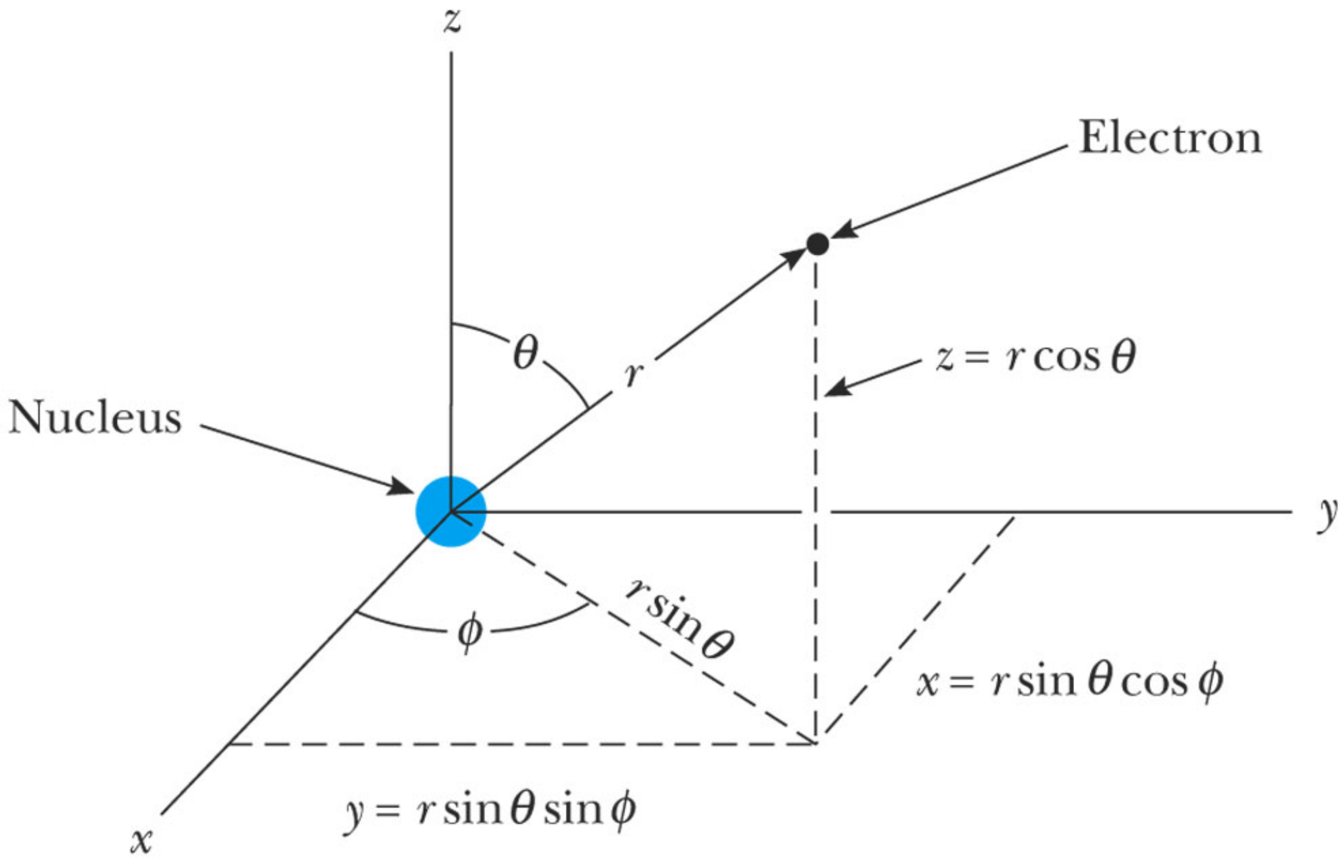
Ch. 6. Quantum Theory of the H Atom

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



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

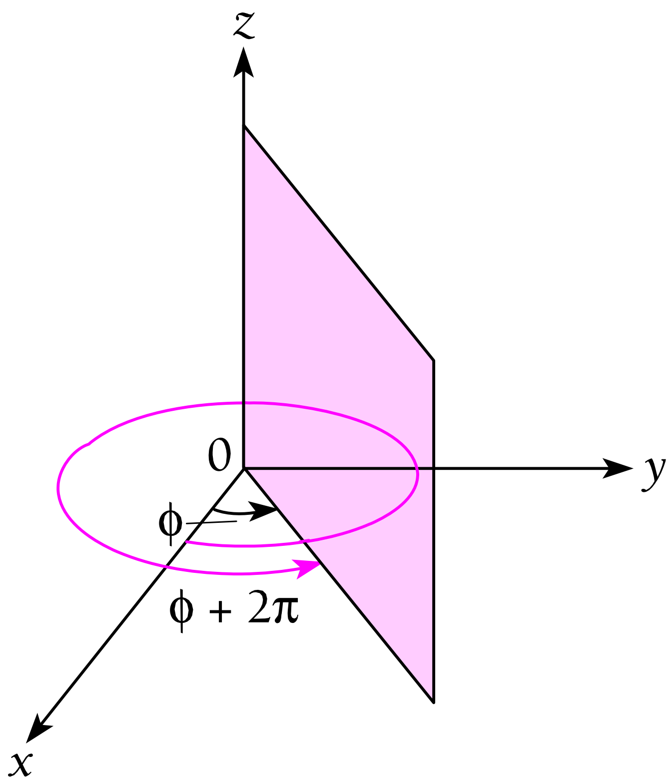
$$\frac{1}{\Phi}\frac{d^2\Phi}{d\phi^2}$$

