1. $\psi(x) = Axe^{-bx}$ gives $d\psi/dx = Ae^{-bx} - bAxe^{-bx}$ and $d^2\psi/dx^2 = -2bAe^{-bx} + b^2Axe^{-bx}$. Then substituting into Equation 7.2 we have

$$-\frac{\hbar^2}{2m}(-2Abe^{-bx} + b^2Axe^{-bx}) - \frac{e^2}{4\pi\varepsilon_0 x}Axe^{-bx} = EAxe^{-bx}$$

Canceling common factors gives

$$\frac{\hbar^2 b}{m} - \frac{\hbar^2 b^2}{2m}x - \frac{e^2}{4\pi\varepsilon_0} = Ex \quad \text{or} \quad \left(\frac{\hbar^2 b}{m} - \frac{e^2}{4\pi\varepsilon_0}\right) + x\left(-\frac{\hbar^2 b^2}{2m} - E\right) = 0$$

For this expression to equal zero for all x, both terms in parentheses must be zero. Thus

$$\frac{\hbar^2 b}{m} = \frac{e^2}{4\pi\varepsilon_0} \quad \text{or} \quad b = \frac{me^2}{4\pi\varepsilon_0\hbar^2} = \frac{1}{a_0} \qquad \text{and} \qquad E = -\frac{\hbar^2 b^2}{2m} = -\frac{me^4}{32\pi^2\varepsilon_0^2\hbar^2}$$

2. The probability density is $P(x) = |\psi(x)|^2 = A^2x^2e^{-2bx}$. To find the maximum, we set the first derivative equal to zero:

$$\frac{dP}{dx} = 2A^2xe^{-2bx} - 2bA^2x^2e^{-2bx} = 0$$

This has solutions at $x = 0$, $x = \infty$, and $x = 1/b = a_0$. The first two give minima and the third gives the maximum.

3. The probability to find the electron in a small interval is $P(x)dx = A^2x^2e^{-2bx}dx$. Substituting the values of A and b, and evaluating the resulting expression for $x = a_0$ and $dx = 0.02a_0$ (appropriate to the interval from $x = 0.99a_0$ to $x = 1.01a_0$), we obtain

$$P(x)dx = \frac{4}{a_0^3}x^2e^{-2x/a_0}dx = \frac{4}{a_0^3}a_0^2e^{-2}(0.02a_0) = 0.0108$$

4. (a) $|\mathbf{L}| = \sqrt{l(l+1)}\hbar = \sqrt{(3)(4)}\hbar = \sqrt{12}\hbar$

(b) There are $2l + 1 = 7$ possible z components: $L_z = m_l\hbar = +3\hbar, +2\hbar, +\hbar, 0, -\hbar, -2\hbar, -3\hbar$.

(c) $\cos\theta = m_l/\sqrt{l(l+1)} = m_l/\sqrt{12}$

$$m_l = +3 \qquad \theta = \cos^{-1} 3/\sqrt{12} = 30°$$

$$m_l = +2 \qquad \theta = \cos^{-1} 2/\sqrt{12} = 55°$$

$$m_l = +1 \qquad \theta = \cos^{-1} 1/\sqrt{12} = 73°$$

$$m_l = 0 \qquad \theta = \cos^{-1} 0 = 90°$$

$$m_l = -1 \qquad \theta = \cos^{-1}(-1/\sqrt{12}) = 107°$$

$$m_l = -2 \qquad \theta = \cos^{-1}(-2/\sqrt{12}) = 125°$$

$$m_l = -3 \qquad \theta = \cos^{-1}(-3/\sqrt{12}) = 150°$$

7. (a) $l_{max} = n - 1 = 5$ so $l = 0, 1, 2, 3, 4, 5$ for $n = 6$.

(b) $m_l = +6, +5, +4, +3, +2, +1, 0, -1, -2, -3, -4, -5, -6$

(c) $n \geq l + 1 = 5$ for $l = 4$, so the smallest possible n is 5.

(d) For $m_l = 4$, $l \geq 4$ so the smallest possible l is 4.

10. With $\psi_{1,0,0}(r,\theta,\phi)=\frac{1}{\sqrt{\pi a_0^3}}e^{-r/a_0}$, $\frac{\partial\psi}{\partial r}=\frac{1}{\sqrt{\pi a_0^3}}\left(-\frac{1}{a_0}\right)e^{-r/a_0}$ and $\frac{\partial^2\psi}{\partial r^2}=\frac{1}{\sqrt{\pi a_0^3}}\left(\frac{1}{a_0^2}\right)e^{-r/a_0}$.

Substituting into Equation 7.10, we have

$$\frac{1}{\sqrt{\pi a_0^3}}\left[-\frac{\hbar^2}{2m}\left(\frac{1}{a_0^2}e^{-r/a_0}-\frac{2}{a_0 r}e^{-r/a_0}\right)-\frac{e^2}{4\pi\varepsilon_0 r}e^{-r/a_0}\right]$$

$$=\frac{1}{\sqrt{\pi a_0^3}}e^{-r/a_0}\frac{e^2}{4\pi\varepsilon_0}\left(-\frac{1}{2a_0}+\frac{1}{r}-\frac{1}{r}\right)=-\frac{1}{2a_0}\frac{e^2}{4\pi\varepsilon_0}\psi_{1,0,0}(r,\theta,\phi)=E\psi_{1,0,0}(r,\theta,\phi)$$

with $E=-\frac{1}{2a_0}\frac{e^2}{4\pi\varepsilon_0}=-\frac{1}{2}\frac{e^2}{4\pi\varepsilon_0}\frac{me^2}{4\pi\varepsilon_0\hbar^2}=-\frac{me^4}{32\pi^2\varepsilon_0^2\hbar^2}$ which is E_1 from Equation 7.13.

12. For $n = 1$, $l = 0$ we have $P(r) = r^2 \left|R_{1,0}(r)\right|^2 = 4r^2 e^{-2r/a_0} / a_0^3$. To find the maximum, we set dP/dr to zero:

$$\frac{dP}{dr} = \frac{4}{a_0^3}\left[2re^{-2r/a_0} - r^2\left(\frac{2}{a_0}\right)e^{-2r/a_0}\right] = \frac{8r}{a_0^3}e^{-2r/a_0}\left(1 - \frac{r}{a_0}\right) = 0$$

There are three solutions to this equation: $r = 0$, $r = \infty$, $r = a_0$. The first two solutions correspond to minima of $P(r)$; only the solution at $r = a_0$ gives a maximum.

