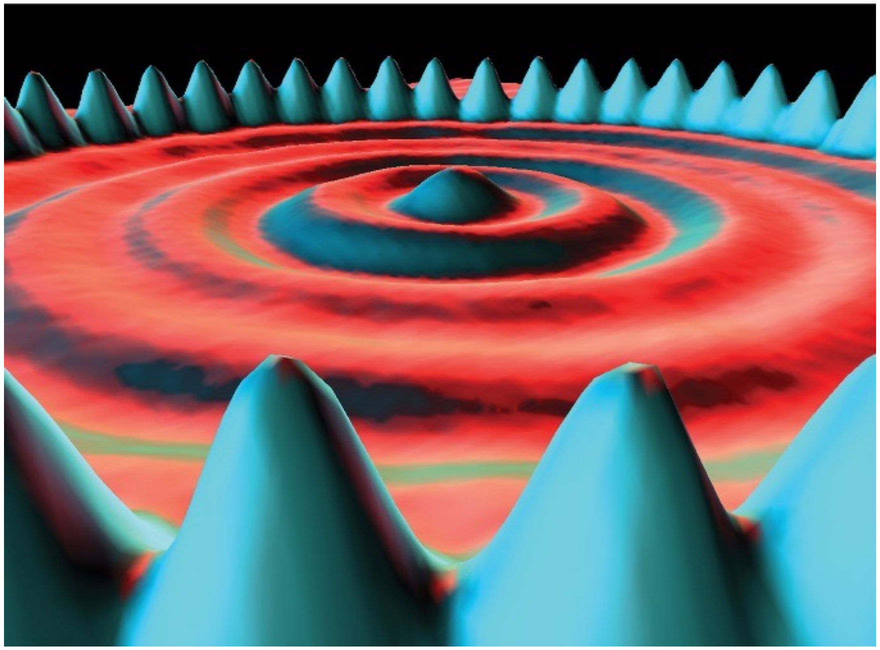
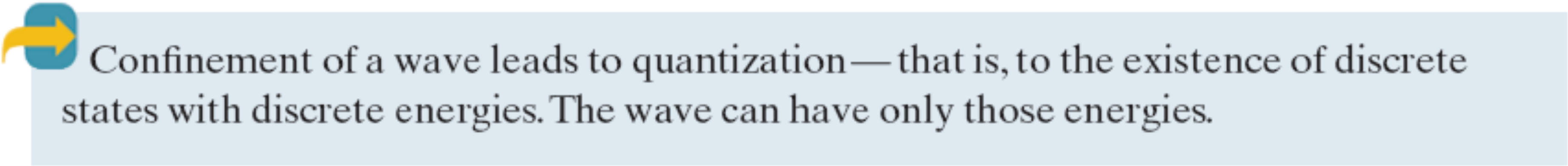
Chapter 39

More About Matter Waves

Energy of Trapped Electron, Two and Three Dimensional Trap, The Hydrogen Atom



39.1: String Waves and Matter Waves:



Confinement of a wave leads to quantization—that is, to the existence of discrete states with discrete energies. The wave can have only those energies.

This observation applies to waves of all kinds, including matter waves.

For matter waves, however, it is more convenient to deal with the energy E of the associated particle than with the frequency f of the wave.

39.2: Energies of a Trapped Electron: One-dimensional trap

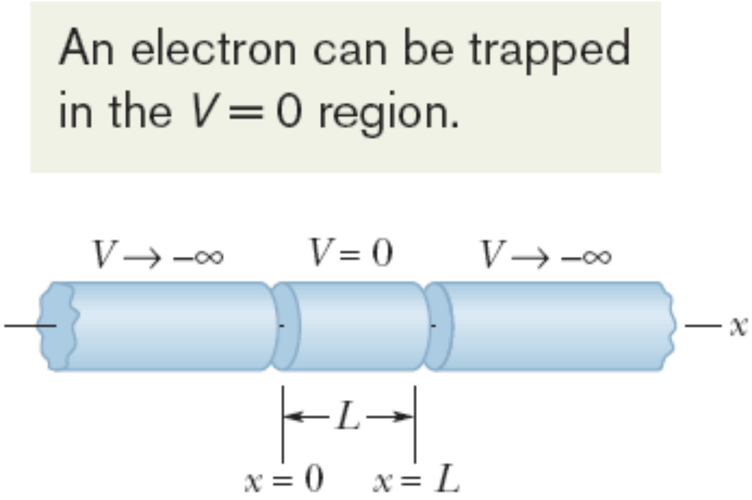


Fig. 39-1 The elements of an idealized "trap" designed to confine an electron to the central cylinder. We take the semi-infinitely long end cylinders to be at an infinitely great negative potential and the central cylinder to be at zero potential.

$$L = \frac{n\lambda}{2}, \qquad \text{for } n = 1, 2, 3, \ldots .$$

Each value of *n* identifies a state of the oscillating string; the integer *n* is a **quantum number.**

For each state of the string, the transverse displacement of the string at any position *x* along the string is given by

$$y_n(x) = A \sin\left(\frac{n\pi}{L} x\right), \qquad \text{for } n = 1, 2, 3, \ldots ,$$

39.2: Energies of a Trapped Electron: Finding the quantized energies:

$$\lambda = \frac{h}{p} = \frac{h}{\sqrt{2mE}}.$$

$$E_n = \left(\frac{h^2}{8mL^2}\right)n^2, \qquad \text{for } n = 1, 2, 3, \ldots .$$

An electron can be trapped in the $U = 0$ region.

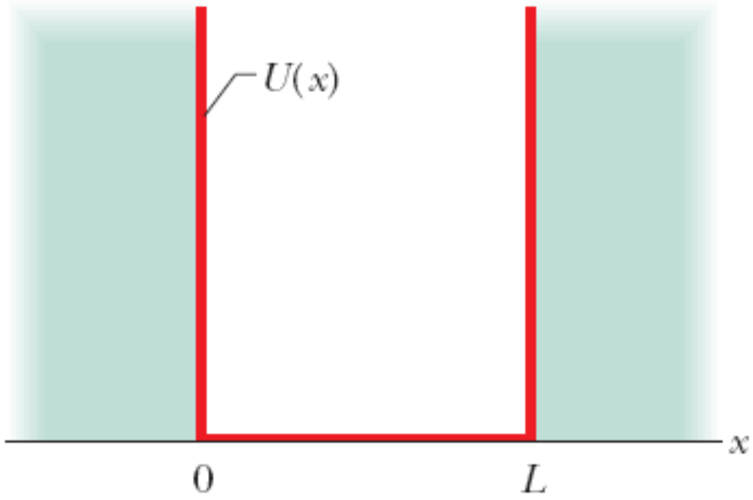


Fig. 39-2 The electric potential energy $U(x)$ of an electron confined to the central cylinder of the idealized trap of Fig. 39-1. We see that $U = 0$ for $0 < x < L$, and $U \rightarrow \infty$ for $x < 0$ and $x > L$.

39.2: Energies of a Trapped Electron: Finding the quantized energies:

$$E_n = \left(\frac{h^2}{8mL^2}\right)n^2, \qquad \text{for } n = 1, 2, 3, \ldots .$$

These are the lowest five energy levels allowed the electron. (No intermediate levels are allowed.)

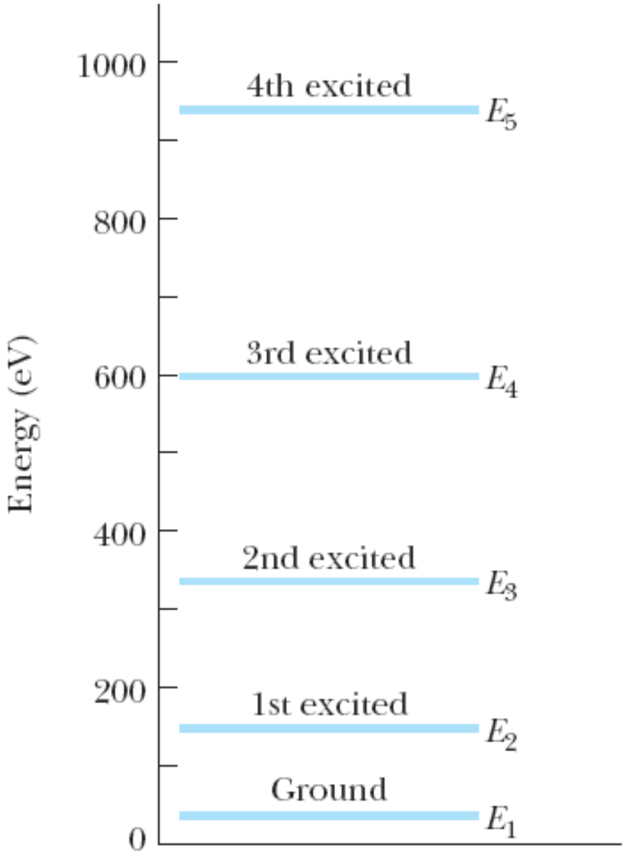


Fig. 39-3 Several of the allowed energies given by Eq. 39-4 for an electron confined to the infinite well of Fig. 39-2. Here width $L = 100$ pm. Such a plot is called an *energy-level diagram.*

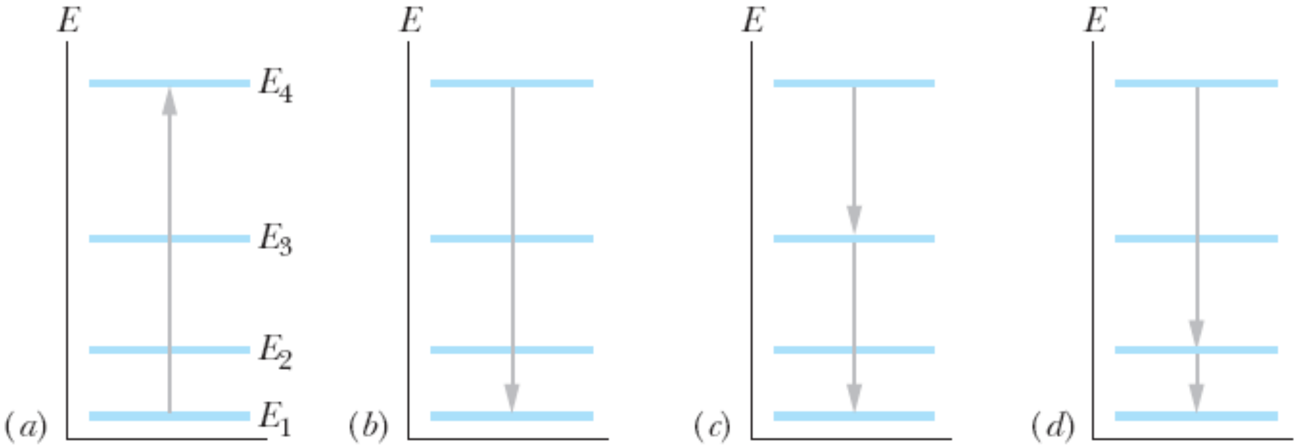
39.2: Energies of a Trapped Electron: Finding the quantized energies:

Fig. 39-4 (*a*) Excitation of a trapped electron from the energy level of its ground state to the level of its third excited state. (*b*)–(*d*) Three of four possible ways the electron can de-excite to return to the energy level of its ground state. (Which way is not shown?)

The electron is excited to a higher energy level.

It can de-excite to a lower level in several ways (set by chance).

$$\Delta E = E_{\text{high}} - E_{\text{low}}.$$



If a confined electron is to absorb a photon, the energy hf of the photon must equal the energy difference ΔE between the initial energy level of the electron and a higher level.

$$hf = \Delta E = E_{\text{high}} - E_{\text{low}}.$$

☑ Checkpoint 1

Rank the following pairs of quantum states for an electron confined to an infinite well according to the energy differences between the states, greatest first: (a) $n = 3$ and $n = 1$, (b) $n = 5$ and $n = 4$, (c) $n = 4$ and $n = 3$.

b, a, c

$$E_n = \left(\frac{h^2}{8mL^2}\right)n^2, \qquad \text{for } n = 1, 2, 3, \ldots .$$

Example, Energy levels in a 1-D infinite potential well:

An electron is confined to a one-dimensional, infinitely deep potential energy well of width $L = 100$ pm.

(a) What is the smallest amount of energy the electron can have?

