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
Lecture a
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:

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

The three dimensional Schrödinger wave equation is

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

Laplace operator
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 $\psi$ 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

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

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 $k_1 L_1 = n_1 \pi$ or $k_1 = n_1 \pi / L_1$. The values for the $k_i$ are

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

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](image)

**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 $x$.

$$\frac{\partial \psi}{\partial x} = \frac{\partial}{\partial x} \left[ A \sin(k_1x)\sin(k_2y)\sin(k_3z) \right]$$

$$= k_1 A \cos(k_1x)\sin(k_2y)\sin(k_3z)$$

$$\frac{\partial^2 \psi}{\partial x^2} = \frac{\partial}{\partial x} \left[ k_1 A \cos(k_1x)\sin(k_2y)\sin(k_3z) \right]$$

$$= -(k_1)^2 A \sin(k_1x)\sin(k_2y)\sin(k_3z)$$

$$= -(k_1)^2 \psi$$

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

$$E = \frac{\pi^2 \hbar^2}{2m} \left( \frac{n_1^2}{L_1^2} + \frac{n_2^2}{L_2^2} + \frac{n_3^2}{L_3^2} \right) \tag{6.49}$$
Problem 6.26

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

\[
E = \frac{\pi^2 \hbar^2}{2mL^2} \left(n_1^2 + n_2^2 + n_3^2\right) = E_0 \left(n_1^2 + n_2^2 + n_3^2\right) \quad \text{where} \quad E_0 = \frac{\pi^2 \hbar^2}{2mL^2}.
\]

Then the second, third, fourth, and fifth levels are

1. : 

\[
E_2 = \left(2^2 + 1^2 + 1^2\right)E_0 = 6E_0 \quad \text{(degenerate)}
\]

\[
E_3 = \left(2^2 + 2^2 + 1^2\right)E_0 = 9E_0 \quad \text{(degenerate)}
\]

\[
E_4 = \left(3^2 + 1^2 + 1^2\right)E_0 = 11E_0 \quad \text{(degenerate)}
\]

\[
E_5 = \left(2^2 + 2^2 + 2^2\right)E_0 = 12E_0 \quad \text{(not degenerate)}
\]
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.

- Consider the Taylor expansion of a potential function:

\[ V(x) = V_0 + V_1(x - x_0) + \frac{1}{2} V_2(x - x_0)^2 + \ldots \]

Redefining the minimum potential and the zero potential, we have

\[ V(x) = \frac{1}{2} V_2 (x - x_0)^2 \]

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)
The mechanical energy $E$ is constant.

(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.
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 $x$. 
The energy levels are given by

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

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>
<thead>
<tr>
<th>Observable</th>
<th>Symbol</th>
<th>Associated Operator</th>
</tr>
</thead>
<tbody>
<tr>
<td>Position</td>
<td>$x$</td>
<td>$x$</td>
</tr>
<tr>
<td>Momentum</td>
<td>$p$</td>
<td>$\frac{\hbar}{i} \frac{\partial}{\partial x}$</td>
</tr>
<tr>
<td>Potential energy</td>
<td>$U$</td>
<td>$U(x)$</td>
</tr>
<tr>
<td>Kinetic energy</td>
<td>$K$</td>
<td>$-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2}$</td>
</tr>
<tr>
<td>Hamiltonian</td>
<td>$H$</td>
<td>$-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + U(x)$</td>
</tr>
<tr>
<td>Total energy</td>
<td>$E$</td>
<td>$i\hbar \frac{\partial}{\partial t}$</td>
</tr>
</tbody>
</table>
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 \( \mu \)
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.

$$\frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial \psi}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial \psi}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2 \psi}{\partial \phi^2} + \frac{2\mu}{\hbar^2} (E - V)\psi = 0$$
The wave function $\psi$ is a function of $r$, $\theta$, $\phi$.

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: $r$, $\theta$, or $\phi$.

