

$$8-1 \quad E = \frac{\hbar^2 \pi^2}{2m} \left[ \left( \frac{n_1}{L_x} \right)^2 + \left( \frac{n_2}{L_y} \right)^2 + \left( \frac{n_3}{L_z} \right)^2 \right]$$

$L_x = L, L_y = L_z = 2L$ . Let  $\frac{\hbar^2 \pi^2}{8mL^2} = E_0$ . Then  $E = E_0(4n_1^2 + n_2^2 + n_3^2)$ . Choose the quantum numbers as follows:

$n_1$	$n_2$	$n_3$	$\frac{E}{E_0}$	
1	1	1	6	ground state
1	2	1	9	* first two excited states
1	1	2	9	*
2	1	1	18	
1	2	2	12	* next excited state
2	1	2	21	
2	2	1	21	
2	2	2	24	
1	1	3	14	* next two excited states
1	3	1	14	*

Therefore the first 6 states are  $\psi_{111}, \psi_{121}, \psi_{112}, \psi_{122}, \psi_{113}$ , and  $\psi_{131}$  with relative energies  $\frac{E}{E_0} = 6, 9, 9, 12, 14, 14$ . First and third excited states are doubly degenerate.

$$8-2 \quad (a) \quad n_1 = 1, n_2 = 1, n_3 = 1$$

$$E_0 = \frac{3\hbar^2 \pi^2}{2mL^2} = \frac{3\hbar^2}{8mL^2} = \frac{3(6.626 \times 10^{-34} \text{ Js})^2}{8(9.11 \times 10^{-31} \text{ kg})(2 \times 10^{-10} \text{ m})^2} = 4.52 \times 10^{-18} \text{ J} = 28.2 \text{ eV}$$

$$(b) \quad n_1 = 2, n_2 = 1, n_3 = 1 \text{ or}$$

$$n_1 = 1, n_2 = 2, n_3 = 1 \text{ or}$$

$$n_1 = 1, n_2 = 1, n_3 = 2$$

$$E_1 = \frac{6\hbar^2}{8mL^2} = 2E_0 = 56.4 \text{ eV}$$

$$8-3 \quad n^2 = 11$$

$$(a) \quad E = \left( \frac{\hbar^2 \pi^2}{2mL^2} \right) n^2 = \frac{11}{2} \left( \frac{\hbar^2 \pi^2}{mL^2} \right)$$

$$(b) \quad \begin{array}{ccc} n_1 & n_2 & n_3 \\ \hline 1 & 1 & 3 \\ 1 & 3 & 1 \\ 3 & 1 & 1 \end{array} \quad \text{3-fold degenerate}$$

$$(c) \quad \psi_{113} = A \sin\left(\frac{\pi x}{L}\right) \sin\left(\frac{\pi y}{L}\right) \sin\left(\frac{3\pi z}{L}\right)$$

$$\psi_{131} = A \sin\left(\frac{\pi x}{L}\right) \sin\left(\frac{3\pi y}{L}\right) \sin\left(\frac{\pi z}{L}\right)$$

$$\psi_{311} = A \sin\left(\frac{3\pi x}{L}\right) \sin\left(\frac{\pi y}{L}\right) \sin\left(\frac{\pi z}{L}\right)$$

- 8-4 (a)  $\psi(x, y) = \psi_1(x)\psi_2(y)$ . In the two-dimensional case,  $\psi = A(\sin k_1 x)(\sin k_2 y)$  where  $k_1 = \frac{n_1\pi}{L}$  and  $k_2 = \frac{n_2\pi}{L}$ .

(b) 
$$E = \frac{\hbar^2 \pi^2 (n_1^2 + n_2^2)}{2mL^2}$$

If we let  $E_0 = \frac{\hbar^2 \pi^2}{mL^2}$ , then the energy levels are:

$n_1$	$n_2$	$\frac{E}{E_0}$		
1	1	1	→	$\psi_{11}$
1	2	$\frac{5}{2}$	→	$\psi_{12}$
2	1	$\frac{5}{2}$	→	$\psi_{21}$
2	2	4	→	$\psi_{22}$

} doubly degenerate

- 8-5 (a)  $n_1 = n_2 = n_3 = 1$  and

$$E_{111} = \frac{3\hbar^2}{8mL^2} = \frac{3(6.63 \times 10^{-34})^2}{8(1.67 \times 10^{-27})(4 \times 10^{-28})} = 2.47 \times 10^{-13} \text{ J} \approx 1.54 \text{ MeV}$$

- (b) States 211, 121, 112 have the same energy and  $E = \frac{(2^2 + 1^2 + 1^2)\hbar^2}{8mL^2} = 2E_{111} \approx 3.08 \text{ MeV}$   
 and states 221, 122, 212 have the energy  $E = \frac{(2^2 + 2^2 + 1^2)\hbar^2}{8mL^2} = 3E_{111} \approx 4.63 \text{ MeV}$ .