15. $$P(r)dr = r^2 \left|R_{1,0}(r)\right|^2 dr = (1.00a_0)^2 \frac{4}{a_0^3} e^{-2}(0.01a_0) = 0.0054$$

17. The angular probability density is $P(\theta,\phi)=\frac{15}{8\pi}\sin^2\theta\cos^2\theta$. To find the locations of the maxima and minima, we set the derivative equal to zero:

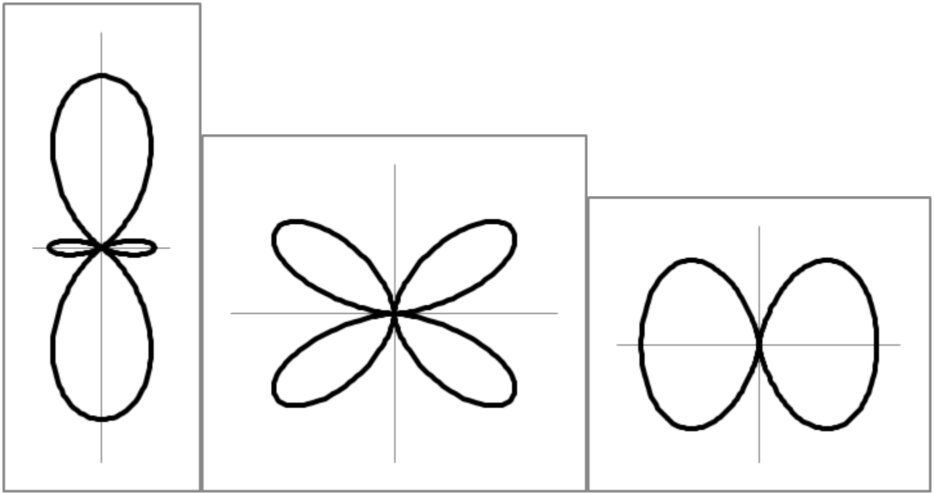
$$\frac{dP}{d\theta}=\frac{15}{8\pi}(2\sin\theta\cos^3\theta-2\sin^3\theta\cos\theta)=\frac{15}{4\pi}(\sin\theta)(\cos\theta)(\cos^2\theta-\sin^2\theta)=0$$

The three angular terms in parentheses give three sets of solutions: $\theta = 0,\pi$; $\theta = \pi/2$; and $\theta = \pi/4, 3\pi/4$. By checking the second derivative, we find that the first two sets give minima (the second derivative is positive) and the third gives maxima (negative second derivative). The angular probability density thus starts at zero along the positive z direction, rises to a maximum at $\theta = 45°$, falls again to zero in the xy plane ($\theta = 90°$), rises again to a maximum at $\theta = 135°$, and finally falls again to zero on the negative z axis.

19. (a) $P(\theta,\phi)=\frac{5}{16\pi}(3\cos^2\theta-1)^2$

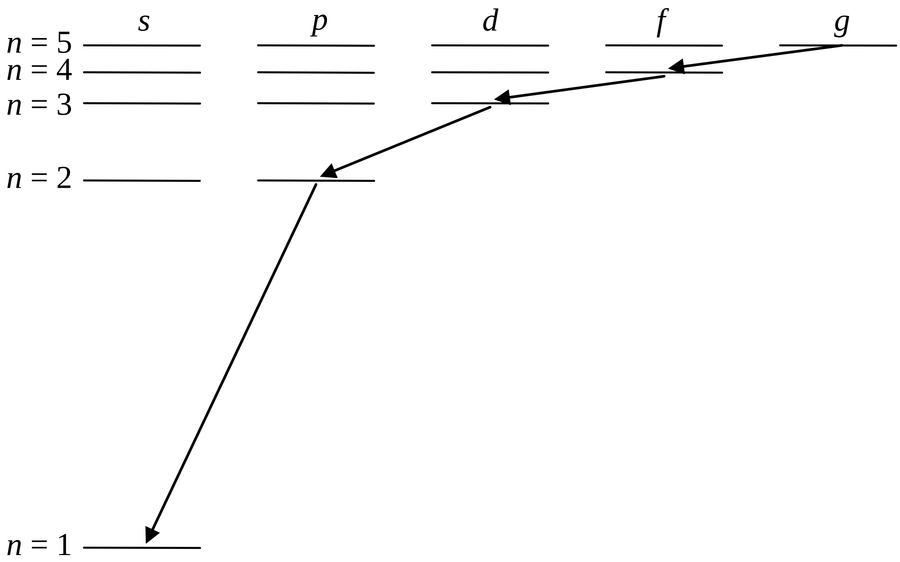
(b) $P(\theta,\phi)=\frac{15}{8\pi}\sin^2\theta\cos^2\theta$

(c) $P(\theta,\phi)=\frac{15}{32\pi}\sin^4\theta$

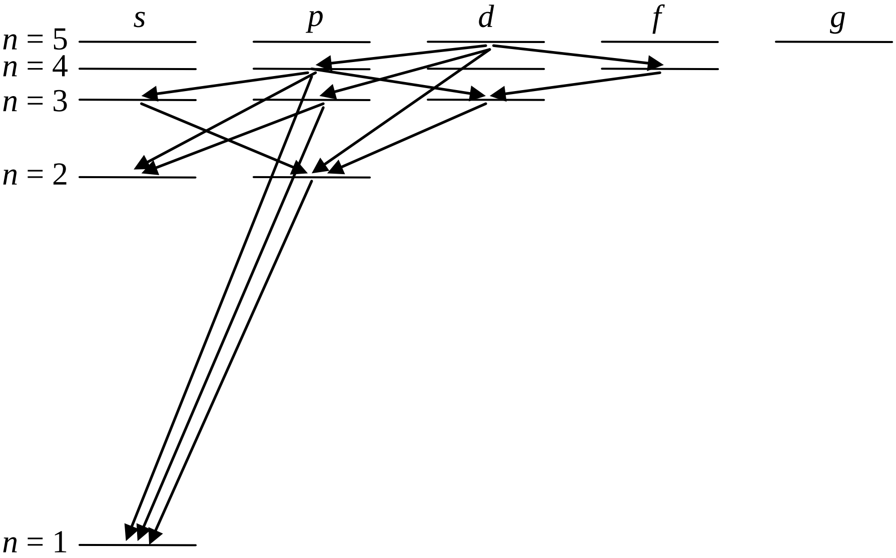


(a) (b) (c)

