Some problems deal with the allowed values of the energy of a hydrogen atom, with the possible
wavelengths and frequencies of the radiation emitted when a hydrogen atom makes a transition
from one state to a lower energy state, or with the frequency and wavelength of radiation that can
be absorbed by a hydrogen atom. The allowed values of the energy are given by

$$E_n = -\frac{m_e^4}{8\varepsilon_0^2} \frac{1}{n^2} = -\frac{13.6 \text{ eV}}{n^2},$$

where $n$ is a positive integer. Remember $E = 0$ means the electron is just free of the proton and
has no kinetic energy. The energy of the photon is the magnitude of the difference in energy of
the two states involved in the transition: $hf = |E_f - E_i|$. $E_f - E_i$ is positive for an absorption event
and negative for an emission event.

Some problems involve the wave functions for the electron in a hydrogen atom. The electron
moves in three-dimensional space and $|\psi|^2 \, dV$ gives the probability it can be found in the
infinitesimal volume $dV$. The radial probability density is given by $P(r) = 4\pi r^2 |\psi|^2$ and $P(r) \, dr$
gives the probability that the particle can be found in the spherical shell with inner radius $r$ and
outer radius $r + dr$.

Questions and Example Problems from Chapter 39

Question 1
The figure below shows three infinite potential wells, each on an x axis. Without written
calculation, determine the wave function $\psi$ for a ground-state electron trapped in each well.

$$\Psi_n(x) = \sqrt{\frac{2}{L}} \sin \left( \frac{n\pi}{L} x \right)$$

$$\Psi_1(x) = \sqrt{\frac{2}{L}} \cos \left( \frac{\pi}{L} x \right)$$

$$\Psi_3(x) = \sqrt{\frac{2}{L}} \sin \left( \frac{2\pi}{L} x \right)$$
Problem 1
A proton is confined to a one-dimensional infinite potential well 100 pm wide. What is its ground-state energy?

\[ E_n = \left( \frac{\hbar^2}{8mL^2} \right) n^2, \quad n = 1, 2, 3, \ldots \]

\[ L = 100 \text{ pm} = 100 \times 10^{-12} \text{ m} \]

\[ E_1 = \frac{\hbar^2}{8mL^2} \]

\[ E_1 = \frac{(6.63 \times 10^{-34} \text{ J s})^2}{8 \times (1.067 \times 10^{-27} \text{ K}) \times (100 \times 10^{-12} \text{ m})^2} \]

\[ E = 3.29 \times 10^{-21} \text{ J} \]

Problem 2
An electron is trapped in a one-dimensional infinite potential well. (a) What pair of adjacent energy levels (if any) will have three times the energy difference that exists between levels \( n = 3 \) and \( n = 4 \)? (b) What pair (if any) will have twice that energy difference?

\[ E_n = \left( \frac{\hbar^2}{8mL^2} \right) n^2 \]

\[ E_{n+1} = \left( \frac{\hbar^2}{8mL^2} \right) (n+1)^2 \]

(a) \[ E_{n+1} - E_n = E_1 (n+1)^2 - E_1 n^2 \]

\[ = E_1 [(n+1)^2 - n^2] = E_1 (2n+1) \]

\[ \Rightarrow \text{ we want } E_{n+1} - E_n = E_1 (2n+1) = 3(E_4 - E_3) \]

\[ E_1 (2n+1) = 3 [E_1 (4)^2 - E_1 (3)^2] \]

\[ E_1 (2n+1) = 3 [7E_1] \Rightarrow 2n+1 = 21 \Rightarrow n = 10 \text{ so adj. energy levels are } E_{10} \text{ and } E_{11}. \]

(b) \[ \text{ we want } E_{n+1} - E_n = E_1 (2n+1) = 2(E_4 - E_3) \]

\[ E_1 (2n+1) = 2 [E_1 (4)^2 - E_1 (3)^2] = 2 [7E_1] \]

\[ E_1 (2n+1) = 14E_1 \Rightarrow 2n+1 = 14 \Rightarrow \text{ no integer valued solutions } \text{ so no adjacent energy levels fit requirement.} \]
Problem 3
Suppose that an electron trapped in a one-dimensional infinite well of width 250 pm is excited from its first excited state to its third excited state. (a) In electron-volts, what energy must be transferred to the electron for this quantum jump? If the electron then de-excites by emitting light, (b) what wavelengths can it emit and (c) in which groupings (and orders) can they be emitted? (d) Show the several possible ways the electron can de-excite on an energy-level diagram.