Lowest energy level: Here, the collection of constants in front of n^2 in Eq. 39-4 is evaluated as

$$\frac{h^2}{8mL^2} = \frac{(6.63 \times 10^{-34}\ \mathrm{J \cdot s})^2}{(8)(9.11 \times 10^{-31}\ \mathrm{kg})(100 \times 10^{-12}\ \mathrm{m})^2}$$
$$= 6.031 \times 10^{-18}\ \mathrm{J}. \tag{39-7}$$

The smallest amount of energy the electron can have corresponds to the lowest quantum number, which is $n = 1$ for the ground state of the electron. Thus, Eqs. 39-4 and 39-7 give us

$$E_1 = \left(\frac{h^2}{8mL^2}\right) n^2 = (6.031 \times 10^{-18}\ \mathrm{J})(1^2)$$
$$\approx 6.03 \times 10^{-18}\ \mathrm{J} = 37.7\ \mathrm{eV}. \qquad \text{(Answer)}$$

(b) How much energy must be transferred to the electron if it is to make a quantum jump from its ground state to its second excited state?

$$\Delta E_{31} = \left(\frac{h^2}{8mL^2}\right)(3)^2 - \left(\frac{h^2}{8mL^2}\right)(1)^2$$
$$= \frac{h^2}{8mL^2}(3^2 - 1^2)$$
$$= (6.031 \times 10^{-18}\ \mathrm{J})(8)$$
$$= 4.83 \times 10^{-17}\ \mathrm{J} = 301\ \mathrm{eV}. \qquad \text{(Answer)}$$

Upward jump: The energies E_3 and E_1 depend on th quantum number n, according to Eq. 39-4. Therefore, subs tuting that equation into Eq. 39-8 for energies E_3 and E_1 ar

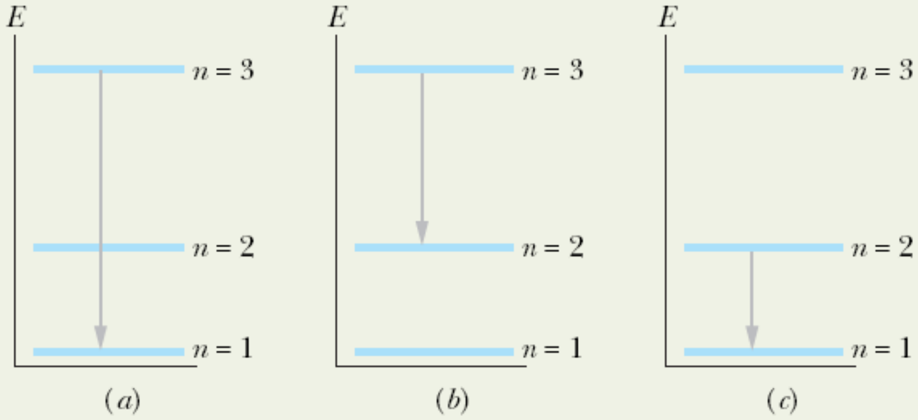


Fig. 39-5 De-excitation from the second excited state to the ground state either directly (*a*) or via the first excited state (*b*, *c*).

Example, Energy levels in a 1-D infinite potential well, cont.:

(c) If the electron gains the energy for the jump from energy level E_1 to energy level E_3 by absorbing light, what light wavelength is required?

KEY IDEAS

(1) If light is to transfer energy to the electron, the transfer must be by photon absorption. (2) The photon's energy must equal the energy difference ΔE between the initial energy level of the electron and a higher level, according to Eq. 39-6 ($hf = \Delta E$). Otherwise, a photon *cannot* be absorbed.

Wavelength: Substituting c/λ for f, we can rewrite Eq. 39-6 as

$$\lambda = \frac{hc}{\Delta E}. \qquad (39\text{-}9)$$

For the energy difference ΔE_{31} we found in (b), this equation gives us

$$\begin{aligned}\lambda &= \frac{hc}{\Delta E_{31}}\\ &= \frac{(6.63 \times 10^{-34}\ \text{J}\cdot\text{s})(2.998 \times 10^{8}\ \text{m/s})}{4.83 \times 10^{-17}\ \text{J}}\\ &= 4.12 \times 10^{-9}\ \text{m}. \qquad \text{(Answer)}\end{aligned}$$

(d) Once the electron has been excited to the second excited state, what wavelengths of light can it emit by de-excitation?

The direct jump involves the same energy difference ΔE_{31} we found in (c). Then the wavelength is the same as we calculated in (c)—except now the wavelength is for light that is emitted, not absorbed. Thus, the electron can jump directly to the ground state by emitting light of wavelength

$$\lambda = 4.12 \times 10^{-9}\ \text{m}. \qquad \text{(Answer)}$$

Following the procedure of part (b), you can show that the energy differences for the jumps of Figs. 39-5*b* and *c* are

$$\Delta E_{32} = 3.016 \times 10^{-17}\ \text{J} \quad \text{and} \quad \Delta E_{21} = 1.809 \times 10^{-17}\ \text{J}.$$

From Eq. 39-9, we then find that the wavelength of the light emitted in the first of these jumps (from $n = 3$ to $n = 2$) is

$$\lambda = 6.60 \times 10^{-9}\ \text{m}, \qquad \text{(Answer)}$$

and the wavelength of the light emitted in the second of these jumps (from $n = 2$ to $n = 1$) is

$$\lambda = 1.10 \times 10^{-8}\ \text{m}. \qquad \text{(Answer)}$$

Upward jump: The energies E_3 and E_1 depend on the quantum number n, according to Eq. 39-4. Therefore, substituting that equation into Eq. 39-8 for energies E_3 and E_1 and

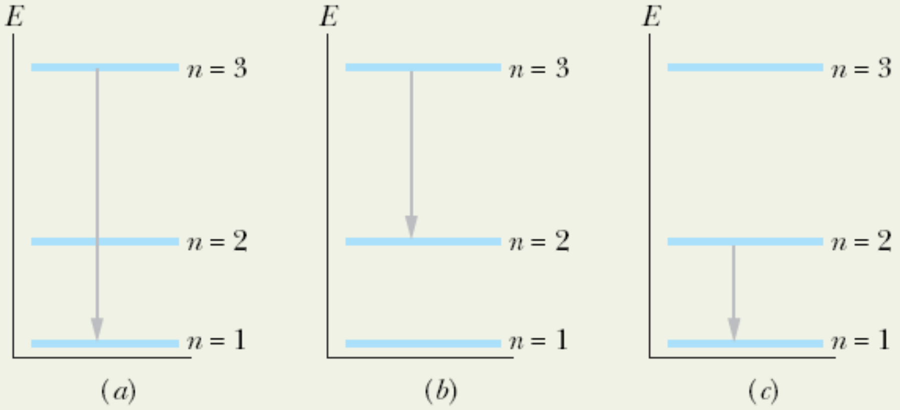


Fig. 39-5 De-excitation from the second excited state to the ground state either directly (*a*) or via the first excited state (*b*, *c*).

39.4: Wave Functions of a Trapped Electron:

The probability density must be zero at the infinite walls.

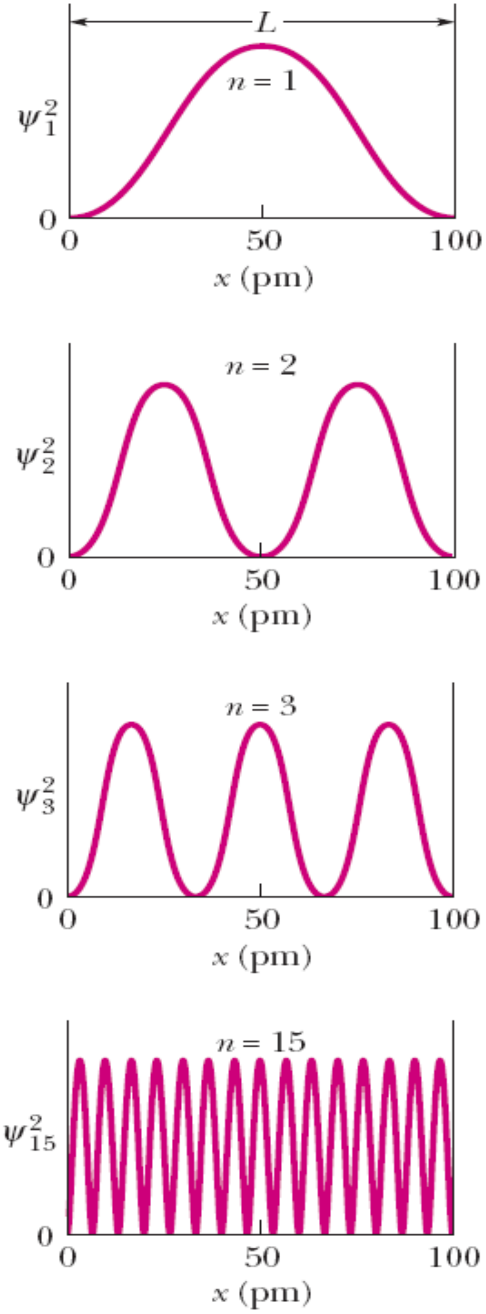


Fig. 39-6 The probability density $\psi_n^2(x)$ for four states of an electron trapped in a one-dimensional infinite well; their quantum numbers are $n = 1, 2, 3,$ and 15. The electron is most likely to be found where $\psi_n^2(x)$ is greatest and least likely to be found where $\psi_n^2(x)$ is least.

$$\begin{pmatrix}\text{probability } p(x)\\ \text{of detection in width } dx\\ \text{centered on position } x\end{pmatrix} = \begin{pmatrix}\text{probability density } \psi_n^2(x)\\ \text{at position } x\end{pmatrix} (\text{width } dx),$$

$$p(x) = \psi_n^2(x)\,dx.$$

$$\psi_n(x) = A \sin\left(\frac{n\pi}{L}x\right), \qquad \text{for } n = 1, 2, 3, \ldots,$$

$$\begin{pmatrix}\text{probability of detection}\\ \text{between } x_1 \text{ and } x_2\end{pmatrix} = \int_{x_1}^{x_2} p(x)$$

$$= \int_{x_1}^{x_2} A^2 \sin^2\left(\frac{n\pi}{L}x\right) dx.$$

39.4: Wave Functions of a Trapped Electron
Normalization and Zero-Point Energy:

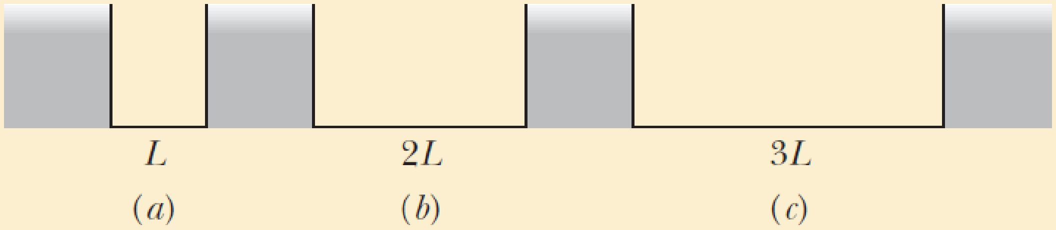
- The product $\psi_n^2(x)\,dx$ gives the probability that an electron in an infinite well can be detected in the interval of the *x* axis that lies between *x* and *x* +*dx*. We know that the electron must be somewhere in the infinite well; so it must be true that

$$\int_{-\infty}^{+\infty} \psi_n^2(x)\,dx = 1 \qquad \text{(normalization equation)}$$

$$E_n = \left(\frac{h^2}{8mL^2}\right)n^2, \qquad \text{for } n = 1, 2, 3, \ldots .$$

- n=1 in the previous equation defines the state of lowest energy for an electron in an infinite potential well, the ground state. Therefore in quantum physics confined systems cannot exist in states with zero energy. They must always have a certain minimum energy called the **zero-point energy.**

Checkpoint 2



The figure shows three infinite potential wells of widths L, $2L$, and $3L$; each contains an electron in the state for which $n = 10$. Rank the wells according to (a) the number of maxima for the probability density of the electron and (b) the energy of the electron, greatest first.

(a) all tie; (b) a, b, c

$$E_n = \left(\frac{h^2}{8mL^2}\right)n^2, \qquad \text{for } n = 1, 2, 3, \ldots .$$

Checkpoint 3

Each of the following particles is confined to an infinite well, and all four wells have the same width: (a) an electron, (b) a proton, (c) a deuteron, and (d) an alpha particle. Rank their zero-point energies, greatest first. The particles are listed in order of increasing mass.

a, b, c, d

Example, Detection probability in a 1D potential well:

$$\psi_n(x) = A \sin\left(\frac{n\pi}{L}x\right), \qquad \text{for } n = 1, 2, 3, \ldots, \tag{39-10}$$

Evaluate the amplitude constant A in Eq. 39-10 for an infinite potential well extending from $x = 0$ to $x = L$.

KEY IDEA

The wave functions of Eq. 39-10 must satisfy the normalization requirement of Eq. 39-14, which states that the probability that the electron can be detected somewhere along the x axis is 1.

Calculations: Substituting Eq. 39-10 into Eq. 39-14 and taking the constant A outside the integral yield

$$A^2 \int_0^L \sin^2\left(\frac{n\pi}{L}x\right) dx = 1. \tag{39-15}$$

We have changed the limits of the integral from $-\infty$ and $+\infty$ to 0 and L because the wave function is zero outside these new limits (so there's no need to integrate out there).

