Chapter 6

Electromagnetic Radiation and the Electronic Structure of the Atom

In This Chapter...

Physical and chemical properties of compounds are influenced by the structure of the molecules that they consist of. Chemical structure depends, in turn, on how electrons are arranged around atoms and how electrons are shared among atoms in molecules. Understanding physical and chemical properties of chemical compounds therefore relies on a detailed understanding of the arrangement of electrons in atoms and molecules. This chapter begins that exploration by examining what we know about atomic electronic structure and how we know it. This is the first of a series of chapters that, in turn, explore the arrangement of electrons in atoms with many electrons (Chapter 7), the manner in which chemical bonds form and control molecular structure (Chapter 8), and two theories of bonding (Chapter 9). In this chapter, we examine the ways we learn about the electronic structure of elements. This, for the most part, involves studying how electromagnetic radiation interacts with atoms. We therefore begin with the nature of electromagnetic radiation.

Chapter Outline

6.1 Electromagnetic Radiation
6.2 Photons and Photon Energy
6.3 Atomic Line Spectra and the Bohr Model of Atomic Structure
6.4 Quantum Theory of Atomic Structure
6.5 Quantum Numbers, Orbitals, and Nodes

Chapter Summary
Chapter Summary Assignment

6.1 Electromagnetic Radiation

Section Outline

6.1a Wavelength and Frequency
6.1b The Electromagnetic Spectrum

Section Summary Assignment

Electromagnetic radiation, energy that travels through space as waves, is made up of magnetic and electric fields oscillating at right angles to one another. Visible light, ultraviolet radiation, and radio waves are all examples of electromagnetic radiation. Although these forms of electromagnetic radiation have different energies, they all have wavelike properties and travel at the same speed in a vacuum.
Opening Exploration 6.1 Electromagnetic Radiation

6.1a Wavelength and Frequency

Waves are characterized by their wavelength, frequency, and speed. The wavelength of a wave (symbolized by the lowercase Greek letter lambda, \( \lambda \)) is the distance between two consecutive peaks or troughs in a wave (Interactive Figure 6.1.1). The frequency of a wave (symbolized by the lowercase Greek letter nu, \( \nu \)) is the number of complete waves that pass a point in space in a given amount of time. Wavelength has units of length (meters) and frequency has units of cycles per second (1/s, s\(^{-1}\)) or hertz (Hz). Waves also have amplitude, the maximum positive displacement from the medium to the top of the crest of a wave.

Interactive Figure 6.1.1 Understand the properties of waves.

![Interactive Figure 6.1.1 Understand the properties of waves.](image)

Wavelength, frequency, and amplitude

The wavelength and frequency of a wave are related by the speed of light, the speed at which all electromagnetic radiation travels in a vacuum. The speed of light in a vacuum, \(2.998 \times 10^8\) m/s, is...
equal to the wavelength (in meters, m) times the frequency (in Hz, 1/s) of the radiation (Equation 6.1)

\[ c = \lambda \nu \]

(Equation 6.1)

Equation 6.1 and the fixed speed of light in a vacuum allow the calculation of the wavelength or frequency of electromagnetic radiation if the other value is known. Notice that wavelength and frequency are inversely related. When light has a very short wavelength, many waves pass a point in space per second and the light has a high frequency. When light has a long wavelength, fewer waves pass a point in space per second and the light has a low frequency.

**EXAMPLE PROBLEM: Calculate wavelength and frequency of waves.**

(a) A local radio station broadcasts at a frequency of 91.7 MHz (91.7 \( \times \) \( 10^6 \) Hz). What is the wavelength of these radio waves?

(b) What is the frequency of blue light with a wavelength of 435 nm?

**SOLUTION:**

You are asked to calculate the wavelength or frequency of electromagnetic radiation.

You are given the frequency or wavelength of the radiation.

(a) First rearrange Equation 6.1 to solve for wavelength (\( \lambda \)). Then substitute the known values into the equation and solve for wavelength.

\[ \lambda = \frac{c}{\nu} = \frac{2.998 \times 10^8 \text{ m/s}}{91.7 \times 10^6 \text{ 1/s}} = 3.27 \text{ m} \]

(b) First rearrange Equation 6.1 to solve for frequency (\( \nu \)). Then substitute the known values into the equation and solve for frequency. Notice that wavelength must be converted to units of meters before using it in Equation 6.1.

\[ \nu = \frac{c}{\lambda} = \frac{2.998 \times 10^8 \text{ m/s}}{4.35 \times 10^{87} \text{ m}} = 6.89 \times 10^{13} \text{ Hz} \]

6.1.1T: Tutorial Assignment
6.1.1: Mastery Assignment

**6.1b The Electromagnetic Spectrum**

The electromagnetic spectrum shows the different types of electromagnetic radiation arranged by wavelength, from gamma rays with very short wavelengths (in the picometer range) to radio waves with very long wavelengths (from about 1 meter to many kilometers in length). Each type of electromagnetic radiation has a range of wavelengths and frequencies, as shown in Interactive Figure 6.1.2.
Interactive Figure 6.1.2 Identify regions of the electromagnetic spectrum.