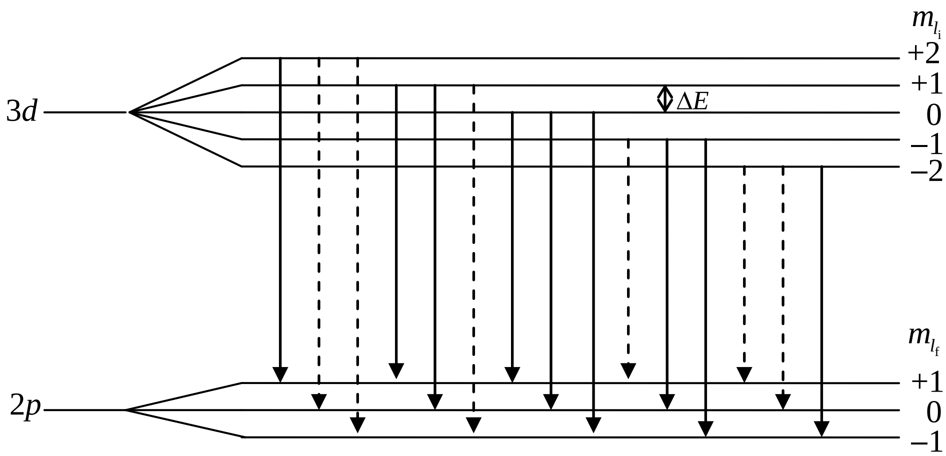
24. (a) The transitions that change l by one unit are



(b) Starting instead with $5d$, the permitted transitions are


s
p
d
f
g
n = 5
n = 4
n = 3
n = 2
n = 1

26. (a)



(b) Transitions shown with dashed lines violate the $\Delta m_l = \pm 1$ selection rule.

(c) The energy of the initial state is $E_i = E_{3d} + m_{l_i}\Delta E$ and the energy of the final state is $E_f = E_{2p} + m_{l_f}\Delta E$ (where ΔE is the spacing between adjacent states). The transition energies can be found from the energy difference:

$$E_i - E_f = (E_{3d} - E_{2p}) + (m_{l_i} - m_{l_f})\Delta E = (E_{3d} - E_{2p}) + \Delta m_l \Delta E$$

There are only three permitted values of Δm_l (0, ±1), so there are only three possible values of the energy difference: $E_{3d} - E_{2p}, E_{3d} - E_{2p} + \Delta E, E_{3d} - E_{2p} + \Delta E$.

27. (a) In the absence of a magnetic field, the 3*d* to 2*p* energy difference is

$$E = (-13.6057\text{ eV})\left(\frac{1}{3^2} - \frac{1}{2^2}\right) = 1.88968\text{ eV}$$

and the wavelength is

$$\lambda = \frac{hc}{E} = \frac{1239.842\text{ eV}\cdot\text{nm}}{1.88968\text{ eV}} = 656.112\text{ nm}$$

The magnetic field gives a change in wavelength of

$$\Delta\lambda = \frac{\lambda^2}{hc}\Delta E = \frac{(656.112\text{ nm})^2}{1239.842\text{ eV}\cdot\text{nm}}(5.79\times10^{-5}\text{ eV/T})(3.50\text{ T}) = 0.0703\text{ nm}$$

The wavelengths of the three normal Zeeman components are then 656.112 nm, 656.112 nm + 0.070 nm = 656.182 nm, and 656.112 nm – 0.070 nm = 656.042 nm.

Chapter 7

1. $\psi(x) = Axe^{-bx}$ gives $d\psi/dx = Ae^{-bx} - bAxe^{-bx}$ and $d^2\psi/dx^2 = -2bAe^{-bx} + b^2Axe^{-bx}$. Then substituting into Equation 7.2 we have

$$-\frac{\hbar^2}{2m}(-2Abe^{-bx} + b^2Axe^{-bx}) - \frac{e^2}{4\pi\varepsilon_0 x}Axe^{-bx} = EAxe^{-bx}$$

Canceling common factors gives

$$\frac{\hbar^2 b}{m} - \frac{\hbar^2 b^2}{2m}x - \frac{e^2}{4\pi\varepsilon_0} = Ex \quad \text{or} \quad \left(\frac{\hbar^2 b}{m} - \frac{e^2}{4\pi\varepsilon_0}\right) + x\left(-\frac{\hbar^2 b^2}{2m} - E\right) = 0$$

For this expression to equal zero for all x, both terms in parentheses must be zero. Thus

$$\frac{\hbar^2 b}{m} = \frac{e^2}{4\pi\varepsilon_0} \quad \text{or} \quad b = \frac{me^2}{4\pi\varepsilon_0\hbar^2} = \frac{1}{a_0} \qquad \text{and} \qquad E = -\frac{\hbar^2 b^2}{2m} = -\frac{me^4}{32\pi^2\varepsilon_0^2\hbar^2}$$

2. The probability density is $P(x) = |\psi(x)|^2 = A^2x^2e^{-2bx}$. To find the maximum, we set the first derivative equal to zero:

$$\frac{dP}{dx} = 2A^2xe^{-2bx} - 2bA^2x^2e^{-2bx} = 0$$

This has solutions at $x = 0$, $x = \infty$, and $x = 1/b = a_0$. The first two give minima and the third gives the maximum.

3. The probability to find the electron in a small interval is $P(x)dx = A^2x^2e^{-2bx}dx$. Substituting the values of A and b, and evaluating the resulting expression for $x = a_0$ and $dx = 0.02a_0$ (appropriate to the interval from $x = 0.99a_0$ to $x = 1.01a_0$), we obtain

$$P(x)dx = \frac{4}{a_0^3}x^2e^{-2x/a_0}dx = \frac{4}{a_0^3}a_0^2e^{-2}(0.02a_0) = 0.0108$$

4. (a) $|\mathbf{L}| = \sqrt{l(l+1)}\hbar = \sqrt{(3)(4)}\hbar = \sqrt{12}\hbar$

(b) There are $2l + 1 = 7$ possible z components: $L_z = m_l\hbar = +3\hbar, +2\hbar, +\hbar, 0, -\hbar, -2\hbar, -3\hbar$.

