Hydrogen Atom

Erwin Schrödinger
(1887-1961)

… Schrödinger gave a talk on de Broglie's notion that a moving particle has a wave character. A colleague remarked to him afterward that to deal properly with a wave, one needs a wave equation. Schrödinger took this to heart, and a few weeks later he was "struggling with a new atomic theory. If only I knew more mathematics! I am very optimistic about this thing and expect that if I can only … solve it, it will be *very* beautiful."

The struggle was successful, and in January 1926 the first of four papers on "Quantization as an Eigenvalue Problem" was completed. In this epochal paper Schrödinger introduced the equation that bears his name and solved it for the hydrogen atom, thereby opening wide the door to the modern view of the atom which others had only pushed ajar.
-- A. Beiser

Spherical Coordinates

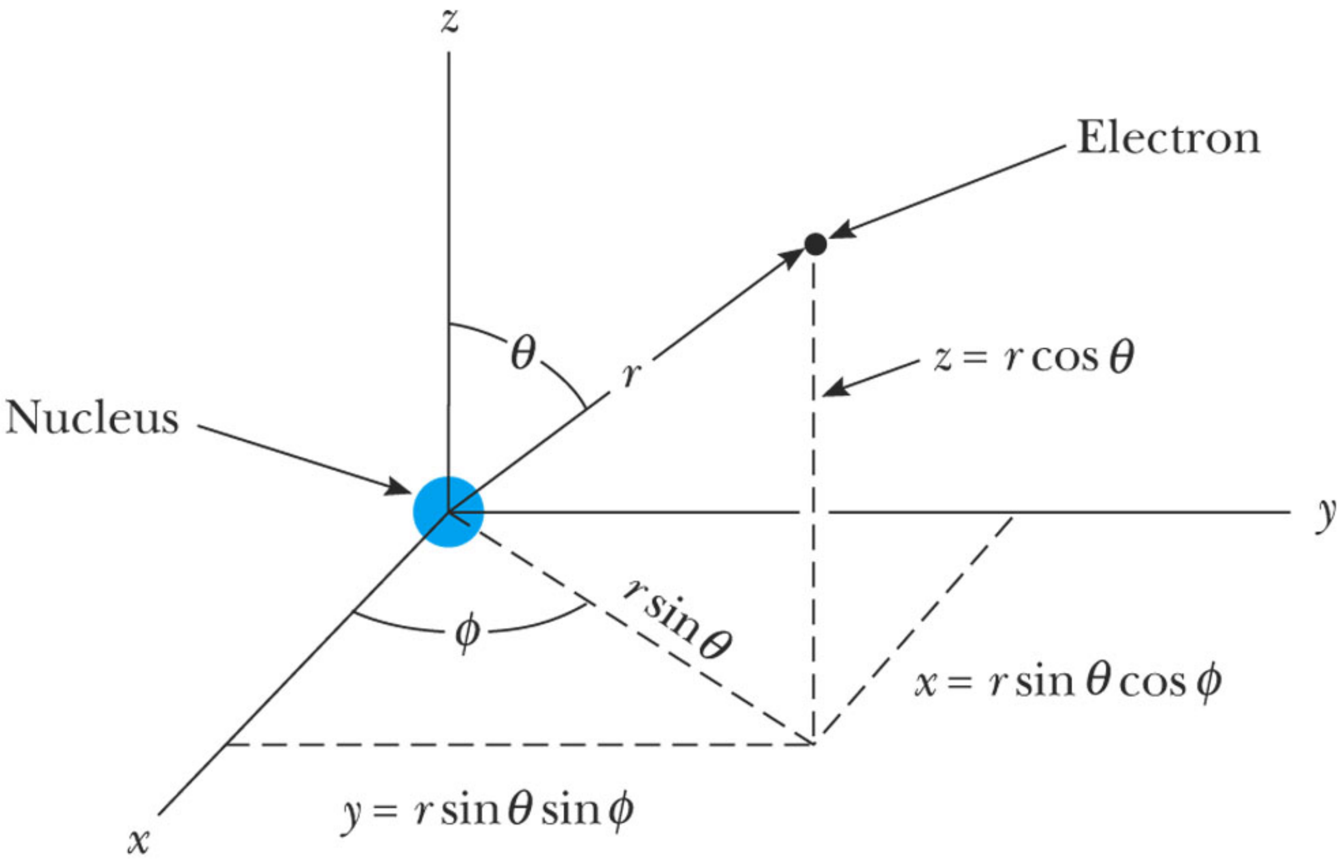


Fig. 8-5, p.266

When Potential Depends on *r* Only

Time-independent 3D Schrödinger Equation

$$-\frac{\hbar^2}{2m}\nabla^2\psi(\mathbf{r})+U(\mathbf{r})\psi(\mathbf{r})=E\psi(\mathbf{r})$$

$U(\mathbf{r})=U(r)$ 일 경우

변수분리

$$\psi(\mathbf{r})=\psi(r,\theta,\phi)=R(r)\Theta(\theta)\Phi(\phi)$$

$$\nabla^2=\frac{\partial^2}{\partial r^2}+\frac{2}{r}\frac{\partial}{\partial r}+\frac{1}{r^2}\left(\frac{\partial^2}{\partial\theta^2}+\cot\theta\frac{\partial}{\partial\theta}+\csc^2\theta\frac{\partial^2}{\partial\phi^2}\right)$$

When Potential Depends on *r* Only

$$\frac{1}{\Phi}\frac{d^2\Phi}{d\phi^2}$$

$$= -\sin^2\theta \left\{ \frac{r^2}{R}\left(\frac{d^2R}{dr^2} + \frac{2}{r}\frac{dR}{dr}\right) + \frac{1}{\Theta}\left(\frac{d^2\Theta}{d\theta^2} + \cot\theta \frac{d\Theta}{d\theta}\right) + \frac{2mr^2}{\hbar^2}\left[E - U(r)\right] \right\}$$

$$= -m_l^2$$

m_l Magnetic quantum number

When Potential Depends on *r* Only

$$\frac{d^2\Phi}{d\phi^2} = -m_l^2\Phi(\phi)$$

$$\Phi(\phi) = \frac{1}{\sqrt{2\pi}} e^{im_l\phi}$$

$$m_l = \cdots, -2, -1, 0, 1, 2, \cdots$$

When Potential Depends on *r* Only

$$\frac{r^2}{R}\left(\frac{d^2R}{dr^2}+\frac{2}{r}\frac{dR}{dr}\right)+\frac{2mr^2}{\hbar^2}\left[E-U(r)\right]=-\frac{1}{\Theta}\left(\frac{d^2\Theta}{d\theta^2}+\cot\theta\frac{d\Theta}{d\theta}\right)+\frac{m_l^2}{\sin^2\theta}$$

$$=l(l+1)$$

l Orbital quantum number

When Potential Depends on *r* Only

$$\frac{d^2\Theta}{d\theta^2} + \cot\theta \frac{d\Theta}{d\theta} - m_l^2 \csc^2\theta\,\Theta(\theta) = -l(l+1)\Theta(\theta)$$

$$l = 0, 1, 2, \cdots$$

$$l \geq |m_l|$$

Associated Legendre polynomials

Table 8.2 Some Associated Legendre Polynomials $P_\ell^{m_\ell}(\cos\theta)$

$$P_0^0 = 1$$
$$P_1^0 = 2\cos\theta$$
$$P_1^1 = \sin\theta$$
$$P_2^0 = 4(3\cos^2\theta - 1)$$
$$P_2^1 = 4\sin\theta\cos\theta$$
$$P_2^2 = \sin^2\theta$$
$$P_3^0 = 24(5\cos^3\theta - 3\cos\theta)$$
$$P_3^1 = 6\sin\theta(5\cos^2\theta - 1)$$
$$P_3^2 = 6\sin^2\theta\cos\theta$$
$$P_3^3 = \sin^3\theta$$

