

7.1 Outline

- Examine the wavelike properties of light (wavelength, frequency, and speed)
- Describe particle behavior of light in terms of quantized energy and photons
- Line spectra and the Bohr model
- Wave behavior of matter and Heisenberg's Uncertainty Principle
- Quantum mechanics and atomic orbitals
- Representations of orbitals and electron configurations

7.2 Electromagnetic Radiation

- **Electromagnetic Radiation** – A form of energy that has wave characteristics and that propagates through a vacuum at the characteristic speed of light 3.00×10^8 m/s.
- Most subatomic particles behave as PARTICLES and obey the physics of waves.

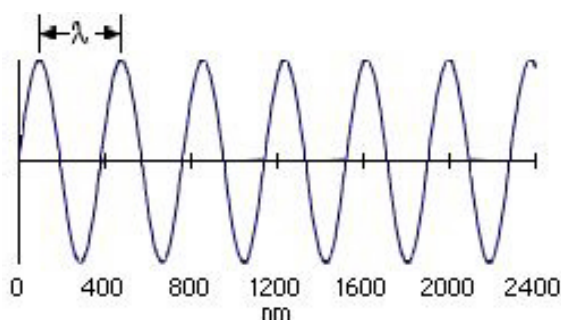


Figure 7.1: A picture of a wave in the ocean.



Figure 7.2: A wave plotted on a 2-dimensional graph.

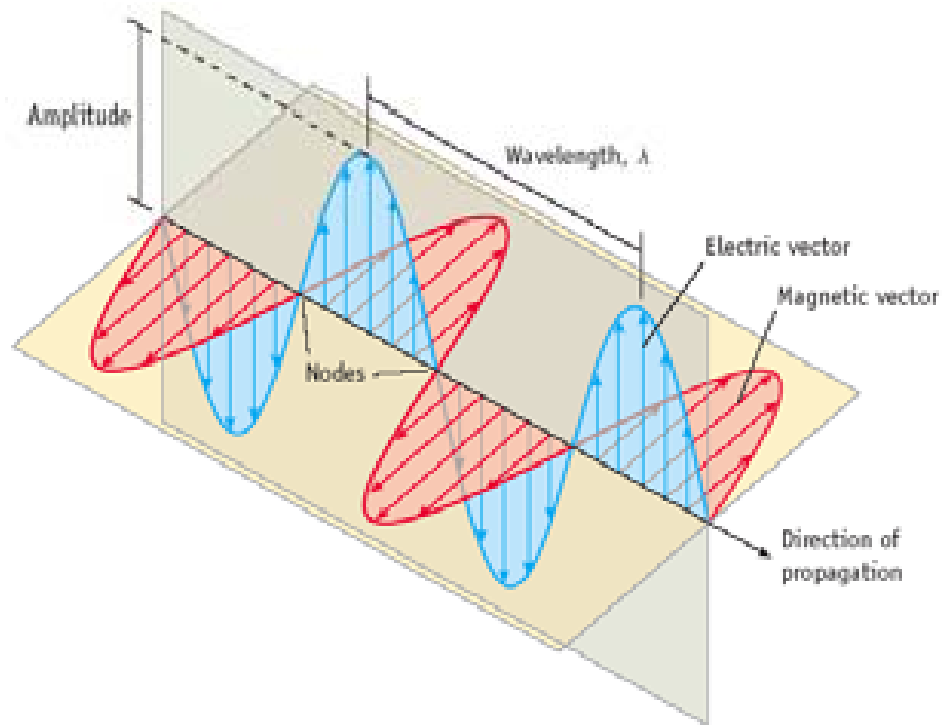


Figure 7.3: A combination of an electric component and magnetic component.

7.3 Wavelength and Frequency

- **Wavelength** – the distance between two adjacent peaks or between two adjacent troughs.
- **Frequency** – the number of times per second that one complete wavelength passes a point.

