Problem 1

Consider an electron in the 3p state of the hydrogen atom. Find the most probable radial position.

Solution:

To find the most probable radial position for an electron in the 3p state of the hydrogen:

\[
P(r) = r^2 |R_{31}|^2
\]

\[
= \frac{r^2}{a_0^2} \left[ \frac{4}{81 \sqrt{6}} \left( 6 - \frac{r}{a_0} \right) \frac{r}{a_0} e^{-r/3a_0} \right]^2
\]

To find the extrema, set \( dP/dr \) to zero and solve for \( r \):

\[
\frac{dP}{dr} = 0 \rightarrow -\frac{2r}{a_0} + 24 - \frac{4r}{a_0} - \frac{12r}{3a_0} + \frac{2r^2}{3a_0^2} = 0
\]

\[
\frac{2}{3} \left( \frac{r}{a_0} \right)^2 - 10 \left( \frac{r}{a_0} \right) + 24 = 0
\]

This equation has a solution when \( r = 12a_0 \) or \( r = 3a_0 \). Notice that in simplifying the expression for we divided out the two obvious solutions \( r = 0 \) and \( r = 6a_0 \) since every term in \( dP/dr \) is going to have a factor of \( r \) and a factor of \( (6 - r/a_0) \). Since \( P(r) \) is zero for \( r = 0 \) and \( r = 6a_0 \), these naturally correspond to minima. Evaluating \( P(6a_0) \) and \( P(12a_0) \), we find that \( P(12a_0) > P(6a_0) \), so \( r = 12a_0 \) is the most probable radial position for an electron in the 3p state of hydrogen.
Problem 2

Consider a hydrogen-like atom (e.g., $\text{He}^+$ or $\text{Li}^{++}$) that has a single electron outside a nucleus of charge $+Ze$.

a.) Rewrite the Schrödinger equation with the new Coulomb potential.
b.) What change does this new potential have on the separation of variables?
c.) Will the radial wave functions be affected? Explain.
d.) Will the spherical harmonics be affected? Explain.
e.) Find the wave function for such an atom when $n = 1$, $l = 0$, and $m = 0$ (i.e., $\psi_{100}$).

Solution:

a) The only change in Equation (7.3) is in the potential energy, with

$$ V = \frac{Ze^2}{4\pi\varepsilon_0 r} $$

$$ \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial \psi}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial \psi}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2 \psi}{\partial \phi^2} + \frac{2\mu}{\hbar^2} \left( E + \frac{Ze^2}{4\pi\varepsilon_0 r} \right) \psi = 0 $$

b) Because $V$ occurs only in the radial part, there is no change in the separation of variables.
c) Yes, from Equation (7.10) it is clear that the radial wave functions will change.
d) No, there is no change in the $\theta$ or $\phi$ dependence.

Carrying $Z$ through the derivation in the text [Equations (7.12) through (7.14)] we find

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

Calculate the probability of an electron in the 2s state of hydrogen to be inside the region of the proton. You can assume that the proton is spherically symmetric with a radius $1 \times 10^{-15}$ m. Repeat for a 2p electron. Hint: note that $r \ll a_0$.

Solution:

For the 2s state:

$$P(r) = r^2 |R(r)|^2 = \frac{1}{8a_0^3} r^2 \left(2 - \frac{r}{a_0}\right)^2 e^{-r/a_0}$$

As in Problem 38 for $r \ll a_0$ we can say $e^{-r/a_0} \approx 1$, so the probability is given by the integral

$$\int_0^{10^{-15}} P(r) \, dr \approx \frac{1}{8a_0^3} \int_0^{10^{-15}} r^2 \left(2 - \frac{r}{a_0}\right)^2 \, dr = \frac{1}{8a_0^3} \int_0^{10^{-15}} \left(4r^2 - \frac{4r^3}{a_0} + \frac{r^4}{5a_0^2}\right) \, dr$$

$$= \frac{1}{8a_0^3} \left[ \frac{4}{3} r^3 - \frac{r^4}{a_0} + \frac{r^5}{5a_0^2} \right]_0^{10^{-15}} = 1.1 \times 10^{-15}$$

Similarly for the 2p state:

$$P(r) = r^2 |R(r)|^2 = \frac{1}{24a_0^5} r^4 e^{-r/a_0}$$

$$\int_0^{10^{-15}} P(r) \, dr \approx \frac{1}{24a_0^5} \int_0^{10^{-15}} r^4 \, dr = \frac{r^5}{120a_0^5} \bigg|_0^{10^{-15}} = 2.01 \times 10^{-26}$$
Problem 4
Which of the following elements can have either (or both) singlet and triplet states and which have neither: He, Al, Ca, Sr? Explain.

Solution:

The ground state in He is a singlet, so an excited state may be a singlet or triplet, and the behavior of Ca ($4s^2$) and Sr ($5s^2$) must be the same. Al has a $3s^23p^1$ configuration. The single unpaired electron gives $S = 1/2$ and $2S + 1 = 2$, which is a doublet.
Problem 5

If the zirconium atom ground state has $S = 1$ and $L = 3$, what are the permissible values of $J$? Write the spectroscopic notation for these possible values of $S$, $L$, and $J$. Which of these is likely to represent the ground state?

Solution:

$J$ ranges from $|L - S|$ to $|L + S|$ or $2, 3, 4$. Then in spectroscopic notation $^{2S+1}L_J$, we have three possibilities: $^3F_2$, $^3F_3$, or $^3F_4$. The ground state has the lowest $J$ value, or $^3F_2$. With $n = 4$ the full notation is $^4F_2$. 