Table 8-2, p.269

$$\Theta(\theta)\Phi(\phi) = Y_l^{m_l}(\theta,\phi)$$

Spherical harmonics

Table 8.3 The Spherical Harmonics $Y_\ell^{m_\ell}(\theta, \phi)$

$$Y_0^0 = \frac{1}{2\sqrt{\pi}}$$

$$Y_1^0 = \tfrac{1}{2}\sqrt{\frac{3}{\pi}} \cdot \cos\theta$$

$$Y_1^{\pm 1} = \mp\tfrac{1}{2}\sqrt{\frac{3}{2\pi}} \cdot \sin\theta \cdot e^{\pm i\phi}$$

$$Y_2^0 = \tfrac{1}{4}\sqrt{\frac{5}{\pi}} \cdot (3\cos^2\theta - 1)$$

$$Y_2^{\pm 1} = \mp\tfrac{1}{2}\sqrt{\frac{15}{2\pi}} \cdot \sin\theta \cdot \cos\theta \cdot e^{\pm i\phi}$$

$$Y_2^{\pm 2} = \tfrac{1}{4}\sqrt{\frac{15}{2\pi}} \cdot \sin^2\theta \cdot e^{\pm 2i\phi}$$

$$Y_3^0 = \tfrac{1}{4}\sqrt{\frac{7}{\pi}} \cdot (5\cos^3\theta - 3\cos\theta)$$

$$Y_3^{\pm 1} = \mp\tfrac{1}{8}\sqrt{\frac{21}{\pi}} \cdot \sin\theta \cdot (5\cos^2\theta - 1) \cdot e^{\pm i\phi}$$

$$Y_3^{\pm 2} = \tfrac{1}{4}\sqrt{\frac{105}{2\pi}} \cdot \sin^2\theta \cdot \cos\theta \cdot e^{\pm 2i\phi}$$

$$Y_3^{\pm 3} = \mp\tfrac{1}{8}\sqrt{\frac{35}{\pi}} \cdot \sin^3\theta \cdot e^{\pm 3i\phi}$$

Table 8-3, p.269

When Potential Depends on *r* Only

Radial wave equation

$$-\frac{\hbar^2}{2m}\left(\frac{d^2R}{dr^2}+\frac{2}{r}\frac{dR}{dr}\right)+\frac{l(l+1)\hbar^2}{2mr^2}R(r)+U(r)R(r)=ER(r)$$

For $U(r)=-k\frac{Ze^2}{r},$

$$E_n=-\frac{ke^2Z^2}{2a_o n^2}=-13.6\text{eV}\cdot\frac{Z^2}{n^2},\quad n=1,2,3,\cdots$$

Principal quantum number

$$\left(a_o=\frac{\hbar^2}{m_e ke^2}\qquad \text{Bohr radius}\right)$$

Table 8.4 The Radial Wavefunctions $R_{n\ell}(r)$ of Hydrogen-like Atoms for $n = 1, 2,$ and 3

n	ℓ	$R_{n\ell}(r)$
1	0	$\left(\frac{Z}{a_0}\right)^{3/2} 2e^{-Zr/a_0}$
2	0	$\left(\frac{Z}{2a_0}\right)^{3/2} \left(2 - \frac{Zr}{a_0}\right) e^{-Zr/2a_0}$
2	1	$\left(\frac{Z}{2a_0}\right)^{3/2} \frac{Zr}{\sqrt{3}\, a_0} e^{-Zr/2a_0}$
3	0	$\left(\frac{Z}{3a_0}\right)^{3/2} 2\left[1 - \frac{2Zr}{3a_0} + \frac{2}{27}\left(\frac{Zr}{a_0}\right)^2\right] e^{-Zr/3a_0}$
3	1	$\left(\frac{Z}{3a_0}\right)^{3/2} \frac{4\sqrt{2}}{3} \frac{Zr}{a_0}\left(1 - \frac{Zr}{6a_0}\right) e^{-Zr/3a_0}$
3	2	$\left(\frac{Z}{3a_0}\right)^{3/2} \frac{2\sqrt{2}}{27\sqrt{5}} \left(\frac{Zr}{a_0}\right)^2 e^{-Zr/3a_0}$

Table 8-4, p.280

Hydrogen-like Atom

$$E_n = -\frac{ke^2 Z^2}{2a_o n^2} = -13.6\text{eV} \cdot \frac{Z^2}{n^2},$$

$$\Psi_{nlm_l}(r,\theta,\phi,t) = R_{nl}(r) Y_l^{m_l}(\theta,\phi) e^{-i\frac{E_n}{\hbar}t}$$

