CHAPTER 7

The Hydrogen Atom

- 7.1 Application of the Schrödinger Equation to the Hydrogen Atom
- 7.2 Solution of the Schrödinger Equation for Hydrogen
- 7.3 Quantum Numbers
- 7.4 Magnetic Effects on Atomic Spectra – The Normal Zeeman Effect

This spherical system has very high symmetry causing very high degeneracy of the wavefunctions

6.5: Three-Dimensional Infinite-Potential Well

- The wave function must be a function of all three spatial coordinates.

  We begin with the conservation of energy $E = K + V = \frac{p^2}{2m} + V$
- Multiply this by the wave function to get

$$\frac{p^2}{2m}\psi + V\psi = E\psi$$

- Now consider momentum as an operator acting on the wave function. In this case, the operator must act twice on each dimension. Given:

$$p^2 = p_x{}^2 + p_y{}^2 + p_z{}^2, \text{ and } \quad \hat{p}_x\psi = -i\hbar\frac{\partial\psi}{\partial x} \quad \hat{p}_y\psi = -i\hbar\frac{\partial\psi}{\partial y} \quad \hat{p}_z\psi = -i\hbar\frac{\partial\psi}{\partial z}$$

- The three dimensional Schrödinger wave equation is

$$-\frac{\hbar^2}{2m}\left(\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2}\right) + V\psi = E\psi \qquad \text{or} \qquad -\frac{\hbar^2}{2m}\nabla^2\psi + V\psi = E\psi$$

Laplace operator

Particle in3-D box

Consider a free particle inside a box with lengths L_1, L_2, and L_3 along the x, y, and z axes, respectively, as shown in Figure 6.6. The particle is constrained to be inside the box. Find the wave functions and energies. Then find the ground-state energy and wave function and the energy of the first excited state for a cube of sides L.

Strategy We employ some of the same strategies to solve this problem as we used for the one-dimensional case. First, because we are considering the walls of the box to be absolutely closed, they are infinite potential barriers, and the wave function ψ must be zero at the walls and beyond. We expect to see standing waves similar to Equation (6.31).

But how should we write the wave function so as to properly include the x, y, and z dependence of the wave function? In this case the mathematics will follow from the physics. The particle is free within the box. Therefore, the x-, y-, and z-dependent parts of the wave function must be independent of each other. Inside the box $V = 0$, so the wave equation we must solve is

$$-\frac{\hbar^2}{2m}\nabla^2\psi = E\psi \tag{6.46}$$

It is therefore reasonable to try a wave function of the form

$$\psi(x, y, z) = A\sin(k_1x)\sin(k_2y)\sin(k_3z) \tag{6.47}$$

where A is a normalization constant. The quantities k_i ($i = 1, 2, 3$) are determined by applying the appropriate boundary conditions. To find the energies, we substitute the wave function into the Schrödinger equation and solve for E.

Solution The condition that $\psi = 0$ at $x = L_1$ requires that $k_1L_1 = n_1\pi$ or $k_1 = n_1\pi/L_1$. The values for the k_i are

$$k_1 = \frac{n_1\pi}{L_1} \qquad k_2 = \frac{n_2\pi}{L_2} \qquad k_3 = \frac{n_3\pi}{L_3} \tag{6.48}$$

where n_1, n_2, and n_3 are integers. Not surprisingly, we have found that in three dimensions, it is necessary to use *three* quantum numbers to describe the physical state.

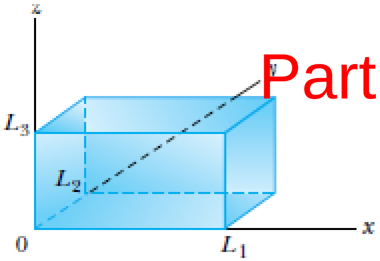


Figure 6.6 A three-dimensional box that contains a free particle. The potential is infinite outside the box, so the particle is constrained to be inside the box.

In order to find the energies using Equation (6.43), we first need to take the appropriate derivatives of the wave function. We do this first for the variable x.

$$\begin{aligned}\frac{\partial\psi}{\partial x} &= \frac{\partial}{\partial x}[A\sin(k_1x)\sin(k_2y)\sin(k_3z)] \\ &= k_1A\cos(k_1x)\sin(k_2y)\sin(k_3z) \\ \frac{\partial^2\psi}{\partial x^2} &= \frac{\partial}{\partial x}[k_1A\cos(k_1x)\sin(k_2y)\sin(k_3z)] \\ &= -(k_1)^2A\sin(k_1x)\sin(k_2y)\sin(k_3z) \\ &= -k_1^2\psi\end{aligned}$$

The derivatives for y and z are similar, and Equation (6.43) becomes

$$\frac{\hbar^2}{2m}(k_1^2 + k_2^2 + k_3^2)\psi = E\psi$$

This gives

$$E = \frac{\hbar^2}{2m}(k_1^2 + k_2^2 + k_3^2)$$

We substitute the values of k_i from Equation (6.48) in this equation to obtain

$$E = \frac{\pi^2\hbar^2}{2m}\left(\frac{n_1^2}{L_1^2} + \frac{n_2^2}{L_2^2} + \frac{n_3^2}{L_3^2}\right) \tag{6.49}$$

Problem6.26

Find the energies of the second, third, fourth, and fifth levels for the three dimensional cubical box. Which energy levels are degenerate?

A given state is degenerate when there is more than one wave function for a given energy

$E=\frac{\pi^2\hbar^2}{2mL^2}\left(n_1^2+n_2^2+n_3^2\right)=E_0\left(n_1^2+n_2^2+n_3^2\right)$ where $E_0=\frac{\pi^2\hbar^2}{2mL^2}$. Then the second, third, fourth, and fifth levels are

1. :

$E_2=\left(2^2+1^2+1^2\right)E_0=6E_0$ (degenerate)

$E_3=\left(2^2+2^2+1^2\right)E_0=9E_0$ (degenerate)

$E_4=\left(3^2+1^2+1^2\right)E_0=11E_0$ (degenerate)

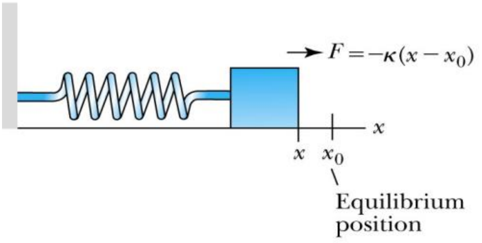
$E_5=\left(2^2+2^2+2^2\right)E_0=12E_0$ (not degenerate)

Degeneracy

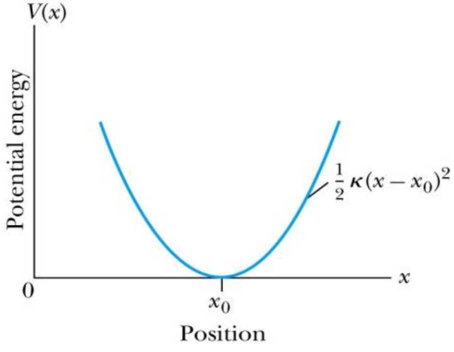
- Analysis of the Schrödinger wave equation in three dimensions introduces three quantum numbers that quantize the energy.
- A quantum state is degenerate when there is more than one wave function for a given energy.
- Degeneracy results from particular properties of the potential energy function that describes the system. A perturbation of the potential energy can remove the degeneracy.
- Use the Schrödinger wave equation for molecules
- We can remove the degeneracy by applying a magnetic field to the atom or molecule

6.6: Simple Harmonic Oscillator

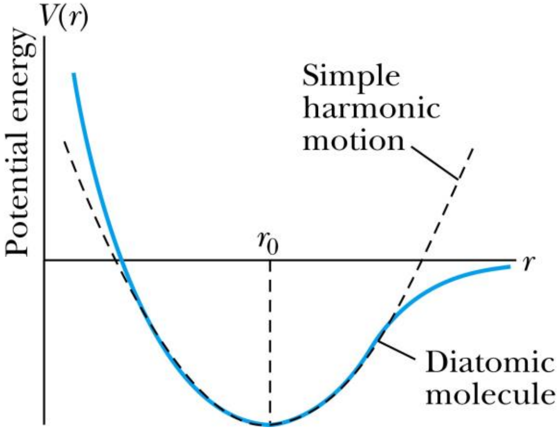
- Simple harmonic oscillators describe many physical situations: springs, diatomic molecules and atomic lattices.



(a)



(b)



- Consider the Taylor expansion of a potential function:

$$V(x) = V_0 + V_1(x-x_0) + \tfrac{1}{2}V_2(x-x_0)^2 + \dots$$

Redefining the minimum potential and the zero potential, we have

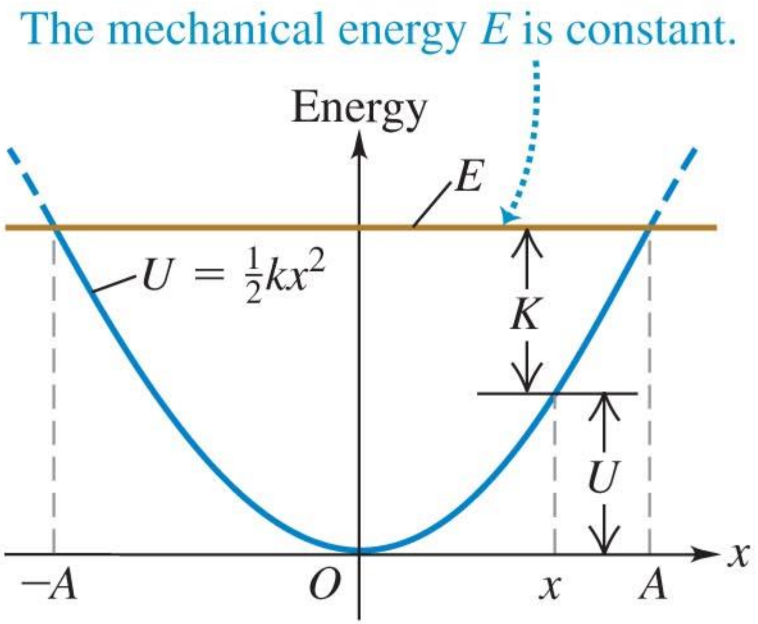
$$V(x) = \tfrac{1}{2}V_2(x-x_0)^2$$

Substituting this into the wave equation:

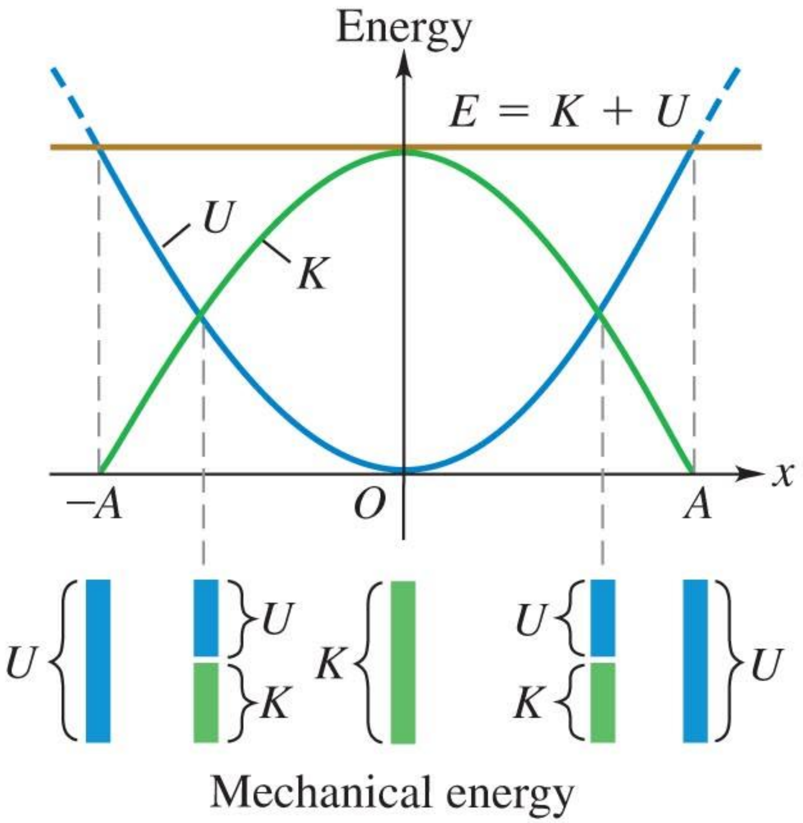
$$\frac{d^2\psi}{dx^2} = -\frac{2m}{\hbar^2}\left(E-\frac{\kappa x^2}{2}\right)\psi = \left(-\frac{2mE}{\hbar^2}+\frac{m\kappa x^2}{\hbar^2}\right)\psi$$

Let $\alpha^2 = \frac{m\kappa}{\hbar^2}$ and $\beta = \frac{2mE}{\hbar^2}$ which yields $\frac{d^2\psi}{dx^2} = (\alpha^2 x^2 - \beta)\psi$.

The pendulum is a simple harmonic oscillator , Foucault pendulum(see miscellaneous on SIBOR)

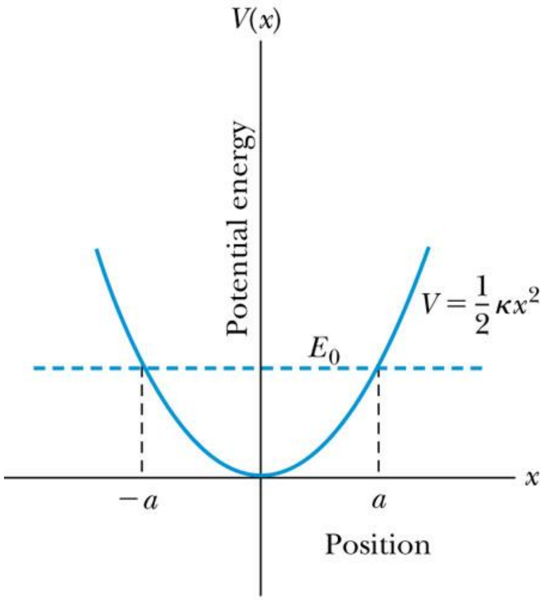


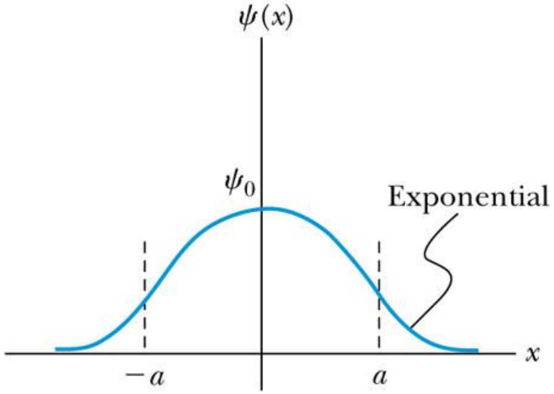
(a) The potential energy U and total energy E of an object in SHM as a function of x position



(b) The same graph as in **(a)**, showing kinetic energy K as well

Parabolic Potential Well

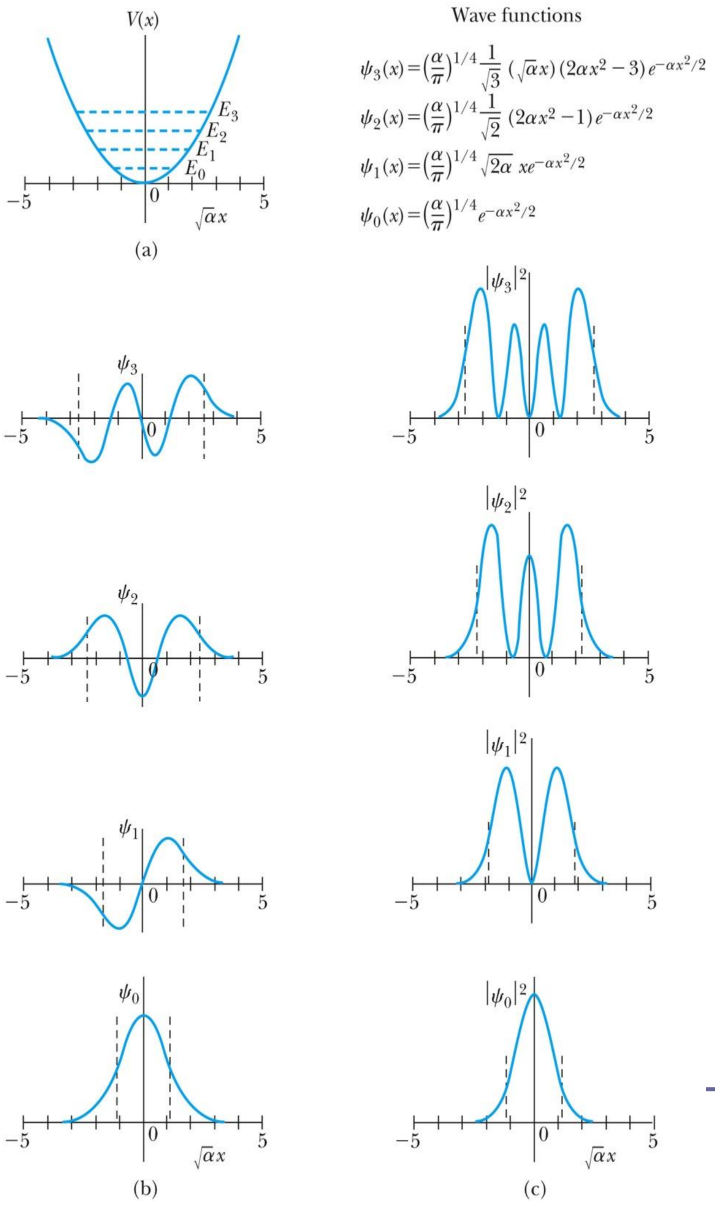


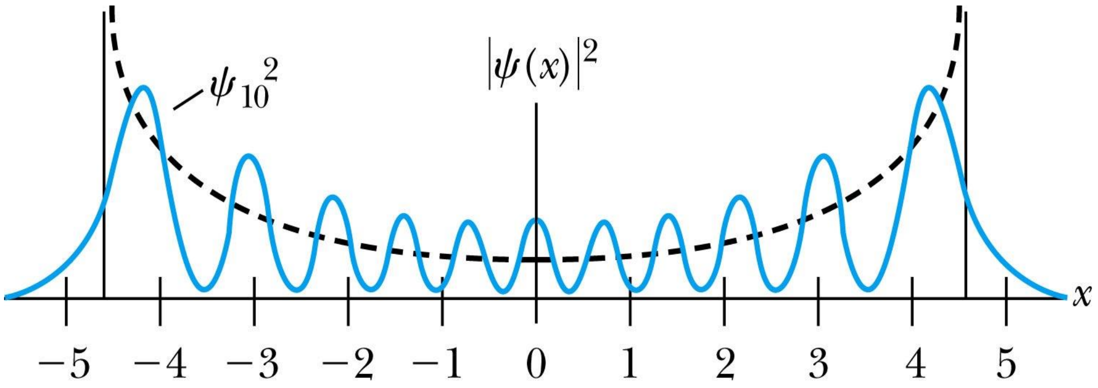


- If the lowest energy level is zero, this violates the uncertainty principle.
- The wave function solutions are $\psi_n = H_n(x)e^{-\alpha x^2/2}$ where $H_n(x)$ are Hermite polynomials of order n.

