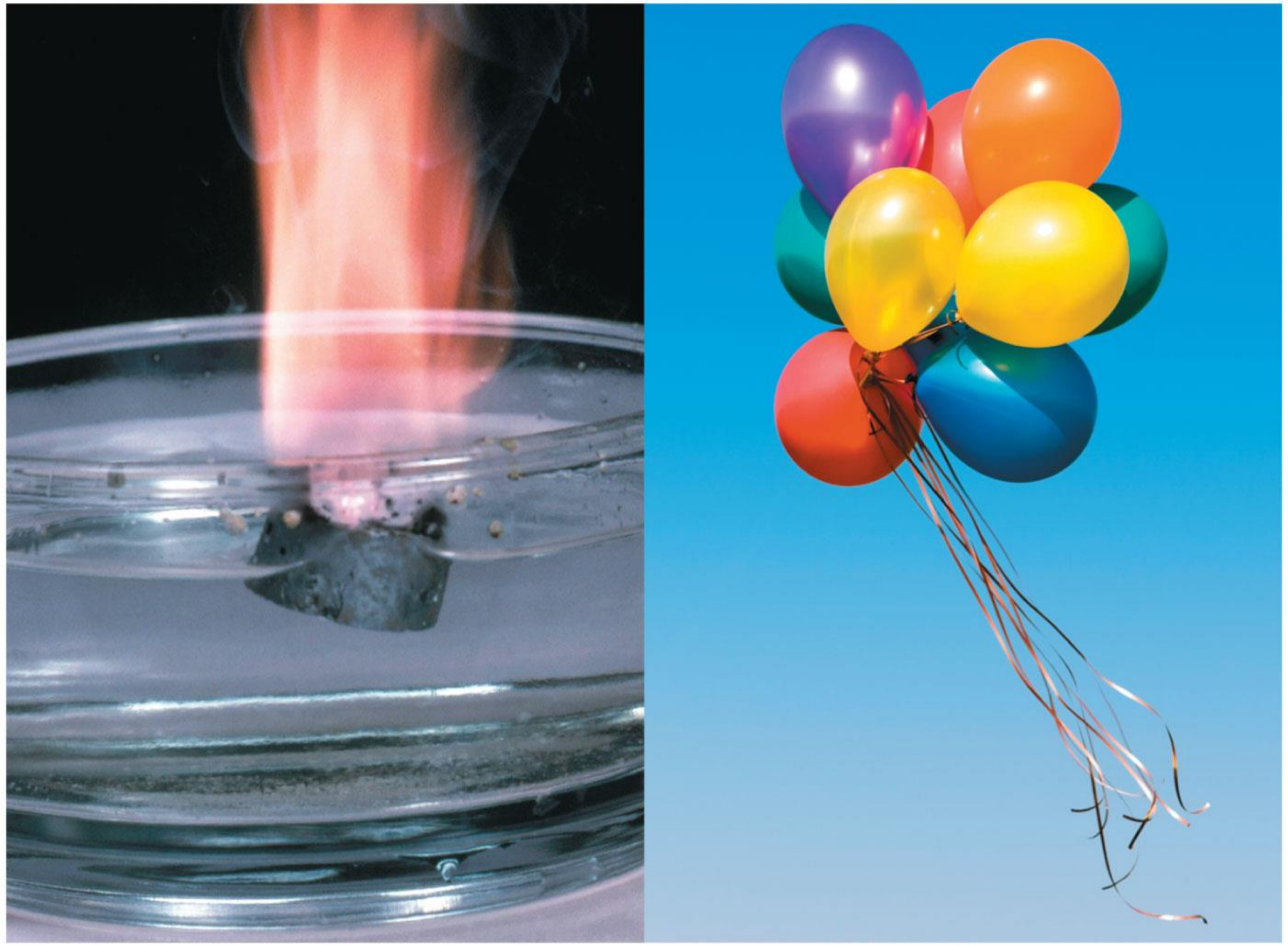
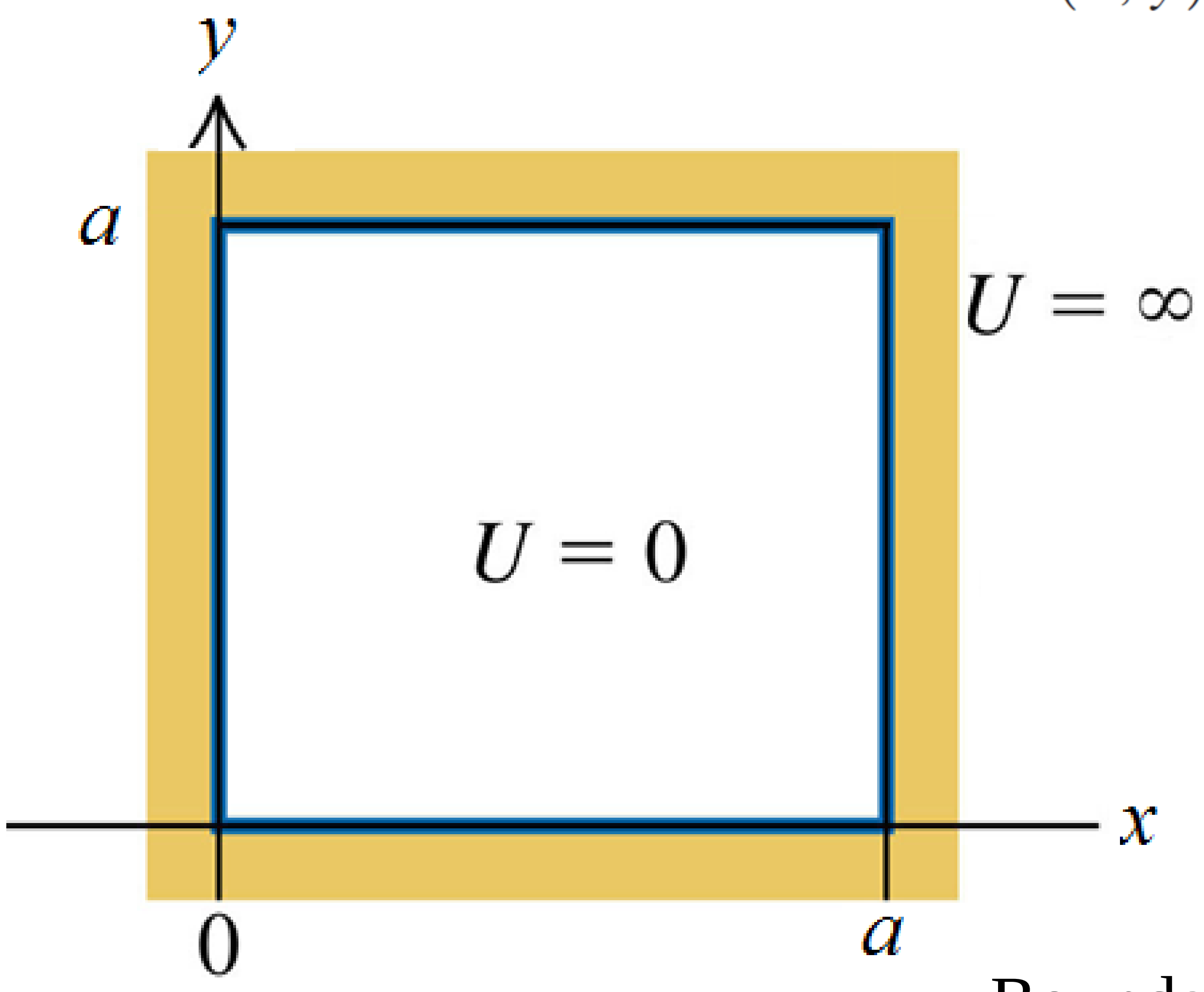
The Three-Dimensional Schrödinger Equation



The 2-D Square Box



$$U(x, y) = \begin{cases} 0 & \text{when } 0 \leq x \leq a \quad \text{and} \quad 0 \leq y \leq a \\ \infty & \text{otherwise} \end{cases} \qquad (8.4)$$

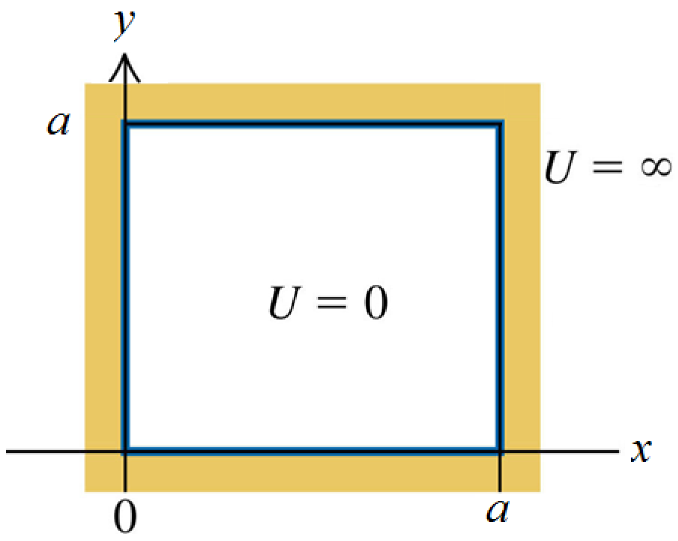
$$\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} = \frac{2M}{\hbar^2}[U - E]\psi \qquad (8.3)$$

$$U(x, y) = 0 \text{ inside the box}$$

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} = -\frac{2ME}{\hbar^2}\psi \qquad (8.6)$$

Boundary Conditions: $\left\{ \psi(x, y) = 0 \quad \begin{matrix} \text{if } x = 0 \text{ or } a \\ \text{and} \\ \text{if } y = 0 \text{ or } a \end{matrix} \right.$

The 2-D Square Box: Separation of Variables in Cartesian Coordinates



$$\frac{\partial^2\psi}{\partial x^2}+\frac{\partial^2\psi}{\partial y^2}=-\frac{2ME}{\hbar^2}\psi \quad \left\{\psi(x,y)=0 \quad \begin{array}{c}\text{if } x=0 \text{ or } a\\ \text{and}\\ \text{if } y=0 \text{ or } a\end{array}\right.$$

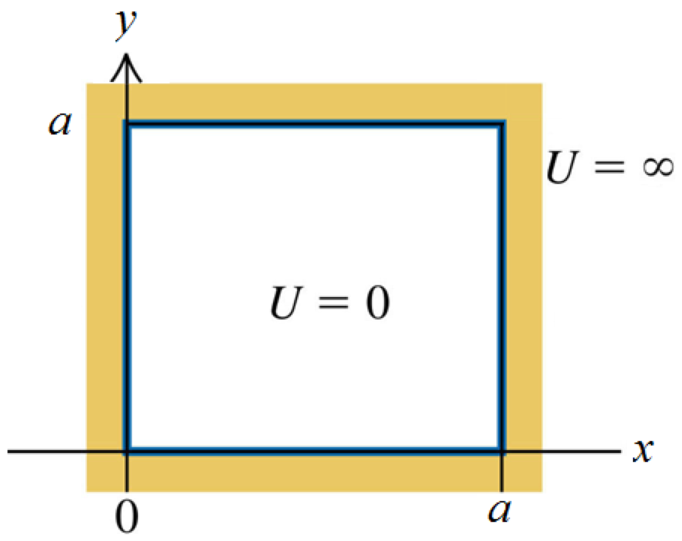
$$\psi(x,y)=X(x)Y(y) \quad (8.7)$$

$$\frac{X''(x)}{X(x)}+\frac{Y''(y)}{Y(y)}=-\frac{2ME}{\hbar^2} \quad (8.10) \qquad X''(x)=-k_x{}^2X(x) \text{ and } Y''(y)=-k_y{}^2Y(y)$$

$$\psi(x,y)=X(x)Y(y)=BC\sin k_x x\sin k_y y=A\sin\frac{n_x\pi x}{a}\sin\frac{n_y\pi y}{a} \quad (8.23)$$

n_x and n_y are any two positive integers

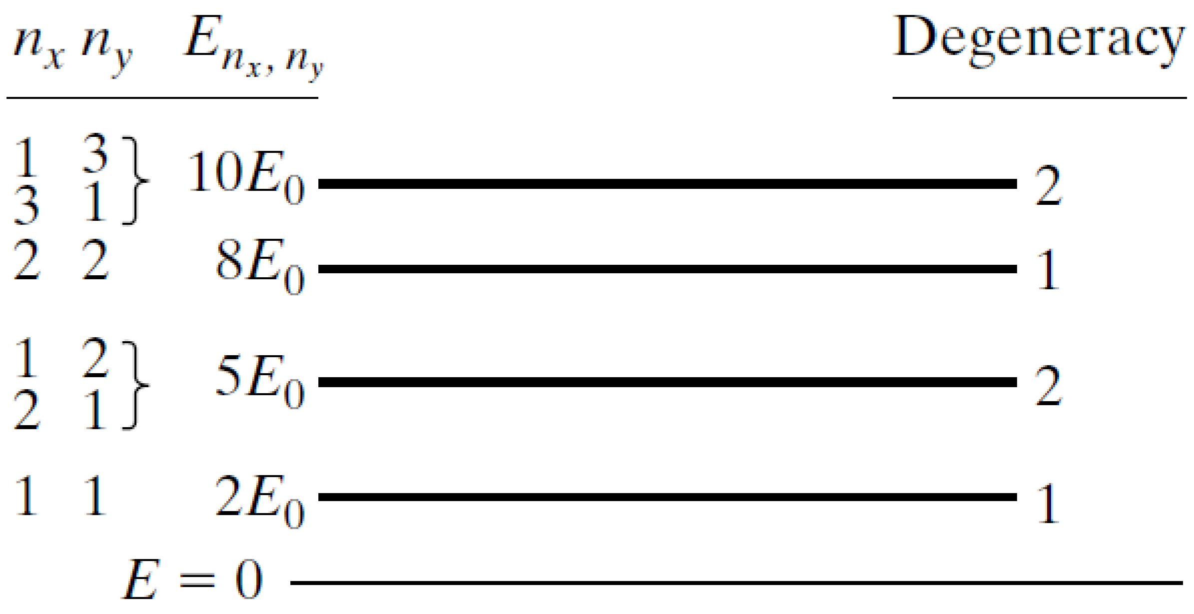
The 2-D Square Box: Allowed Energies, Quantum Numbers and Degeneracy