\[
E_n = \left( \frac{\hbar^2}{8mL^2} \right) n^2 = \left[ \frac{(6.63 \times 10^{-34} \text{ J} \cdot \text{s})^2}{8 \left( 9.11 \times 10^{-31} \text{ kg} \right) \left( 250 \times 10^{-12} \text{ m} \right)^2} \right] n^2
\]

\[
E_n = (9.65 \times 10^{-19} \text{ J}) n^2
\]

\[
= (6.03 \text{ eV}) n^2
\]

(a) First excited state → \( n = 2 \)
Second excited state → \( n = 3 \)
Third excited state → \( n = 4 \)

\[
\Delta E = E_4 - E_2 = (6.03 \text{ eV})(4^2 - 2^2)
\]

\[
\Delta E = 72.4 \text{ eV}
\]

(b) \( hf = \Delta E \)

\[
hc/\lambda = \Delta E \rightarrow \lambda = \frac{hc}{\Delta E}
\]

Possible transitions
\[
\begin{align*}
n = 4 & \rightarrow n = 3 & \lambda = 29.4 \text{ nm} \\
n = 4 & \rightarrow n = 2 & \lambda = 17.1 \text{ nm} \\
n = 3 & \rightarrow n = 2 & \lambda = 41.2 \text{ nm} \\
n = 3 & \rightarrow n = 1 & \lambda = 25.7 \text{ nm} \\
n = 2 & \rightarrow n = 1 & \lambda = 68.5 \text{ nm}
\end{align*}
\]

(c) 4 → 1
4 → 2, 2 → 1
4 → 3, 3 → 1
4 → 3, 3 → 2, 2 → 1

(d) Energy-level diagram
Problem 4
A particle is confined to the one-dimensional infinite potential well of the figure below. If the particle is in its first excited state (n = 2), what is its probability of detection between (a) x = 0 and x = 0.25L, (b) x = 0 and x = 0.50L, and (c) x = 0.25L and x = L?

\[
\psi_n(x) = \sqrt{\frac{2}{L}} \sin \left( \frac{n \pi x}{L} \right) \rightarrow \psi_2(x) = \sqrt{\frac{2}{L}} \sin \left( \frac{2 \pi x}{L} \right).
\]

(a) \[\int_{x=0}^{0.25L} 2 \sqrt{\frac{L}{2}} \sin^2 \left( \frac{2 \pi x}{L} \right) \, dx \]

\[= \frac{1}{\pi} \left[ \frac{\pi}{2} - \frac{1}{4} \sin \pi x - \left( \frac{1}{2} \cos \frac{\pi}{4} - \frac{1}{2} \sin \frac{\pi}{4} \right) \right] = \frac{1}{4} \]

(b) Using some equation and integrating from x = 0 to x = 0.50L, \[\int_{x=0}^{0.50L} \psi_2^2(x) \, dx \rightarrow \frac{1}{2} \]

(c) \[1 - \int_{x=0.25L}^{0.50L} \psi_2^2(x) \, dx = 1 - \frac{1}{4} = \frac{3}{4} \]

Problem 5
(a) The figure below gives the energy levels for an electron trapped in a finite potential energy well 450 eV deep. If the electron is in the n = 3 state, what is its kinetic energy? (b) The electron then absorbs 500 eV of energy from an external source. What is its kinetic energy after this absorption, assuming that the electron moves to a position for which x > L?

\[
E_2 = 280 \text{ eV} = K + U \quad U = 0 \rightarrow K = 280 \text{ eV}
\]

(b) \[E_{\text{total}} = 280 \text{ eV} + 500 \text{ eV} = 780 \text{ eV} = K + U \]

\[U = 450 \text{ eV} \quad \frac{\text{eV}}{x > L} \]

\[K = 780 \text{ eV} - 450 \text{ eV} \rightarrow K = 330 \text{ eV} \]
Problem 6
An electron is contained in the rectangular box of the figure below, with widths \( L_x = 800 \) pm, \( L_y = 1600 \) pm, and \( L_z = 400 \) pm. What is the electron's ground-state energy in electron-volts?