(c) $\cos\theta = m_l/\sqrt{l(l+1)} = m_l/\sqrt{12}$

$m_l = +3 \qquad \theta = \cos^{-1} 3/\sqrt{12} = 30°$

$m_l = +2 \qquad \theta = \cos^{-1} 2/\sqrt{12} = 55°$

$m_l = +1 \qquad \theta = \cos^{-1} 1/\sqrt{12} = 73°$

$m_l = 0 \qquad \theta = \cos^{-1} 0 = 90°$

$m_l = -1 \qquad \theta = \cos^{-1}(-1/\sqrt{12}) = 107°$

$m_l = -2 \qquad \theta = \cos^{-1}(-2/\sqrt{12}) = 125°$

$m_l = -3 \qquad \theta = \cos^{-1}(-3/\sqrt{12}) = 150°$

5. For $l = 2$, $m_l = +2, +1, 0, -1, -2$. With $\cos\theta = m_l/\sqrt{l(l+1)} = m_l/\sqrt{6}$, we have

$m_l = +2 \qquad \theta = \cos^{-1} 2/\sqrt{6} = 35°$

$m_l = +1 \qquad \theta = \cos^{-1} 1/\sqrt{6} = 66°$

$m_l = 0 \qquad \theta = \cos^{-1} 0 = 90°$

$m_l = -1 \qquad \theta = \cos^{-1}(-1/\sqrt{6}) = 114°$

$m_l = -2 \qquad \theta = \cos^{-1}(-2/\sqrt{6}) = 145°$

6. $l = 0$: (4, 0, 0)

   $l = 1$: (4, 1, +1), (4, 1, 0), (4, 1, –1)

   $l = 2$: (4, 2, +2), (4, 2, +1), (4, 2, 0), (4, 2, –1), (4, 2, –2)

   $l = 3$: (4, 3, +3), (4, 3, +2), (4, 3, +1), (4, 3, 0), (4, 3, –1), (4, 3, –2), (4, 3, –3)

7. (a) $l_{\max} = n - 1 = 5$ so $l = 0, 1, 2, 3, 4, 5$ for $n = 6$.

   (b) $m_l = +6, +5, +4, +3, +2, +1, 0, -1, -2, -3, -4, -5, -6$

   (c) $n \geq l + 1 = 5$ for $l = 4$, so the smallest possible n is 5.

   (d) For $m_l = 4$, $l \geq 4$ so the smallest possible l is 4.

8. The normalization integral for the (1, 0, 0) wave function is

$$\int_0^\infty r^2 dr \int_0^\pi \sin\theta \, d\theta \int_0^{2\pi} d\phi \left|\psi_{1,0,0}(r,\theta,\phi)\right|^2 = \int_0^\infty 4a_0^{-3} e^{-2r/a_0} r^2 dr \int_0^\pi \tfrac{1}{2}\sin\theta \, d\theta \int_0^{2\pi} \tfrac{1}{2\pi} d\phi$$

$$= 4a_0^{-3} \int_0^\infty e^{-2r/a_0} r^2 dr = \frac{4}{a_0^3} \frac{2!}{(2/a_0)^3} = 1$$

The last integral is evaluated using the standard form $\int_0^\infty x^n e^{-ax}dx = n!/a^{n+1}$.

The normalization integral for the (2, 0, 0) wave function is

$$\int_0^\infty r^2 dr \int_0^\pi \sin\theta\, d\theta \int_0^{2\pi} d\phi \left|\psi_{2,0,0}(r,\theta,\phi)\right|^2 = \int_0^\infty \tfrac{1}{8} a_0^{-3}(2-r/a_0)^2 e^{-r/a_0} r^2 dr \int_0^\pi \tfrac{1}{2}\sin\theta\, d\theta \int_0^{2\pi} \tfrac{1}{2\pi}\, d\phi$$

$$= \tfrac{1}{8} a_0^{-3} \int_0^\infty e^{-r/a_0}\left(4r^2 - 4\frac{r^3}{a_0} + \frac{r^4}{a_0^2}\right)dr = \tfrac{1}{8} a_0^{-3}\left[4\frac{2!}{(1/a_0)^3} - \frac{4}{a_0}\frac{3!}{(1/a_0)^4} + \frac{1}{a_0^2}\frac{4!}{(1/a_0)^5}\right] = \tfrac{1}{8}(8-24+24) = 1$$

9. With $\psi_{2,0,0}(r,\theta,\phi) = \dfrac{1}{\sqrt{4\pi}}\dfrac{1}{\sqrt{8a_0^3}}\left(2-\dfrac{r}{a_0}\right)e^{-r/2a_0}$, we then have $\dfrac{\partial\psi}{\partial\theta} = 0$ and $\dfrac{\partial\psi}{\partial\phi} = 0$.

$$\frac{\partial\psi}{\partial r} = \frac{1}{\sqrt{32\pi a_0^3}}\left[-\frac{1}{a_0}e^{-r/2a_0} - \frac{1}{2a_0}\left(2-\frac{r}{a_0}\right)e^{-r/2a_0}\right] = \frac{1}{\sqrt{32\pi a_0^3}}\left(-\frac{2}{a_0} + \frac{r}{2a_0^2}\right)e^{-r/2a_0}$$

$$\frac{\partial^2\psi}{\partial r^2} = \frac{1}{\sqrt{32\pi a_0^3}}\left[\frac{1}{2a_0^2}e^{-r/2a_0} + \frac{1}{2a_0^2}e^{-r/2a_0} + \frac{1}{4a_0^2}\left(2-\frac{r}{a_0}\right)e^{-r/2a_0}\right] = \frac{1}{\sqrt{32\pi a_0^3}}\left(\frac{3}{2a_0^2} - \frac{r}{4a_0^3}\right)e^{-r/2a_0}$$