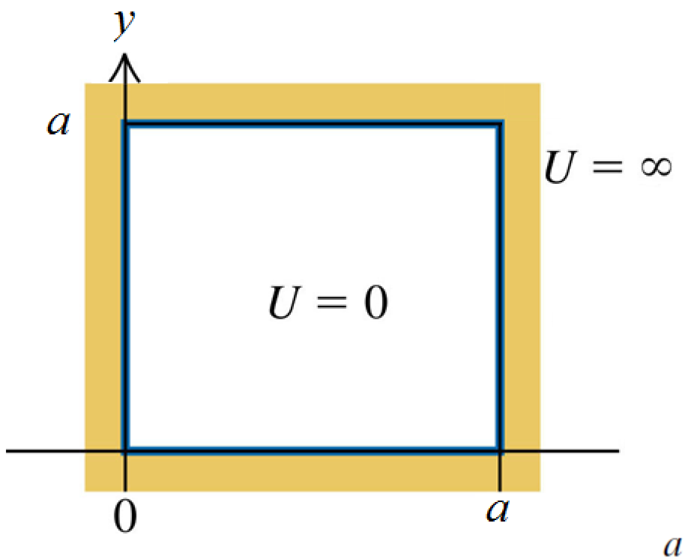
$$E = E_{n_x, n_y} = \frac{\hbar^2 \pi^2}{2Ma^2}(n_x^2 + n_y^2) \quad (8.26)$$

FIGURE 8.2

The energy levels of a particle in a two-dimensional, square rigid box. The lowest allowed energy is $2E_0$; the line at $E = 0$ is merely to show the zero of the energy scale. The degeneracies, listed on the right, refer to the number of independent wave functions with the same energy.



The 2-D Square Box: Normalization Constant; Contour Maps of |ψ|²



$$|\psi(x, y)|^2 = A^2 \sin^2\left(\frac{\pi x}{a}\right) \sin^2\left(\frac{\pi y}{a}\right) \quad (8.31)$$

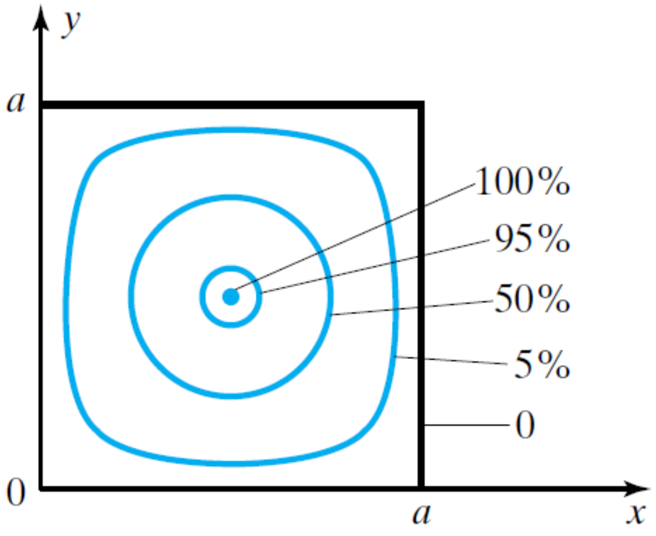


FIGURE 8.3

Contour map of the probability density $|\psi|^2$ for the ground state of the square box. The percentages shown give the value of $|\psi|^2$ as a percentage of its maximum value.

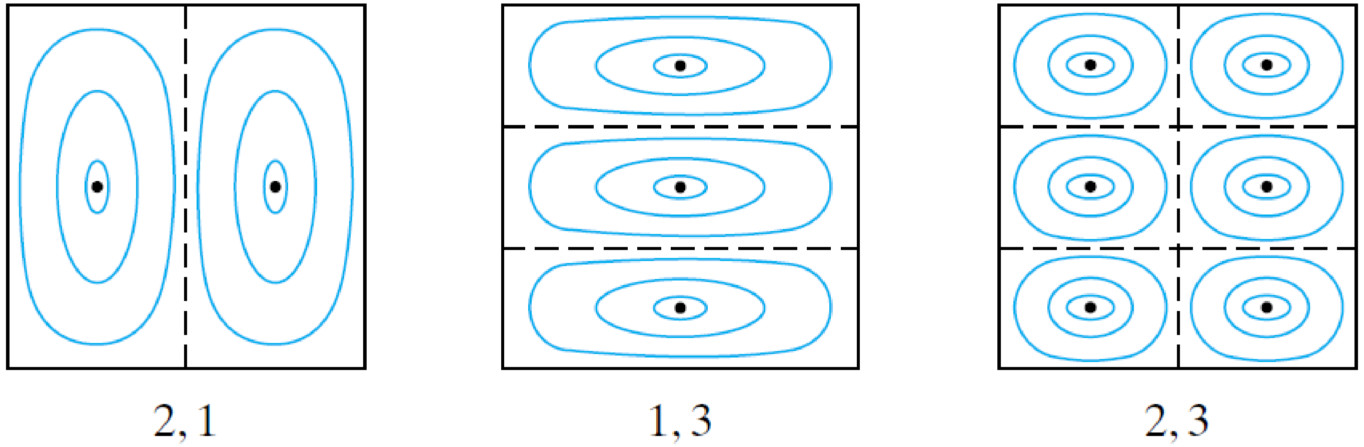
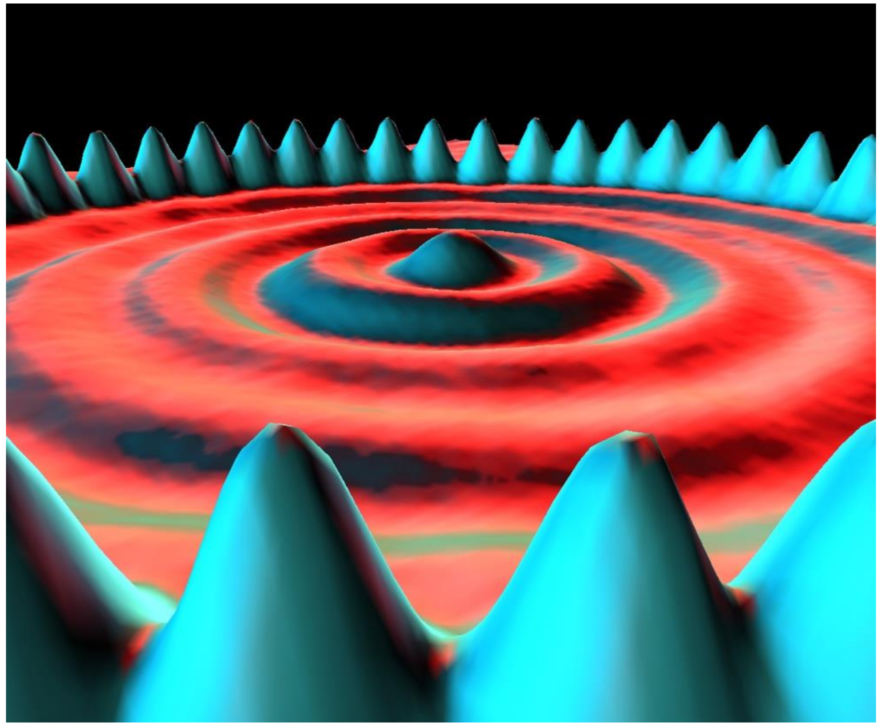
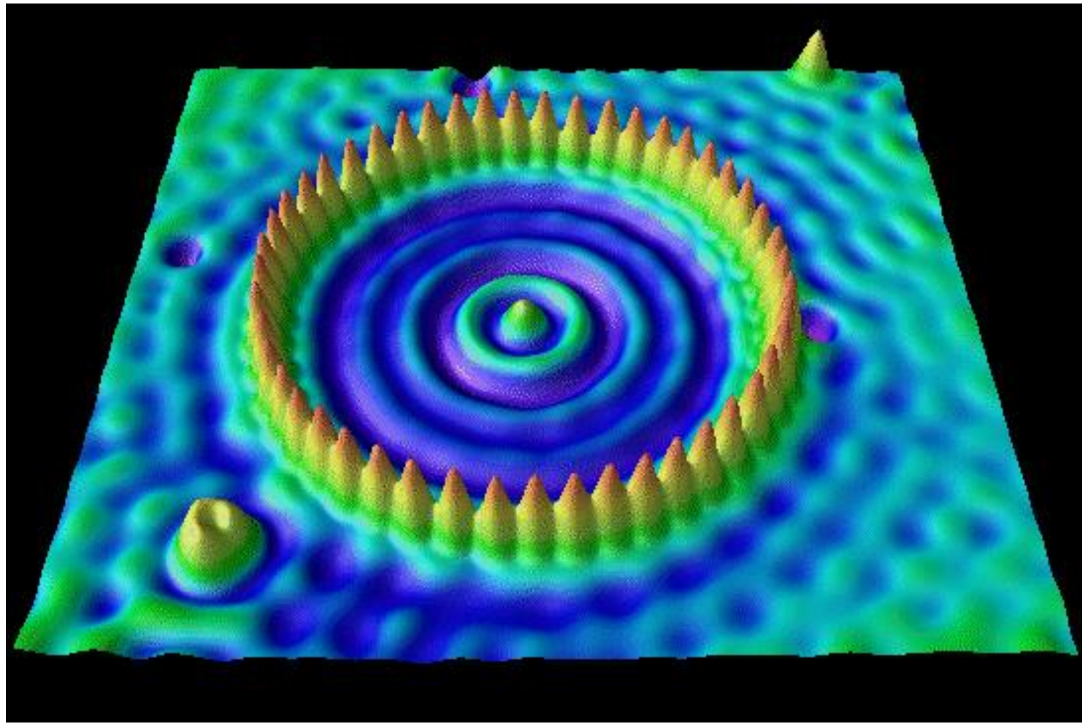


FIGURE 8.4

Contour maps of $|\psi|^2$ for three excited states of the square box. The two numbers under each picture are n_x and n_y. The dashed lines are nodal lines, where $|\psi|^2$ vanishes; these occur where ψ passes through zero as it oscillates from positive to negative values.

A 2-D Circular "Hard Box"





The particle-in-a-box problem is well known among chemistry students taking quantum mechanics. It describes the wavelike behavior of an electron trapped inside an imaginary box. In 1993, Eigler and IBM colleagues Michael F. Crommie and Christopher P. Lutz physically constructed their own box—or in this case, a ring. They used an STM to position 48 iron atoms on a cold copper surface in a ring roughly 71 Å in diameter. The atomically engineered **quantum corral** confined copper's surface electrons to the interior of the ring. The now-famous image published at that time (shown) depicts concentric waves—a rippled interference pattern—caused by surface electrons being reflected from the ring of atoms (*Science* 1993, DOI: **10.1126/science.262.5131.218**).

