Problem Set 8

P20.7) Calculate the distance from the nucleus for which the radial distribution function for the $2p$ orbital has its main and subsidiary maxima.

$$r^2 R_{21}^2(r) = \frac{1}{\sqrt{24}}\left(\frac{1}{a_0}\right)^{3/2} \frac{r^4}{a_0} e^{-r/a_0}$$

The maxima and minima are found by setting the derivative of this function equal to zero.

$$\frac{d}{dr}\left(\frac{r^4}{a_0} e^{-r/a_0}\right) = \frac{4r^3}{a_0} e^{-r/a_0} - \frac{r^4}{a_0^2} e^{-r/a_0} = \frac{r^3 e^{-r/a_0}}{a_0}\left(4 - \frac{r}{a_0}\right) = 0$$

The solutions are $r = 0, r = 4a_0$.

There are no subsidiary maxima.

P20.10) Ions with a single electron such as He^+, Li^{2+}, and Be^{3+} are described by the H atom wave functions with Z/a_0 substituted for $1/a_0$, where Z is the nuclear charge. The $1s$ wave function becomes $\psi(r) = 1/\sqrt{\pi}\,(Z/a_0)^{3/2} e^{-Zr/a_0}$. Using this result, calculate the total energy for the $1s$ state in H, He^+, Li^{2+}, and Be^{3+} by substitution in the Schrödinger equation.

We substitute in the radial equation

$$-\frac{\hbar^2}{2m_e r^2}\frac{d}{dr}\left[r^2 \frac{dR(r)}{dr}\right] + \left[\frac{\hbar^2 l(l+1)}{2m_e r^2} - \frac{Ze^2}{4\pi\varepsilon_0 r}\right] R(r) = ER(r)$$

$$-\frac{\hbar^2}{2m_e r^2}\frac{d}{dr}\left[r^2 \frac{d\,1/\sqrt{\pi}\,(Z/a_0)^{3/2} e^{-Zr/a_0}}{dr}\right] + \left[\frac{\hbar^2 0(0+1)}{2m_e r^2} - \frac{Ze^2}{4\pi\varepsilon_0 r}\right] 1/\sqrt{\pi}\,(Z/a_0)^{3/2} e^{-Zr/a_0}$$

$$= -\frac{\hbar^2}{2\sqrt{\pi} m_e r^2}\frac{d}{dr}\left[-r^2 (Z/a_0)^{5/2} e^{-Zr/a_0}\right] - \frac{e^2}{4\pi\sqrt{\pi}\varepsilon_0 r}(Z/a_0)^{3/2} e^{-Zr/a_0}$$

$$= -\frac{\hbar^2}{2\sqrt{\pi} m_e r^2}\left[-2r (Z/a_0)^{5/2} e^{-Zr/a_0} + r^2 (Z/a_0)^{7/2} e^{-Zr/a_0}\right] - \frac{Ze^2}{4\pi\sqrt{\pi}\,\varepsilon_0 r}(Z/a_0)^{3/2} e^{-Zr/a_0}$$

$$= \left(\frac{\hbar^2}{\sqrt{\pi} m_e r}(Z/a_0)^{5/2} e^{-Zr/a_0} - \frac{e^2}{4\pi\sqrt{\pi}\varepsilon_0 r}(Z/a_0)^{3/2} e^{-Zr/a_0}\right) - \frac{\hbar^2}{2\sqrt{\pi} m_e}(Z/a_0)^{7/2} e^{-Zr/a_0}$$

Using the relation $a_0 = \dfrac{\varepsilon_0 h^2}{\pi m_e e^2}$

$$= \frac{1}{\sqrt{\pi}}(Z/a_0)^{3/2}\left[\left(\frac{Z}{4\pi}\frac{e^2}{\varepsilon_0 r} - \frac{Ze^2}{4\pi\varepsilon_0 r}\right) e^{-Zr/a_0} - \frac{\hbar^2}{2m_e}(Z/a_0)^2 e^{-Zr/a_0}\right]$$

$$= -\frac{1}{\sqrt{\pi}}(Z/a_0)^{3/2}\frac{\hbar^2}{2m_e}(Z/a_0)^2 e^{-Zr/a_0} = -\frac{1}{\sqrt{\pi}}(Z/a_0)^{3/2}\frac{Z^2 e^2}{8\pi\varepsilon_0 a_0} e^{-Zr/a_0} = -\frac{Z^2 e^2}{8\pi\varepsilon_0 a_0}\psi(r)$$