- In contrast to the particle in a box, where the oscillatory wave function is a sinusoidal curve, in this case the oscillatory behavior is due to the polynomial, which dominates at small x. The exponential tail is provided by the Gaussian function, which dominates at large x.

Analysis of the Parabolic Potential Well





- The energy levels are given by

$$E_n = (n+\tfrac{1}{2})\hbar\sqrt{\kappa/m} = (n+\tfrac{1}{2})\hbar\omega$$

- The zero point energy is called the Heisenberg limit:

$$E_0 = \frac{1}{2}\hbar\omega$$

- Classically, the probability of finding the mass is greatest at the ends of motion and smallest at the center (that is, proportional to the amount of time the mass spends at each position).
- Contrary to the classical one, the largest probability for this lowest energy state is for the particle to be at the center.

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Table 6.2 Common Observables and Associated Operators

Observable	Symbol	Associated Operator
Position	x	x
Momentum	p	$\frac{\hbar}{i}\frac{\partial}{\partial x}$
Potential energy	U	$U(x)$
Kinetic energy	K	$-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}$
Hamiltonian	H	$-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + U(x)$
Total energy	E	$i\hbar\frac{\partial}{\partial t}$

7.1: Application of the Schrödinger Equation to the Hydrogen Atom

- The approximation of the potential energy of the electron-proton system is electrostatic:

$$V(r) = -\frac{e^2}{4\pi\varepsilon_0 r}$$

- Rewrite the three-dimensional time-independent Schrödinger Equation.

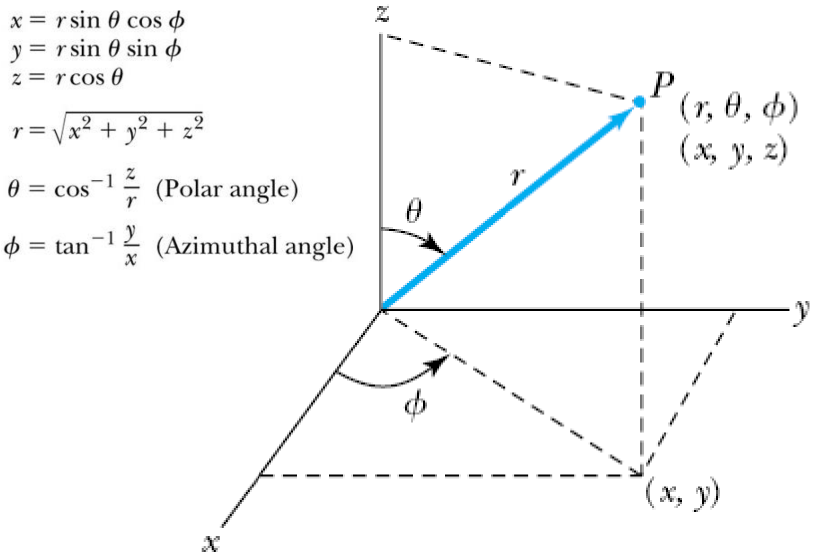
$$-\frac{\hbar^2}{2m}\frac{1}{\psi(x,y,z)}\left[\frac{\partial^2\psi(x,y,z)}{\partial x^2}+\frac{\partial^2\psi(x,y,z)}{\partial y^2}+\frac{\partial^2\psi(x,y,z)}{\partial z^2}\right]=E-V(r)$$

For Hydrogen-like atoms (He^+ or Li^{++})

- Replace e^2 with Ze^2 (Z is the atomic number)
- Use appropriate reduced mass μ

Application of the Schrödinger Equation

- The potential (central force) *V*(*r*) depends on the distance *r* between the proton and electron.



$x = r\sin\theta\cos\phi$
$y = r\sin\theta\sin\phi$
$z = r\cos\theta$

$r = \sqrt{x^2 + y^2 + z^2}$

$\theta = \cos^{-1}\frac{z}{r}$ (Polar angle)

$\phi = \tan^{-1}\frac{y}{x}$ (Azimuthal angle)

Transform to spherical polar coordinates because of the radial symmetry.

Insert the Coulomb potential into the transformed Schrödinger equation.

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right)+\frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right)+\frac{1}{r^2\sin^2\theta}\frac{\partial^2\psi}{\partial\phi^2}+\frac{2\mu}{\hbar^2}(E-V)\psi=0$$

Application of the Schrödinger Equation

- The wave function ψ is a function of r, θ, ϕ

→ Equation is separable.

→ Solution may be a product of three functions.

→ $\psi(r,\theta,\phi) = R(r)f(\theta)g(\phi)$ Equation 7.3

- We can separate Equation 7.3 into three separate differential equations, each depending on one coordinate: r, θ, or ϕ.

Divide and conquer !!

7.2: Solution of the Schrödinger Equation for Hydrogen

- Substitute Eq (7.4) into Eq (7.3) and separate the resulting equation into three equations: $R(r)$, $f(\theta)$, and $g(\phi)$.

Separation of Variables

- The derivatives from Eq (7.4)

$$\frac{\partial\psi}{\partial r} = fg\frac{\partial R}{\partial r} \qquad \frac{\partial\psi}{\partial\theta} = Rg\frac{\partial f}{\partial\theta} \qquad \frac{\partial^2\psi}{\partial\phi^2} = Rf\frac{\partial^2 g}{\partial\phi^2}$$

- Substitute them into Eq (7.3)

$$\frac{fg}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right) + \frac{Rg}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial f}{\partial\theta}\right) + \frac{Rf}{r^2\sin^2\theta}\frac{\partial^2 g}{\partial\phi^2} + \frac{2\mu}{\hbar^2}(E-V)Rfg = 0$$

- Multiply both sides of Eq (7.6) by $r^2\sin^2\theta / Rfg$

$$-\frac{\sin^2\theta}{R}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right) - \frac{2\mu}{\hbar^2}r^2\sin^2\theta(E-V) - \frac{\sin\theta}{f}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial f}{\partial\theta}\right) = \frac{1}{g}\frac{\partial^2 g}{\partial\phi^2}$$

Solution of the Schrödinger Equation

- Only r and θ appear on the left side and only ϕ appears on the right side of Eq (7.7)
- The left side of the equation cannot change as ϕ changes.
- The right side cannot change with either r or θ.

- Each side needs to be equal to a constant for the equation to be true. Set the constant $-m_\ell^2$ equal to the right side of Eq (7.7)

  $\frac{d^2 g}{d\phi^2} = -m_\ell^2 g$ -------- **azimuthal equation**

- It is convenient to choose a solution to be $e^{im_\ell \phi}$.

Solution of the Schrödinger Equation

- $e^{im_\ell\phi}$ satisfies Eq (7.8) for any value of m_ℓ.
- The solution be single valued in order to have a valid solution for any ϕ, which is $g(\phi) = g(\phi + 2\pi)$
  $g(\phi = 0) = g(\phi = 2\pi) \longrightarrow e^{0} = e^{2\pi i m_\ell}$
- m_ℓ to be zero or an integer (positive or negative) for this to be true.
- If Eq (7.8) were positive, the solution would not be realized.

- Set the left side of Eq (7.7) equal to $-m_\ell^2$ and rearrange it.

$$\frac{1}{R}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right)+\frac{2\mu r^2}{\hbar^2}(E-V)=\frac{m_\ell{}^2}{\sin^2\theta}-\frac{1}{f\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial f}{\partial\theta}\right)$$

- Everything depends on r on the left side and θ on the right side of the equation.

Solution of the Schrödinger Equation

- Set each side of Eq (7.9) equal to constant ℓ(ℓ + 1).

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)+\frac{2\mu}{\hbar^2}\left[E-V-\frac{\hbar^2}{2\mu}\frac{\ell(\ell+1)}{r^2}\right]R=0$$ **----Radial equation**

$$\frac{1}{\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{df}{d\theta}\right)+\left[\ell(\ell+1)-\frac{m_\ell^{\ 2}}{\sin^2\theta}\right]f=0$$ **----Angular equation**

- Schrödinger equation has been separated into three ordinary second-order differential equations [Eq (7.8), (7.10), and (7.11)], each containing only one variable.

Solution of the Radial Equation

- The radial equation is called the **associated Laguerre equation** and the *solutions R* that satisfy the appropriate boundary conditions are called *associated Laguerre functions*.

- Assume the ground state has ℓ = 0 and this requires $m_\ell = 0$.

  Eq (7.10) becomes

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)+\frac{2\mu}{\hbar^2}(E-V)R=0$$

- The derivative of $r^2\frac{dR}{dr}$ yields two terms.

  Write those terms and insert Eq (7.1)

$$\frac{d^2R}{dr^2}+\frac{2}{r}\frac{dR}{dr}+\frac{2\mu}{\hbar^2}\left(E+\frac{e^2}{4\pi\varepsilon_0 r}\right)R=0$$

Solution of the Radial Equation

- Try a solution $R = Ae^{-r/a_0}$
  A is a normalization constant.
  a_0 is a constant with the dimension of length.
  Take derivatives of *R* and insert them into Eq (7.13).

$$\left(\frac{1}{a_0{}^2} + \frac{2\mu}{\hbar^2}E\right) + \left(\frac{2\mu e^2}{4\pi\varepsilon_0\hbar^2} - \frac{2}{a_0}\right)\frac{1}{r} = 0$$

- To satisfy Eq (7.14) for any *r* is for each of the two expressions in parentheses to be zero.
  Set the second parentheses equal to zero and solve for a_0.

$$a_0 = \frac{4\pi\varepsilon_0\hbar^2}{\mu e^2}$$

Set the first parentheses equal to zero and solve for *E*.

$$E = -\frac{\hbar^2}{2\mu a_0{}^2} = -E_0$$

Both equal to the Bohr result

Quantum Numbers

- The appropriate boundary conditions to Eq (7.10) and (7.11) leads to the following restrictions on the quantum numbers ℓ and m_ℓ:
    - $\ell = 0, 1, 2, 3, \ldots$
    - $m_\ell = -\ell, -\ell + 1, \ldots, -2, -1, 0, 1, 2, . \ell . , \ell - 1, \ell$
    - $|m_\ell| \leq \ell$ and $\ell < 0$.

- The predicted energy level is

$$E_n = -\frac{E_0}{n^2}$$

Problem7.8

The wave function Ψ for the ground state of hydrogen is given by

$$\Psi_{100}(r,\phi,\theta) = A\, e^{-r/a_o}$$

Find the constant A that will normalize this wave function over all space.

1. The wave function given is $\psi_{100}(r,\theta,\phi) = Ae^{-r/a_0}$ so $\psi^*\psi$ is given by $\psi_{100}{}^*\psi_{100} = A^2e^{-2r/a_0}$. To normalize the wave function, compute the triple integral over all space $\iiint \psi^*\psi\, dV = A^2\int_0^{2\pi}\int_0^{\pi}\int_0^{\infty} r^2 \sin\theta e^{-2r/a_0}\, dr\, d\theta\, d\phi$. The ϕ integral yields 2π, and the θ integral yields 2. This leaves $\iiint \psi^*\psi\, dV = 4\pi A^2\int_0^{\infty} r^2 e^{-2r/a_0}\, dr = 4\pi A^2 \dfrac{2}{(2/a_0)^3} = \pi a_0^3 A^2$ This integral must equal 1 due to normalization which leads to $\pi a_0^3 A^2 = 1$ so $A = \dfrac{1}{\sqrt{\pi a_0^3}}$.

Hydrogen Atom Radial Wave Functions

- First few radial wave functions $R_{n\ell}$

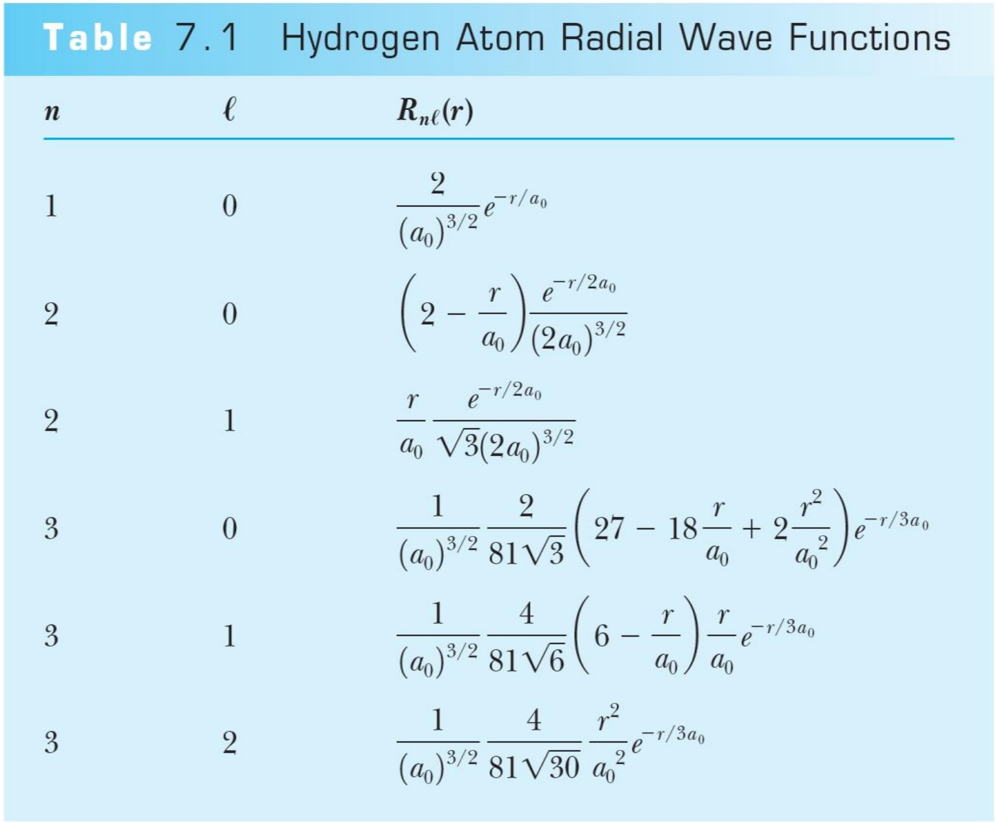


Table 7.1 Hydrogen Atom Radial Wave Functions

n	ℓ	$R_{n\ell}(r)$
1	0	$\frac{2}{(a_0)^{3/2}}e^{-r/a_0}$
2	0	$\left(2-\frac{r}{a_0}\right)\frac{e^{-r/2a_0}}{(2a_0)^{3/2}}$
2	1	$\frac{r}{a_0}\frac{e^{-r/2a_0}}{\sqrt{3}(2a_0)^{3/2}}$
3	0	$\frac{1}{(a_0)^{3/2}}\frac{2}{81\sqrt{3}}\left(27-18\frac{r}{a_0}+2\frac{r^2}{a_0{}^2}\right)e^{-r/3a_0}$
3	1	$\frac{1}{(a_0)^{3/2}}\frac{4}{81\sqrt{6}}\left(6-\frac{r}{a_0}\right)\frac{r}{a_0}e^{-r/3a_0}$
3	2	$\frac{1}{(a_0)^{3/2}}\frac{4}{81\sqrt{30}}\frac{r^2}{a_0{}^2}e^{-r/3a_0}$