$n = 1, 2, 3, \cdots$ Principal quantum number

$l = 0, 1, 2, \cdots, (n-1)$ Orbital quantum number

$m_l = -l, (-l+1), \cdots, -2, -1, 0, 1, 2, \cdots, (l-1), l$

Magnetic quantum number

$m_s = -\frac{1}{2}, \frac{1}{2}$ Spin magnetic quantum number

Table 6.1 Normalized Wave Functions of the Hydrogen Atom for $n = 1$, 2, and 3*

n	l	m_l	$\Phi(\phi)$	$\Theta(\theta)$	$R(r)$	$\psi(r, \theta, \phi)$
1	0	0	$\frac{1}{\sqrt{2\pi}}$	$\frac{1}{\sqrt{2}}$	$\frac{2}{a_0^{3/2}} e^{-r/a_0}$	$\frac{1}{\sqrt{\pi}\, a_0^{3/2}} e^{-r/a_0}$
2	0	0	$\frac{1}{\sqrt{2\pi}}$	$\frac{1}{\sqrt{2}}$	$\frac{1}{2\sqrt{2}\, a_0^{3/2}} \left(2 - \frac{r}{a_0}\right) e^{-r/2a_0}$	$\frac{1}{4\sqrt{2\pi}\, a_0^{3/2}} \left(2 - \frac{r}{a_0}\right) e^{-r/2a_0}$
2	1	0	$\frac{1}{\sqrt{2\pi}}$	$\frac{\sqrt{6}}{2} \cos\theta$	$\frac{1}{2\sqrt{6}\, a_0^{3/2}} \frac{r}{a_0} e^{-r/2a_0}$	$\frac{1}{4\sqrt{2\pi}\, a_0^{3/2}} \frac{r}{a_0} e^{-r/2a_0} \cos\theta$
2	1	± 1	$\frac{1}{\sqrt{2\pi}} e^{\pm i\phi}$	$\frac{\sqrt{3}}{2} \sin\theta$	$\frac{1}{2\sqrt{6}\, a_0^{3/2}} \frac{r}{a_0} e^{-r/2a_0}$	$\frac{1}{8\sqrt{\pi}\, a_0^{3/2}} \frac{r}{a_0} e^{-r/2a_0} \sin\theta\, e^{\pm i\phi}$
3	0	0	$\frac{1}{\sqrt{2\pi}}$	$\frac{1}{\sqrt{2}}$	$\frac{2}{81\sqrt{3}\, a_0^{3/2}} \left(27 - 18\frac{r}{a_0} + 2\frac{r^2}{a_0^2}\right) e^{-r/3a_0}$	$\frac{1}{81\sqrt{3\pi}\, a_0^{3/2}} \left(27 - 18\frac{r}{a_0} + 2\frac{r^2}{a_0^2}\right) e^{-r/3a_0}$
3	1	0	$\frac{1}{\sqrt{2\pi}}$	$\frac{\sqrt{6}}{2} \cos\theta$	$\frac{4}{81\sqrt{6}\, a_0^{3/2}} \left(6 - \frac{r}{a_0}\right) \frac{r}{a_0} e^{-r/3a_0}$	$\frac{\sqrt{2}}{81\sqrt{\pi}\, a_0^{3/2}} \left(6 - \frac{r}{a_0}\right) \frac{r}{a_0} e^{-r/3a_0} \cos\theta$
3	1	± 1	$\frac{1}{\sqrt{2\pi}} e^{\pm i\phi}$	$\frac{\sqrt{3}}{2} \sin\theta$	$\frac{4}{81\sqrt{6}\, a_0^{3/2}} \left(6 - \frac{r}{a_0}\right) \frac{r}{a_0} e^{-r/3a_0}$	$\frac{1}{81\sqrt{\pi}\, a_0^{3/2}} \left(6 - \frac{r}{a_0}\right) \frac{r}{a_0} e^{-r/3a_0} \sin\theta\, e^{\pm i\phi}$
3	2	0	$\frac{1}{\sqrt{2\pi}}$	$\frac{\sqrt{10}}{4} (3\cos^2\theta - 1)$	$\frac{4}{81\sqrt{30}\, a_0^{3/2}} \frac{r^2}{a_0^2} e^{-r/3a_0}$	$\frac{1}{81\sqrt{6\pi}\, a_0^{3/2}} \frac{r^2}{a_0^2} e^{-r/3a_0} (3\cos^2\theta - 1)$
3	2	± 1	$\frac{1}{\sqrt{2\pi}} e^{\pm i\phi}$	$\frac{\sqrt{15}}{2} \sin\theta\cos\theta$	$\frac{4}{81\sqrt{30}\, a_0^{3/2}} \frac{r^2}{a_0^2} e^{-r/3a_0}$	$\frac{1}{81\sqrt{\pi}\, a_0^{3/2}} \frac{r^2}{a_0^2} e^{-r/3a_0} \sin\theta\cos\theta\, e^{\pm i\phi}$
3	2	± 2	$\frac{1}{\sqrt{2\pi}} e^{\pm 2i\phi}$	$\frac{\sqrt{15}}{4} \sin^2\theta$	$\frac{4}{81\sqrt{30}\, a_0^{3/2}} \frac{r^2}{a_0^2} e^{-r/3a_0}$	$\frac{1}{162\sqrt{\pi}\, a_0^{3/2}} \frac{r^2}{a_0^2} e^{-r/3a_0} \sin^2\theta\, e^{\pm 2i\phi}$

*The quantity $a_0 = 4\pi\epsilon_0\hbar^2/me^2 = 5.292 \times 10^{-11}$ m is equal to the radius of the innermost Bohr orbit.

Table 8.5 Spectroscopic Notation for Atomic Shells and Subhells

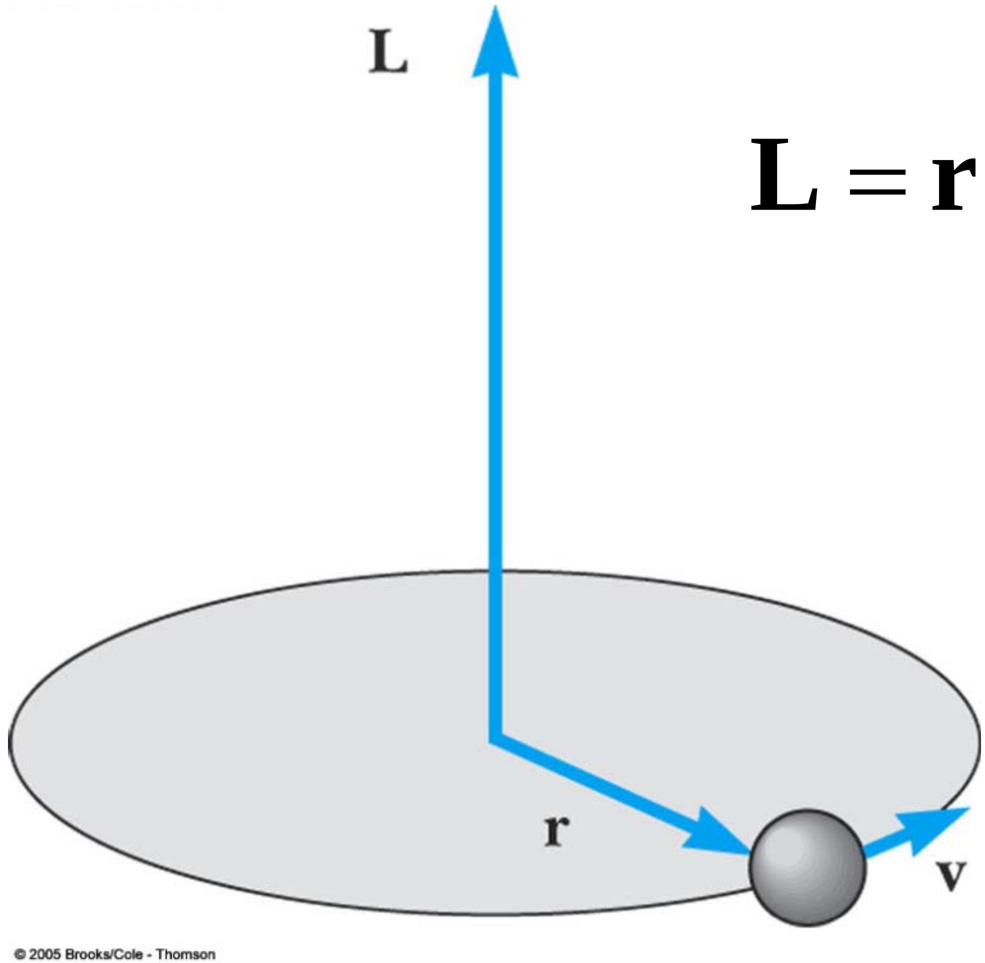
n	Shell Symbol	ℓ	Shell Symbol
1	K	0	s
2	L	1	p
3	M	2	d
4	N	3	f
5	O	4	g
6	P	5	h
. . .		. . .	

