PROBLEM SET 2
SOLUTION KEY

P9.1) Show by substitution that $\psi_{100}(r,\theta,\phi) = \frac{1}{\sqrt{\pi}}\left(\frac{1}{a_0}\right)^{3/2} e^{-r/a_0}$ is a solution of

$$-\frac{\hbar^2}{2m_e}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi(r,\theta,\phi)}{\partial r}\right)+\frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi(r,\theta,\phi)}{\partial\theta}\right)+\frac{1}{r^2\sin\theta}\frac{\partial^2\psi(r,\theta,\phi)}{\partial\phi^2}\right]$$
$$-\frac{e^2}{4\pi\varepsilon_0 r}\psi(r,\theta,\phi)=E\psi(r,\theta,\phi)$$

What is the eigenvalue for total energy? Use the relation $a_0=\varepsilon_0 h^2/(\pi m_e e^2)$.

Because the wavefunction does not depend on the angles, we need not consider the portion of the Schrödinger equation that involves partial derivatives with respect to θ and ϕ.

$$-\frac{\hbar^2}{2m_e}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi(r,\theta,\phi)}{\partial r}\right)+\frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi(r,\theta,\phi)}{\partial\theta}\right)+\frac{1}{r^2\sin\theta}\frac{\partial^2\psi(r,\theta,\phi)}{\partial\phi^2}\right]$$
$$-\frac{e^2}{4\pi\varepsilon_0|\vec{r}|}\psi(r,\theta,\phi)$$
$$=-\frac{1}{\sqrt{\pi}}\left(\frac{1}{a_0}\right)^{3/2}\frac{\hbar^2}{2\mu}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial e^{-r/a_0}}{\partial r}\right)\right]-\frac{1}{\sqrt{\pi}}\left(\frac{1}{a_0}\right)^{3/2}\frac{e^2}{4\pi\varepsilon_0|\vec{r}|}e^{-r/a_0}$$
$$-\frac{1}{\sqrt{\pi}}\left(\frac{1}{a_0}\right)^{3/2}\frac{\hbar^2}{2\mu}\left[\frac{1}{r^2}e^{-r/a_0}\left(\frac{r^2}{a_0^2}-\frac{2r}{a_0}\right)\right]-\frac{1}{\sqrt{\pi}}\left(\frac{1}{a_0}\right)^{3/2}\frac{e^2}{4\pi\varepsilon_0|\vec{r}|}e^{-r/a_0}$$
$$=-\frac{1}{\sqrt{\pi}}\left(\frac{1}{a_0}\right)^{3/2}\left(\frac{\hbar^2}{2\mu a_0^2}\right)e^{-r/a_0}-\frac{1}{\sqrt{\pi}}\left(\frac{1}{a_0}\right)^{3/2}\left[-\frac{\hbar^2}{\mu a_0}+\frac{e^2}{4\pi\varepsilon_0 r}\right]\frac{1}{r}e^{-r/a_0}$$
$$=-\frac{1}{\sqrt{\pi}}\left(\frac{1}{a_0}\right)^{3/2}\left(\frac{\hbar^2}{2\mu a_0^2}\right)e^{-r/a_0}-\frac{1}{\sqrt{\pi}}\left(\frac{1}{a_0}\right)^{3/2}\left[-\frac{\hbar^2\pi\mu e^2}{\mu\varepsilon_0 h^2}+\frac{e^2}{4\pi\varepsilon_0 r}\right]\frac{1}{r}e^{-r/a_0}$$
$$=-\frac{1}{\sqrt{\pi}}\left(\frac{1}{a_0}\right)^{3/2}\left(\frac{\hbar^2}{2\mu a_0^2}\right)e^{-r/a_0}-\frac{1}{\sqrt{\pi}}\left(\frac{1}{a_0}\right)^{3/2}\left[-\frac{e^2}{4\pi\varepsilon_0}+\frac{e^2}{4\pi\varepsilon_0}\right]\frac{1}{r}e^{-r/a_0}$$
$$=-\frac{1}{\sqrt{\pi}}\left(\frac{1}{a_0}\right)^{3/2}\left(\frac{\hbar^2}{2\mu a_0}\frac{\pi\mu e^2}{4\pi^2\hbar^2\varepsilon_0}\right)e^{-r/a_0}=\frac{1}{\sqrt{\pi}}\left(\frac{1}{a_0}\right)^{3/2}\left(\frac{-e^2}{8\pi\varepsilon_0 a_0}\right)e^{-r/a_0}$$