We can simplify the indicated integration by changing the variable from x to the dimensionless variable y, where

$$y = \frac{n\pi}{L}x, \tag{39-16}$$

hence

$$dx = \frac{L}{n\pi}\,dy.$$

When we change the variable, we must also change the integration limits (again). Equation 39-16 tells us that $y = 0$ when $x = 0$ and that $y = n\pi$ when $x = L$; thus 0 and $n\pi$ are our new limits. With all these substitutions, Eq. 39-15 becomes

$$A^2 \frac{L}{n\pi} \int_0^{n\pi} (\sin^2 y)\, dy = 1.$$

We can use integral 11 in Appendix E to evaluate the integral, obtaining the equation

$$\frac{A^2 L}{n\pi}\left[\frac{y}{2} - \frac{\sin 2y}{4}\right]_0^{n\pi} = 1.$$

Evaluating at the limits yields

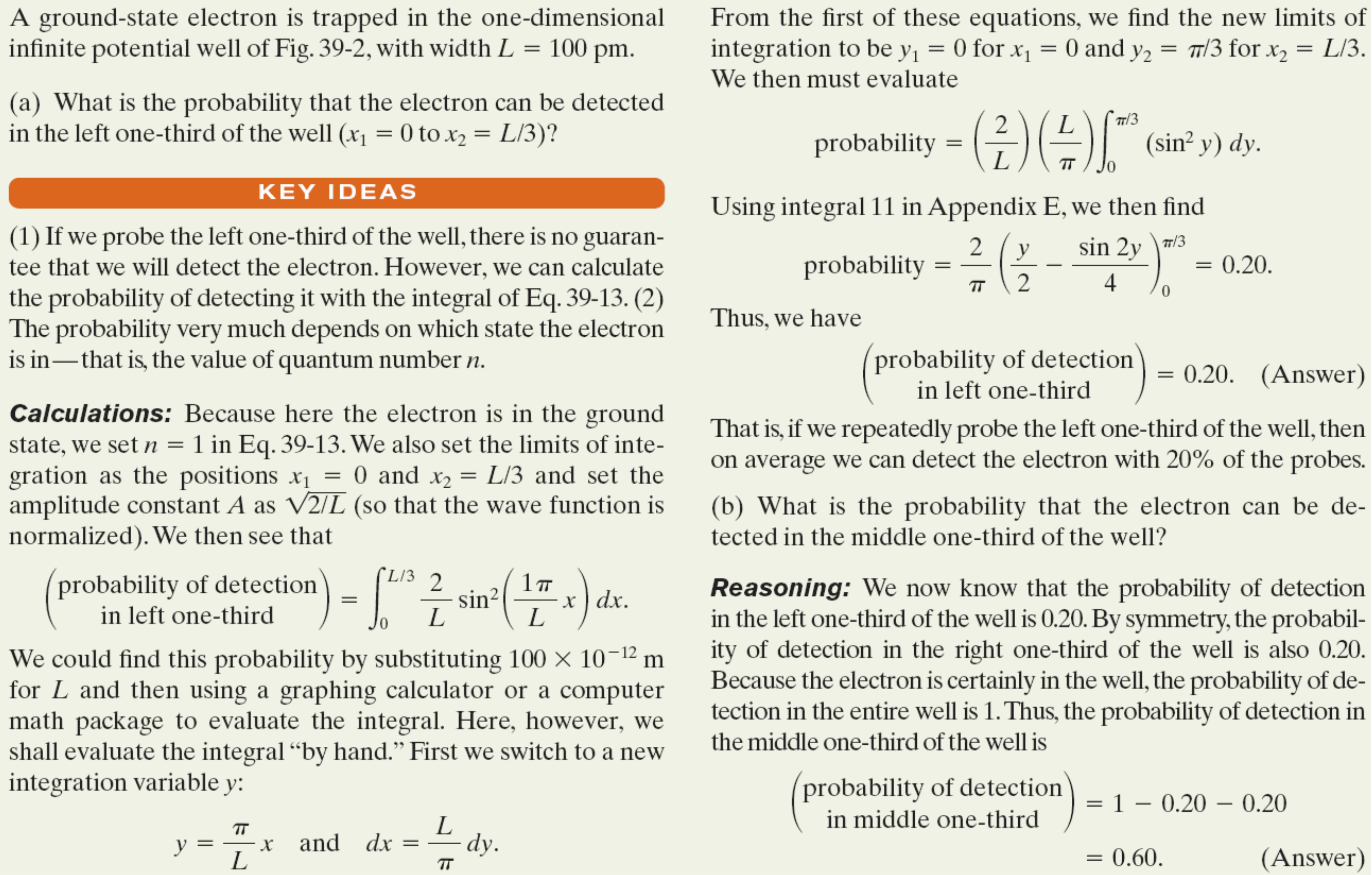
$$\frac{A^2 L}{n\pi}\,\frac{n\pi}{2} = 1;$$

thus

$$A = \sqrt{\frac{2}{L}}. \qquad \text{(Answer)} \tag{39-17}$$

This result tells us that the dimension for A^2, and thus for $\psi_n^2(x)$, is an inverse length. This is appropriate because the probability density of Eq. 39-12 is a probability *per unit length.*

Example, Detection probability in a 1D potential well:



A ground-state electron is trapped in the one-dimensional infinite potential well of Fig. 39-2, with width $L = 100$ pm.

(a) What is the probability that the electron can be detected in the left one-third of the well ($x_1 = 0$ to $x_2 = L/3$)?

KEY IDEAS

(1) If we probe the left one-third of the well, there is no guarantee that we will detect the electron. However, we can calculate the probability of detecting it with the integral of Eq. 39-13. (2) The probability very much depends on which state the electron is in—that is, the value of quantum number n.

Calculations: Because here the electron is in the ground state, we set $n = 1$ in Eq. 39-13. We also set the limits of integration as the positions $x_1 = 0$ and $x_2 = L/3$ and set the amplitude constant A as $\sqrt{2/L}$ (so that the wave function is normalized). We then see that

$$\begin{pmatrix}\text{probability of detection}\\ \text{in left one-third}\end{pmatrix} = \int_0^{L/3} \frac{2}{L} \sin^2\left(\frac{1\pi}{L}x\right) dx.$$

We could find this probability by substituting 100×10^{-12} m for L and then using a graphing calculator or a computer math package to evaluate the integral. Here, however, we shall evaluate the integral "by hand." First we switch to a new integration variable y:

$$y = \frac{\pi}{L}x \quad \text{and} \quad dx = \frac{L}{\pi}dy.$$

From the first of these equations, we find the new limits of integration to be $y_1 = 0$ for $x_1 = 0$ and $y_2 = \pi/3$ for $x_2 = L/3$. We then must evaluate

$$\text{probability} = \left(\frac{2}{L}\right)\left(\frac{L}{\pi}\right)\int_0^{\pi/3} (\sin^2 y)\, dy.$$

Using integral 11 in Appendix E, we then find

$$\text{probability} = \frac{2}{\pi}\left(\frac{y}{2} - \frac{\sin 2y}{4}\right)_0^{\pi/3} = 0.20.$$

Thus, we have

$$\begin{pmatrix}\text{probability of detection}\\ \text{in left one-third}\end{pmatrix} = 0.20. \qquad \text{(Answer)}$$

That is, if we repeatedly probe the left one-third of the well, then on average we can detect the electron with 20% of the probes.

(b) What is the probability that the electron can be detected in the middle one-third of the well?

Reasoning: We now know that the probability of detection in the left one-third of the well is 0.20. By symmetry, the probability of detection in the right one-third of the well is also 0.20. Because the electron is certainly in the well, the probability of detection in the entire well is 1. Thus, the probability of detection in the middle one-third of the well is

$$\begin{aligned}\begin{pmatrix}\text{probability of detection}\\ \text{in middle one-third}\end{pmatrix} &= 1 - 0.20 - 0.20\\ &= 0.60. \qquad \text{(Answer)}\end{aligned}$$

An Electron in a Finite Well:

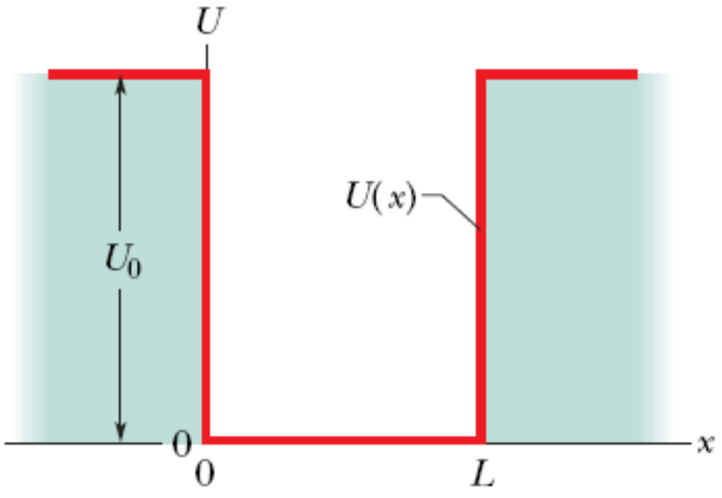


Fig. 39-7 A *finite* potential energy well. The depth of the well is U_0 and its width is L. As in the infinite potential well of Fig. 39-2, the motion of the trapped electron is restricted to the x direction.

To find the wave functions describing the quantum states of an electron in the finite well of Fig. 39-7, one needs to consider Schrödinger's equation.

For motion in one dimension, Schrödinger's equation in the form is:

$$\frac{d^2\psi}{dx^2} + \frac{8\pi^2 m}{h^2}[E - U(x)]\psi = 0.$$

An Electron in a Finite Well:

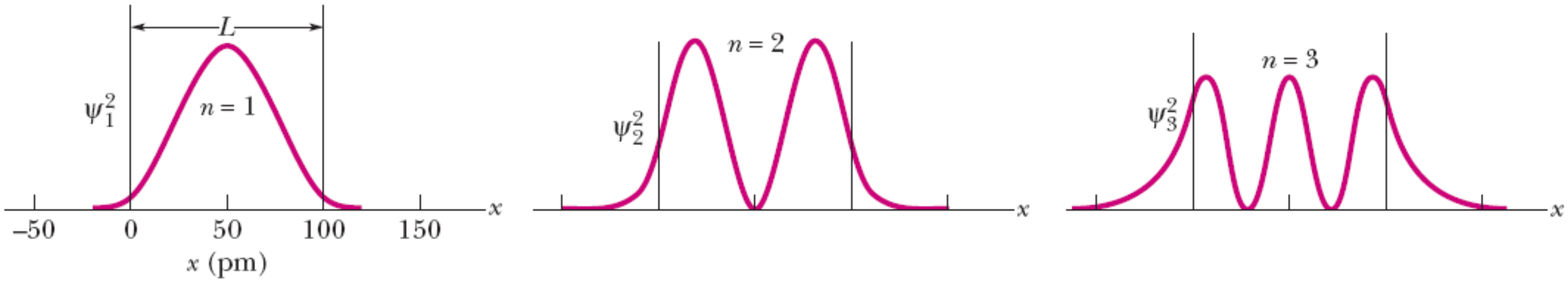


Fig. 39-8 The first three probability densities for an electron confined to a finite potential well of depth U_0 =450 eV and width L =100 pm. Only states n =1, 2, 3, and 4 are allowed.

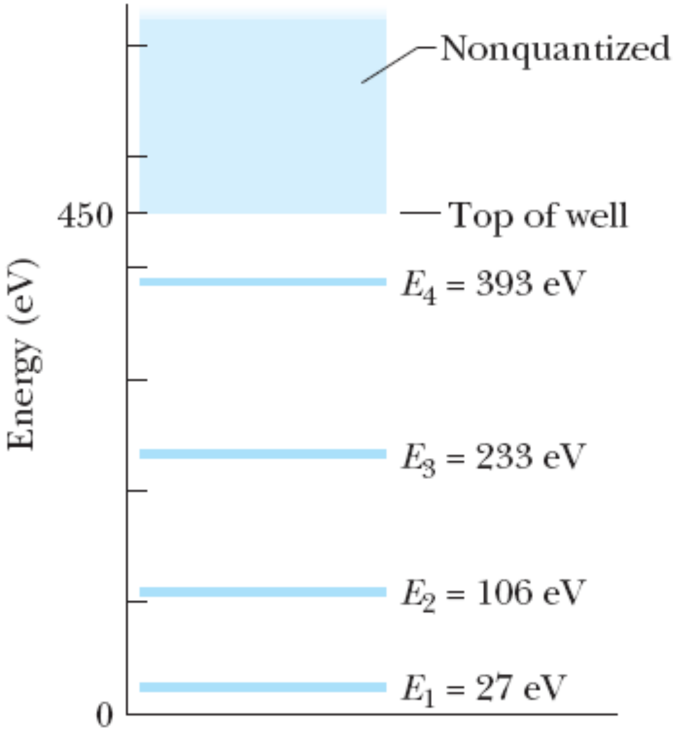
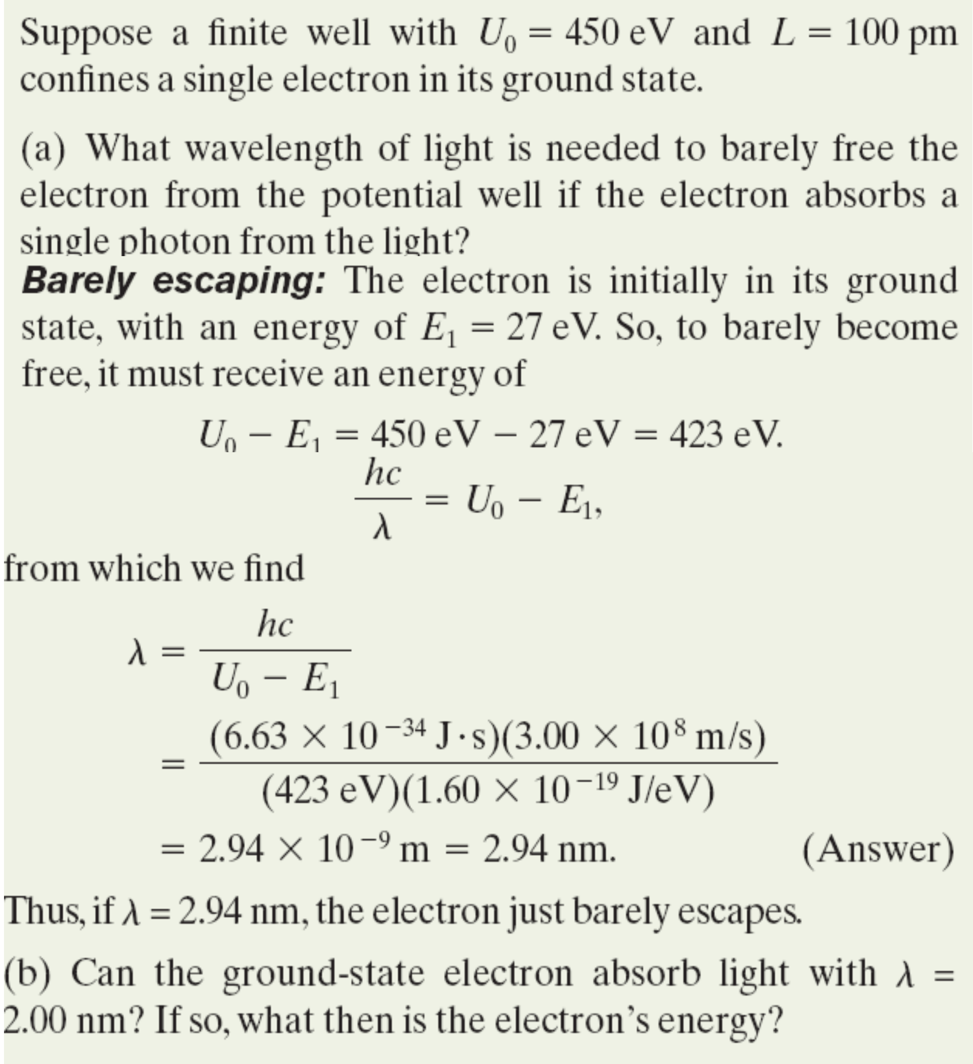