- Subscripts on *R* specify the values of *n* and *ℓ*

Solution of the Angular and Azimuthal Equations

- The solutions for Eq (7.8) are $e^{im_\ell \phi}$ or $e^{-im_\ell \phi}$
- Solutions to the angular and azimuthal equations are linked because both have m_ℓ
- Group these solutions together into functions

$$Y(\theta, \phi) = f(\theta) g(\phi)$$ ---- **spherical harmonics**

Normalized Spherical Harmonics

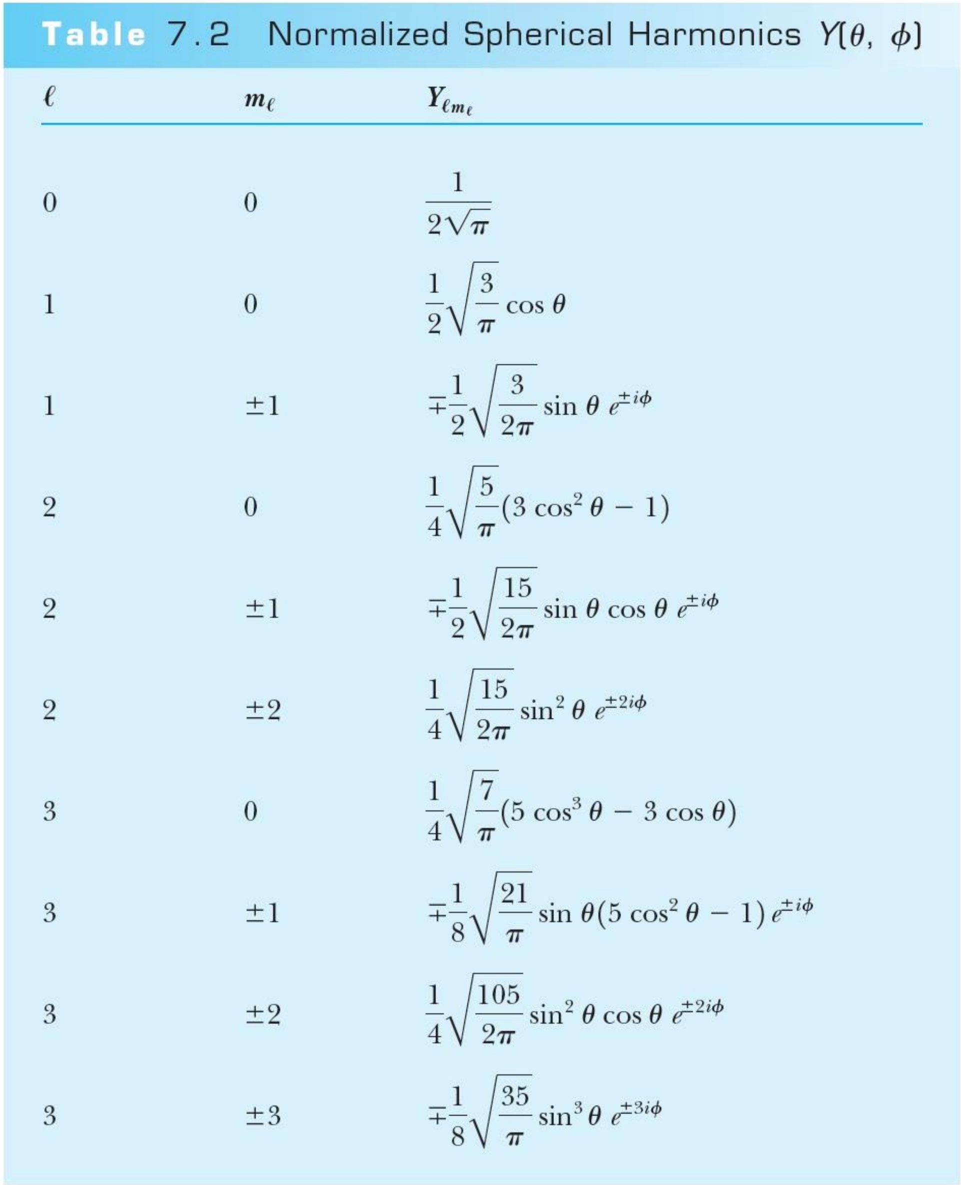


Table 7.2 Normalized Spherical Harmonics $Y(\theta, \phi)$

ℓ	m_ℓ	$Y_{\ell m_\ell}$
0	0	$\frac{1}{2\sqrt{\pi}}$
1	0	$\frac{1}{2}\sqrt{\frac{3}{\pi}}\cos\theta$
1	±1	$\mp\frac{1}{2}\sqrt{\frac{3}{2\pi}}\sin\theta\, e^{\pm i\phi}$
2	0	$\frac{1}{4}\sqrt{\frac{5}{\pi}}(3\cos^2\theta - 1)$
2	±1	$\mp\frac{1}{2}\sqrt{\frac{15}{2\pi}}\sin\theta\cos\theta\, e^{\pm i\phi}$
2	±2	$\frac{1}{4}\sqrt{\frac{15}{2\pi}}\sin^2\theta\, e^{\pm 2i\phi}$
3	0	$\frac{1}{4}\sqrt{\frac{7}{\pi}}(5\cos^3\theta - 3\cos\theta)$
3	±1	$\mp\frac{1}{8}\sqrt{\frac{21}{\pi}}\sin\theta(5\cos^2\theta - 1)\, e^{\pm i\phi}$
3	±2	$\frac{1}{4}\sqrt{\frac{105}{2\pi}}\sin^2\theta\cos\theta\, e^{\pm 2i\phi}$
3	±3	$\mp\frac{1}{8}\sqrt{\frac{35}{\pi}}\sin^3\theta\, e^{\pm 3i\phi}$

Solution of the Angular and Azimuthal Equations

- The radial wave function *R* and the spherical harmonics *Y* determine the probability density for the various quantum states. The total wave function $\psi(r,\theta,\phi)$ depends on *n*, ℓ, and m_ℓ. The wave function becomes

$$\psi_{n\ell m_\ell}(r,\theta,\phi)=R_{n\ell}(r)Y_{\ell m_\ell}(\theta,\phi)$$

7.3: Quantum Numbers

The three quantum numbers:

n	Principal quantum number
ℓ	Orbital angular momentum quantum number
m_ℓ	Magnetic quantum number

The boundary conditions:

$n = 1, 2, 3, 4, \dots$	Integer
$\ell = 0, 1, 2, 3, \dots, n - 1$	Integer
$m_\ell = -\ell, -\ell + 1, \dots, 0, 1, \dots, \ell - 1, \ell$	Integer

The restrictions for quantum numbers:

- $n > 0$
- $\ell < n$
- $|m_\ell| \leq \ell$

Clicker - Questions

1) For what levels in the hydrogen atom will we not find $l=2$ states??

a) $n = 4, 5$

b) $n = 3, 4$

c) $n = 2, 1$

d) $n = 5, 6$

Clicker - Questions

2) Which of the following states of the hydrogen atom is allowed?

a) $n = 6, l = 2, m_l = 0$

b) $n = 2, l = 2, m_l = 0$

c) $n = 5, l = 2, m_l = 3$

d) $n = 1, l = 2, m_l = 1$

Problem7.11

List all quantum numbers (n,l,m_l) for the n=5 level in atomic hydrogen.

1. It is required that $\ell < 5$ and $|m_\ell| \le \ell$.

$\ell = 4$: $m_\ell = 0, \pm 1, \pm 2, \pm 3, \pm 4$; $\ell = 3$: $m_\ell = 0, \pm 1, \pm 2, \pm 3$;

$\ell = 2$: $m_\ell = 0, \pm 1, \pm 2$ $\ell = 1$: $m_\ell = 0, \pm 1$ $\ell = 0$: $m_\ell = 0$

Principal Quantum Number *n*

- It results from the solution of *R*(*r*) in Eq (7.4) because *R*(*r*) includes the potential energy *V*(*r*).

  The result for this quantized energy is

$$E_n = \frac{-\mu}{2}\left(\frac{e^2}{4\pi\varepsilon_0\hbar}\right)^2 \frac{1}{n^2} = -\frac{E_0}{n^2}$$

- The negative means the energy *E* indicates that the electron and proton are bound together.

Orbital Angular Momentum Quantum Number ℓ

- It is associated with the $R(r)$ and $f(\theta)$ parts of the wave function.

- Classically, the orbital angular momentum $\vec{L} = \vec{r} \times \vec{p}$ with $L = mv_{\text{orbital}}r$.

- ℓ is related to L by $L = \sqrt{\ell(\ell+1)}\hbar$.

- In an ℓ = 0 state, $L = \sqrt{0(1)}\hbar = 0$

It disagrees with Bohr's semi-classical "planetary" model of electrons orbiting a nucleus $L = n\hbar$.

Orbital Angular Momentum Quantum Number ℓ

- A certain energy level is **degenerate** with respect to ℓ when the energy is independent of ℓ.

- Use letter names for the various ℓ values

ℓ =	0	1	2	3	4	5 . . .
Letter =	*s*	*p*	*d*	*f*	*g*	*h* . . .

- Atomic states are referred to by their n and ℓ
- A state with $n = 2$ and $\ell = 1$ is called a $2p$ state
- The boundary conditions require $n > \ell$

Uncertainty principle for angular momentum

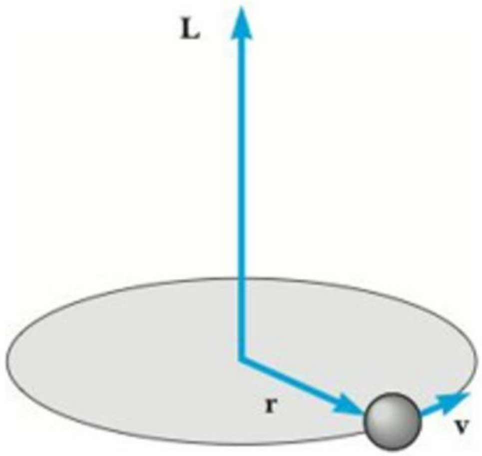


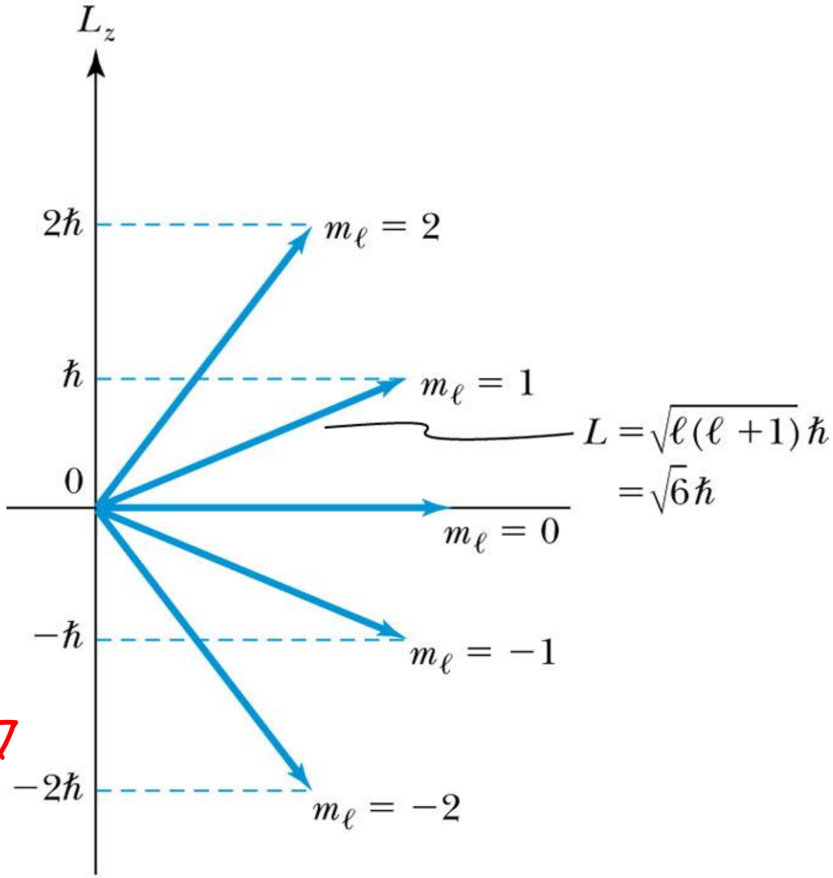
Figure 8.6 The angular momentum **L** of an orbiting particle is perpendicular to the plane of the orbit. If the direction of **L** were known precisely, both the coordinate and momentum in the direction perpendicular to the orbit would be known, in violation of the uncertainty principle.

Magnetic Quantum Number m_ℓ

- The angle ϕ is a measure of the rotation about the z axis.
- The solution for $g(\phi)$ specifies that m_ℓ is an integer and related to the *z* component of *L*.

$$L_z = m_\ell \hbar$$

- The relationship of *L*, L_z, ℓ, and m_ℓ for ℓ = 2.
- $L = \sqrt{\ell(\ell+1)}\hbar = \sqrt{6}\hbar$ is fixed.
- Because L_z is quantized, only certain orientations of $\vec{L}$ are possible and this is called **space quantization**.



$$\cos\theta = \frac{L_z}{|L|} = \frac{m_\ell}{\sqrt{\ell(\ell+1)}}$$

Magnetic Quantum Number m_ℓ

- Quantum mechanics allows $\vec{L}$ to be quantized along only one direction in space. Because of the relation $L^2 = L_x^2 + L_y^2 + L_z^2$ the knowledge of a second component would imply a knowledge of the third component because we know $\vec{L}$.

- We expect the average of the angular momentum components squared to be $\langle L_x{}^2 \rangle = \langle L_y{}^2 \rangle = \langle L_z{}^2 \rangle$

$$\langle L^2 \rangle = 3\langle L_z{}^2 \rangle = \frac{3}{2\ell+1}\sum_{m_\ell=-\ell}^{\ell} m_\ell{}^2\hbar^2 = \ell(\ell+1)\hbar^2$$

Since the sum $\displaystyle\sum_{i=-\ell}^{\ell} i^2 = \frac{1}{3}\ell(\ell+1)(2\ell+1)$

Use a math table for the summation result

Fuzzyness of angular momentum

mechanical analogy: wheel in gravitational field

rotating wheel

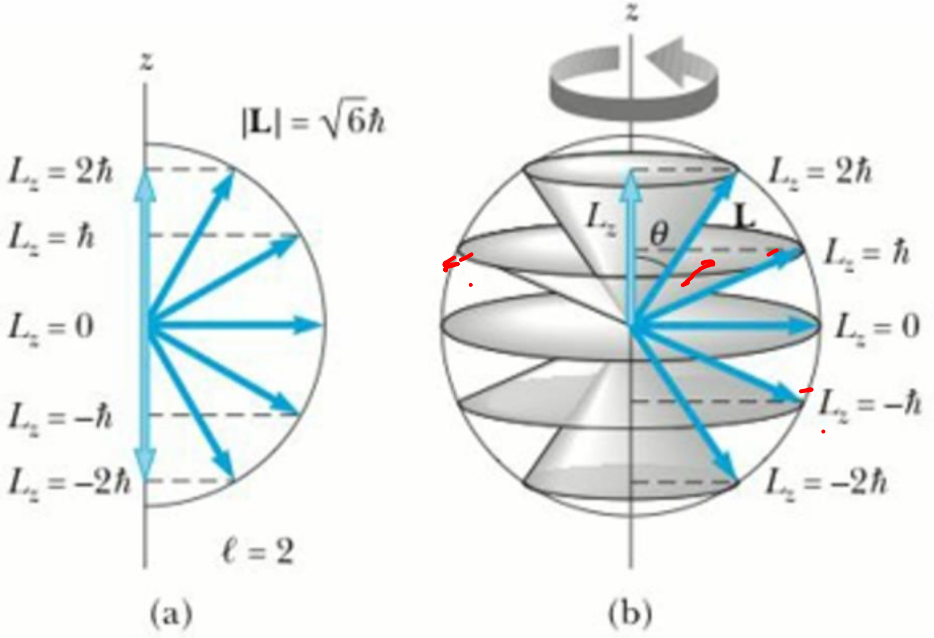


Figure 8.7 (a) The allowed projections of the orbital angular momentum for the case $\ell = 2$. (b) From a three-dimensional perspective, the orbital angular momentum vector **L** lies on the surface of a cone. The fuzzy character of L_x and L_y is depicted by allowing **L** to precess about the z-axis, so that L_x and L_y change continually while L_z maintains the fixed value $m_\ell \hbar$.

Honda 600RR

Who races this bike?

Why can anybody race it, if he just dares to go fast?

The oval track of the Texas World Speedway allows speeds of 250 mph.

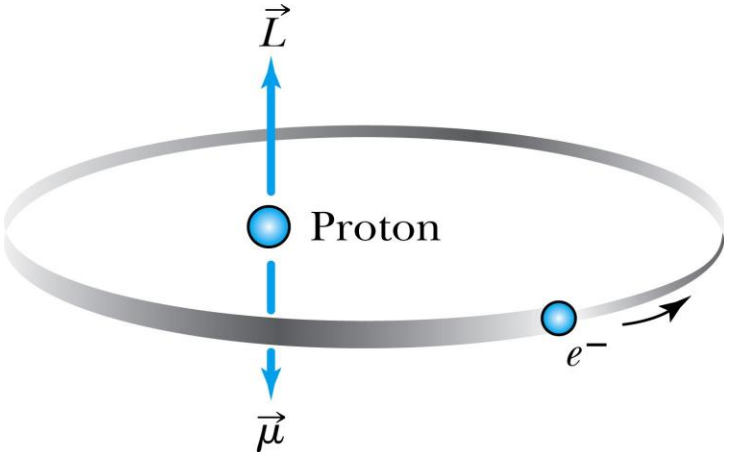
7.4: Magnetic Effects on Atomic Spectra—The Normal Zeeman Effect

- The Dutch physicist Pieter Zeeman showed the spectral lines emitted by atoms in a magnetic field split into multiple energy levels. It is called the **Zeeman effect**.