The 3-D Central Force Problem. Spherical Coordinates

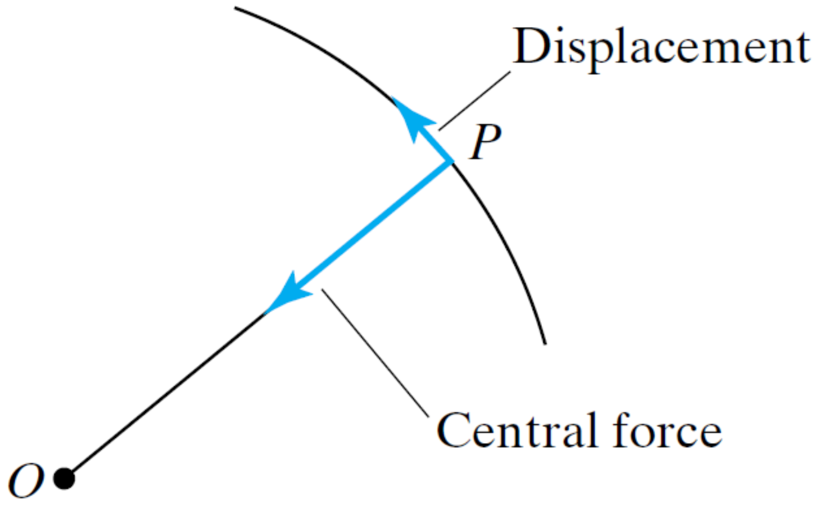
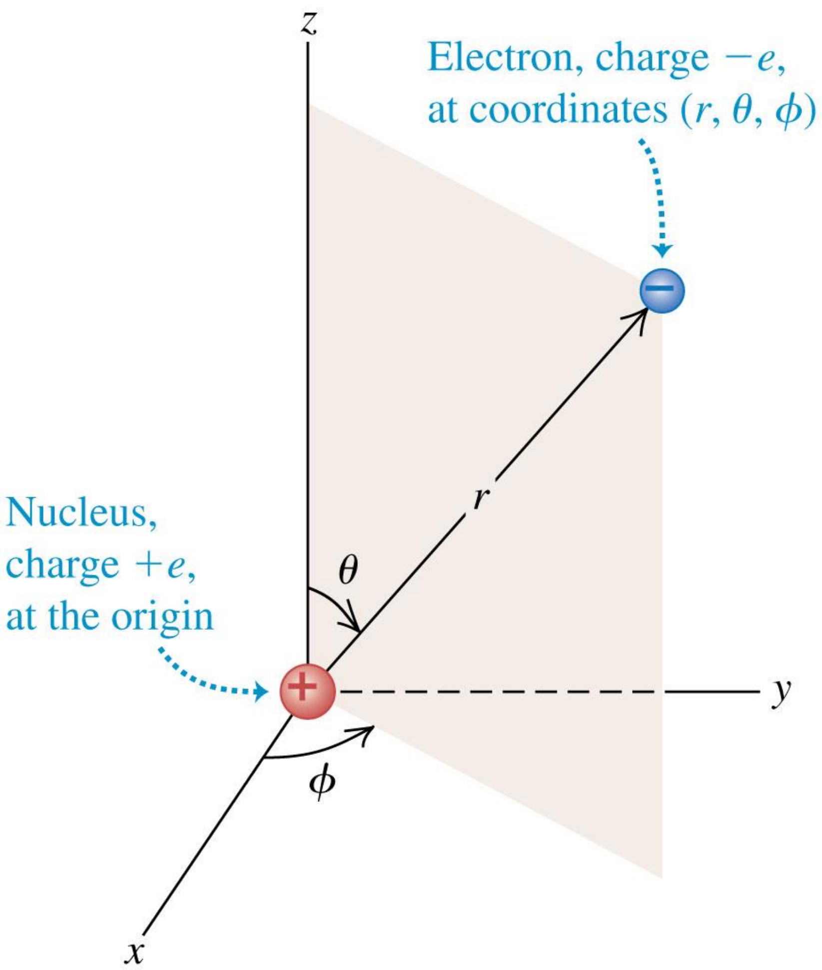


FIGURE 8.6

A central force points exactly toward or away from O. If the particle undergoes a displacement perpendicular to the radius vector OP, the force does no work and the potential energy U is therefore constant.



$$\frac{d^2\psi}{dx^2} = \frac{2M}{\hbar^2}[U - E]\psi$$

$$\psi = \psi(x, y, z) = \psi(\mathbf{r})$$

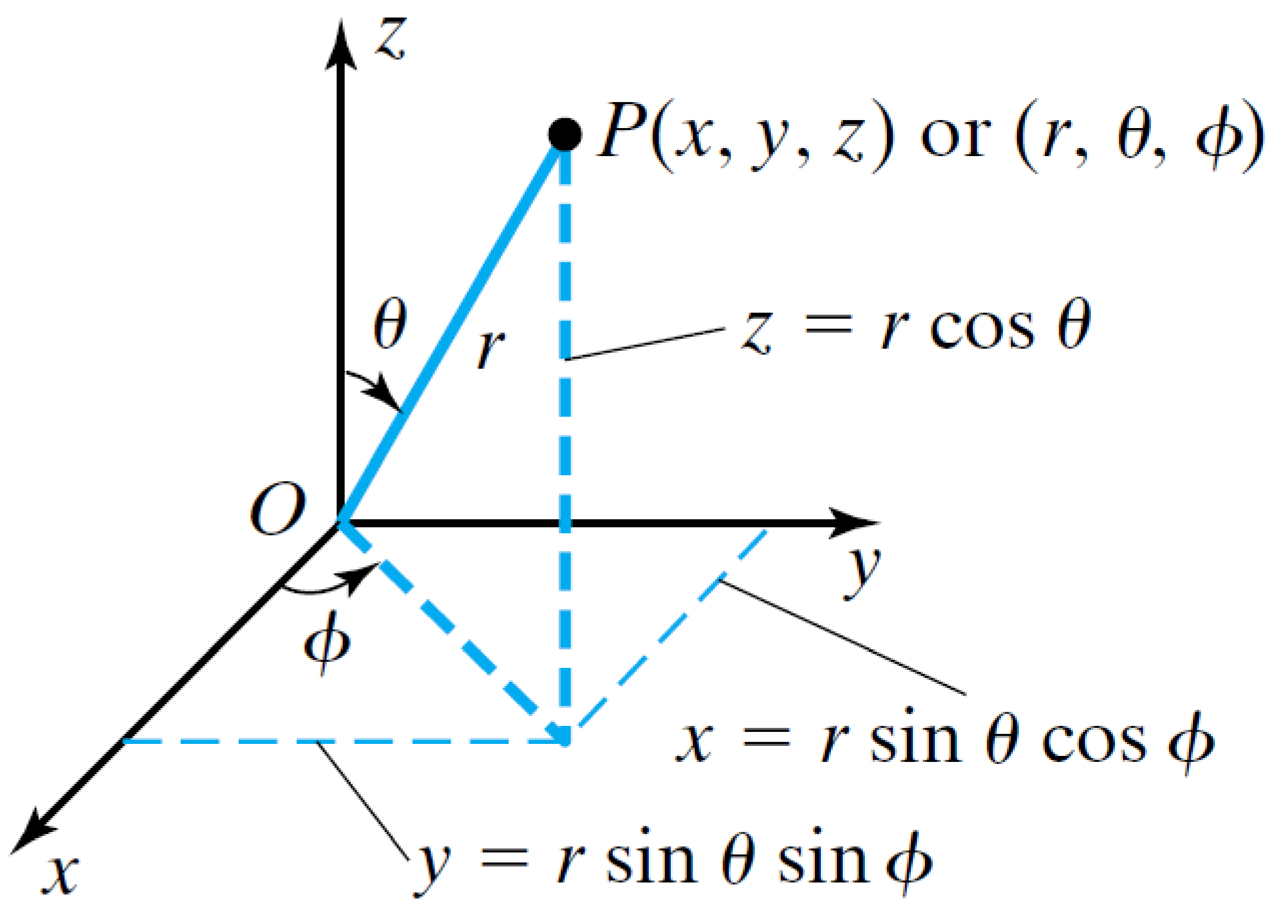
$$U = U(x, y, z) = U(\mathbf{r})$$

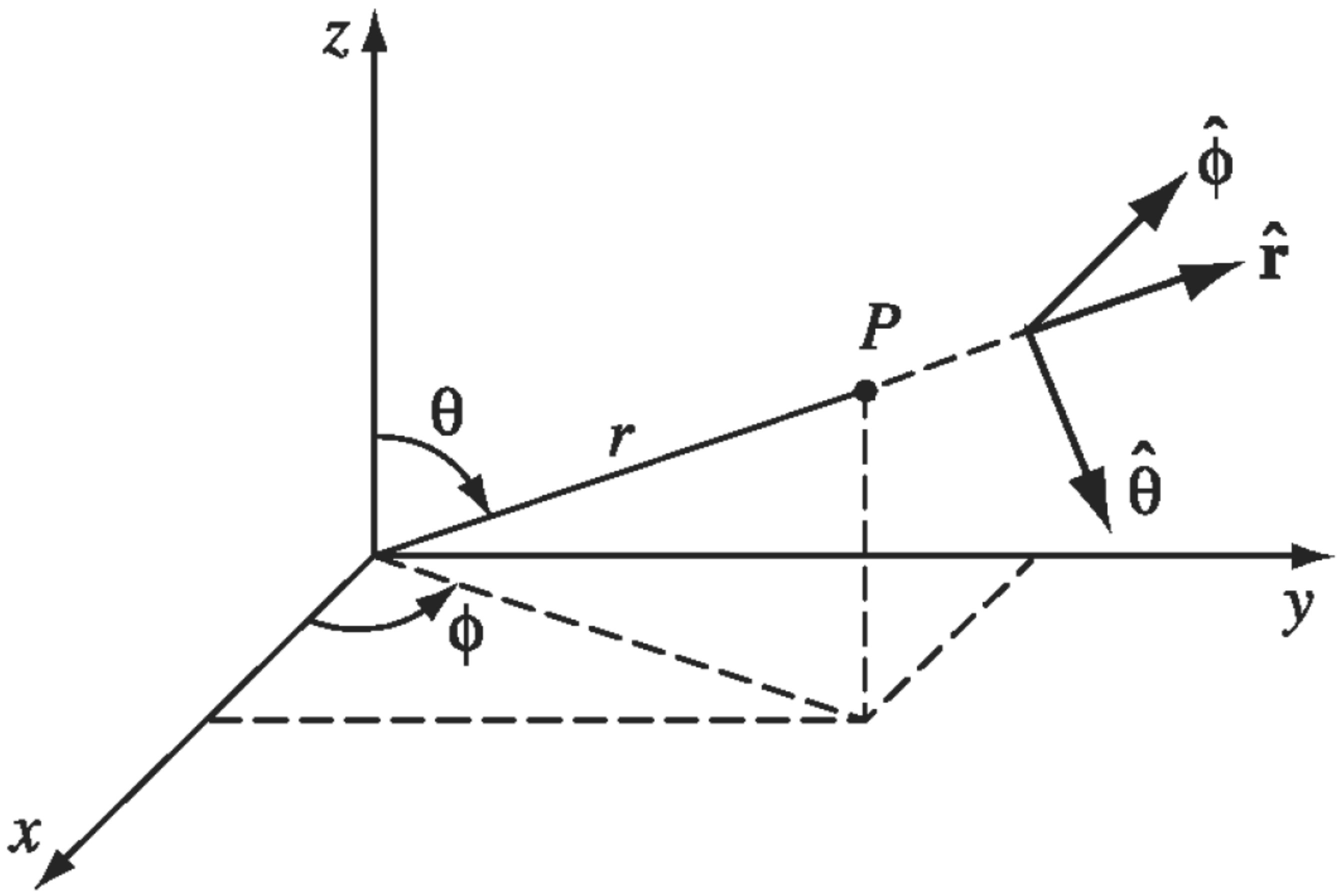
For central forces:

$$U(\mathbf{r}) = U(\mathrm{r})$$

$$\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2} = \frac{2M}{\hbar^2}[U - E]\psi$$

Spherical Coordinates and Unit Vectors





The direction of the spherical unit vectors depends on location!