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)

\[
\frac{\partial \psi}{\partial r} = fg \frac{\partial R}{\partial r} \quad \frac{\partial \psi}{\partial \theta} = Rg \frac{\partial f}{\partial \theta} \quad \frac{\partial^2 \psi}{\partial \phi^2} = Rf \frac{\partial^2 g}{\partial \phi^2}
\]

- 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 $r^2 \sin^2 \theta / Rfg$

\[
-\frac{\sin^2 \theta}{R} \frac{\partial}{\partial r} \left( r^2 \frac{\partial R}{\partial r} \right) - \frac{2\mu}{\hbar^2} r^2 \sin^2 \theta (E - V) - \frac{1}{f} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial f}{\partial \theta} \right) = \frac{1}{g} \frac{\partial^2 g}{\partial \phi^2}
\]
Solution of the Schrödinger Equation

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

- 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)
  \[
  \frac{d^2 g}{d\phi^2} = -m_\ell^2 g \quad \text{-------- azimuthal equation} \quad \text{Eq (7.8)}
  \]
- It is convenient to choose a solution to be $e^{im_\ell \phi}$.  

Solution of the Schrödinger Equation

- $e^{im_ℓ \phi}$ satisfies Eq (7.8) for any value of $m_ℓ$.
- The solution be single valued in order to have a valid solution for any $\phi$, which is $g(\phi) = g(\phi + 2\pi)$
  
  $g(\phi = 0) = g(\phi = 2\pi) \quad \rightarrow \quad e^0 = e^{2\pi im_ℓ}$

- $m_ℓ$ 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 $-m_ℓ^2$ and rearrange it.
  
  \[
  \frac{1}{R} \frac{\partial}{\partial r} \left( r^2 \frac{\partial R}{\partial r} \right) + \frac{2\mu r^2}{\hbar^2} (E - V) = \frac{m_ℓ^2}{\sin^2 \theta} - \frac{1}{f \sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial f}{\partial \theta} \right)
  \]

- Everything depends on $r$ on the left side and $\theta$ on the right side of the equation.
Solution of the Schrödinger Equation

- Set each side of Eq (7.9) equal to constant $\ell(\ell + 1)$.

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

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

- 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.

This was divide
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 $\ell = 0$ 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)

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

- Try a solution \( R = A e^{-r/a_0} \)
  - \( A \) 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
The appropriate boundary conditions to Eq (7.10) and (7.11) leads to the following restrictions on the quantum numbers $\ell$ and $m_\ell$:

- $\ell = 0, 1, 2, 3, \ldots$
- $m_\ell = -\ell, -\ell + 1, \ldots, -2, -1, 0, 1, 2, \ldots, \ell - 1, \ell$
- $|m_\ell| \leq \ell$ and $\ell < 0$.

The predicted energy level is

$$E_n = -\frac{E_0}{n^2}$$
The wave function given is  

\[ \psi_{100}(r, \phi, \theta) = A e^{-r/a_0} \]

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

1. The wave function given is  \( \psi_{100}(r, \theta, \phi) = A e^{-r/a_0} \) so  \( \psi^* \psi \) is given by  \( \psi_{100}^* \psi_{100} = A^2 e^{-2r/a_0} \).

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  \( \phi \) integral yields 2\( \pi \), and the  \( \theta \) integral yields 2. This leaves

\[
\iiint \psi^* \psi \, dV = 4\pi A^2 \int_0^\infty r^2 e^{-2r/a_0} \, dr = 4\pi A^2 \frac{2}{(2/a_0)^3} = \pi a_0^3 A^2
\]

This integral must equal 1 due to normalization which leads to  \( \pi a_0^3 A^2 = 1 \) so  \( A = \frac{1}{\sqrt{\pi a_0^3}} \).
Hydrogen Atom Radial Wave Functions