$\psi(r)$ is an eigenfunction with the value $-\dfrac{Z^2 e^2}{8\pi\varepsilon_0 a_0}$

$$E_H = -\frac{e^2}{8\pi\varepsilon_0 a_0} = 2.179\times10^{-18}\,\text{J}$$

$$E_{He^+} = -\frac{4e^2}{8\pi\varepsilon_0 a_0} = 8.717\times10^{-18}\,\text{J}$$

$$E_{Li^{2+}} = -\frac{9e^2}{4\pi\varepsilon_0 a_0} = 19.61\times10^{-18}\,\text{J}$$

$$E_{Be^{3+}} = -\frac{16e^2}{8\pi\varepsilon_0 a_0} = 34.87\times10^{-18}\,\text{J}$$

P20.11) Ions with a single electron such as He^+, Li^{2+}, and Be^{3+} are described by the H atom wave functions with Z/a_0 substituted for $1/a_0$, where Z is the nuclear charge. The 1*s* wave function becomes $\psi(r) = 1/\sqrt{\pi}\,(Z/a_0)^{3/2} e^{-Zr/a_0}$. Using this result, compare the mean value of the radius $\langle r \rangle$ at which you would find the 1*s* electron in H, He^+, Li^{2+}, and Be^{3+}.

$$\langle r \rangle = \frac{Z^3}{\pi a_0^3}\int_0^{2\pi} d\phi \int_0^{\pi} \sin\theta\, d\theta \int_0^{\infty} r^3 e^{-\frac{2Zr}{a_0}}\, dr$$

$$\langle r \rangle = \frac{4Z^3}{a_0^3}\int_0^{\infty} r^3 e^{-\frac{2Zr}{a_0}}\, dr$$

Using the standard integral $\int_0^{\infty} r^n e^{-\alpha r} = \frac{n!}{\alpha^{n+1}}$

$$\langle r \rangle = \frac{4Z^3}{a_0^3}\frac{6a_0^4}{16Z^4} = \frac{3}{2Z}a_0$$

$$\langle r \rangle_H = \frac{3}{2}a_0;\quad \langle r \rangle_{He^+} = \frac{3}{4}a_0;\quad \langle r \rangle_{Li^{2+}} = \frac{1}{2}a_0;\quad \langle r \rangle_{Be^{3+}} = \frac{3}{8}a_0$$

P20.13) In this problem, you will calculate the probability density of finding an electron within a sphere of radius *r* for the H atom in its ground state.

a. Show using integration by parts, $\int u\, dv = uv - \int v\, du$, that $\int r^2 e^{-r/\alpha} dr = e^{-r/\alpha}(-2\alpha^3 - 2\alpha^2 r - \alpha r^2)$.

b. Using this result, show that the probability density of finding the electron within a sphere of radius *r* for the hydrogen atom in its ground state is

$$1 - e^{-2r/a_0} - \frac{2r}{a_0}\left(1 + \frac{r}{a_0}\right)e^{-2r/a_0}$$

c. Evaluate this probability density for $r = 0.10\ a_0$, $r = 1.0\ a_0$, and $r = 4.0\ a_0$.

a) Show using integration by parts, $\int u\,d\mathrm{v} = uv - \int \mathrm{v}\,du$, that $\int r^2 e^{-\frac{r}{\alpha}} dr = e^{-\frac{r}{\alpha}}\left(-2\alpha^3 - 2\alpha^2 r - \alpha r^2\right)$

Let $u = r^2$ and $d\mathrm{v} = e^{-\frac{r}{\alpha}} dr$

$$\int r^2 e^{-\frac{r}{\alpha}} dr = -\alpha r^2 e^{-\frac{r}{\alpha}} + 2\alpha \int r\, e^{-\frac{r}{\alpha}} dr$$

