CEM 483/881 Problem Set 10 Fall 2017

(due Monday, November 27)

1. Write the Slater determinant for the ground state of Be.

2. The ground state wave function of Li^{2+} is $\psi = \frac{1}{\sqrt{\pi}}\left(\frac{Z}{a_o}\right)^{3/2} e^{-Zr/a_o}$ where Z is the nuclear charge. Calculate the expectation value of the potential energy for Li^{2+}.

3. The operator for the total spin of two electrons is

$\hat{S}_{total}^2 = (\hat{S}_1 + \hat{S}_2)^2 = \hat{S}_1^2 + \hat{S}_2^2 + 2(\hat{S}_{1x}\hat{S}_{2x} + \hat{S}_{1y}\hat{S}_{2y} + \hat{S}_{1z}\hat{S}_{2z})$. Given that

$$\hat{S}_x\alpha = \frac{\hbar}{2}\beta \qquad \hat{S}_y\alpha = \frac{i\hbar}{2}\beta \qquad \hat{S}_z\alpha = \frac{\hbar}{2}\alpha$$

$$\hat{S}_x\beta = \frac{\hbar}{2}\alpha \qquad \hat{S}_y\beta = \frac{-i\hbar}{2}\alpha \qquad \hat{S}_z\beta = -\frac{\hbar}{2}\beta \ ,$$

show that $\alpha(1)\alpha(2)$ and $\beta(1)\beta(2)$ are eigenfunctions of the operator $\hat{S}_{total}^2$. What is the eigenvalue in each case?

4. Using Hund's Rules, write the term symbols for the ground state of the atoms H through F in the form ${}^{2S+1}L_J$.

5. Derive the ground state term symbols for the following electron configurations:

a) d^5 b) f^3 c) p^4

d) How many ways are there to place 3 electrons in an f subshell?

6. The principal peak in the emission spectrum of atomic sodium is yellow. On close examination, this emission peak is a doublet consisting of wavelengths 589.0 and 589.6 nm. Construct an energy level diagram that explains the origin of this observation.

7. The atomic emission experiments of a mixture show a calcium peak at 422.673 nm corresponding to a ${}^1P_1 \rightarrow {}^1S_0$ transition and a doublet due to potassium ${}^2P_{3/2} \rightarrow {}^2S_{1/2}$ and ${}^2P_{1/2} \rightarrow {}^2S_{1/2}$ transitions at 764.494 and 769.901 nm, respectively.

a. Calculate the ratio of g_{upper}/g_{lower} for each of these transitions (g refers to the degeneracy of a particular state).

b. Calculate N_{upper}/N_{lower} for a temperature of 1600 ºC for each transition (remember that N_{upper} and N_{lower} refer to the populations of each state).

8. Consider the 1s np $^3P \rightarrow$ 1s nd ^3D transition in He. Draw an energy level diagram taking the spin orbit coupling that splits terms into levels into account. Into how many levels does each term split? The selection rule for transitions in this case is $\Delta J = 0, \pm 1$. How many transitions will be observed in an absorbance spectrum? Show the allowed transitions in your energy level diagram.