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

<table>
<thead>
<tr>
<th>$n$</th>
<th>$\ell$</th>
<th>$R_{n\ell}(r)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>$\frac{2}{(a_0)^{3/2}} e^{-r/a_0}$</td>
</tr>
<tr>
<td>2</td>
<td>0</td>
<td>$\left(2 - \frac{r}{a_0}\right) \frac{e^{-r/2a_0}}{(2a_0)^{3/2}}$</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>$\frac{r}{a_0} \frac{e^{-r/2a_0}}{\sqrt{3}(2a_0)^{3/2}}$</td>
</tr>
<tr>
<td>3</td>
<td>0</td>
<td>$\frac{1}{(a_0)^{3/2}} \frac{2}{81\sqrt{3}} \left(27 - 18 \frac{r}{a_0} + 2 \frac{r^2}{a_0^2}\right) e^{-r/3a_0}$</td>
</tr>
<tr>
<td>3</td>
<td>1</td>
<td>$\frac{1}{(a_0)^{3/2}} \frac{4}{81\sqrt{6}} \left(6 - \frac{r}{a_0}\right) \frac{r}{a_0} e^{-r/3a_0}$</td>
</tr>
<tr>
<td>3</td>
<td>2</td>
<td>$\frac{1}{(a_0)^{3/2}} \frac{4}{81\sqrt{30}} \frac{r^2}{a_0^2} e^{-r/3a_0}$</td>
</tr>
</tbody>
</table>

- Subscripts on $R$ specify the values of $n$ and $\ell$
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 $m_\ell$
- Group these solutions together into functions

$$Y(\theta, \phi) = f(\theta)g(\phi) \quad ---- \text{spherical harmonics}$$
# Normalized Spherical Harmonics

<table>
<thead>
<tr>
<th>$\ell$</th>
<th>$m_\ell$</th>
<th>$Y_{\ell m_\ell}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>$\frac{1}{2\sqrt{\pi}}$</td>
</tr>
<tr>
<td>1</td>
<td>0</td>
<td>$\frac{1}{2\sqrt{\pi}} \cos \theta$</td>
</tr>
<tr>
<td>1</td>
<td>$\pm 1$</td>
<td>$\pm \frac{1}{2} \sqrt{\frac{3}{2\pi}} \sin \theta \ e^{\pm i\phi}$</td>
</tr>
<tr>
<td>2</td>
<td>0</td>
<td>$\frac{1}{4\sqrt{\pi}} (3 \cos^2 \theta - 1)$</td>
</tr>
<tr>
<td>2</td>
<td>$\pm 1$</td>
<td>$\pm \frac{1}{2} \sqrt{\frac{15}{2\pi}} \sin \theta \cos \theta \ e^{\pm i\phi}$</td>
</tr>
<tr>
<td>2</td>
<td>$\pm 2$</td>
<td>$\frac{1}{4\sqrt{\pi}} \sin^2 \theta \ e^{\pm 2i\phi}$</td>
</tr>
<tr>
<td>3</td>
<td>0</td>
<td>$\frac{1}{4\sqrt{\pi}} (5 \cos^3 \theta - 3 \cos \theta)$</td>
</tr>
<tr>
<td>3</td>
<td>$\pm 1$</td>
<td>$\pm \frac{1}{8\sqrt{\pi}} \sin \theta (5 \cos^2 \theta - 1) \ e^{\pm i\phi}$</td>
</tr>
<tr>
<td>3</td>
<td>$\pm 2$</td>
<td>$\frac{1}{4\sqrt{\pi}} \sin^2 \theta \cos \theta \ e^{\pm 2i\phi}$</td>
</tr>
<tr>
<td>3</td>
<td>$\pm 3$</td>
<td>$\pm \frac{1}{8\sqrt{\pi}} \sin^3 \theta \ e^{\pm 3i\phi}$</td>
</tr>
</tbody>
</table>
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 $n$, $\ell$, and $m_\ell$. 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
- $\ell$  Orbital angular momentum quantum number
- $m_\ell$  Magnetic quantum number

