Assignment 3: solutions:

1. Problem 2, p. 226: Show that

$$\Theta_{20}(\theta) = \frac{\sqrt{10}}{4}\left(3\cos^2\theta - 1\right)$$

is a solution of the Eq.

$$\frac{1}{\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right) + \left[l(l+1) - \frac{m_l^2}{\sin^2\theta}\right]\Theta = 0$$

and that it is normalized.

Ans : To show that $\Theta_{20} is$ a solution, we need not worry about the constant factor. Let us consider $f(\theta) = 3\cos^2\theta - 1$.In the L.H.S of the differential equation

1st term :

$\frac{df}{d\theta} = -6\cos\theta\sin\theta$

$$\sin\theta\frac{df}{d\theta} = -6\cos\theta\sin^2\theta$$

$$\frac{1}{\sin\theta}\frac{d}{d\theta}\sin\theta\frac{df}{d\theta} = -\frac{6}{sin\theta}[-\sin^3\theta + 2\cos^2\theta\sin\theta] = 6[\sin^2\theta - 2\cos^2\theta] = -6f$$

2ndterm:

$$\left[l(l+1) - \frac{m_l^2}{\sin^2\theta}\right]f = 2(2+1)f = 6f$$

$$\therefore \text{L.H.S} = -6f + 6f = 0 = \text{R.H.S}$$

$\Longrightarrow \Theta_{20}$ is a solution .

And $\int|\Theta_{20}|^2\sin\theta d\theta = \frac{10}{16}\int_0^\pi(3\cos^2\theta - 1)^2\sin\theta d\theta$

$$= \frac{5}{8}\int_{-1}^{+1}(3X^2-1)^2dX = \frac{5}{8}\int_{-1}^{+1}(9X^4 - 6X^2 + 1)dX = \frac{5}{8}\left[\frac{9}{5}X^5|_{-1}^{+1} - 2X^3|_{-1}^{+1} + X|_{-1}^{+1}\right]$$

$$\Longrightarrow \frac{5}{8}\left[\frac{18}{5} - 4 + 2\right] = \frac{5}{8}.\frac{8}{5} = 1$$

Hence $\Theta_{20}$is normalised in θ - space.

2. Problem 3, p. 226: Show that

$$R_{10}(r) = \frac{2}{a_0^{\frac{3}{2}}}e^{-\frac{r}{a_0}}$$

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) + \left[\frac{2m}{\hbar^2}\left(\frac{e^2}{4\pi\epsilon_0 r} + E\right) - \frac{l(l+1)}{r^2}\right]R = 0$$

and that it is normalized.

Ans. Consider $f(r) = \exp(\frac{-r}{a_0})$

1st term

$\frac{1}{r^2}\frac{d}{dr}r^2\frac{df}{dr} = -\frac{a_0}{r^2}\frac{d}{dr}[r^2\exp\frac{-r}{a_0}] = -\frac{1}{a_0 r^2}[2r - \frac{1}{a_0}r^2]\exp\frac{-r}{a_0} = -\frac{1}{a_0}[-\frac{1}{a_0} + \frac{2}{r}]e^{\frac{-r}{a_0}}$

2nd term: using $a_0 = \frac{\hbar^2}{m}\frac{4\pi\epsilon_0}{e^2}$; $\quad E = \frac{e^2}{8\pi\epsilon_0 a_0}$; and $\frac{2m}{\hbar^2}E = \frac{1}{a_0^2}$

$$\left[\frac{2m}{\hbar^2}\left(\frac{e^2}{4\pi\epsilon_0 r} + E\right) - \frac{l(l+1)}{r^2}\right] e^{\frac{-r}{a_0}} \overset{l=0}{\Longrightarrow} \frac{1}{a_0}[-\frac{1}{a_0} + \frac{2}{r}]e^{-\frac{r}{a_0}}$$

$$\therefore \text{L.H.S}=-\frac{1}{a_0}[-\frac{1}{a_0}+\frac{2}{r}]e^{-\frac{r}{a_0}}+\frac{1}{a_0}[-\frac{1}{a_0}+\frac{2}{r}]e^{-\frac{r}{a_0}} = 0 = \text{R.H.S}$$

To prove the normalisation, we show using $\int x^2 e^{ax}dx = \left(\frac{x^2}{a} - \frac{2x}{a^2} + \frac{2}{a^3}\right)e^{ax}$,

$$\int_0^\infty \left(\frac{2}{a_0^{\frac{3}{2}}}e^{-\frac{r}{a_0}}\right)^2 r^2 dr = \frac{4}{a_0^3}\left[\left(-\frac{r^2}{\frac{2}{a_0}} - \frac{2r}{\left(\frac{2}{a_0}\right)^2} - \frac{2}{\left(\frac{2}{a_0}\right)^3}\right)e^{-\frac{2r}{a_0}}\right]_0^\infty = 1$$

3. Problem 21, p. 227: The probability of finding an atomic electron whose radial wave function is $R(r)$ outside a sphere of radius r_0 centered on th nucleus is

$$\int_{r_0}^\infty |R(r)|^2 r^2 dr$$

(a) Calculate the probability of finding a 1s electron in a hydrogen atom at a distance greater than a_0 from the nucleus.

(b) When a 1s electron in a hydrogen atom is $2a_0$ from the nucleus, all its energy is potential energy. According to classical physics, the electron therefore cannot ever exceed the distance $2a_0$ from the nucleus. Find the probability $r > 2a_0$ for a ls electron in a hydrogen atom.