\[
E_{n_x, n_y, n_z} = \frac{\hbar^2}{8m} \left( \frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} + \frac{n_z^2}{L_z^2} \right)
\]

Ground state is given by \( n_x = n_y = n_z = 1 \)

\[
E_{1,1,1} = \frac{\hbar^2}{8m} \left( \frac{1}{L_x^2} + \frac{1}{L_y^2} + \frac{1}{L_z^2} \right)
\]

\[
E_{1,1,1} = \frac{\left( 4.63 \times 10^{-39} \text{ J} \right)}{8 \left( 9.1 \times 10^{-31} \text{ kg} \right)} \left[ \frac{1}{(800 \times 10^{-12} \text{ m})^2} + \frac{1}{(1600 \times 10^{-12} \text{ m})^2} + \frac{1}{(400 \times 10^{-12} \text{ m})^2} \right]
\]

\[
E_{1,1,1} = 4.95 \times 10^{-19} \text{ J} = 3.10 \text{ eV}
\]

Problem 7
A rectangular box of widths \( L_x = L \) and \( L_y = 2L \) contains an electron. What multiple of \( \hbar^2/8mL^2 \), where \( m \) is the electron's mass, are (a) the energy of the electron's ground state, (b) the energy of its first excited state, (c) the energy of its lowest degenerate states, and (d) the difference between the energies of its second and third excited states?

\[
E_{n_x, n_y} = \left( \frac{\hbar^2}{8mL^2} \right) \left( \frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} \right) = \left( \frac{\hbar^2}{8mL^2} \right) \left[ \frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} \right]
\]

\[
E_{1,1} = \left( \frac{\hbar^2}{8mL^2} \right) \left( 1 + \frac{1}{4} \right) = \frac{5}{4} \left( \frac{\hbar^2}{8mL^2} \right)
\]

(b) first excited state \( n_x = 1, n_y = 2 \)

\[
E_{1,2} = \left( \frac{\hbar^2}{8mL^2} \right) \left( 1 + \frac{3}{4} \right) = \frac{2}{4} \left( \frac{\hbar^2}{8mL^2} \right)
\]

(c) lowest degenerate state \( n_x = 1, n_y = 4 \)

\[
E_{1,4} = \left( \frac{\hbar^2}{8mL^2} \right) \left( 1 + \frac{4}{4} \right) = 5 \left( \frac{\hbar^2}{8mL^2} \right)
\]

\[
E_{2,2} = \left( \frac{\hbar^2}{8mL^2} \right) \left( 2^2 + \frac{2}{4} \right) = 5 \left( \frac{\hbar^2}{8mL^2} \right)
\]

(d) second excited state \( n_x = 1, n_y = 3 \)

\[
E_{1,3} = \left( \frac{\hbar^2}{8mL^2} \right) \left( 1 + \frac{3}{4} \right) = \frac{13}{4} \left( \frac{\hbar^2}{8mL^2} \right)
\]

\[
E_{2,1} = \left( \frac{\hbar^2}{8mL^2} \right) \left( 2 + \frac{1}{4} \right) = \frac{17}{4} \left( \frac{\hbar^2}{8mL^2} \right)
\]

\[
\Delta E = (1) \left( \frac{\hbar^2}{8mL^2} \right)
\]
Problem 8
(a) What is the wavelength of light for the least energetic photon emitted in the Paschen series of the hydrogen atom spectrum lines? (b) What is the wavelength of the series limit for the Paschen series?

\[ \text{Paschen series} \rightarrow n_f = 3 \quad hf = \Delta E = (-13.6 \text{ eV}) \left( \frac{1}{n_{\text{high}}^2} - \frac{1}{n_{\text{low}}^2} \right) \]

\[ \Delta E = (13.6 \text{ eV}) \left( \frac{1}{3^2} - \frac{1}{n_{\text{high}}^2} \right) \]

(a) least energetic if \( n_{\text{high}} = 4 \):

\[ hf = \Delta E \rightarrow \frac{hc}{\lambda} = \Delta E \rightarrow \lambda = \frac{hc}{\Delta E} = \frac{1240 \text{ eV nm}}{0.661 \text{ eV}} = 1875 \text{ nm} \]