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

$$= -m_l^2$$

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 $P_\ell^{m_\ell}(\cos\theta)$

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

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

Spherical harmonics

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

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

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

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

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

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

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

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

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

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

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

Hydrogen-like Atom

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 $$U(r)=-\frac{Ze^2}{4\pi\varepsilon_0 r},$$

$$E_n=-\frac{e^2Z^2}{8\pi\varepsilon_0 a_o n^2}=-\frac{me^4Z^2}{32\pi^2\varepsilon_0^2\hbar^2n^2}=-13.6\text{eV}\cdot\frac{Z^2}{n^2},\quad n=1,2,3,\cdots$$

Principal quantum number

$$\left(a_o=\frac{\hbar^2}{4\pi\varepsilon_0 me^2}\qquad \text{Bohr radius}\right)$$

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	$\left(\frac{Z}{3a_0}\right)^{3/2} \frac{2\sqrt{2}}{27\sqrt{5}} \left(\frac{Zr}{a_0}\right)^2 e^{-Zr/3a_0}$

Hydrogen-like Atom

$$E_n = -\frac{me^4Z^2}{32\pi^2\varepsilon_0^2\hbar^2n^2} = -13.6\text{eV}\cdot\frac{Z^2}{n^2},$$

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

$n = 1, 2, 3, \cdots$ 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

표 6.1 수소원자의 규격화된 파동함수; n = 1, 2, 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	$\frac{1}{\sqrt{2\pi}} e^{\pm 2i\phi}$	$\frac{\sqrt{15}}{4} \sin^2\theta$	$\frac{4}{81\sqrt{30}\, a_0^{3/2}} \frac{r^2}{a_0^2} e^{-r/3a_0}$	$\frac{1}{162\sqrt{\pi}\, a_0^{3/2}} \frac{r^2}{a_0^2} e^{-r/3a_0} \sin^2\theta\, e^{\pm 2i\phi}$

Table 8.5 Spectroscopic Notation for Atomic Shells and Subhells

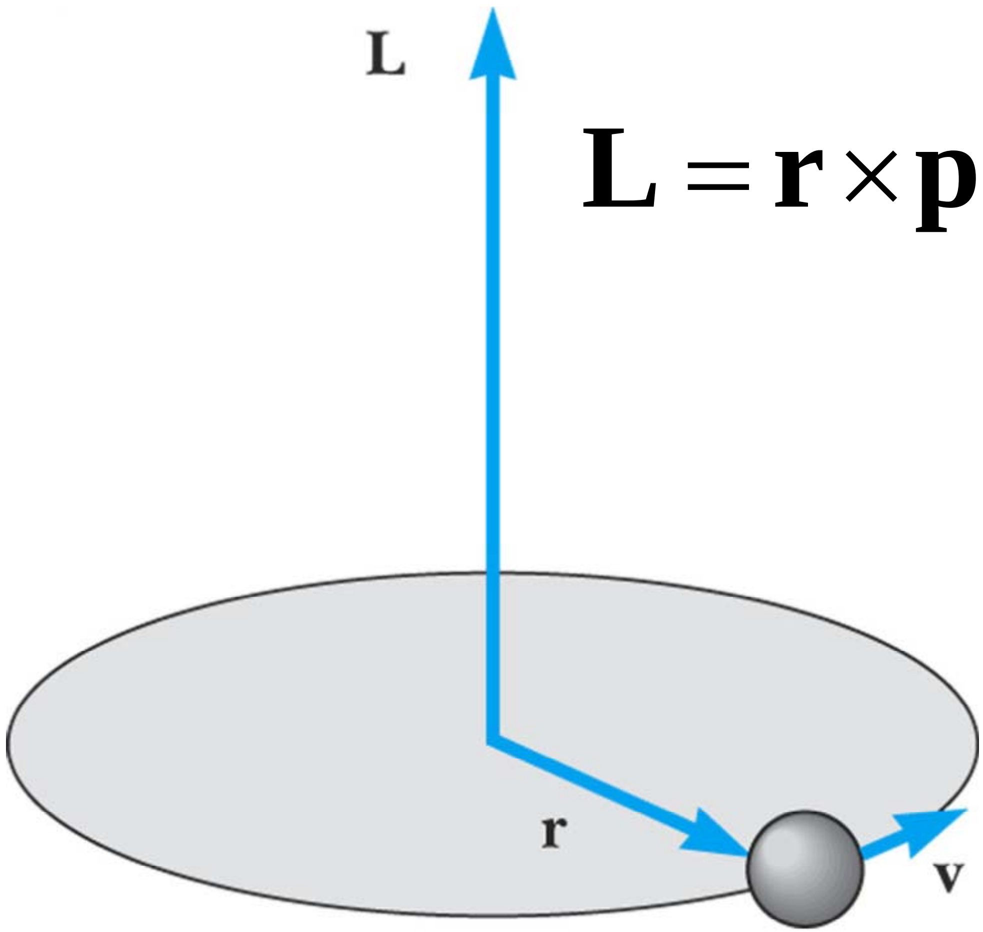
n	Shell Symbol	ℓ	Shell Symbol
1	K	0	s
2	L	1	p
3	M	2	d
4	N	3	f
5	O	4	g
6	P	5	h
. . .		. . .	

