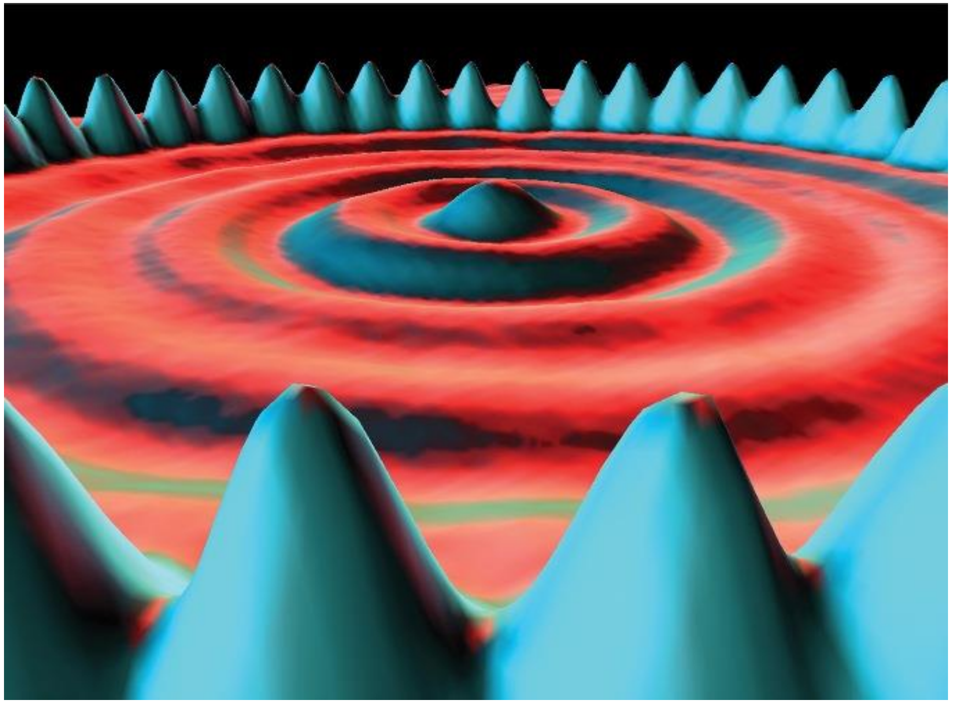
Chapter 39

More About Matter Waves



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:

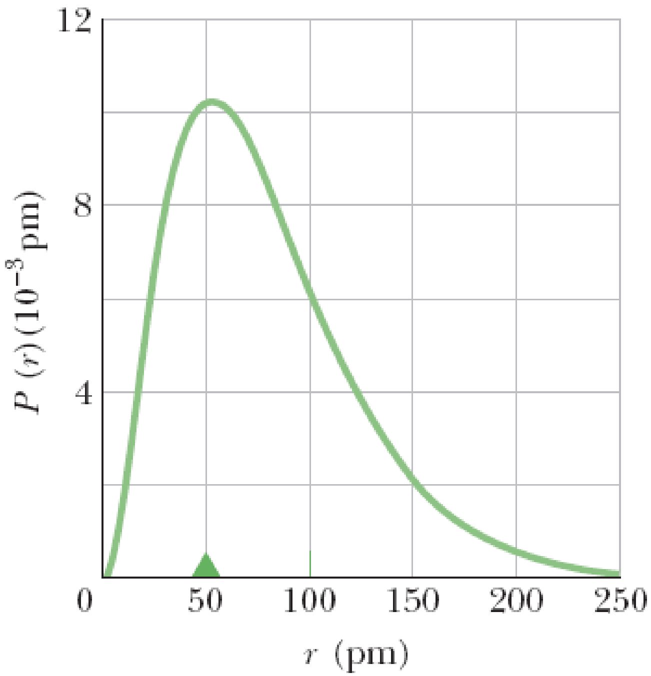


Fig. 39-19 A plot of the radial probability density $P(r)$ for the ground state of the hydrogen atom. The triangular marker is located at one Bohr radius from the origin, and the origin represents the center of the atom.

