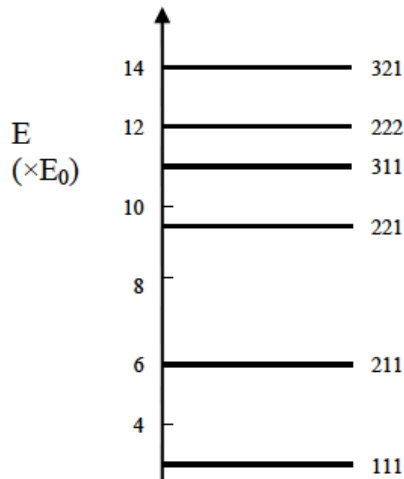


7-1.  $E_{n_1 n_2 n_3} = \frac{\hbar^2 \pi^2}{2mL^2} (n_1^2 + n_2^2 + n_3^2)$  (Equation 7-4)

$$E_{311} = \frac{\hbar^2 \pi^2}{2mL^2} (3^2 + 1^2 + 1^2) = 11E_0 \quad \text{where } E_0 = \frac{\hbar^2 \pi^2}{2mL^2}$$

$$E_{222} = E_0 (2^2 + 2^2 + 2^2) = 12E_0 \quad \text{and} \quad E_{321} = E_0 (3^2 + 2^2 + 1^2) = 14E_0$$

The 1<sup>st</sup>, 2<sup>nd</sup>, 3<sup>rd</sup>, and 5<sup>th</sup> excited states are degenerate.



7-2.  $E_{n_1 n_2 n_3} = \frac{\hbar^2 \pi^2}{2m} \left( \frac{n_1^2}{L_1^2} + \frac{n_2^2}{L_2^2} + \frac{n_3^2}{L_3^2} \right) = \frac{\hbar^2 \pi^2}{2mL_1^2} \left( n_1^2 + \frac{n_2^2}{4} + \frac{n_3^2}{9} \right)$  (Equation 7-5)

$n_1 = n_2 = n_3 = 1$  is the lowest energy level.

$$E_{111} = E_0 (1 + 1/4 + 1/9) = 1.361E_0 \quad \text{where } E_0 = \frac{\hbar^2 \pi^2}{2mL_1^2}$$

The next nine levels are, increasing order,

$n_1$	$n_2$	$n_3$	$E (\times E_0)$
1	1	2	1.694
1	2	1	2.111
1	1	3	2.250
1	2	2	2.444
1	2	3	3.000
1	1	4	3.028
1	3	1	3.360
1	3	2	3.472
1	2	4	3.778

7-3. (a)  $\psi_{n_1 n_2 n_3}(x, y, z) = A \cos \frac{n_1 \pi x}{L} \sin \frac{n_2 \pi y}{L} \sin \frac{n_3 \pi z}{L}$

(b) They are identical. The location of the coordinate origin does not affect the energy level structure.

7-4.  $\psi_{111}(x, y, z) = A \sin \frac{\pi x}{L_1} \sin \frac{\pi y}{2L_1} \sin \frac{\pi z}{3L_1}$        $\psi_{112}(x, y, z) = A \sin \frac{\pi x}{L_1} \sin \frac{\pi y}{2L_1} \sin \frac{2\pi z}{3L_1}$

$\psi_{121}(x, y, z) = A \sin \frac{\pi x}{L_1} \sin \frac{\pi y}{L_1} \sin \frac{\pi z}{3L_1}$        $\psi_{122}(x, y, z) = A \sin \frac{\pi x}{L_1} \sin \frac{\pi y}{L_1} \sin \frac{2\pi z}{3L_1}$

$\psi_{113}(x, y, z) = A \sin \frac{\pi x}{L_1} \sin \frac{\pi y}{2L_1} \sin \frac{\pi z}{L_1}$