The boundary conditions:

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

The restrictions for quantum numbers:

- $n > 0$
- $\ell < n$
- $|m_\ell| \leq \ell$
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) \( n = 5, 6 \)
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) $n = 1, l = 2, m_l = 1$
Problem 7.11

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

1. It is required that \(\ell < 5\) and \(|m_\ell| \leq \ell\).

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

\(\ell = 2\): \(m_\ell = 0, \pm 1, \pm 2\) \(\ell = 1\): \(m_\ell = 0, \pm 1\) \(\ell = 0\): \(m_\ell = 0\)
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.
Lecture b
Orbital Angular Momentum Quantum Number $\ell$

- 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 $L = mv_{\text{orbital}} r$.

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

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

It disagrees with Bohr’s semi-classical “planetary” model of electrons orbiting a nucleus $L = n\hbar$. 
A certain energy level is **degenerate** with respect to \( \ell \) when the energy is independent of \( \ell \).

- Use letter names for the various \( \ell \) values
  - \( \ell = 0\ 1\ 2\ 3\ 4\ 5 \ldots \)
  - Letter = \( s\ p\ d\ f\ g\ h \ldots \)

Atomic states are referred to by their \( n \) and \( \ell \)

- A state with \( n = 2 \) and \( \ell = 1 \) is called a \( 2p \) state
- The boundary conditions require \( n > \ell \)

---

Degeneracy: Number of \( m \) states namely \( 2\ell+1 \)
Uncertainty principle for angular momentum

Figure 8.6 The angular momentum \( \mathbf{L} \) of an orbiting particle is perpendicular to the plane of the orbit. If the direction of \( \mathbf{L} \) 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 $m_\ell$

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

$$L_z = m_\ell \hbar$$

- The relationship of $L$, $L_z$, $\ell$, and $m_\ell$ for $\ell = 2$.
- $L = \sqrt{\ell(\ell + 1)}\hbar = \sqrt{6}\hbar$ 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 $m_\ell$

- 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

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

Use a math table for the summation result.
Fuzzyness of angular momentum

Mechanical analogy: wheel in gravitational field

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 $\mathbf{L}$ lies on the surface of a cone. The fuzzy character of $L_x$ and $L_y$ is depicted by allowing $\mathbf{L}$ 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.
Lecture b
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**.

**External magnetic field reduces spherical symmetry**

**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 $T = \frac{2\pi r}{v}$.
- Think of an electron as an orbiting circular current loop of $I = \frac{dq}{dt}$ around the nucleus.

$$\vec{\mu} = -\frac{e}{2m} \vec{L}$$ where $L = mvr$ is the magnitude of the orbital angular momentum
The Zeeman effect (magnetic effect on atomic spectra)

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

\[ \mu = IA = \frac{I A}{c} \]

\[ I = \frac{d\varphi}{dt}, \quad L = mv_r \mu L \]

\[ \mu = IA = \frac{e}{c} A = \frac{-e}{2\hbar} \frac{\hbar r^2}{L} = -eLv = -\frac{eL}{2m} \]

\[ \vec{\mu} = -\frac{eL}{2m} \]

note: without magnetic field there is no handle to align the atom and \( \vec{L} \) and \( \vec{\mu} \) are opposite, but in random orientations

\[ \vec{S} = \vec{P} \times B \]

\[ \vec{V}_B = -\vec{P} \times \vec{B} \]

\[ L = \left( \frac{eL}{2m} \right) m_e = -\mu_B m_e \]

unit of magnetic moment = Bohr magneton

\[ \text{ Hydrogen beam } \]

\[ \begin{array}{c}
\text{Magnet} \\
\text{Screen} \\
\text{+1} \\
\text{0} \\
\text{-1}
\end{array} \]
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.

$$\vec{\mu} = -\mu_B \vec{L} / \hbar$$
Example 7.5

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 $\omega_L$ 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 $\omega_L$ is given by

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

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

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

![Diagram of an atom with magnetic moment $\vec{\mu}$ and external magnetic field $\vec{B}$ showing precession and the Larmor frequency $\omega_L$.]