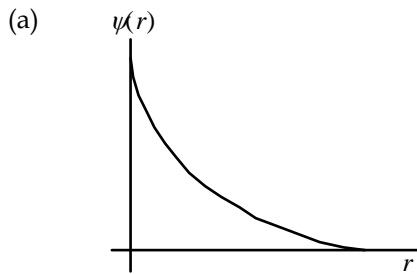
- (c) Both states are threefold degenerate.

8-10  $n = 4$ ,  $l = 3$ , and  $m_l = 3$ .

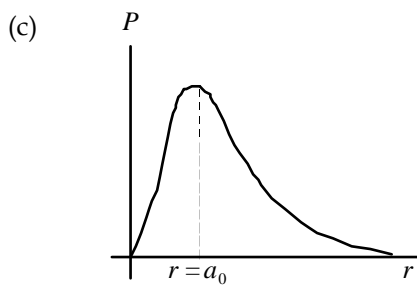
(a) 
$$L = [l(l+1)]^{1/2} \hbar = [3(3+1)]^{1/2} \hbar = 2\sqrt{3}\hbar = 3.65 \times 10^{-34} \text{ Js}$$

(b) 
$$L_z = m_l \hbar = 3\hbar = 3.16 \times 10^{-34} \text{ Js}$$

8-12  $\psi(r) = \left(\frac{1}{\pi}\right)^{1/2} \left(\frac{1}{a_0}\right)^{3/2} e^{-r/a_0}$



- (b) The probability of finding the electron in a volume element  $dV$  is given by  $|\psi|^2 dV$ . Since the wave function has spherical symmetry, the volume element  $dV$  is identified here with the volume of a spherical shell of radius  $r$ ,  $dV = 4\pi r^2 dr$ . The probability of finding the electron between  $r$  and  $r + dr$  (that is, within the spherical shell) is  $P = |\psi|^2 dV = 4\pi r^2 |\psi|^2 dr$ .



(d)  $\int |\psi|^2 dV = 4\pi \int |\psi|^2 r^2 dr = 4\pi \left(\frac{1}{\pi}\right) \left(\frac{1}{a_0^3}\right) \int_0^\infty e^{-2r/a_0} r^2 dr = \left(\frac{4}{a_0^3}\right) \int_0^\infty e^{-2r/a_0} r^2 dr$

Integrating by parts, or using a table of integrals, gives

$$\int |\psi|^2 dV = \left(\frac{4}{a_0^3}\right) \left[ 2 \left(\frac{a_0}{2}\right)^3 \left(\frac{2}{a_0}\right)^3 \right] = 1.$$

(e)  $P = 4\pi \int_{r_1}^{r_2} |\psi|^2 r^2 dr$  where  $r_1 = \frac{a_0}{2}$  and  $r_2 = \frac{3a_0}{2}$

$$\begin{aligned}
P &= \left( \frac{4}{a_0^3} \right) \int_{r_1}^{r_2} r^2 e^{-2r/a_0} dr \quad \text{let } z = \frac{2r}{a_0} \\
&= \frac{1}{2} \int_1^3 z^2 e^{-z} dz \\
&= -\frac{1}{2} (z^2 + 2z + 2) e^{-z} \Big|_1^3 \quad (\text{integrating by parts}) \\
&= -\frac{17}{2} e^{-3} + \frac{5}{2} e^{-1} = 0.496
\end{aligned}$$

8-13  $Z=2$  for  $\text{He}^+$

(a) For  $n=3$ ,  $l$  can have the values of 0, 1, 2

$$l=0 \rightarrow m_l = 0$$

$$l=1 \rightarrow m_l = -1, 0, +1$$

$$l=2 \rightarrow m_l = -2, -1, 0, +1, +2$$

(b) All states have energy  $E_3 = \frac{-Z^2}{3^2} (13.6 \text{ eV})$

$$E_3 = -6.04 \text{ eV}.$$

8-14  $Z=3$  for  $\text{Li}^{2+}$

(a)  $n=1 \rightarrow l=0 \rightarrow m_l = 0$

$n=2 \rightarrow l=0 \rightarrow m_l = 0$

and  $l=1 \rightarrow m_l = -1, 0, +1$

(b) For  $n=1$ ,  $E_1 = -\left(\frac{3^2}{1^2}\right)(13.6) = -122.4 \text{ eV}$

