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:

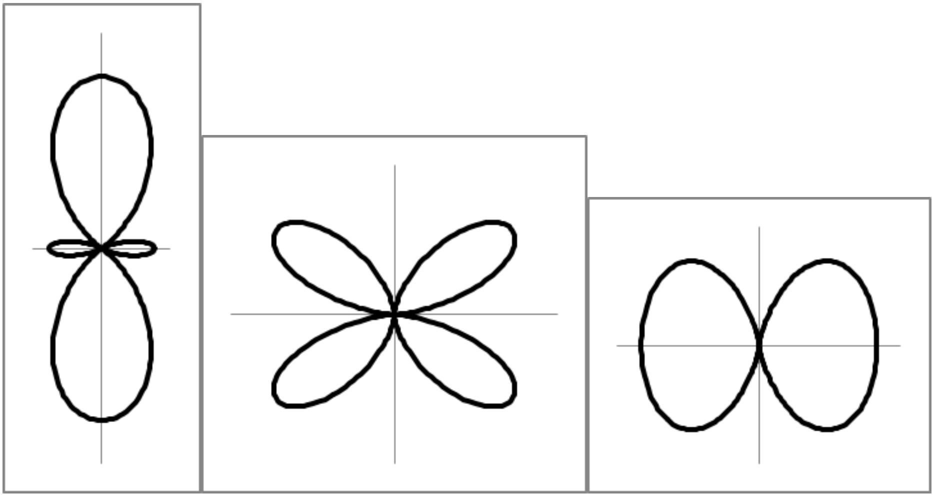
$$\frac{dP}{d\theta}=\frac{15}{8\pi}(2\sin\theta\cos^3\theta-2\sin^3\theta\cos\theta)=\frac{15}{4\pi}(\sin\theta)(\cos\theta)(\cos^2\theta-\sin^2\theta)=0$$

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

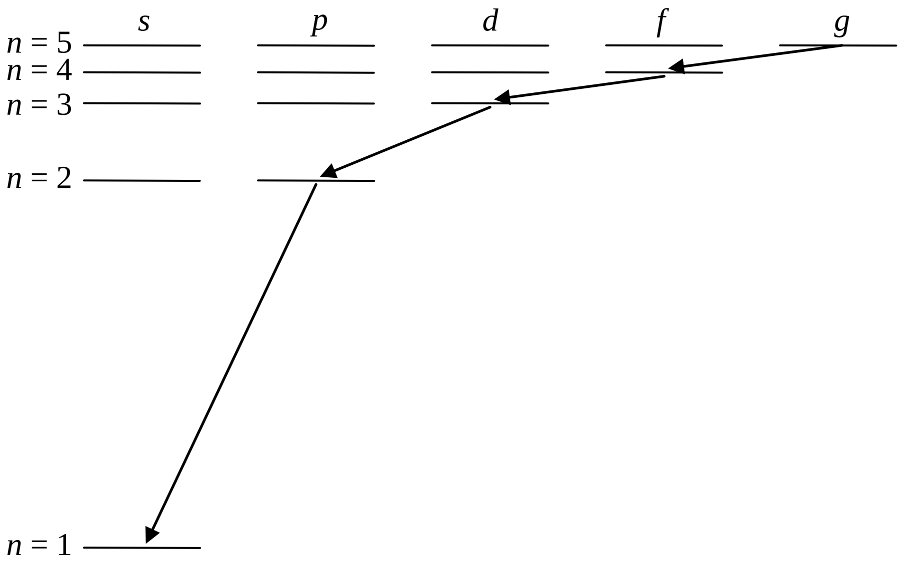
(b) $P(\theta,\phi)=\frac{15}{8\pi}\sin^2\theta\cos^2\theta$