Table 8-5, p.280

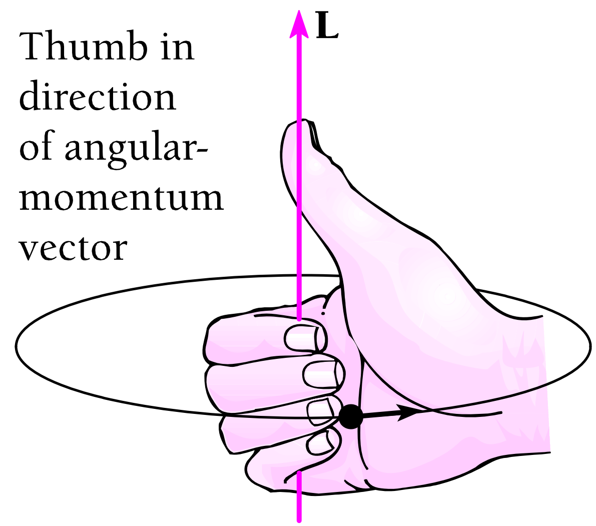
표 6.2 원자 전자 상태

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

Angular Momentum



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



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

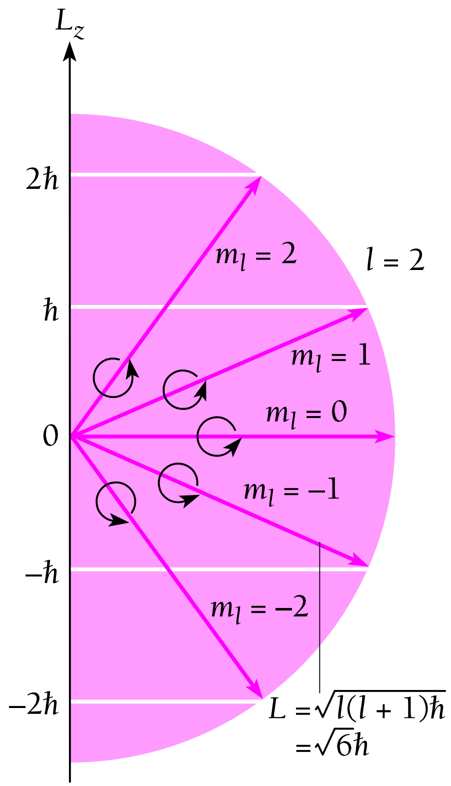


그림 6.4 궤도 각운동량의 공간 양자화

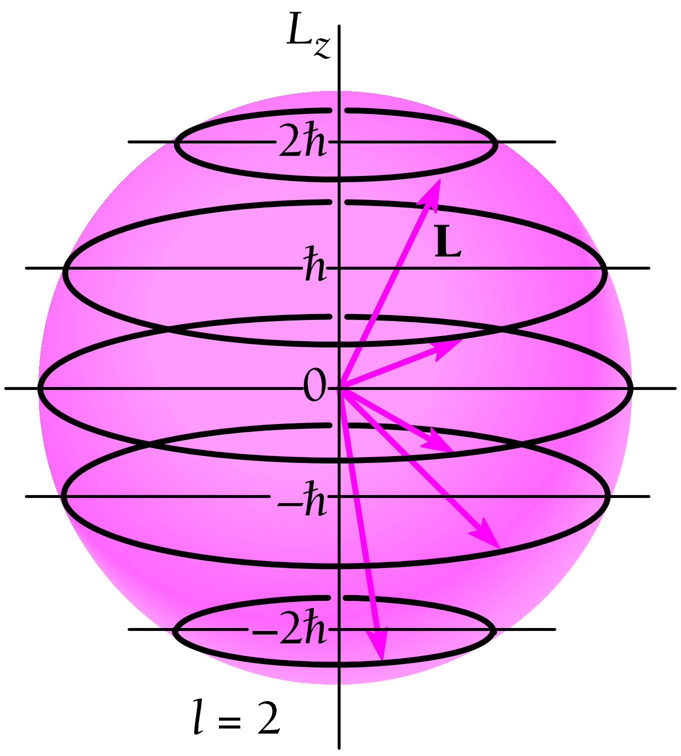


그림 6.6 각운동량 벡터 L은 z축 주위로 계속하여 세차 운동을 한다.

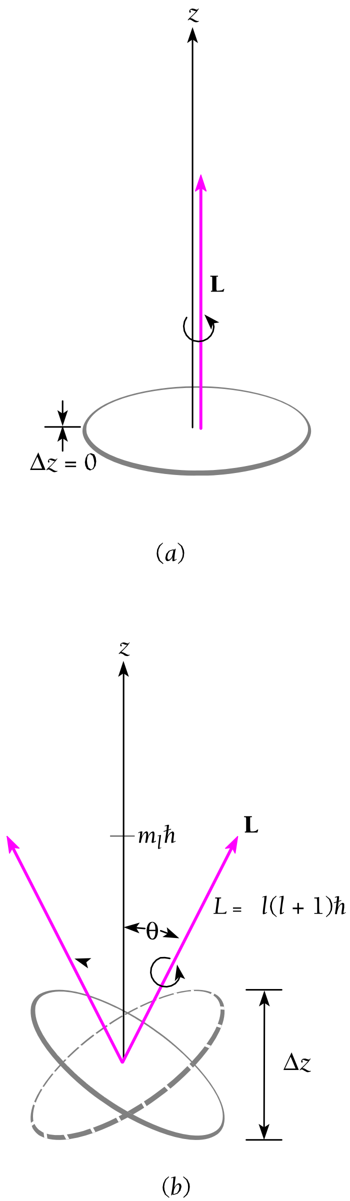


그림 6.5 불확정성 원리에 의해 각운동량 벡터 L은 공간에서 확정된 방향을 가질 수 없다.