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

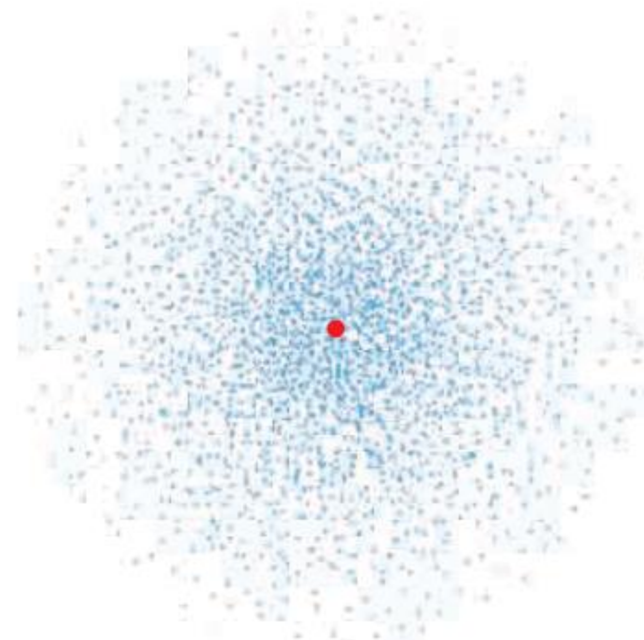


Fig. 39-20 A "dot plot" showing the volume probability density $\psi^2(r)$—not the *radial* probability density $P(r)$—for the ground state of the hydrogen atom. The density of dots drops exponentially with increasing distance from the nucleus, which is represented here by a red spot.

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:

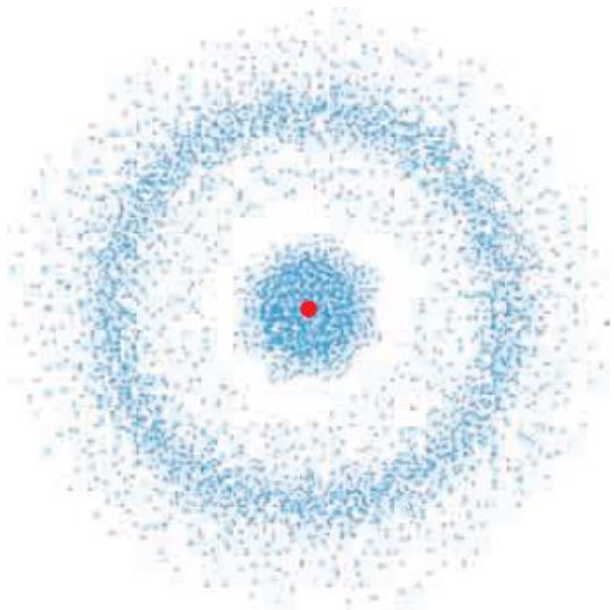


Fig. 39-21 A dot plot showing the volume probability density $\psi^2(r)$ for the hydrogen atom in the quantum state with $n = 2$, $\ell = 0$, and $m_\ell = 0$. The plot has spherical symmetry about the central nucleus. The gap in the dot density pattern marks a spherical surface over which $\psi^2(r)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