Table 8-5, p.280

Table 6.2 Atomic Electron States

	$l = 0$	$l = 1$	$l = 2$	$l = 3$	$l = 4$	$l = 5$
$n = 1$	1*s*					
$n = 2$	2*s*	2*p*				
$n = 3$	3*s*	3*p*	3*d*			
$n = 4$	4*s*	4*p*	4*d*	4*f*		
$n = 5$	5*s*	5*p*	5*d*	5*f*	5*g*	
$n = 6$	6*s*	6*p*	6*d*	6*f*	6*g*	6*h*

Angular Momentum



$$\mathbf{L} = \mathbf{r} \times \mathbf{p}$$

Fig. 8-6, p.267

When Potential Depends on *r* Only

Radial wave equation

$$-\frac{\hbar^2}{2m}\left(\frac{d^2R}{dr^2}+\frac{2}{r}\frac{dR}{dr}\right)+\frac{l(l+1)\hbar^2}{2mr^2}R(r)+U(r)R(r)=ER(r)$$

$$K_{orb}=\frac{1}{2}mv^2=\frac{L^2}{2mr^2}$$

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

Angular Momentum

$$\hat{\mathbf{L}} = \hat{\mathbf{r}} \times \hat{\mathbf{p}}$$

$$\hat{\mathbf{L}} = \begin{vmatrix} \mathbf{a_x} & \mathbf{a_y} & \mathbf{a_z} \\ x & y & z \\ -i\hbar\partial/\partial x & -i\hbar\partial/\partial y & -i\hbar\partial/\partial z \end{vmatrix}$$

$$\hat{L}_x = i\hbar\left(\sin\phi\frac{\partial}{\partial\theta} + \cot\theta\cos\phi\frac{\partial}{\partial\phi}\right)$$

$$\hat{L}_y = -i\hbar\left(\cos\phi\frac{\partial}{\partial\theta} - \cot\theta\sin\phi\frac{\partial}{\partial\phi}\right)$$