Integrating by parts again,

$$\int r^2 e^{-\frac{r}{\alpha}} dr = -\alpha r^2 e^{-\frac{r}{\alpha}} + 2\alpha\left(-\alpha r e^{-\frac{r}{\alpha}} + \alpha \int e^{-\frac{r}{\alpha}} dr\right) = -\alpha r^2 e^{-\frac{r}{\alpha}} - 2\alpha\left(\alpha r e^{-\frac{r}{\alpha}} - \alpha^2 e^{-\frac{r}{\alpha}}\right)$$

$$\int r^2 e^{-\frac{r}{\alpha}} dr = e^{-\frac{r}{\alpha}}\left(-\alpha r^2 - 2\alpha^2 r - 2\alpha^3\right)$$

b) Using this result, show that the probability density of finding the electron within a sphere of radius r for the hydrogen atom in its ground state is $1 - e^{-\frac{2r}{a_0}} - \frac{2r}{a_0}\left(1 + \frac{r}{a_0}\right) e^{-\frac{2r}{a_0}}$.

Setting $\alpha = \frac{a_0}{2}$,

$$\frac{1}{\pi a_0^3}\int_0^{2\pi} d\phi \int_0^{\pi} \sin\theta\, d\theta \int_0^{\infty} r'^2 e^{-\frac{2r'}{a_0}} dr' = \frac{4}{a_0^3}\left[e^{-\frac{2r'}{\alpha}}\left(-\frac{a_0}{2} r'^2 - \frac{a_0^2}{2} r' - \frac{a_0^3}{4}\right)\right]_0^r$$

$$= \frac{4}{a_0^3}\left[e^{-\frac{2r}{\alpha}}\left(-\frac{a_0}{2} r^2 - \frac{a_0^2}{2} r - \frac{a_0^3}{4}\right) + \frac{a_0^3}{4}\right] = -2\frac{r^2}{a_0^2} e^{-\frac{2r}{a_0}} - 2\frac{r}{a_0} e^{-\frac{2r}{a_0}} - e^{-\frac{2r}{a_0}} + 1$$

$$= 1 - e^{-\frac{2r}{a_0}} - 2\frac{r}{a_0}\left(1 + \frac{r}{a_0}\right) e^{-\frac{2r}{a_0}}$$

c) Evaluate this probability density for $r = 0.10\ a_0$, $r = 1.0\ a_0$, and $r = 4.0\ a_0$.

The probability evaluated at $r = 0.10\ a_0 = 1.1 \times 10^{-3}$. The probability evaluated at $r = 1.0\ a_0 = 0.32$. The probability evaluated at $r = 4.0\ a_0 = 0.99$.

P20.15) In spherical coordinates, $z = r\cos\theta$. Calculate $\langle z \rangle$ and $\langle z^2 \rangle$ for the H atom in its ground state. Without doing the calculation, what would you expect for $\langle x \rangle$ and $\langle y \rangle$, and $\langle x^2 \rangle$ and $\langle y^2 \rangle$? Why?

$$\langle z \rangle = \frac{1}{\pi a_0^3}\int_0^{2\pi} d\phi \int_0^{\pi} \cos\theta \sin\theta \, d\theta \int_0^{\infty} r^3 e^{-\frac{2r}{a_0}} dr$$

$$\langle z \rangle = \frac{2\pi}{\pi a_0^3}\left[-\frac{\cos^2\theta}{2}\right]_0^{\pi} \int_0^{\infty} r^5 e^{-\frac{r}{a_0}} dr = 0 \text{ because the integral over } \theta \text{ is zero.}$$

$$\left\langle z^2 \right\rangle = \frac{1}{\pi a_0^3}\int_0^{2\pi} d\phi \int_0^{\pi} \cos^2\theta \sin\theta \, d\theta \int_0^{\infty} r^4 e^{-\frac{2r}{a_0}} dr$$

$$\left\langle z^2 \right\rangle = \frac{2\pi}{\pi a_0^3}\left[-\frac{\cos^3\theta}{3}\right]_0^{\pi} \int_0^{\infty} r^4 e^{-\frac{2r}{a_0}} dr = \frac{4}{3a_0^3}\int_0^{\infty} r^4 e^{-\frac{2r}{a_0}} dr$$

Using the standard integral $\int_0^{\infty} r^n e^{-\alpha r} = \frac{n!}{\alpha^{n+1}}$

$$\left\langle z^2 \right\rangle = \frac{4}{3a_0^3}\frac{24a_0^5}{32} = a_0^2$$

Because the H atom is spherically symmetrical, $\langle x \rangle$ and $\langle y \rangle$, $\left\langle x^2 \right\rangle$ and $\left\langle y^2 \right\rangle$ will have the same values as $\langle z \rangle$ and $\left\langle z^2 \right\rangle$.

