Chapter 7: Quantum Mechanics in three Dimensions

#7.1

$$E_{n_1,n_2,n_3} = \frac{\hbar^2 \pi^2}{2m}\left[\left(\frac{n_1}{L}\right)^2 + \left(\frac{n_2}{2L}\right)^2 + \left(\frac{n_3}{2L}\right)^2\right]$$

$$= \frac{\hbar^2 \pi^2}{8mL^2}\left[4n_1^2 + n_2^2 + n_3^2\right]$$

* Ground state $n_1 = n_2 = n_3 = 1$

$$E_{111} = \frac{6\hbar^2\pi^2}{8mL^2} = \boxed{\frac{3\hbar^2\pi^2}{4mL^2}} \quad ①$$

* First excited state $n_1 = 1 \quad n_2 = 2 \quad n_3 = 1$

$$E_{121} = \boxed{\frac{9\hbar^2\pi^2}{8mL^2}} \quad ②$$

and $n=1 \quad n_2 = 1 \quad n_3 = 2$

$$E_{112} = \boxed{\frac{9\hbar^2\pi^2}{8mL^2}} \quad ③$$

this state is doubly degenerate.

* Second excited state $n_1 = 1 \quad n_2 = 2 \quad n_3 = 2$

$$E_{122} = \frac{12\hbar^2\pi^2}{8mL^2} = \boxed{\frac{3\hbar^2\pi^2}{4mL^3}} \quad ④$$

* Third excited state $n_1 = 1 \quad n_2 = 3 \quad n_3 = 1$

$$E_{131} = \frac{14\hbar^2\pi^2}{8mL^2} = \boxed{\frac{7\hbar^2\pi^2}{4mL^2}} \quad ⑤$$

and $n_1 = 1 \quad n_2 = 1 \quad n_3 = 3$

$$E_{131} = \frac{14\hbar^2\pi^2}{8mL^2} = \boxed{\frac{7\hbar^2\pi^2}{4mL^2}} \quad ⑥$$

this state is doubly degenerate.

The corresponding wavefunctions are ψ_{111}, ψ_{121}, ψ_{112}, ψ_{113}, and ψ_{131}.

7.9

$$|\vec{L}| = \sqrt{\ell(\ell+1)}\,\hbar \quad \Rightarrow \quad \hbar^2 \ell(\ell+1) = |\vec{L}|^2$$

$$\ell^2 + \ell - \frac{|\vec{L}|^2}{\hbar^2} = 0$$

$$\ell^2 + \ell - \frac{(4.714 \times 10^{-34})^2}{(1.05 \times 10^{-34})^2} = 0$$

$$\ell^2 + \ell - 20.2 = 0 \qquad \ell = \frac{-1 \pm \sqrt{(1)^2 + 4 \times 20.2}}{2} = \frac{8}{2} = 4.$$

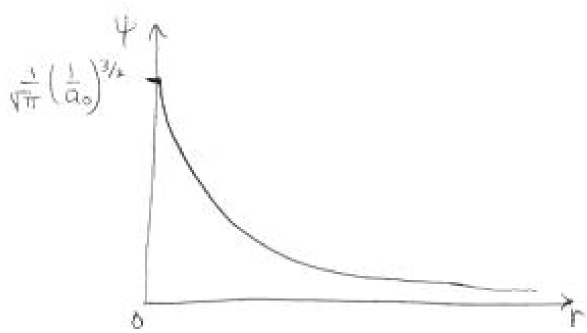
So $\boxed{\ell = 4}$ ⇐ orbital quantum number

#7.12.

$$\psi(r,\theta,\phi) = \frac{1}{\sqrt{\pi}}\left(\frac{1}{a_0}\right)^{3/2} e^{-r/a_0}$$ is the ground state wavefunction for the hydrogen atom.

a) $r \to 0 \qquad \psi \longrightarrow \frac{1}{\sqrt{\pi}}\left(\frac{1}{a_0}\right)^{3/2}$