The function is an eigenfunction of the Schrödinger equation with the eigenvalue $E=\frac{-e^2}{8\pi\varepsilon_0 a_0}$

P9.6) How many radial and angular nodes are there in the following H orbitals set?

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

The functions have $n-l-1$ radial nodes and l angular nodes. Therefore

a) $\psi_{2p_z}(r,\theta,\phi)$ 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.

P9.9)) The d orbitals have the nomenclature $d_{z^2}, d_{xy}, d_{xz}, d_{yz}$, and $d_{x^2-y^2}$. Show how the d orbital $\psi_{3d_{yz}}(r,\theta,\phi) = \frac{\sqrt{2}}{81\sqrt{\pi}}\left(\frac{1}{a_0}\right)^{3/2}\frac{r^2}{a_0^2}e^{-r/3a_0}\sin\theta\cos\theta\sin\phi$ can be written in the form $yzF(r)$.

In spherical coordinates, $x = r\sin\theta\cos\phi$, $y = r\sin\theta\sin\phi$, and $z = r\cos\theta$. Therefore,

$$\psi_{3d_{yz}}(r,\theta,\phi) = \frac{\sqrt{2}}{81\sqrt{\pi}}\left(\frac{1}{a_0}\right)^{3/2}\frac{r^2}{a_0^2}e^{-r/3a_0}\sin\theta\cos\theta\sin\phi$$

$$= \frac{\sqrt{2}}{81\sqrt{\pi}}\left(\frac{1}{a_0}\right)^{3/2}\frac{1}{a_0^2}e^{-r/3a_0}(r\cos\theta)(r\sin\theta\sin\phi) = \frac{\sqrt{2}}{81\sqrt{\pi}}\left(\frac{1}{a_0}\right)^{3/2}\frac{1}{a_0^2}e^{-r/3a_0}(yz)$$

P9.10) Show that the function $\frac{r}{a_0}e^{-r/2a_0}$ is a solution of the differential equation for $R(r)$

$$-\frac{\hbar^2}{2m_e r^2}\frac{d}{dr}\left[r^2\frac{dR(r)}{dr}\right] + \left[\frac{\hbar^2 l(l+1)}{2\mu r^2} - \frac{e^2}{4\pi\varepsilon_0 r}\right]R(r) = E\,R(r) \text{ for } l = 1$$

What is the eigenvalue? Using this result, what is the value for the principal quantum number n for this function?

$$-\frac{\hbar^2}{2m_e r^2}\frac{d}{dr}\left[r^2\frac{d\frac{r}{a_0}e^{-r/2a_0}}{dr}\right] + \left[\frac{\hbar^2}{m_e r^2} - \frac{e^2}{4\pi\varepsilon_0 r}\right]\frac{r}{a_0}e^{-r/2a_0}$$

$$= -\frac{\hbar^2}{2m_e r^2}\frac{d}{dr}\left[\frac{r^2}{a_0}e^{-r/2a_0} - \frac{r^3}{2a_0^2}e^{-r/2a_0}\right] + \left[\frac{\hbar^2}{m_e r^2} - \frac{e^2}{4\pi\varepsilon_0 r}\right]\frac{r}{a_0}e^{-r/2a_0}$$