For  $n=2$ ,  $E_2 = -\left(\frac{3^2}{2^2}\right)(13.6) = -30.6 \text{ eV}$

8-16 For a  $d$  state,  $l=2$ . Thus,  $m_l$  can take on values -2, -1, 0, 1, 2. Since  $L_z = m_l \hbar$ ,  $L_z$  can be  $\pm 2\hbar$ ,  $\pm \hbar$ , and zero.

8-17 (a) For a  $d$  state,  $l=2$

$$L = [l(l+1)]^{1/2} \hbar = (6)^{1/2} (1.055 \times 10^{-34} \text{ Js}) = 2.58 \times 10^{-34} \text{ Js}$$

(b) For an  $f$  state,  $l=3$

$$L = [l(l+1)]^{1/2} \hbar = (12)^{1/2} (1.055 \times 10^{-34} \text{ Js}) = 3.65 \times 10^{-34} \text{ Js}$$

8-18 The state is  $6g$

(a)  $n=6$

(b)  $E_n = -\frac{13.6 \text{ eV}}{n^2}$        $E_6 = \frac{-13.6}{6^2} \text{ eV} = -0.378 \text{ eV}$

(c) For a g-state,  $l = 4$

$$L = [l(l+1)]^{1/2} \hbar = (4 \times 5)^{1/2} \hbar = \sqrt{20} \hbar = 4.47 \hbar$$

(d)  $m_l$  can be -4, -3, -2, -1, 0, 1, 2, 3, or 4

$$L_z = m_l \hbar; \cos \theta = \frac{L_z}{L} = \frac{m_l}{[l(l+1)]^{1/2}} \hbar = \frac{m_l}{\sqrt{20}}$$

$m_l$	-4	-3	-2	-1	0	1	2	3	4
$L_z$	$-4\hbar$	$-3\hbar$	$-2\hbar$	$-\hbar$	0	$\hbar$	$2\hbar$	$3\hbar$	$4\hbar$
$\theta$	$153.4^\circ$	$132.1^\circ$	$116.6^\circ$	$102.9^\circ$	$90^\circ$	$77.1^\circ$	$63.4^\circ$	$47.9^\circ$	$26.6^\circ$

8-21 (a)  $\psi_{2s}(r) = \frac{1}{4(2\pi)^{1/2}} \left(\frac{1}{a_0}\right)^{3/2} \left(2 - \frac{r}{a_0}\right) e^{-r/2a_0}$ . At  $r = a_0 = 0.529 \times 10^{-10} \text{ m}$  we find

$$\begin{aligned} \psi_{2s}(a_0) &= \frac{1}{4(2\pi)^{1/2}} \left(\frac{1}{a_0}\right)^{3/2} (2-1)e^{-1/2} = (0.380) \left(\frac{1}{a_0}\right)^{3/2} \\ &= (0.380) \left[ \frac{1}{0.529 \times 10^{-10} \text{ m}} \right]^{3/2} = 9.88 \times 10^{14} \text{ m}^{-3/2} \end{aligned}$$

(b)  $|\psi_{2s}(a_0)|^2 = (9.88 \times 10^{14} \text{ m}^{-3/2})^2 = 9.75 \times 10^{29} \text{ m}^{-3}$

(c) Using the result to part (b), we get  $P_{2s}(a_0) = 4\pi a_0^2 |\psi_{2s}(a_0)|^2 = 3.43 \times 10^{10} \text{ m}^{-1}$ .

8-22  $R_{2p}(r) = A r e^{-r/2a_0}$  where  $A = \frac{1}{2(6)^{1/2} a_0^{5/2}}$

$$P(r) = r^2 R_{2p}^2(r) = A^2 r^4 e^{-r/a_0}$$

$$\langle r \rangle = \int_0^\infty r P(r) dr = A^2 \int_0^\infty r^5 e^{-r/a_0} dr = A^2 a_0^6 5! = 5a_0 = 2.645 \text{ \AA}$$