**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 $\phi$) about the magnetic field $\vec{B}$.
The Normal Zeeman Effect

- The potential energy is quantized due to the magnetic quantum number $m_\ell$.

\[ V_B = -\mu_z B = +\mu_B m_\ell B \]

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

<table>
<thead>
<tr>
<th>$m_\ell$</th>
<th>Energy</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$E_0 + \mu_B B$</td>
</tr>
<tr>
<td>0</td>
<td>$E_0$</td>
</tr>
<tr>
<td>-1</td>
<td>$E_0 - \mu_B B$</td>
</tr>
</tbody>
</table>

\[
\begin{align*}
\ell = 1 & \\
\Delta E = \mu_B B & \\
\Delta E & \\
\vec{B} = B_0 \hat{k} & \\
\vec{B} = 0 & \\
m_\ell & \\
1 & \\
0 & \\
-1 &
\end{align*}
\]
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 \( m_\ell \) 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 \( \mu_B \) [see text after Equation (7.28)]. The energy difference is determined from Equation (7.31).

Solution The Bohr magneton is determined to be

\[
\mu_B = \frac{e\hbar}{2m} = \frac{(1.602 \times 10^{-19} \text{ C})(1.055 \times 10^{-34} \text{ J} \cdot \text{s})}{2(9.11 \times 10^{-31} \text{ kg})} = 9.27 \times 10^{-24} \text{ J/T}
\]

\( \Delta E = \mu_B B \Delta m_e = (9.27 \times 10^{-24} \text{ J/T}) \times 2T = 1.85 \times 10^{-4} \text{ eV} \)
Spectrum of atomic hydrogen

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 $2p$ to $1s$

\[ \ell = 0 \]
\[ \ell = 1 \]

\[ \vec{B} = 0 \]
\[ \vec{B} = B_0 \hat{k} \]
History of Hydrogen Spectroscopy
Space quantization in 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.

Stearn Gerlach used silver atoms
The Normal Zeeman Effect

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

- 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 \( m_\ell \), \( m_\ell \) states is always odd (\( 2\ell + 1 \)) and should have produced an odd number of lines.

\[
V_B = -\mu_z B
\]

\[
F_z = -(dV_B / dz) = \mu_z (dB / dz)
\]

- The \( m_\ell = +1 \) state will be deflected down, the \( m_\ell = -1 \) state up, and the \( m_\ell = 0 \) state will be undeflected.

Strum Gerlach saw only 2 states!
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 \( \Delta x \) 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

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

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 \( \frac{1}{2} m (v_x^2) = \frac{3}{2} kT \).

**Solution** We calculate \( \langle v_x^2 \rangle \) to be

\[ v_x^2 = \frac{3kT}{m} = \frac{3(1.38 \times 10^{-23} \text{ J/K})(663 \text{ K})}{1.67 \times 10^{-27} \text{ kg}} = 1.64 \times 10^7 \text{ m}^2/\text{s}^2 \]

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

\[ d = \frac{1}{2(1.67 \times 10^{-27} \text{ kg})} (9.27 \times 10^{-24} \text{ J/T})(1240 \text{ T/m}) \times \frac{(0.03 \text{ m})^2}{(1.64 \times 10^7 \text{ m}^2/\text{s}^2)} = 0.19 \times 10^{-3} \text{ m} \]

---

*Saw only 2 states = Controversy!
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 $s = \frac{1}{2}$. 
Intrinsic Spin

- The spinning electron reacts similarly to the orbiting electron in a magnetic field.
- We should try to find $L$, $L_z$, $\ell$, and $m_\ell$.
- The magnetic spin quantum number $m_s$ has only two values, $m_s = \pm \frac{1}{2}$.

