of Li USING A TABLE AS SHOWN IN LECTURE (i.e. NOT by "looking up" the answer). Use Hund's rules to determine which is the lowest energy term.

2) A word on "Atomic Units." You may have noticed many of our equations are accumulating a large number of complicated constants that appear repeatedly. For instance, the Bohr Radius:

$$a_0 = \frac{4\pi\varepsilon_0\hbar^2}{me^2}$$

Many of our equations can be made simpler by "giving up" SI units, and working in units more suited to the problem at hand, then "coverting back" to SI units at the end (it can also save you from dropping that darn factor of h in the derivative and so on). If we pick any set of units, we might pick a set where $\hbar = 1$, the electron mass = 1, the electron charge = 1, and the permittivity of free space, $4\pi\varepsilon_0 = 1$. If we work in such "atomic units" (theorists often do) then the formula for the allowed energy levels for a Hydrogen-like atom with nuclear charge Z becomes just:

$$E = \frac{Z^2}{2n^2}$$

where the units are given in "hartrees" (after the Hartree in Hartree-Fock).

3A) How many eV are in 1 hartree? How many J?

3B) Variational treatment of He (Lite version: We will take much of the "character-building" [as Calvin would say] out and leave only a few steps the end for you to do):

In atomic units the Hamitonian of He is $H = -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - \frac{2}{r_1} - \frac{2}{r_2} + \frac{1}{r_{12}}$

3C) Write out a trial wavefunction of the form 1s(1)1s(2) and show that in atomic units it has the form:

$$\Psi(r_1, r_2) = \frac{Z^3}{\pi} e^{-Z(r_1+r_2)}$$

where r_1 and r_2 are the radial positions of the two electrons. We can use the variational thereom to minimize the energy by varying Z.

If you evaluated $< E >= \int\int \Psi^*(r_1, r_2) \hat{H} \Psi(r_1, r_2) dr_1 dr_2$ you would, after a *lot* of math come to:

$$< E >= -Z^2 + \frac{2(Z-2)Z^3}{\pi} \int_0^\infty \frac{e^{-2Zr}}{r} 4\pi r^2 dr + \frac{5}{8}Z$$

3D) Complete the evaluation of this integral, and then find the value of Z that minimizes E.

Your value of E will be in Hartrees.

3E) Compare this value of the total energy of the He atom with the value you would get by assuming each electron occupied a normal hydrogen-like 1s orbital around a nucleus of charge Z (ignoring e-/e- repulsion , and also with the experimental value of –79.0 eV.   Is this result consistent with the variational theorem?

3F) Why does the calculation not match the experimental energy (i.e. what real effect has our calculation ignored? Hint: read the textbook)

3G) Interpret the value of Z that minimizes E.

4) Explain why the energy of an orbital depend on l for electrons in atoms other than hydrogen? **Annotate your discussion with a plot of the radial wave functions for 3s, 3p and 3d.**