7-7.  $E_0 = \frac{\hbar^2 \pi^2}{2mL^2} = \frac{(1.055 \times 10^{-34} \text{ J}\cdot\text{s})^2 \pi^2}{2(9.11 \times 10^{-31} \text{ kg})(0.10 \times 10^{-9} \text{ m})^2 (1.609 \times 10^{-19} \text{ J/eV})} = 37.68 \text{ eV}$

$E_{311} - E_{111} = \Delta E = 11E_0 - 3E_0 = 8E_0 = 301 \text{ eV}$

$E_{222} - E_{111} = \Delta E = 12E_0 - 3E_0 = 9E_0 = 339 \text{ eV}$

$E_{321} - E_{111} = \Delta E = 14E_0 - 3E_0 = 11E_0 = 415 \text{ eV}$

7-8. (a) Adapting Equation 7-3 to two dimensions (i.e., setting  $k_3 = 0$ ), we have

$$\psi_{n_1 n_2} = A \sin \frac{n_1 \pi x}{L} \sin \frac{n_2 \pi y}{L}$$

(b) From Equation 7-5,  $E_{n_1 n_2} = \frac{\hbar^2 \pi^2}{2mL^2} (n_1^2 + n_2^2)$

(c) The lowest energy degenerate states have quantum numbers  $n_1 = 1, n_2 = 2$ , and  $n_1 = 2, n_2 = 1$ .

7-9. (a) For  $n = 3, \ell = 0, 1, 2$

(b) For  $\ell = 0, m = 0$ . For  $\ell = 1, m = -1, 0, +1$ . For  $\ell = 2, m = -2, -1, 0, +1, +2$ .

(c) There are nine different  $m$ -states, each with two spin states, for a total of 18 states for  $n = 3$ .

7-10. (a) For  $\ell = 4$

$$L = \sqrt{\ell(\ell+1)} \hbar = \sqrt{4(5)} \hbar = \sqrt{20} \hbar$$

$$m_\ell = 4\hbar$$

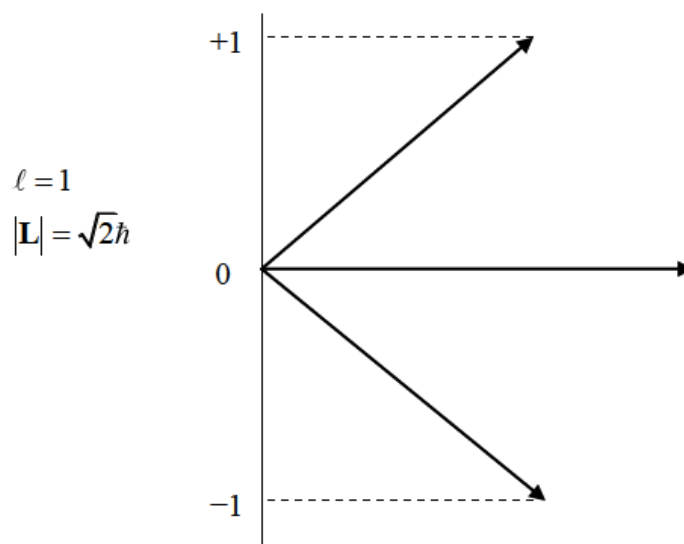
$$\theta_{\min} = \cos^{-1} \frac{4}{\sqrt{20}} \rightarrow \theta_{\min} = 26.6^\circ$$

(b) For  $\ell = 2$

$$L = \sqrt{6} \hbar \quad m_\ell = 2\hbar$$

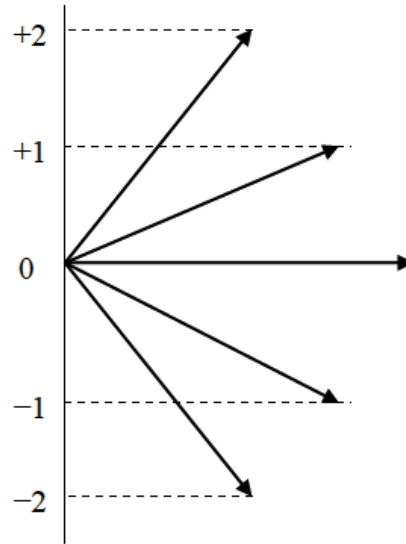
$$\theta_{\min} = \cos^{-1} \frac{2}{\sqrt{6}} \rightarrow \theta_{\min} = 35.3^\circ$$