(b) series limit \( n_{\text{high}} = \infty \):

\[ \Delta E = (13.6 \text{ eV}) \left( \frac{1}{3^2} - \frac{1}{\infty} \right) = 1.51 \text{ eV} \]

\[ \lambda = \frac{1240 \text{ eV nm}}{1.51 \text{ eV}} \rightarrow \lambda = 821 \text{ eV nm} \]

Problem 9
A hydrogen atom, initially at rest in the \( n = 4 \) quantum state, undergoes a transition to the ground state, emitting a photon in the process. What is the speed of the recoiling hydrogen atom?

\[ \Rightarrow \text{if the hydrogen atom is initially at rest (} P_c^\text{=}0\text{), then from conservation of momentum, the momentum of the photon and the momentum of the recoiling hydrogen atom must have the same magnitude (but opposite directions) so that } P_f^\text{=}0 \]

\[ P_H = P_{\text{photon}} \rightarrow m_H V_H = hf/c \]

\[ \Rightarrow \text{energy of photon equals difference in energy states:} \quad hf = E_f - E_i \]

\[ hf = -13.6 \text{ eV} - \frac{13.6 \text{ eV}}{4^2} = 12.75 \text{ eV} \]

\[ m_H V_H = hf/c = \frac{(12.75 \text{ eV})}{c} \rightarrow V_H = \frac{(12.75 \text{ eV})}{m_H c} \quad m_H = 1.673 \times 10^{-27} \text{ kg} \]

\[ V_H = \frac{(12.75 \text{ eV}) (1.602 \times 10^{-19} \text{ J/eV})}{(1.673 \times 10^{-27} \text{ kg}) (3.0 \times 10^8 \text{ m/s})} \rightarrow V_H = 4.1 \text{ m/s} \]
Problem 10
(a) Find, using the energy-level diagram of the figure below, the quantum numbers corresponding to a transition in which the wavelength of the emitted radiation is 121.6 nm. (b) To what series does this transition belong?

\[ E = \frac{hf}{\lambda} \]

\[ E = \frac{1240 \text{ eV} \cdot \text{nm}}{121.6 \text{ nm}} \]

\[ E = 10.2 \text{ eV} \]

Must be part of Lyman series

(b) Lyman series

(a) \[ hf = \Delta E = E_{\text{high}} - E_{\text{low}} \]

\[ 10.2 \text{ eV} = \frac{-13.6 \text{ eV}}{n^2} - \left( \frac{-13.6 \text{ eV}}{n^2} \right) \]

\[ -3.4 \text{ eV} = \frac{-13.6 \text{ eV}}{n^2} \rightarrow n^2 = \frac{-13.6 \text{ eV}}{3.4 \text{ eV}} = 4 \]

\[ n = 2 \]
Problem 11
A hydrogen atom in a state having a binding energy (the energy required to remove an electron) of 0.85 eV makes a transition to a state with an excitation energy (the difference between the energy of the state and that of the ground state) of 10.2 eV. (a) What is the energy of the photon emitted as a result of the transition? (b) Identify this transition, using the energy-level diagram of the figure below.

\[ E_i = -0.85 \text{ eV} \]

\[ E_f = -13.6 \text{ eV} + 10.2 \text{ eV} = -3.4 \text{ eV} \]

(a) \[ E_{\text{photon}} = E_i - E_f = -0.85 \text{ eV} - (-3.4 \text{ eV}) \]

\[ E_{\text{photon}} = 2.55 \text{ eV} \]

(b) From the figure, you can see that a photon whose energy is 2.55 eV must correspond to the Balmer series which are transitions to \( n = 2 \).

Balmer series \( \rightarrow \Delta E = E_n - E_\infty = -\frac{13.6 \text{ eV}}{n^2} - \left(\frac{-13.6 \text{ eV}}{2^2}\right) \)

\[ -\frac{13.6 \text{ eV}}{n^2} - \left(\frac{-13.6 \text{ eV}}{4}\right) = 2.55 \text{ eV} \]

\[ -\frac{13.6 \text{ eV}}{n^2} + 3.4 \text{ eV} = 2.55 \text{ eV} \quad \rightarrow \quad -\frac{13.6 \text{ eV}}{n^2} = -0.85 \text{ eV} \]

\[ n = 4 \]