CHAPTER 9

Contents

Electrons in Atoms

At the end of the 19th century, some observers of the scientific scene believed that it was nearly time to close the books on the field of physics. They thought that with the accumulated knowledge of the previous two or three centuries, the main work left to be done was to apply this body of physics–*classical physics*–to such fields as chemistry and biology.

Only a few fundamental problems remained, including an explanation of certain details of *light emission* and a phenomenon known as *the photoelectric effect*. But the solution to these problems, rather than marking an end in the study of physics, spelled the beginning of a new golden age of physics. **These problems were solved through a bold new proposal–*the quantum theory*–a scientific breakthrough of epic proportions.**

In this chapter, we will see that to explain phenomena at the atomic and molecular level, classical physics is inadequate only the quantum theory will do.

Electromagnetic Radiation

Electromagnetic radiation is a form of energy transmission in which electric and magnetic fields are propagated as waves through empty space (a vacuum) or through a medium, such as glass.

Wave

A ***wave*** is a disturbance that transmits energy through space or a material medium (Figure 1).

↘ Water waves, sound waves, and seismic waves (which produce earthquakes) are unlike electromagnetic radiation. They require a material medium for their transmission.

Amplitude

The maximum height of the wave above the center line or the maximum depth below is called the ***amplitude***.

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Wavelength

The distance between the tops of two successive crests (or the bottoms of two troughs) is called the **wavelength**, designated by the Greek letter lambda, λ.

Frequency

Another feature, **frequency**, designated by the Greek letter nu, ν, is the number of *crests* or *troughs* that pass through a given point per unit of time. Frequency has the unit, $time^{-1}$, usually s^{-1} (per second), meaning the number of events or cycles per second.

Figure 1. **Electromagnetic waves:** This sketch of two different electromagnetic waves shows the propagation of mutually perpendicular oscillating electric and magnetic fields. For a given wave, the wavelengths, frequencies, and amplitudes of the electric and magnetic field components are identical. If these views are of the same instant of time, we would say that **(a)** has the longer wavelength and lower frequency, and **(b)** has the shorter wavelength and higher frequency.

Speed of the Wave

The product of the length of a wave (λ) and the frequency (ν) shows how far the wave front travels in a unit of time. This is the speed of the wave. The SI unit for frequency (s^{-1}), is the hertz (Hz), and the basic SI wavelength unit is the meter (m).

$$\text{Speed of the wave} = \lambda \times \nu \ (ms^{-1})$$

Some units that are used for electromagnetic radiation are listed below

1 cm (cm)	10^{-2} m
1 micrometer (μm)	10^{-6} m
1 nanometer (nm)	10^{-9} m
1 Angstrom (Å)	10^{-10} m $= 10^{-7}$ cm $= 10$ Å
1 picometer (pm)	10^{-12} m $= 10^{-10}$ cm $= 10^{-2}$ Å

↘ We cannot actually see an electromagnetic wave as we do the traveling wave in a rope, but we can try to represent it as in Figure 1.
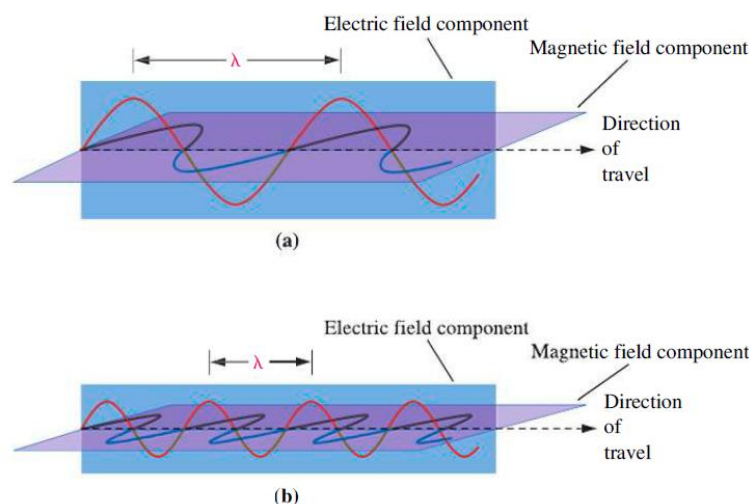
- According to a theory proposed by James Clerk Maxwell (1831–1879) in 1865, *electromagnetic radiation* (a propagation of electric and magnetic fields) is produced by an accelerating electrically charged particle (a charged particle whose velocity changes).

▷ **Example:**   Radio waves, for example, are a form of electromagnetic radiation produced by causing oscillations (fluctuations) of the electric current in a specially designed electrical circuit.

With visible light, another form of electromagnetic radiation, the accelerating charged particles are the electrons in atoms or molecules.

Speed of Light

A distinctive feature of electromagnetic radiation is its **constant** speed of 2.99792458×10^8 m s^{-1} in a vacuum, often referred to as the **speed of light**. The speed of light is represented by the symbol c.