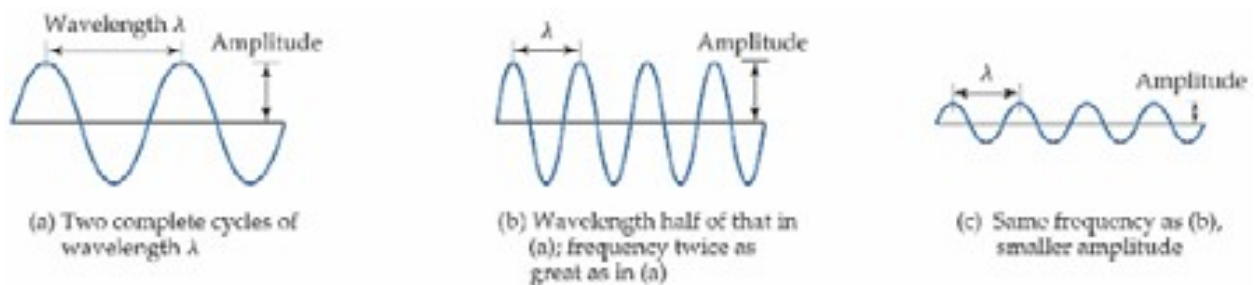


Figure 7.4: Wavelength and Frequency

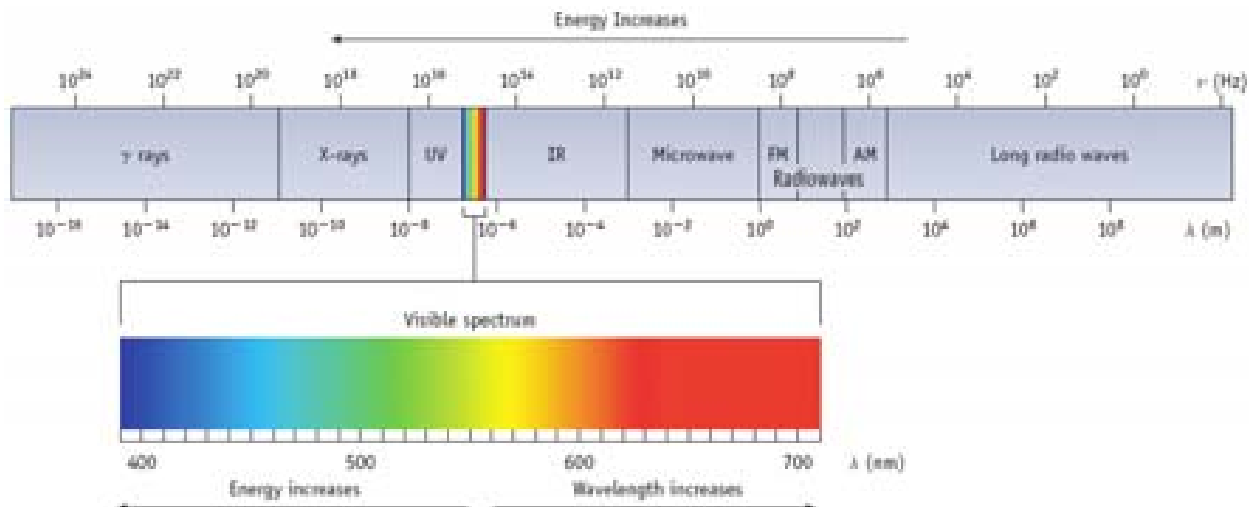


Figure 7.5: Electromagnetic Spectrum

- long wavelength $\epsilon \rightarrow$ small frequency
- short wavelength $\epsilon \rightarrow$ high frequency
- Therefore, wavelength and frequency are inversely related.

7.4 Wavelength-Frequency Relationship

- All electromagnetic radiation moves at the same speed, specifically the speed of light.
 $c = 2.998 \times 10^8 \text{ m/s}$.
- The inverse relationship between frequency and wavelength for electromagnetic radiation is

$$\nu = \frac{c}{\lambda} \quad (7.1)$$

where c is the speed of light, λ (lambda) is the wavelength, and ν (nu) is the frequency.

Table 7.1: Common Wavelength Units

Unit	Symbol	Length (m)	Type of Radiation
Angstrom	Å	10^{-10}	X-ray
Nanometer	nm	10^{-9}	Ultraviolet, visible
Micrometer	μm	10^{-6}	Infrared
Millimeter	mm	10^{-3}	Microwave
Centimeter	cm	10^{-2}	Microwave
Meter	m	1	TV, radio
Kilometer	km	1000	Radio

7.5 Common Frequency Unit

- Frequency is typically expressed in cycles per second, a unit also called a **hertz (Hz)**. A **hertz** is equivalent to reciprocal second.
- A particular FM radio station at a frequency of 101.3 MHz, which could also be expressed as:

$$101.3 \times 10^6 \text{ or } 101.3 \times 10^6 \text{ s}^{-1}$$

7.6 Hot Objects

- Solids emit radiation when heated (referred to as *Blackbody radiation*).
- For example, a stove burner glows bright red, while the filament in a tungsten light bulb glows white.
- Hotter objects glow more white.
- Wavelength distribution of radiation clearly depends on temperature.