$$\hat{L}_z = -i\hbar\frac{\partial}{\partial\phi}$$

Angular Momentum

$$\hat{L}^2 Y_l^{m_l}(\theta,\phi) = l(l+1)\hbar^2 Y_l^{m_l}(\theta,\phi)$$

$$\hat{L}_z Y_l^{m_l}(\theta,\phi) = m_l \hbar Y_l^{m_l}(\theta,\phi)$$

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

$$L_z = m_l \hbar$$

Space Quantization

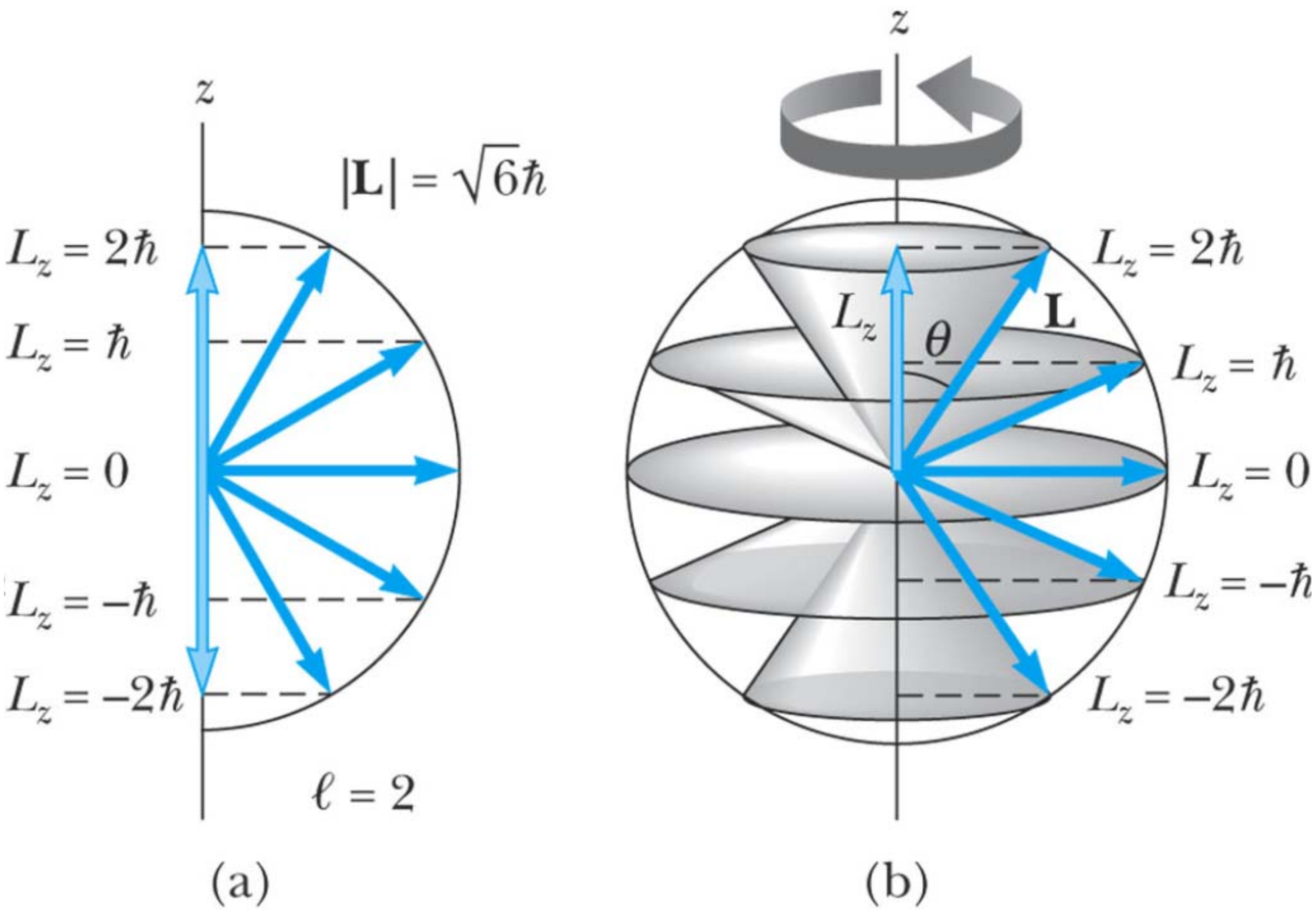


Fig. 8-7, p.272

Selection Rule

$$|l_f - l_i| = 1$$

$$\text{or} \quad \Delta l = \pm 1$$