$$c = \nu \times \lambda$$

The electromagnetic spectrum

Figure 2 indicates the wide range of possible wavelengths and frequencies for some common types of electromagnetic radiation and illustrates this important fact: The wavelength of electromagnetic radiation is shorter for high frequencies and longer for low frequencies.
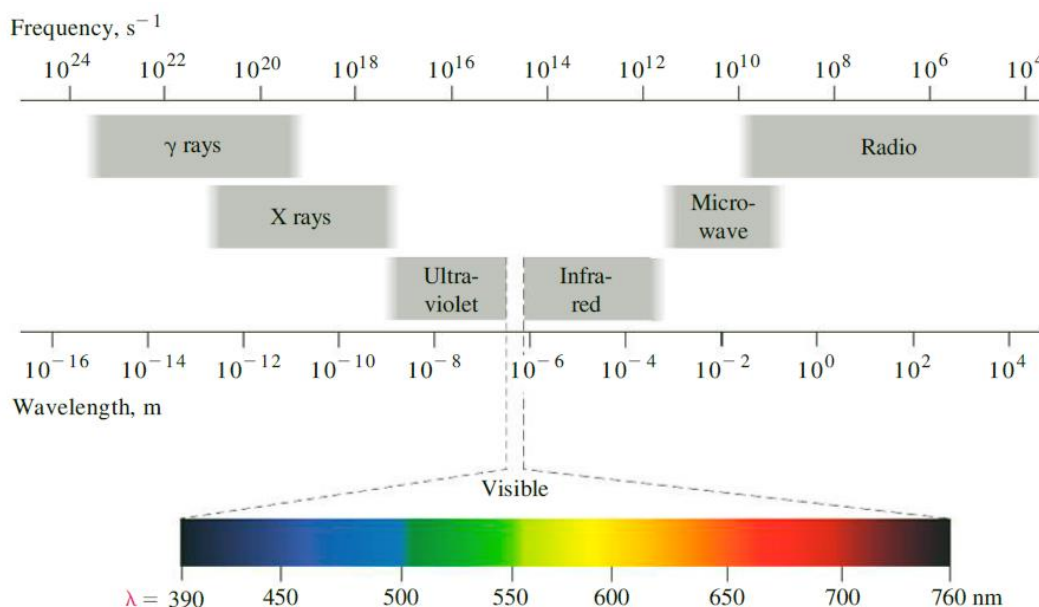

Figure 2. The visible region, which extends from violet at the shortest wavelength to red at the longest wavelength, is only a small portion of the entire spectrum. The approximate wavelength and frequency ranges of some other forms of electromagnetic radiation are also indicated.

▷ **Example:** Most of the light from a sodium vapor lamp has a wavelength of 589 nm. What is the frequency of this radiation?

Change the units of from nanometers to meters.

$$\lambda = 589\ nm\ \times\ \frac{10^{-9}\ m}{1\ nm} = 5.89\ \times 10^{-7} m$$

$$c = 2.998\ \times 10^8\ m\ s^{-1}$$

$$\nu = ?$$

$$c = \nu \times \lambda \Rightarrow \nu = \frac{c}{\lambda} = \frac{2.998\ \times 10^8\ m\ s^{-1}}{5.89\ \times 10^{-7} m} = 5.09 \times 10^{14}\ s^{-1} = 5.09\ \times 10^{14} Hz$$

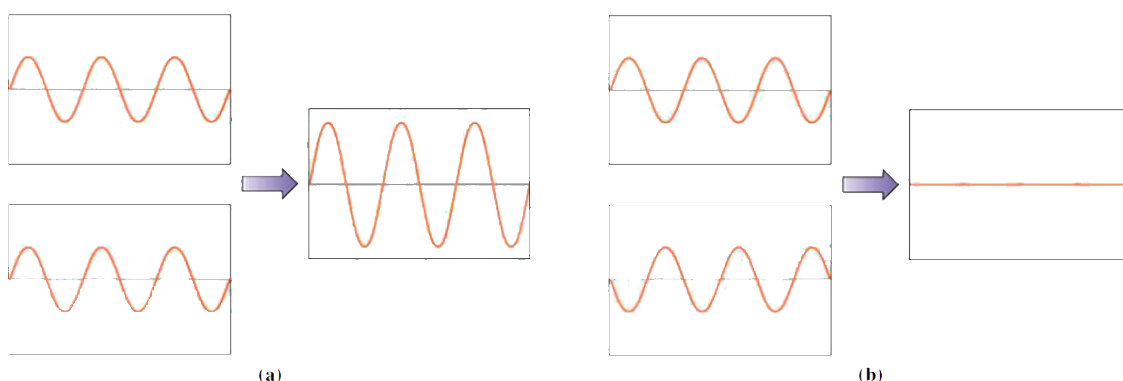*An Important Characteristic of Electromagnetic Waves*

Figure 3. **Interference in two overlapping light waves:** (a) In constructive interference, the troughs and crests are in step (in phase), leading to addition of the two waves. (b) In destructive interference, the troughs and crests are out of step (out of phase), leading to cancellation of the two waves.

The waves combine to produce the highest crests and deepest troughs in the water. The waves are said to be in phase, and the addition of the waves is called ***constructive interference*** (Figure 3a). Where the waves meet in such a way that the peak of one wave occurs at the trough of another, the waves cancel and the water is flat (Figure 3b). These out-of-step waves are said to be out of phase, and the cancellation of the waves is called ***destructive interference***.

The Visible Spectrum

The speed of light is lower in any medium (e.g., glass, water) than it is in a vacuum. Also, the speed is different in different media. As a consequence, light is refracted, or bent, when it passes from one medium to another (Figure 4). Thus, when a beam of white light is passed through a transparent medium, the wavelength components are refracted differently.
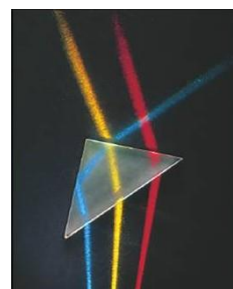

Figure 4. Refraction of light.

Thus, when a beam of white light is passed through a transparent medium, the wavelength components are refracted differently. The light is dispersed into a band

of colors, a *spectrum*. In Figure 5, a beam of white light (for example, sunlight) is dispersed by a glass prism into a continuous band of colors corresponding to all the wavelength components from red to violet.
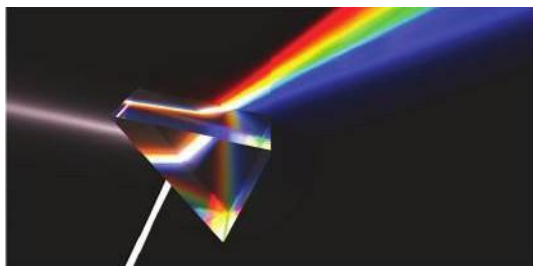

Figure 5. The spectrum of white light Dispersion of light through a prism. Red light is refracted the least and violet light the most when white light is passed through a glass prism. The other colors of the visible spectrum are found between red and violet.