P20.20) Calculate the mean value of the radius $\langle r \rangle$ at which you would find the electron if the H atom wave function is $\psi_{210}(r,\theta,\phi)$.

$$\langle r \rangle = \frac{1}{32\pi a_0^5}\int_0^{2\pi} d\phi \int_0^{\pi} \cos^2\theta \sin\theta \, d\theta \int_0^{\infty} r^5 e^{-\frac{r}{a_0}} dr$$

$$\langle r \rangle = \frac{2\pi}{32\pi a_0^5}\left[-\frac{\cos^3\theta}{3}\right]_0^{\pi} \int_0^{\infty} r^5 e^{-\frac{r}{a_0}} dr = \frac{2\pi}{32\pi a_0^5}\frac{2}{3}\int_0^{\infty} r^5 e^{-\frac{r}{a_0}} dr = \frac{1}{24 a_0^5}\int_0^{\infty} r^5 e^{-\frac{r}{a_0}} dr$$

Using the standard integral $\int_0^{\infty} r^n e^{-\alpha r} = \frac{n!}{\alpha^{n+1}}$

$$\langle r \rangle = \frac{1}{24a_0^5} 5!\, a_0^6 = 5a_0$$

P20.23) Calculate the average value of the kinetic and potential energies for the H atom in its ground state.

$$\langle E_{kinetic}\rangle = \int \psi^*(\tau)\,\hat{E}_{kinetic}\,\psi(\tau)\,d\tau$$

$$\langle E_{kinetic}\rangle = -\frac{\hbar^2}{2m_e}\frac{1}{\pi a_0^3}\int_0^{2\pi} d\phi \int_0^{\pi}\sin\theta\, d\theta \int_0^{\infty} e^{-r/a_0}\left(\frac{1}{r^2}\frac{d}{dr}\left[r^2\frac{d}{dr}e^{-r/a_0}\right]\right) r^2\,dr$$

$$\langle E_{kinetic}\rangle = -\frac{\hbar^2}{2m_e}\frac{4}{a_0^3}\int_0^{\infty}\left[-\frac{2r}{a_0}e^{-2r/a_0} + \frac{r^2}{a_0^2}e^{-2r/a_0}\right] dr = \frac{\hbar^2}{m_e}\frac{4}{a_0^4}\int_0^{\infty} r\,e^{-2r/a_0}\,dr - \frac{\hbar^2}{m_e}\frac{2}{a_0^5}\int_0^{\infty} r^2 e^{-2r/a_0}\,dr$$

Using the standard integral $\int_0^{\infty} r^n e^{-\alpha r} = \frac{n!}{\alpha^{n+1}}$

$$\langle E_{kinetic}\rangle = \frac{\hbar^2}{m_e}\frac{4}{a_0^4}\frac{a_0^2}{4} - \frac{\hbar^2}{m_e}\frac{2}{a_0^5}\frac{2a_0^3}{8} = \frac{\hbar^2}{2m_e a_0^2} = \frac{\hbar^2 \pi m_e e^2}{2m_e a_0 \varepsilon_0 h^2} = \frac{e^2}{8\pi a_0 \varepsilon_0}$$

$$\langle E_{potential}\rangle = \int \psi^*(\tau)\hat{E}_{potential}\psi(\tau)\,d\tau$$

$$\langle E_{potential}\rangle = -\frac{e^2}{4\pi\varepsilon_0}\frac{1}{\pi a_0^3}\int_0^{2\pi} d\phi \int_0^{\pi}\sin\theta\, d\theta \int_0^{\infty}\left[e^{-r/a_0}\right]\left(\frac{1}{r}\right)\left[e^{-r/a_0}\right] r^2\,dr$$

$$\langle E_{potential}\rangle = -\frac{e^2}{4\pi\varepsilon_0}\frac{4}{a_0^3}\int_0^{\infty} r\,e^{-2r/a_0}\,dr = -\frac{e^2}{4\pi\varepsilon_0}\frac{4}{a_0^3}\frac{a_0^2}{4} = -\frac{e^2}{4\pi\varepsilon_0 a_0}$$