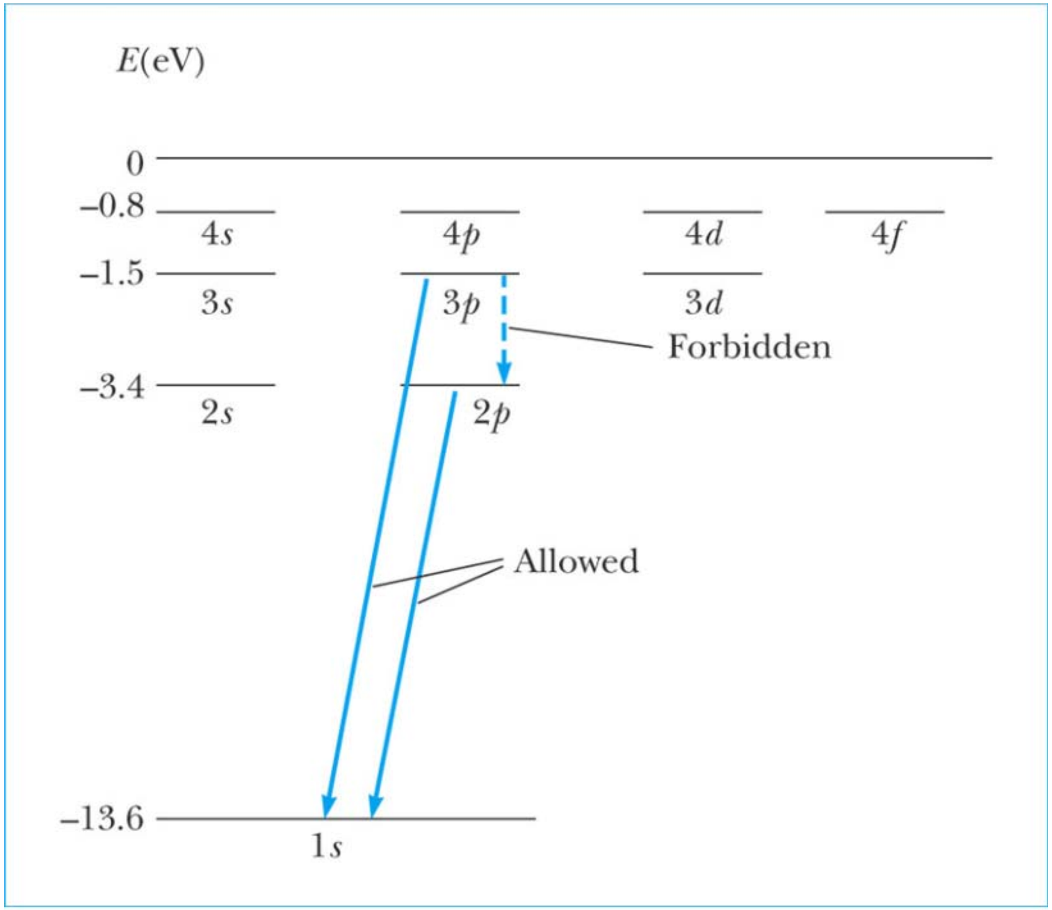


Fig. 8-8, p.281

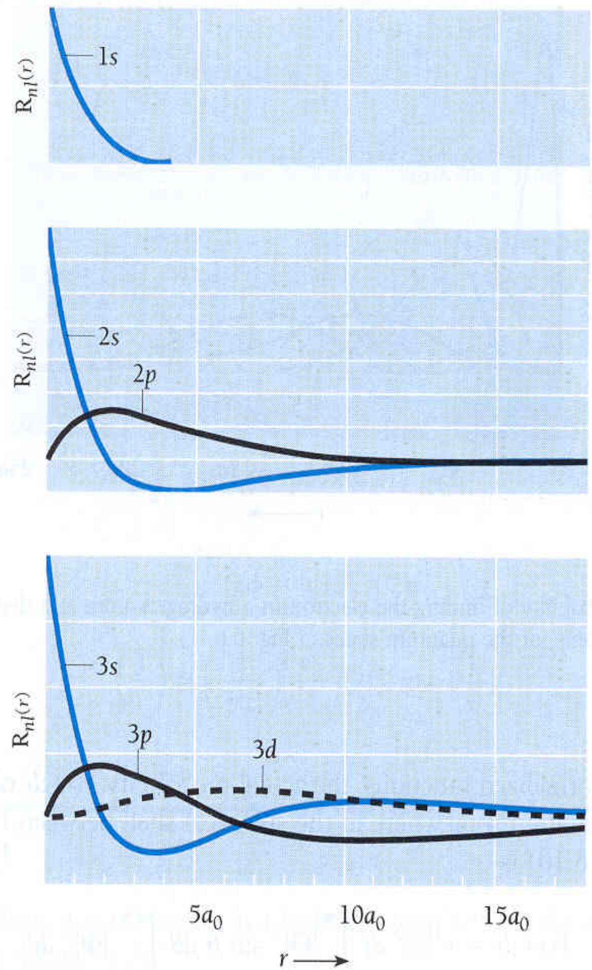


Figure 6.8 The variation with distance from the nucleus of the radial part of the electron wave function in hydrogen for various quantum states. The quantity $a_0 = 4\pi\epsilon_0\hbar^2/me^2 = 0.053$ nm is the radius of the first Bohr orbit.

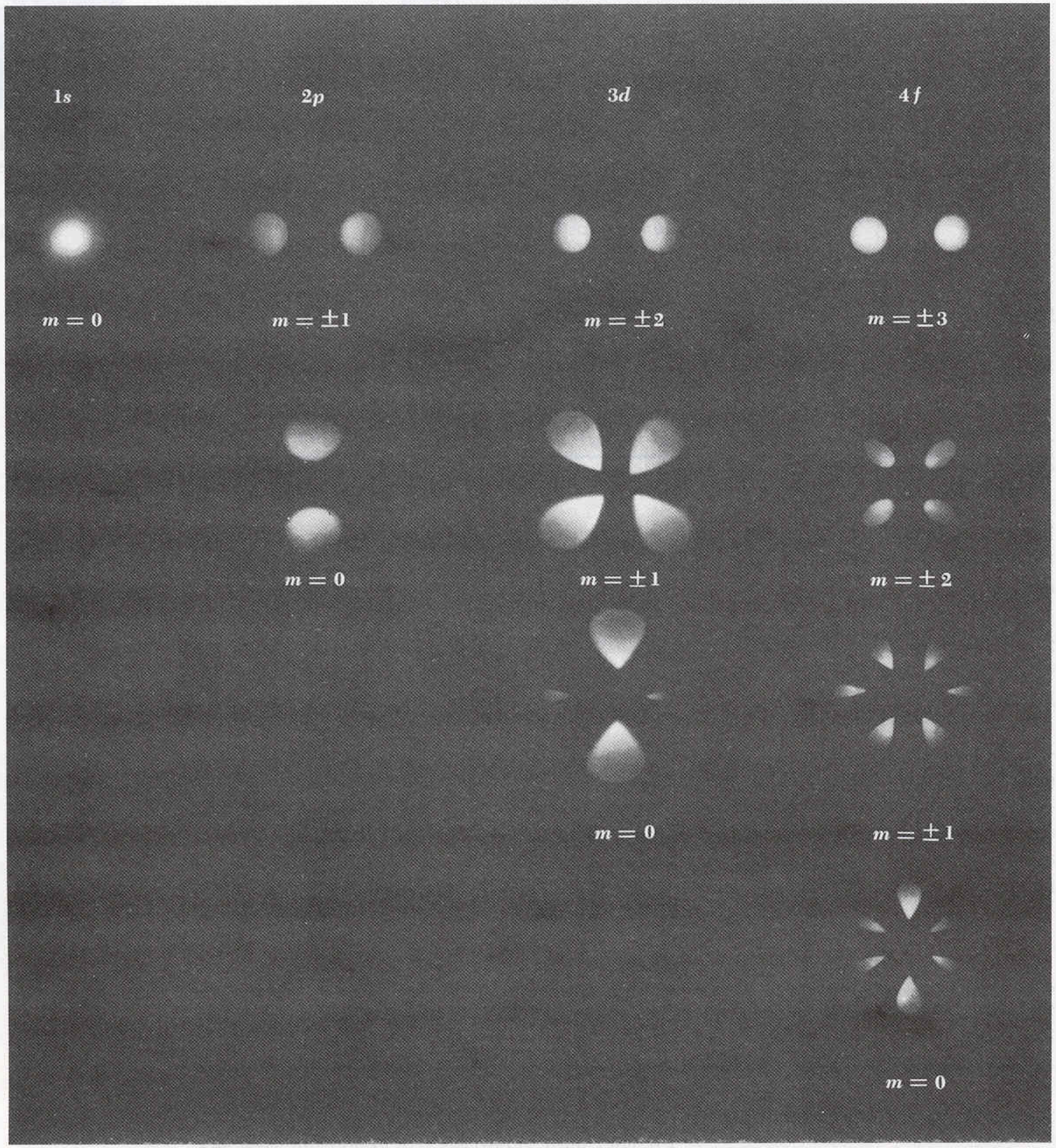
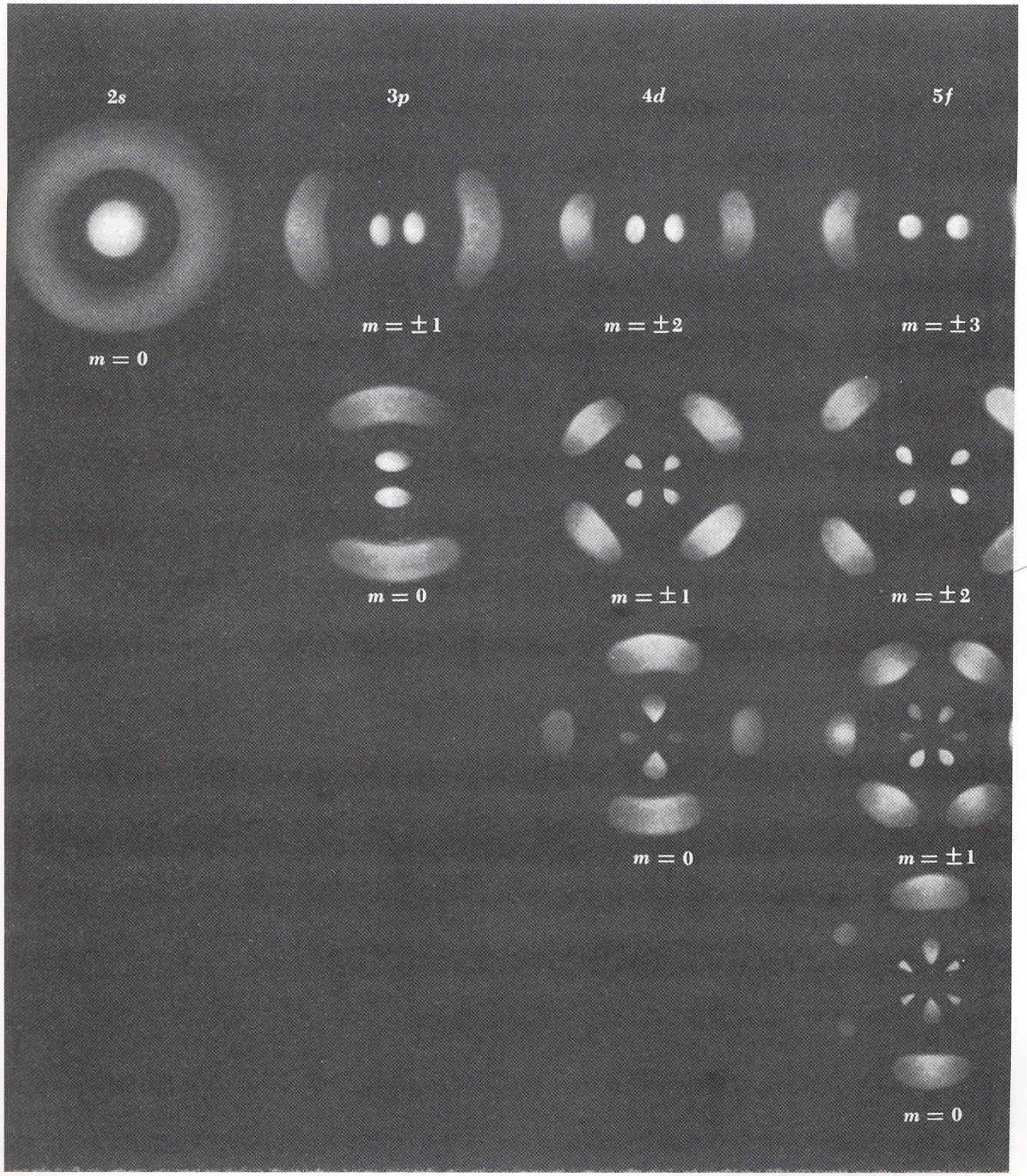