Normal Zeeman effect:

- A spectral line is split into three lines.
- Consider the atom to behave like a small magnet.
- The current loop has a magnetic moment $\mu = IA$ and the period $T = 2\pi r / v$.
- Think of an electron as an orbiting circular current loop of $I = dq / dt$ around the nucleus.
- $\vec{\mu} = -\frac{e}{2m}\vec{L}$ where $L = mvr$ is the magnitude of the orbital angular momentum

The Normal Zeeman Effect



- Since there is no magnetic field to align them, $\vec{\mu}$ point in random directions. The dipole has a potential energy

$$V_B = -\vec{\mu} \cdot \vec{B}$$

- The angular momentum is aligned with the magnetic moment, and the torque between $\vec{\mu}$ and $\vec{B}$ causes a precession of $\vec{\mu}$.

$$\mu_z = \frac{e\hbar}{2m} m_\ell = -\mu_B m_\ell$$

Where $\mu_B = e\hbar / 2m$ is called a **Bohr magneton**.

- $\vec{\mu}$ cannot align exactly in the z direction and has only certain allowed quantized orientations.

$$\vec{\mu} = -\mu_B \vec{L} / \hbar$$

Precession frequency

EXAMPLE 7.5

$L = \sqrt{\ell(\ell+1)}\,\hbar > m_\ell \hbar$ length

$\vec{L}$ = vector

Determine the precessional frequency of an atom having magnetic moment $\vec{\mu}$ in an external magnetic field $\vec{B}$. This precession is known as the *Larmor precession*.

Strategy We have already seen that the torque $\vec{\tau}$ is equal to $\vec{\mu} \times \vec{B}$, but we also know from classical mechanics that the torque is $d\vec{L}/dt$. The torque in Figure 7.5 is perpendicular to $\vec{\mu}$, $\vec{L}$, and $\vec{B}$ and is out of the page. This must also be the direction of the change in momentum $d\vec{L}$ as seen in Figure 7.5. Thus $\vec{L}$ and $\vec{\mu}$ precess about the magnetic field. The Larmor frequency ω_L is given by $d\phi/dt$.

Solution The magnitude of $d\vec{L}$ is given by $L \sin\theta\, d\phi$ (see Figure 7.5), so ω_L is given by

$$\omega_L = \frac{d\phi}{dt} = \frac{1}{L\sin\theta}\frac{dL}{dt} \qquad (7.29)$$

We now insert the magnitude of $L = 2m\mu/e$ from Equation (7.26). The value of dL/dt, the magnitude of $\vec{\mu} \times \vec{B}$, can be determined from Figure 7.5 to be $\mu B \sin\theta$. Equation (7.29) becomes

$$\omega_L = \left(\frac{e}{2m\mu\sin\theta}\right)\mu B\sin\theta = \frac{eB}{2m} \qquad (7.30)$$

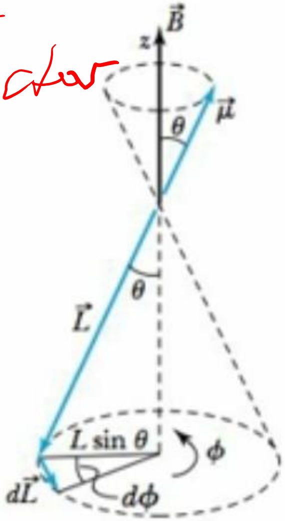


Figure 7.5 An atom having magnetic moment $\vec{\mu}$ feels a torque $\vec{\tau} = \vec{\mu} \times \vec{B}$ due to an external magnetic field $\vec{B}$. This torque must also be equal to $d\vec{L}/dt$. The vectors $\vec{\mu}$ and $\vec{L}$ are antiparallel, so the vector $d\vec{L}/dt$ must be perpendicular to $\vec{\mu}$, $\vec{B}$, and $\vec{L}$. As shown in the figure, $d\vec{L}/dt$ requires both $\vec{\mu}$ and $\vec{L}$ to precess (angle ϕ) about the magnetic field $\vec{B}$.

$\mu_z = \frac{e\hbar}{2m} m_\ell = -\mu_B m_\ell$

$\boxed{\vec{\mu} = -\mu_B \vec{L}/\hbar \quad \text{vector!!}}$

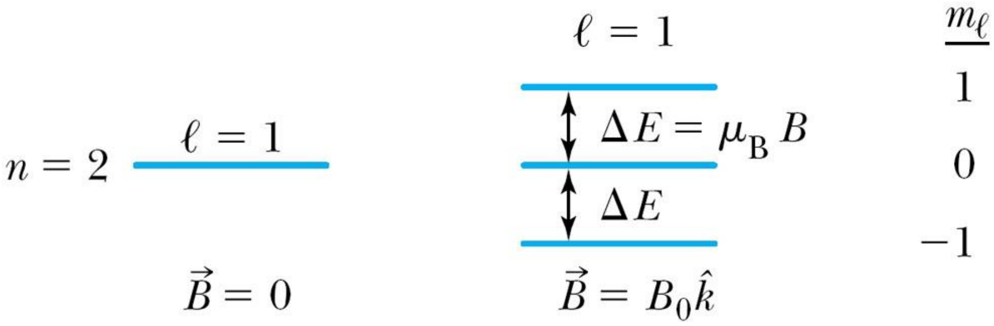
The Normal Zeeman Effect

- The potential energy is quantized due to the magnetic quantum number m_ℓ.

$$V_B = -\mu_z B = +\mu_B m_\ell B$$

- When a magnetic field is applied, the 2*p* level of atomic hydrogen is split into three different energy states with energy difference of $\Delta E = \mu_B B\, \Delta m_\ell$.

m_ℓ	**Energy**
1	$E_0 + \mu_B B$
0	E_0
−1	$E_0 - \mu_B B$



CONCEPTUAL EXAMPLE 7.6

What is the lowest $n\ell$ state in the hydrogen atom that has a degeneracy of 5?

Solution We want to find the lowest energy $n\ell$ state that has five m_ℓ states. This is true for a $\ell = 2$ state, because $2\ell + 1 = 5$. The lowest possible $\ell = 2$ state will be $3d$, because $n > \ell$ is required.

EXAMPLE 7.7

What is the value of the Bohr magneton? Use that value to calculate the energy difference between the $m_\ell = 0$ and $m_\ell = +1$ components in the $2p$ state of atomic hydrogen placed in an external field of 2.00 T.

Strategy To find the Bohr magneton we insert the known values of e, $\hbar$, and m into the equation for μ_B [see text after Equation (7.28)]. The energy difference is determined from Equation (7.31).

Solution The Bohr magneton is determined to be

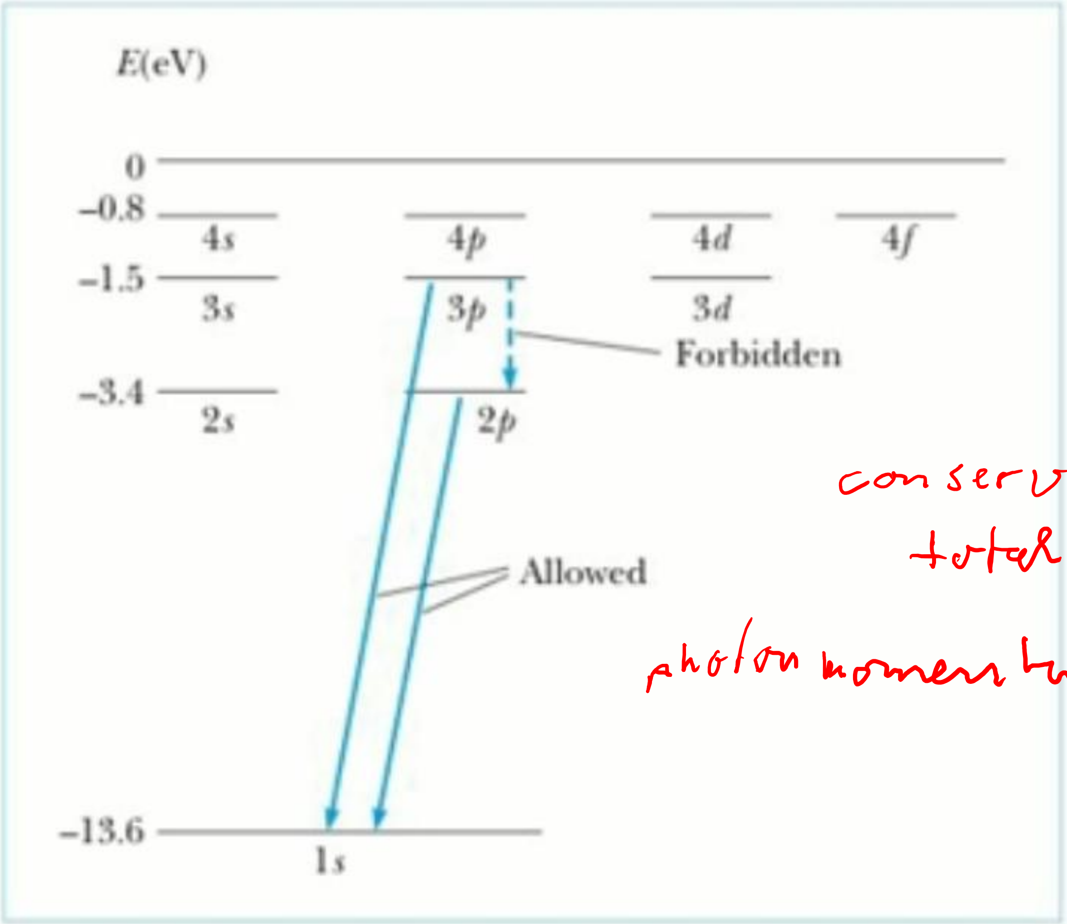
$$\mu_B = \frac{e\hbar}{2m}$$

$$= \frac{(1.602 \times 10^{-19}\ \text{C})(1.055 \times 10^{-34}\ \text{J}\cdot\text{s})}{2(9.11 \times 10^{-31}\ \text{kg})}$$

$$\mu_B = 9.27 \times 10^{-24}\ \text{J/T} \tag{7.32}$$

$\Delta E = \mu_B B \Delta m_e = (9.27 \times 10^{-24} J/T) \times 2T = 1.16 \times 10^{-4} eV$

Spectrum of atomic hydrogen



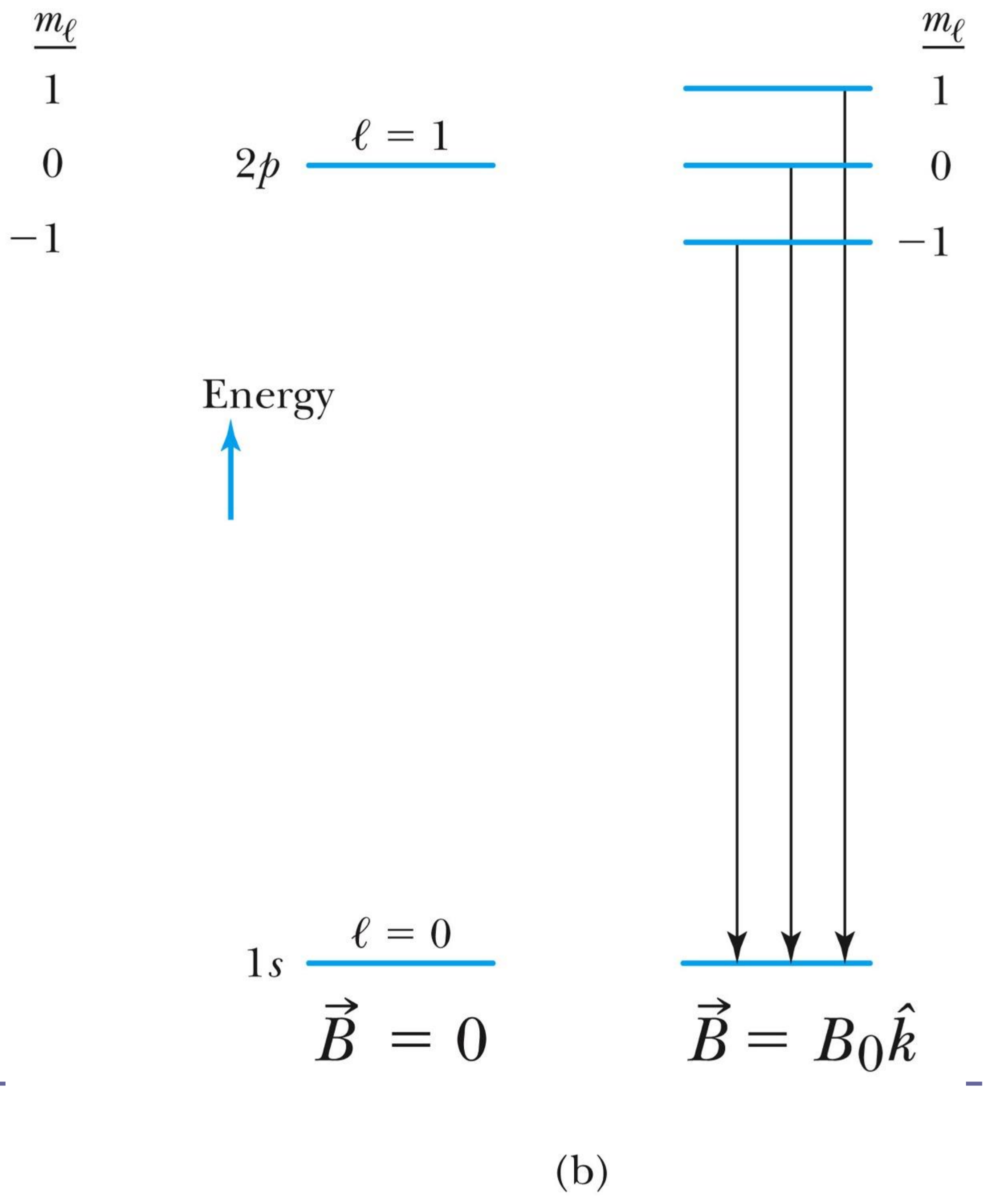
conservation of total momentum

photon momentum = 1ħ

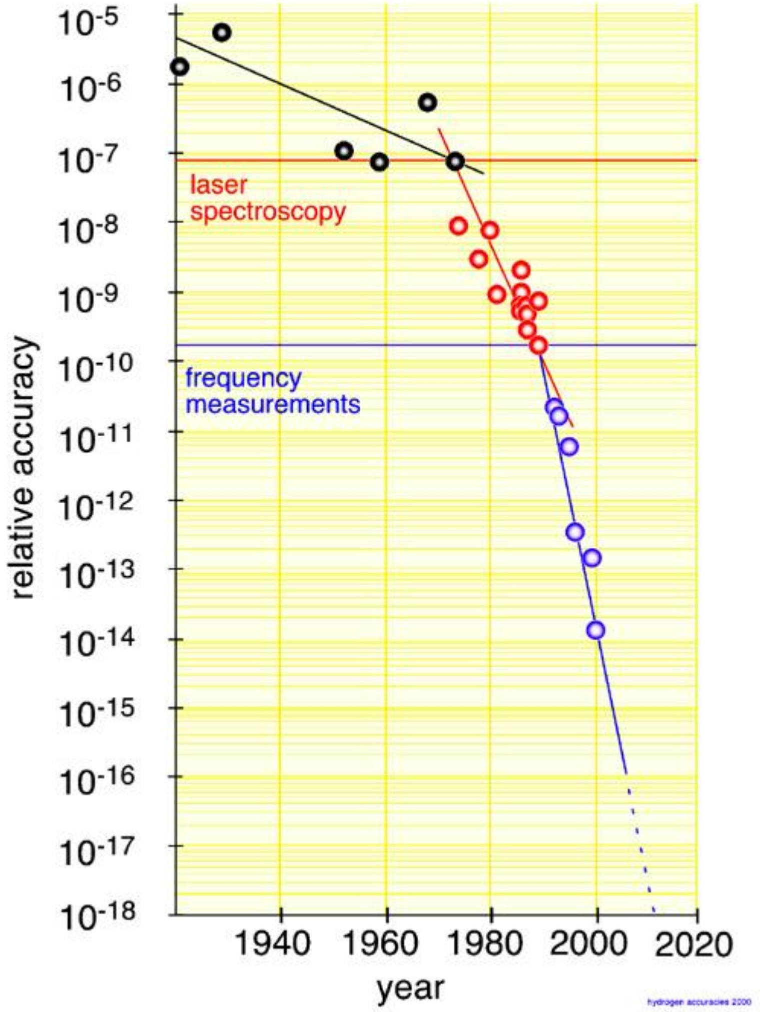
Figure 8.8 Energy-level diagram of atomic hydrogen. Allowed photon transitions are those obeying the selection rule $\Delta\ell = \pm 1$. The $3p \rightarrow 2p$ transition ($\Delta\ell = 0$) is said to be forbidden, though it may still occur (but only rarely).