The electron’s spin will be either “up” or “down” and can never be spinning with its magnetic moment $\mu_s$ exactly along the z axis.

The intrinsic spin angular momentum vector

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

(a) (b)
How fast does the earth rotate?

Approximately 1,675 km/h (1,040 mph) at the equator, slightly less near the poles.
8. Stern and Gerlach performed an experiment that showed the space quantization of silver atoms in an inhomogeneous magnetic field. Their experiment demonstrated that

a. space quantization is a property that only exists for energy levels, governed by quantum number n.

b. the differences in magnetic moment of the atom demonstrated space quantization in external magnetic fields.

c. the classically defined Bohr magneton was inaccurate because it did not take into account the space quantization of external magnetic fields within the atom.

d. an additional angular momentum factor within the atom was causing the observed space quantization.
1. For an atom of hydrogen where the quantum number \( n = 3 \), how many possible independent configurations of the atom exist (consider principal quantum number \( n \), angular momentum quantum number \( l \), magnetic quantum number \( m_l \), and magnetic spin quantum number \( m_s \))?

- 18
- 8
- 32
- 26
- infinite
Lecture c
Intrinsic Spin

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

- The gyromagnetic ratio ($\ell$ or $s$).
- $g_\ell = 1$ and $g_s = 2$, then
  \[
  \mathbf{\mu}_\ell = -\frac{g_\ell\mu_B\mathbf{\hat{L}}}{\hbar} = -\frac{\mu_B\mathbf{\hat{L}}}{\hbar}
  \quad \text{and} \quad
  \mathbf{\mu}_s = -\frac{g_s\mu_B\mathbf{\hat{S}}}{\hbar} = -2\frac{\mu_B\mathbf{\hat{S}}}{\hbar}
  \]
- The z component of $\mathbf{\hat{S}}$ is $S_z = m_s\hbar = \pm\hbar/2$.
- In $\ell = 0$ state
  - no splitting due to $\mathbf{\mu}_s$.
  - there is space quantization due to the intrinsic spin.
- Apply $m_\ell$ and the potential energy becomes
  \[
  V_B = -\mathbf{\mu}_s \cdot \mathbf{\hat{B}} = +\frac{e}{m} \mathbf{\hat{S}} \cdot \mathbf{\hat{B}}
  \]

The numerical factor relating the magnetic moment to each angular momentum vector is the gyromagnetic ratio.
Hans Georg Dehmelt (9 September 1922 – 7 March 2017) was a German and American physicist, who was awarded a Nobel Prize in Physics in 1989, for co-developing the ion trap technique (Penning trap) with Wolfgang Paul,
Space quantization of the electron spin angular momentum

Doublet splitting due to the electron spin magnetic moment

In the frame of the electron there is an internal magnetic field created by the orbiting proton. The doublet splitting due to the electron spin magnetic moment is demonstrated in the figure.
The gyromagnetic ratio

- a. is 1 for the magnetic moment associated with the spin and 2 for the magnetic moment associated with the angular momentum.
- b. relates the Bohr magneton to the elementary charge.
- c. does not help explain the result of the Stern and Gerlach experiment.
- d. relates the magnetic moments of spin and angular momentum to the total angular momentum.
- e. gives the values of intrinsic spin quantum number of the electron as 1/2 and -1/2
Problem 7.29

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

1. For the 4f state n = 4 and ℓ = 3. The possible m_ℓ values are 0, ±1, ±2, and ±3 with m_s = ±1/2 for each possible m_ℓ value. The degeneracy of the 4f state is then (with 2 spin states per m_ℓ) equal to 2(7) = 14.
Problem 7.32