Figure 6.12 Photographic representation of the electron probability-density distribution $|\psi|^2$ for several energy states. These may be regarded as sectional views of the distribution in a plane containing the polar axis, which is vertical and in the plane of the paper. The scale varies from figure to figure.


2s
3p
4d
5f
m = 0
m = ±1
m = ±2
m = ±3
m = 0
m = ±1
m = ±2
m = 0
m = ±1
m = 0

$$P(r)dr = |\psi|^2 \, 4\pi r^2 dr$$

$$P(r) = r^2 |R(r)|^2$$

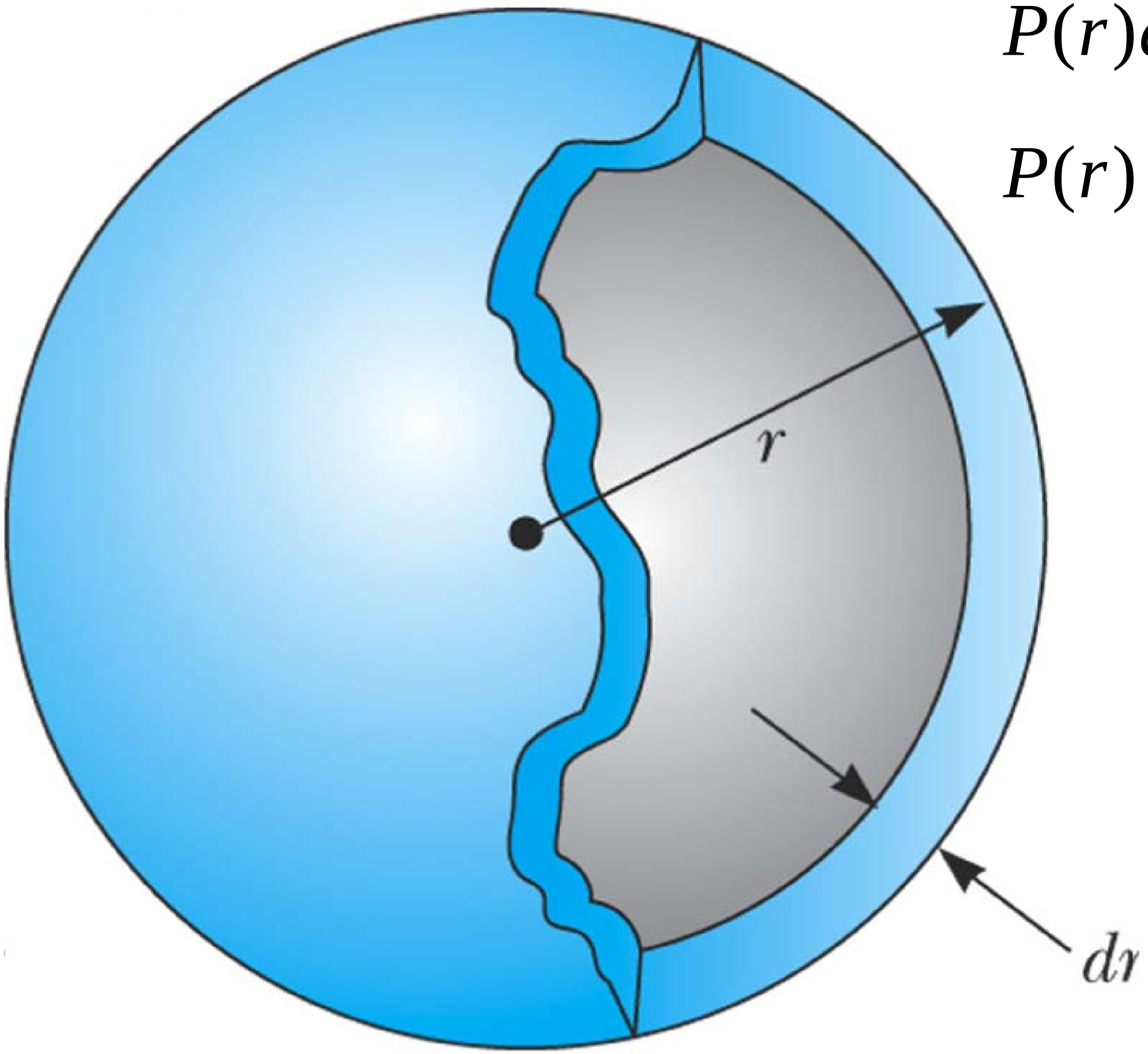


Fig. 8-9, p.282

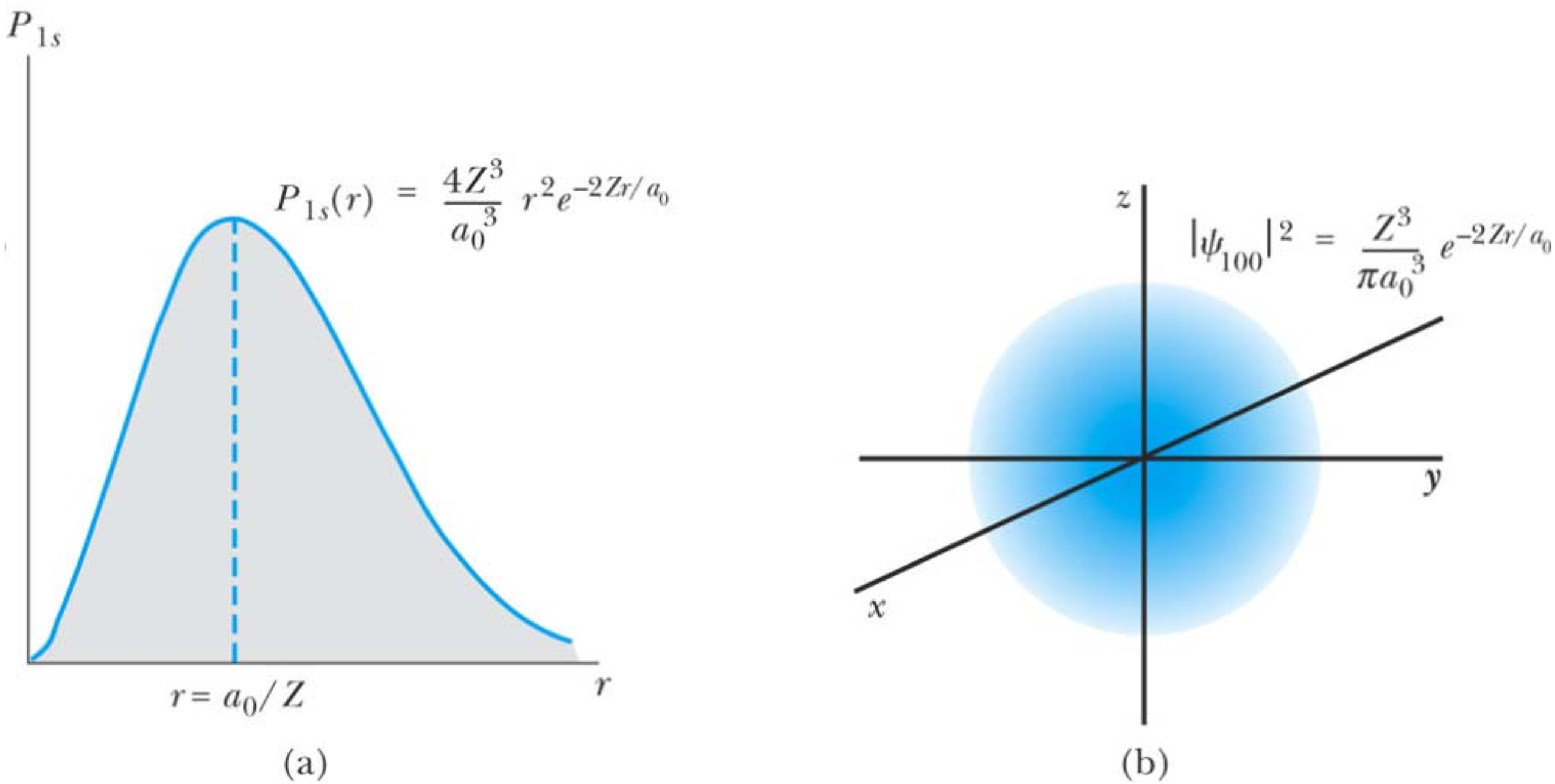

P_{1s}
$P_{1s}(r) = \frac{4Z^3}{a_0^3} r^2 e^{-2Zr/a_0}$
$r = a_0/Z$
r
(a)
z
$|\psi_{100}|^2 = \frac{Z^3}{\pi a_0^3} e^{-2Zr/a_0}$
y
x
(b)