$$= -\frac{\hbar^2}{2m_e r^2}\left[-2\frac{r^2}{a_0^2}e^{-r/2a_0} + \frac{r^3}{4a_0^3}e^{-r/2a_0} + 2\frac{r}{a_0}e^{-r/2a_0}\right] + \left[\frac{\hbar^2}{m_e r^2} - \frac{e^2}{4\pi\varepsilon_0 r}\right]\frac{r}{a_0}e^{-r/2a_0}$$

$$= -\frac{\hbar^2}{2m_e r^2}\left[-2\frac{r^2}{a_0^2}e^{-r/2a_0} + \frac{r^3}{4a_0^3}e^{-r/2a_0}\right] - \frac{e^2}{4\pi\varepsilon_0 a_0}e^{-r/2a_0}$$

$$= -\frac{\hbar^2}{2m_e r^2}\left[-2\frac{r^2\pi m_e e^2}{a_0\varepsilon_0 h^2}e^{-r/2a_0} + \frac{r^3}{4a_0^3}e^{-r/2a_0}\right] - \frac{e^2}{4\pi\varepsilon_0 a_0}e^{-r/2a_0}$$

where we have used the definition $a_0 = \frac{\varepsilon_0 h^2}{\pi m_e e^2}$

$$= -\frac{\hbar^2}{2m_e r^2}\frac{r^3}{4a_0^3}e^{-r/2a_0} + \frac{e^2}{4\pi a_0\varepsilon_0}e^{-r/2a_0} - \frac{e^2}{4\pi\varepsilon_0 a_0}e^{-r/2a_0} = -\frac{\hbar^2}{2m_e r^2}\frac{r^3}{4a_0^3}e^{-r/2a_0}$$

$$= -\frac{e^2}{32\pi\, a_0\varepsilon_0}\frac{r}{a_0}e^{-r/2a_0}$$

By comparison with $E_n = -\frac{e^2}{8\pi\varepsilon_0 a_0 n^2}$, $n = 2$.

P9.17) 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 $\langle y \rangle$, $\langle x^2 \rangle$ and $\langle y^2 \rangle$? Why?

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

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

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

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

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

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

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

(1) **Angular momentum states of a hydrogenic atom**

Since the energy eigenfunction $\psi_{nlm}(r,\theta,\phi)$ of a hydrogenic atom is also an eigenfunction of $\hat{L}^2$ and $\hat{L}_z$, then:

a) For a 2p orbital (*l=1*): $L = \hbar\sqrt{l(l+1)} = \sqrt{2}\hbar$, and the allowed (measurable) values of L_z are $-\hbar, 0, \hbar$.

b) For a 2d orbital (*l=2*), $L = \hbar\sqrt{2(2+1)} = \sqrt{6}\hbar$, and the allowed (measurable) values of L_z are $-2\hbar, -\hbar, 0, \hbar, 2\hbar$.

(2) **Average radial distance of the electron from the nucleus in an energy eigenstate of a hydrogenic atom.** For a hydrogenic atom ($H, He^+, Li^{2+}, \ldots$), it can be shown that:

$$< r >_{nl} = \frac{n^2 a_0}{Z}\left[1 + \frac{1}{2}(1 - \frac{l(l+1)}{n^2})\right] \quad \text{[Engel, P9.24]}$$

where Z is the atomic number of the atom and a_0 is the Bohr radius for the H-atom ($a_0 \cong 0.53$ Å).

Thus:

a) For an *H* atom (Z=1),

i) 2s (n=2,l=0): $< r >_{20} = 6a_0 = 3.18$ Å

ii) 3p (n=3,l=1), $< r >_{31} = 12.5a_0 = 6.63$ Å

b) For a Li^{2+} atom (Z=3),

i) 2s (n=2,l=0): $< r >_{20} = 2a_0 = 1.06$ Å

ii) 3p (n=3,l=1), $< r >_{31} = 4.167a_0 = 2.21$ Å