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

1. For the 5d state \(n = 5\) and \(\ell = 2\). The possible \(m_\ell\) values are 0, ±1, and ±2, with \(m_s = \pm 1/2\) for each possible \(m_\ell\) value. The degeneracy of the 5d state is then (with 2 spin states per \(m_\ell\)) 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.
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,
  \[ P(r) \, dr = r^2 R^2(R(r)) \int_0^\pi |f(\theta)|^2 \sin \theta \, d\theta \int_0^{2\pi} |g(\phi)|^2 \, d\phi \]
- 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
\[ (e^{im_l\theta})^* e^{im_l\theta} = e^{-im_l\theta + im_l\theta} = e^0 = 1 \]
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,

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

(7.38)

We are integrating over $\theta$ and $\phi$, 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

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

(7.39)

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

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

(7.40)
Normalizing a hydrogenic wave function

**EXAMPLE 7.2**

Show that the hydrogen wave function $\psi_{211}$ 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

$$\int \psi_{nlm}^* \psi_{nlm} \, d\tau = 1 = \int \psi_{211}^* \psi_{211} r^2 \sin \theta \, dr \, d\theta \, d\phi \quad (7.18)$$

where $d\tau = r^2 \sin \theta \, dr \, d\theta \, d\phi$ is the volume element. We look up the wave function $\psi_{211}$ 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 $\psi_{211}$ into Equation (7.18), insert the integration limits for $r$, $\theta$, and $\phi$, and do the integration. First we find $\psi_{211}^* \psi_{211}$:

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

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

$$\int \psi_{211}^* \psi_{211} r^2 \sin \theta \, dr \, d\theta \, d\phi$$

$$= \frac{1}{64\pi a_0^5} \int_0^\infty r^4 e^{-r/a_0} \, dr \int_0^\pi \sin^3 \theta \, d\theta \int_0^{2\pi} d\phi$$

$$= \frac{1}{64\pi a_0^5} \left[ \frac{24a_0^5}{3} \right] \left[ \frac{4}{3} \right] \left[ 2\pi \right]$$

$$= 1$$

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

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

Table 7.1 Hydrogen Atom Radial Wave Functions

<table>
<thead>
<tr>
<th>$n$</th>
<th>$\ell$</th>
<th>$R_n\ell(r)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>$\frac{2}{(a_0)^{5/2}} e^{-r/a_0}$</td>
</tr>
<tr>
<td>2</td>
<td>0</td>
<td>$\left(\frac{2}{a_0} - \frac{r}{a_0}\right) e^{-r/(2a_0)}$</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>$\frac{r}{a_0} e^{-r/(2a_0)} \sqrt{3(2a_0)^{5/2}}$</td>
</tr>
<tr>
<td>3</td>
<td>0</td>
<td>$\frac{1}{(a_0)^{5/2}} \frac{2}{81 \sqrt{3}} \left(27 - 18 \frac{r}{a_0} + 2 \frac{r^2}{a_0^2}\right) e^{-r/3a_0}$</td>
</tr>
<tr>
<td>3</td>
<td>1</td>
<td>$\frac{1}{(a_0)^{5/2}} \frac{4}{81 \sqrt{6}} \left(6 - \frac{r}{a_0}\right) e^{-r/3a_0}$</td>
</tr>
<tr>
<td>3</td>
<td>2</td>
<td>$\frac{1}{(a_0)^{5/2}} \frac{4}{81 \sqrt{30}} \frac{r^2}{a_0^2} e^{-r/3a_0}$</td>
</tr>
</tbody>
</table>

Horizontal axis in units of the Bohr radius.
Lecture d
3-D Probability Distribution Functions

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

![Diagrams showing probability density for different electron states.](image)
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 1s and 2p 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 \( R_{nl}(r) \) from Table 7.1.

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

1s state:

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

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

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

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

\[
\frac{2r^2}{a_0} = 2r
\]

\[
r = a_0 \quad \text{Most probable radius for 1s state electron}
\]

2p state:

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

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

\[
\frac{r^4}{a_0} = 4r^3
\]

\[
r = 4a_0 \quad \text{Most probable radius for 2p state electron}
\]

Notice that the most probable radii for the 1s and 2p states agree with the Bohr radii. This occurs only for the largest possible \( \ell \) value for each \( n \) (see Problem 36).
Calculate the average orbital radius of a 1s 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 $\theta$ and $\phi$. We use Equation (7.39) for the probability density and find the radial wave function $R_{1s}(r)$ in Table 7.1.