Substituting into the left side of Equation 7.10, we have

$$-\frac{\hbar^2}{2m}\left[\frac{1}{\sqrt{32\pi a_0^3}}\left(\frac{3}{2a_0^2} - \frac{r}{4a_0^3}\right)e^{-r/2a_0} + \frac{2}{r}\frac{1}{\sqrt{32\pi a_0^3}}\left(-\frac{2}{a_0} + \frac{r}{2a_0^2}\right)e^{-r/2a_0}\right] - \frac{e^2}{4\pi\varepsilon_0 r}\frac{1}{\sqrt{32\pi a_0^3}}\left(2-\frac{r}{a_0}\right)e^{-r/2a_0}$$

$$= \frac{1}{\sqrt{32\pi a_0^3}}e^{-r/2a_0}\left[-\frac{\hbar^2}{2m}\left(\frac{3}{2a_0^2} - \frac{r}{4a_0^3} - \frac{4}{ra_0} + \frac{1}{a_0^2}\right) - \frac{e^2}{2\pi\varepsilon_0 r} + \frac{e^2}{4\pi\varepsilon_0 a_0}\right]$$

$$= \frac{1}{\sqrt{32\pi a_0^3}}e^{-r/2a_0}\,\frac{e^2}{4\pi\varepsilon_0}\left(-\frac{5}{4a_0} + \frac{r}{8a_0^2} + \frac{2}{r} - \frac{2}{r} + \frac{1}{a_0}\right)$$

$$= \frac{1}{\sqrt{32\pi a_0^3}}e^{-r/2a_0}\,\frac{e^2}{4\pi\varepsilon_0}\left(-\frac{1}{4a_0} + \frac{r}{8a_0^2}\right) = \frac{e^2}{4\pi\varepsilon_0}\left(-\frac{1}{8a_0}\right)\psi_{2,0,0}(r,\theta,\phi) = E\psi_{2,0,0}(r,\theta,\phi)$$

with $E = \dfrac{e^2}{4\pi\varepsilon_0}\left(-\dfrac{1}{8a_0}\right) = \dfrac{e^2}{4\pi\varepsilon_0}\left(-\dfrac{me^2}{32\pi\varepsilon_0\hbar^2}\right) = \dfrac{1}{4}\left(-\dfrac{me^4}{32\pi^2\varepsilon_0^2\hbar^2}\right)$, which is the energy E_2 as defined in Equation 7.13.

Starting with $\psi_{2,1,0}(r,\theta,\phi) = \dfrac{1}{\sqrt{32\pi a_0^5}}re^{-r/2a_0}\cos\theta$,

$$\frac{\partial\psi}{\partial r}=\frac{1}{\sqrt{32\pi a_0^5}}\left(e^{-r/2a_0}-\frac{r}{2a_0}e^{-r/2a_0}\right)\cos\theta$$

$$\frac{\partial^2\psi}{\partial r^2}=\frac{1}{\sqrt{32\pi a_0^5}}\left(-\frac{1}{2a_0}e^{-r/2a_0}-\frac{1}{2a_0}e^{-r/2a_0}+\frac{r}{4a_0^2}e^{-r/2a_0}\right)\cos\theta$$

$$\frac{\partial\psi}{\partial\theta}=\frac{1}{\sqrt{32\pi a_0^5}}re^{-r/2a_0}(-\sin\theta)$$

$$\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right)=-\frac{1}{\sqrt{32\pi a_0^5}}re^{-r/2a_0}(2\sin\theta\cos\theta)$$

Equation 7.10 then gives

$$\frac{\cos\theta}{\sqrt{32\pi a_0^5}}e^{-r/2a_0}\left(-\frac{\hbar^2}{2m}\left[-\frac{1}{a_0}+\frac{r}{4a_0^2}+\frac{2}{r}\left(1-\frac{r}{2a_0}\right)-\frac{2}{r}\right]-\frac{e^2}{4\pi\varepsilon_0}\right)$$

$$=\frac{e^2}{4\pi\varepsilon_0}\psi_{2,1,0}(r,\theta,\phi)\left(\frac{1}{2r}-\frac{1}{8a_0}+\frac{1}{2r}-\frac{1}{r}\right)=\frac{e^2}{4\pi\varepsilon_0}\left(-\frac{1}{8a_0}\right)\psi_{2,1,0}(r,\theta,\phi)=E_2\psi_{2,1,0}(r,\theta,\phi)$$

10. With $\psi_{1,0,0}(r,\theta,\phi)=\frac{1}{\sqrt{\pi a_0^3}}e^{-r/a_0}$, $\frac{\partial\psi}{\partial r}=\frac{1}{\sqrt{\pi a_0^3}}\left(-\frac{1}{a_0}\right)e^{-r/a_0}$ and $\frac{\partial^2\psi}{\partial r^2}=\frac{1}{\sqrt{\pi a_0^3}}\left(\frac{1}{a_0^2}\right)e^{-r/a_0}$. Substituting into Equation 7.10, we have

$$\frac{1}{\sqrt{\pi a_0^3}}\left[-\frac{\hbar^2}{2m}\left(\frac{1}{a_0^2}e^{-r/a_0}-\frac{2}{a_0 r}e^{-r/a_0}\right)-\frac{e^2}{4\pi\varepsilon_0 r}e^{-r/a_0}\right]$$

$$=\frac{1}{\sqrt{\pi a_0^3}}e^{-r/a_0}\frac{e^2}{4\pi\varepsilon_0}\left(-\frac{1}{2a_0}+\frac{1}{r}-\frac{1}{r}\right)=-\frac{1}{2a_0}\frac{e^2}{4\pi\varepsilon_0}\psi_{1,0,0}(r,\theta,\phi)=E\psi_{1,0,0}(r,\theta,\phi)$$

with $E=-\frac{1}{2a_0}\frac{e^2}{4\pi\varepsilon_0}=-\frac{1}{2}\frac{e^2}{4\pi\varepsilon_0}\frac{me^2}{4\pi\varepsilon_0\hbar^2}=-\frac{me^4}{32\pi^2\varepsilon_0^2\hbar^2}$ which is E_1 from Equation 7.13.