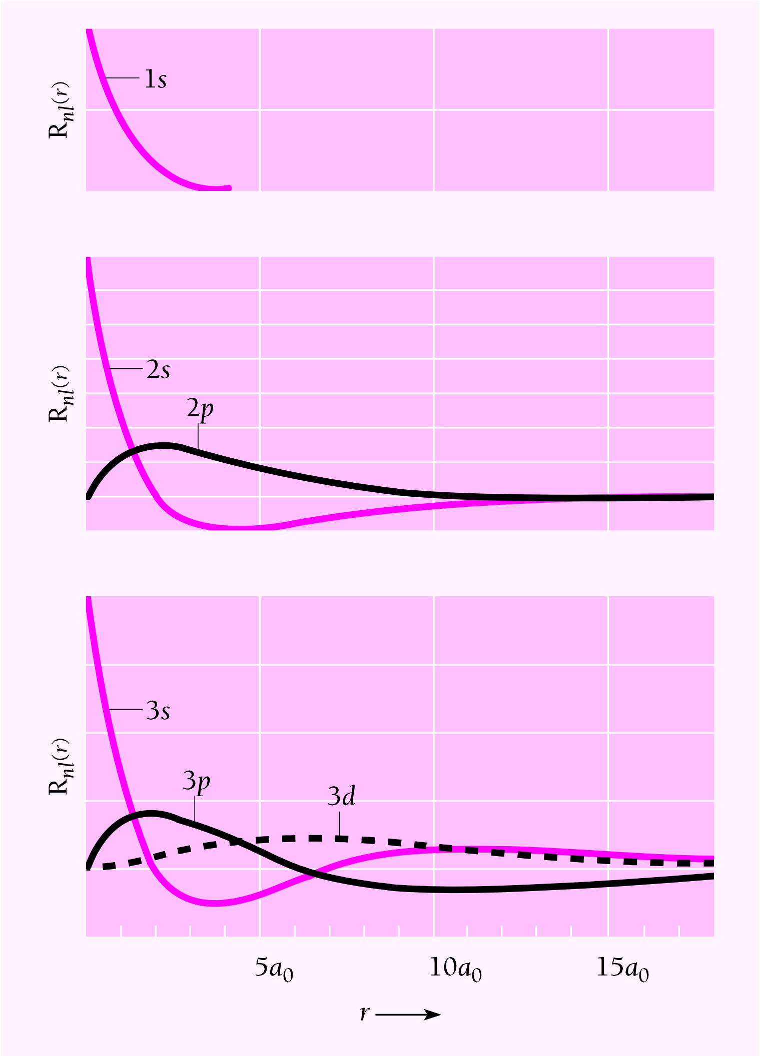


그림 6.8 다양한 양자 상태에서의 수소원자 지름 파동함수의 핵으로부터의 거리에 따른 변화.