7.7 Quantization of Energy

- An object can gain or lose energy by absorbing or emitting radiant energy in discrete QUANTA.
- **Energy of radiation is proportional to frequency**

$$E = h \cdot \nu \tag{7.2}$$

where $h = 6.626 \times 10^{-34} \text{ J} \cdot \text{s}$ is Planck's constant.

7.8 Photoelectric Effect

- Shining light on a clean metal surface causes electrons to be ejected.
- For example, cesium metal will emit electrons when irradiated by light with a frequency of $4.60 \times 10^{14} \text{ Hz}$ or greater. Electrons from cesium will not be ejected if lower frequencies are used.
- Einstein suggested that an incident stream of tiny energy packets (quanta) were responsible for causing electrons to be ejected from the metals surface.
- These discrete energy packets/particles are referred to as "photons".
- Once electrons were ejected, a current could be measured.

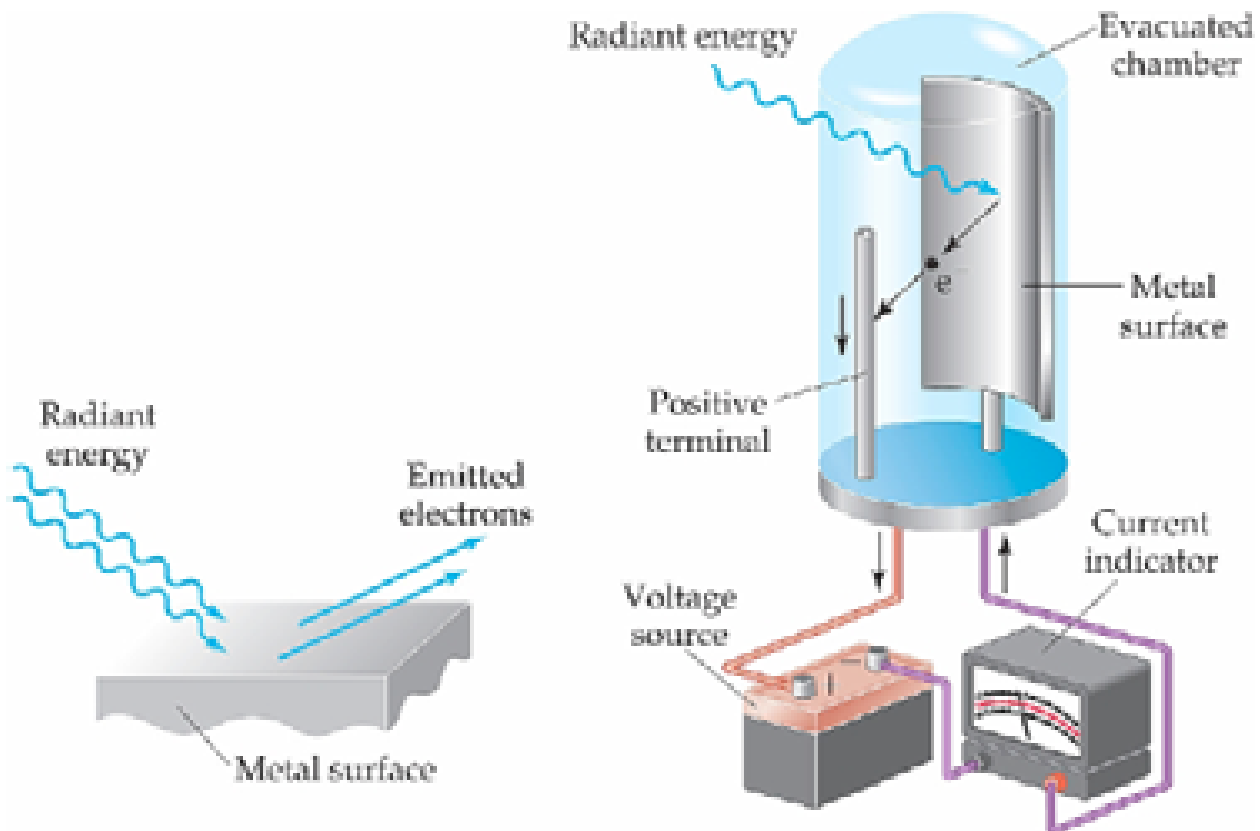


Figure 7.6: Photoelectric Effect

- Einstein was awarded the Nobel Prize in Physics in 1921 for his work on the photoelectric effect.
- **Energy of Photon** $= E = h\nu$, where the radiant energy is quantized.