Fig. 39-9 The energy-level diagram corresponding to the probability densities of Fig. 39-8. If an electron is trapped in the finite potential well, it can have only the energies corresponding to $n = 1, 2, 3,$ and 4. If it has an energy of 450 eV or greater, it is not trapped and its energy is not quantized.

For a finite well, the electron matter wave penetrates the walls of the well—into a region in which Newtonian mechanics says the electron cannot exist.

However, from the plots in Fig. 39-8, we see there is leakage into the walls, and that the leakage is greater for greater values of quantum number *n*.

Example, Electron escaping from a finite well:



Suppose a finite well with $U_0 = 450$ eV and $L = 100$ pm confines a single electron in its ground state.

(a) What wavelength of light is needed to barely free the electron from the potential well if the electron absorbs a single photon from the light?

Barely escaping: The electron is initially in its ground state, with an energy of $E_1 = 27$ eV. So, to barely become free, it must receive an energy of

$$U_0 - E_1 = 450\text{ eV} - 27\text{ eV} = 423\text{ eV}.$$

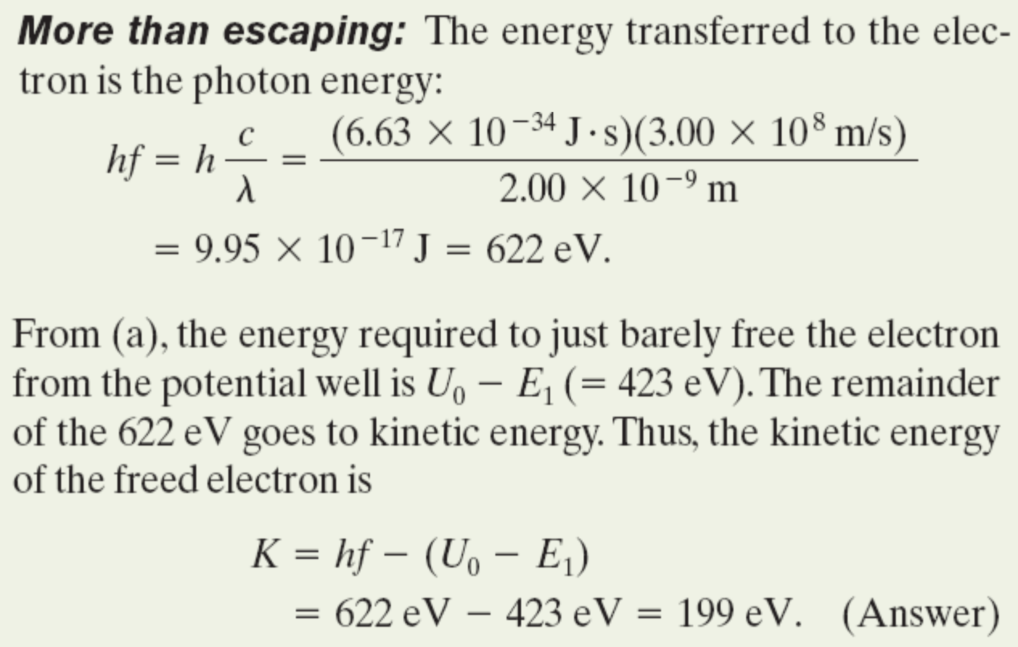
$$\frac{hc}{\lambda} = U_0 - E_1,$$

from which we find

$$\begin{aligned}\lambda &= \frac{hc}{U_0 - E_1} \\ &= \frac{(6.63 \times 10^{-34}\text{ J}\cdot\text{s})(3.00 \times 10^{8}\text{ m/s})}{(423\text{ eV})(1.60 \times 10^{-19}\text{ J/eV})} \\ &= 2.94 \times 10^{-9}\text{ m} = 2.94\text{ nm}. \qquad \text{(Answer)}\end{aligned}$$

Thus, if $\lambda = 2.94$ nm, the electron just barely escapes.

(b) Can the ground-state electron absorb light with $\lambda = 2.00$ nm? If so, what then is the electron's energy?



More than escaping: The energy transferred to the electron is the photon energy:

$$\begin{aligned}hf = h\frac{c}{\lambda} &= \frac{(6.63 \times 10^{-34}\text{ J}\cdot\text{s})(3.00 \times 10^{8}\text{ m/s})}{2.00 \times 10^{-9}\text{ m}} \\ &= 9.95 \times 10^{-17}\text{ J} = 622\text{ eV}.\end{aligned}$$

From (a), the energy required to just barely free the electron from the potential well is $U_0 - E_1$ (= 423 eV). The remainder of the 622 eV goes to kinetic energy. Thus, the kinetic energy of the freed electron is

$$\begin{aligned}K &= hf - (U_0 - E_1) \\ &= 622\text{ eV} - 423\text{ eV} = 199\text{ eV}. \qquad \text{(Answer)}\end{aligned}$$

More Electron Traps, Nanocrystallites:

Fig. 39-10 Two samples of powdered cadmium selenide, a semiconductor, differing only in the size of their granules. Each granule serves as an electron trap. The lower sample has the larger granules and consequently the smaller spacing between energy levels and the lower photon energy threshold for the absorption of light. Light not absorbed is scattered, causing the sample to scatter light of greater wavelength and appear red. The upper sample, because of its smaller granules, and consequently its larger level spacing and its larger energy threshold for absorption, appears yellow. *(From Scientific American, January 1993,page 122.Reproduced with permission of Michael Steigerwald, Bell Labs–Lucent Technologies)*

$$(E = (h^2/8mL^2)n^2)$$

A given nanocrystallite can absorb photons with an energy above a certain threshold energy E_t $(=hf_t)$ and thus wavelengths below a corresponding threshold wavelength $\lambda_t = \frac{c}{f_t} = \frac{ch}{E_t}$.

More Electron Traps, Quantum Dots:

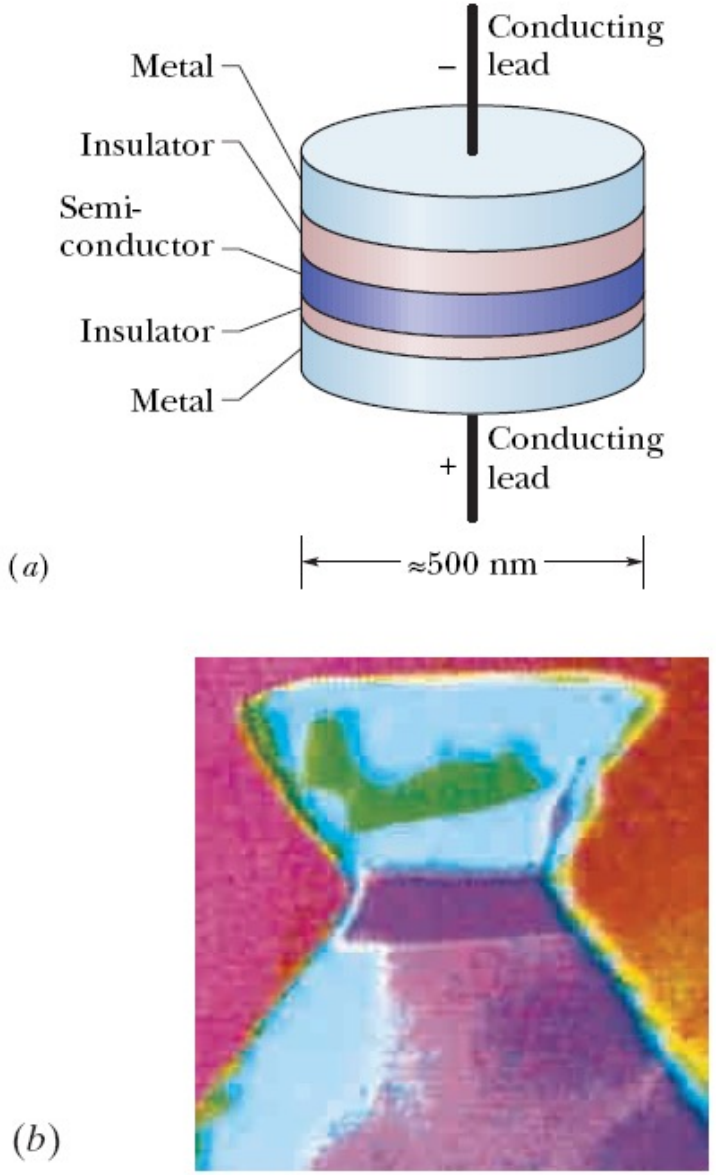
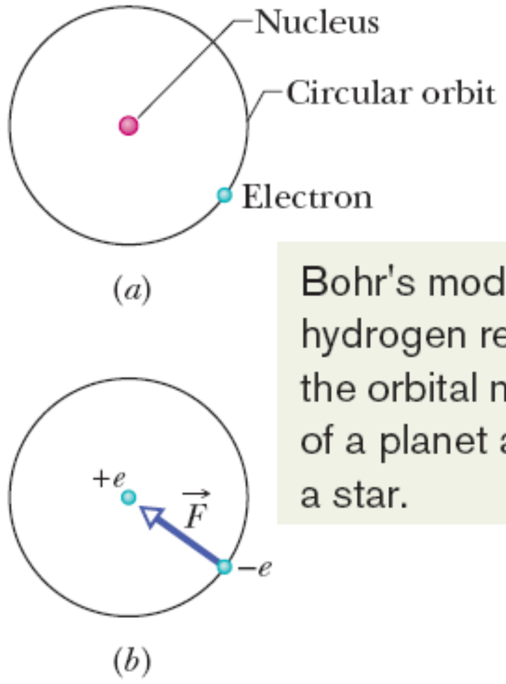


Fig. 39-11 A quantum dot, or "artificial atom." (*a*) A central semiconducting layer forms a potential energy well in which electrons are trapped. The lower insulating layer is thin enough to allow electrons to be added to or removed from the central layer by barrier tunneling if an appropriate voltage is applied between the leads. (*b*) A photograph of an actual quantum dot. The central purple band is the electron confinement region. *(From* Scientific American, *September 1995, page 67. Image reproduced with permission of H. Temkin, Texas Tech University)*

39.5: The Bohr Model of the Hydrogen Atom:



(a)

(b)

Bohr's model for hydrogen resembles the orbital model of a planet around a star.