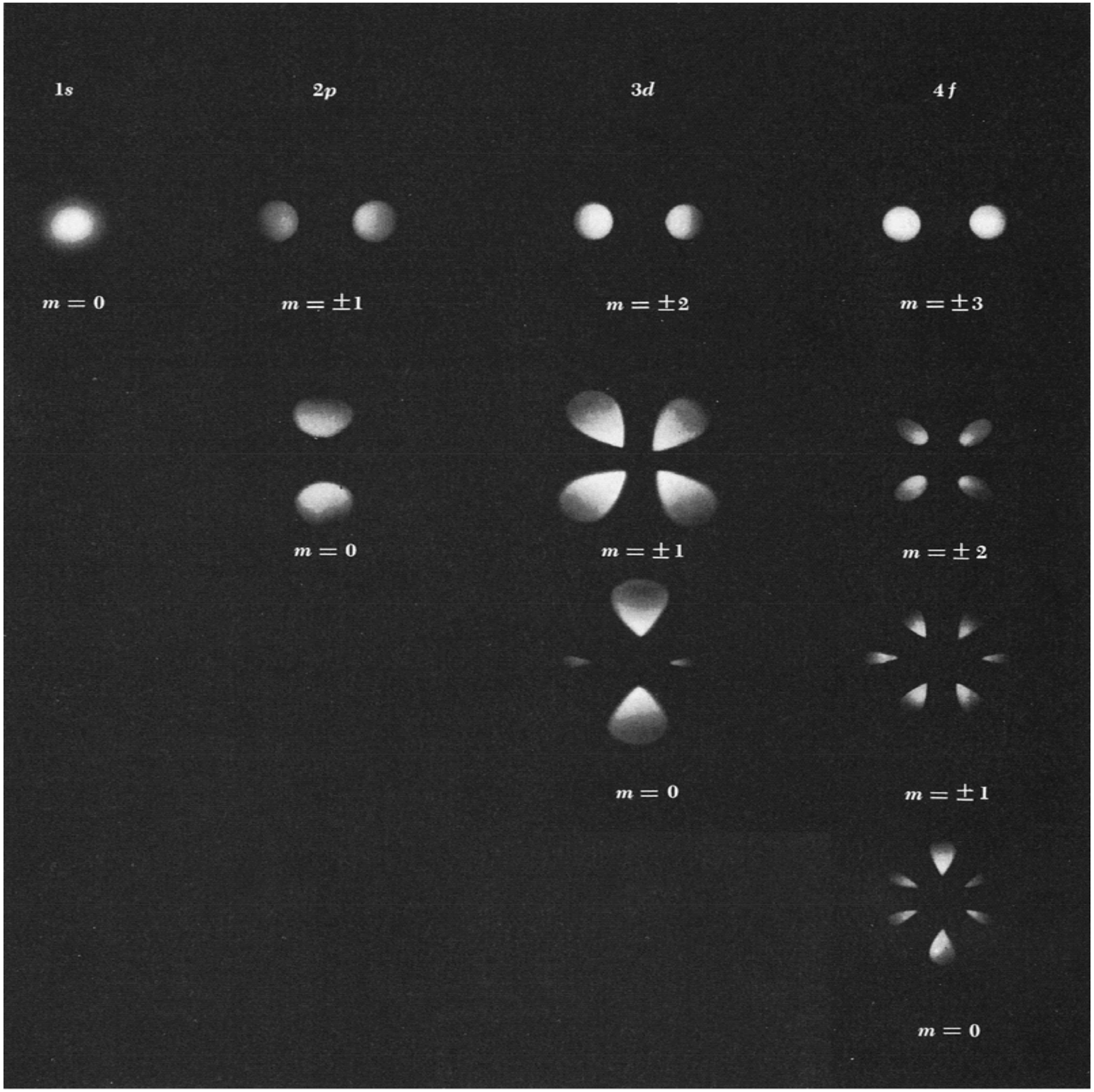


그림 6.12