The Normal Zeeman Effect

- A transition from 2*p* to 1*s*



History of Hydrogen Spectroscopy



Space quantizationin the Stern Gerlach experiment

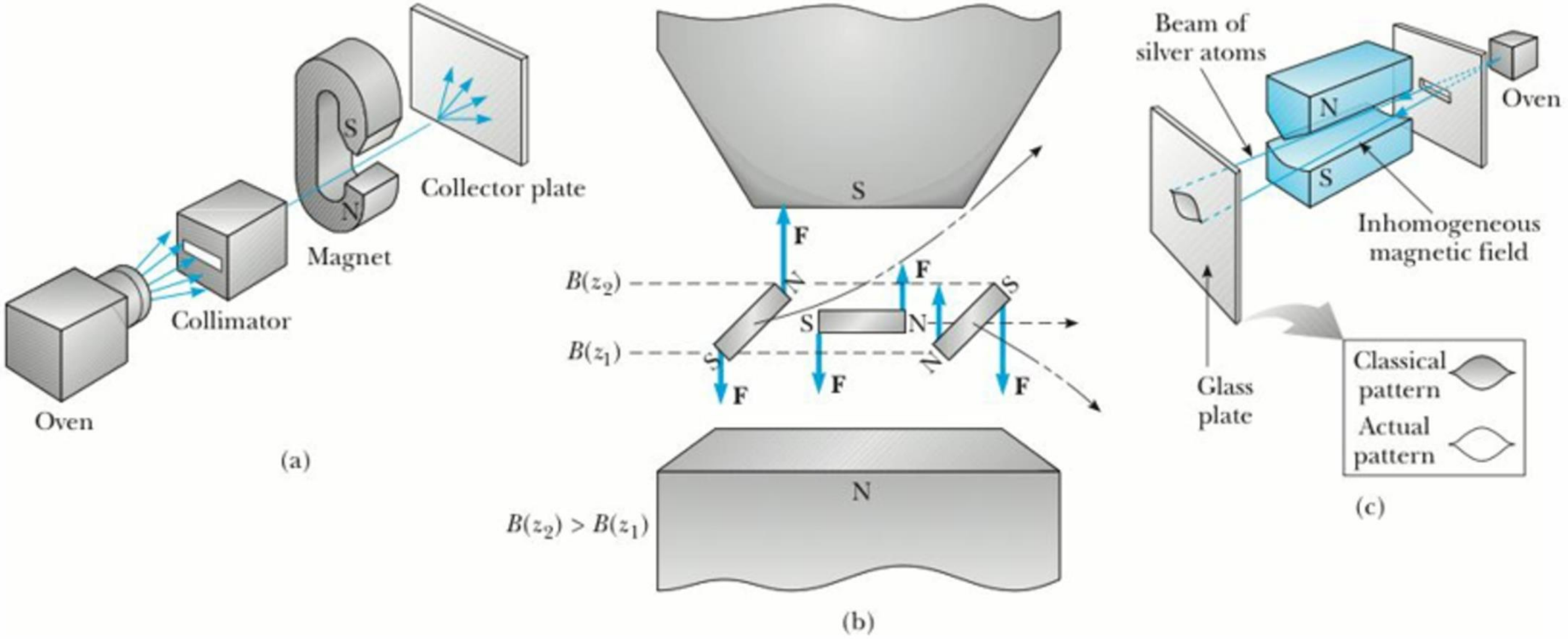
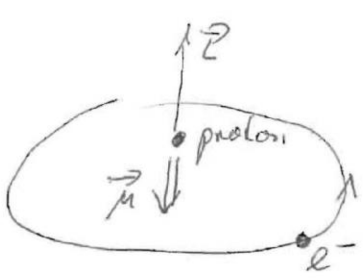


Figure 9.7 The Stern–Gerlach experiment to detect space quantization. (a) A beam of silver atoms is passed through a nonuniform magnetic field and detected on a collector plate. (b) The atoms, with their magnetic moment, are equivalent to tiny bar magnets. In a nonuniform field, each atomic magnet experiences a net force that depends on its orientation. (c) If any moment orientation were possible, a continuous fanning of the beam would be seen at the collector. For space quantization, the fanning is replaced by a set of discrete lines, one for each distinct moment orientation present in the beam.

The Zeeman effect (magnetic effect on atomic spectra)



classical consideration: electron circulating around proton is like an electrical current loop

$$\mu = \underset{\substack{\uparrow\\ \text{current}}}{I}\,\underset{\substack{\nwarrow\\ \text{area}}}{A} \qquad =$$

$$I = \frac{dq}{dt}\ ,\quad L = m v\cdot r \qquad v \perp r$$

$$\mu = IA = \frac{q}{T}A = \frac{-e}{\cancel{2}\cancel{\pi} r/v}\cancel{\pi} r^2 = \frac{-erv}{2} = -\frac{e}{2m}L \qquad \boxed{\vec\mu = -\frac{e}{2m}\vec L}$$

note: without magnetic field there is <u>no</u> handle to align the atom and $\vec L$ and $\vec\mu$ are opposite, but in random orientations

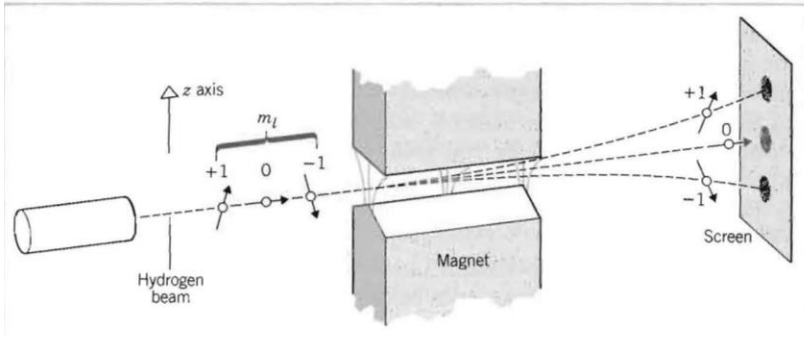
$$\vec\tau = \vec\mu \times \vec B$$

$$V_B = -\vec\mu\cdot\vec B$$

<u>note</u>: magnetic moment cannot align itself exactly in the z-direction L

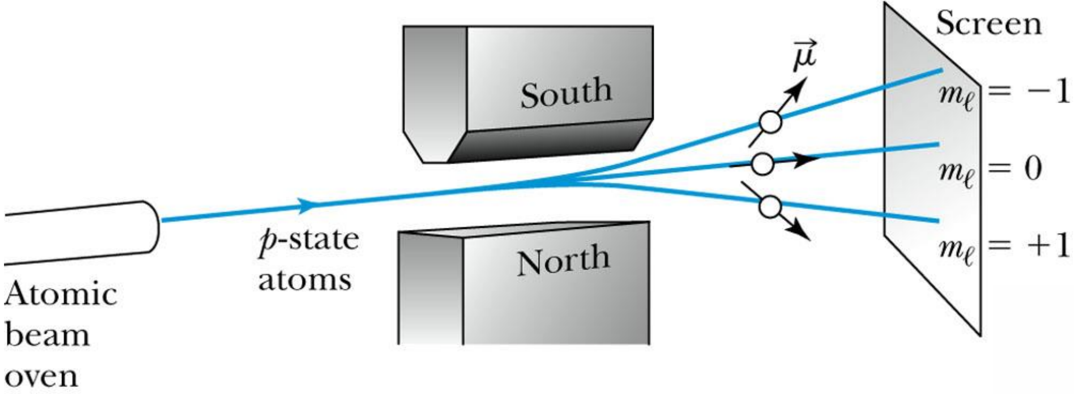
$$\mu_z = \boxed{\frac{e\hbar}{2m}}\, m_e = -\mu_B\, m_e$$

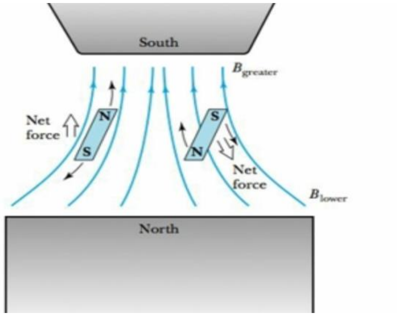
unit of magnetic moment = Bohr magneton



The Normal Zeeman Effect

- An atomic beam of particles in the $\ell = 1$ state pass through a inhomogeneous magnetic field along the *z* direction.





- $V_B = -\mu_z B$
- $F_z = -(dV_B / dz) = \mu_z (dB / dz)$
- The $m_\ell = +1$ state will be deflected down, the $m_\ell = -1$ state up, and the $m_\ell = 0$ state will be undeflected.
- If the space quantization were due to the magnetic quantum number m_ℓ, m_ℓ states is always odd $(2\ell + 1)$ and should have produced an odd number of lines.

Stern Gerlach saw only 2 states!

EXAMPLE 7.8

In 1927 T. E. Phipps and J. B. Taylor of the University of Illinois reported an important experiment similar to the Stern-Gerlach experiment but using hydrogen atoms instead of silver. This was done because hydrogen is the simplest atom, and the separation of the atomic beam in the inhomogeneous magnetic field would allow a clearer interpretation. The atomic hydrogen beam was produced in a discharge tube having a temperature of 663 K. The highly collimated beam passed along the x direction through an inhomogeneous field (of length 3 cm) having an average gradient of 1240 T/m along the z direction. If the magnetic moment of the hydrogen atom is 1 Bohr magneton, what is the separation of the atomic beam?

Strategy The force can be found from the potential energy of Equation (7.31).

$$F_z = -\frac{dV}{dz} = \mu_z \frac{dB}{dz}$$

The acceleration of the hydrogen atom along the z direction is $a_z = F_z/m$. The separation of the atom along the z direction due to this acceleration is $d = a_z t^2/2$. The time that the atom spends within the inhomogeneous field is $t = \Delta x/v_x$ where Δx is the length of the inhomogeneous field, and v_x is the constant speed of the atom within the field. The separation d is therefore found from

$$d = \frac{1}{2} a_z t^2 = \frac{1}{2}\left(\frac{F_z}{m}\right) t^2 = \frac{1}{2m}\left(\mu_z \frac{dB}{dz}\right)\left(\frac{\Delta x}{v_x}\right)^2$$

We know all the values needed to determine d except the speed v_x, but we do know the temperature of the hydrogen gas. The average energy of the atoms collimated along the x direction is $\frac{1}{2}m\langle v_x^2\rangle = \frac{3}{2}kT$.

Solution We calculate $\langle v_x^2\rangle$ to be

$$v_x^2 = \frac{3kT}{m} = \frac{3(1.38 \times 10^{-23}\ \mathrm{J/K})(663\ \mathrm{K})}{1.67 \times 10^{-27}\ \mathrm{kg}}$$

$$= 1.64 \times 10^{7}\ \mathrm{m^2/s^2}$$

The separation d of the one atom is now determined to be

$$d = \frac{1}{2(1.67 \times 10^{-27}\ \mathrm{kg})}(9.27 \times 10^{-24}\ \mathrm{J/T})(1240\ \mathrm{T/m})$$

$$\times \frac{(0.03\mathrm{m})^2}{(1.64 \times 10^{7}\ \mathrm{m^2/s^2})} = 0.19 \times 10^{-3}\ \mathrm{m}$$

saw only 2 states = controversy!

7.5: Intrinsic Spin

- Samuel Goudsmit and George Uhlenbeck in Holland proposed that *the electron must have an intrinsic angular momentum* and therefore a magnetic moment.

- Paul Ehrenfest showed that the surface of the spinning electron should be moving faster than the speed of light!

- In order to explain experimental data, Goudsmit and Uhlenbeck proposed that the electron must have an **intrinsic spin quantum number** $s = ½$.

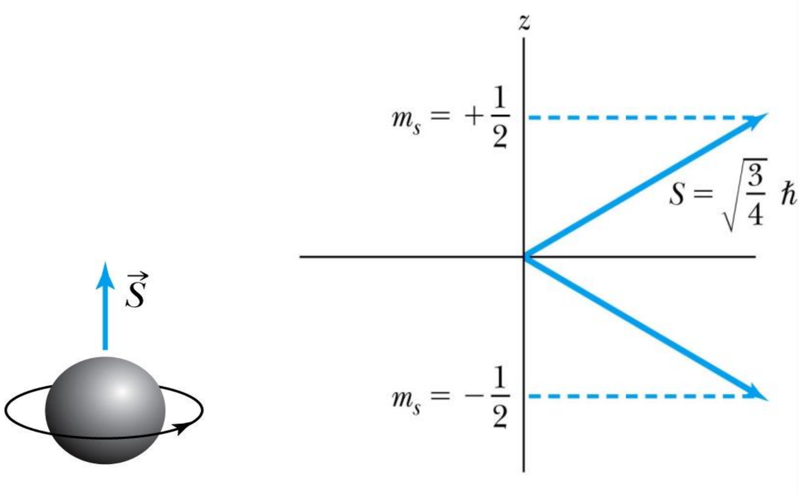
Intrinsic Spin

- The spinning electron reacts similarly to the orbiting electron in a magnetic field.
- We should try to find L, L_z, ℓ, and m_ℓ.
- The **magnetic spin quantum number** m_s has only two values, $m_s = \pm ½$.

The electron's spin will be either "up" or "down" and can never be spinning with its magnetic moment μ_s exactly along the z axis.

The **intrinsic spin angular momentum** vector

$$\left|\vec{S}\right| = \sqrt{s(s+1)}\hbar = \sqrt{3/4}\hbar\ .$$



(a)　(b)

Intrinsic Spin

- The magnetic moment is $\vec{\mu}_s = -(e/m)\vec{S}$, or $-2\mu_B \vec{S}/\hbar$.
- The coefficient of $\vec{S}/\hbar$ is $-2\mu_B$ as with $\vec{L}$ is a consequence of theory of relativity.

- The **gyromagnetic ratio** (ℓ or *s*).
- $g_\ell = 1$ and $g_s = 2$, then

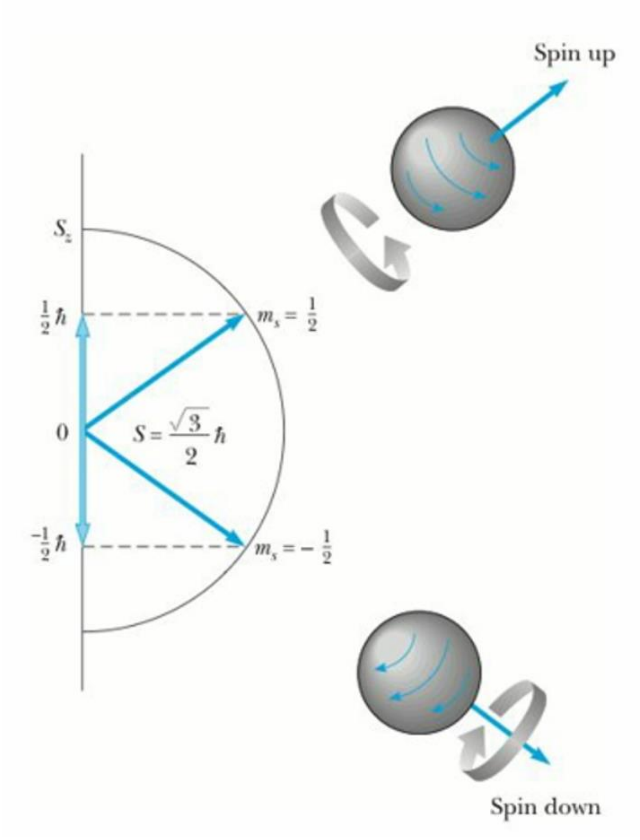
$$\overrightarrow{\mu_l} = -\frac{g_l \mu_B \vec{L}}{\hbar} = -\frac{\mu_B \vec{L}}{\hbar} \quad \text{and} \quad \overrightarrow{\mu_s} = -\frac{g_s \mu_B \vec{S}}{\hbar} = -2\frac{\mu_B \vec{S}}{\hbar}$$

- The z component of $\vec{S}$ is $S_z = m_s \hbar = \pm\hbar/2$.
- In ℓ = 0 state → no splitting due to $\vec{\mu}_s$.

  → there is space quantization due to the intrinsic spin.
- Apply m_ℓ and the potential energy becomes

$$V_B = -\vec{\mu}_s \cdot \vec{B} = +\frac{e}{m}\vec{S} \cdot \vec{B}$$

Space quantization of the electron spin angular momentum



Doublet splitting due to the electron spin magnetic moment

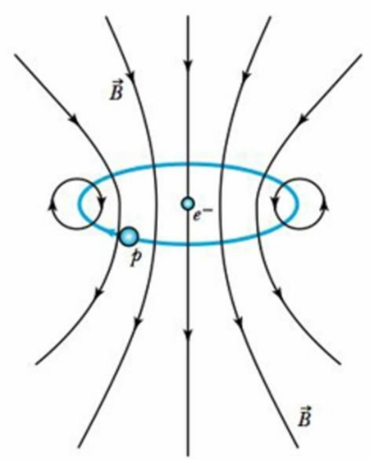


Figure 7.10 The hydrogen atom in the frame of reference of the electron. In this case, the orbiting proton creates a magnetic field at the position of the electron.

In the frame of the electron there is an internal magnetic field created by the orbiting proton= doubled splitting

Problem7.29

Use all four quantum numbers (n,l.m_l,m_s) to write down all possible sets of quantum numbers for the 4*f* state of atomic hydrogen. What is the total degeneracy?

1. For the 4*f* state $n = 4$ and $\ell = 3$. The possible m_ℓ values are $0, \pm1, \pm2,$ and ±3 with $m_s = \pm1/2$ for each possible m_ℓ value. The degeneracy of the 4*f* state is then (with 2 spin states per m_ℓ) equal to 2(7) = 14.