Fig. 39-16 (*a*) Circular orbit of an electron in the Bohr model of the hydrogen atom. (*b*) The Coulomb force $\vec{F}$ on the electron is directed radially inward toward the nucleus.

$$F = k\frac{|q_1||q_2|}{r^2},$$

$$-\frac{1}{4\pi\varepsilon_0}\frac{e^2}{r^2} = m\left(-\frac{v^2}{r}\right),$$

The angular momentum: $\ell = rmv \sin\phi,$

$$= rmv \sin 90^\circ$$

For quantization of *l*, $rmv = n\hbar,$

$$v = \frac{n\hbar}{rm}.$$

$$r = \frac{h^2\varepsilon_0}{\pi m e^2}n^2, \qquad \text{for } n = 1, 2, 3, \ldots .$$

$$r = an^2, \qquad \text{for } n = 1, 2, 3, \ldots ,$$

$$a = \frac{h^2\varepsilon_0}{\pi m e^2} = 5.291\,772 \times 10^{-11}\ \text{m} \approx 52.92\ \text{pm}.$$

39.5: The Bohr Model of the Hydrogen Atom, Orbital energy is quantized:

$$
\begin{aligned}
E &= K + U \\
&= \tfrac{1}{2}mv^2 + \left(-\frac{1}{4\pi\varepsilon_0}\frac{e^2}{r}\right).
\end{aligned}
$$

$$rmv = n\hbar,$$

$$v = \frac{n\hbar}{rm}.$$

⇨ $$E = -\frac{1}{8\pi\varepsilon_0}\frac{e^2}{r}.$$

⇨ $$E_n = -\frac{me^4}{8\varepsilon_0^2h^2}\frac{1}{n^2}, \qquad \text{for } n = 1, 2, 3, \ldots,$$

⇨ $$E_n = -\frac{2.180 \times 10^{-18}\,\text{J}}{n^2} = -\frac{13.61\,\text{eV}}{n^2}, \qquad \text{for } n = 1, 2, 3, \ldots.$$

39.5: The Bohr Model of the Hydrogen Atom, Energy Changes:

$$hf = \Delta E = E_{\text{high}} - E_{\text{low}}.$$

⬇

$$\frac{1}{\lambda} = -\frac{me^4}{8\varepsilon_0^2 h^3 c}\left(\frac{1}{n_{\text{high}}^2} - \frac{1}{n_{\text{low}}^2}\right).$$

⬇

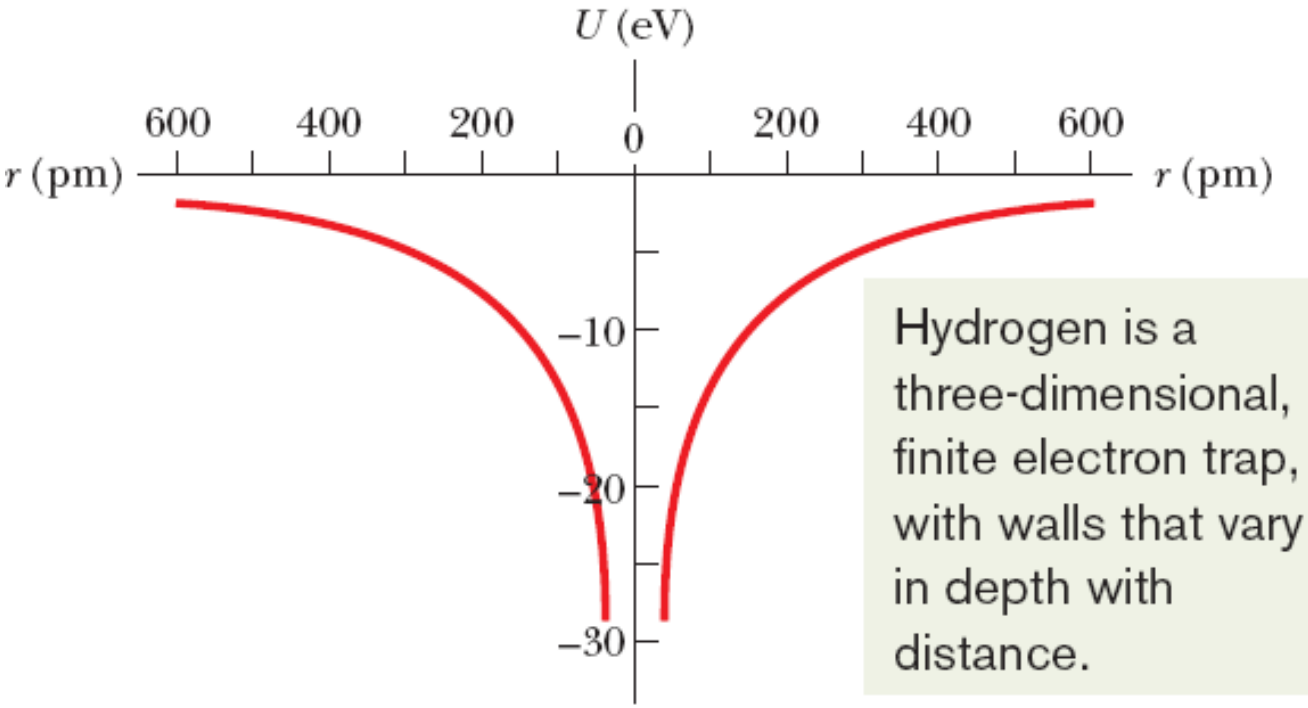
$$\frac{1}{\lambda} = R\left(\frac{1}{n_{\text{low}}^2} - \frac{1}{n_{\text{high}}^2}\right),$$

$$R = \frac{me^4}{8\varepsilon_0^2 h^3 c} = 1.097\,373 \times 10^7\ \text{m}^{-1} \qquad \text{(Rydberg Constant)}$$

$h = 4.1357 \times 10^{-15}$ eV s

R= 13.6 eV

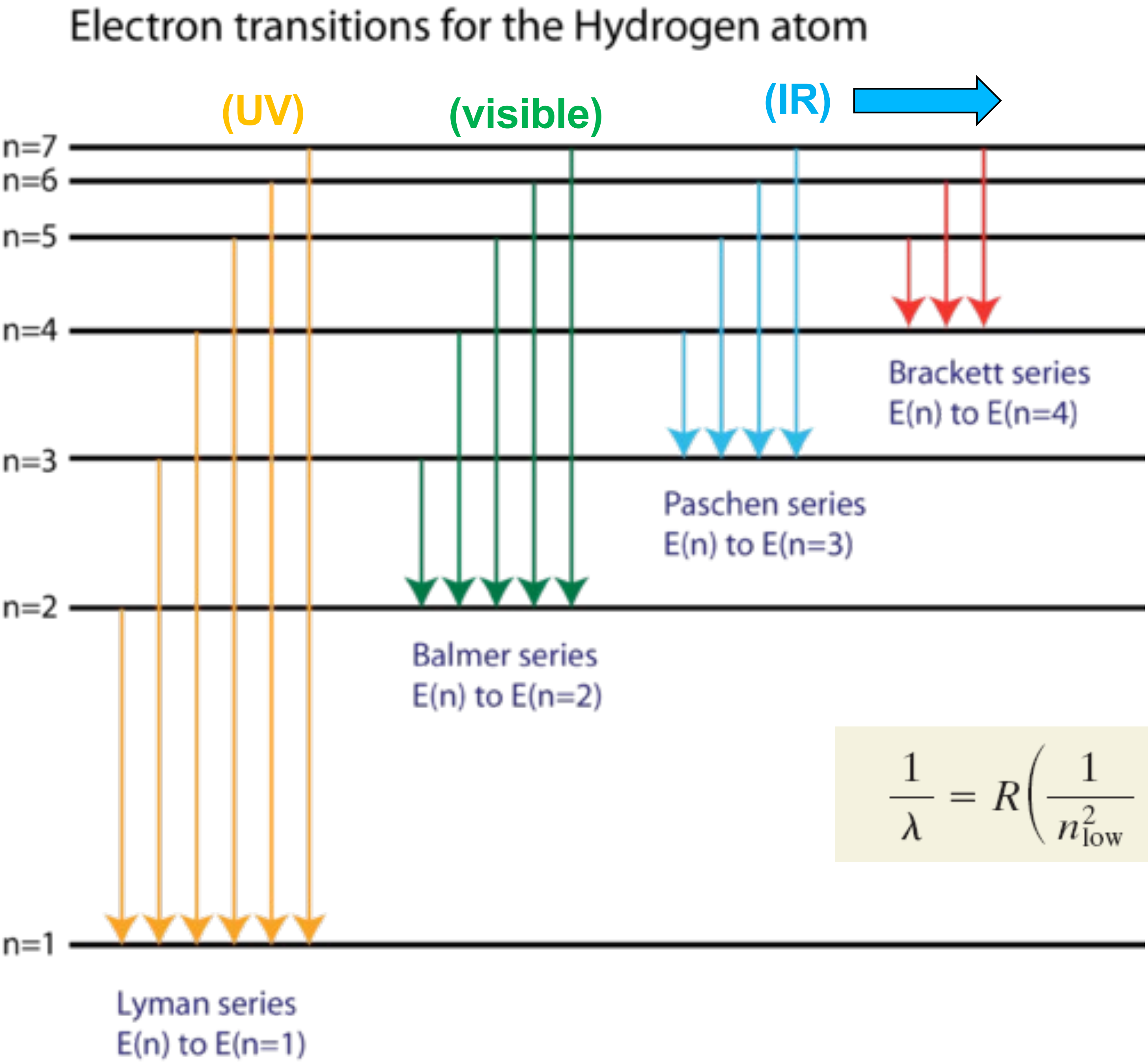
39.9: Schrodinger’s Equation and The Hydrogen Atom:



Hydrogen is a three-dimensional, finite electron trap, with walls that vary in depth with distance.

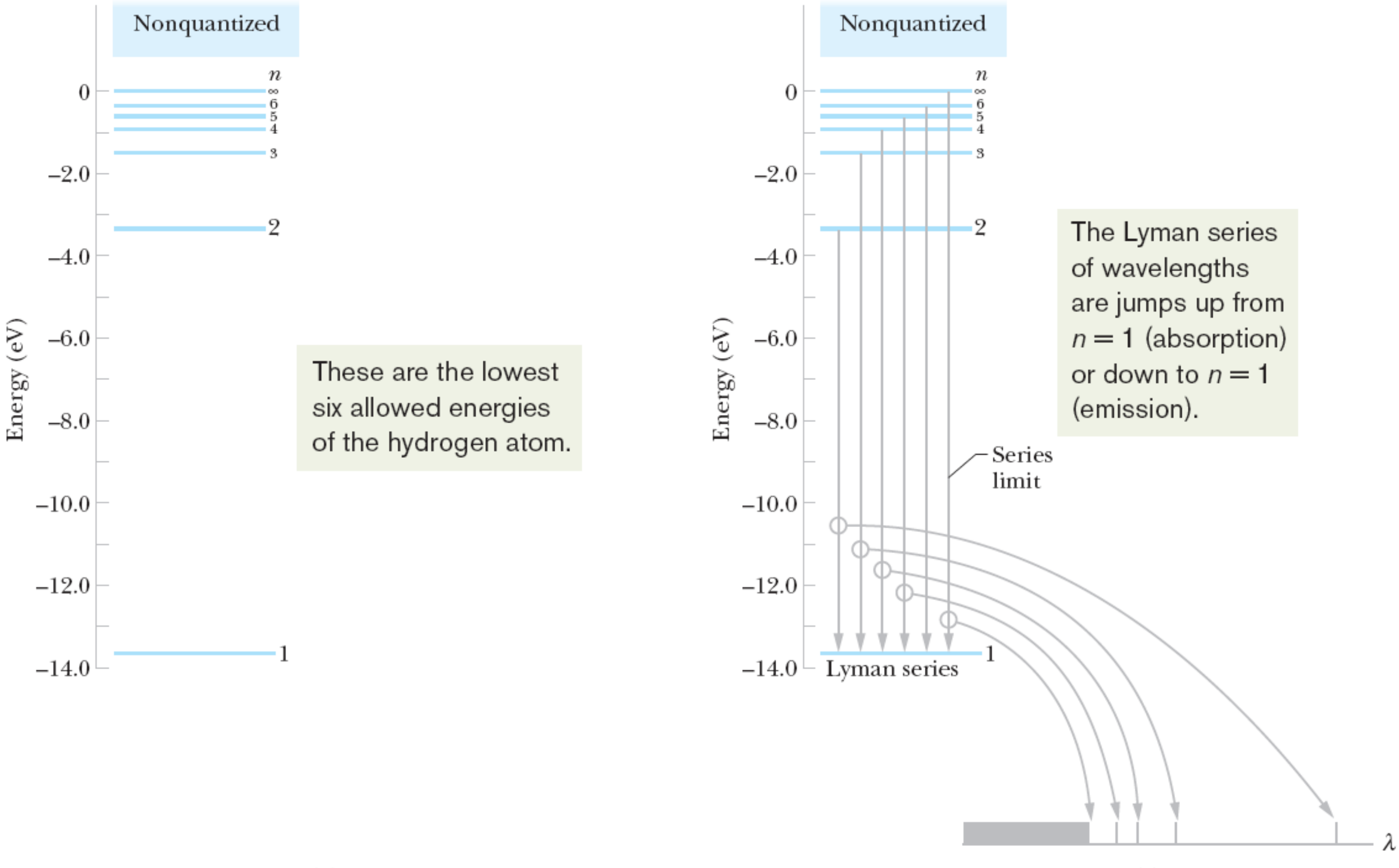
Fig. 39-17 The potential energy U of a hydrogen atom as a function of the separation r between the electron and the central proton. The plot is shown twice (on the left and on the right) to suggest the three-dimensional spherically symmetric trap in which the electron is confined.