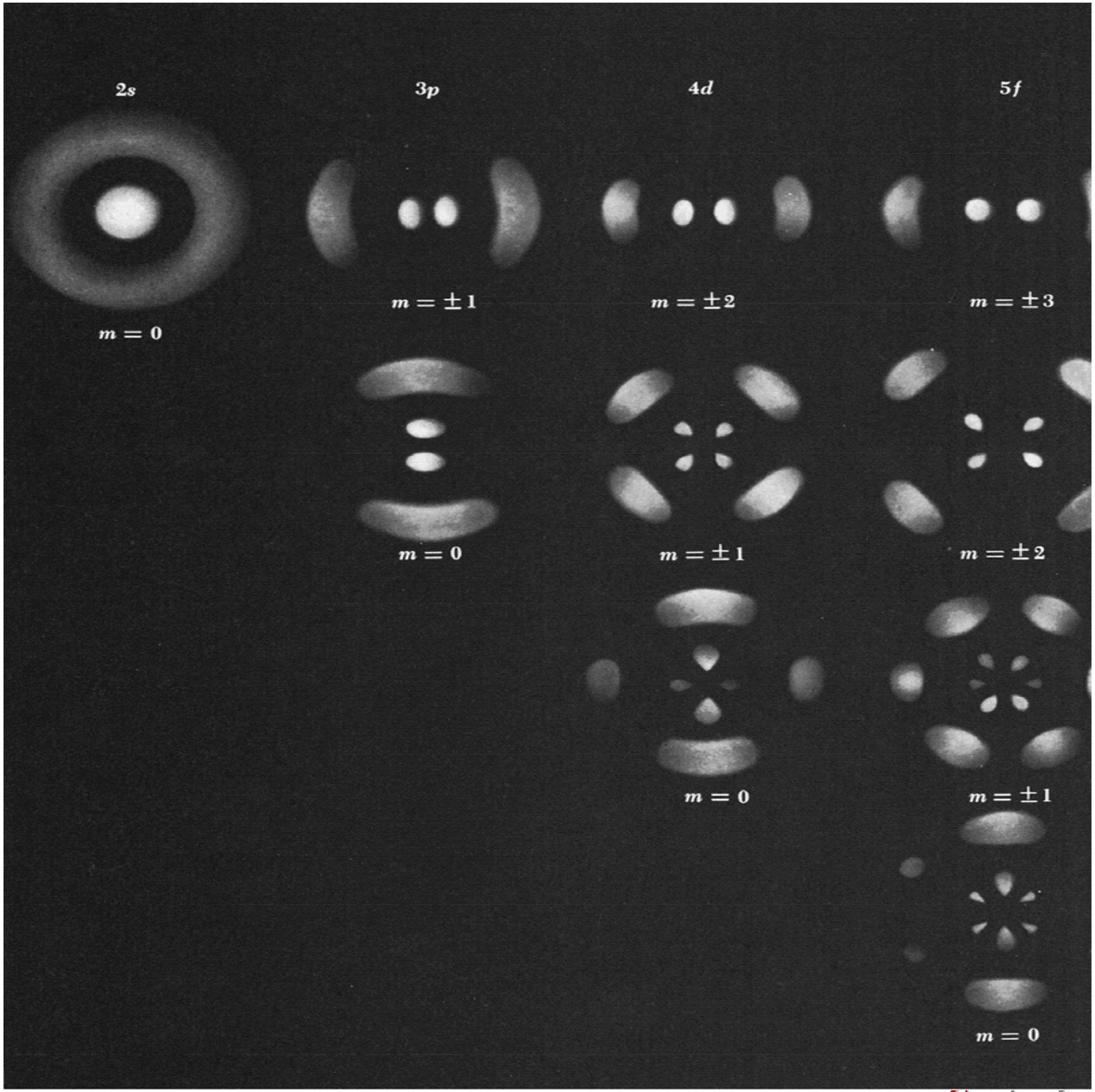
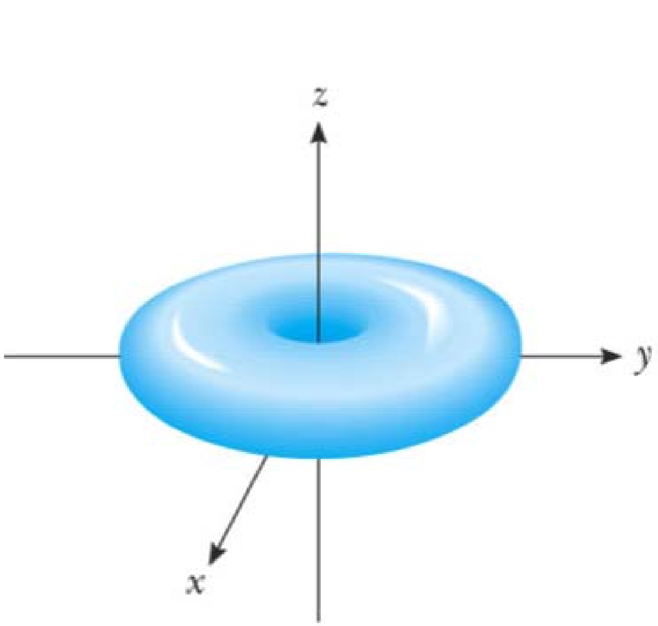