Vector Calculus

$$\vec{\nabla} = \hat{\imath}\frac{\partial}{\partial x} + \hat{\jmath}\frac{\partial}{\partial y} + \hat{k}\frac{\partial}{\partial z}$$

The "Del" Operator

$$\vec{\nabla}T = \frac{\partial T}{\partial x}\hat{\imath} + \frac{\partial T}{\partial y}\hat{\jmath} + \frac{\partial T}{\partial z}\hat{k}$$

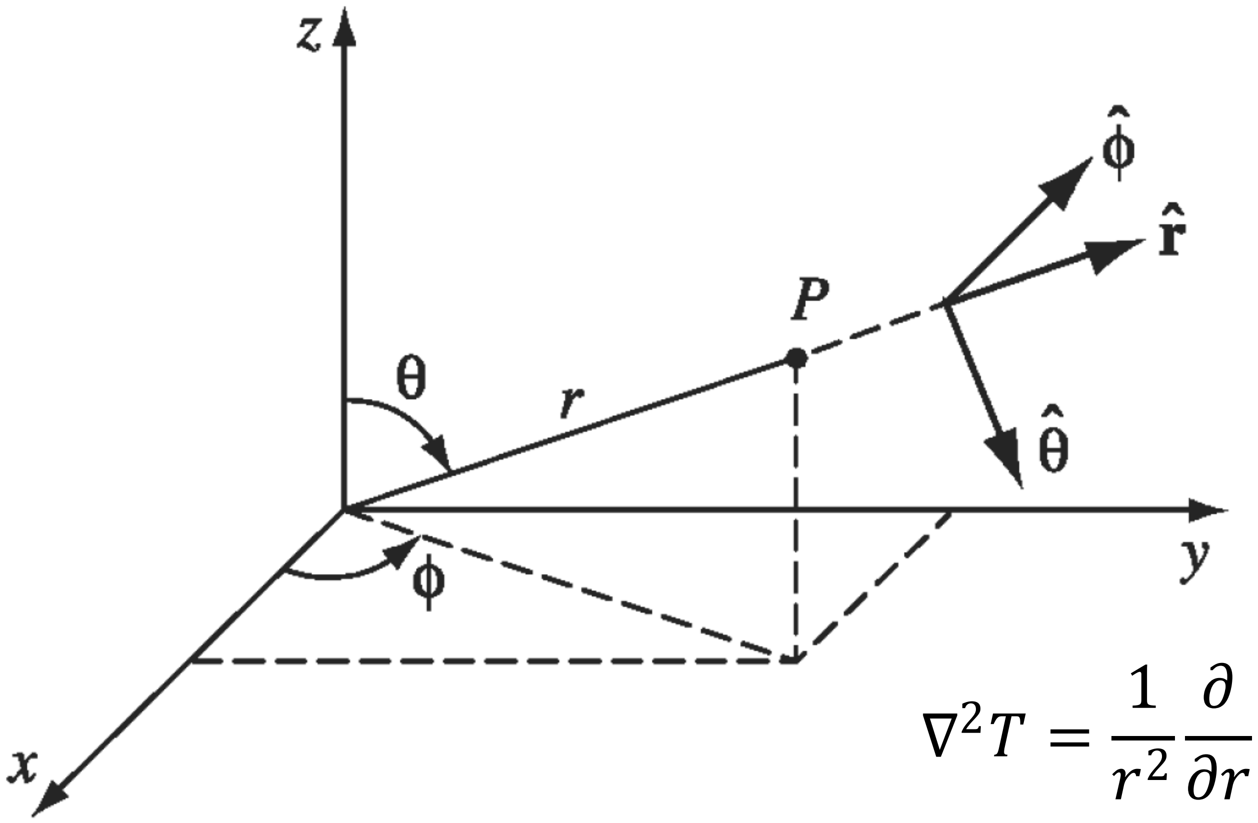
Gradient of a scalar T

$$\nabla^2 T = \frac{\partial^2 T}{\partial x^2} + \frac{\partial^2 T}{\partial y^2} + \frac{\partial^2 T}{\partial z^2}$$

Laplacian of a scalar T

Because the spherical unit vectors are not constant vectors (unlike their Cartesian counterparts) they also need to be differentiated. Gradients and laplacians will look a lot more complicated in spherical coordinates.

Vector Calculus in Spherical Coordinates



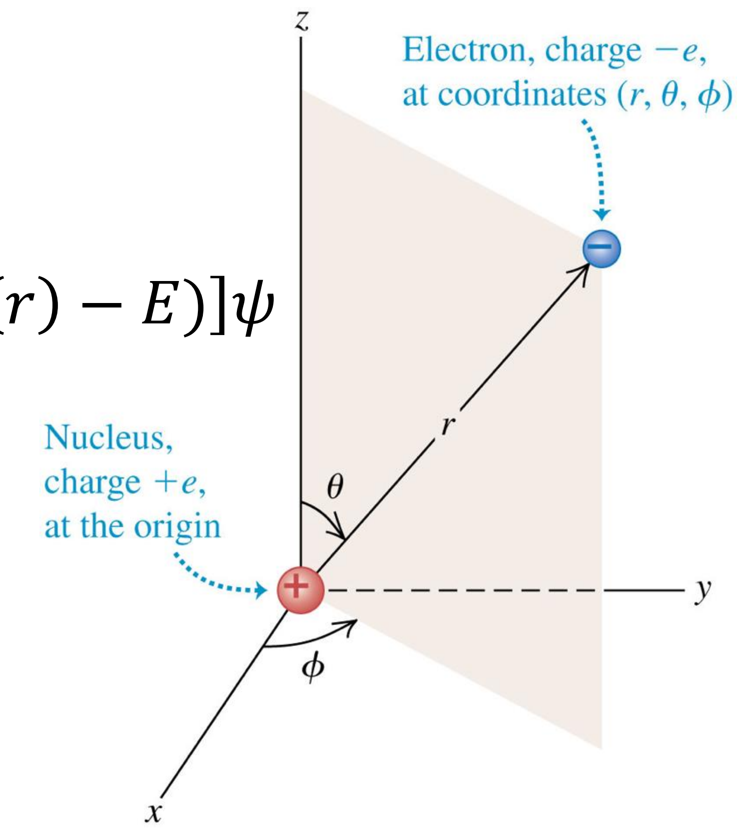
$$\vec{\nabla}T = \frac{\partial T}{\partial r}\hat{r} + \frac{1}{r}\frac{\partial T}{\partial \theta}\hat{\theta} + \frac{1}{r sin\theta}\frac{\partial T}{\partial \varphi}\hat{\varphi}$$

$$\nabla^2 T = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial T}{\partial r}\right) + \frac{1}{r^2 sin\theta}\frac{\partial}{\partial \theta}\left(sin\theta\frac{\partial T}{\partial \theta}\right) + \frac{1}{r^2 sin^2\theta}\frac{\partial^2 T}{\partial \varphi^2}$$

$$= \frac{1}{r}\frac{\partial^2}{\partial r^2}(rT) + \frac{1}{r^2 sin\theta}\frac{\partial}{\partial \theta}\left(sin\theta\frac{\partial T}{\partial \theta}\right) + \frac{1}{r^2 sin^2\theta}\frac{\partial^2 T}{\partial \varphi^2}$$

The 3-D Central Force Problem

$$\underbrace{\frac{1}{r}\frac{\partial^2}{\partial r^2}(r\psi)+\frac{1}{r^2 sin\theta}\frac{\partial}{\partial\theta}\left(sin\theta\frac{\partial\psi}{\partial\theta}\right)+\frac{1}{r^2 sin^2\theta}\frac{\partial^2\psi}{\partial\varphi^2}}_{\nabla^2\psi(r,\theta,\varphi)}=\frac{2M}{\hbar^2}[U(r)-E)]\psi$$



$$\psi(r,\theta,\varphi)=R(r)Y(\theta,\varphi)$$

$$\frac{Y}{r}\frac{d^2}{dr^2}(rR)+\frac{R}{r^2 sin\theta}\frac{\partial}{\partial\theta}\left(sin\theta\frac{\partial Y}{\partial\theta}\right)+\frac{R}{r^2 sin^2\theta}\frac{\partial^2 Y}{\partial\varphi^2}=\frac{2M}{\hbar^2}[U(r)-E)]RY \qquad \left|\frac{r^2}{RY}\right.$$

$$\underbrace{\left\{\frac{r}{R}\frac{d^2}{dr^2}(rR)-\frac{2Mr^2}{\hbar^2}[U(r)-E]\right\}}_{f(r)=l(l+1)}+\underbrace{\left\{\frac{1}{Y}\left[\frac{1}{sin\theta}\frac{\partial}{\partial\theta}\left(sin\theta\frac{\partial Y}{\partial\theta}\right)+\frac{1}{sin^2\theta}\frac{\partial^2 Y}{\partial\varphi^2}\right]\right\}}_{g(\theta,\varphi)=-l(l+1)}=0$$

The Angular Equations: Quantization of the Orbital Angular Momentum

$$\frac{1}{Y}\left[\frac{1}{sin\theta}\frac{\partial}{\partial\theta}\left(sin\theta\frac{\partial Y}{\partial\theta}\right)+\frac{1}{sin^2\theta}\frac{\partial^2 Y}{\partial\varphi^2}\right]=-l(l+1) \qquad |sin^2\theta$$

$$\frac{1}{Y}\left[sin\theta\frac{\partial}{\partial\theta}\left(sin\theta\frac{\partial Y}{\partial\theta}\right)+\frac{\partial^2 Y}{\partial\varphi^2}\right]=-l(l+1)sin^2\theta$$

$$\left[\frac{1}{Y}sin\theta\frac{\partial}{\partial\theta}\left(sin\theta\frac{\partial Y}{\partial\theta}\right)+l(l+1)sin^2\theta\right]+\frac{\partial^2 Y}{\partial\varphi^2}=0$$

$$Y(\theta,\varphi)=\Theta(\theta)\Phi(\varphi)$$

$$\left[\frac{1}{\Theta\Phi}sin\theta\frac{d}{d\theta}\left(sin\theta\Phi\frac{d\Theta}{d\theta}\right)+l(l+1)sin^2\theta\right]+\Theta\frac{d^2\Phi}{d\varphi^2}=0$$

$$\left[\frac{1}{\Theta}sin\theta\frac{d}{d\theta}\left(sin\theta\frac{d\Theta}{d\theta}\right)+l(l+1)sin^2\theta\right]+\frac{1}{\Phi}\frac{d^2\Phi}{d\varphi^2}=0$$

The Angular Equations: Quantization of the Orbital Angular Momentum (Continued)

$$\underbrace{\left[\frac{1}{\Theta}sin\theta\frac{d}{d\theta}\left(sin\theta\frac{d\Theta}{d\theta}\right)+l(l+1)sin^2\theta\right]}_{f(\theta)=m^2}+\underbrace{\frac{1}{\Phi}\frac{d^2\Phi}{d\varphi^2}}_{g(\varphi)=-m^2}=0$$

$$\frac{1}{\Theta}sin\theta\frac{d}{d\theta}\left(sin\theta\frac{d\Theta}{d\theta}\right)+l(l+1)sin^2\theta=m^2$$

$$\frac{1}{\Phi}\frac{d^2\Phi}{d\varphi^2}=-m^2$$

The Φ Equation: Quantization of the Orientation of the Angular Momentum (Space Quantization)

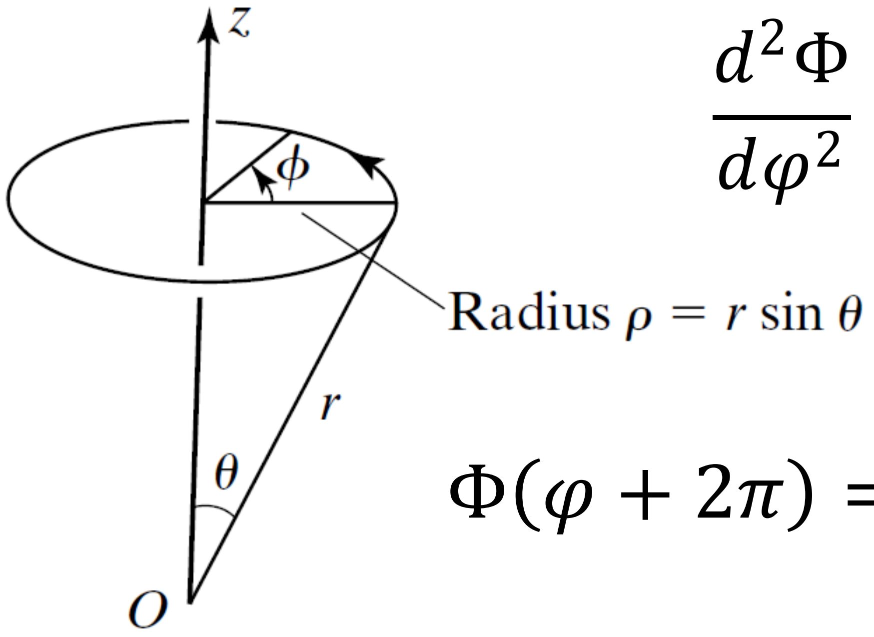


FIGURE 8.12

If we fix r and θ and let ϕ vary, we move around a circle of radius $\rho = r \sin\theta$.