Atomic Spectra

The visible spectrum in Figure 5 is said to be a *continuous spectrum* because the light being diffracted consists of many wavelength components. If the source of a spectrum produces light having only a relatively small number of wavelength components, then a *discontinuous spectrum* is observed.

Atomic or Line Spectra

For example, if the light source is an electric discharge passing through a gas, only certain colors are seen in the spectrum (Figure 6a and b). Or, if the light source is a gas flame into which an ionic compound has been introduced, the flame may acquire a distinctive color indicative of the metal ion present (Figure 6c and e).
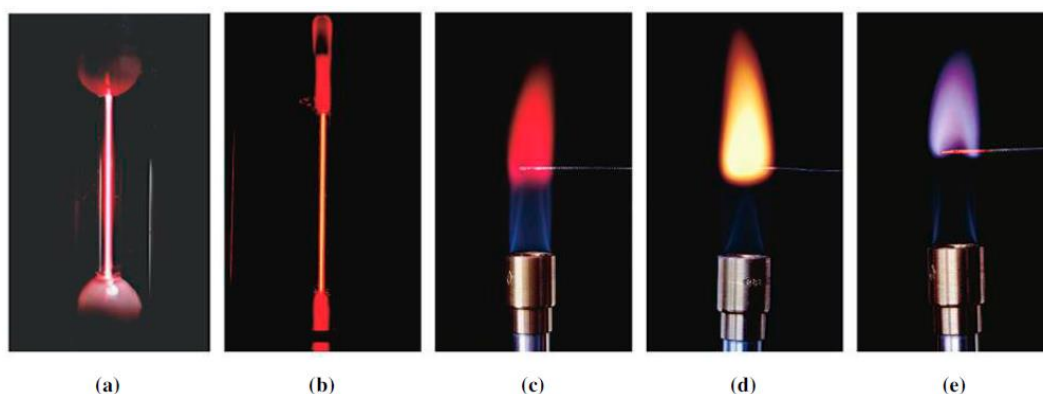
Figure 6. **Sources for light emission:** Light emitted by an electric discharge through (a) hydrogen gas and (b) neon gas. Light emitted when compounds of the alkali metals are excited in the gas flames: (c) lithium, (d) sodium, and (e) potassium.

In each of these cases, the emitted light produces a spectrum consisting of only a limited number of discrete wavelength components, observed as colored lines with dark spaces between them. These discontinuous spectra are called *atomic*, or *line*, *spectra*.

Source: R. H. Petrucci, General Chemistry, 10th Edition   A. Aydogan

Among the most extensively studied atomic spectra has been the hydrogen spectrum. Light from a hydrogen lamp appears to the eye as a reddish purple color (Figure 6a). The principal wavelength component of this light is red light of wavelength 656.3 nm. Three other lines appear in the visible spectrum of atomic hydrogen, however: a greenish blue line at 486.1 nm, a violet line at 434.0 nm, and another violet line at 410.1 nm.

Figure 7. **The Balmer series for hydrogen atoms–a line spectrum:** The four lines shown are the only ones visible to the unaided eye. Additional, closely spaced lines lie in the ultraviolet (UV) region.

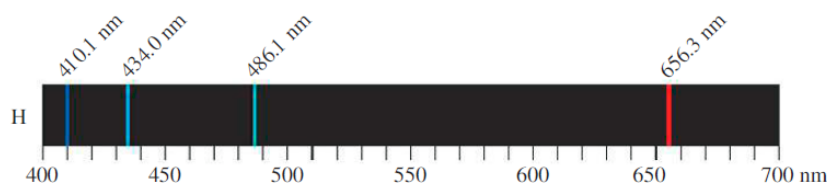The visible atomic spectrum of hydrogen is shown in Figure 7. In 1885, Johann Balmer, apparently through trial and error, deduced a formula for the wavelengths of these spectral lines. Balmer's equation, rearranged to a form based on frequency, is:

$$\nu = 3.2881 \times 10^{15}\ s^{-1} \left(\frac{1}{2^2} - \frac{1}{n^2} \right)$$

In this equation, is the frequency of the spectral line, and n must be an integer (whole number) greater than two. If is substituted n = 3 into the equation, the frequency of the red line is obtained. If n=4 is used, the frequency of the greenish blue line is obtained, and so on.

Blackbody Radiation

As with atomic spectra, classical physics could not provide a complete explanation of light emission by heated solids, a process known as **blackbody radiation**. Light emitted by a hot radiating object can be dispersed by a prism to produce a continuous color spectrum. As seen in Figure 8, the light intensity varies smoothly with wavelength, peaking at a wavelength fixed by the source temperature. Classical theory predicts that the intensity of the radiation emitted would increase indefinitely, as indicated by the dashed lines in Figure 8.
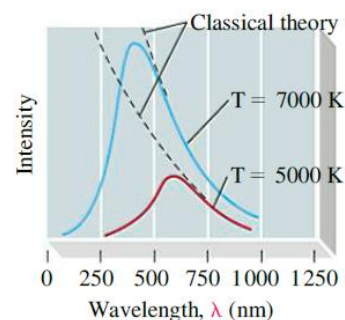

Figure 8. Spectrum of radiation given off by a heated body

Max Planck

In 1900, to explain the fact that the intensity does not increase indefinitely, Max Planck (1858−1947) made a revolutionary proposal: ***Energy, like matter, is discontinuous***. Classical physics places no

limitations on the amount of energy a system may possess, whereas quantum theory limits this energy to a discrete set of specific values.

The *difference* between any two allowed energies of a system also has a specific value, called a **quantum** of energy. This means that when the energy increases from one allowed value to another, it increases by a tiny jump, or quantum.

