Quantum Mechanics and Spectroscopy
CHEM 3PA3
Assignment 11 **Name:** ______________________

1. What is the wavelength associated to the following transitions in the hydrogen atom?
   (a) $2p$-orbital to $3s$-orbital
   (b) $3s$-orbital to $3d$-orbital

2. What is the ionization energy for the ground state hydrogen atom?

3. Write a Slater determinant wavefunction for the ground state of the Lithium atom, with electron configuration $1s^2 2s^1$.

4. Calculate the probability of finding an electron within a sphere of radius 1 a.u. for a $1s$-orbital, a $2s$-orbital, and a $2p_0$-orbital of the hydrogen atom (Z=1).

$$\psi_{1s}(\mathbf{r}) = \psi_{1,0,0}(\mathbf{r}) = \sqrt{\frac{Z^3}{\pi}} \cdot e^{-Zr},$$

$$\psi_{2s}(\mathbf{r}) = \psi_{2,0,0}(\mathbf{r}) = \sqrt{\frac{Z^3}{2^5\pi}} \cdot (2 - Zr)e^{-Zr/2},$$

$$\psi_{2p}(\mathbf{r}) = \psi_{2,1,0}(\mathbf{r}) = \sqrt{\frac{Z^3}{2^5\pi}} \cdot Zre^{-Zr/2}\cos\theta.$$

5. Calculate the mean kinetic and potential energy of an electron in the ground state of the hydrogen atom. In other words, evaluate $< T >= -(\hbar^2/2\mu)\int \psi_{1s}^\star(\mathbf{r})\nabla^2\psi_{1s}(\mathbf{r})\mathrm{d}\mathbf{r}$, and $< V >= -(e^2/4\pi\epsilon_0)\int \psi_{1s}^\star(\mathbf{r})(1/r)\psi_{1s}(\mathbf{r})\mathrm{d}\mathbf{r}$. Is the virial theorem satisfied, $< T >= -0.5 < V >$?

6. In the third-year chemistry laboratory, you made "quantum dots." An electron in a quantum dot can be approximated as a particle in a spherical well,

$$V(r) = \begin{cases} 0, & r \leq a \\ \infty, & r > a \end{cases}$$

The eigenfunctions of this system are products of spherical Bessel functions and spherical Harmonics,

$$\Psi_{klm}(r,\theta,\phi) \propto j_l(kr)Y_l^m(\theta,\phi).$$

The two lowest-order spherical Bessel funtions are:

$$j_0(x) = \frac{\sin(x)}{x} \qquad j_1(x) = \frac{sin(x)}{x^2} - \frac{cos(x)}{x}$$

These functions have the property that they are zero at the following values:

$$0 = j_0(x_i) \qquad x_0 = \pi;\ x_1 = 2\pi;\ x_3 = 3\pi; ...$$
$$0 = j_1(x_i) \qquad x_0 = 4.493409;\ x_1 = 7.725252;\ x_3 = 10.904122; ...$$

The spherical Bessel functions are eigenfunctions of the following differential equation:

$$\left(-\frac{1}{2}\left[\frac{1}{r^2}\frac{d}{dr}r^2\frac{d}{dr}\right] + \frac{l(l+1)}{2r^2}\right) j_l(kr) = \frac{k^2}{2} j_l(kr).$$

(a) Confirm, by explicit substitution, that the proposed wavefunction, $\Psi_{klm}(r, \theta, \phi) \propto j_l(kr)Y_l^m(\theta, \phi)$ is and aigenfunction for the "electron in a spherical well" Hamiltonian.

(b) What are the energy levels for the s-type "electron in a spherical well" states? What is the ground-state energy for the electron in a spherical well?

(c) Suppose you want to design a quantum dot that absorbs red light, with wavelength $\lambda = 680 \cdot 10^{-9}$ m, and assume that the "electron in a spherical wll" is an adequate model for the quntum dot. What radius for the quantum dot will cause the lowest-energy electric-dipole-allowed abosrption from the ground state to have wavelength $\lambda = 680$ nm? You will probably find it helpful to work this problem in atomic units. The atomic unit of length is the Bohr, and 1 Bohr$= 0.52917725 \cdot 10^{-10}$ m.