The electromagnetic spectrum

Visible light, the electromagnetic radiation that can be observed by the human eye, ranges in wavelength from about 400 to 700 nm. Each color in the visible spectrum (Interactive Figure 6.1.2) has a different wavelength and frequency. Light with a wavelength of 450 nm is blue, for example, and light with a wavelength of 675 nm is red.

The visible spectrum is a very small portion of the entire electromagnetic spectrum. The different types of radiation that make up the entire spectrum are all important to humans. For example, x-rays are used for imaging living tissues, microwave radiation is used in microwave ovens to cause water molecules to rotate and generate heat, and radio waves are used in radio and cell phone communication as well as in television and digital satellite signals.

6.2 Photons and Photon Energy

Section Outline
6.2a The Photoelectric Effect
Section Summary Assignment

The wavelike properties of electromagnetic radiation are demonstrated by experiments that show wave interference and diffraction. At the beginning of the 20th century, other experiments puzzled the scientific community because they suggested that light acts more like it is composed of particles of energy. That light acts alternately as a wave and as a particle is known as the matter–wave duality of electromagnetic radiation.
Opening Exploration 6.2: The Photoelectric Effect

The photoelectric effect

6.2a The Photoelectric Effect

One experiment that could not easily be explained by the wavelike properties of electromagnetic radiation is the **photoelectric effect**. The photoelectric effect is exhibited when light is shone on a metal and electrons are ejected from the surface of the metal. In a typical experiment, a piece of metal is placed in a vacuum tube. If light with a long wavelength (low frequency) is directed at the metal surface, nothing happens—even if the light has high intensity. However, if the light has a short wavelength (high frequency) and low or moderate intensity, electrons are ejected from the metal surface. The ejection of electrons from the metal depends not on the total energy of the light, but only on the wavelength of the light. This experiment suggests that light has particle-like properties.

The explanation for photoelectric effect is that light travels in packets, called **photons**, and that the energy of a single packet is related to the wavelength of the light. If a photon has low energy, it will be unable to knock an electron out of the metal. Hitting the metal with large numbers of these low-energy photons (very bright light with long wavelength) has no effect because no single photon can do the job (Interactive Figure 6.2.1).

Interactive Figure 6.2.1 Identify the properties of photons.
Missing figure 6.5

On the other hand, a photon of high energy (short wavelength) can lead to the ejection of electrons. Thus, even low-intensity light with high energy (short wavelength) will lead to a measurable current. This implies that a photon carries an explicit amount of energy, called a quantum of energy, and that energy itself is quantized.

The relationship between frequency and the energy of a photon is given by Planck’s equation,

\[ E_{\text{photon}} = h \nu \quad (6.2) \]

where \( h \) is Planck’s constant, \( 6.626 \times 10^{-34} \) J·s. Planck’s constant is named for Max Planck (1858–1947), the scientist who first proposed the idea that energy is quantized.
Notice that the energy of a photon is directly related to the frequency of the radiation. Also notice that Planck’s constant is very small, which means that a single photon of light carries a small amount of energy.

**EXAMPLE PROBLEM: Use Planck’s equation to calculate photon energy.**

(a) Calculate the energy of a single photon of light with a frequency of $8.66 \times 10^{14}$ Hz.

(b) Calculate the energy of a single photon of yellow light with a wavelength of 582 nm.

**SOLUTION:**

**You are asked** to calculate the energy of a photon of light. 

**You are given** the frequency or wavelength of the radiation.

(a) Use Planck’s equation to calculate the energy of this light.

$$E = h \nu = (6.626 \times 10^{-34} \text{ J} \cdot \text{s})(8.66 \times 10^{14} \text{ s}^{-1}) = 5.74 \times 10^{-19} \text{ J}$$

(b) First, convert wavelength to frequency and then use Planck’s equation to calculate the energy of this light.

$$\nu = \frac{c}{\lambda} = \frac{2.998 \times 10^{8} \text{ m/s}}{582 \text{ nm} \left( \frac{10^{-9} \text{ m}}{1 \text{ nm}} \right)} = 5.15 \times 10^{14} \text{ s}^{-1}$$

$$E = h \nu = (6.626 \times 10^{-34} \text{ J} \cdot \text{s})(5.15 \times 10^{14} \text{ s}^{-1}) = 3.41 \times 10^{-19} \text{ J}$$

### 6.3 Atomic Line Spectra and the Bohr Model of Atomic Structure

**Section Outline**

6.3a Atomic Line Spectra

6.3b The Bohr Model

**Section Summary Assignment**

When sunlight passes through a prism hanging in a window, the white light is separated into a band that shows the colors of the rainbow, called a continuous spectrum. When the light emitted by “excited” gas phase elements is passed through a prism, a different kind of spectrum is seen—one that led scientists to a better understanding of electronic structure.