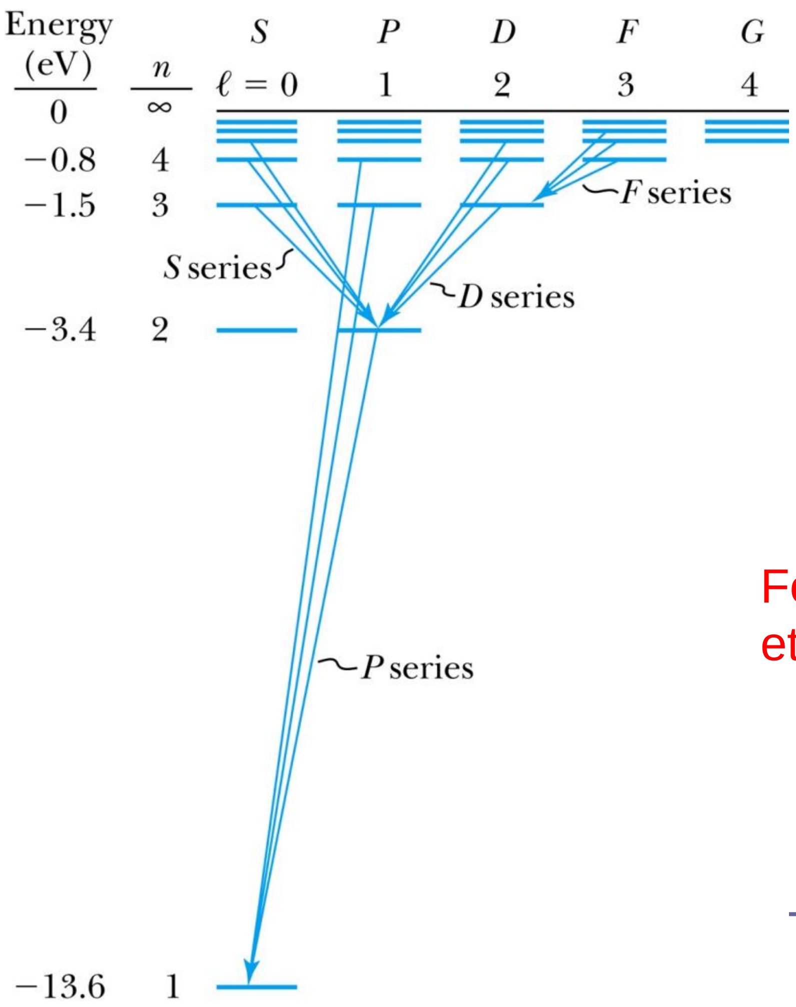
Problem7.32

Use all four quantum numbers $(n,l.m_l,m_s)$ to write down all possible sets of quantum numbers for the 5*d* state of atomic hydrogen. What is the total degeneracy?

1. For the 5*d* state $n = 5$ and $\ell = 2$. The possible m_ℓ values are $0, \pm1,$ and $\pm2,$ with $m_s = \pm1/2$ for each possible m_ℓ value. The degeneracy of the 5*d* state is then (with 2 spin states per m_ℓ) equal to 2(5) = 10.

7.6: Energy Levels and Electron Probabilities

- For hydrogen, the energy level depends on the principle quantum number *n*.



- In ground state an atom cannot emit radiation. It can absorb electromagnetic radiation, or gain energy through inelastic bombardment by particles.

Forbidden transitions: 3P-2P, 3d-2S,4F-3S, etc

Selection Rules

- We can use the wave functions to calculate transition probabilities for the electron to change from one state to another.

Allowed transitions:

- Electrons absorbing or emitting photons to change states when $\Delta\ell = \pm 1$.

Forbidden transitions:

- Other transitions possible but occur with much smaller probabilities when $\Delta\ell \neq \pm 1$.

$$\Delta n = \text{anything}$$

$$\Delta\ell = \pm 1$$

$$\Delta m_\ell = 0, \pm 1$$

Conservation of angular momentum: photon carries one unit of angular momentum. The atom changes by one unit of angular momentum in the radiation process

3-D Probability Distribution Functions

- We must use wave functions to calculate the probability distributions of the electrons.

- The "position" of the electron is spread over space and is not well defined.

- We may use the radial wave function $R(r)$ to calculate radial probability distributions of the electron.
- The probability of finding the electron in a differential volume element $d\tau$ is $dP = \psi^*(r,\theta,\phi)\ \psi(r,\theta,\phi)\ d\tau$.

3-D Probability Distribution Functions

- The differential volume element in spherical polar coordinates is

$$d\tau = r^2 \sin\theta \, dr \, d\theta \, d\phi$$

Therefore,

$$P(r)\,dr = r^2 R^*(r) R(r)\,dr \int_0^{\pi} |f(\theta)|^2 \sin\theta \, d\theta \int_0^{2\pi} |g(\phi)|^2 \, d\phi$$

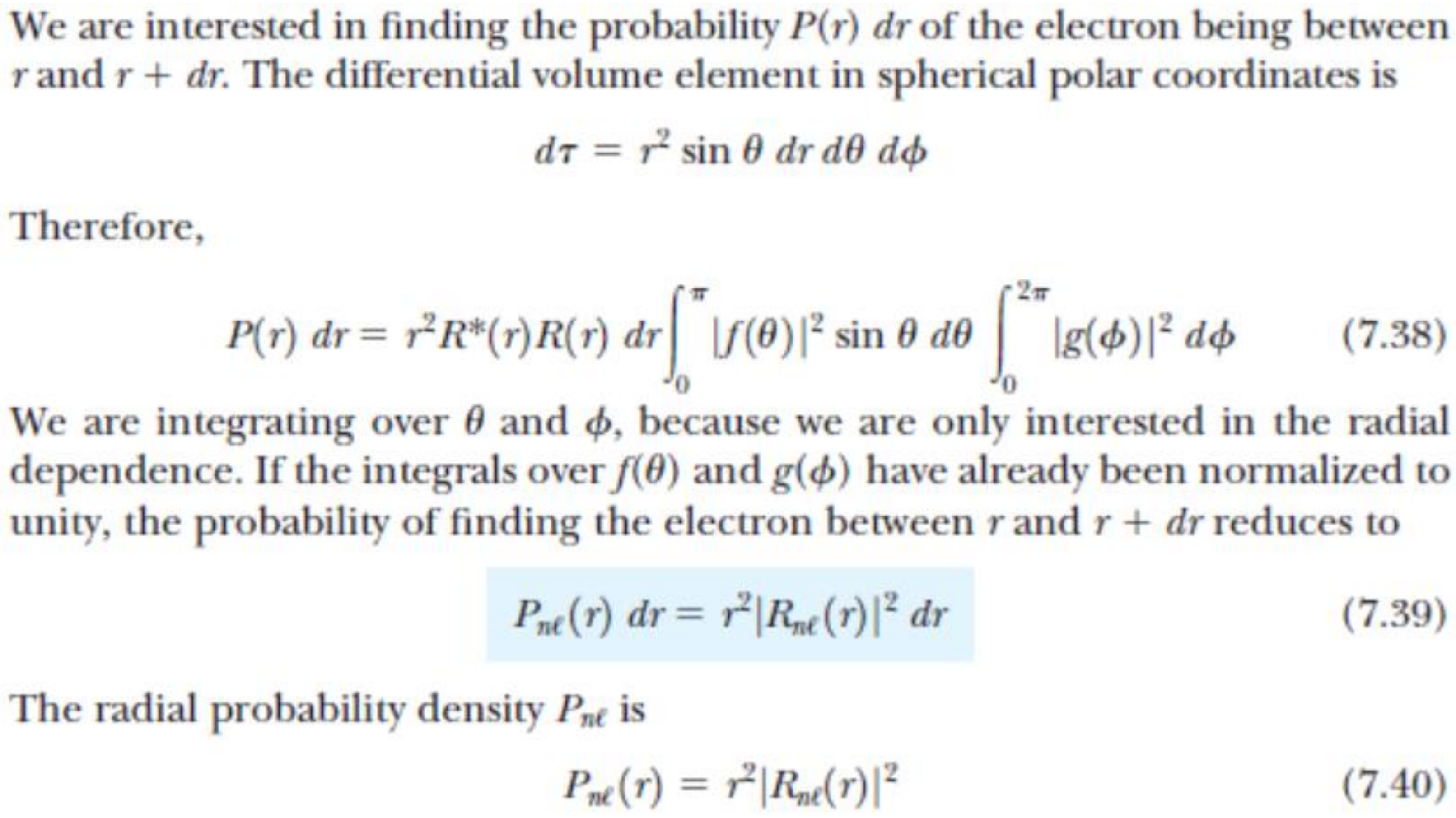
- We are only interested in the radial dependence.

$$P(r)\,dr = r^2 |R(r)|^2 \, dr$$

- The radial probability density is $P(r) = r^2|R(r)|^2$ and it depends only on *n* and *l*.

The integrals have been normalized to unity. For the azimuthal part we have $(e^{im_l\emptyset})^* e^{im_l\emptyset} = e^{-im_l\emptyset + im_l\emptyset} = e^0 = 1$

Probability distributions in 3D space(as shown before)



We are interested in finding the probability $P(r)\,dr$ of the electron being between r and $r + dr$. The differential volume element in spherical polar coordinates is

$$d\tau = r^2 \sin\theta \, dr \, d\theta \, d\phi$$

Therefore,

$$P(r)\,dr = r^2 R^*(r) R(r)\,dr \int_0^{\pi} |f(\theta)|^2 \sin\theta \, d\theta \int_0^{2\pi} |g(\phi)|^2 \, d\phi \qquad (7.38)$$

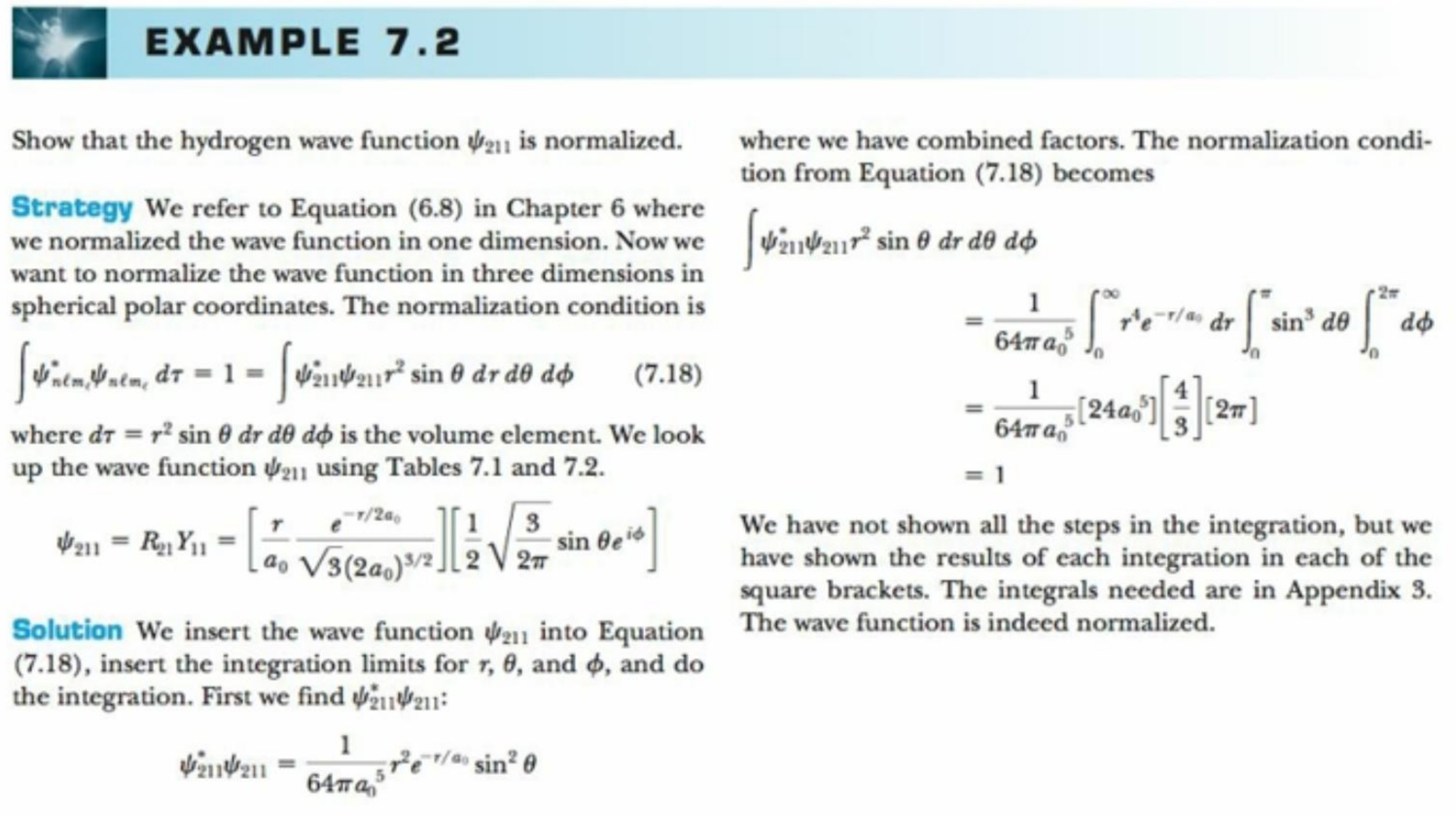
We are integrating over θ and ϕ, because we are only interested in the radial dependence. If the integrals over $f(\theta)$ and $g(\phi)$ have already been normalized to unity, the probability of finding the electron between r and $r + dr$ reduces to

$$P_{n\ell}(r)\,dr = r^2 |R_{n\ell}(r)|^2 \, dr \qquad (7.39)$$

The radial probability density $P_{n\ell}$ is

$$P_{n\ell}(r) = r^2 |R_{n\ell}(r)|^2 \qquad (7.40)$$

Normalizing a hydrogenic wave function



EXAMPLE 7.2

Show that the hydrogen wave function ψ_{211} is normalized.

Strategy We refer to Equation (6.8) in Chapter 6 where we normalized the wave function in one dimension. Now we want to normalize the wave function in three dimensions in spherical polar coordinates. The normalization condition is

$$\int \psi^*_{n\ell m_\ell}\psi_{n\ell m_\ell}\,d\tau = 1 = \int \psi^*_{211}\psi_{211}r^2\sin\theta\,dr\,d\theta\,d\phi \qquad (7.18)$$

where $d\tau = r^2\sin\theta\,dr\,d\theta\,d\phi$ is the volume element. We look up the wave function ψ_{211} using Tables 7.1 and 7.2.

$$\psi_{211} = R_{21}Y_{11} = \left[\frac{r}{a_0}\frac{e^{-r/2a_0}}{\sqrt{3}(2a_0)^{3/2}}\right]\left[\frac{1}{2}\sqrt{\frac{3}{2\pi}}\sin\theta\, e^{i\phi}\right]$$

Solution We insert the wave function ψ_{211} into Equation (7.18), insert the integration limits for r, θ, and ϕ, and do the integration. First we find $\psi^*_{211}\psi_{211}$:

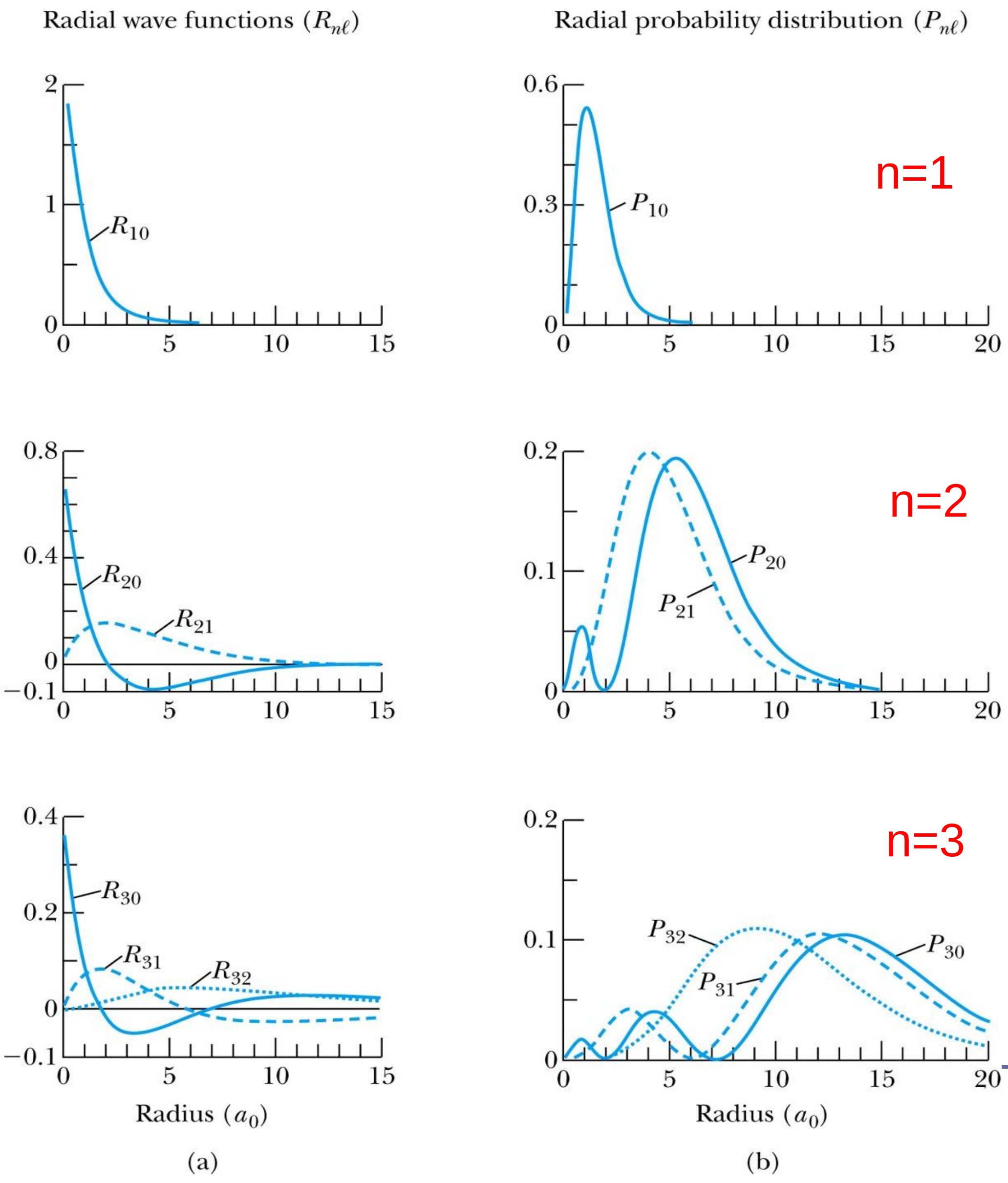
$$\psi^*_{211}\psi_{211} = \frac{1}{64\pi a_0^5}r^2e^{-r/a_0}\sin^2\theta$$

where we have combined factors. The normalization condition from Equation (7.18) becomes

$$\begin{aligned}\int \psi^*_{211}\psi_{211}r^2\sin\theta\,dr\,d\theta\,d\phi &= \frac{1}{64\pi a_0^5}\int_0^\infty r^4e^{-r/a_0}\,dr\int_0^\pi \sin^3 d\theta\int_0^{2\pi} d\phi\\ &= \frac{1}{64\pi a_0^5}[24a_0^5]\left[\frac{4}{3}\right][2\pi]\\ &= 1\end{aligned}$$

We have not shown all the steps in the integration, but we have shown the results of each integration in each of the square brackets. The integrals needed are in Appendix 3. The wave function is indeed normalized.

