CHEM 352: Homework for chapter 2.

1. The quantum mechanical state of a hydrogen atom is described by the following superposition:

$$\psi = \frac{1}{\sqrt{14}} \left(2\psi_{1,0,0} - 3\psi_{2,0,0} - \psi_{3,2,2}\right)$$

where $\psi_{n,l,m}$ are eigenfunctions of the Hamiltonian. The subscripts refer to quantum numbers n, l, m.

   (a) What is the probability of finding the hydrogen atom in states $(n = 1, l = 0, m = 0), (n = 2, l = 0, m = 0), (n = 3, l = 2, m = 2)$ or in some other state?

   (b) What are the expectation values for energy, $\hat{\vec{L}}^2$ and $\hat{L}_z$?

2. Show that operators $\hat{L}_z$ and $\hat{\vec{L}}^2 = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2$ commute with the hydrogen atom Hamiltonian operator:

$$\left[-\frac{\hbar^2}{2m}\Delta + \hat{V}, \hat{L}_z\right] = \left[-\frac{\hbar^2}{2m}\Delta + \hat{V}, \hat{\vec{L}}^2\right] = 0$$

where $\hat{V}$ is the operator corresponding to electron - nuclear Coulomb interaction. Use spherical coordinates and remember that operators commute, for example, if they depend on different variables. What is the significance of this result?

3. Demonstrate that the Cartesian hydrogen like p_x and p_y orbitals are not eigenfunctions of $\hat{L}_z$ but their linear combinations $p_x \pm ip_y$ are.

4. (a) Consider a hydrogenlike atom with on electron on $2s$ orbital. What is the most probable distance from the nucleus? Use the radial wavefunction in your calculation.

   (b) Show that the following hydrogenlike atom orbital pairs are orthogonal: $(1s, 2s)$ and $(2p_x, 2p_y)$.

5. (a) Write the electron configuration for V^{2+} ion. What quantum numbers for the total electron spin are possible in this configuration?

(b) If two electrons reside on two different orbitals, what are the possible values for total spin and the multiplicity? What values are possible for three electrons on different orbitals?

6. (a) What information do the following term symbols provide about a given atom: $^1D_2$ and $^3F_4$?

   (b) Consider the emission spectrum of potassium atom, which exhibits lines at $\lambda_1 = 766.70$ nm and $\lambda_2 = 770.11$ nm. What is the value of the spin-orbit coupling constant? The emission lines originate from the ^2P excited state (spin-orbit split).

   (c) Which of the following atomic transitions are (dipole) allowed: $5d \rightarrow 2s, 5p \rightarrow 3s, 5p \rightarrow 3f$?

7. (a) Write all the term symbols that can be obtained from the following electron configurations: $2s^1 2p^1$, $2p^1 3d^1$ and Ar$4s^2 3d^{10} 4p^5$ (Br atom).

   (b) Write the term symbols for carbon atom (He$2s^2 2p^2$), which has two equivalent p-electrons. Hint: tabulate all possible $m_{l_1}, m_{l_2}, m_{s_1}$ and m_{s_2} values and calculate the total L and S values. Remember to exculde the Pauli forbidden states.