**Opening Exploration 6.3 Line Spectra**

[Figure ID #6-6]

#### 6.3a Atomic Line Spectra

If a sample of a gas is placed in a sealed glass tube and “excited” with an electric current, the atoms absorb energy and begin to glow, emitting light. A common example of this is the light emitted by sealed tubes containing neon (neon lights), but the same principle is at work in fluorescent lightbulbs. When the radiation emitted by these samples is analyzed by passing it through a prism, a line spectrum (Interactive Figure 6.3.1) is observed that shows only very specific wavelengths of light.
Interactive Figure 6.3.1 Explore the hydrogen line spectrum.

Notice that the line spectra for different elements in Interactive Figure 6.3.1 show a finite number of lines (the spectra are not continuous) and that the number of lines and the wavelengths of the lines are different for each element. The fact that only certain wavelengths of light are emitted when atoms of a given element are excited suggests that the energy of an atom is quantized.

6.3b The Bohr Model

Niels Bohr (1885–1962) was the first scientist to explain atomic line spectra. He proposed that electrons in atoms could occupy only certain energy levels. That is, the energy of electrons in atoms is quantized. According to his model of atomic electronic structure, electrons move around the nucleus of an atom in defined energy levels, called orbits. He assigned a number to each energy level, known as the principle quantum number \( n \). Electrons in low-energy levels can absorb energy and be promoted to higher-energy levels. When an electron moves from a high-energy level to a lower-energy level, energy is emitted in the form of light. Hydrogen, for example, is in its ground state when its electron is in the lowest energy level, \( n = 1 \). When a hydrogen atom absorbs energy, the electron moves to an excited state where \( n > 1 \).

Using his model, Bohr was able to explain the energies and wavelengths of the lines observed in the visible portion of the hydrogen spectrum.

<table>
<thead>
<tr>
<th>Color</th>
<th>( \lambda ) (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Red</td>
<td>656</td>
</tr>
<tr>
<td>Blue–green</td>
<td>486</td>
</tr>
<tr>
<td>Blue</td>
<td>434</td>
</tr>
<tr>
<td>Violet</td>
<td>410</td>
</tr>
</tbody>
</table>

Using Bohr’s equation relating the energy \( (E_n) \) and energy level \( (n) \) for an electron, it is possible to calculate the energy of a single electron in a ground state or excited state, or the energy change when an electron moves between two energy levels.

\[
E_n = \frac{\hbar^2}{2m} \times 10^{6\text{J}} \left( \frac{1}{n^2} \right) \tag{6.3}
\]

For example, the calculation of the energy of an electron in the \( n = 2 \) and the \( n = 3 \) energy levels follows:

\[
n = 2 \quad E_2 = \frac{\hbar^2}{2m} \times 10^{6\text{J}} \left( \frac{1}{2^2} \right) = 6.448 \times 10^{6\text{J}} \]

\[
n = 3 \quad E_3 = \frac{\hbar^2}{2m} \times 10^{6\text{J}} \left( \frac{1}{3^2} \right) = 4.489 \times 10^{6\text{J}} \]
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\[ n = 3 \quad E_3 = \frac{\hbar}{2} \cdot 1.79 \times 10^{38} \text{J} \left(\frac{1}{2}\right) = 2.421 \times 10^{39} \text{J} \]

The energy emitted when an electron moves from the \( n = 3 \) to the \( n = 2 \) energy level is therefore

\[ \Delta E = \frac{\hbar}{2} \cdot 1.79 \times 10^{38} \text{J} \left(\frac{1}{2}\right) = 3.026 \times 10^{39} \text{J} \]

and the frequency and wavelength of light that corresponds to this energy change is

\[
\nu = \frac{E}{\hbar} = \frac{3.026 \times 10^{39} \text{J}}{6.626 \times 10^{-34} \text{J} \cdot \text{s}} = 4.567 \times 10^{14} \text{s}^{-1} \\
\lambda = \frac{c}{\nu} = \frac{2.998 \times 10^8 \text{m/s}}{4.567 \times 10^{14} \text{s}^{-1}} = 6.564 \times 10^{-7} \text{m} = 656.4 \text{nm}
\]

The wavelength and energy of the red line in the hydrogen spectrum corresponds to an electron moving from the \( n = 3 \) energy level to the \( n = 2 \) energy level.

As shown in Interactive Figure 6.3.2, all of the lines in the visible region of the hydrogen spectrum result from an electron moving from an excited state \((n > 2)\) to the \( n = 2 \) energy level. Notice in the figure that electron energy becomes more negative as it occupies lower energy levels and is closer to the nucleus (as \( n \) decreases).