- Radiant energy must be sufficient to overcome the attractive force between the electron and the metal itself.
- If an incident photon has more energy than required to remove an electron, the additional energy will be transferred to the electron's kinetic energy (i.e., energy associated with the electron's motion). See photoelectric worked example!

7.9 Continuous Spectrum of Wavelengths from White Light

- **Continuous spectrum** – a spectrum that contains radiation distributed over all wavelengths.
- In the schematic above, a white light source is used that is separated into its component colors by use of a prism.

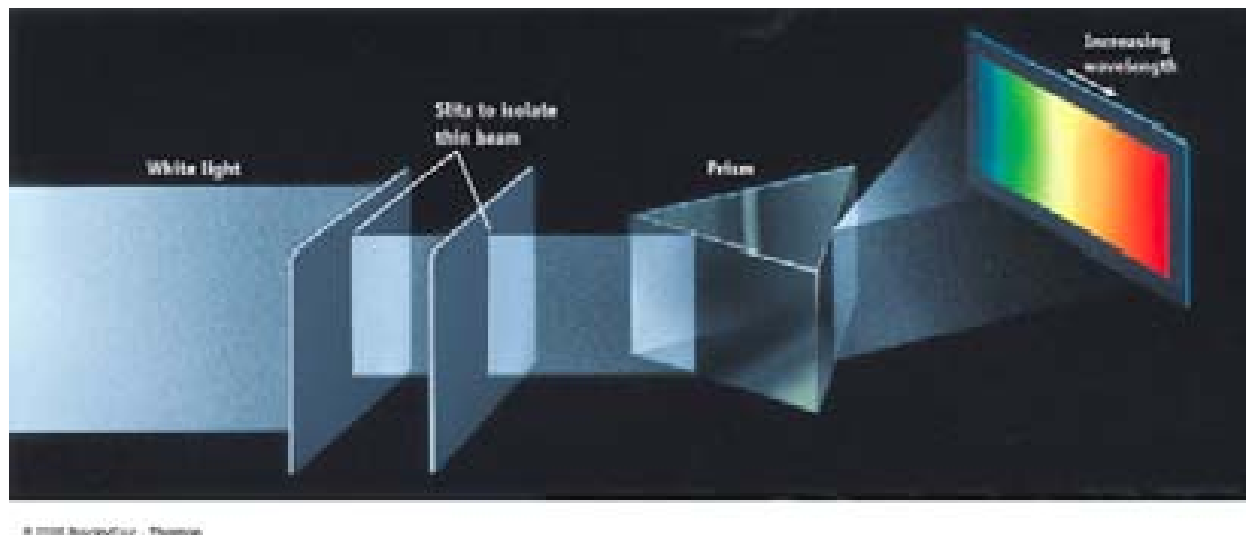


Figure 7.7: Continuous Spectrum of Wavelengths from White Light

7.10 Line Emission Spectrum of Hydrogen

- **Line spectrum** – a spectrum that contains radiation at only specific wavelengths.
- In the schematic above, a potential is applied to a sealed tube of hydrogen at reduced pressure. Passing this light through a prism results in a 4 line pattern, each with its own specific wavelength. The wavelengths in the hydrogen spectrum are: 410 nm (violet), 434 nm (blue), 486 nm (blue-green), and 656 nm (red).