11. (a) For $n = 2$, $l = 1$, $m_l = 0$, the probability to find the electron in a volume element dV is given by Equation 7.16:

$$\left|\psi_{2,1,0}(r,\theta,\phi)\right|^2 dV=\frac{1}{24a_0^3}\frac{r^2}{a_0^2}e^{-r/a_0}\left(\frac{3}{4\pi}\cos^2\theta\right)r^2\sin\theta\,dr\,d\theta\,d\phi$$

and for $m_l = \pm 1$,

$$\left|\psi_{2,1,\pm1}(r,\theta,\phi\right|^2 dV = \frac{1}{24a_0^3}\frac{r^2}{a_0^2}e^{-r/a_0}\left(\frac{3}{8\pi}\sin^2\theta\right)r^2\sin\theta\, dr\, d\theta\, d\phi$$

For $\theta = 0$, both probabilities are zero due to the sin θ terms.
(b) For $\theta = 90°$, the 2,1,0 probability is zero due to the cos θ term. With $dr = 0.02a_0$, $d\theta = 0.11° = 0.00192$ rad, and $d\phi = 0.25° = 0.00436$ rad, the 2,1,±1 probability is

$$\left|\psi_{2,1,\pm1}(r,\theta,\phi\right|^2 dV = \frac{(0.50a_0)^2}{24a_0^5}e^{-0.5a_0/a_0}\left(\frac{3}{8\pi}\sin^2 90°\right)(0.50a_0)^2(\sin 90°)$$
$$\times(0.02a_0)(0.00192\,\text{rad})(0.00436\,\text{rad}) = 3.2\times10^{-11}$$

(c) Because the probability density associated with any particular state in hydrogen is always independent of ϕ, the 2,1,0 probability is again zero and the 2,1,±1 probability is again 3.2×10^{-11}. (*d*) The only change in the 2,1,±1 probability is to replace sin 90° with sin 45° in three locations, so the new probability is $(3.2\times10^{-11})(\frac{1}{2}\sqrt{2})^3 = 1.1\times10^{-11}$. For the 2,1,0 probability, the angular factors are the same because cos 45° = sin 45°. The only change comes about because of the change from $3/8\pi$ to $3/4\pi$ in the $\Theta(\theta)$ term, so the 2,1,0 probability is 2.2×10^{-11}.

12. For $n = 1$, $l = 0$ we have $P(r) = r^2\left|R_{1,0}(r)\right|^2 = 4r^2e^{-2r/a_0}/a_0^3$. To find the maximum, we set *dP/dr* to zero:

$$\frac{dP}{dr} = \frac{4}{a_0^3}\left[2re^{-2r/a_0} - r^2\left(\frac{2}{a_0}\right)e^{-2r/a_0}\right] = \frac{8r}{a_0^3}e^{-2r/a_0}\left(1-\frac{r}{a_0}\right) = 0$$

There are three solutions to this equation: $r = 0$, $r = \infty$, $r = a_0$. The first two solutions correspond to minima of $P(r)$; only the solution at $r = a_0$ gives a maximum.

13. For $n = 2$, $l = 0$, $P(r) = r^2\left|R_{2,0}(r)\right|^2 = r^2\frac{1}{8a_0^3}\left(2-\frac{r}{a_0}\right)^2 e^{-r/a_0} = \frac{1}{8a_0^3}\left(4r^2 - \frac{4r^3}{a_0}+\frac{r^4}{a_0^2}\right)e^{-r/a_0}$

Setting *dP/dr* to zero, we have

$$\frac{1}{8a_0^3}re^{-r/a_0}\left(8-\frac{16r}{a_0}+\frac{8r^2}{a_0^2}-\frac{r^3}{a_0^3}\right) = \frac{1}{8a_0^3}re^{-r/a_0}\left(2-\frac{r}{a_0}\right)\left(4-\frac{6r}{a_0}+\frac{r^2}{a_0^2}\right) = 0$$

The five solutions are: $r = 0, r = \infty, r = 2a_0, r = (3\pm\sqrt{5})a_0$. The first three solutions give minima and the last two give maxima.

14. For $n = 2$, $l = 1$, we have $P(r) = r^2 \left|R_{2,1}(r)\right|^2 = r^2 \dfrac{1}{24a_0^3}\dfrac{r^2}{a_0^2}e^{-r/a_0}$. The total probability between $r = a_0$ and $r = 2a_0$ is

$$P(a_0 : 2a_0) = \int_{a_0}^{2a_0} P(r)\,dr = \frac{1}{24a_0^5}\int_{a_0}^{2a_0} r^4 e^{-r/a_0} dr$$

We can use Equation 7.4 to evaluate this integral. The result is

$$P(a_0 : 2a_0) = \frac{1}{24a_0^5}\left[-a_0 e^{-r/a_0}(r^4 + 4a_0r^3 + 12a_0^2r^2 + 24a_0^3r + 24)\right]_{a_0}^{2a_0} = 0.0490$$

15. $P(r)dr = r^2\left|R_{1,0}(r)\right|^2 dr = (1.00a_0)^2 \dfrac{4}{a_0^3}e^{-2}(0.01a_0) = 0.0054$

16. The kinetic energy is zero where $E = U$. With the potential energy from Eq. 6.24, we have

$$E_n = -\frac{me^4}{32\pi^2\varepsilon_0^2\hbar^2}\frac{1}{n^2} = -\frac{e^2}{4\pi\varepsilon_0 r}$$

$$r = \frac{8\pi\varepsilon_0\hbar^2}{me^2}n^2 = 2a_0n^2$$

So the turning points are $2a_0$ for $n = 1$, $8a_0$ for $n = 2$, and $18a_0$ for $n = 3$. The probability densities in Figure 7.10 do change from oscillatory to decreasing exponential at those radial coordinates.

17. The angular probability density is $P(\theta,\phi) = \frac{15}{8\pi}\sin^2\theta\cos^2\theta$. To find the locations of the maxima and minima, we set the derivative equal to zero:

$$\frac{dP}{d\theta} = \frac{15}{8\pi}(2\sin\theta\cos^3\theta - 2\sin^3\theta\cos\theta) = \frac{15}{4\pi}(\sin\theta)(\cos\theta)(\cos^2\theta - \sin^2\theta) = 0$$

The three angular terms in parentheses give three sets of solutions: $\theta = 0, \pi$; $\theta = \pi/2$; and $\theta = \pi/4, 3\pi/4$. By checking the second derivative, we find that the first two sets give minima (the second derivative is positive) and the third gives maxima (negative second derivative). The angular probability density thus starts at zero along the positive z direction, rises to a maximum at $\theta = 45°$, falls again to zero in the xy plane ($\theta = 90°$), rises again to a maximum at $\theta = 135°$, and finally falls again to zero on the negative z axis.