$$\frac{d^2\Phi}{d\varphi^2} = -m^2\Phi \qquad \Rightarrow \quad \Phi(\varphi) = e^{im\varphi}$$

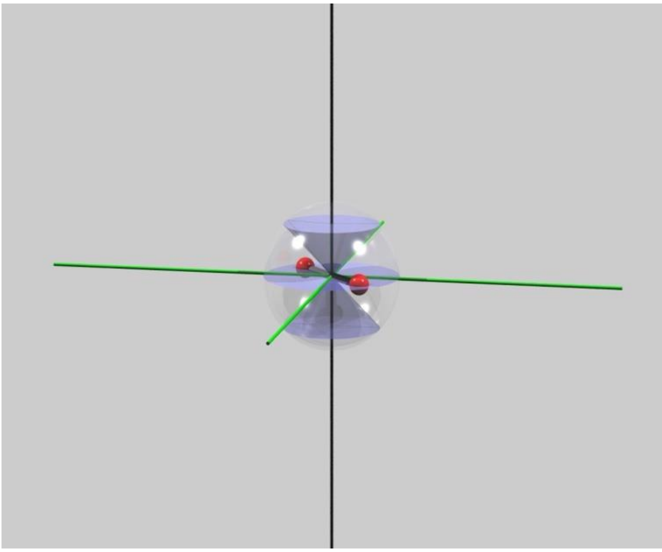
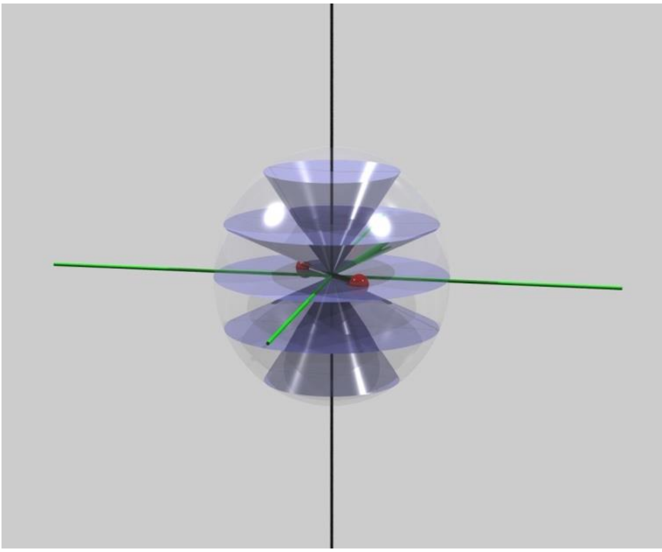
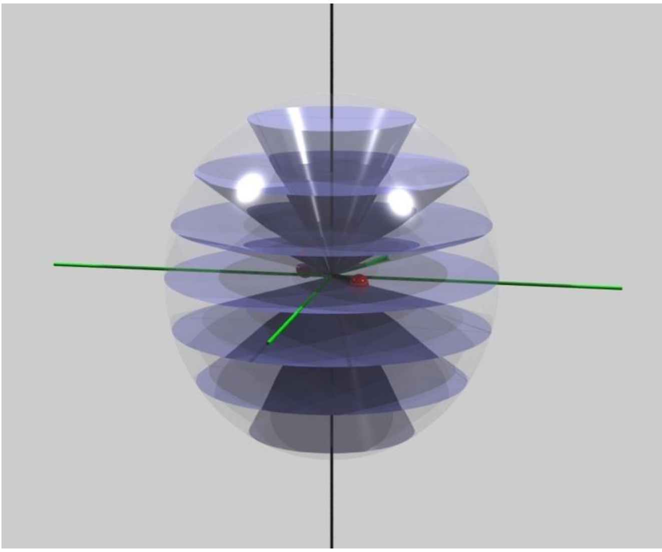
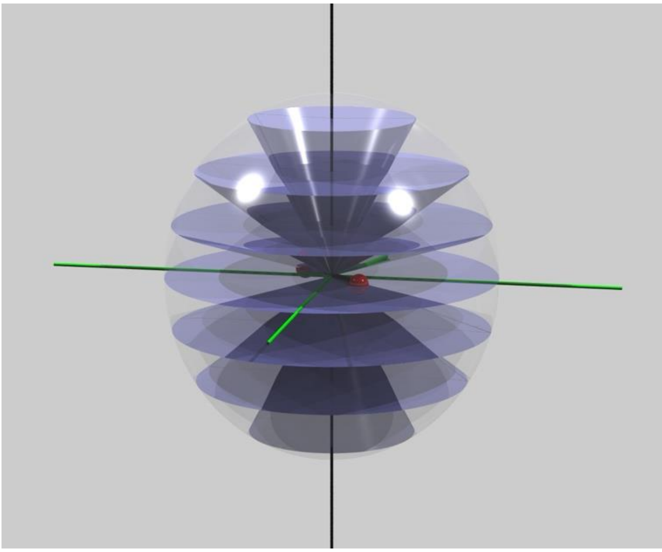
$$\Phi(\varphi + 2\pi) = \Phi(\varphi) \qquad \Rightarrow \quad m = 0, \pm 1, \pm 2, \pm 3, \ldots$$

"magnetic quantum number"

$$L_z = m\hbar \qquad m = 0, \pm 1, \pm 2, \pm 3, \ldots$$

quantization of the orientation of the angular momentum

The Φ Equation: Quantization of the Orientation of the Angular Momentum (Space Quantization)

The Θ Equation

$$sin\theta \frac{d}{d\theta}\left(sin\theta \frac{d\Theta}{d\theta}\right) + [l(l+1)sin^2\theta - m^2]\Theta = 0$$

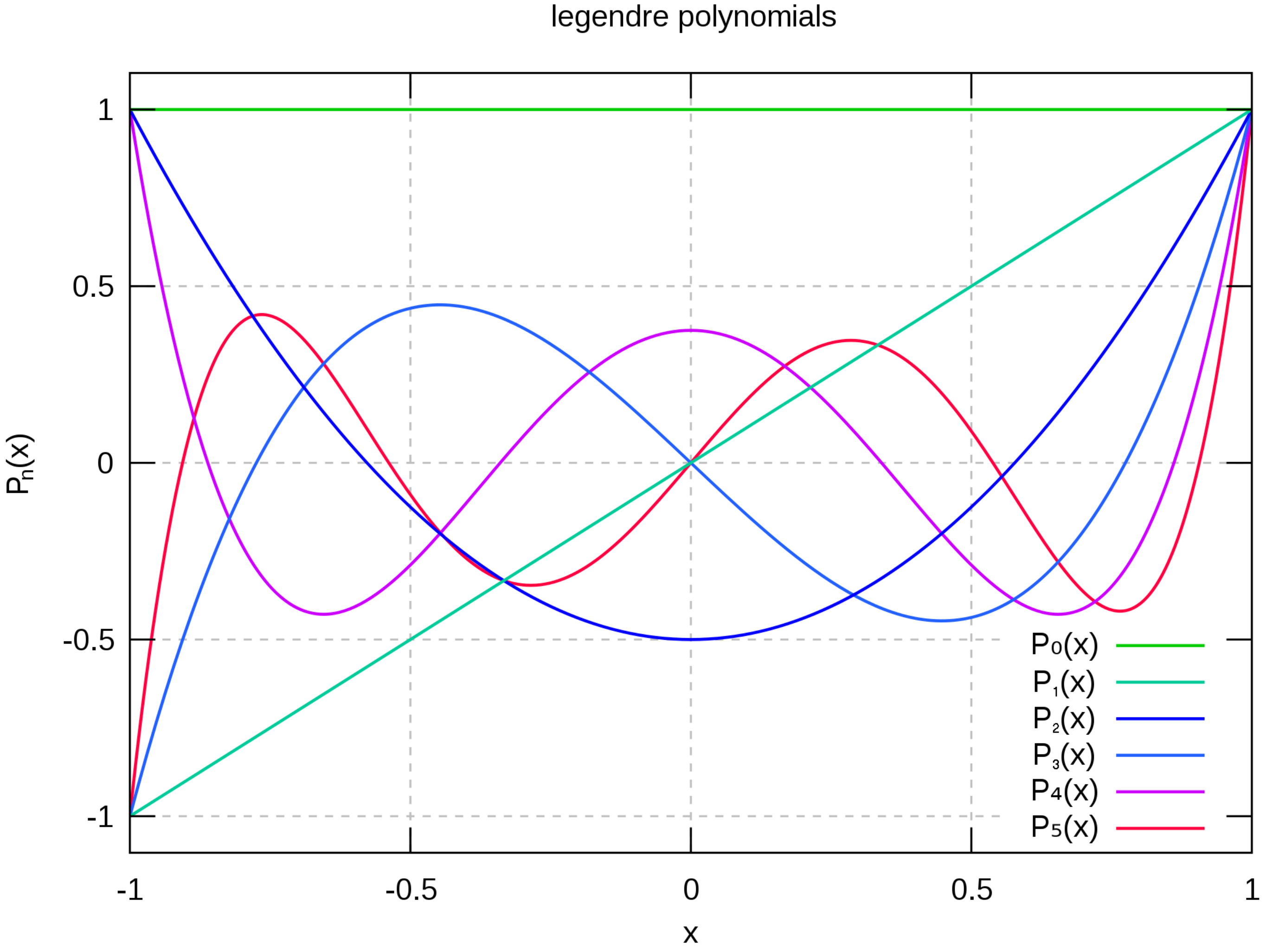
$$\boxed{\Theta(\theta) = AP_l^m(cos\theta)}$$

$$P_l^m(cos\theta) - \ associated\ Legendre\ functions$$

$$P_l^m(x) \equiv (1-x^2)^{\frac{|m|}{2}}\left(\frac{d}{dx}\right)^{|m|} P_l(x)$$

$$P_l(x) - \ l^{th} order\ Legendre\ polynomial$$

Legendre Polynomials



Adrien-Marie Legendre
1752-1833

$$P_l(x) \equiv \frac{1}{2^l l!}\left(\frac{d}{dx}\right)^l (x^2-1)^l$$

The Rodriguez Formula

$$P_0(x) = 1$$

$$P_1(x) = x$$

$$P_2(x) = \frac{1}{2}(3x^2-1)$$

$$P_3(x) = \frac{1}{2}(5x^3-3x)$$

$$P_4(x) = \frac{1}{8}(35x^4-30x^2+3)$$

$$l = 0, 1, 2, 3, \ldots$$

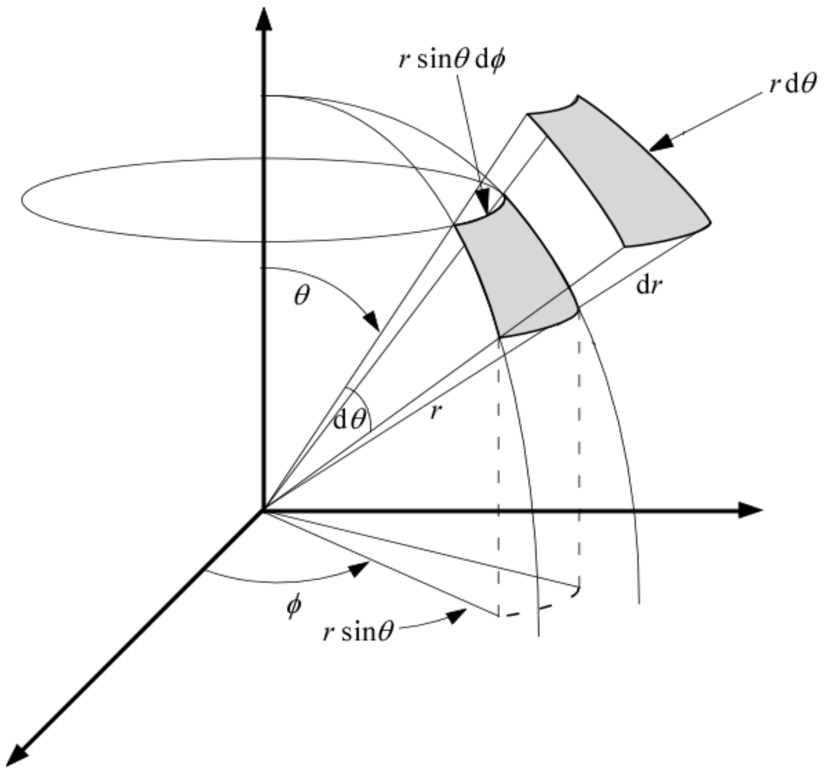
"orbital quantum number"

$$|m| \leq l$$

$$m = 0, \pm 1, \pm 2, \pm 3, \ldots, \pm l$$

$$2l + 1 \; values$$

Normalization



$$\psi(r,\theta,\varphi) = R(r)Y(\theta,\varphi)$$

$$Y(\theta,\varphi) = \Theta(\theta)\Phi(\varphi) \quad \begin{cases} \Theta(\theta) = AP_l^m(cos\theta) \\ \Phi(\varphi) = e^{im\varphi} \end{cases}$$

$$\int_{all\ space} |\psi|^2 dV = 1 \qquad dV = r^2 \sin\theta\, dr d\theta d\varphi \quad \Rightarrow \int_0^\infty |R|^2 r^2 dr \iint_{\theta=0\ \varphi=0}^{\theta=\pi\ \varphi=2\pi} |Y|^2 \sin\theta\, d\theta d\varphi = 1$$

For convenience, we normalize *R* and *Y* separately:

$$\int_0^\infty |R|^2 r^2 dr = 1 \qquad \text{and} \qquad \iint_{\theta=0\ \varphi=0}^{\theta=\pi\ \varphi=2\pi} |Y|^2 \sin\theta\, d\theta d\varphi = 1$$

Spherical Harmonics

$$Y_l^m(\theta,\varphi) = \underbrace{\varepsilon\sqrt{\frac{2l+1}{4\pi}\frac{(l-|m|)!}{(l+|m|)!}}P_l^m(cos\theta)}_{\Theta(\theta)}\underbrace{e^{im\varphi}}_{\Phi(\varphi)}$$

$$\varepsilon = \begin{cases} (-1)^m, & m \geq 0 \\ 1, & m < 0 \end{cases}$$

The normalized angular wave functions are called the *spherical harmonics*.