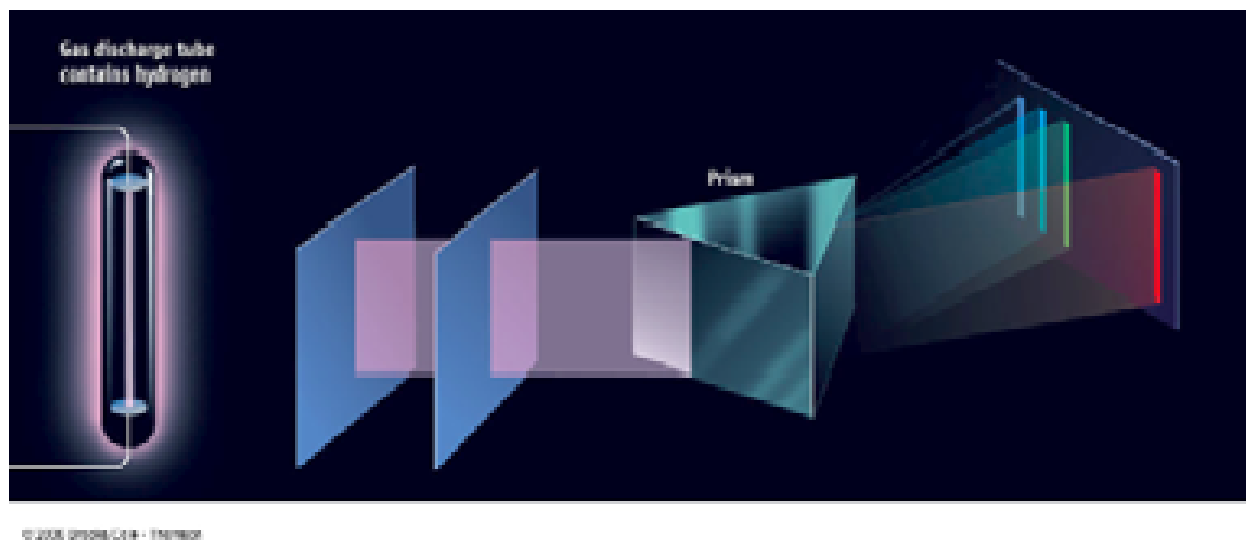


Figure 7.8: Line Emission Spectrum of Hydrogen

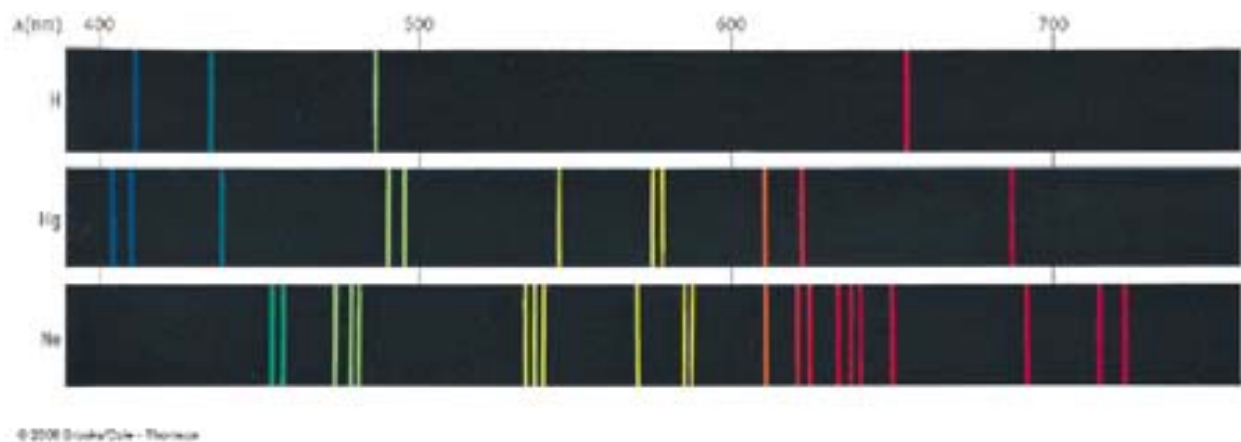


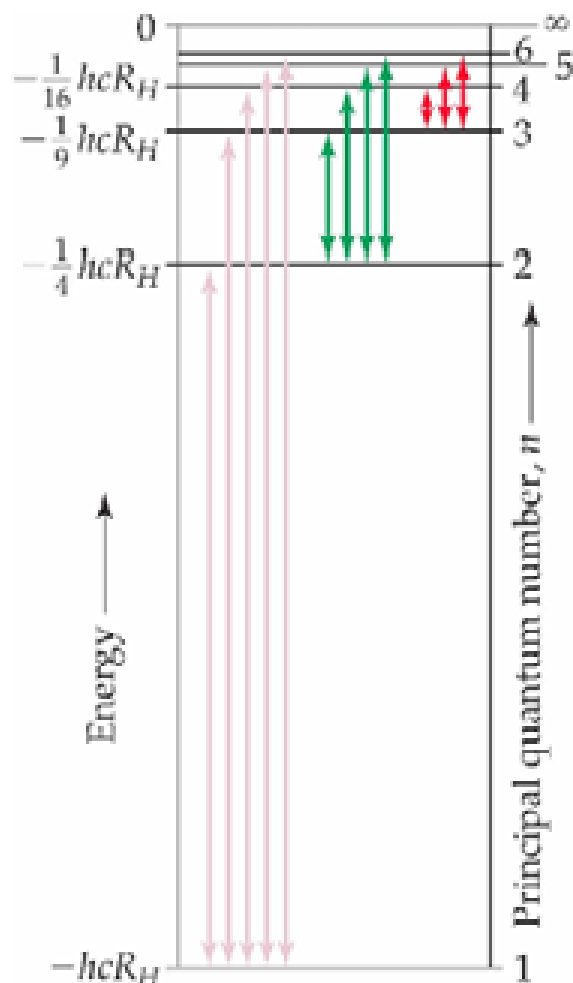
Figure 7.9: Line Emission Spectra of Hydrogen, Mercury, and Neon

7.11 Niels Bohr's Model of the Hydrogen Atom

Model based on the following three postulates:

- Only orbits of certain radii, corresponding to certain definite energies, are permitted for the electron in the hydrogen atom.
- An electron in a permitted orbit has a specific energy and is in an “allowed” energy state. An electron in an allowed energy state will not radiate energy and therefore will not spiral into the nucleus.