Planck s assumption was that the group of atoms must have an energy corresponding to the equation

$$\in = nh\nu$$

where ϵ is the energy, n is a positive integer, ν is the oscillator frequency, and **h** is a constant that had to be determined by experiment (**Planck's constant**).

$$h = 6.62607 \times 10^{-34} \text{ J s} = 6.62607 \times 10^{-27} \text{ erg s}$$

The energy of a quantum of electromagnetic radiation is proportional to the frequency of the radiation the higher the frequency, the greater the energy. This is summarized by what we now call Planck's equation.

$$E = h\nu$$

The Photoelectric Effect

↘ In 1888, Heinrich Hertz discovered that when light strikes the surface of certain metals, electrons are ejected. This phenomenon is called the ***photoelectric effect***. In this phenomenon:

- Electron emission only occurs when the frequency of the incident light exceeds a particular threshold value (ν_0).
- The number of electrons emitted depends on the intensity of the incident light, but
- The kinetic energies of the emitted electrons depend on the frequency of the light.

In 1905, Einstein proposed that electromagnetic radiation has particle-like qualities and that particles of light, subsequently called ***photons*** by G. N. Lewis, have a characteristic energy given by Planck's equation.

In the particle model, a photon of energy strikes a bound electron, which absorbs the photon energy. If the photon energy, hν, is greater than the energy binding the electron to the surface (a quantity known as the work function), a photoelectron is liberated.

The kinetic energy of the photoelectrons has been converted to potential energy, expressed through the following equation.

$$\frac{1}{2}mu^2 = eV_s$$

where *m, u* and *e* are the mass, speed, and charge of an electron, respectively. Thus

$$hv = \frac{1}{2}mu^2 + eV_p$$

where V_p is the potential energy of electron.

▷ **Example:** For radiation of wavelength 242.4 nm, the longest wavelength that will bring about the photodissociation of what is the energy of (a) one photon, and (b) a mole of photons of this light?

(a) First, calculate the frequency of the radiation.

$$v = \frac{c}{\lambda} = \frac{2.998 \times 10^8 \text{ ms}^{-1}}{242.4 \times 10^{-9} \text{ m}} = 1.237 \times 10^{15} \text{ s}^{-1}$$

Then, calculate the energy of a single photon.

$$E = hv = 6.626 \times 10^{-34} \times \frac{\text{Js}}{\text{photon}} \times 1.237 \times 10^{15} \text{ s}^{-1} = 8.196 \times 10^{-19} \text{ J/photon}$$

(b) Calculate the energy of a mole of photons

$$E = 8.196 \times 10^{-19} \frac{\text{J}}{\text{photon}} \times 6.022 \times 10^{23} \frac{\text{photons}}{\text{mol}} = 4.936 \times 10^5 \text{ J/mol}$$

The Bohr Atom

The Rutherford model of a nuclear atom does not indicate how electrons are arranged outside the nucleus of an atom. According to classical physics, stationary, negatively charged electrons would be pulled into the positively charged nucleus. However, again according to classical physics, orbiting electrons should be constantly accelerating and should radiate energy.

In 1913, Niels Bohr (1885−1962) resolved this problem by using Planck s quantum hypothesis. Bohr postulated that for a hydrogen atom:

1. The electron moves in circular orbits about the nucleus with the motion.
2. The electron has only a fixed set of allowed orbits, called ***stationary states***. According to that, as long as an electron remains in a given orbit, <u>its energy is constant and no energy is emitted</u>. The angular momentum values of an electron is described by $nh/2\pi$, where *n* must be an integer.

Thus the quantum numbers progress: $n = 1$ for the first orbit; $n = 2$ for the second orbit; and so on.

3. An electron can pass only from one allowed orbit to another. In such transitions, fixed discrete quantities of energy (quanta) are involved–either absorbed or emitted.
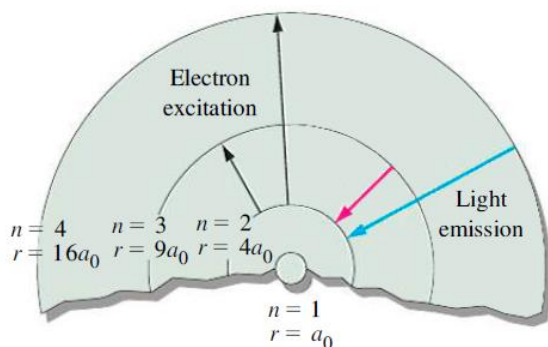

Figure 9. **Bohr model of the hydrogen atom:** A portion of the hydrogen atom is pictured. The nucleus is at the center, and the electron is found in one of the discrete orbits, $n = 1, 2$, and so on. Excitation of the atom raises the electron to higher-numbered orbits, as shown with black arrows. Light is emitted when the electron falls to a lower-numbered orbit. Two transitions that produce lines in the Balmer series of the hydrogen spectrum are shown in the approximate colors of the spectral lines.

↘ The atomic model of hydrogen based on these ideas is pictured in Figure 9. The allowed states for the electron are numbered, $n = 1, n = 2, n = 3$, and so on. These numbers are called as *quantum numbers*.