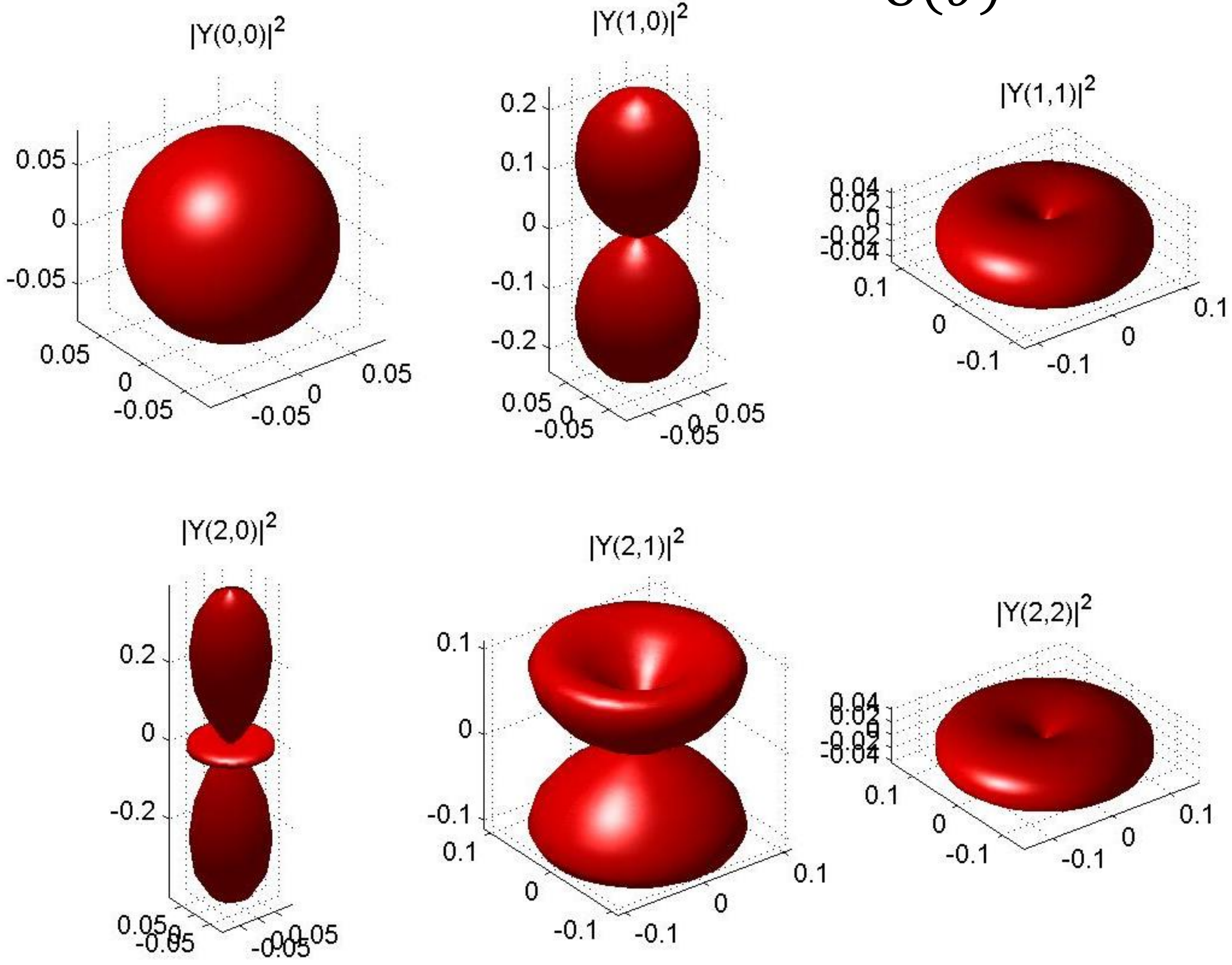


TABLE 8.1

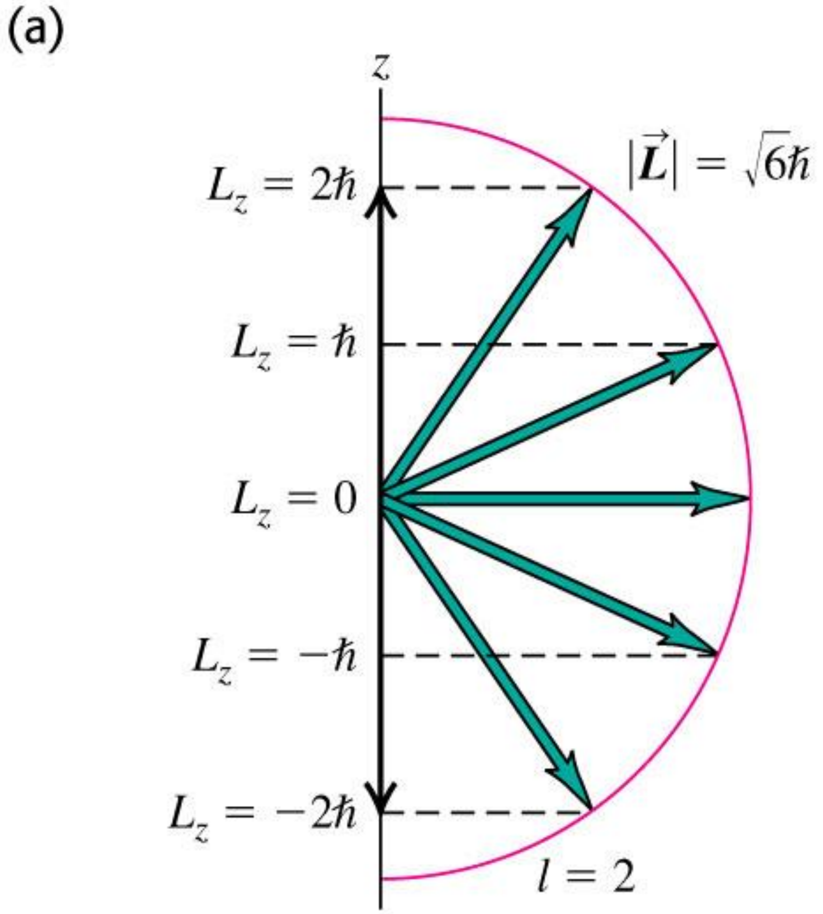
The first few angular functions $\Theta_{l,m}(\theta)$. The functions with m negative are given by $\Theta_{l,-m} = (-1)^m\Theta_{l,m}$.

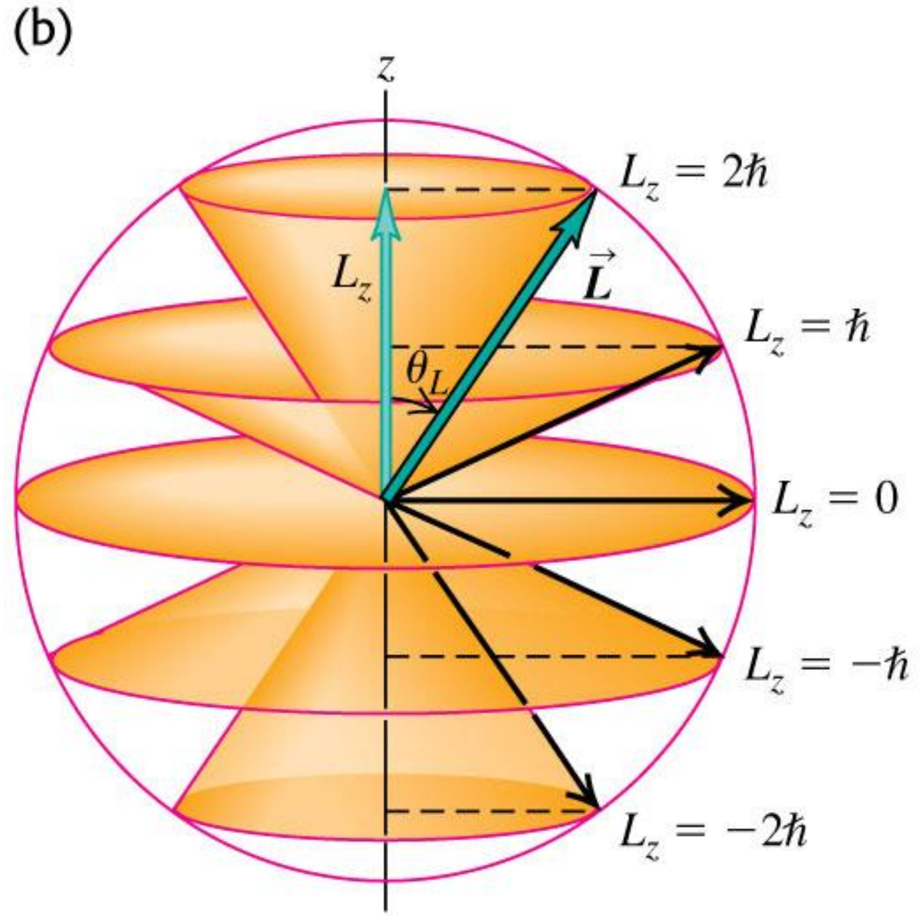
	$l = 0$	$l = 1$	$l = 2$
$m = 0$	$\sqrt{1/4\pi}$	$\sqrt{3/4\pi}\cos\theta$	$\sqrt{5/16\pi}\,(3\cos^2\theta - 1)$
$m = 1$		$-\sqrt{3/8\pi}\sin\theta$	$-\sqrt{15/8\pi}\sin\theta\cos\theta$
$m = 2$			$\sqrt{15/32\pi}\sin^2\theta$

The Θ Equation: Quantization of the Magnitude of the Angular Momentum

The requirement that $\Theta(\theta)$ be finite at $\theta = 0$ and $\theta = \pi$ determines the possible values of the magnitude of the orbital angular momentum $\vec{\boldsymbol{L}}$:

$$L = \sqrt{l(l+1)}\hbar \quad l = 0, 1, 2, \dots$$





The Radial Equation

$$\frac{r}{R}\frac{d^2}{dr^2}(rR) - \frac{2Mr^2}{\hbar^2}[U(r) - E] = l(l+1)$$

$$Let\ u(r) = rR$$

$$\frac{d^2u}{dr^2} = \frac{2M}{\hbar^2}\left[U(r) + \frac{\hbar^2}{2M}\frac{l(l+1)}{r^2} - E\right]u$$

$$\int_0^\infty |u|^2 dr = 1$$

$$normalization$$

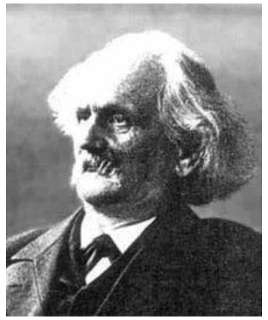
$$U_{eff} = U(r) + \frac{\hbar^2}{2M}\frac{l(l+1)}{r^2} \quad effective\ potential$$