Bohr Model of the Hydrogen Atom, Electron Transitions, Atomic Energy Levels, Lyman & Balmer Series



$$\frac{1}{\lambda} = R\left(\frac{1}{n_{\text{low}}^2} - \frac{1}{n_{\text{high}}^2}\right),$$

Schrodinger’s Equation and The Hydrogen Atom:



These are the lowest six allowed energies of the hydrogen atom.

The Lyman series of wavelengths are jumps up from $n = 1$ (absorption) or down to $n = 1$ (emission).

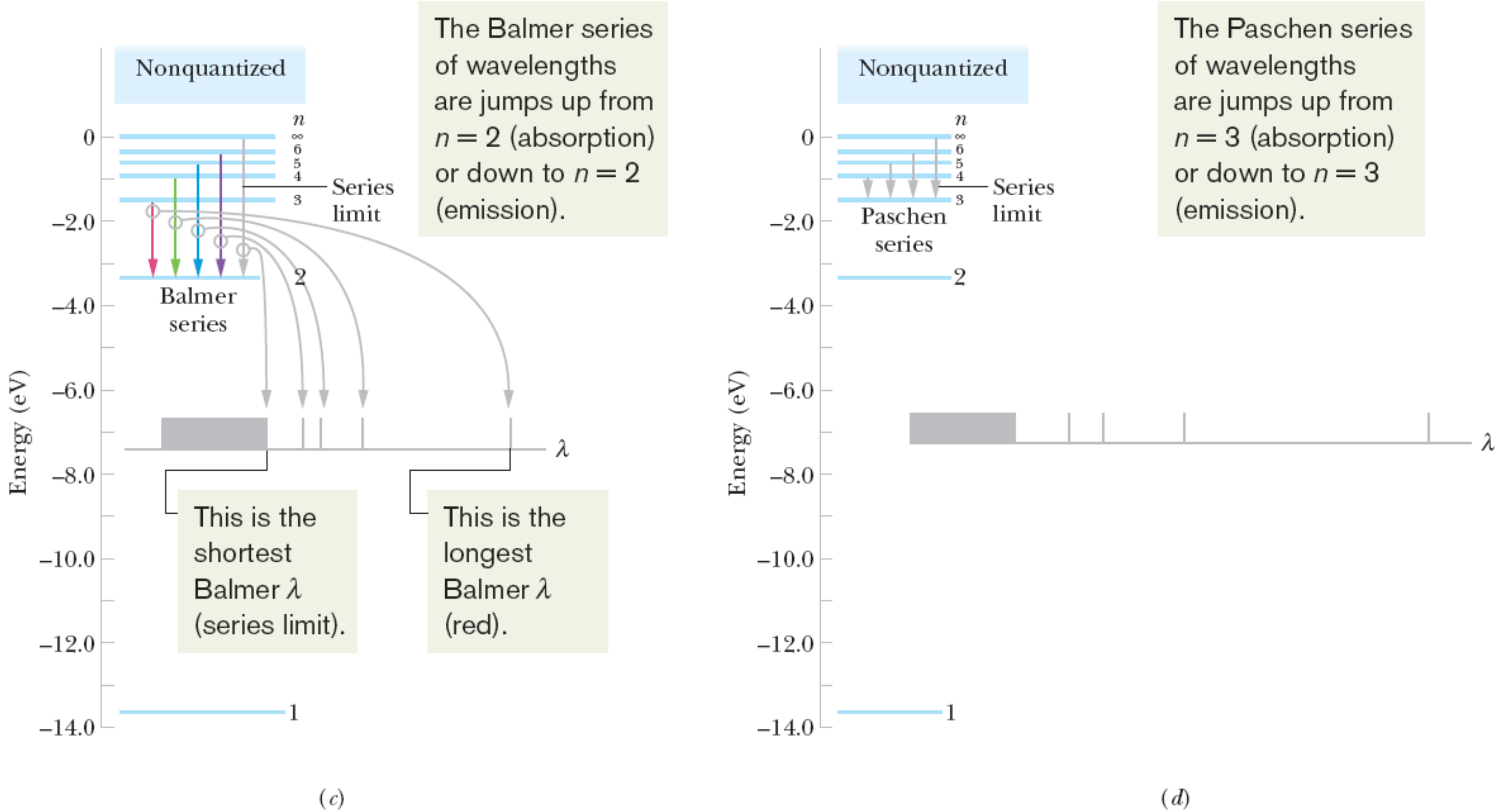
(a)

(b)

Fig. 39-18 (a) An energy-level diagram for the hydrogen atom. Some of the transitions for (b) the Lyman series. For each, the longest four wavelengths and the series-limit wavelength are plotted on a wavelength axis. Any wavelength shorter than the series-limit wavelength is allowed.

Schrodinger’s Equation and The Hydrogen Atom:

Fig. 39-18 Some of the transitions for (c) the Balmer series, and (d) the Paschen series. For each, the longest four wavelengths and the series-limit wavelength are plotted on a wavelength axis. Any wavelength shorter than the series-limit wavelength is allowed.



The Balmer series of wavelengths are jumps up from $n = 2$ (absorption) or down to $n = 2$ (emission).

This is the shortest Balmer λ (series limit).

This is the longest Balmer λ (red).

The Paschen series of wavelengths are jumps up from $n = 3$ (absorption) or down to $n = 3$ (emission).

Q: A photon is emitted as an atom makes a transition from n = 4 to n = 2 level. What is the frequency, wavelength and energy of the emitted photon?

Solution:

$$\begin{aligned} E &= -13.6\left[\frac{1}{n_f^2}-\frac{1}{n_i^2}\right] \text{ eV} \\ &= -13.6\left[\frac{1}{2^2}-\frac{1}{4^2}\right] \text{ eV} \\ &= -13.6\left[\frac{1}{4}-\frac{1}{16}\right] \text{ eV} \\ &= -13.6 \times \frac{3}{16} \text{ eV} \\ &= \text{-}2.55 \text{ eV.} \end{aligned}$$

The negative sign shows that photon has been emitted.

$$\begin{aligned} c &= f\lambda \\ \Rightarrow \lambda &= \frac{c}{f} = \frac{3\times10^{8} \text{ m/s}}{6.15\times10^{14} \text{ Hz}} \\ &= 4.875\times10^{-7} \text{ m} \\ &= 488 \text{ nm.} \end{aligned}$$

Thus frequency of photon will be,

$$\begin{aligned} f &= \frac{E}{h} = \frac{2.55 \text{ eV}}{6.63\times10^{-34} \text{ Js}} \\ &= \frac{2.55\times1.6\times10^{-19} \text{ J}}{6.63\times10^{-34} \text{ Js}} \\ &= 6.15\times10^{14} \text{ Hz.} \end{aligned}$$

Q: A Hydrogen atom initially in its ground state i.e., n = 1 level, absorbs a photon and ends up in n = 4 level. What must have been the frequency of the photon? Now the electron makes spontaneous emission and comes back to the ground state. What are the possible frequencies of the photons emitted during this process.

Solution:

We are given that,

$$\begin{aligned} \text{Initial state of electron} &= n_i = 1 \\ \text{final state of electron} &= n_f = 4. \end{aligned}$$

We want to calculate the frequency of photon absorbed by the electron to make this transition. As we know that energy of photon absorbed is given by,

$$\begin{aligned} E &= -13.6\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right) \text{ eV} \\ hf &= -13.6\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right) \text{ eV} \\ f &= -\frac{13.6}{h}\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right) \text{ eV} \\ &= -\frac{13.6}{4.14 \times 10^{-15} \text{ eVs}}\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right) \text{ eV} \\ &= -3.28 \times 10^{15}\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right) \text{ Hz} \\ f_{1\to 4} &= -3.28 \times 10^{15}\left(\frac{1}{4^2} - \frac{1}{1^2}\right) \text{ Hz} \\ &= -3.28 \times 10^{15}\left(\frac{1}{16} - 1\right) \text{ Hz} \\ &= -3.28 \times 10^{15} \times \frac{-15}{16} \text{ Hz} \\ &= +3.08 \times 10^{15} \text{ Hz,} \end{aligned}$$

The positive sign shows that photon has been absorbed.

Direct Transition from n = 4 to n = 1

$$f_{4\to 1} = -3.08 \times 10^{15} \text{ Hz,}$$

Indirect Transitions

(a) From level 4 to level 2 and then from 2 to level 1.
(b) From level 4 to level 3 and then from 3 to level 1.
(c) From level 4 to level 3, then from level 3 to level 2 and then finally from level 2 to level 1.

From $n = 4$ **to** $n = 2$

$$\begin{aligned} f_{4\to 2} &= -3.28 \times 10^{15}\left(\frac{1}{2^2} - \frac{1}{4^2}\right) \text{ Hz} \\ &= -6.15 \times 10^{14} \text{ Hz.} \end{aligned}$$

From $n = 2$ **to** $n = 1$

$$\begin{aligned} f_{2\to 1} &= -3.28 \times 10^{15}\left(\frac{1}{1^2} - \frac{1}{2^2}\right) \text{ Hz} \\ &= -2.46 \times 10^{15} \text{ Hz.} \end{aligned}$$

From $n = 4$ **to** $n = 3$

$$\begin{aligned} f_{4\to 3} &= -3.28 \times 10^{15}\left(\frac{1}{3^2} - \frac{1}{4^2}\right) \text{ Hz} \\ &= -1.6 \times 10^{14} \text{ Hz.} \end{aligned}$$

From $n = 3$ **to** $n = 1$

$$\begin{aligned} f_{3\to 1} &= -3.28 \times 10^{15}\left(\frac{1}{1^2} - \frac{1}{3^2}\right) \text{ Hz} \\ &= -2.92 \times 10^{15} \text{ Hz.} \end{aligned}$$

From $n = 3$ **to** $n = 2$

$$\begin{aligned} f_{3\to 2} &= -3.28 \times 10^{15}\left(\frac{1}{2^2} - \frac{1}{3^2}\right) \text{ Hz} \\ &= -4.57 \times 10^{1} \text{ Hz.} \end{aligned}$$

Negative sign with each frequency represents that photon has been emitted.

Quantum Numbers and The Hydrogen Atom:

Each set of quantum numbers (n, l, m_l) identifies the wave function of a particular quantum state. The quantum number n, is called the **principal quantum number.** The **orbital quantum number** l is a measure of the magnitude of the angular momentum associated with the quantum state. The **orbital magnetic quantum number** m_l is related to the orientation in space of this angular momentum vector.

The restrictions on the values of the quantum numbers for the hydrogen atom, as listed in Table 39-2, are not arbitrary but come out of the solution to Schrödinger's equation.

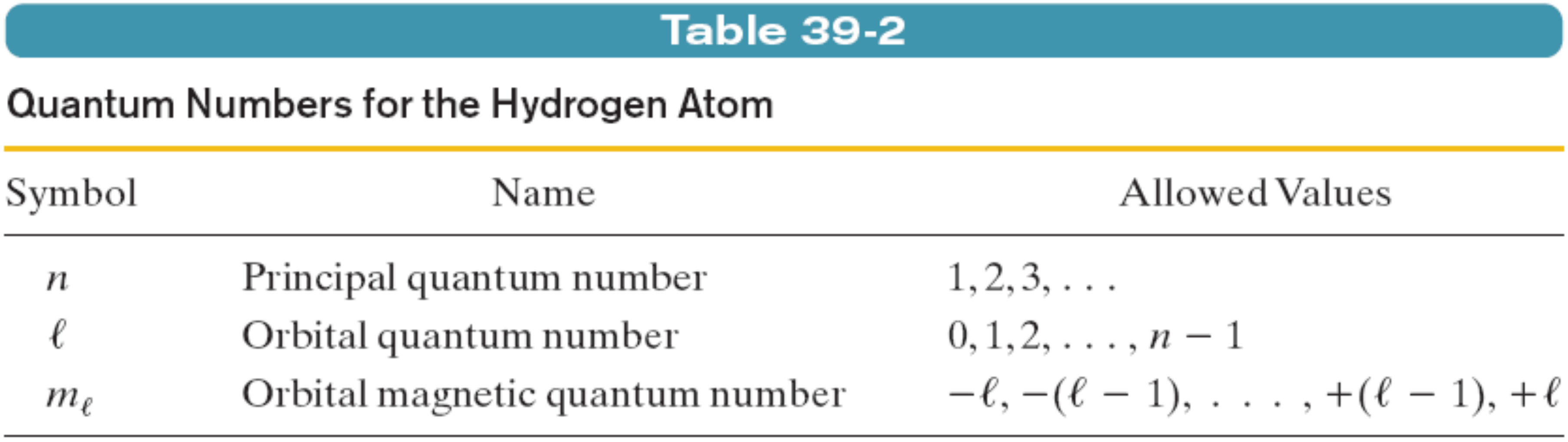


Table 39-2

Quantum Numbers for the Hydrogen Atom

Symbol	Name	Allowed Values
n	Principal quantum number	$1, 2, 3, \ldots$
ℓ	Orbital quantum number	$0, 1, 2, \ldots, n-1$
m_ℓ	Orbital magnetic quantum number	$-\ell, -(\ell-1), \ldots, +(\ell-1), +\ell$

☑ Checkpoint 5

(a) A group of quantum states of the hydrogen atom has $n = 5$. How many values of ℓ are possible for states in this group? (b) A subgroup of hydrogen atom states in the $n = 5$ group has $\ell = 3$. How many values of m_ℓ are possible for states in this subgroup?