그림 6.12 계속



$n = 2,\ \ell = 1,\ m_\ell = \pm 1$

(a)

$n = 3,\ \ell = 1,\ m_\ell = 0$

(b)

$n = 3,\ \ell = 2,\ m_\ell = 0$

(c)

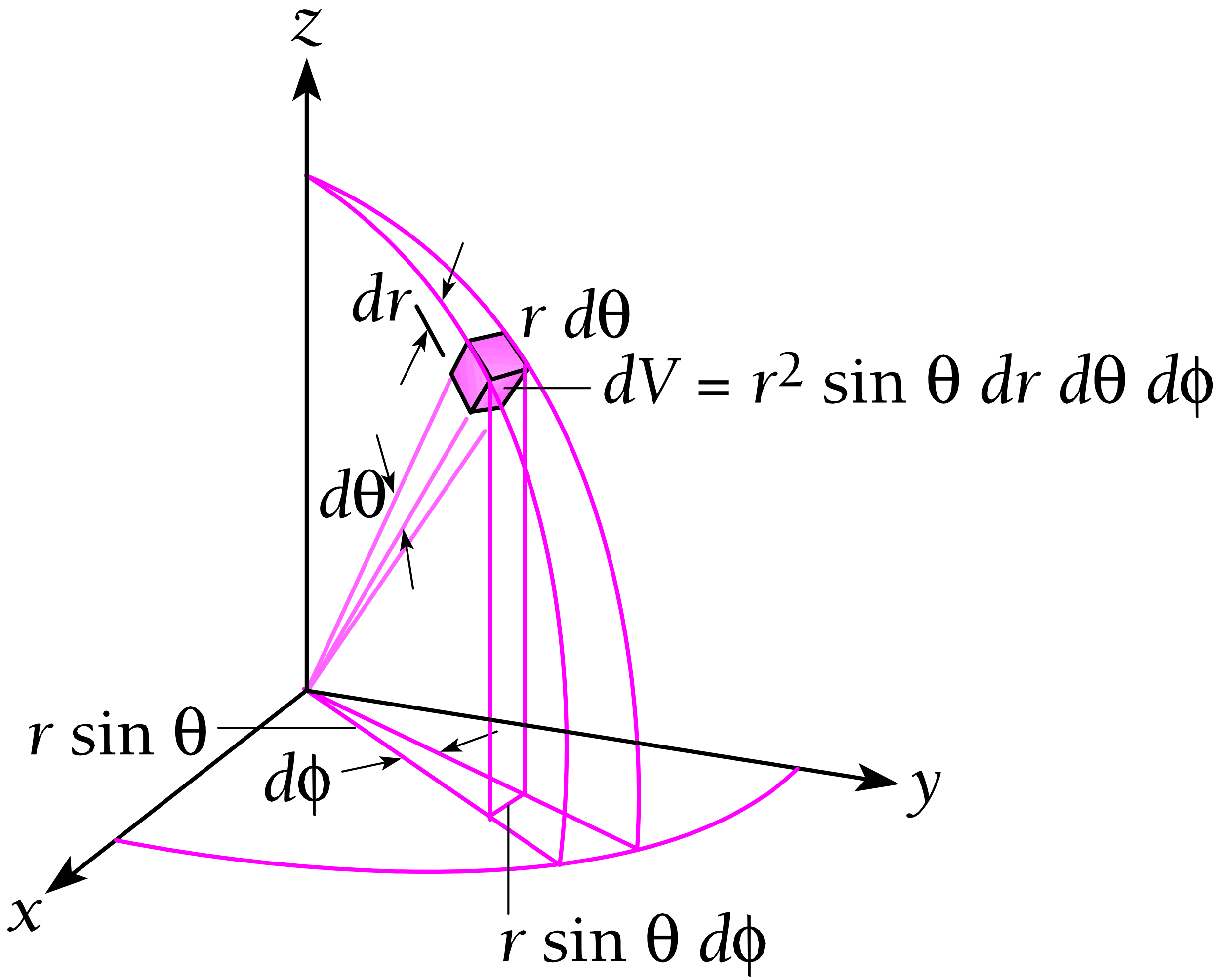
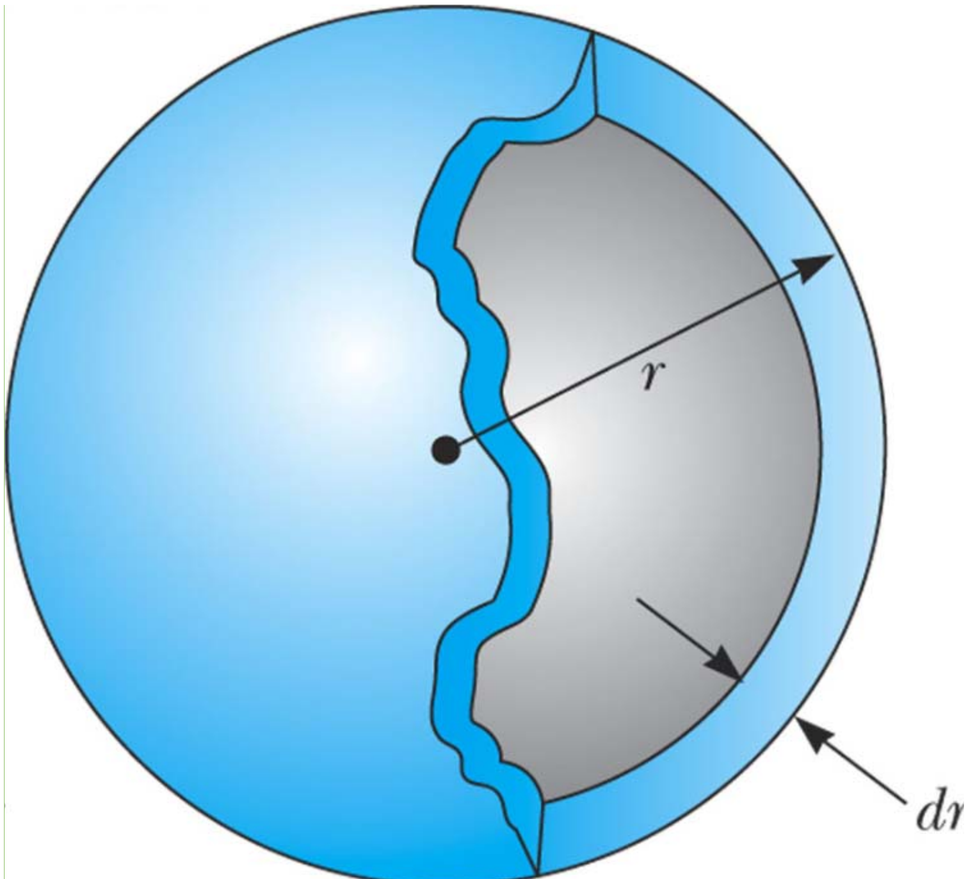