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

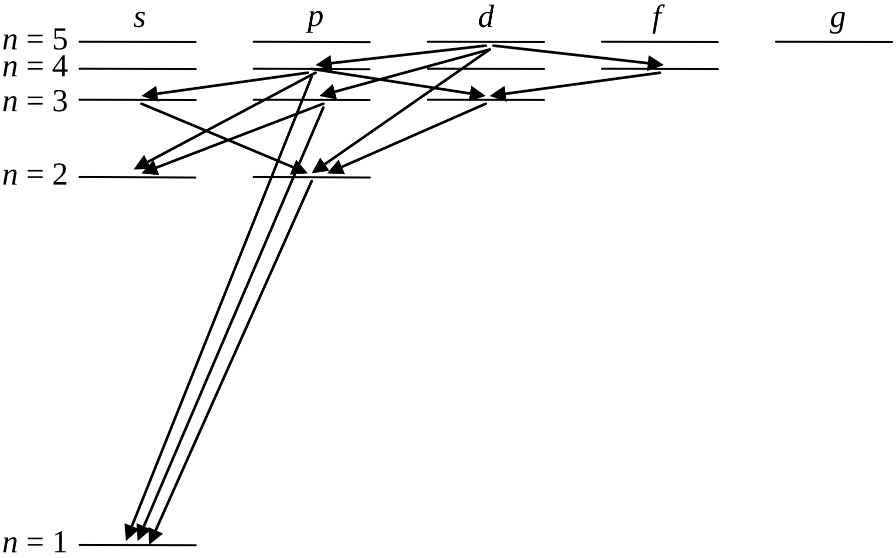


(a) (b) (c)

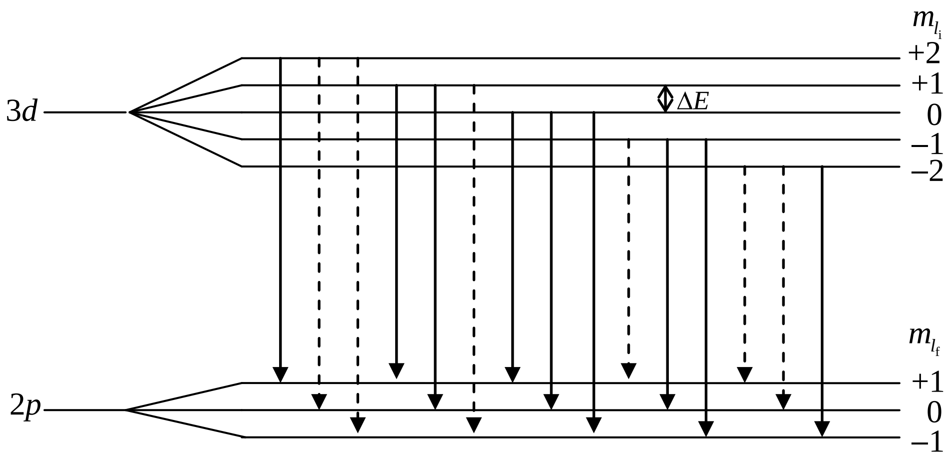
24. (a) The transitions that change l by one unit are



(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 3d to 2p 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.

28. The energy of the $2p$ to $1s$ Lyman transition is

$$E = (-13.60570\ \text{eV})\left(\frac{1}{2^2} - \frac{1}{1^2}\right) = 10.20428\ \text{eV}$$

and its wavelength (in the absence of fine structure) is

$$\lambda = \frac{hc}{E} = \frac{1239.842\ \text{eV}\cdot\text{nm}}{10.20428\ \text{eV}} = 121.5022\ \text{eV}$$

With the fine structure energy splitting of 4.5×10^{-5} eV, the wavelength splitting is

$$\Delta\lambda = \frac{\lambda^2}{hc}\Delta E = \frac{(121.5\ \text{nm})^2}{1240\ \text{eV}\cdot\text{nm}}(4.5\times10^{-5}\ \text{eV}) = 0.00054\ \text{nm}$$

The fine structure splits one level up by $0.5\Delta E$ and the other down by the same amount, so the wavelengths are

$$\lambda + \tfrac{1}{2}\Delta\lambda = 121.5024\ \text{nm} \qquad \text{and} \qquad \lambda - \tfrac{1}{2}\Delta\lambda = 121.5019\ \text{nm}$$