Radial Probability Distribution Functions



n=1

n=2

n=3

- *R*(*r*) and *P*(*r*) for the lowest-lying states of the hydrogen atom

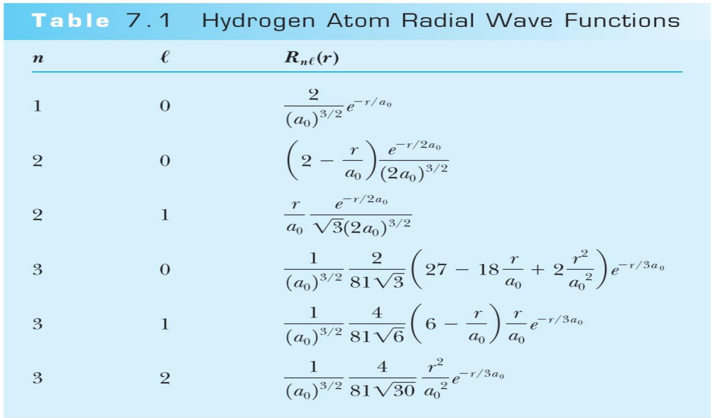
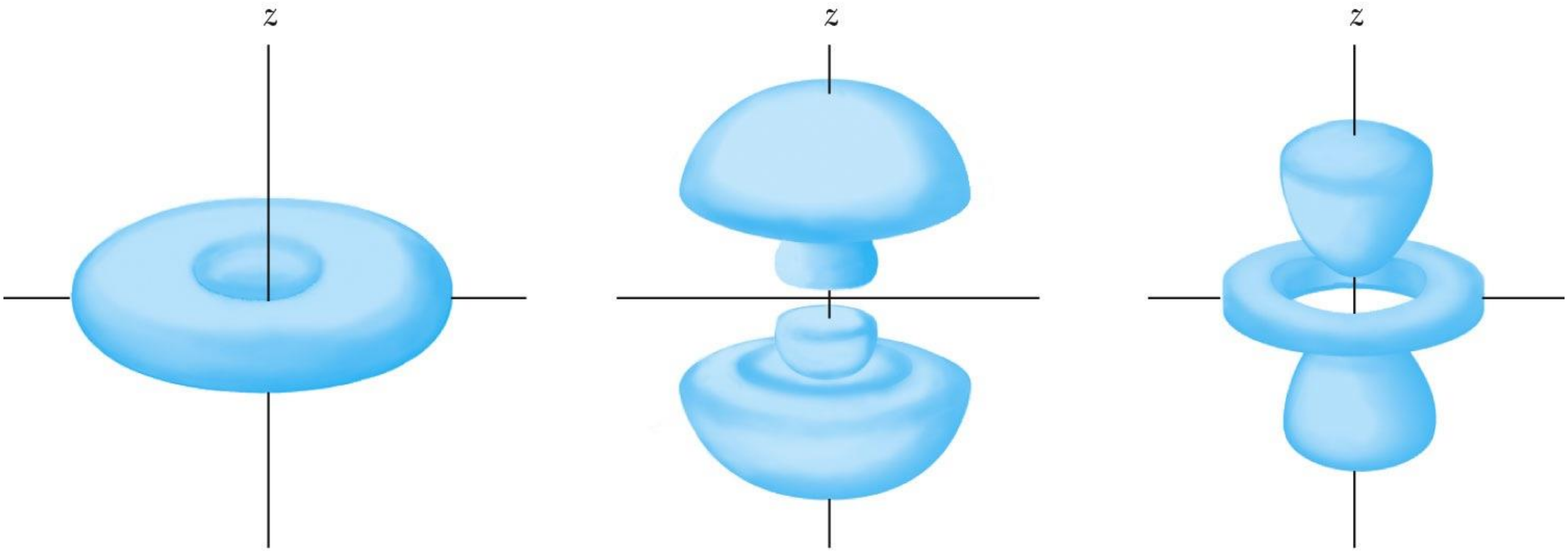


Table 7.1 Hydrogen Atom Radial Wave Functions

n	ℓ	$R_{n\ell}(r)$
1	0	$\frac{2}{(a_0)^{3/2}}e^{-r/a_0}$
2	0	$\left(2 - \frac{r}{a_0}\right)\frac{e^{-r/2a_0}}{(2a_0)^{3/2}}$
2	1	$\frac{r}{a_0}\frac{e^{-r/2a_0}}{\sqrt{3}(2a_0)^{3/2}}$
3	0	$\frac{1}{(a_0)^{3/2}}\frac{2}{81\sqrt{3}}\left(27 - 18\frac{r}{a_0} + 2\frac{r^2}{a_0{}^2}\right)e^{-r/3a_0}$
3	1	$\frac{1}{(a_0)^{3/2}}\frac{4}{81\sqrt{6}}\left(6 - \frac{r}{a_0}\right)\frac{r}{a_0}e^{-r/3a_0}$
3	2	$\frac{1}{(a_0)^{3/2}}\frac{4}{81\sqrt{30}}\frac{r^2}{a_0{}^2}e^{-r/3a_0}$

3-D Probability Distribution Functions

- The probability density for the hydrogen atom for three different electron states

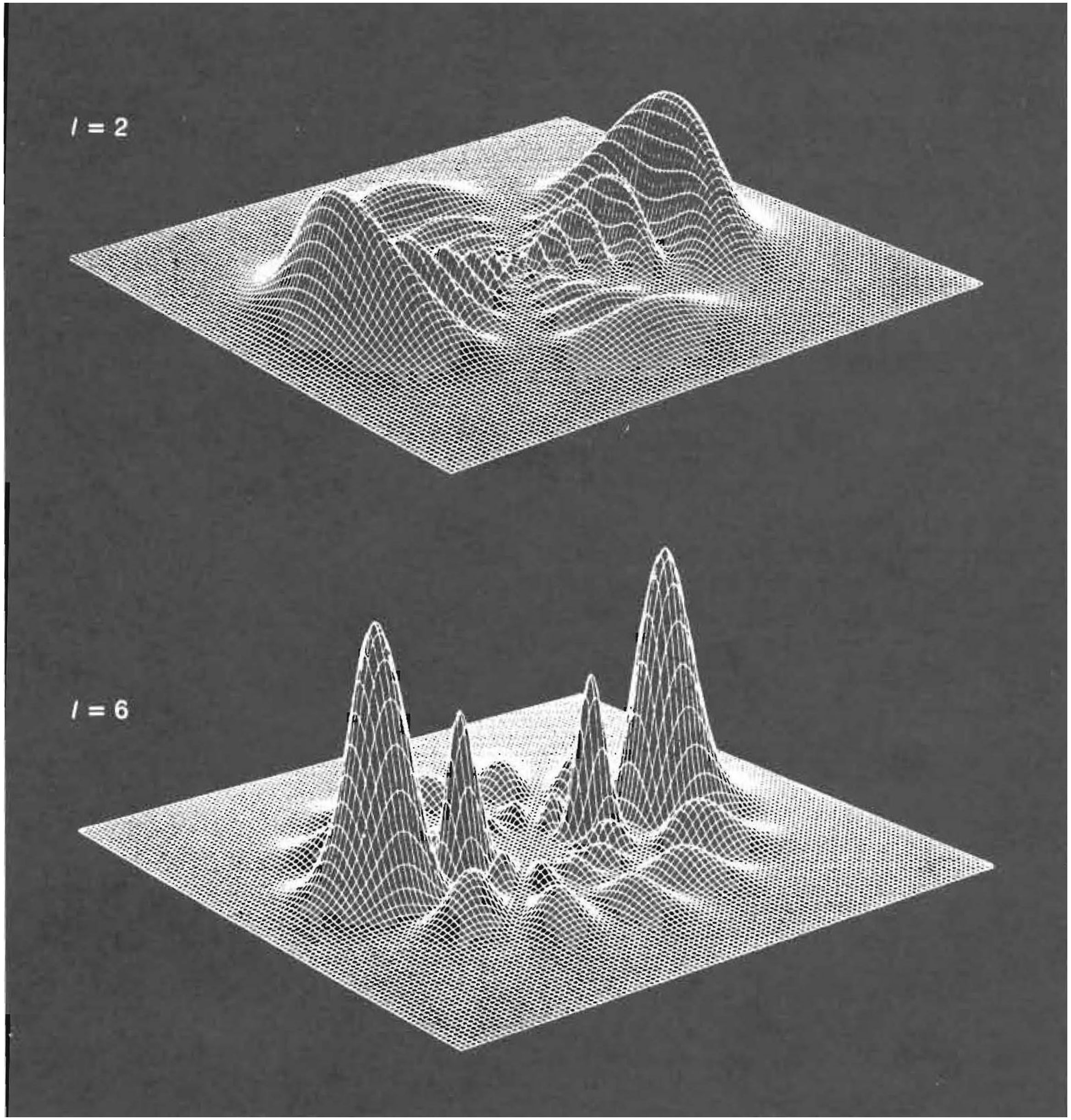


$n = 2$
$\ell = 1$
$m_\ell = \pm 1$

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

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

(b)



These computer-drawn graphs represent the probability to locate the electron in the $n = 8$ *state of hydrogen for angular momentum quantum number* $l = 2$ *and* $l = 6$*; the vertical coordinate at any point gives the probability to find the electron in a small volume element at that point. The nucleus of the atom would be at the center of each graph.*

EXAMPLE 7.11

Find the most probable radius for the electron of a hydrogen atom in the 1*s* and 2*p* states.

Strategy To find the maximum and minimum of a function we take the derivative of the function with respect to the variable and set the derivative equal to zero. To find the most probable radial value we take the derivative of the probability density $P(r)$ (see Equation (7.39)) with respect to r and set it equal to zero. We use the $R_{n\ell}(r)$ from Table 7.1.

Solution We use Equation (7.40) for the probability density for both the 1*s* and 2*p* states and find the $R_{n\ell}$ values from Table 7.1.

$$P_{10} = \frac{4r^2}{a_0^{\,3}} e^{-2r/a_0}$$

$$P_{21} = \frac{r^4}{24a_0^{\,5}} e^{-r/a_0}$$

1s state:

$$\frac{d}{dr}P_{10}(r) = 0 = \frac{d}{dr}\left(\frac{4e^{-2r/a_0}}{a_0^3} r^2\right)$$

$$0 = \frac{4}{a_0^{\,3}}\left(-\frac{2}{a_0} r^2 + 2r\right) e^{-2r/a_0}$$

$$\frac{2r^2}{a_0} = 2r$$

$$r = a_0 \quad \text{Most probable radius for 1}s\text{ state electron} \qquad (7.41)$$

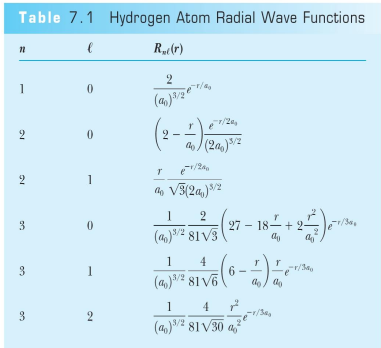


Table 7.1 Hydrogen Atom Radial Wave Functions

n	ℓ	$R_{n\ell}(r)$
1	0	$\frac{2}{(a_0)^{3/2}} e^{-r/a_0}$
2	0	$\left(2 - \frac{r}{a_0}\right)\frac{e^{-r/2a_0}}{(2a_0)^{3/2}}$
2	1	$\frac{r}{a_0}\frac{e^{-r/2a_0}}{\sqrt{3}(2a_0)^{3/2}}$
3	0	$\frac{1}{(a_0)^{3/2}}\frac{2}{81\sqrt{3}}\left(27 - 18\frac{r}{a_0} + 2\frac{r^2}{a_0^2}\right)e^{-r/3a_0}$
3	1	$\frac{1}{(a_0)^{3/2}}\frac{4}{81\sqrt{6}}\left(6 - \frac{r}{a_0}\right)\frac{r}{a_0}e^{-r/3a_0}$
3	2	$\frac{1}{(a_0)^{3/2}}\frac{4}{81\sqrt{30}}\frac{r^2}{a_0^2}e^{-r/3a_0}$

2*p* state:

$$\frac{d}{dr}P_{21}(r) = \frac{d}{dr}\left[\frac{r^4}{24a_0^{\,5}} e^{-r/a_0}\right] = 0$$

$$\frac{e^{-r/a_0}}{24a_0^{\,5}}\left(4r^3 - \frac{r^4}{a_0}\right) = 0$$

$$\frac{r^4}{a_0} = 4r^3$$

$$r = 4a_0 \quad \text{Most probable radius for 2}p\text{ state electron} \qquad (7.42)$$

Notice that the most probable radii for the 1*s* and 2*p* states agree with the Bohr radii. This occurs only for the largest possible ℓ value for each n (see Problem 36).

EXAMPLE 7.12

Calculate the average orbital radius of a 1*s* electron in the hydrogen atom.

Strategy To find the average value, we shall find the expectation value.

Solution The expectation (or average) value of r is (see Section 6.2)

$$\langle r \rangle = \int \psi^*(r, \theta, \phi) r \psi(r, \theta, \phi)\, d\tau = \int r P(r)\, dr$$

where we have again integrated over θ and ϕ. We use Equation (7.39) for the probability density and find the radial wave function $R_{1s}(r)$ in Table 7.1.

$$\langle r \rangle = \int_0^\infty \frac{4}{a_0^3} e^{-2r/a_0}\, r^3\, dr$$

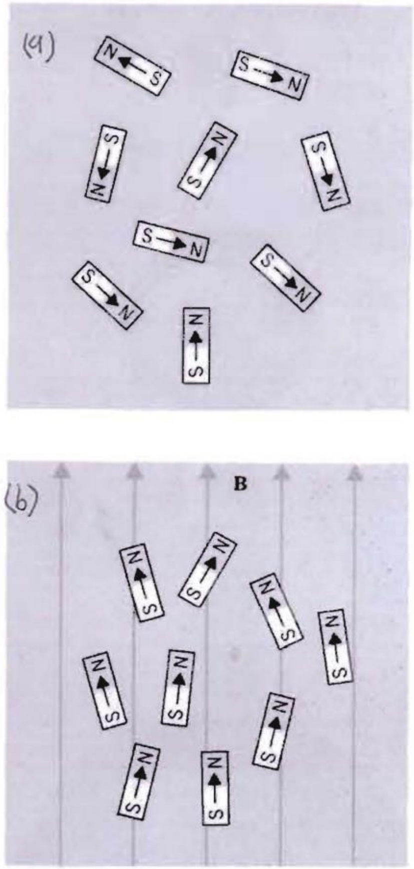
We look up this integral in Appendix 3 and determine

$$\int_0^\infty r^3 e^{-2r/a_0}\, dr = \frac{3a_0^4}{8}$$

so that

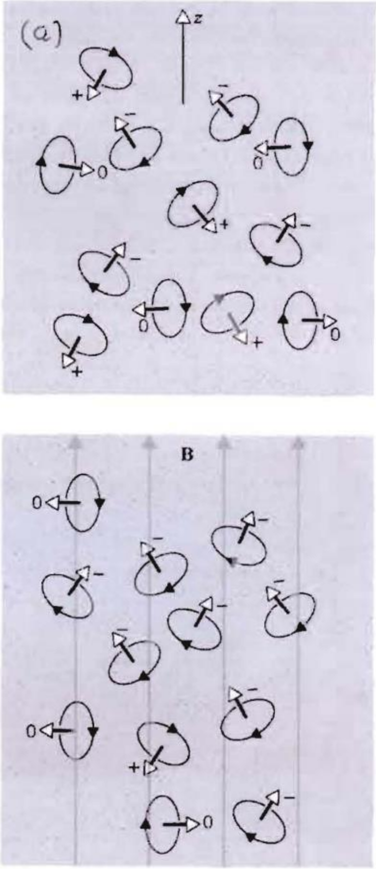
$$\langle r \rangle = \frac{4}{a_0^3} \frac{3a_0^4}{8} = \frac{3}{2} a_0 \qquad \text{For the 1}s\text{ state electron}$$

Therefore, the average electron radius in the 1*s* state is larger than the most probable value, the Bohr radius. We can see that this result is reasonable by examining the radial probability distribution for the 1*s* state displayed in Figure 7.12. The maximum (or most probable) value occurs at a_0, but the average is greater than a_0 because of the shape of the "tail" of the distribution.