18. The angular probability density is $P(\theta,\phi) = \frac{5}{16\pi}(3\cos^2\theta - 1)^2$. To find the locations of the maxima and minima, we set the derivative equal to zero:

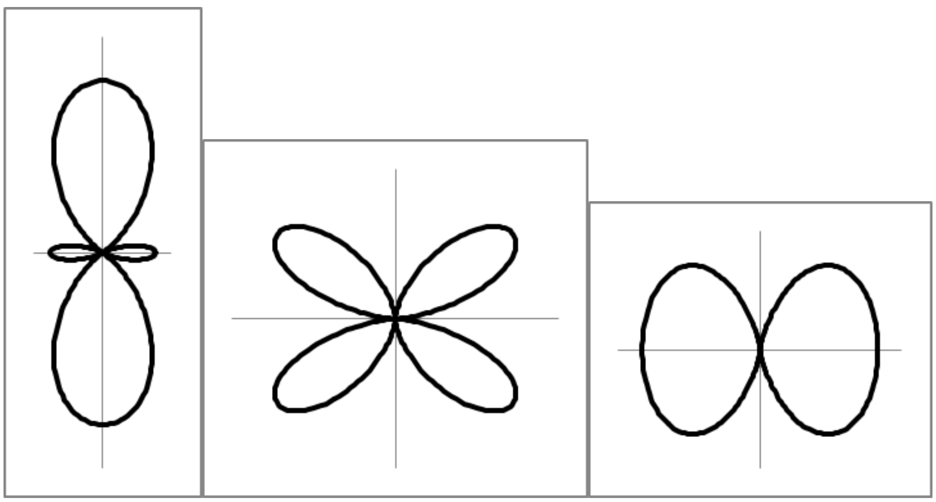
$$\frac{dP}{d\theta} = \frac{5}{8\pi}(3\cos^2\theta - 1)(-6\sin\theta\cos\theta) = -\frac{15}{4\pi}(\sin\theta)(\cos\theta)(3\cos^2\theta - 1)$$

The three angular terms in parentheses give three sets of solutions: $\theta = 0, \pi$; $\theta = \pi/2$; and $\theta = \cos^{-1}(\pm 1/\sqrt{3}) = 0.955, 2.186$. The first two give maxima and the third gives minima. The angular probability density is a maximum on the positive z axis, falls to zero at θ = 55°, rises again to a maximum in the xy plane (θ = 90°), falls to zero at θ = 125°, and rises to a maximum on the negative z axis.

19. (a) $P(\theta,\phi) = \frac{5}{16\pi}(3\cos^2\theta - 1)^2$

(b) $P(\theta,\phi) = \frac{15}{8\pi}\sin^2\theta\cos^2\theta$

(c) $P(\theta,\phi) = \frac{15}{32\pi}\sin^4\theta$



(a) (b) (c)

20. (a) degeneracy = $2n^2 = 2(5)^2 = 50$

(b) For each value of l, the degeneracy is $2(2l+1)$.

$l = 0$:	2(0+1) = 2
$l = 1$:	2(2+1) = 6
$l = 2$:	2(4+1) = 10
$l = 3$:	2(6+1) = 14
$l = 4$:	2(8+1) = 18
total:	50

21. $$\sum_{l=0}^{n-1} 2(2l+1) = 4\sum_{l=0}^{n-1} l + 2\sum_{l=0}^{n-1} 1 = 4\frac{n(n-1)}{2} + 2n = 2n^2$$

22. (a) l exceeds the maximum permitted value (n – 1).

(b) m_l exceeds the maximum permitted value (l)