Ans.

$$p_{r>a_0} = \int_{a_0}^\infty |R(r)|^2 r^2 dr = \int_{a_0}^\infty \left(\frac{2}{a_0^{\frac{3}{2}}}\right)^2 \left(e^{-\frac{r}{a_0}}\right)^2 r^2 dr = \frac{4}{a_0^3}\int_{a_0}^\infty e^{-\frac{2r}{a_0}} r^2 dr$$

$$\text{using } \int x^2 e^{ax}dx = \left(\frac{x^2}{a} - \frac{2x}{a^2} + \frac{2}{a^3}\right)e^{ax}$$

we get

$$p_{r>a_0} = \frac{4}{a_0^3}\left[\left(-\frac{a_0}{2}.r^2 - 2\left(\frac{a_0}{2}\right)^2.r - \left(\frac{a_0}{2}\right)^3.2\right)e^{\frac{-2r}{a_0}}\right]_{a_0}^\infty$$

$$= \frac{4}{a_0^3}\left[\frac{a_0^3}{2} + \frac{a_0^3}{2} + \frac{a_0^3}{4}\right]e^{-2}$$

$$= 5.e^{-2} = 0.677$$

(b)

$$p_{r>2a_0} = \frac{4}{a_0^3}\left[2^2.\frac{a_0^3}{2} + 2.\frac{a_0^3}{2} + \frac{a_0^3}{4}\right]e^{-2\times 2}$$

$$= 13e^{-4} = 0.238$$

4. Problem 22, p. 227: According to Fig. 6.11 (p. 214), a 2s electron in a hydrogen atom is more

likely than a 2p electron to be closer to the nucleus than $r = a_0$ (that is, to be between $r = 0$ and $r = a_0$). Verify thLs by calculating the relevant probabilities,

Ans.Using the results from above ,

$$p^{1s}_{r<a_0} = \frac{4}{a_0^3}\left[-\left(\frac{a_0}{2}.r^2 + \frac{a_0^2}{2}r + \frac{a_0^3}{4}\right)e^{-\frac{2r}{a_0}}\right]_0^{a_0}$$

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

$$= 1 - 0.677 = 0.323$$

(we could have obtained this as $p^{1s}_{r<a_0} = 1 - p^{1s}_{r>a_0}$)

$$p^{2p}_{r<a_0} = \int_0^{a_0}\left(\frac{1}{2\sqrt{6}a_0^{\frac{2}{3}}}.\frac{r}{a_0}e^{-\frac{r}{2a_0}}\right)^2 r^2 dr$$

$$= \frac{1}{24a_0^5}\int_0^{a_0} r^4 e^{-\frac{r}{a_0}} dr$$

using $\int x^4 e^{ax}dx = \left[\frac{x^4}{a} - \frac{4}{a^2}x^3 + \frac{12}{a^3}x^2 - \frac{24}{a^4}x + \frac{24}{a^5}\right]e^{ax}$

$$p^{2p}_{r<a_0} = \left(\frac{1}{24a_0^5}\left[-a_0r^4 - 4a_0^2r^3 - 12a_0^3r^2 - 24a_0^4r - 24a_0^5\right]e^{\frac{-r}{a_0}}\right)_0^{a_0}$$

$$= 1 - \frac{1}{24}\left[1 + 4 + 12 + 24 + 24\right]e^{-1}$$

$$= 1 - \frac{65}{24}e^{-1} = 1 - 0.996 = 0.004$$

5.. Problem 23, p. 227: Unsöld's theorem states that for any value of the orbital quantum number l, the probability densities summed over all possible states from $m_l = -l$ to $m_l = +l$ yield a constant independent of angles θ or ϕ; that is,

$$\sum_{m_l=-l}^{m_l=+l} |\Theta|^2|\Phi|^2 = \text{constant}$$

This theorem means that every closed subshell atom or ion has a spherically symmetric distribution of electric charge. Verify Unsöld theorem for $l = 0$, $l = 1$, and $l = 2$ with the help of Table 6.1.

Ans:

$$S = \sum_{ml=-l}^{+l} |\Theta|^2|\Phi|^2$$

For $l = 0$

$$S = |\Theta_{00}|^2|\Phi_{00}|^2 = \frac{1}{4\pi}$$

For $l = 1$

$$S = |\Theta_{1,0}|^2|\Phi_0|^2 + 2|\Theta_{1,\pm1}|^2|\Phi_{\pm1}|^2$$

$$= \frac{6}{2}\cos^2\theta.\frac{1}{2\pi} + 2.\frac{3}{2}\sin^2\theta.\frac{1}{2\pi}$$

$$= \frac{3}{2\pi}(\cos^2\theta + \sin^2\theta) = \frac{3}{2\pi}$$

For $l = 2$

$$S = |\Theta_{2,0}|^2|\Phi_0|^2 + 2.|\Theta_{2,\pm1}|^2|\Phi_\pm|^2 + 2|\Theta_{2,\pm2}|^2|\Phi_{\pm2}|^2$$

$$= \frac{10}{16}(3\cos^2\theta - 1)^2.\frac{1}{2\pi} + 2.\frac{15}{4}\sin^2\theta\cos^2\theta\frac{1}{2\pi} + 2.\frac{15}{16}\sin^4\theta.\frac{1}{2\pi}$$

$$= \frac{5}{16\pi}\left[(3\cos^2\theta - 1)^2 + 12\sin^2\theta\cos^2\theta + 3\sin^4\theta\right]$$

$$\frac{5}{16\pi}\left[(3 - 3\sin^2\theta - 1)^2 + 12\sin^2\theta(1 - \sin^2\theta) + 3\sin^4\theta\right]$$

$$\frac{5}{16\pi}\left[4 - 12\sin^2\theta + 9\sin^4\theta + 12\sin^2\theta - 12\sin^4\theta + 3\sin^4\theta\right]$$

$$= \frac{5}{16\pi}[4] = \frac{5}{4\pi}$$