$r \to \infty \qquad \psi \longrightarrow 0$



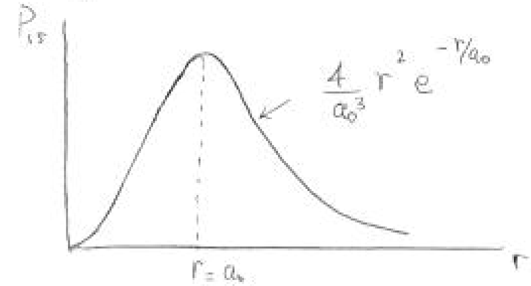
b) Probability of finding the electron between r and $r+dr$ is

$$= |\psi(r,\theta,\phi)|^2 \, dV$$

Since the wavefunction depends only on r (has spherical symmetry) $dV = 4\pi r^2 dr$

$$\Rightarrow \boxed{P(r)dr = |\psi|^2 4\pi r^2 dr}$$

c) See figure 7.10 in the textbook



The electron is most likely to be found at $r = a_0$ where the probability is maximum (see figure).

d) $P = \int_0^\infty P(r)\, dr \stackrel{?}{=} 1$

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

apply the change of variables $z = \frac{2r}{a_0}$ $\quad dr = \frac{a_0}{2} dz$

and $r^2 = \left(\frac{a_0}{2}\right)^2 z^2$

$$\Rightarrow P = \frac{4}{a_0^3} \int_0^\infty \left(\frac{a_0}{2}\right)^2 z^2 \left(\frac{a_0}{2}\right) e^{-z} dz = \frac{4}{a_0^3} \left(\frac{a_0}{2}\right)^3 \int_0^\infty z^2 e^{-z} dz$$

note that $\int_0^\infty z^n e^{-z} dz = n!$

$$\Rightarrow \int_0^\infty z^2 e^{-z} dz = 2! = 2\times 1 = 2 \Rightarrow P = \frac{8}{a_0^3} \times \frac{a_0^3}{8} = 1$$

$\Rightarrow$ The wavefunction is normalized.

e)
$$P = \int_{\frac{a_0}{2}}^{\frac{3a_0}{2}} P(r)\,dr = \frac{4}{a_0^3} \int_{\frac{a_0}{2}}^{\frac{3a_0}{2}} r^2 e^{-\frac{2r}{a_0}}\,dr$$

Change variable $z = \frac{2r}{a_0}$

$$P = \frac{4}{a_0^3} \int_1^3 \left(\frac{a_0}{2}\right)^3 z^2 e^{-z}\,dz = \frac{1}{2} \int_1^3 z^2 e^{-z}\,dz$$

$$= -\frac{1}{2}\left(z^2 + 2z + 2\right)e^{-z}\Big|_1^3 = -\frac{17}{2}e^{-3} + \frac{5}{2}e^{-1} = -0.42 + 0.92$$

$$= 0.5$$

$$= \boxed{50\%}$$

7.18

a) $4d \Rightarrow n = 4$ and $l = 2$

$$|\vec{L}| = \sqrt{l(l+1)}\,\hbar = \sqrt{2\times 3}\,\hbar = \sqrt{6}\,\hbar = 2.57\times 10^{-34}\ \text{J.s}$$

b) $6f \Rightarrow n = 6$ and $l = 3$

$$|\vec{L}| = \sqrt{3\times 4}\,\hbar = \sqrt{12}\,\hbar = 3.64\times 10^{-34}\ \text{J.s}$$

7.23

The radial part of the wavefunction for the hydrogen atom in the 2p state is given by

$$R_{2p}(r) = A\,r\,e^{-\frac{r}{2a_0}}$$

From table 7.4 in your textbook $A = \left(\frac{1}{2a_0}\right)^{3/2} \frac{1}{\sqrt{3}\,a_0}$

$$\langle r \rangle = \int_0^\infty r P(r)\,dr$$

where $P(r) = r^2 |R_{2p}|^2 = r^2 \left(\frac{1}{2a_0}\right)^3 \frac{1}{3a_0^2} r^2 e^{-\frac{r}{a_0}}$

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

$$\langle r \rangle = \frac{1}{24 a_0^5} \int_0^\infty r^5 e^{-r/a_0} \, dr$$

Change variable $\frac{r}{a_0} = z$ $\quad r^5 = a_0^5 z \quad dr = a_0 \, dz$

$$\langle r \rangle = \frac{1}{24 a_0^5} a_0^6 \underbrace{\int_0^\infty z^5 e^{-z} \, dz}_{5!} = \frac{a_0}{24} 5! = 5 a_0$$

since $a_0 = 0.529$ Å

$$\boxed{\langle r \rangle = 2.65 \text{ Å}}$$