PHYS 2380 - Assignment 5

Due April 17, 2017

April 5, 2017

1.) In this problem, we will examine some properties of the wavefunctions of hydrogen-like atoms.

a.) When we investigated the quantum simple harmonic oscillator we showed that the eigenstates are orthogonal. The hydrogen-like wavefunctions also form an orthogonal set, and must obey the relationship

$$\int_0^{2\pi} \int_0^{\pi} \int_0^{\infty} \psi^*_{n'l'm'} \psi_{nlm} r^2 \sin\theta dr d\theta d\phi = \delta_n^{n'} \delta_l^{l'} \delta_m^{m'} \tag{1}$$

where the Kronecker $\delta_a^{a'}$ gives 1 if $a = a'$ and 0 if $a \neq a'$. We will not prove the orthogonality relationship in general, but simply demonstrate it for the following pairs:
i.) ψ_{100} and ψ_{200},
ii.) ψ_{200} and ψ_{210},
iii.) ψ_{210} and ψ_{211}.
When evaluating these expressions, the following integral identity may be useful:

$$\int_0^{\infty} x^q e^{-\alpha x} dx = \frac{q!}{a^{q+1}} \tag{2}$$

b.) Any eigenstate of a hydrogen-like atom is degenerate with respect to several other states with the same n (except for the ground state, $n = 1$, $l = 0$, $m = 0$). For example, the $n = 2$ state has a four-fold degeneracy since this state has orbital quantum number $l = 0$ (with magnetic quantum number $m = 0$) and $l = 1$ (with $m = -1, 0, 1$). The most general probability density for atoms in the $n = 2$ state is a superposition of these four states with equal amplitudes,

$$\Psi_2 = \frac{1}{2}\psi_{200} + \frac{1}{2}\psi_{210} + \frac{1}{2}\psi_{211} + \frac{1}{2}\psi_{21-1}. \tag{3}$$

Using the orthogonality condition from part a, find the probability density $P_2(r, \theta, \phi)$ that comes from the state Ψ_2 above. Does the probability density have any symmetry (ie, does it depend on all of the coordinates)?

c.) Now consider the superposition of the $n = 3$ eigenstates. Do an analogous calculation for $P_3(r, \theta, \phi)$ where Ψ_3 is written as an evenly-weighted superposition. Recall from the last assignment that the squares of the real amplitude coefficients must sum to 1 to give a realistic superposition. You do not have to simplify the calculation of P_3 fully, just find which coordinates it depends on. You may also find it easier to complete this problem by working on groups of terms arranged by orbital quantum number l.

d.) Do the solutions to parts b and c have the same type of symmetry?

2 a.) Calculate the location at which the radial probability density is a maximum for the $n = 2$, $l = 1$ state of the hydrogen atom.

b.) Calculate the expectation value of the radial coordinate in this state.

c.) Explain the physical significance of the difference in the answers to a and b. According to the Bohr model, the radius of an electron orbital is given by

$$r_{Bohr} = \frac{n^2 a_0}{Z} \tag{4}$$

3 a.) Calculate the expectation value $< V >$ of the potential energy in the $n = 2$, $l = 0$ state of the hydrogen atom.

b.) Do the same for the $n = 2$, $l = 1$ state.

c.) Discuss the results of part a and b in connection with the Virial theorem, and explain how they relate to the orbital (l) degeneracy.

The first 10 wave functions of hydrogen-like atoms:

$$\psi_{100} = \frac{1}{\sqrt{\pi}} \left(\frac{Z}{a_0}\right)^{3/2} e^{-Zr/a_0} \tag{5}$$

$$\psi_{200} = \frac{1}{4\sqrt{2\pi}} \left(\frac{Z}{a_0}\right)^{3/2} \left(2 - \frac{Zr}{a_0}\right) e^{-Zr/2a_0} \tag{6}$$

$$\psi_{210} = \frac{1}{4\sqrt{2\pi}} \left(\frac{Z}{a_0}\right)^{3/2} \frac{Zr}{a_0} e^{-Zr/2a_0} \cos\theta \tag{7}$$

$$\psi_{21\pm1} = \frac{1}{8\sqrt{\pi}} \left(\frac{Z}{a_0}\right)^{3/2} \frac{Zr}{a_0} e^{-Zr/2a_0} \sin\theta e^{\pm i\phi} \tag{8}$$

$$\psi_{300} = \frac{1}{81\sqrt{3\pi}} \left(\frac{Z}{a_0}\right)^{3/2} \left(27 - 18\frac{Zr}{a_0} + 2\frac{Z^2r^2}{a_0^2}\right) e^{-Zr/3a_0} \tag{9}$$

$$\psi_{310} = \frac{\sqrt{2}}{81\sqrt{\pi}} \left(\frac{Z}{a_0}\right)^{3/2} \left(6 - \frac{Zr}{a_0}\right) \frac{Zr}{a_0} e^{-Zr/3a_0} \cos\theta \tag{10}$$

$$\psi_{31\pm1} = \frac{1}{81\sqrt{\pi}} \left(\frac{Z}{a_0}\right)^{3/2} \left(6 - \frac{Zr}{a_0}\right) \frac{Zr}{a_0} e^{-Zr/3a_0} \sin\theta e^{\pm i\phi} \tag{11}$$

$$\psi_{320} = \frac{1}{81\sqrt{6\pi}} \left(\frac{Z}{a_0}\right)^{3/2} \frac{Z^2r^2}{a_0^2} e^{-Zr/3a_0} \left(3\cos^2\theta - 1\right) \tag{12}$$

$$\psi_{32\pm1} = \frac{1}{81\sqrt{\pi}} \left(\frac{Z}{a_0}\right)^{3/2} \frac{Z^2r^2}{a_0^2} e^{-Zr/3a_0} \sin\theta\cos\theta e^{\pm i\phi} \tag{13}$$

$$\psi_{32\pm2} = \frac{1}{162\sqrt{\pi}} \left(\frac{Z}{a_0}\right)^{3/2} \frac{Z^2r^2}{a_0^2} e^{-Zr/3a_0} \sin^2\theta e^{\pm 2i\phi} \tag{14}$$

These wavefunctions are given in terms of the Bohr radius,

$$a_0 = \frac{4\pi\epsilon_0\hbar^2}{\mu e^2} = 5.29 \times 10^{-11} m \tag{15}$$