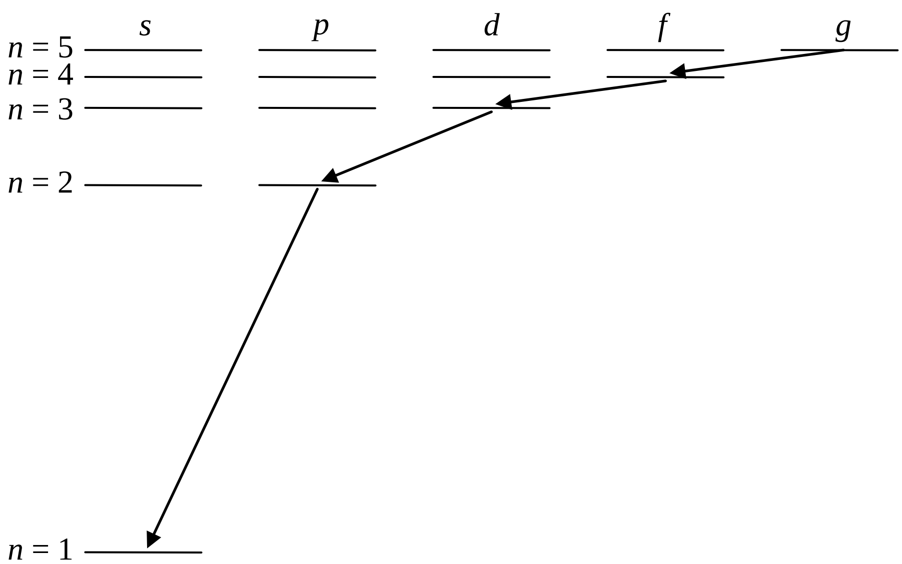
(c) m_s can be only +1/2 or -1/2

(d) negative values of l are not permitted

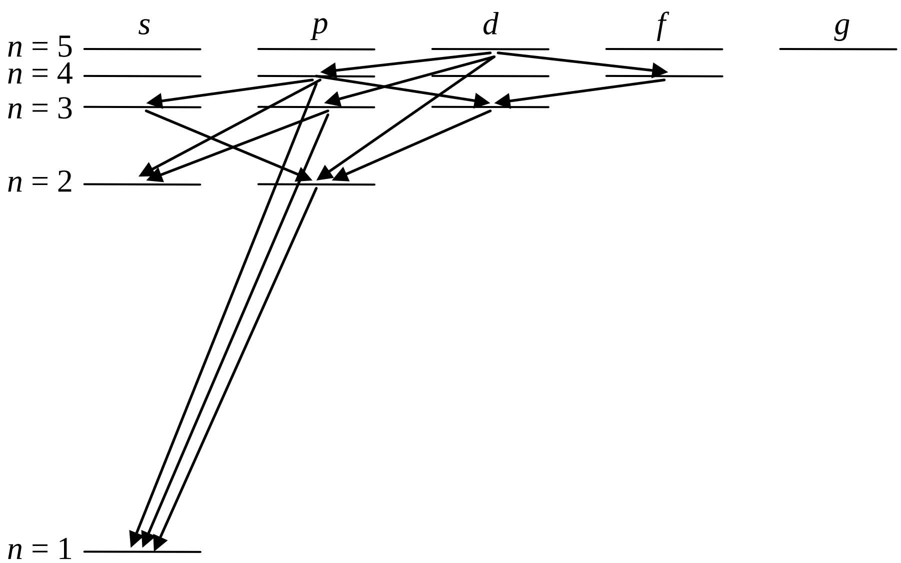
23. The selection rule is $\Delta l = \pm 1$, so the 4p state can make transitions to any lower s state ($\Delta l = -1$) or d state ($\Delta l = +1$). The possible transitions are then:

$$4p \to 3s,\ 4p \to 2s,\ 4p \to 1s, \text{ and } 4p \to 3d$$

24. (a) The transitions that change l by one unit are

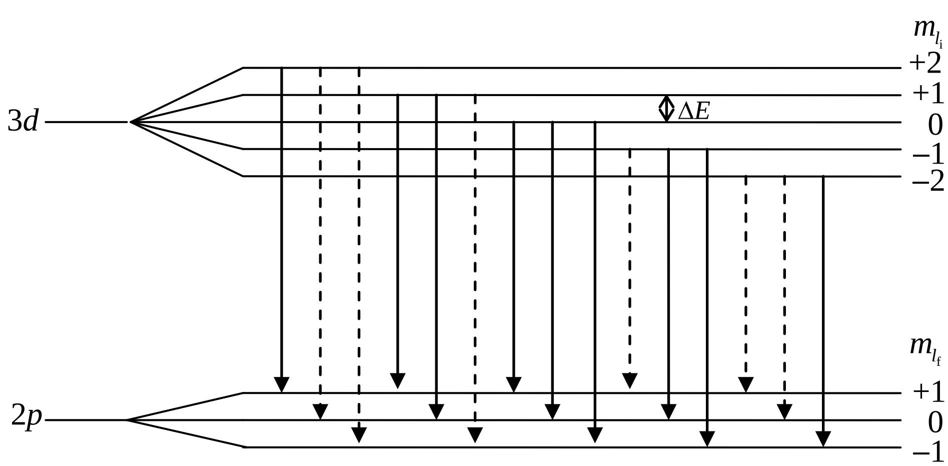


(b) Starting instead with 5d, the permitted transitions are



25. (a) 7*s*, 7*p*, 7*d*, 7*f*, 7*g*, 7*h*, 7*i* (b) 6*p*, 6*f*, 5*p*, 5*f*, 4*p*, 4*f*, 3*p*, 2*p*

26. (a)



(b) Transitions shown with dashed lines violate the $\Delta m_l = \pm 1$ selection rule.

(c) The energy of the initial state is $E_\mathrm{i} = E_{3d} + m_{l_\mathrm{i}}\Delta E$ and the energy of the final state is $E_\mathrm{f} = E_{2p} + m_{l_\mathrm{f}}\Delta E$ (where ΔE is the spacing between adjacent states). The transition energies can be found from the energy difference:

$$E_\mathrm{i} - E_\mathrm{f} = (E_{3d} - E_{2p}) + (m_{l_\mathrm{i}} - m_{l_\mathrm{f}})\Delta E = (E_{3d} - E_{2p}) + \Delta m_l \Delta E$$

There are only three permitted values of Δm_l (0, ±1), so there are only three possible values of the energy difference: $E_{3d} - E_{2p}, E_{3d} - E_{2p} + \Delta E, E_{3d} - E_{2p} + \Delta E$.

27. (a) In the absence of a magnetic field, the 3*d* to 2*p* energy difference is

$$E = (-13.6057\ \text{eV})\left(\frac{1}{3^2} - \frac{1}{2^2}\right) = 1.88968\ \text{eV}$$

and the wavelength is

$$\lambda = \frac{hc}{E} = \frac{1239.842\ \text{eV}\cdot\text{nm}}{1.88968\ \text{eV}} = 656.112\ \text{nm}$$

The magnetic field gives a change in wavelength of

$$\Delta\lambda = \frac{\lambda^2}{hc}\Delta E = \frac{(656.112\ \text{nm})^2}{1239.842\ \text{eV}\cdot\text{nm}}(5.79\times10^{-5}\ \text{eV/T})(3.50\ \text{T}) = 0.0703\ \text{nm}$$

The wavelengths of the three normal Zeeman components are then 656.112 nm, 656.112 nm + 0.070 nm = 656.182 nm, and 656.112 nm – 0.070 nm = 656.042 nm.

33. $$r_{\text{av}} = \int_0^\infty rP(r)dr = \int_0^\infty r^3 \left|R_{1,0}(r)\right|^2 dr = \frac{4}{a_0^3}\int_0^\infty r^3 e^{-2r/a_0} dr = \frac{4}{a_0^3}\frac{3!}{(2/a_0)^4} = \frac{3}{2}a_0$$

35.

$$U_{\mathrm{av}} = \int_0^\infty U(r)P(r)\,dr = \int_0^\infty \left(-\frac{e^2}{4\pi\varepsilon_0 r}\right) r^2 \left|R_{1,0}(r)\right|^2 dr = -\frac{e^2}{4\pi\varepsilon_0}\frac{4}{a_0^3}\int_0^\infty r e^{-2r/a_0}\,dr$$

$$= -\frac{e^2}{4\pi\varepsilon_0}\frac{4}{a_0^3}\frac{1}{(2/a_0)^2} = -\frac{e^2}{4\pi\varepsilon_0 a_0}$$