Fig. 8-10, p.283

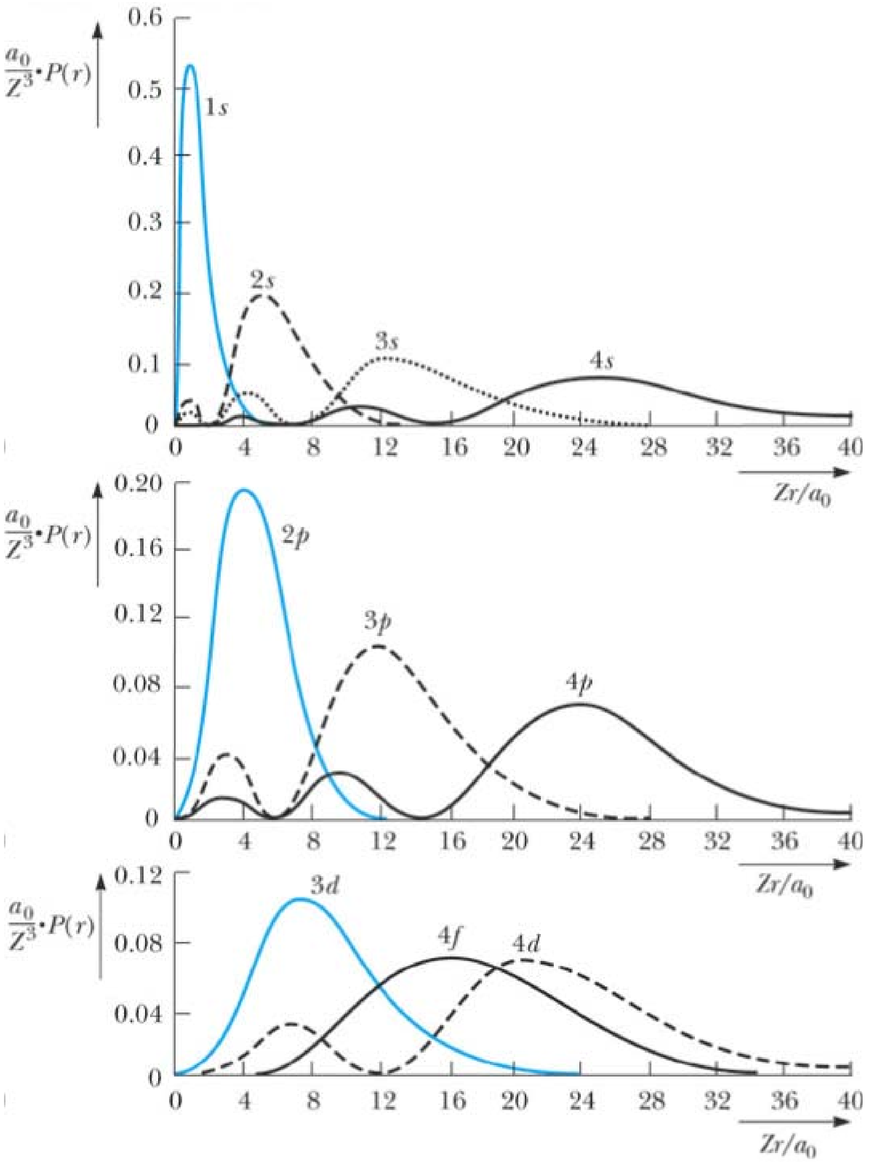
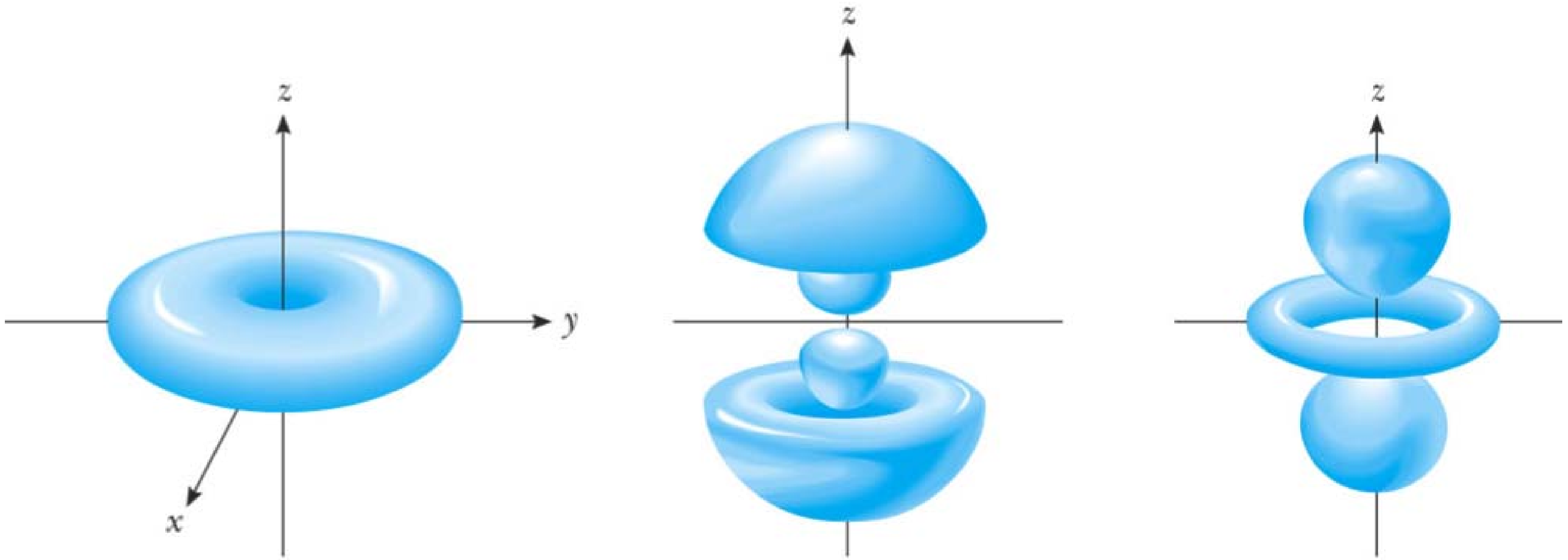

$\frac{a_0}{Z^3}\cdot P(r)$
0.6
0.5
0.4
0.3
0.2
0.1
0
1s
2s
3s
4s
0 4 8 12 16 20 24 28 32 36 40
Zr/a_0
0.20
0.16
0.12
0.08
0.04
2p
3p
4p
0.12
0.08
0.04
3d
4f
4d

Fig. 8-11, p.285



$n = 2, \ell = 1, m_\ell = \pm 1$
(a)

$n = 3, \ell = 1, m_\ell = 0$
(b)

$n = 3, \ell = 2, m_\ell = 0$
(c)

Fig. 8-12, p.286

$$\psi_{210} = R_{21}(r)Y_1^0(\theta,\phi) = \psi_{2p_z} \quad \psi_{2p_x} = \frac{1}{\sqrt{2}}\left(\psi_{211} + \psi_{21-1}\right) \quad \psi_{2p_y} = \frac{1}{\sqrt{2}}\left(\psi_{211} - \psi_{21-1}\right)$$

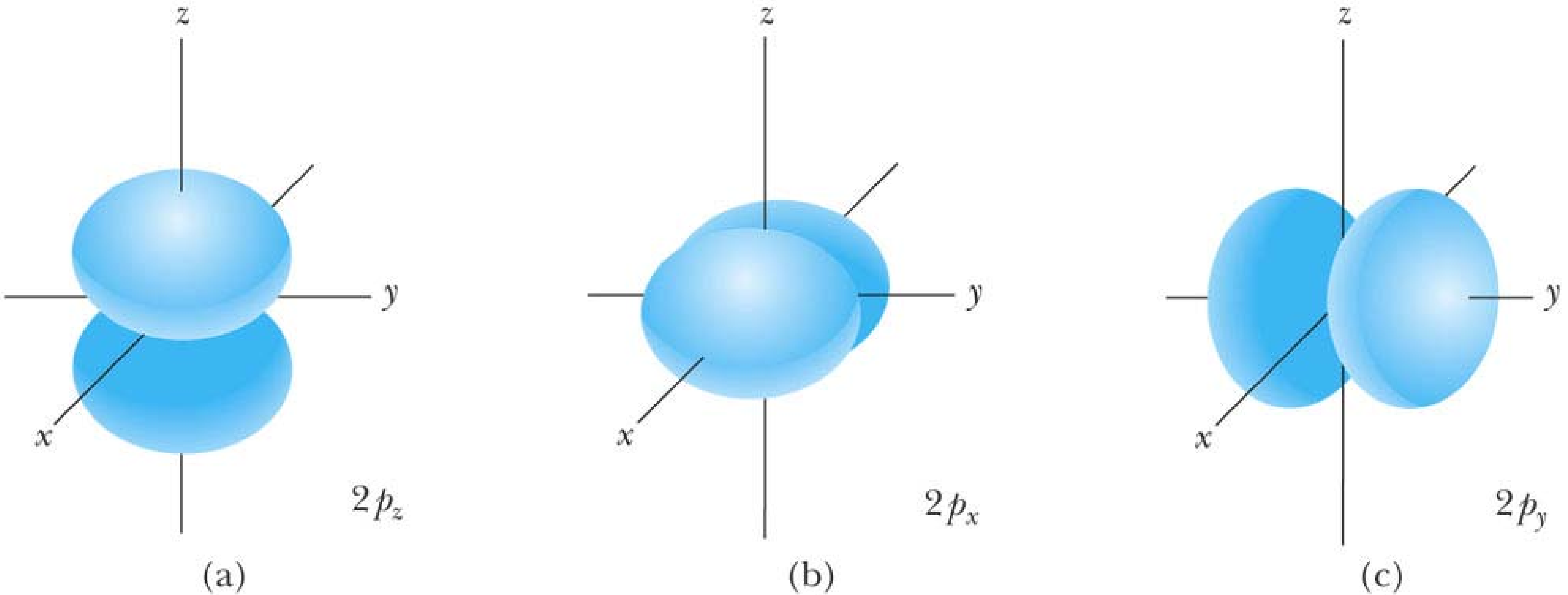


Fig. 8-13, p.286