The Bohr theory predicts the radii of the allowed orbits in a hydrogen atom.

$$r_n = n^2 a_0, \text{ where } n = 1, 2, 3, ... \text{ and } a_0 = 53 \text{ pm } (0.53 \text{ Å})$$

The theory also allows us to calculate the electron velocities in these orbits and, most important, the energy. When the electron is free of the nucleus, by convention, it is said to be at a zero of energy. When a free electron is attracted to the nucleus and confined to the orbit n, the electron energy becomes negative.

$$E_n = \frac{-R_H}{n^2} \quad (R_H = 2.179 \times 10^{-18} \text{ J})$$

With this expression, we can calculate the energies of the allowed energy states, or *energy levels*, of the hydrogen atom. These levels can be represented schematically as in Figure 8-14. This representation is called an *energy-level diagram*.
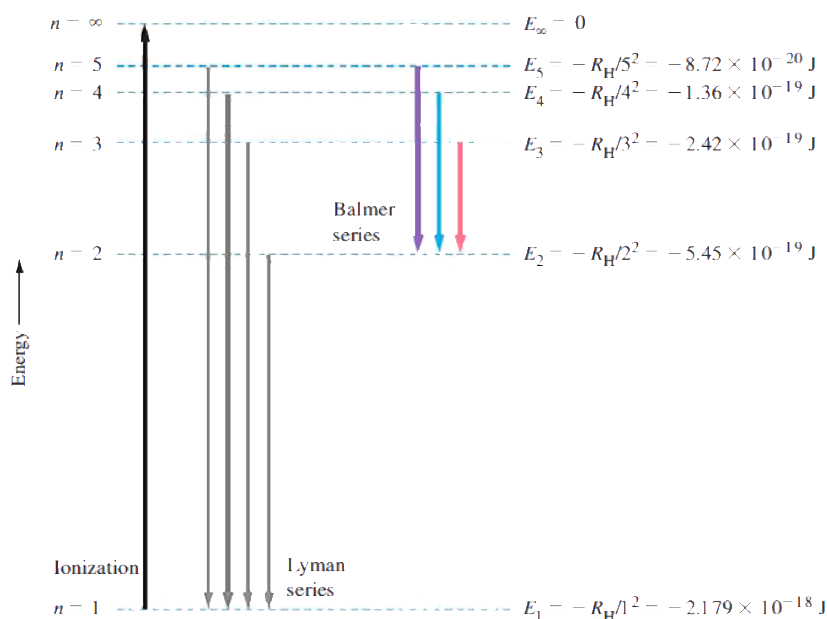
Figure 10. **Energy-level diagram for the hydrogen atom:** If the electron acquires of 2.179 × 10⁻¹⁸ J energy, it moves to the orbit $n = \infty$; ionization of the H atom occurs (black arrow). Energy emitted when the electron falls from higher-numbered orbits to the orbit $n = 1$ is in the form of ultraviolet light, which produces a spectral series called the Lyman series (gray lines). Electron transitions to the orbit $n = 2$ yield lines in the Balmer series (recall Figure 7); three of the lines are shown here (in color). Transitions to $n = 3$ yield spectral lines in the infrared.

Ground state

Normally, the electron in a hydrogen atom is found in the orbit closest to the nucleus ($n = 1$). This is the lowest allowed energy, or the **ground state**.

Excited state

When the electron gains a quantum of energy, it moves to a higher level ($n = 2, 3$, and so on) and the atom is in an **excited state**.

When the electron drops from a higher to a lower numbered orbit, a unique quantity of energy is emitted −the difference in energy between the two levels.

$$\Delta E = E_f - E_i = \frac{-R_H}{n_f^2} - \frac{-R_H}{n_i^2} = R_H \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right) = 2.179 \times 10^{-18} \text{ J} \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right)$$

where n_f is the final level and n_i is the initial one.

The energy of the photon (E_{photon}) either absorbed or emitted, is equal to the magnitude of this energy difference. Because and we can write $E_{photon} = h\nu$ and $E_{photon} = |\Delta E|$, we can write

$$|\Delta E| = E_{photon} = h\nu$$

where $|\Delta E|$ represents the magnitude of the energy difference between the energy levels involved in the electronic transition.

▷ **Example:** Is it likely that there is an energy level for the hydrogen atom, $E_n = -1.00 \times 10^{-20}$ J?

Let us rearrange the energy level equation, solve for n^2 and then for n.

$$E_n = \frac{-R_\mathrm{H}}{n^2} \Rightarrow n^2 = \frac{-R_\mathrm{H}}{E_n}$$

$$= \frac{-2.179 \times 10^{-18} \text{ J}}{-1.00 \times 10^{-20} \text{ J}} = 2.179 \times 10^2 = 217.9$$

$$n = \sqrt{217.9} = 14.76$$

Because the value of *n* is not an integer, this is *not an allowed energy level* for the hydrogen atom.

▷ **Example:** Determine the wavelength of the line in the Balmer series of hydrogen corresponding to the transition from *n* = 5 to *n* = 2.

The specific data $n_\mathrm{i} = 5$ and $n_\mathrm{f} = 2$.

$$\Delta E = 2.179 \times 10^{-18} \text{ J} \left(\frac{1}{5^2} - \frac{1}{2^2} \right)$$
$$= 2.179 \times 10^{-18} \times (0.04000 - 0.25000)$$
$$= -4.576 \times 10^{-19} \text{ J}$$

Rearranging $E_\mathrm{photon} = \Delta E = h\nu$ gives the frequency

$$\nu = \frac{E_\mathrm{photon}}{h} = \frac{-4.576 \times 10^{-19} \text{ J photon}^{-1}}{6.626 \times 10^{-34} \text{ J s photon}^{-1}} = 6.906 \times 10^{-19} \text{ s}^{-1}$$

Rearranging $c = h\nu$ for the wavelength gives the following result:

$$\lambda = \frac{c}{\nu} = \frac{2.998 \times 10^8 \text{ m s}^{-1}}{6.906 \times 10^{-19} \text{ s}^{-1}} = 4.341 \times 10^{-7} \text{ m} = 434.1 \text{ nm}$$

Inadequacies of the Bohr Model

Despite the accomplishments of the Bohr model for the hydrogen atom and hydrogen-like ions, the Bohr theory has a number of weaknesses.

- The theory cannot explain the emission spectra of atoms and ions with more than one electron
- The theory cannot explain the effect of magnetic fields on emission spectra.

Modern quantum mechanics replaced the Bohr theory in 1926.