7-12. (a)



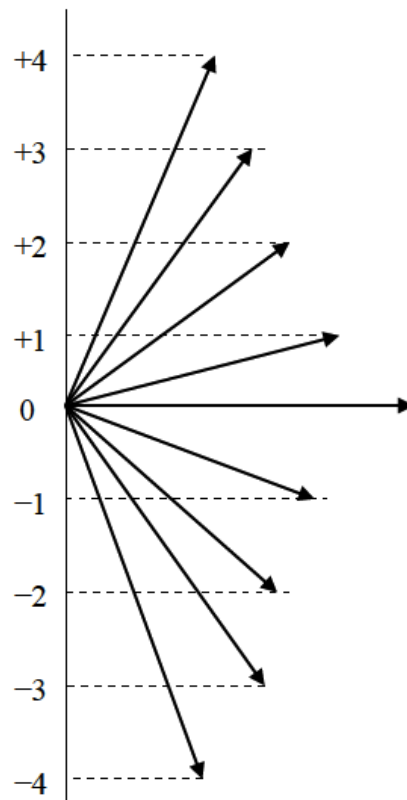
(b)

$$\ell = 2$$
$$|\mathbf{L}| = \sqrt{6}\hbar$$



(c)

$$\ell = 4$$
$$|\mathbf{L}| = \sqrt{20}\hbar$$



(d)  $|\mathbf{L}| = \sqrt{\ell(\ell+1)}\hbar$  (See diagrams above.)

7-13.  $L^2 = L_x^2 + L_y^2 + L_z^2 \rightarrow L_x^2 + L_y^2 = L^2 - L_z^2 = \ell(\ell+1)\hbar^2 - (m\hbar)^2 = (6 - m^2)\hbar^2$

$$(a) (L_x^2 + L_y^2)_{\min} = (6 - 2^2)\hbar^2 = 2\hbar^2$$

$$(b) (L_x^2 + L_y^2)_{\max} = (6 - 0^2)\hbar^2 = 6\hbar^2$$

$$(c) L_x^2 + L_y^2 = (6 - 1)\hbar^2 = 5\hbar^2 \quad L_x \text{ and } L_y \text{ cannot be determined separately.}$$

$$(d) n = 3$$

$$7-15. \quad \mathbf{L} = \mathbf{r} \times \mathbf{p} \quad \frac{d\mathbf{L}}{dt} = \frac{d\mathbf{r}}{dt} \times \mathbf{p} + \mathbf{r} \times \frac{d\mathbf{p}}{dt}$$

$$\frac{d\mathbf{r}}{dt} \times \mathbf{p} = \mathbf{v} \times m\mathbf{v} = m\mathbf{v} \times \mathbf{v} = 0 \quad \text{and} \quad \mathbf{r} \times \frac{d\mathbf{p}}{dt} = \mathbf{r} \times \mathbf{F}. \quad \text{Since for } V = V(r), \text{ i.e., central forces,}$$

$$\mathbf{F} \text{ is parallel to } \mathbf{r}, \text{ then } \mathbf{r} \times \mathbf{F} = 0 \quad \text{and} \quad \frac{d\mathbf{L}}{dt} = 0$$

$$7-16. (a) \text{ For } \ell = 3, n = 4, 5, 6, \dots \text{ and } m = -3, -2, -1, 0, 1, 2, 3$$

$$(b) \text{ For } \ell = 4, n = 5, 6, 7, \dots \text{ and } m = -4, -3, -2, -1, 0, 1, 2, 3, 4$$

$$(c) \text{ For } \ell = 0, n = 1 \text{ and } m = 0$$

$$(d) \text{ The energy depends only on } n. \text{ The minimum in each case is:}$$