**Interactive Figure 6.3.2 Understand the Bohr model of the atom.**
The observed emissions in the ultraviolet region are the result of a transition from an excited state to the \( n = 1 \) level, and emissions in the infrared region result from transitions from \( n > 3 \) or 4 to the \( n = 3 \) or 4 energy level. The energy change for each of these transitions is calculated using the general form of the Bohr equation:

\[
\Delta E = \mathcal{G}2.179 \times 10^{18} \text{ J} \left( \frac{1}{n_{\text{final}}} - \frac{1}{n_{\text{initial}}} \right)
\]

where \( n_{\text{final}} \) and \( n_{\text{initial}} \) are the final energy level and initial energy level, respectively.

It is important to keep in mind that a simple relationship between energy and the integer \( n \) is true only for species with a single electron such as hydrogen. The line spectra observed for all other species are more complex (Interactive Figure 6.3.1) and follow no clear, defined mathematical relationship.

**EXAMPLE PROBLEM: Calculate energy change for electron transitions between energy levels.**

Calculate the wavelength of the radiation emitted when an electron in a hydrogen atom moves from the \( n = 5 \) to the \( n = 3 \) energy level. Is the radiation visible?

**SOLUTION:**

You are asked to calculate the wavelength of light emitted when an electron moves between energy levels in a hydrogen atom. **You are given** the initial and final energy levels for the electron.

Use the general form of the Bohr equation to calculate the energy of the transition and then calculate the wavelength of the radiation.

\[
\Delta E = \mathcal{G}2.179 \times 10^{18} \text{ J} \left( \frac{1}{n_{\text{final}}} - \frac{1}{n_{\text{initial}}} \right) = \mathcal{G}1.550 \times 10^{19} \text{ J}
\]

\[
\nu = \frac{E}{\hbar} = \frac{1.550 \times 10^{19} \text{ J}}{6.626 \times 10^{-34} \text{ J} \cdot \text{s}} = 2.339 \times 10^{14} \text{ s}^{-1}
\]

\[
\lambda = \frac{c}{\nu} = \frac{2.998 \times 10^8 \text{ m/s}}{2.339 \times 10^{14} \text{ s}^{-1}} = 1.282 \times 10^{-6} \text{ m} = 1282 \text{ nm}
\]

This radiation is not visible. It is in the infrared region of the electromagnetic spectrum.

6.3.1T: Tutorial Assignment
6.3.1: Mastery Assignment

### 6.4 Quantum Theory of Atomic Structure

#### Section Outline

6.4a Wave Properties of Matter

6.4b The Schrödinger Equation and Wave Functions

Section Summary Assignment

The Bohr model of an electron orbiting around the nucleus like a planet around the sun fails to explain almost all properties of atoms. Indeed, the planetary view of one charged particle orbiting another particle of opposite charge violates some of the best known laws of classical physics. Because of this deficiency, scientists have developed a different view of how electrons are arranged about the nucleus in the atom. This view depends on two central concepts: the wave behavior of matter and the
uncertainty principle. These two ideas combined lead to a mathematical description of electronic structure.

**Opening Exploration 6.4 Anatomy of a Wave Function**

6.4a Wave Properties of Matter

Bohr’s model of the electronic structure of the atom failed when it was applied to species with more than a single electron. Although his theory is still useful in thinking about electron transitions between energy levels, it ultimately failed because it addressed only the particle nature of electrons. Similar to the way that light energy can act as a wave or as a particle, matter such as an electron displays properties of wave motion in addition to its particle behavior.

In the early 20th century, Louis de Broglie proposed that all matter in motion has a characteristic wavelength, according to a relationship now known as the de Broglie equation.

\[ \lambda = \frac{h}{mv} \]  

(6.5)

where \( h \) is Plank’s constant, \( m \) is the mass of the particle (in kg), and \( v \) is the velocity (m/s). For any macroscopic object, the calculated wavelength is vanishingly small and not observable. For an electron, though, the wavelength is significant and measurable.

**EXAMPLE PROBLEM:** Calculate the wavelength of moving particles using de Broglie’s equation.

Calculate the wavelength of the following:

(a) An electron (mass = \( 9.11 \times 10^{-31} \text{ kg} \)) moving at a speed of \( 2.2 \times 10^6 \text{ m/s} \)

(b) A golf ball (mass = 45 g) moving at a speed of 72 m/s

**SOLUTION:**

**You are asked** to calculate the wavelength of a moving particle.

**You are given** the mass and velocity of the particle.

(a) \[ \lambda = \frac{h}{mv} = \frac{6.626 \times 10^{-34} \text{ J} \cdot \text{s}}{(9.11 \times 10^{-31} \text{ kg})(2.2 \times 10^6 \text{ m/s})} = 3.3 \times 10^{-10} \text{ m} \]
(b) \( \lambda = \frac{h}{mv} = \frac{6.626 \times 10^{-34} \text{ J} \cdot \text{s}}{(0.045 \text{ kg})(72 \text{ m/s})} = 2.0 \times 10^{-34} \text{ m} \)

**Is your answer reasonable?** The electron has a wavelength similar to the wavelength of x-rays, whereas the heavier, slower golf ball has a wavelength too small to be measured by any known instrument.