Two Ideas Leading to a New Quantum Mechanics

Wave Particle Duality

To explain the photoelectric effect, Einstein suggested that light has particlelike properties, which are displayed through photons. Other phenomena, however, such as the dispersion of light into a spectrum by a prism, are best understood in terms of the wave theory of light. Light, then, appears to have a ***dual nature***.

In 1924, Louis de Broglie, considering the nature of light and matter, offered a startling proposition: *Small particles of matter may at times display wave-like properties*. He was aware of Einstein s famous equation and Planck relationship for the energy of a photon.

$$h\nu = mc^2$$

$$\frac{h\nu}{c} = mc = p$$

where p is the momentum of the photon. Using $\nu\lambda = c$, we have

$$p = \frac{h}{\lambda}$$

In order to use this equation for a material particle, such as an electron, de Broglie substituted for the momentum, p, its equivalent–the product of the mass of the particle, m, and its velocity, u. When this is done, we arrive at de Broglie s famous relationship.

$$\lambda = \frac{h}{p} = \frac{h}{mu}$$

↘ De Broglie called the waves associated with material particles ***matter waves***. If matter waves exist for small particles, then beams of particles, such as electrons, should exhibit the characteristic properties of waves, namely diffraction.

↘ George P. Thomson was the son of J.J. Thomson, who had won the Nobel Prize in physics in 1906 for his discovery of the electron. It is interesting to note that **Thomson the father** showed that the electron is a particle, and **Thomson the son** showed that the electron is a wave. Father and son together demonstrated the **wave–particle duality** of electrons.

The Uncertainty Principle

During the 1920s, Niels Bohr and Werner Heisenberg considered hypothetical experiments to establish just how precisely the behavior of subatomic particles can be determined.

The two variables that must be measured are the position of the particle (x) and its momentum ($p = mu$). The conclusion they reached is that there must always be uncertainties in measurement such that the product of the uncertainty in position (Δx), and the uncertainty in momentum (Δp), is

$$\Delta x \Delta p \geq \frac{h}{4\pi}$$

The significance of this expression, called the **Heisenberg uncertainty principle**, is that we **cannot** measure **position** and **momentum** with great precision **simultaneously**.
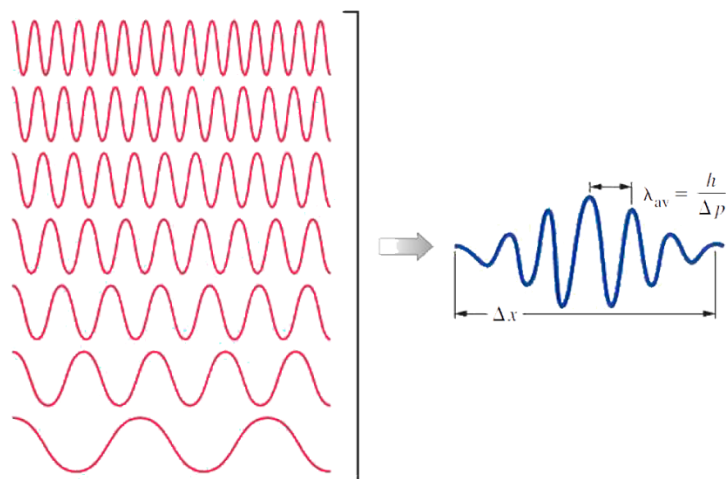

Figure 11. **The uncertainty principle interpreted graphically:** A collection of waves with varying wavelengths (left) can combine into a wave packet (right). The superposition of the different wavelengths yields an average wavelength (λ_{av}) and causes the wave packet to be more localized (Δx) than the individual waves. The greater the number of wavelengths that combine, the more precisely an associated particle can be located, that is, the smaller (Δx). However, because each of the wavelengths corresponds to a different value of momentum according to the de Broglie relationship, the greater is the uncertainty in the resultant momentum.

▷**Example:**   A 12 eV electron can be shown to have a speed of 2.05×10^6 m/s. Assuming that the precision (uncertainty) of this value is 1.5%, with what precision can we simultaneously measure the position of the electron?

The uncertainty in the electron speed is

$$\Delta u = 0.015 \times 2.05 \times 10^6 \text{ ms}^{-1} = 3.1 \times 10^4 \text{ m s}^{-1}$$

The electron mass (9.109×10^{-31} kg) is known much more precisely than the electron speed, which means that

$$\Delta p = m\Delta u = 9.109 \times 10^{-31} \text{ kg} \times 3.1 \times 10^4 \text{ m s}^{-1}$$
$$= 2.8 \times 10^{-26} \text{ kg m s}^{-1}$$

The uncertainty in the electron s position is

$$\Delta x = \frac{h}{4\pi\Delta p} = \frac{6.63 \times 10^{-34} \text{ kg m}^2\text{s}^{-1}}{4 \times 3.14 \times 2.8 \times 10^{-26} \text{ kg m s}^{-1}} = 1.9 \times 10^{-9} \text{ m} = 1.9 \times 10^3 \text{ pm}$$

Wave Mechanics

De Broglie's relationship suggests that electrons are matter waves and thus should display wavelike properties. A consequence of this wave particle duality is the limited precision in determining an electron's position and momentum imposed by the Heisenberg uncertainty principle.

How are we to view electrons in atoms? To answer this question, we must begin by identifying two types of waves.

Standing Waves

The characteristics of a standing wave:

- The crests and troughs of the wave occur at fixed positions and the amplitude of the wave at the fixed ends is zero.
- The magnitudes of the oscillations differ from point to point along the wave, including certain points, called **nodes**, that undergo no displacement at all.

Figure 12. Standing waves in a string

We might say that the permitted wavelengths of standing waves are quantized. They are equal to twice the path length (L) divided by a whole number (n) that is,

$$\lambda = \frac{2L}{n}$$

Where $n = 1,2,3, ...$ and the total number of nodes $= n + 1$

⬊ The plucked guitar string represents a one-dimensional standing wave, and so does an electron in a Bohr orbit. Also, the fact that Bohr orbits are one dimensional also points up a serious deficiency in the Bohr model: **The matter waves of electrons in the hydrogen atom must be three dimensional**.