Friedrich Wilhelm Bessel
1784-1846

$$u(r) = Arj_l(kr) + Brn_l(kr) \quad general\ solution\ for\ an\ arbitrary\ integer\ n$$

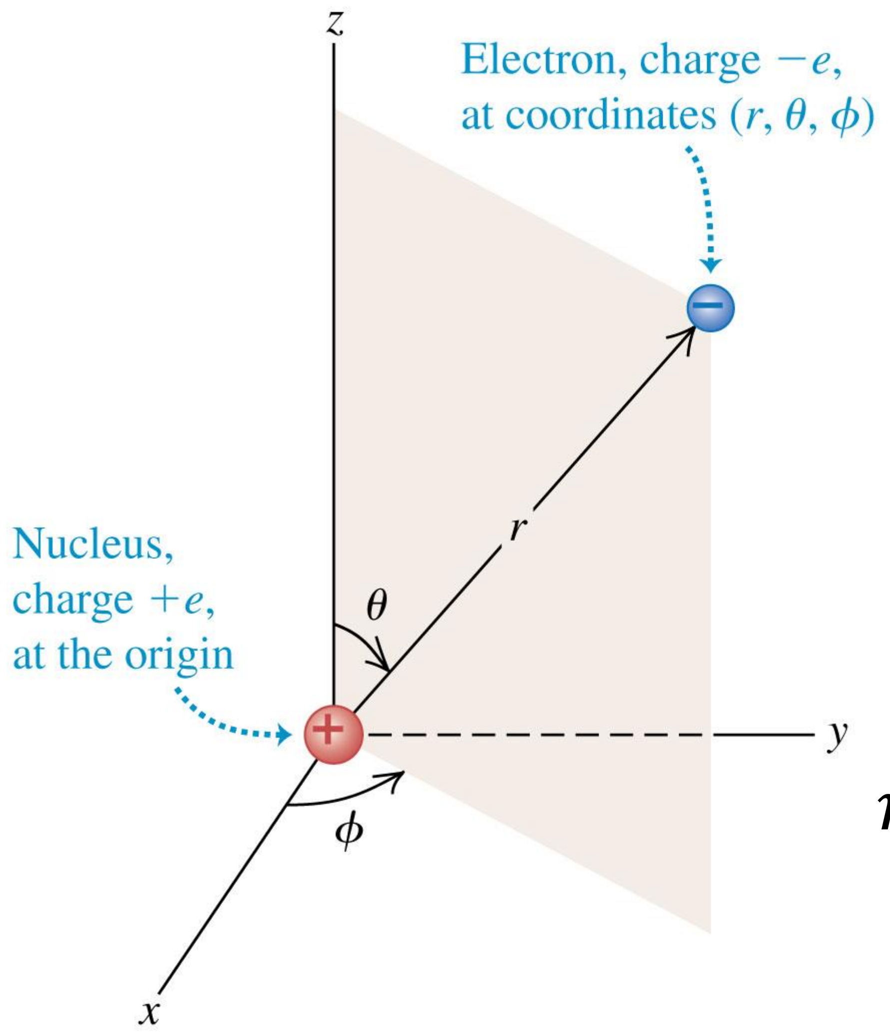
$$j_l(x) \quad spherical\ Bessel\ function\ of\ order\ l \qquad k \equiv \frac{\sqrt{2ME}}{\hbar}$$

$$n_l(x) \quad spherical\ Neumann\ function\ of\ order\ l$$



Carl Gottfried Neumann
1832-1925

The Energy Levels of the Hydrogen Atom



$$E_n = -\left[\frac{M}{2\hbar^2}\left(\frac{e^2}{4\pi\varepsilon_0}\right)^2\right]\frac{1}{n^2} = -\left[\frac{M(ke^2)^2}{2\hbar^2}\right]\frac{1}{n^2}$$

$$E_n = -\frac{E_R}{n^2} \qquad E_R = 13.6\ eV$$

$$n = 1, 2, 3, \ldots \quad principal\ quantum\ number$$

$$n > l$$

Quantum Numbers Recap

$$n = 1, 2, 3, \ldots \quad \textit{principal quantum number}$$

$$E_n = -\frac{E_R}{n^2}$$

$$l = 0, 1, 2, 3, \ldots n - 1 \quad \textit{orbital (azimuthal) quantum number}$$

$$L = \sqrt{l(l+1)}\hbar$$

$$m = 0, \pm 1, \pm 2, \pm 3, \ldots, \pm l \quad \textit{magnetic quantum number}$$

$$L_z = m\hbar$$

Degeneracy

ground state: $n = 1, \quad l = 0, \quad m = 0$

The ground state is *nondegenerate*.

first excited level: $n = 2, \quad l = \begin{cases} 0 & m = 0 \\ \text{or} & \\ 1 & m = 1, 0, \text{or } -1 \end{cases}$

The first excited level is *fourfold degenerate*.

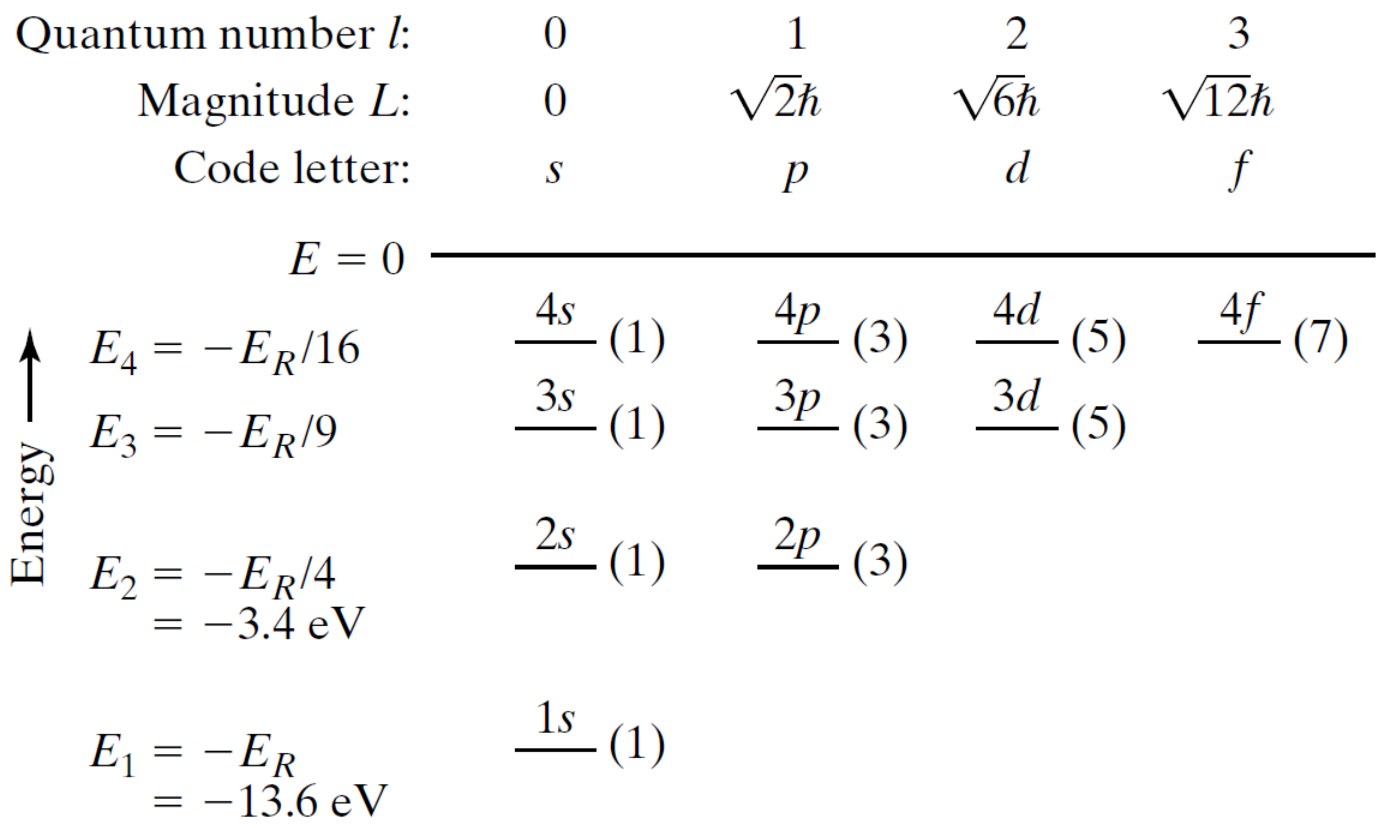


FIGURE 8.16

Energy-level diagram for the hydrogen atom, with energy plotted upward and angular momentum to the right. The letters $s, p, d, f, \ldots$ are code letters traditionally used to indicate $l = 0, 1, 2, 3, \ldots$. (Energy spacing not to scale.)

For a level n, the total degeneracy is $2n^2$.

Hydrogenic Wave Functions

$$\psi_{nlm}(r,\theta,\varphi) = R_{nl}(r)Y_l^m(\theta,\varphi) = R_{nl}(r)\Theta_{lm}(\theta)\Phi_m(\varphi)$$

$$Y_l^m(\theta,\varphi) = \varepsilon\sqrt{\frac{2l+1}{4\pi}\frac{(l-|m|)!}{(l+|m|)!}}\, e^{im\varphi}\, P_l^m(cos\theta) \qquad \varepsilon = \begin{cases}(-1)^m\,, m \geq 0\\ 1\,, \quad\quad m < 0\end{cases}$$

$$\psi_{nlm} = \sqrt{\left(\frac{2}{na_B}\right)^3 \frac{(n-l-1)!}{2n[(n+l)!]^3}}\, e^{-r/na_B}\left(\frac{2r}{na_B}\right)^l \left[L_{n-l-1}^{2l+1}(2r/na_B)\right]Y_l^m(\theta,\varphi)$$

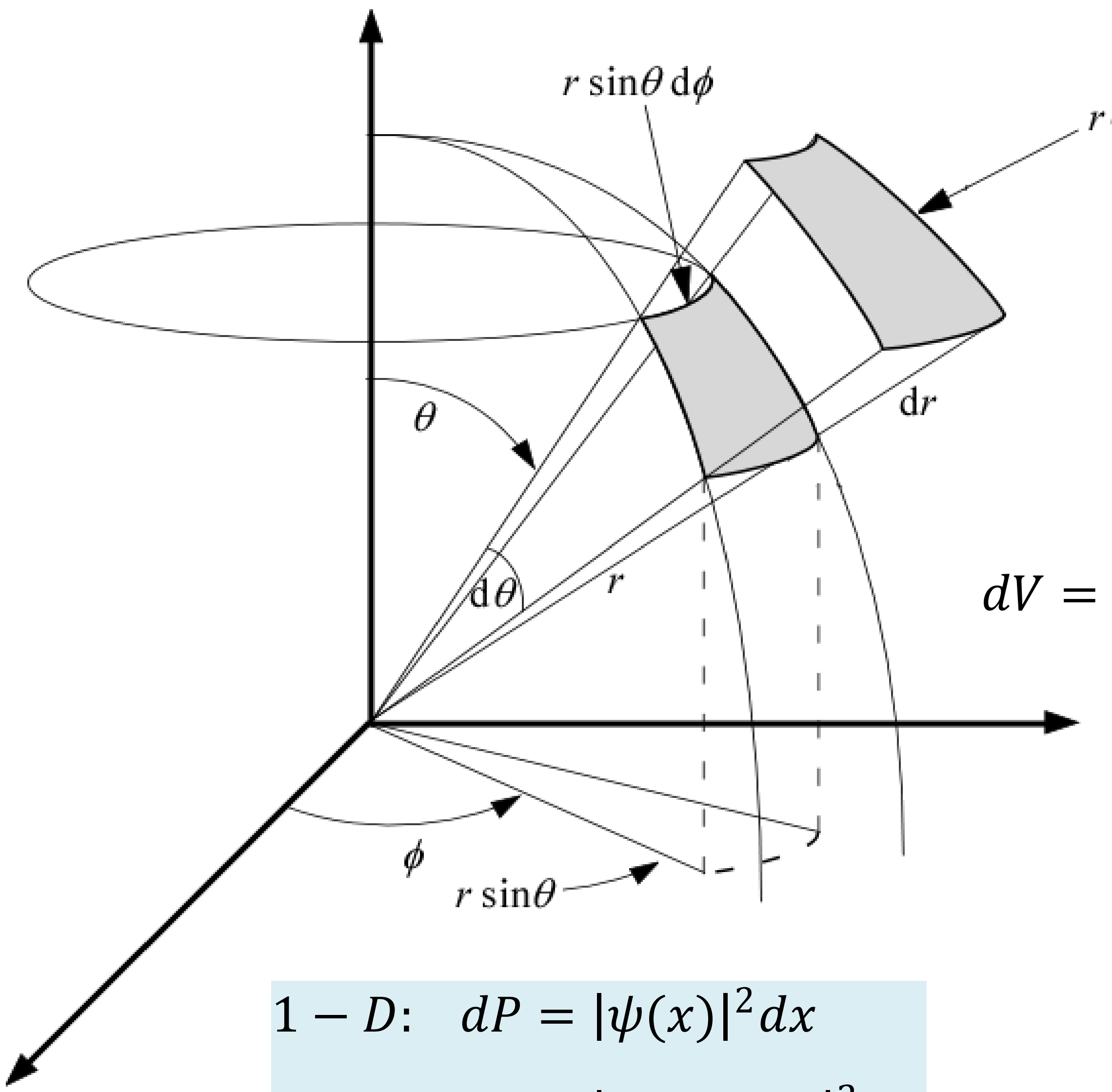
$L_{q-p}^p(x) \equiv (-1)^p\left(\frac{d}{dx}\right)^p L_q(x)$ *associated Laguerre polynomial*