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**6.4.1T: Tutorial Assignment**

**6.4.1: Mastery Assignment**

**The Heisenberg Uncertainty Principle** A few years after de Broglie proposed that all particles have wavelike properties, Werner Heisenberg (1901–1976) proposed the uncertainty principle, which states that it is not possible to know with great certainty both an electron’s position and its momentum (which is related to its kinetic energy) at the same time. Equation 6.6 shows the mathematical expression of this principle, where \( \Delta x \) is the uncertainty in the position of the electron and \( \Delta p \) is the uncertainty in the electron’s momentum.

\[
\Delta x \Delta p \geq \frac{h}{4\pi} \tag{6.6}
\]

As shown earlier with calculations involving line spectra, it is possible to determine with great certainty the energy of an electron. Therefore, according to Heisenberg’s uncertainty principle, we cannot know the position of the electron with any certainty. This principle demonstrated another weakness in Bohr’s atomic theory. Bohr proposed that electrons moved in defined orbits around the nucleus, implying that both the position and the energy of an electron could be known with great certainty.

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**6.4b The Schrödinger Equation and Wave Functions**

In the early 20th century, Erwin Schrödinger (1877–1961) derived a new mathematical equation to describe the wavelike behavior of electrons. Solutions to this equation produced wave functions \( \psi \), mathematical equations that predict the energy of an electron and the regions in space where an electron is most likely to be found. The square of a wave function, \( \psi^2 \), is equal to the probability of finding an electron in a given region around the nucleus of an atom. These probability functions, called orbitals, are represented using two- or three-dimensional shapes as shown in Interactive Figure 6.4.1, Figure 6.4.2, and Figure 6.4.3.

We will not examine the mathematical form of wave functions in detail, but it is worth examining one to make clear how orbital shapes are derived. In Interactive Figure 6.4.1, the wave function \( \psi \) and the probability density \( \psi^2 \) for the lowest-energy electron in a hydrogen atom are plotted as a function of \( r \), the distance from the nucleus.
Interactive Figure 6.4.1 Describe wave functions and orbitals.

Wave function ($\psi$) and probability density ($\psi^2$) for the lowest-energy electron in a hydrogen atom. Notice that as the distance from the nucleus ($r$) decreases, the value of $\psi^2$ becomes larger. This suggests that the lowest-energy electron in a hydrogen atom is most likely to be found close to the nucleus.

This probability function is usually visualized in two ways. First, imagine visualizing the position of an electron as a dot, sampling the position once every second over a very long period of time. If this is done for an electron in a hydrogen atom, the “dot picture” would look like that shown in Figure 6.4.2.

Figure 6.4.2 Dot picture representation of an electron in a hydrogen atom

Notice that the density of dots is greatest close to the nucleus. This is the region of greatest electron density, the region of greatest probability of finding an electron.

The second way to visualize the electron in a hydrogen atom is to think about a boundary surface that encloses the region of space where the electron is likely to be found most of the time. In this view, the electron is much more likely to be found within the boundary surface than outside the boundary surface. The boundary surface for the lowest-energy orbital is shown in Figure 6.4.3.
6.5 Quantum Numbers, Orbitals, and Nodes

Section Outline
6.5a Quantum Numbers
6.5b Orbital Shapes
6.5c Nodes
6.5d Orbital Energy Diagrams and Changes in Electronic State

Section Summary Assignment

The organization of the periodic table is intimately related to the organization of electrons in atoms, which can be expressed in terms of quantum numbers. Quantum numbers refers to a series of numbers that results from solving Schrödinger’s wave equation for the hydrogen atom. In this section we explore quantum numbers and how they relate to orbital shapes and the energy of electrons.

Opening Exploration 6.5 Waves and Nodes

6.5a Quantum Numbers
Three quantum numbers are used to characterize an orbital. The principal quantum number (n) describes the size and energy of the shell in which the orbital resides. Recall that Bohr’s atomic structure model also included a principal quantum number (n). The allowed values of n are positive integers (n = 1, 2, 3, 4, …). The angular momentum quantum number (l) indicates the shape of the orbital. For any given value of n, l can have values that range from 0 to (n – 1). For example, in the n = 4 shell, l has values of 0, 1, 2, and 3. Each value of l corresponds to an orbital label and an orbital shape.
Beyond $\ell = 3$, the orbitals are labeled alphabetically ($\ell = 4$ is a $g$ orbital, for example). The magnetic quantum number ($m_\ell$) is related to an orbital’s orientation in space. For a specific value of $\ell$, $m_\ell$ can have values that range from $-\ell$ to $+\ell$. For example, when $\ell = 1$, the possible values of $m_\ell$ are $-1, 0,$ and $+1$. Thus, there are three $p$ ($\ell = 1$) orbitals (because there are three $m_\ell$ values when $\ell = 1$) in any shell.