32. (a)

$$U = -\frac{e^2}{8\pi\varepsilon_0 r} = -\frac{e^2}{4\pi\varepsilon_0}\frac{1}{2r} = -\frac{1.44\ \text{eV}\cdot\text{nm}}{2(0.0529\ \text{nm})} = -27.2\ \text{eV}$$

$$K = E - U = -13.6\ \text{eV} - (-27.2\ \text{eV}) = 13.6\ \text{eV}$$

(b) $K = 0$ where $E = U = -13.6$ eV:

$$U = -13.6\ \text{eV} = \frac{-1.44\ \text{eV}\cdot\text{nm}}{2r} \quad \text{so} \quad r = \frac{-1.44\ \text{eV}\cdot\text{nm}}{2(-13.6\ \text{eV})} = 0.106\ \text{nm} = 2a_0$$

(c)

$$P(2a_0:\infty)=\int_{2a_0}^{\infty} r^2\frac{4}{a_0^3}e^{-2r/a_0}dr=\frac{4}{a_0^3}\frac{e^{-2r/a_0}}{2/a_0}\left(r^2+\frac{2r}{2/a_0}+\frac{2}{(2/a_0)^2}\right)\Bigg|_{2a_0}^{\infty}=6.5e^{-4}=0.238$$

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.

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

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

38. (a) In Cartesian coordinates, the solution can be found using Eq. 7.9, which is separable for this potential energy. The solutions can be written $\psi_{n_x n_y n_z}(x, y, z) = X_{n_x}(x) Y_{n_y}(y) Z_{n_z}(z)$, and for each of the 3 functions there is an energy of $(n_i + \frac{1}{2})\hbar\omega$, where $i = x, y,$ or z. The total energy is then $E_{n_x n_y n_z} = (n_x + n_y + n_z + \frac{3}{2})\hbar\omega$.

(b)

Ground state: $E = \frac{3}{2}\hbar\omega \quad (n_x n_y n_z) = (000)$

1st excited state: $E = \frac{5}{2}\hbar\omega \quad (n_x n_y n_z) = (100), (010), (001)$

2nd excited state: $E = \frac{7}{2}\hbar\omega \quad (n_x n_y n_z) = (200), (020), (002), (110), (101), (011)$

(c) The ground state has $n = 0$ and therefore only $l = 0$, so it is non-degenerate. The first excited state has $n = 1$ and therefore $l = 1$, which has degeneracy 3 ($m_l = +1, 0, -1$). The second excited state has $n = 2$ and therefore includes $l = 0$ (degeneracy = 1) and $l = 2$ (degeneracy = 5), for a total degeneracy of 6.

39. (a) The radial dependence of the 3 functions is e^{-r/a_0} for $n = 1$, $l = 0$; $re^{-r/2a_0}$ for $n = 2$, $l = 1$; and $r^2e^{-r/3a_0}$ for $n = 3$, $l = 2$. A guess for the next function in the series is $r^3e^{-r/4a_0}$ for $n = 4$, $l = 3$.

(b) The necessary derivatives are:

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

$$\frac{d^2R}{dr^2} = 6re^{-r/4a_0} - 3r^2e^{-r/4a_0} / 4a_0 - 3r^2e^{-r/4a_0} / 4a_0 + r^3e^{-r/4a_0} / 16a_0^2$$

Substituting into Eq. 7.12 and canceling the common exponential factor gives:

$$-\frac{\hbar^2}{2m}\left[6r - \frac{3r^2}{2a_0} + \frac{r^3}{16a_0^2} + \frac{2}{r}\left(3r^2 - \frac{r^3}{4a_0}\right)\right] + \left(\frac{-e^2}{4\pi\varepsilon_0} + \frac{12\hbar^2}{2mr^2}\right)r^3 = Er^3$$

The terms linear in r cancel, leaving us with

$$\frac{\hbar^2r^2}{2ma_0} - \frac{\hbar^2r^3}{32ma_0^2} - \frac{e^2r^2}{4\pi\varepsilon_0} = Er^3$$

When the value of a_0 is inserted, the 2 terms in r^2 cancel, leaving us with

$$E = -\frac{\hbar^2}{2m}\frac{1}{16a_0^2} = -\frac{1}{16}\frac{\hbar^2}{2m}\left(\frac{me^2}{4\pi\varepsilon_0\hbar^2}\right)^2 = -\frac{1}{16}\frac{me^4}{32\pi^2\varepsilon_0^2\hbar^2}$$

which is the expected energy for the $n = 4$ state.