(a) 5; (b) 7

The Wave Functions of the Hydrogen Atom's Ground State:

The wave function for the ground state of the hydrogen atom, obtained by solving the three-dimensional Schrödinger equation and normalizing is

$$\psi(r) = \frac{1}{\sqrt{\pi} a^{3/2}} e^{-r/a} \qquad \text{(ground state)}$$

where a is the *Bohr radius.*

The probability that an electron can be detected in any given (infinitesimal) volume element dV located at radius r, of width dr, from the center of the atom is

$$\psi^2(r)\, dV = \frac{4}{a^3} e^{-2r/a} r^2\, dr.$$

in which $4\pi r^2$ is the surface area of the inner shell and dr is the radial distance between the two shells.

The **radial probability density** $P(r)$ is a linear probability density such that

$$P(r)\, dr = \psi^2(r)\, dV.$$

This leads to:

$$\boxed{P(r) = \frac{4}{a^3} r^2 e^{-2r/a} \qquad \text{(radial probability density, hydrogen atom ground state).}}$$

The Wave Functions of the Hydrogen Atom's Ground State:

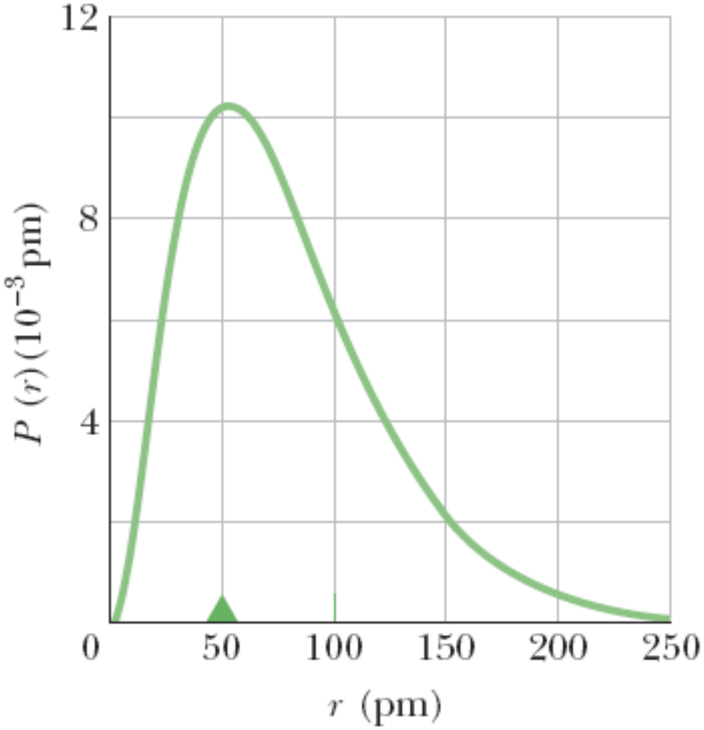


Fig. 39-19 A plot of the radial probability density $P(r)$ for the ground state of the hydrogen atom. The triangular marker is located at one Bohr radius from the origin, and the origin represents the center of the atom.

$$\boxed{\int_0^\infty P(r)\,dr = 1.}$$

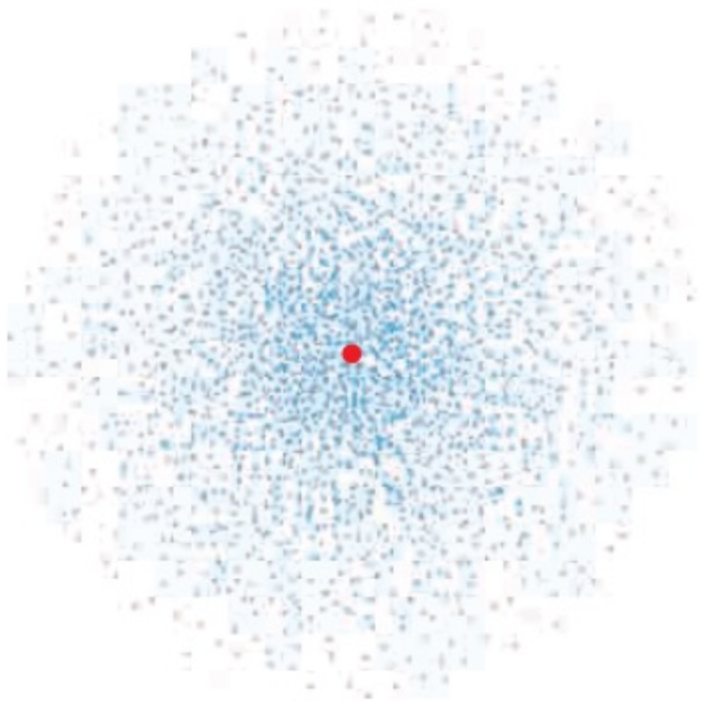
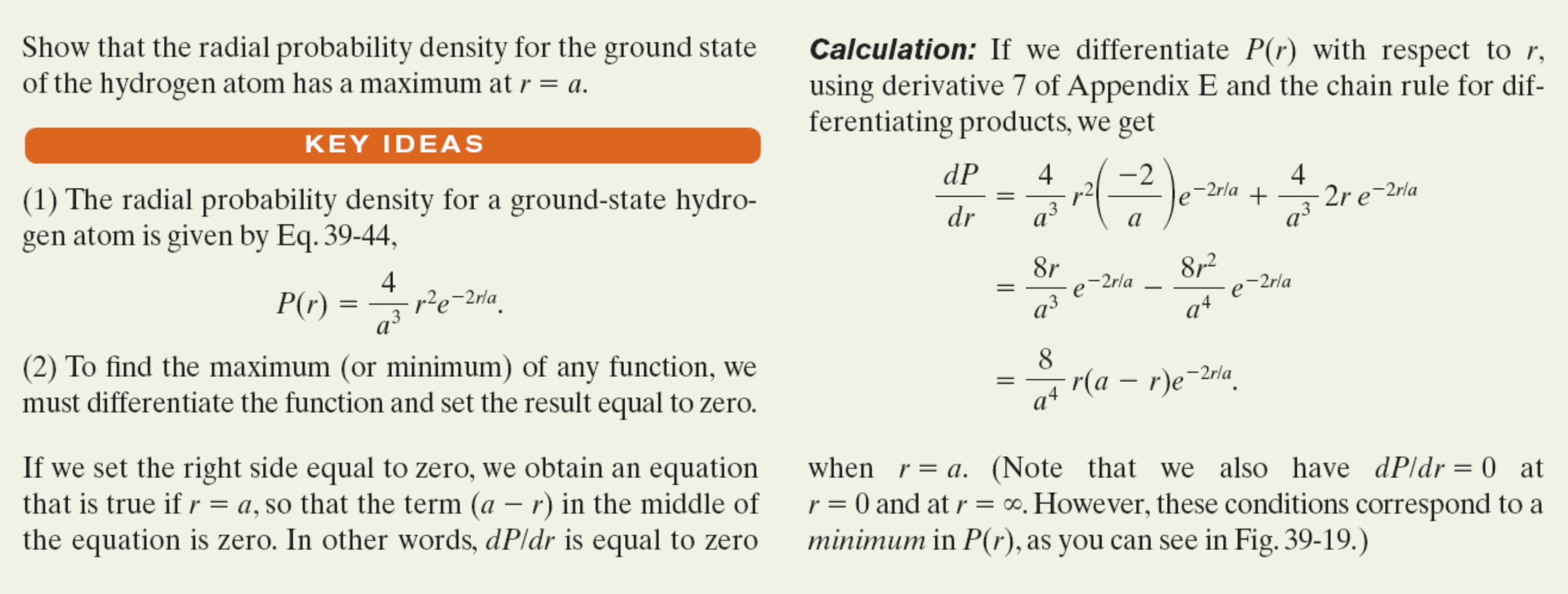


Fig. 39-20 A "dot plot" showing the volume probability density $\psi^2(r)$—not the *radial* probability density $P(r)$—for the ground state of the hydrogen atom. The density of dots drops exponentially with increasing distance from the nucleus, which is represented here by a red spot.

Example, Probability of detection of an electron in a hydrogen atom:



Show that the radial probability density for the ground state of the hydrogen atom has a maximum at $r = a$.

KEY IDEAS

(1) The radial probability density for a ground-state hydrogen atom is given by Eq. 39-44,

$$P(r) = \frac{4}{a^3} r^2 e^{-2r/a}.$$

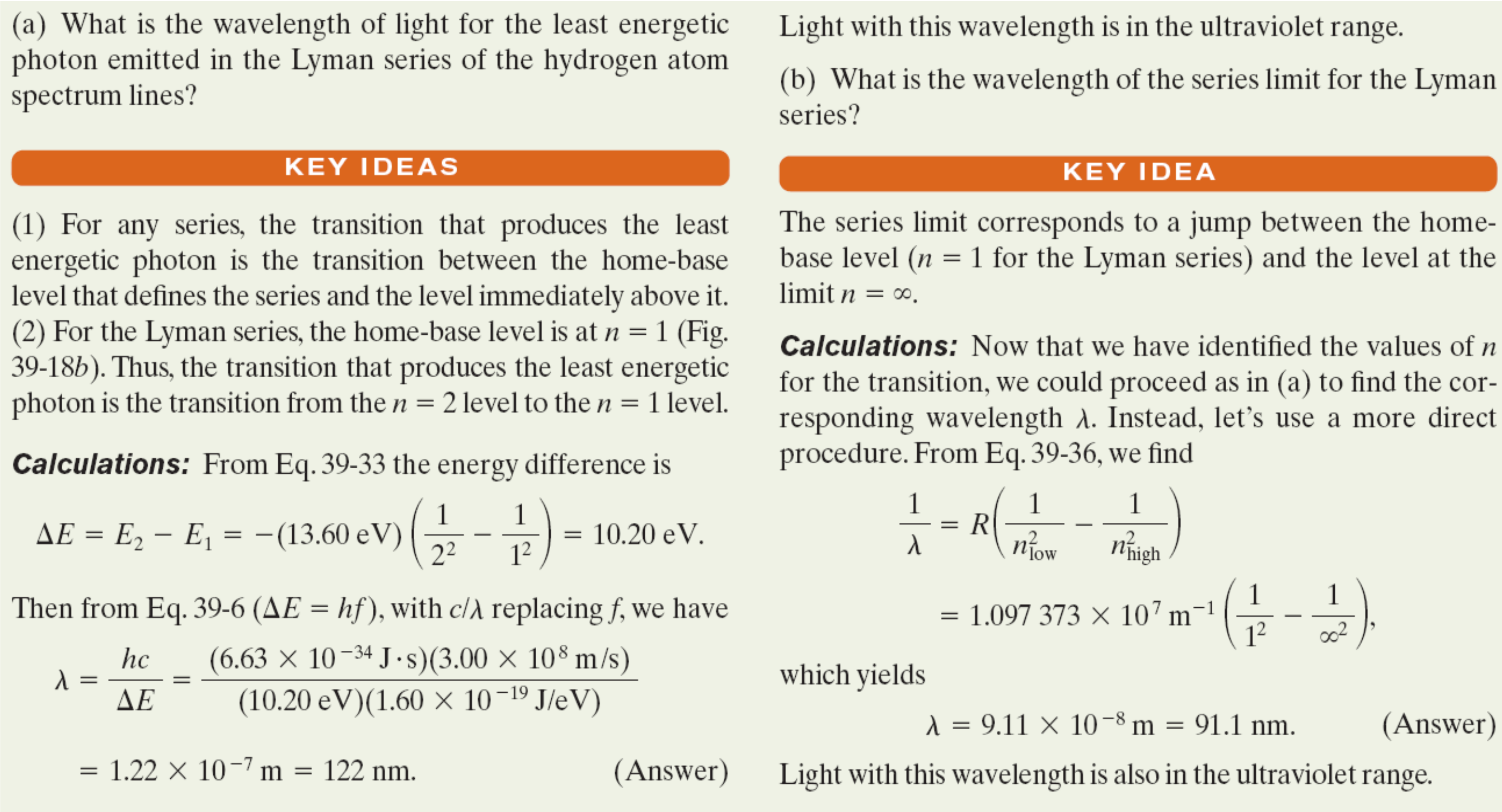
(2) To find the maximum (or minimum) of any function, we must differentiate the function and set the result equal to zero.

Calculation: If we differentiate $P(r)$ with respect to r, using derivative 7 of Appendix E and the chain rule for differentiating products, we get

$$\begin{aligned}\frac{dP}{dr} &= \frac{4}{a^3} r^2 \left(\frac{-2}{a}\right) e^{-2r/a} + \frac{4}{a^3} 2r\, e^{-2r/a} \\ &= \frac{8r}{a^3} e^{-2r/a} - \frac{8r^2}{a^4} e^{-2r/a} \\ &= \frac{8}{a^4} r(a - r) e^{-2r/a}.\end{aligned}$$

If we set the right side equal to zero, we obtain an equation that is true if $r = a$, so that the term $(a - r)$ in the middle of the equation is zero. In other words, dP/dr is equal to zero when $r = a$. (Note that we also have $dP/dr = 0$ at $r = 0$ and at $r = \infty$. However, these conditions correspond to a *minimum* in $P(r)$, as you can see in Fig. 39-19.)