<table>
<thead>
<tr>
<th>$\ell$</th>
<th>Orbital Label</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>$s$</td>
</tr>
<tr>
<td>1</td>
<td>$p$</td>
</tr>
<tr>
<td>2</td>
<td>$d$</td>
</tr>
<tr>
<td>3</td>
<td>$f$</td>
</tr>
</tbody>
</table>

**Example Problem: Use quantum numbers.**

(a) List all possible values for $\ell$ in the sixth energy level ($n = 6$).

(b) List all possible values for $m_\ell$ for an $f$ orbital.

**Solution:**

**You are asked** to list all possible quantum numbers.

**You are given** a specific orbital or group of orbitals.

(a) For any given value of $n$, $\ell$ can have values that range from 0 to $(n - 1)$. When $n = 6$, $\ell$ can have values of 0, 1, 2, 3, 4, and 5. Thus, there are six different types of orbitals in the sixth energy level.

(b) For a specific value of $\ell$, $m_\ell$ can have values that range from $-\ell$ to $+\ell$. An $f$ orbital corresponds to an $\ell$ value of 3. Therefore, the possible values of $m_\ell$ are $-3, -2, -1, 0, 1, 2,$ and $3$. Thus, there are seven unique $f$ orbitals, one for each $m_\ell$ value.

**6.5.1T: Tutorial Assignment**

**6.5.1: Mastery Assignment**

**6.5b Orbital Shapes**

The three-dimensional shapes of orbitals play a vital and important role in the behavior of electrons and thus control chemical processes and determine the shapes of molecules. Everything from the physical states of compounds to the selective way biological molecules react with one another is a facet of the way electrons are arranged in orbitals about the atom’s nucleus.

Schrödinger’s wave equation can be solved to produce wave functions and orbitals for single-electron species such as hydrogen. More complicated mathematical treatment leads to comparable orbitals for multielectron atoms. Orbitals are given designations, such as $1s$, $3p_x$, and $4d_{xz}$, that provide information about the orbital’s energy, shape, and orientation in space. The lowest-energy orbitals for a hydrogen atom are shown in **Interactive Figure 6.5.1**.
Interactive Figure 6.5.1 Explore orbital shapes.

Atomic orbitals (boundary surfaces, n = 1–3)

Each boundary surface contains the volume in space where an electron is most likely to be found. The surfaces also contain regions of high electron density, and some orbitals, such as the 2px orbital (Figure 6.5.2), contain regions of space called nodes, where there is no probability of finding an electron (no electron density).

Figure 6.5.2 The node in a 2px orbital.

Orbitals are classified by energy, shape, and orientation in space. The main classification is the energy of the orbital, designated by the value of the principal quantum number, n. The principal quantum number indicates the relative size of the orbital. For example, the 2s orbital (n = 2) is higher in energy and larger than the 1s orbital (n = 1). Orbitals with the same n value are said to be in the same shell. Higher n values indicate orbitals where electrons are located, on average, farther from the nucleus. These electrons are less attracted to the positively charged nucleus (because it is farther away) and have a higher relative energy. Electrons closer to the nucleus have relatively large,
negative energy. Electrons farther from the nucleus have energy closer to zero or a smaller negative energy. In summary,

**High-Energy Electrons**
- Have a higher \( n \) value
- Are farther from the nucleus
- Have a small, negative energy (close to zero)

**Low-Energy Electrons**
- Have a lower \( n \) value
- Are closer to the nucleus
- Have a large, negative energy

Each shell contains one or more **subshells**, each defined by a different value of \( \ell \) and designated by a different letter (\( s, p, d, \) and \( f \) are the letters assigned to the first four subshells). The subshell label indicates the shape of the orbitals in that subshell. An \( s \) orbital has a spherical shape, \( p \) orbitals have two regions of electron density on either side of the nucleus, and most of the \( d \) orbitals have four regions of electron density surrounding the nucleus. When an orbital has more than one region of electron density, the different regions are separated by a node.

Each subshell is made up of one or more orbitals. The number of orbitals in a subshell is given by the number of \( m_\ell \) values for that subshell. For subshells with more than one orbital, subscript letters are used to differentiate between orbitals. The subshells and orbitals that exist for the first four shells are shown in **Table 6.5.1**.