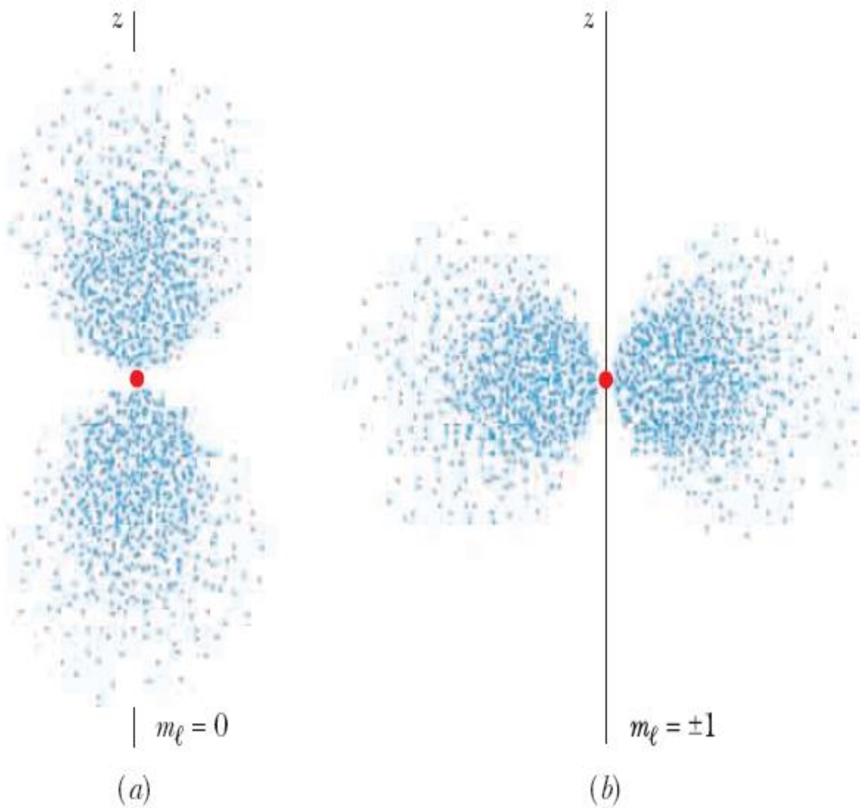


Fig. 39-23 Dot plots of the volume probability density $\psi^2(r, \theta)$ for the hydrogen atom in states with $n = 2$ and $\ell = 1$. (a) Plot for $m_\ell = 0$. (b) Plot for $m_\ell = +1$ and $m_\ell = -1$. Both plots show that the probability density is symmetric about the z axis.

Hydrogen Atom States with large n:

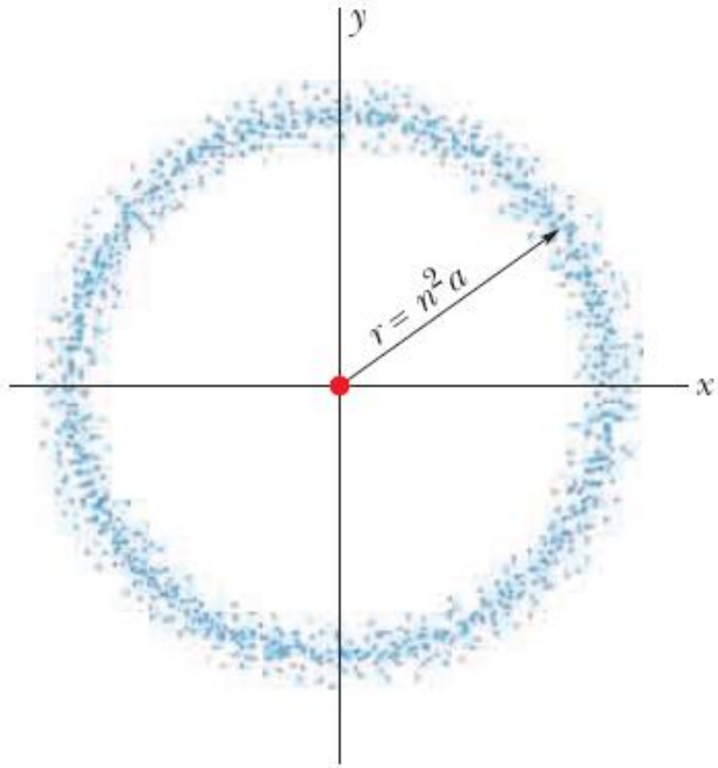


Fig. 39-24 A dot plot of the radial probability density $P(r)$ for the hydrogen atom in a quantum state with a relatively large principal quantum number—namely, $n = 45$—and angular momentum quantum number $\ell = n - 1 = 44$. The dots lie close to the xy plane, the ring of dots suggesting a classical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

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