Particle in a Box: Standing Waves, Quantum Particles, and Wave Functions

In 1927, Erwin Schrödinger, suggested that an electron (or any other particle) exhibiting wavelike properties should be describable by a mathematical equation called a ***wave function***. Greek letter psi (ψ), should correspond to a standing wave within the boundary of the system being described.

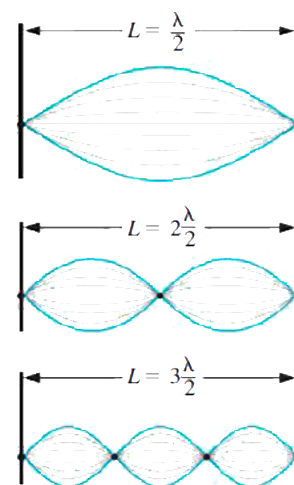$$\psi_n(x) = \sqrt{\frac{2}{L}} sin\left(\frac{n\pi x}{L}\right) \quad n = 1, 2, 3, ...$$

Solutions of the Schrödinger equation for the hydrogen atom give the wave functions for the electron in the hydrogen atom. These wave functions are called orbitals to distinguish them from the orbits of the Bohr theory.

Quantum Numbers and Electron Orbitals

By specifying three quantum numbers in a wave function ψ we obtain an orbital. Combinations of quantum numbers produce different orbitals. Orbitals state a region where electron in an atom have the highest possibility of presence.

Assigning Quantum Numbers

The following relationships involving the three quantum numbers arise from the solution of the Schrödinger wave equation for the hydrogen atom. In this solution the values of the quantum numbers are fixed in the order listed.

Principal quantum number (n)

Principal quantum number, n, which may have only a positive, nonzero integral value.

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

Angular momentum quantum number (l)

Orbital angular momentum quantum number (l), which may be zero or a positive integer, but not larger than $n - 1$.

$$l = 0, 1, 2, 3, \dots, n - 1$$

Magnetic quantum number (m_l)

Magnetic quantum number (m_l), which may be a negative or positive integer, including zero, and ranging from $-l$ to $+l$.

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

Spin quantum number (m_s)

$$m_s = \pm \frac{1}{2}$$

▷ **Example:**   Can an orbital have the quantum numbers $n = 2, l = 2$, and $m_l = 2$?

No. The l quantum number cannot be greater than $n - 1$. Thus, if $n = 2$, l can be only 0 or 1. And if l can be only 0 and 1, m_l cannot be 2; m_l must be 0 if $l = 0$ and may be $-1, 0$, or $+1$ if $l = 1$.

Principal Shells and Subshells

- All orbitals with the same value of n are in the same **principal electronic shell** or **principal level**, and all orbitals with the same n and l values are in the same **subshell**, or **sublevel**.

- The value of n relates to the energy and most probable distance of an electron from the nucleus. The higher the value of n, the greater the electron energy and the farther, on average, the electron is from the nucleus.

- The quantum number l determines the angular distribution, or shape, of an orbital.

- m_l determines the orientation of the orbital.

➥ The number of subshells in a principal electronic shell is the same as the number of allowed values of the orbital angular momentum quantum number, l.

n	l	Number of subshells	m_l
1	0	1	0
2	0, 1	2	-1, 0, 1
3	0, 1, 2	3	-2, -1, 0, 1, 2

➥ The name given to a subshell, regardless of the principal shell in which it is found, depends on the value of the l quantum number. The first four subshells are

s subshell	p subshell	d subshell	f subshell
$l = 0$	$l = 1$	$l = 2$	$l = 3$

➥ Total number of orbitals in a subshell is $2l + 1$. The names of the orbitals are the same as the names of the subshells in which they appear.

s **orbitals**	p **orbitals**	d **orbitals**	f **orbitals**
$l = 0$	$l = 1$	$l = 2$	$l = 3$
$m_l = 0$	$m_l = 0, \pm1$	$m_l = 0, \pm1, \pm2$	$m_l = 0, \pm1, \pm2, \pm3$
one s orbital in an s subshell	three p orbitals in a p subshell	five d orbitals in a d subshell	seven f orbitals in an f subshell

Orbitals table

	s ($\ell = 0$)	p ($\ell = 1$)			d ($\ell = 2$)				
	$m_l = 0$	$m_l = 0$	$m_l = \pm 1$		$m_l = 0$	$m_l = \pm 1$		$m_l = \pm 2$	
	s	p_z	p_x	p_y	d_{z^2}	d_{xz}	d_{yz}	d_{xy}	$d_{x^2-y^2}$
$n = 1$	.								
$n = 2$	.								
$n = 3$	.								
$n = 4$									
$n = 5$									
$n = 6$					...	...	...	...	...
$n = 7$		...	...	...	...	...	...	...	...

Figure 13. Orbital configurations for the real hydrogen-like wave functions. (Source: http://en.wikipedia.org/wiki/Atomic_orbital 3/19/2014 10:42 AM)

Electron Spin: A Fourth Quantum Number

In 1925, George Uhlenbeck and Samuel Goudsmit proposed that some unexplained features of the hydrogen spectrum could be understood by assuming that an electron acts as if it spins, much as Earth spins on its axis. There are two possibilities for *electron spin* (Figure 14**Error! Reference source not found.**).

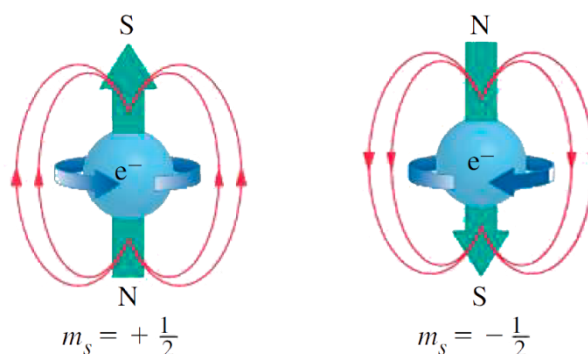The value of m_s does not depend on any of the other three quantum numbers.