### Table 6.5.1 Subshells and Orbitals in \( n = 1–4 \) Energy Levels

<table>
<thead>
<tr>
<th>Principal Quantum Number</th>
<th>( \ell )</th>
<th>Subshell</th>
<th>Number of ( m_\ell ) Values</th>
<th>Orbitals in the Subshell</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>( s )</td>
<td>1</td>
<td>(1s orbital)</td>
</tr>
<tr>
<td>2</td>
<td>0</td>
<td>( s )</td>
<td>1</td>
<td>(2s orbital)</td>
</tr>
<tr>
<td>3</td>
<td>1</td>
<td>( p )</td>
<td>3</td>
<td>(2p(_x), 2p(_y), 2p(_z) orbitals)</td>
</tr>
<tr>
<td>3</td>
<td>0</td>
<td>( s )</td>
<td>1</td>
<td>(3s orbital)</td>
</tr>
<tr>
<td>1</td>
<td>1</td>
<td>( p )</td>
<td>3</td>
<td>(3p(_x), 3p(_y), 3p(_z) orbitals)</td>
</tr>
<tr>
<td>2</td>
<td>2</td>
<td>( d )</td>
<td>5</td>
<td>(3d(<em>{xy}), 3d(</em>{xz}), 3d(<em>{yz}), 3d(</em>{z^2}), and 3d(_{x'y'}) orbitals)</td>
</tr>
<tr>
<td>4</td>
<td>0</td>
<td>( s )</td>
<td>1</td>
<td>(4s orbital)</td>
</tr>
<tr>
<td>1</td>
<td>1</td>
<td>( p )</td>
<td>3</td>
<td>(4p(_x), 4p(_y), and 4p(_z) orbitals)</td>
</tr>
<tr>
<td>3</td>
<td>2</td>
<td>( d )</td>
<td>5</td>
<td>(4d(<em>{xy}), 4d(</em>{xz}), 4d(<em>{yz}), 4d(</em>{z^2}), and 4d(_{x'y'}) orbitals)</td>
</tr>
<tr>
<td>4</td>
<td>3</td>
<td>( f )</td>
<td>7</td>
<td>(4f(<em>{1}^{\pm}), 4f(</em>{2}^{\pm}), 4f(<em>{3}^{\pm}), 4f(</em>{4}^{\pm}), 4f(<em>{5}^{\pm}), 4f(</em>{6}^{\pm}), and 4f(_{7}^{\pm}) orbitals)</td>
</tr>
</tbody>
</table>

Notice that as \( n \) increases, so does the number of subshells in that shell. Also, the number of subshells for any shell is equal to the principal quantum number, \( n \), and the total number of orbitals in a given energy level is equal to \( n^2 \).
6.5c Nodes

Nodes are regions of space where there is zero probability of finding an electron. Two types of nodes are found in orbitals: planar nodes (also called angular nodes and sometimes take the shape of a cone) and radial nodes (also called spherical nodes).

Planar nodes are found in all orbitals other than the s orbitals. As shown in Interactive Figure 6.5.2, each p orbital has a planar node that is perpendicular to the axis where there are regions of high electron density. The d orbitals generally have two planar nodes that are perpendicular to each other. For example, the 3d_{xy} orbital has two planar nodes, one in the xz plane and one in the yz plane. The number of planar nodes in a subshell is given by the value of the angular momentum quantum number, \( \ell \).

<table>
<thead>
<tr>
<th>( \ell )</th>
<th>Subshell</th>
<th>Number of Planar Nodes</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>s</td>
<td>0</td>
</tr>
<tr>
<td>1</td>
<td>p</td>
<td>1</td>
</tr>
<tr>
<td>2</td>
<td>d</td>
<td>2</td>
</tr>
<tr>
<td>3</td>
<td>f</td>
<td>3</td>
</tr>
</tbody>
</table>

Radial nodes are more difficult to visualize than planar nodes. Consider the 2s orbital, which has a single radial node. The boundary surface for a 2s orbital looks much like that of a 1s orbital. But, if we “slice” the orbital in half, we can see that the 2s orbital has a spherical region where there is no electron density. This is a radial node, and it separates two regions of electron density: one near the nucleus and the other farther from the nucleus (on the other side of the node) (Interactive Figure 6.5.3).

Interactive Figure 6.5.3  Relate quantum numbers to nodes.
[Figure ID #6-16]

Radial nodes in the 2s and 3s orbitals

The number of radial nodes increases as the value of \( n \) increases. For example, a 3s orbital has two radial nodes separating three regions of electron density, and a 4s orbital has three radial nodes. Likewise, a 2p orbital has no radial nodes, and a 3p orbital has one. The number of radial nodes for an orbital is related to both \( n \) and \( \ell \) and is equal to \( (n - \ell - 1) \). The total number of nodes (planar and radial) for an orbital is equal to \( n - 1 \).

6.5d Orbital Energy Diagrams and Changes in Electronic State

We use energy diagrams as a means for depicting orbital energies (Figure 6.5.4).

Figure 6.5.4  Energy diagram for hydrogen orbitals (\( n = 1–4 \)).

Notice that the energy of each orbital depends only on its shell, not its subshell. This is true only for hydrogen, and we will see in the next chapter that the energy of orbitals for all other atoms depends
on both the shell and the subshell. The energy of each shell is the same as that seen earlier in the Bohr model of the hydrogen atom, \( E_n = \frac{\hbar^2}{2m} \left( \frac{1}{n^2} \right) \).