$$E_4 = -13.6eV/n^2 = -13.6eV/4^2 = -0.85eV$$

$$E_5 = -13.6eV/5^2 = -0.54eV$$

$$E_1 = -13.6eV$$

$$7-17. (a) 6f \text{ state: } n = 6, \ell = 3$$

$$(b) E_6 = -13.6eV/n^2 = -13.6eV/6^2 = -0.38eV$$

$$(c) L = \sqrt{\ell(\ell+1)}\hbar = \sqrt{3(3+1)}\hbar = \sqrt{12}\hbar = 3.65 \times 10^{-34} \text{ J}\cdot\text{s}$$

$$(d) L_z = m\hbar \quad L_z = -3\hbar, -2\hbar, -1\hbar, 0, 1\hbar, 2\hbar, 3\hbar$$

7-21. (a) For the ground state,  $P(r)\Delta r = \psi^2(4\pi r^2)\Delta r = \frac{4r^2}{a_0^3}e^{-2r/a_0}\Delta r$

For  $\Delta r = 0.03a_0$ , at  $r = a_0$  we have  $P(r)\Delta r = \frac{4a_0^2}{a_0^3}e^{-2}(0.03a_0) = 0.0162$

(b) For  $\Delta r = 0.03a_0$ , at  $r = 2a_0$  we have  $P(r)\Delta r = \frac{4(2a_0)^2}{a_0^3}e^{-4}(0.03a_0) = 0.0088$

7-22.  $P(r) = Cr^2e^{-2Zr/a_0}$  For  $P(r)$  to be a maximum,

$$\frac{dP}{dr} = C \left[ r^2 \left( -\frac{2Z}{a_0} \right) e^{-2Zr/a_0} + 2r e^{-2Zr/a_0} \right] = 0 \rightarrow C \times \frac{2Zr}{a_0} \left( \frac{a_0}{Z} - r \right) e^{-2Zr/a_0} = 0$$

This condition is satisfied with  $r = 0$  or  $r = a_0/Z$ . For  $r = 0$ ,  $P(r) = 0$  so the maximum  $P(r)$  occurs for  $r = a_0/Z$ .

7-27. For the most likely value of  $r$ ,  $P(r)$  is a maximum, which requires that (see Problem 7-25)

$$\frac{dP}{dr} = A \cos^2 \theta \left[ r^4 \left( -\frac{Z}{a_0} \right) e^{-Zr/a_0} + 4r^3 e^{-Zr/a_0} \right] = 0$$

For hydrogen  $Z = 1$  and  $A \cos^2 \theta (r^3/a_0)(4a_0 - r)e^{-r/a_0} = 0$ . This is satisfied for  $r = 0$  and  $r = 4a_0$ . For  $r = 0$ ,  $P(r) = 0$  so the maximum  $P(r)$  occurs for  $r = 4a_0$ .

7-65.  $\psi_{100} = \frac{1}{\sqrt{\pi}} \left( \frac{Z}{a_0} \right)^{3/2} e^{-Zr/a_0}$  (Equations 7-30 and 7-31)

$$P(r) = 4\pi r^2 \psi_{100}^* \psi_{100} \quad (\text{Equation 7-32})$$

$$= 4\pi r^2 \frac{Z^3}{\pi a_0^3} e^{-Zr/a_0} = \frac{4Z^3}{a_0^3} r^2 e^{-2Zr/a_0}$$

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

$$= \frac{a_0}{4Z} \int_0^\infty \left( \frac{2Zr}{a_0} \right)^3 e^{-2Zr/a_0} d(2Zr/a_0) = \frac{a_0}{4Z} \times 3! = \frac{3a_0}{2Z}$$

7-68.  $\theta_{\min} = \cos^{-1} \left[ m_\ell \hbar / \sqrt{\ell(\ell+1)} \hbar \right]$  with  $m_\ell = \ell$ .