Figure 14. **Electron spin visualized:** Two possibilities for electron spin are shown with their associated magnetic fields. Two electrons with opposing spins have opposing magnetic fields that cancel, leaving no net magnetic field for the pair.

- An electron, because of its spin, generates a magnetic field.

- A pair of electrons with opposing spins has no net magnetic field.
- The direction of the net magnetic field produced depends only on the spin of the unpaired electron.

Multielectron Atoms

Schrödinger developed his wave equation for the hydrogen atom–an atom containing just one electron. In multielectron atoms, the attractive force of the nucleus for a given electron increases as the nuclear charge increases. As a result, we find that

- Orbital energies become lower (more negative) with increasing atomic number of the atom.
- Orbital energies in multielectron atoms depend on the type of orbital; the orbitals with different values of l.

Penetration and Shielding

Shielding

Electrons in orbitals closer to the nucleus **screen** or **shield** the nucleus from electrons farther away. The screening electrons reduce the effectiveness of the nucleus in attracting the particular more-distant electron and reduce the nuclear charge effectively. This effect is called as ***shielding*** or ***screening***.

The magnitude of the reduction of the nuclear charge depends on the **types of orbitals** the **inner electrons** are in and the **type of orbital that the screened electron** is in. Thus, electrons in s orbitals are more effective at screening the nucleus from outer electrons than are electrons in p or d orbitals.

Penetration

The ability of electrons in orbitals that allows them to get close to the nucleus is called ***penetration***. An electron in an orbital with good penetration is better at screening than one with low penetration.

Electron Configurations

The ***electron configuration*** of an atom is a designation of how electrons are distributed among various orbitals in principal shells and subshells. Many of the physical and chemical properties of elements can be correlated with electron configurations.

Rules for Assigning Electrons to Orbitals

1. **Electrons occupy orbitals in a way that minimizes the energy of the atom.**

$$1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s, 4d, 5p, 6s, 4f, 5d, 6p, 7s, 5f, 6d, 7p$$
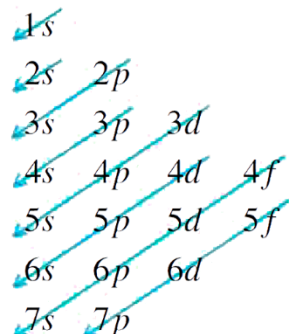

Figure 15. **The order of filling of electronic subshells:** Beginning with the top line, follow the arrows, and the order obtained is the same as in expression.

2. **No two electrons in an atom can have all four quantum numbers alike–the Pauli Exclusion Principle.**

   The first three quantum numbers, and determine a specific orbital. Two electrons may have these three quantum numbers alike; but if they do, they must have different values of m_s. Another way to state this result is that only two electrons may occupy the same orbital, and these electrons must have opposing spins.

3. When orbitals of identical energy (degenerate orbitals) are available, electrons initially occupy these orbitals singly.

   This rule, known as **Hund's rule**, an atom tends to have as many unpaired electrons as possible.

Representing Electron Configurations

The electron configuration of a carbon atom is shown in three different ways:

spdf notation (condensed):   C $1s^2 2s^2 2p^2$

spdf notation (expanded):   C $1s^2 2s^2 2p_x^1 2p_y^1$
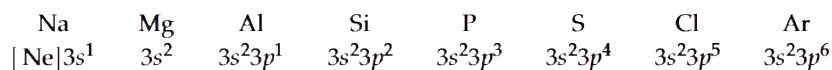
orbital diagram: C

$$1s \qquad 2s \qquad 2p$$

$Z = 7 - 10$, N through Ne

$$1s \quad 2s \qquad 2p$$

$Z = 11 - 18$, Na through Ar.

Because the configuration $1s^2 2s^2 2p^6$ is that of neon, we will call this the neon core, represent it as [Ne].

Na	Mg	Al	Si	P	S	Cl	Ar
[Ne]$3s^1$	$3s^2$	$3s^2 3p^1$	$3s^2 3p^2$	$3s^2 3p^3$	$3s^2 3p^4$	$3s^2 3p^5$	$3s^2 3p^6$

$Z = 19 - 20$, K through Ca.

After argon, instead of $3d$ the next subshell to fill is $4s$.

$$K: [Ar]4s^1 \quad \text{and} \quad Ca: [Ar]4s^2$$

$Z = 21 - 30$, Sc through Zn.

		$3d$					$4s$	
Sc:	[Ar]	↑					↑↓	[Ar]$3d^1 4s^2$
Ti:	[Ar]	↑	↑				↑↓	[Ar]$3d^2 4s^2$
V:	[Ar]	↑	↑	↑			↑↓	[Ar]$3d^3 4s^2$
Cr:	[Ar]	↑	↑	↑	↑	↑	↑	[Ar]$3d^5 4s^1$
Mn:	[Ar]	↑	↑	↑	↑	↑	↑↓	[Ar]$3d^5 4s^2$
Fe:	[Ar]	↑↓	↑	↑	↑	↑	↑↓	[Ar]$3d^6 4s^2$
Co:	[Ar]	↑↓	↑↓	↑	↑	↑	↑↓	[Ar]$3d^7 4s^2$
Ni:	[Ar]	↑↓	↑↓	↑↓	↑	↑	↑↓	[Ar]$3d^8 4s^2$
Cu:	[Ar]	↑↓	↑↓	↑↓	↑↓	↑↓	↑	[Ar]$3d^{10} 4s^1$
Zn:	[Ar]	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	[Ar]$3d^{10} 4s^2$