P20.26) As will be discussed in Chapter 10, core electrons shield valence electrons so that they experience an effective nuclear charge Z_{eff} rather than the full nuclear charge. Given that the first ionization energy of Li is 5.39 eV, use the formula in Problem P20.15 to estimate the effective nuclear charge experienced by the 2*s* electron in Li

$$I = 13.60\frac{Z^2}{n^2}\text{eV};\; Z_{eff} = \sqrt{\frac{n^2 I}{13.60\text{ eV}}} = \sqrt{\frac{4\times 5.39\text{ eV}}{13.60\text{ eV}}} = 1.26$$

P20.29) Calculate $\langle r \rangle$ and the most probable value of r for the H atom in its ground state. Explain why they differ with a drawing.

$$\langle r \rangle = \frac{1}{\pi a_0^3}\int_0^{2\pi} d\phi \int_0^{\pi} \sin\theta \, d\theta \int_0^{\infty} r^3 e^{-\frac{2r}{a_0}} dr$$

$$\langle r \rangle = \frac{4}{a_0^3}\int_0^{\infty} r^3 e^{-\frac{2r}{a_0}} dr$$

Using the standard integral $\int_0^{\infty} r^n e^{-\alpha r} = \frac{n!}{\alpha^{n+1}}$

$$\langle r \rangle = \frac{4}{a_0^3}\frac{6a_0^4}{16} = \frac{3}{2}a_0$$

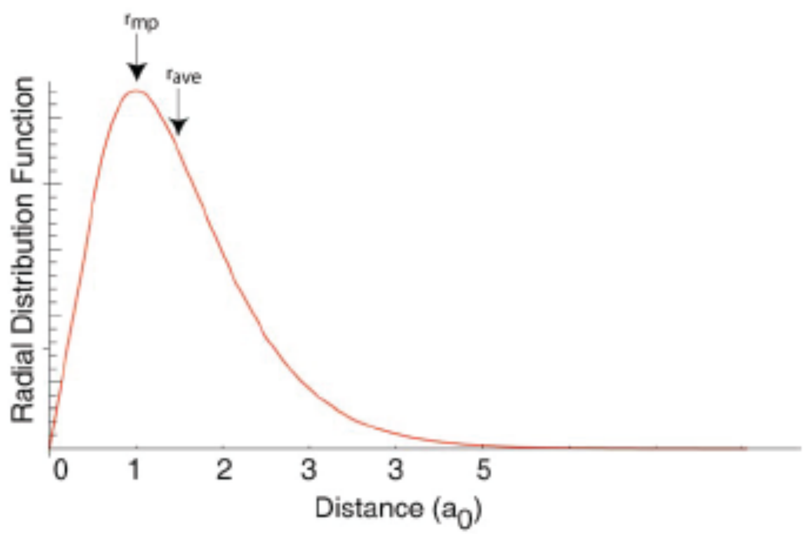
The most probable value of r is found by setting the derivative of the radial probability distribution equal to zero.

$$r^2 R_{10}^2(r) = 4\left(\frac{1}{a_0}\right)^3 r^2 e^{-2r/a_0}$$

$$\frac{d}{dr}\left(r^2 e^{-2r/a_0}\right) = 2r\, e^{-2r/a_0} - \frac{2r^2}{a_0} e^{-2r/a_0} = 2e^{-2r/a_0} r\left(1 - \frac{r}{a_0}\right) = 0$$

The solutions are $r = 0, r = a_0$.

The mean and most probable values are not equal because $r^2 R_{10}^2(r)$ is not symmetric with respect to r about its maximum value as shown in the following figure.



P20.30) How many radial and angular nodes are there in the following H orbitals?

a. $\psi_{2p_x}(r,\theta,\phi)$ c. $\psi_{3d_{xz}}(r,\theta,\phi)$

b. $\psi_{2s}(r)$ d. $\psi_{3d_{x^2-y^2}}(r,\theta,\phi)$

The functions have *n*–*l*–1 radial nodes and *l* angular nodes. Therefore

a) $\psi_{2p_x}(r,\theta,\phi)$ has no radial nodes and one angular node.

b) $\psi_{2s}(r)$ has one radial node and no angular nodes.

c) $\psi_{3d_{xz}}(r,\theta,\phi)$ has no radial nodes and 2 angular nodes.

d) $\psi_{3d_{x^2-y^2}}(r,\theta,\phi)$ has no radial nodes and 2 angular nodes.