$\cos \theta_{\min} = \ell / \sqrt{\ell(\ell+1)}$ . Thus,  $\cos^2 \theta_{\min} = \ell^2 / [\ell(\ell+1)] = 1 - \sin^2 \theta_{\min}$

or,  $\sin^2 \theta_{\min} = 1 - \frac{\ell^2}{\ell(\ell+1)} = \frac{\ell(\ell+1) - \ell^2}{\ell(\ell+1)} = \frac{\ell^2 + \ell - \ell^2}{\ell(\ell+1)}$

And,  $\sin \theta_{\min} = \left( \frac{1}{\ell+1} \right)^{1/2}$  For large  $\ell$ ,  $\theta_{\min}$  is small.

Then  $\sin \theta_{\min} \approx \theta_{\min} = \left( \frac{1}{\ell+1} \right)^{1/2} \approx \frac{1}{(\ell)^{1/2}}$

7-70.  $P(r) = \frac{4Z^3}{a_0^3} r^2 e^{-2Zr/a_0}$  (See Problem 7-65)

For hydrogen,  $Z = 1$  and at the edge of the proton  $r = R_0 = 10^{-15} m$ . At that point, the exponential factor in  $P(r)$  has decreased to:

$$e^{-2R_0/a_0} = e^{-2(10^{-15})/(0.529 \times 10^{-10} m)} = e^{-(3.78 \times 10^{-5})} \approx 1 - 3.78 \times 10^{-5} \approx 1$$

Thus, the probability of the electron in the hydrogen ground state being inside the nucleus, to better than four figures, is:

$$\begin{aligned} P(r) &= \frac{4r^2}{a_0^3} & P &= \int_0^{R_0} P(r) dr = \int_0^{R_0} \frac{4r^2}{a_0^3} = \frac{4}{a_0^3} \int_0^{R_0} r^2 dr = \frac{4}{a_0^3} \left. \frac{r^3}{3} \right|_0^{R_0} \\ & & &= \frac{4}{a_0^3} \left( \frac{R_0^3}{3} \right) = \frac{4(10^{-15} m)^3}{3(0.529 \times 10^{-10} m)^3} = 9.0 \times 10^{-15} \end{aligned}$$

7-72. (a) Substituting  $\psi(r, \theta)$  into Equation 7-9 and carrying out the indicated operations yields (eventually)

$$-\frac{\hbar^2}{2\mu} \psi(r, \theta) \left[ 2/r^2 - 1/4a_0^2 \right] - \frac{\hbar^2}{2\mu} \psi(r, \theta) (-2/r^2) + V\psi(r, \theta) = E\psi(r, \theta)$$

Canceling  $\psi(r, \theta)$  and recalling that  $r^2 = 4a_0^2$  (because  $\psi$  given is for  $n = 2$ ) we

$$\text{have } -\frac{\hbar^2}{2\mu}(-1/4a_0^2) + v = E$$

The circumference of the  $n = 2$  orbit is:  $C = 2\pi(4a_0) = 2\lambda \rightarrow a_0 = \lambda/4\pi = 1/2k$ .

$$\text{Thus, } -\frac{\hbar^2}{2\mu}\left(-\frac{1}{4/4k^2}\right) + V = E \rightarrow \frac{\hbar^2 k^2}{2\mu} + V = E$$

(b) or  $\frac{p^2}{2m} + v = E$  and Equation 7-9 is satisfied.

$$\int_0^\infty \psi^2 dx = \int A^2 \left(\frac{r}{a_0}\right)^2 e^{-r/a_0} \cos^2 \theta r^2 \sin \theta dr d\theta d\phi = 1$$

$$A^2 \int_0^\infty \left(\frac{r}{a_0}\right)^2 e^{-r/a_0} r^2 dr \int_0^\pi \cos^2 \theta \sin \theta d\theta \int_0^{2\pi} d\phi = 1$$

Integrating (see Problem 7-23),

$$A^2 (6a_0^3)(2/3)(2\pi) = 1$$

$$A^2 = 1/8a_0^3\pi \rightarrow A = \sqrt{1/8a_0^3\pi}$$