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

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

$$\langle r \rangle = \frac{4}{a_0^3} \frac{3a_0^4}{8} = \frac{3}{2} a_0$$

For the 1s state electron.

Therefore, the average electron radius in the 1s 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 1s 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 \( B \) 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 space quantization. The \( z \)-components are indicated as \(+ (\hbar \omega +1)\)
\( \ell \) (\( \ell \omega \)) and \(- \ell \omega -1\).
\[ M_z = -\frac{\ell \hbar}{2m} \quad m_e = \frac{\hbar}{2m} \quad \text{m.e.} \]

Fine structure:

\[
\mu_s = -\frac{\ell}{2m} = \mu_0 \quad m_s = \pm \frac{1}{2}
\]

Two viewpoints: 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.

(a) An electron circulates about the nucleus with orbital angular momentum \( \ell \). The spin of the electron is parallel to \( \ell \). (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*

\[ B = -M_0 B \]

\[ F_z = -\frac{dN}{dz} = M_0 \frac{dB}{dz} \]

There is a different force on each of the 3 $m_z$-state down; $m_z = +1$ up: $m_z = -1$ undeflected $m_z = 0$

Hydrogen is most abundant gas in the Milky Way galaxy (9% by mass).

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

\[ \lambda \cdot v = C \]

\[ 21 \text{ cm} \times 14 \times 10^{20} \text{ Hz} = 3 \times 10^{20} \text{ cm} \]

Hyperfine structure: Interaction between electron and nuclear magnetic moments

Search for extra terrestrial 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 1983 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 \(5.9 \times 10^{-6} \text{eV}\) 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 \(5.9 \times 10^{-6} \text{eV} = \frac{3}{2} kT = \frac{3}{2} \left(8.617 \times 10^{-5} \text{eV/K}\right)T\). This gives \(T = 0.0456 \text{K}\).
Table 8.5  Spectroscopic Notation for Atomic Shells and Subhells

<table>
<thead>
<tr>
<th>$n$</th>
<th>Shell Symbol</th>
<th>$\ell$</th>
<th>Shell Symbol</th>
</tr>
</thead>
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<tr>
<td>1</td>
<td>$K$</td>
<td>0</td>
<td>$s$</td>
</tr>
<tr>
<td>2</td>
<td>$L$</td>
<td>1</td>
<td>$p$</td>
</tr>
<tr>
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<td>$M$</td>
<td>2</td>
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<td>3</td>
<td>$f$</td>
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<tr>
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<td>$O$</td>
<td>4</td>
<td>$g$</td>
</tr>
<tr>
<td>6</td>
<td>$P$</td>
<td>5</td>
<td>$h$</td>
</tr>
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<td>...</td>
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</tr>
</tbody>
</table>
10. A wave function $\Psi$ 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 $x = \pi/4$.

Integrate by substitution $u=2x$
$du/dx=2$ \hspace{10pt} dx=du/2

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

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

Normalization

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

Integrate by substitution $u=2x$
$du/dx=2$ \hspace{10pt} dx=du/2

(c) $P = \int_{-\pi/8}^{\pi/8} \Psi^* \Psi \, dx = \frac{1}{16} \left[ \frac{\pi}{2} + \frac{1}{4} \sin(2x) \right]_{-\pi/8}^{\pi/8} = \frac{1}{16} + \frac{1}{4\pi^2} = 0.511$

(b) $P = \int_{0}^{\pi} \Psi^* \Psi \, dx = \frac{1}{8} + \frac{1}{4\pi} \left[ 0, 0.205 \right]$