We can now give a more complete view of what occurs when a hydrogen atom absorbs a photon of light. The ground state for the hydrogen atom finds its electron in the lowest-energy orbital, the 1s orbital. When an atom absorbs a photon of light, the electron is promoted to a higher-energy orbital \((n > 1)\). The photon of light causes the electron to move farther away from the nucleus, as shown in Interactive Figure 6.5.5.

**Interactive Figure 6.5.5** Add energy to a hydrogen atom.

![Interactive Figure 6.5.5](image)

A hydrogen atom absorbs energy.

Note that although Interactive Figure 6.5.5 shows a hydrogen atom absorbing energy and promoting an electron from a 1s orbital to a 3px orbital, absorption of a photon with a wavelength of 93.8 nm can promote the electron to any p orbital in the \( n = 3 \) shell. Absorption of light with a different wavelength can promote the electron to an orbital with a different energy.

**Chapter Review**

**Key Concepts**

**6.1 Electromagnetic Radiation**

- Electromagnetic radiation is made up of magnetic and electric fields oscillating at right angles to one another (6.1).
- Waves are characterized by their wavelength, frequency, and speed (6.1a).
- Wavelength and speed are related by the speed of light (6.1a).
- The electromagnetic spectrum shows the different types of electromagnetic radiation (6.1b).
- Visible light is a small portion of the electromagnetic spectrum (6.1b).

**6.2 Photons and Photon Energy**

- The photoelectric effect suggests that light has particle-like properties (6.2a).
- Light travels in packets called photons, and the energy of a photon is related to the wavelength and frequency of the light (6.2a).
- Planck’s equation relates the energy of a photon to its frequency (6.2a).
6.3 Atomic Line Spectra and the Bohr Model of Atomic Structure

- When light emitted by excited atoms is passed through a prism, the resulting spectrum is called a line spectrum and is characteristic for a given element (6.3a).
- Niels Bohr’s atomic theory states that electrons in an atom can occupy only certain energy levels and that they move from lower- to higher-energy levels when they absorb energy (6.3b).
- Bohr’s equation relates the energy of an electron to its energy state as indicated by \( n \), the principle quantum number (6.3b).

6.4 Quantum Theory of Atomic Structure

- Louis de Broglie proposed that all matter in motion has a characteristic wavelength (6.4a).
- Werner Heisenberg proposed the uncertainty principle, which states that it is not possible to know with great certainty both an electron’s position and its momentum at the same time (6.4a).
- Erwin Schrödinger proposed a mathematical system that produced wave function equations that predict the energy of an electron and the regions in space where it is most likely to be found (6.4b).
- The square of a wave function is equal to the probability of finding an electron in a given region of space around the nucleus of an atom (6.4b).
- An orbital is the probability function visualized as a two- or three-dimensional shape (6.4b).

6.5 Quantum Numbers, Orbitals, and Nodes

- The quantum numbers \( n \), \( \ell \), and \( m_\ell \) are a series of numbers that result from solving Schrödinger’s wave equation for the hydrogen atom and are used to characterize orbitals (6.5a).
- Each energy level (shell) contains one or more subshells, and each subshell is made up of one or more orbitals (6.5b).
- Orbitals can contain planar and radial nodes, regions of space where there is no probability of finding an electron (6.5c).
- The number of nodes in an orbital is related to the quantum numbers \( n \) and \( \ell \) (6.5c).
- Energy diagrams are used to depict relative orbital energies (6.5d).
Chapter 6  Electromagnetic Radiation and the Electronic Structure of the Atom

Key Equations

\[ c = \lambda \nu \quad (6.1) \]
\[ E_{\text{photon}} = h \nu \quad (6.2) \]
\[ E_n = \mathcal{G}2.179 \times 10^{18} J \left( \frac{1}{n^2} \right) \quad (6.3) \]
\[ \Delta E = \mathcal{G}2.179 \times 10^{18} J \left( \frac{1}{n_{\text{final}}^2} - \frac{1}{n_{\text{initial}}^2} \right) \quad (6.4) \]
\[ \lambda = \frac{h}{m \nu} \quad (6.5) \]
\[ \Delta x \Delta \rho^3 \geq \frac{h}{4\pi} \quad (6.6) \]

Key Terms

6.1 Electromagnetic Radiation
- electromagnetic radiation
- wavelength
- frequency
- amplitude
- speed of light
- electromagnetic spectrum

6.2 Photons and Photon Energy
- photoelectric effect
- photons

6.3. Atomic Line Spectra and the Bohr Model of Atomic Structure
- line spectrum
- principle quantum number
- ground state
- excited state

6.4. Quantum Theory of Atomic Structure
- uncertainty principle
- wave functions
- orbitals
- electron density

6.5 Quantum Numbers, Orbitals, and Nodes
- quantum numbers
- principal quantum number
- angular momentum quantum number
- magnetic quantum number
- nodes
- subshells