$L_q(x) \equiv e^x\left(\frac{d}{dx}\right)^q (e^{-x}x^q)$ q^{th} *Laguerre polynomial*

$a_B \equiv \frac{4\pi\varepsilon_0}{e^2}\frac{\hbar}{M} = 0.529 \times 10^{-10}m$ *Bohr radius*

Edmond Nicolas Laguerre
1834-1886

Probabilities and Average Values in Three Dimensions



$$dV = r^2 \sin\theta \, dr d\theta d\varphi$$

$1 - D$: $\quad dP = |\psi(x)|^2 dx$

$3 - D$: $\quad dP = |\psi(r,\theta,\varphi)|^2 dV$

Hydrogenic Wave Functions: The Ground State

The Ground State

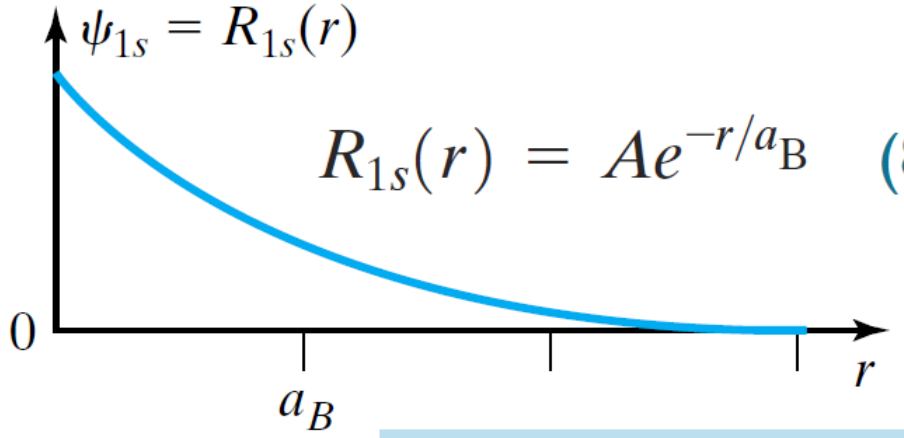
$$n = 1 \text{ and } l = 0$$

$$\psi_{1s}(r, \theta, \phi) = R_{1s}(r) \qquad (8.78)$$

$$\frac{d^2}{dr^2}(rR) = \frac{2m_e}{\hbar^2}\left[-\frac{ke^2}{r} + \frac{E_R}{n^2}\right](rR) \qquad (8.79)$$

$$a_B = \hbar^2/(m_e ke^2) \qquad E_R = ke^2/2a_B$$

$$\frac{d^2}{dr^2}(rR) = \left(\frac{1}{n^2 a_B^2} - \frac{2}{a_B r}\right)(rR) \qquad (8.80)$$



$$R_{1s}(r) = Ae^{-r/a_B} \qquad (8.81)$$

FIGURE 8.17 The wave function (8.81) for the ground state of hydrogen, as a function of *r*.

$$P(\text{between } r \text{ and } r + dr) = P(r)\, dr \qquad (8.83)$$

$$P(r) = 4\pi r^2 |R(r)|^2 \qquad (8.84)$$

radial probability density

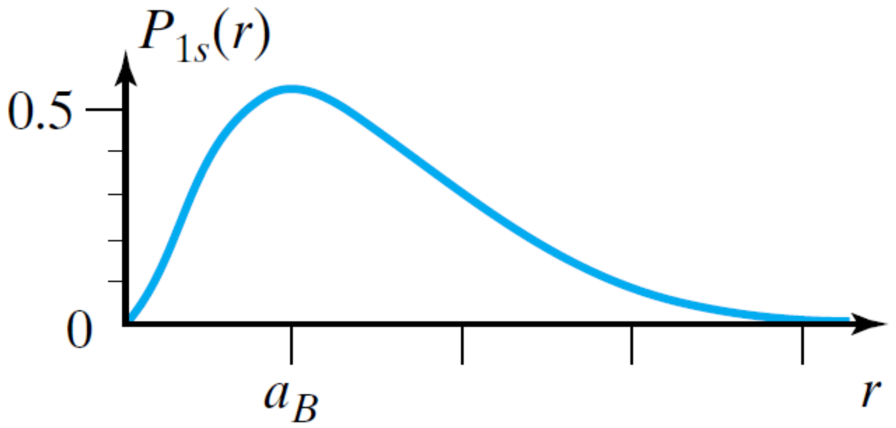
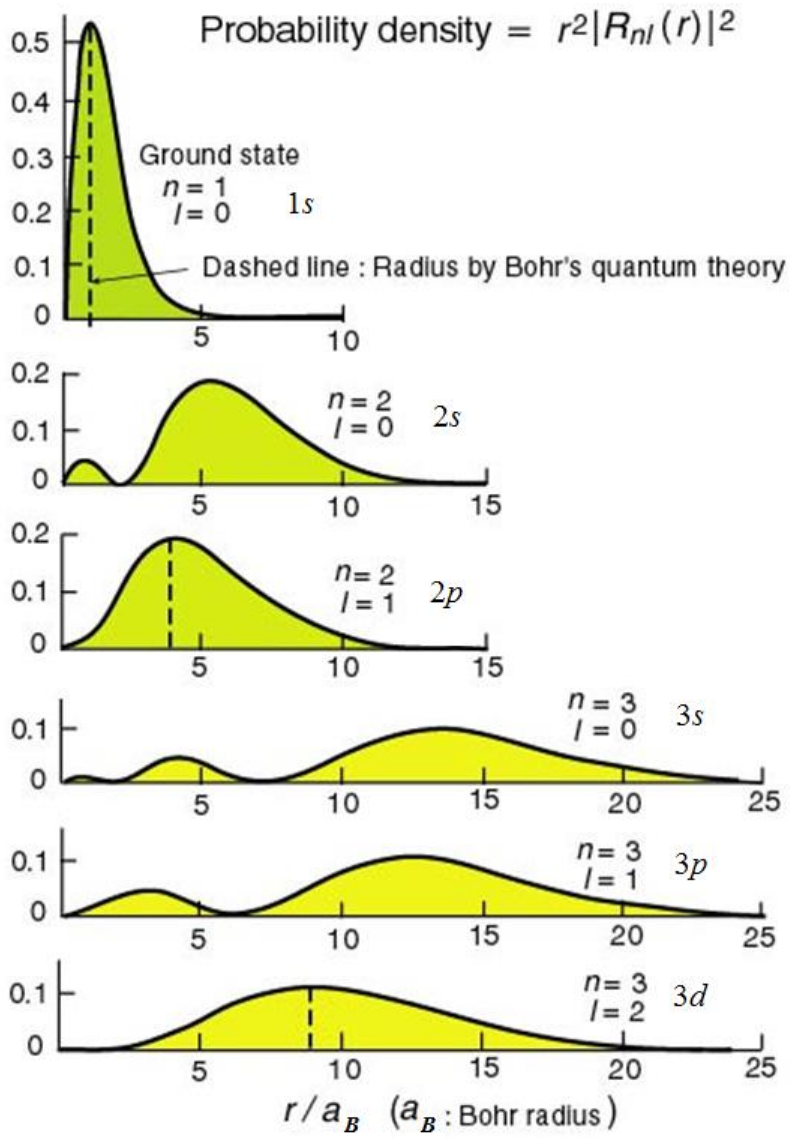
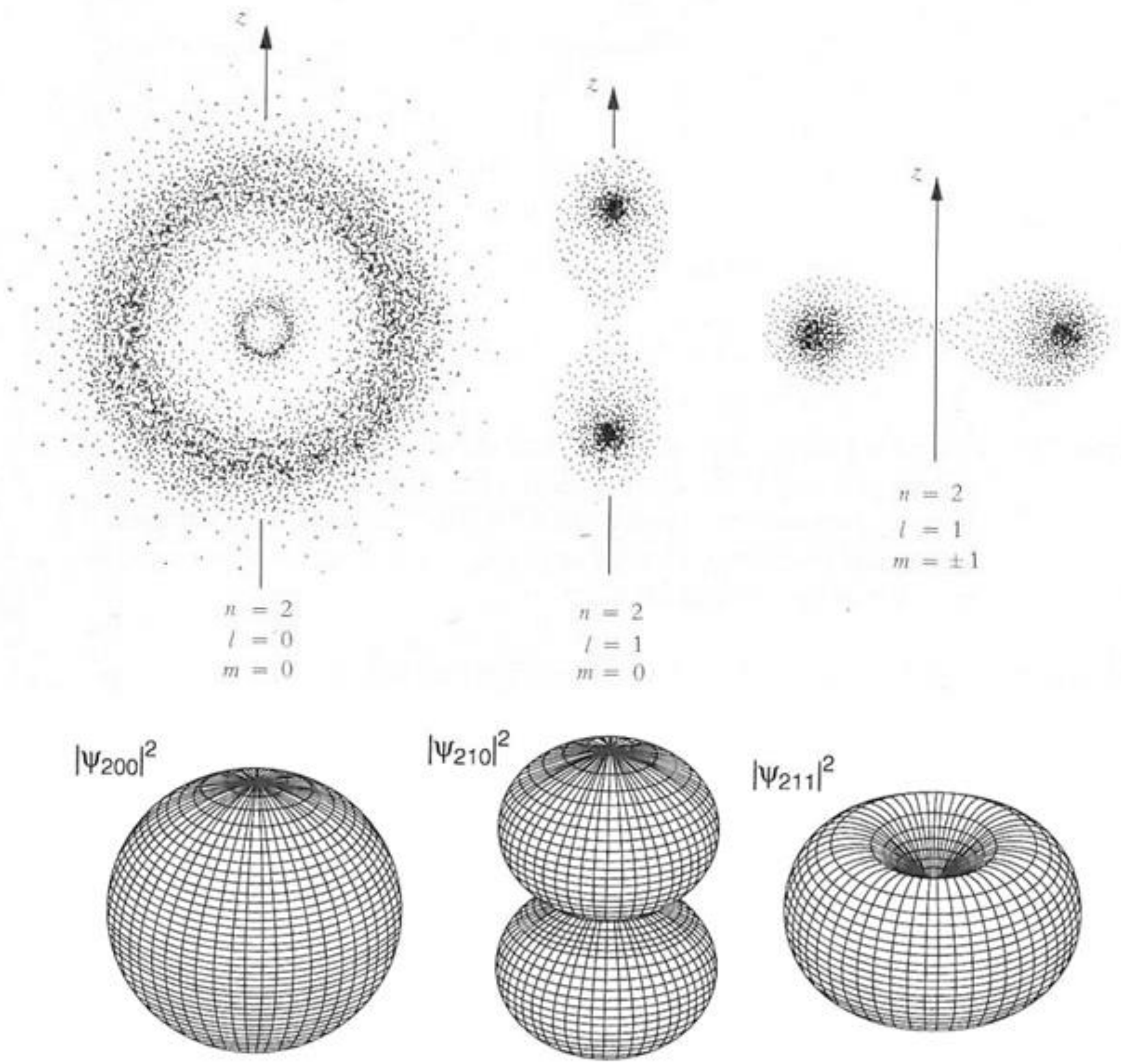


FIGURE 8.18 The probability of finding the electron a distance *r* from the nucleus is given by the radial probability density $P(r)$. For the $1s$ or ground state of hydrogen $P(r)$ is maximum at $r = a_B$. The density $P(r)$ has the dimensions of inverse length and is shown here in units of $1/a_B$.

The Radial Wave Function. Probability Density Plots. Shells





Probability Density Plots for the First Few Hydrogen Wave Functions