Example, Light emission from a hydrogen atom:



(a) What is the wavelength of light for the least energetic photon emitted in the Lyman series of the hydrogen atom spectrum lines?

KEY IDEAS

(1) For any series, the transition that produces the least energetic photon is the transition between the home-base level that defines the series and the level immediately above it. (2) For the Lyman series, the home-base level is at $n = 1$ (Fig. 39-18*b*). Thus, the transition that produces the least energetic photon is the transition from the $n = 2$ level to the $n = 1$ level.

Calculations: From Eq. 39-33 the energy difference is

$$\Delta E = E_2 - E_1 = -(13.60\ \text{eV})\left(\frac{1}{2^2} - \frac{1}{1^2}\right) = 10.20\ \text{eV}.$$

Then from Eq. 39-6 ($\Delta E = hf$), with c/λ replacing f, we have

$$\lambda = \frac{hc}{\Delta E} = \frac{(6.63 \times 10^{-34}\ \text{J}\cdot\text{s})(3.00 \times 10^{8}\ \text{m/s})}{(10.20\ \text{eV})(1.60 \times 10^{-19}\ \text{J/eV})}$$

$$= 1.22 \times 10^{-7}\ \text{m} = 122\ \text{nm}. \qquad \text{(Answer)}$$

Light with this wavelength is in the ultraviolet range.

(b) What is the wavelength of the series limit for the Lyman series?

KEY IDEA

The series limit corresponds to a jump between the home-base level ($n = 1$ for the Lyman series) and the level at the limit $n = \infty$.

Calculations: Now that we have identified the values of n for the transition, we could proceed as in (a) to find the corresponding wavelength λ. Instead, let's use a more direct procedure. From Eq. 39-36, we find

$$\frac{1}{\lambda} = R\left(\frac{1}{n_{\text{low}}^2} - \frac{1}{n_{\text{high}}^2}\right)$$

$$= 1.097\,373 \times 10^{7}\ \text{m}^{-1}\left(\frac{1}{1^2} - \frac{1}{\infty^2}\right),$$

which yields

$$\lambda = 9.11 \times 10^{-8}\ \text{m} = 91.1\ \text{nm}. \qquad \text{(Answer)}$$

Light with this wavelength is also in the ultraviolet range.

Hydrogen Atom States with n = 2:

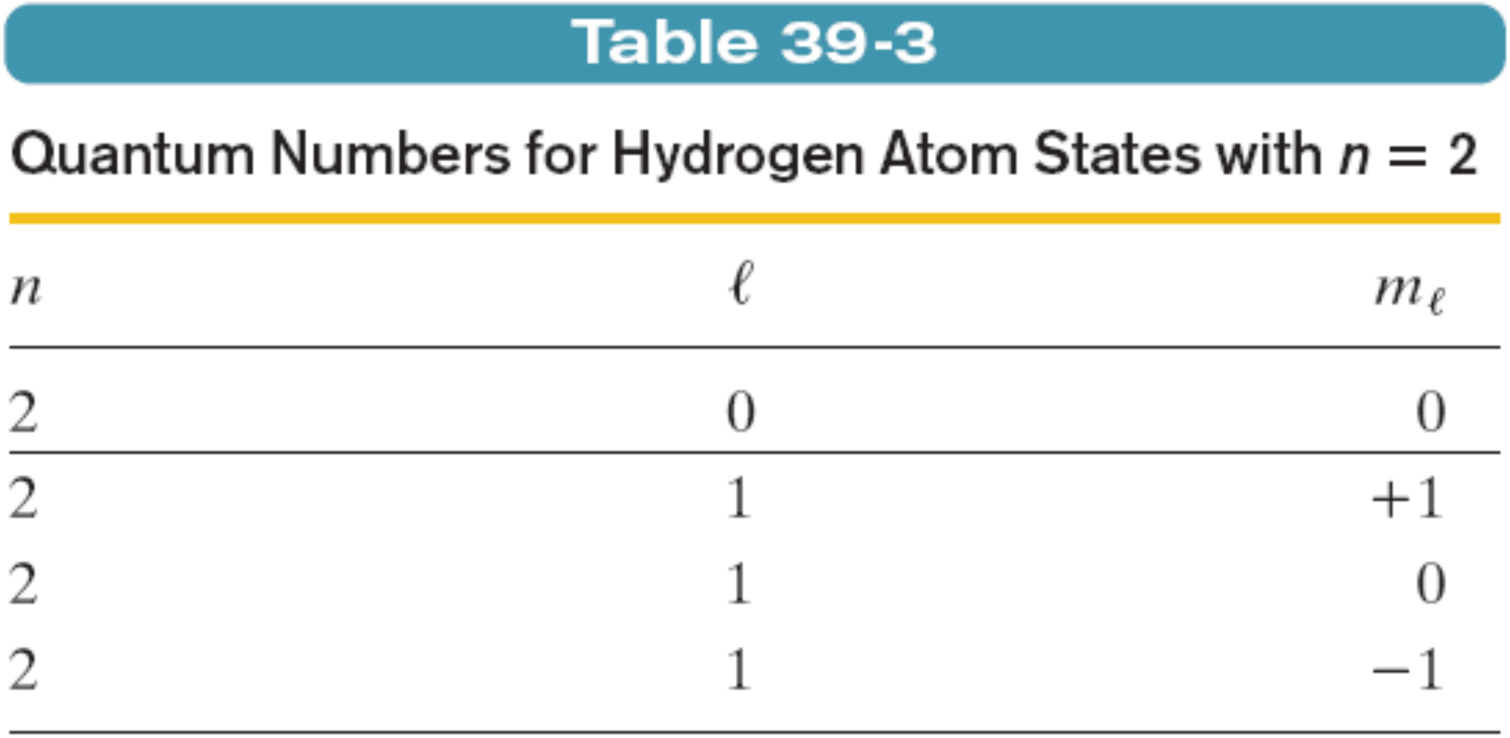


Table 39-3

Quantum Numbers for Hydrogen Atom States with $n = 2$

n	ℓ	m_ℓ
2	0	0
2	1	+1
2	1	0
2	1	−1

Hydrogen Atom States with n = 2:

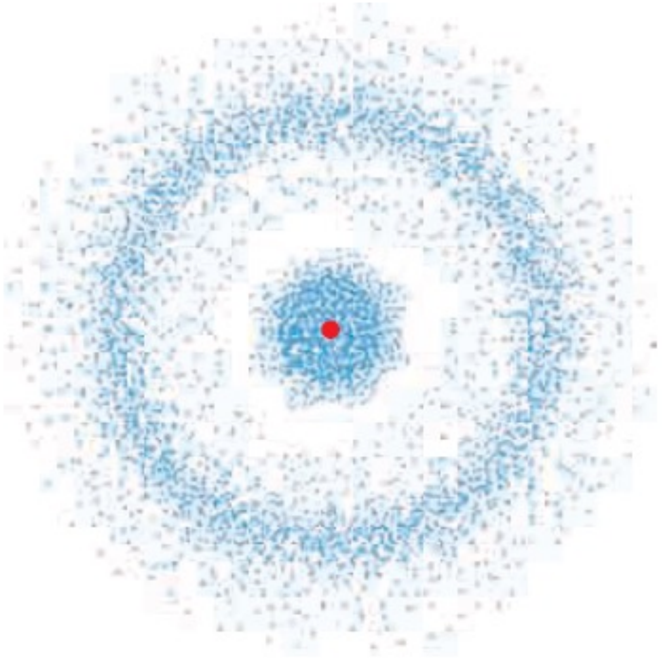


Fig. 39-21 A dot plot showing the volume probability density $\psi^2(r)$ for the hydrogen atom in the quantum state with $n = 2$, $\ell = 0$, and $m_\ell = 0$. The plot has spherical symmetry about the central nucleus. The gap in the dot density pattern marks a spherical surface over which $\psi^2(r) = 0$.

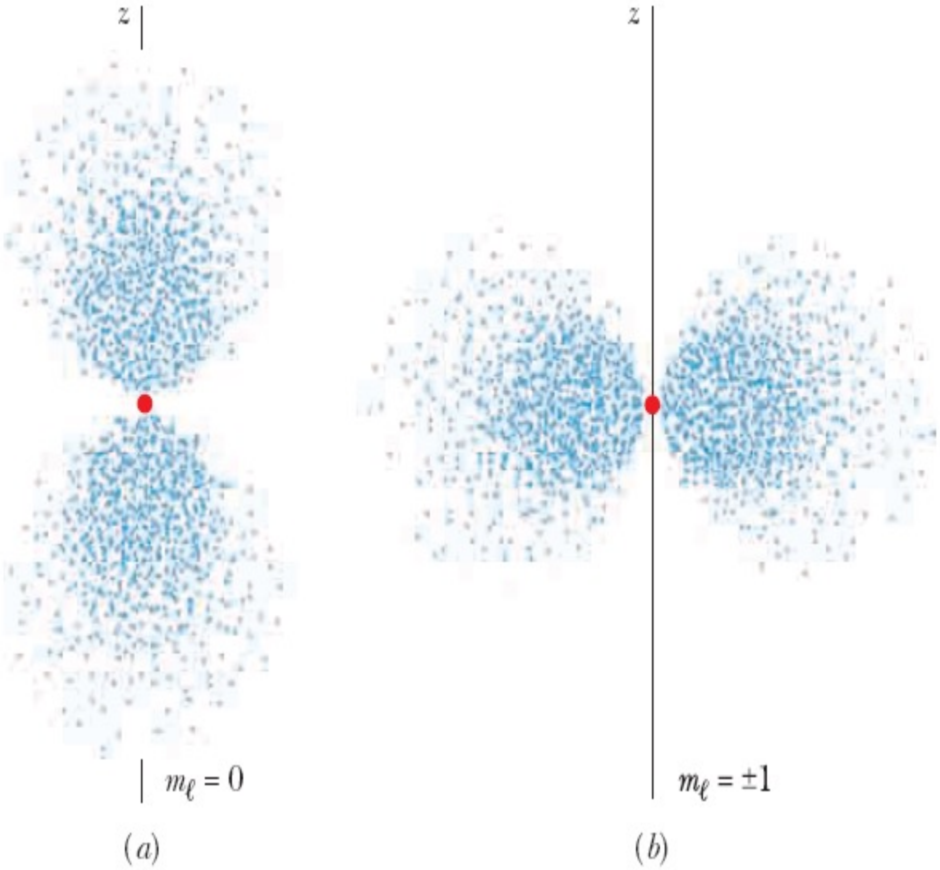


Fig. 39-23 Dot plots of the volume probability density $\psi^2(r, \theta)$ for the hydrogen atom in states with $n = 2$ and $\ell = 1$. (a) Plot for $m_\ell = 0$. (b) Plot for $m_\ell = +1$ and $m_\ell = -1$. Both plots show that the probability density is symmetric about the z axis.

Hydrogen Atom States with large n:

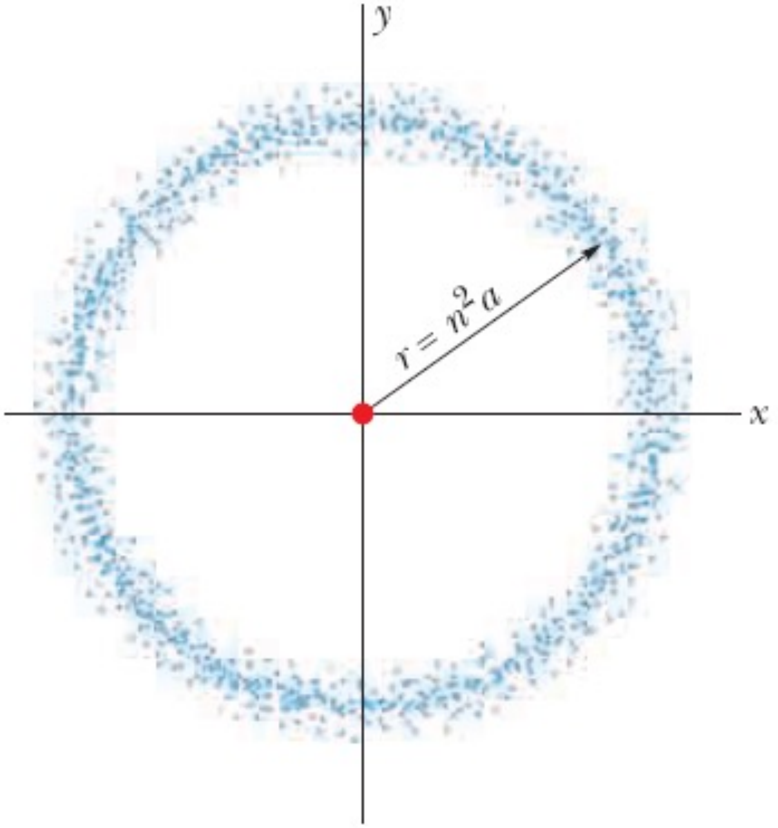


Fig. 39-24 A dot plot of the radial probability density $P(r)$ for the hydrogen atom in a quantum state with a relatively large principal quantum number—namely, $n = 45$—and angular momentum quantum number $\ell = n - 1 = 44$. The dots lie close to the xy plane, the ring of dots suggesting a classical electron orbit.