(a) A collection of small non interacting magnets

(b) An applied magnetic field $\vec{B}$ rotates the magnetic moments into the direction of the field.



(a) A collection of non interacting atomic moments

(b) with an applied magnetic field there is <u>space quantization</u> The z-components are indicated as + (for +1) 0 (for 0) and – (for -1)

$$\mu_z = -\frac{e\hbar}{2m} m_\ell = -\mu_B \cdot m_\ell$$

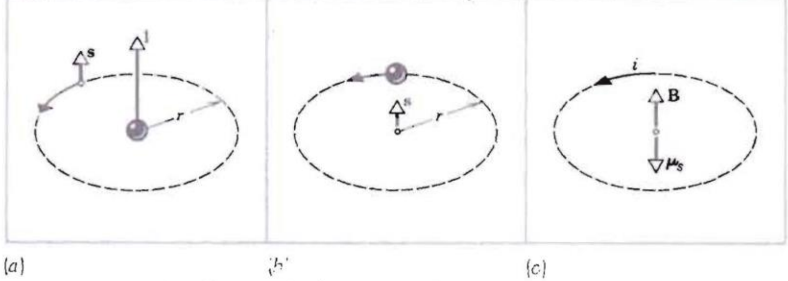
Fine structure:

$$\vec{\mu}_s = -\frac{e}{m}\vec{s} \qquad m_s = \pm\frac{1}{2}$$

↑ magnetic — intrinsic spin

Two view points: both are correct

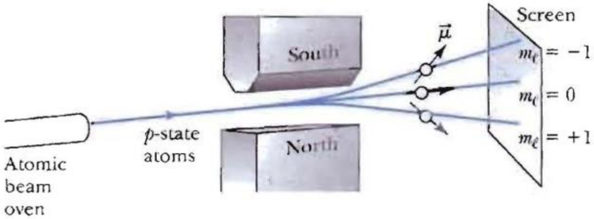
For many centuries it was believed that the earth was the center of the solar system and that the sun moved around the earth. Today we know that the earth moves around the sun



similar for electron

(a) An electron circulates about the nucleus with orbital angular momentum **l**. The spin of the electron is parallel to **l**. (b) From the point of view of the electron, the proton circulates as shown. (c) The apparently circulating proton is represented by the current i and causes a magnetic field **B** at the electron. The spin magnetic moment of the electron is opposite to its spin angular momentum.

"Landmark" experiments in atomic physics



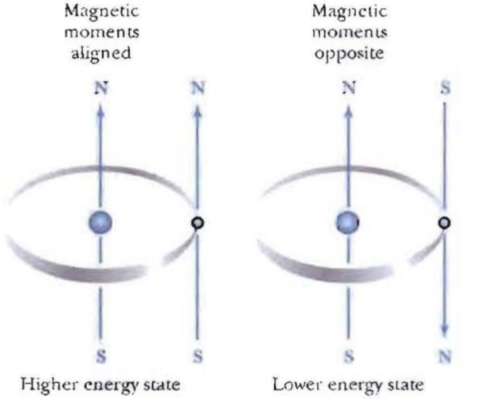
Stern Gerlach experiment

$$V_B = -\mu_z B \qquad F_z = -\frac{dV_B}{dz} = \mu_z \frac{dB}{dz}$$

magnetic field gradient

There is a different force on each of the 3 m_ℓ-states

down; $m_\ell = +1$ up : $m_\ell = -1$ not deflected $m_\ell = 0$



Hydrogen is most abundant gas in ~~the~~ Milky way galaxy $n \approx 1$ atom/cm³.

The 21 cm line in atomic hydrogen (1420 MHz) is observed in astronomical telescopes

$$\lambda \cdot \nu = c$$

$$21\,\text{cm} \; 1.4 \times 10^{9}\,\text{Hz} = 3 \times 10^{10}\ \frac{\text{cm}}{\text{s}}$$

Hyperfine structure: Interaction between electron and nuclear magnetic moments

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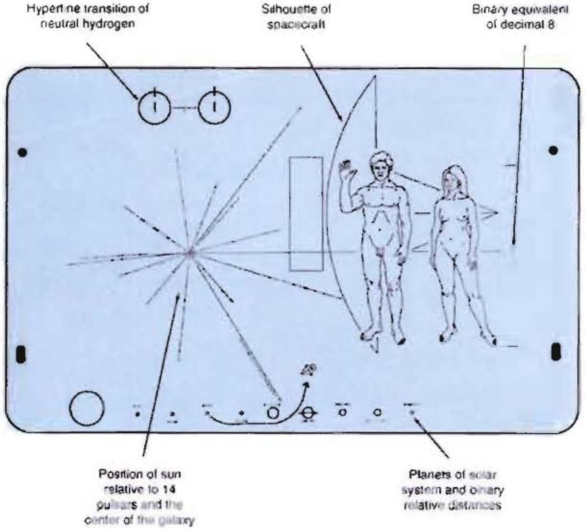

Hyperfine transition of neutral hydrogen

Silhouette of spacecraft

Binary equivalent of decimal 8

Position of sun relative to 14 pulsars and the center of the galaxy

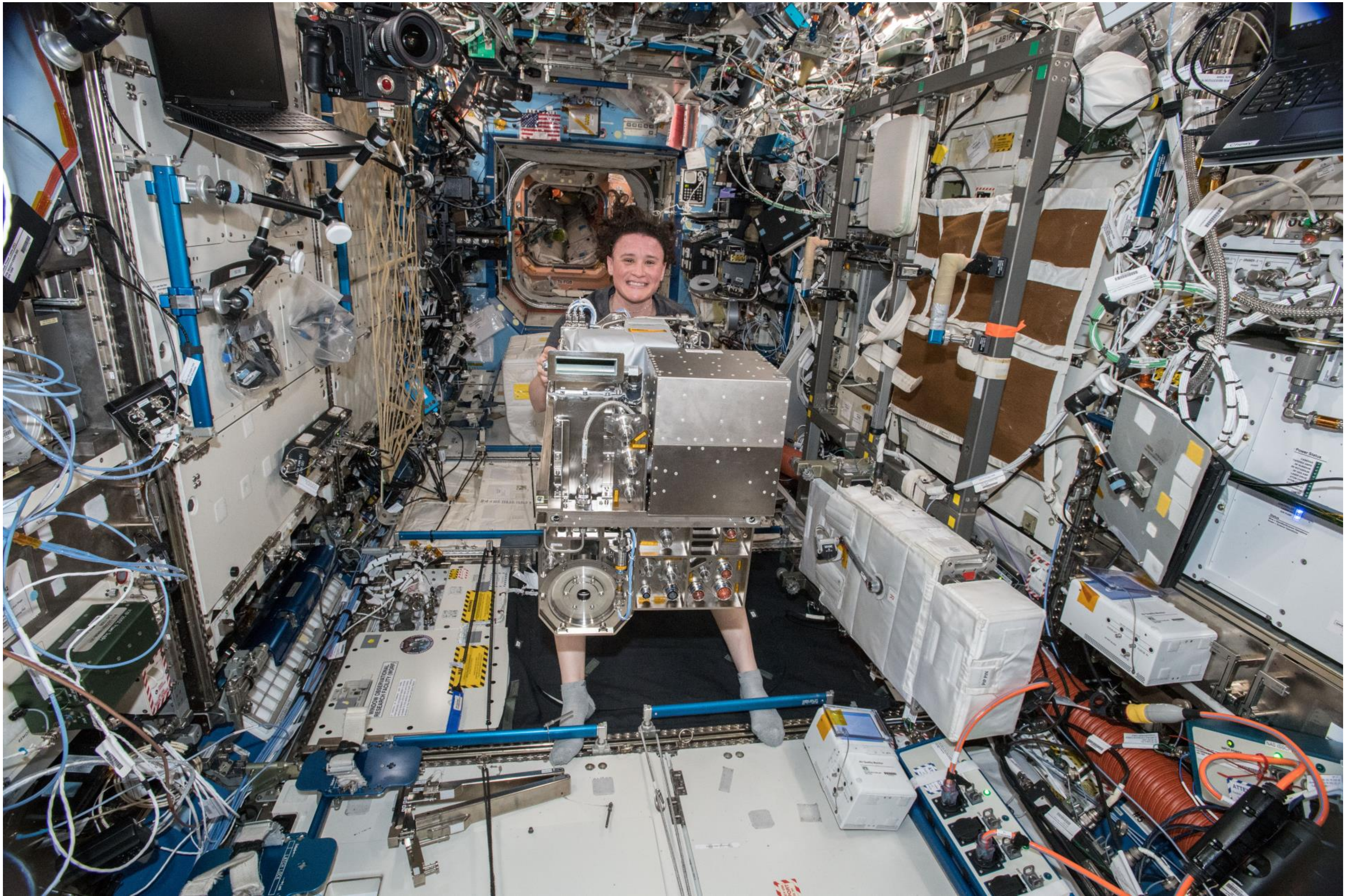
Planets of solar system and binary relative distances

Search for extraterrestrial intelligence

Voyagers 1 and 2 are exiting the solar system

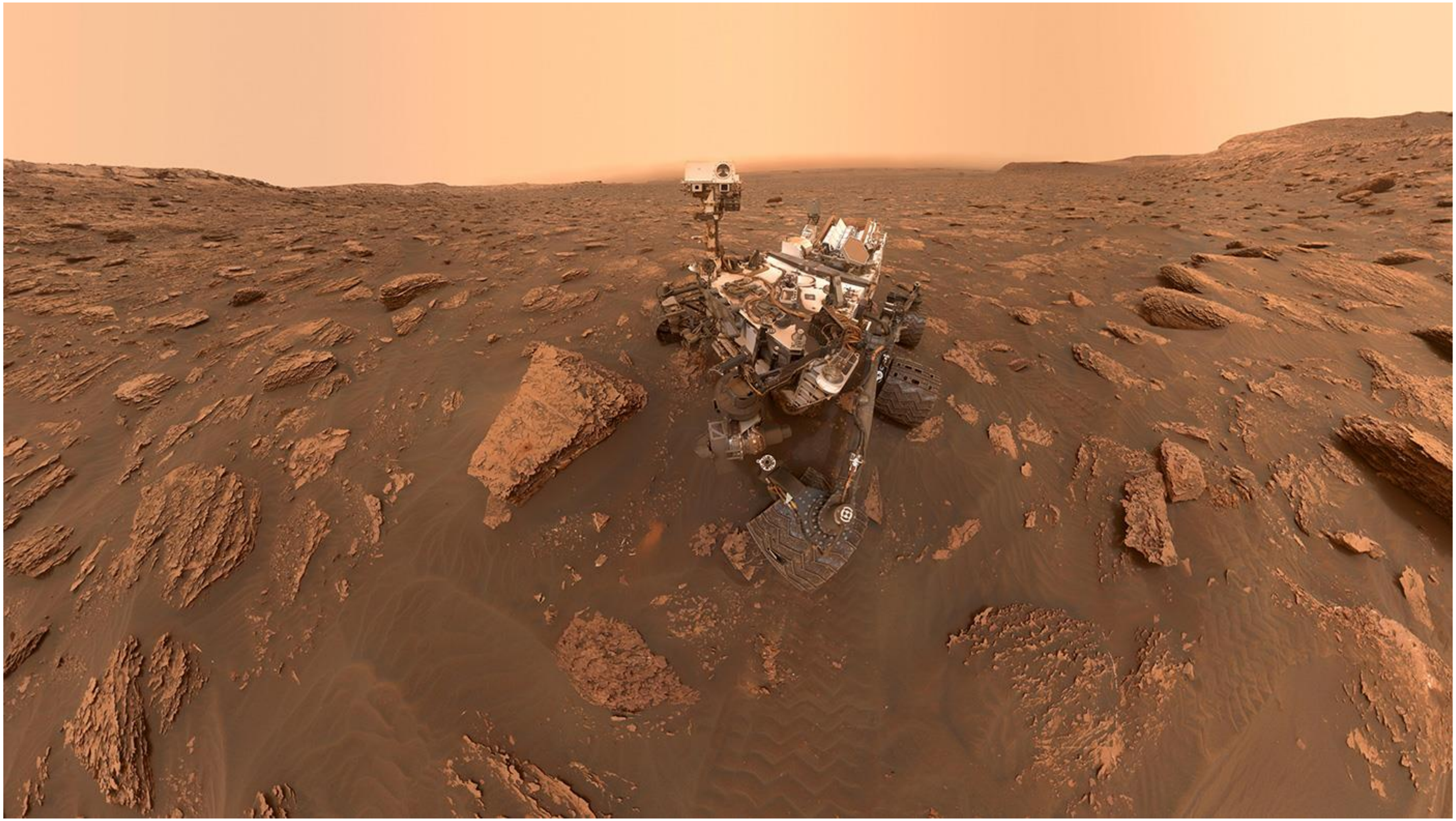
This plaque is on board of Pioneer 10 and Pioneer 11 space crafts. Pioneer 10 was launched in 1980's and is now more than 10^{10} km from earth to far to send signals

Space Station



The **SPHERES Tether Slosh** investigation combines fluid dynamics equipment with robotic capabilities aboard the station. In space, the fuels used by spacecraft can slosh around in unpredictable ways making space maneuvers difficult. This investigation uses two SPHERES robots tethered to a fluid-filled container covered in sensors to test strategies for safely steering spacecraft such as dead satellites that might still have fuel in the tank.

Selfie of the Mars Rover in a Dust Storm



Problem 7.31

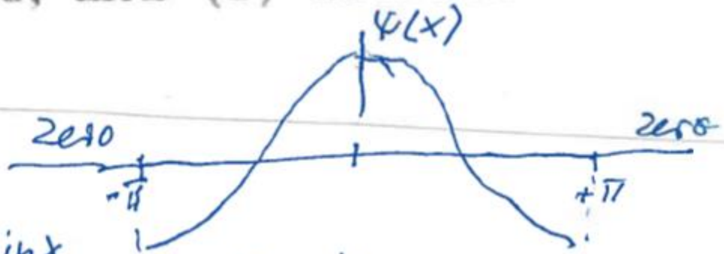
The 21-cm line transition of atomic hydrogen results from a spin-flip transition for the electron in the parallel state of the n=1 state. What temperature in interstellar space gives a hydrogen atom enough energy ($5.9\text{x}10^{-6}$eV) to excite another hydrogen atom in a collision?

1. If we determine the thermal energy that equals the energy required for the spin-flip transition, we have $5.9\times10^{-6}\,\text{eV} = \frac{3}{2}kT = \frac{3}{2}\left(8.617\times10^{-5}\,\text{eV/K}\right)T$. This gives $T = 0.0456\,\text{K}$.

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
. . .		. . .	

10. A wave function Ψ is $A(e^{ix} + e^{-ix})$ in the region $-\pi < x < \pi$ and zero elsewhere. Normalize the wave function and find the probability of the particle being (a) between $x = 0$ and $x = \pi/8$, and (b) between $x = 0$ and $x = \pi/4$.



$\psi = A(e^{ix} + e^{-ix})$ use Euler $e^{ix} = \cos x + i\sin x$

$e^{-x} = \cos x - i\sin x$

$e^{ix} + e^{-ix} = 2\cos x$

$\boxed{\psi = 2A\cos x}$

normalization

$$\int_{-\pi}^{+\pi}\psi^*\psi\,dx = 4A^2\int_{-\pi}^{\pi}\cos^2 x\,dx = 4A^2\int_{-\pi}^{+\pi}\frac{1+\cos(2x)}{2}\,dx = 4A^2\frac{1}{2}\left[x + \frac{\sin 2x}{2}\right]\Bigg|_{-\pi}^{\pi}$$

Integrate by substitution u=2x
du/dx=2 dx=du/2

$$= 4A^2\left[\frac{1}{2}x + \underbrace{\frac{1}{4}\sin(2x)}_{0}\right]\Bigg|_{-\pi}^{\pi} = 4A^2\pi = 1 \quad \boxed{A = \frac{1}{2\sqrt{\pi}}}$$

(a) $P = \int_0^{\pi/8}\psi^*\psi\,dx = \frac{1}{\pi}\int_0^{\pi/8}\cos^2(x)\,dx = \frac{1}{\pi}\left(\frac{x}{2} + \frac{1}{4}\sin(2x)\right)\Big|_0^{\pi/8} = \frac{1}{16} + \frac{1}{4\pi\sqrt{2}} \boxed{= 0.119}$

(b) $P = \int_0^{\pi/4}\psi\psi^*\,dx = \frac{1}{8} + \frac{1}{4\pi} \boxed{= 0.205}$

note: ψ(x) is in the region $-\pi < x < \pi$ and zero elsewhere