그림 6.9 구면 극좌표계에서의 부피 요소 dV

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

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



핵으로부터의 거리가 r과 r+dr 사이인 공 껍질에서 수소원자의 전자를 발견할 확률은 P(r)dr이다.

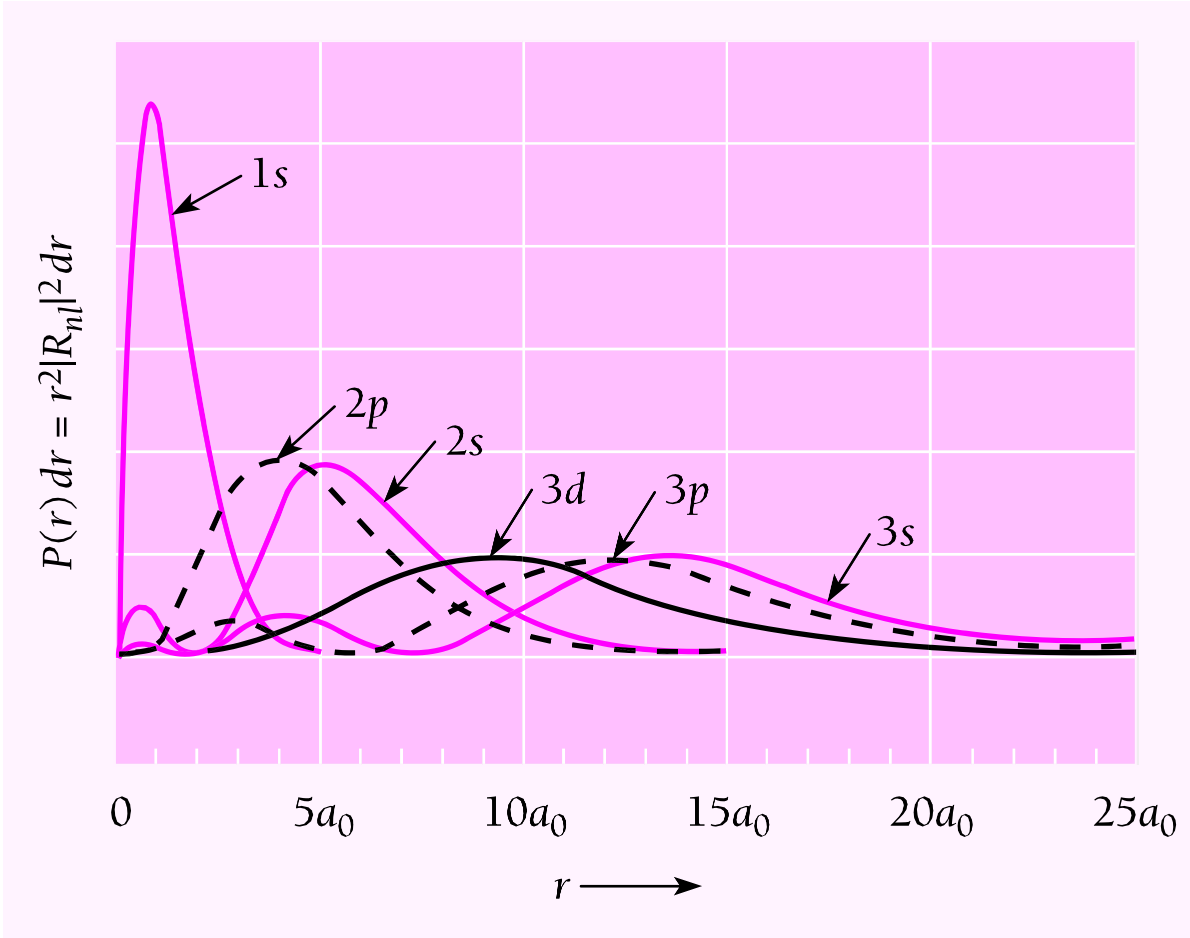
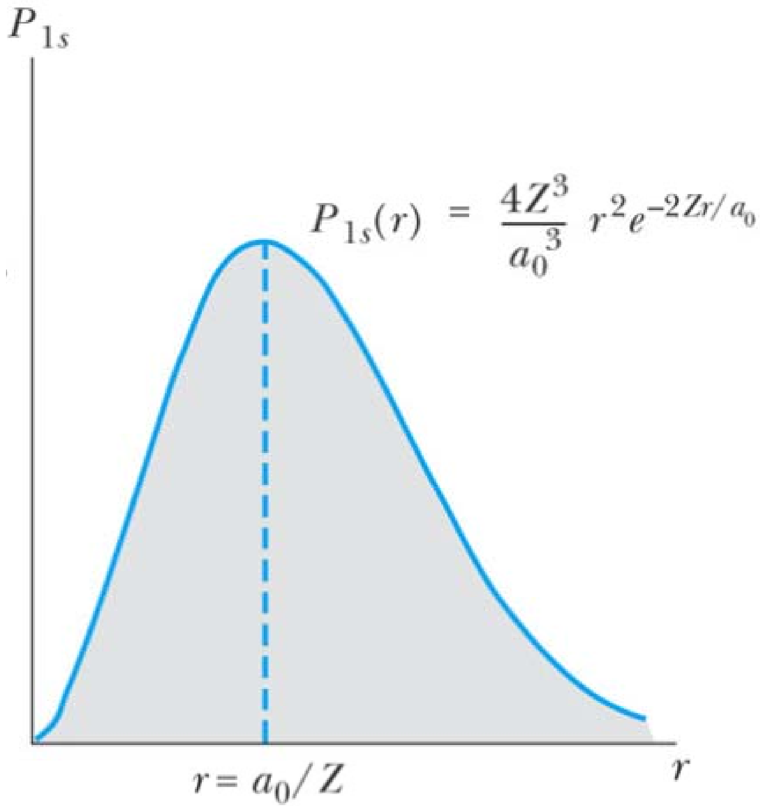
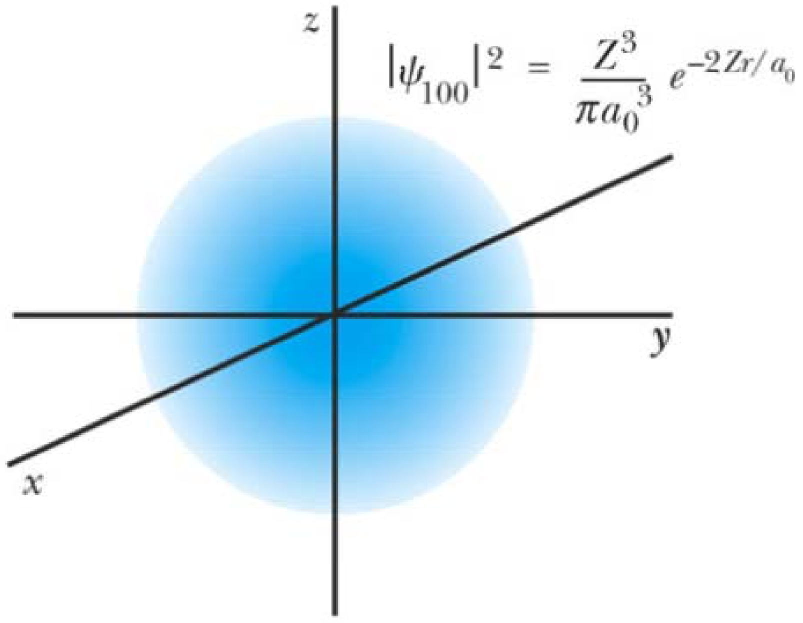


그림 6.11 그림 6.8에서 나타낸 상태들에 대한, 핵으로부터의 거리 r과 r+dr 사이에서 수소원자의 전자를 발견할 확률.


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)