- Energy is emitted or absorbed by the electron only as the electron changes from one allowed energy state to another. (This energy is emitted or absorbed as a **photon** (7.2))

7.12 The Energy States of the Hydrogen Atom



$$E_n = -hcR_H \left(\frac{1}{n^2} \right) \quad (7.3)$$

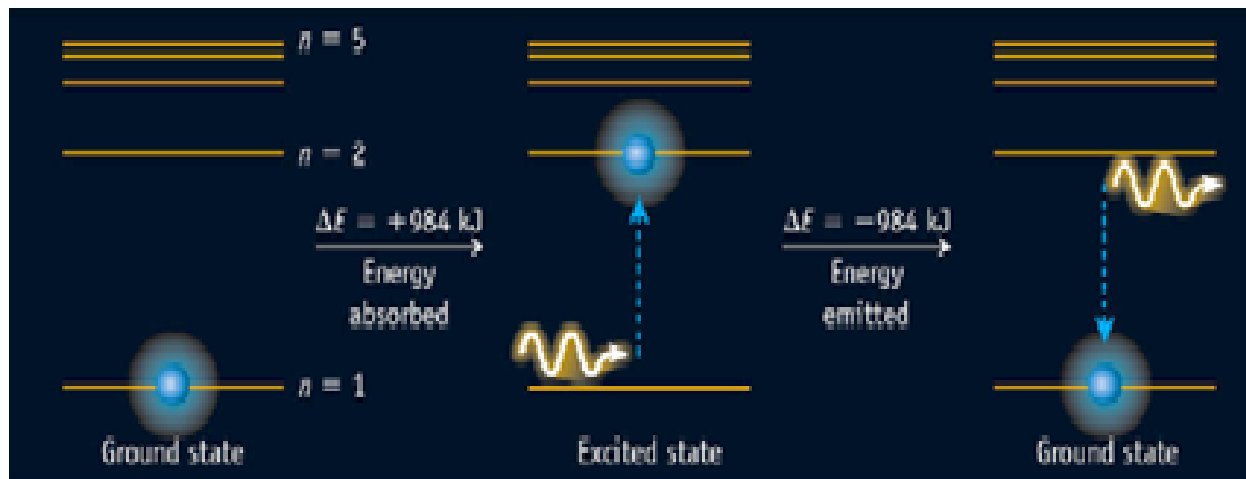
$$= -2.18 \times 10^{-18} J \left(\frac{1}{n^2} \right)$$

- h , c and R_H are **Planck's constant**, the speed of light, and Rydberg's constant, respectively.
- n is called the **principal quantum number**, and takes on whole integer values in $[1, \infty)$.
- The lowest energy state ($n = 1$) is called the **ground state**.
- When an electron occupies the $n = 2$ orbit or higher, the atom is said to be in an **excited state**.

Figure 7.10: The Energy States of the Hydrogen Atom

7.13 Electronic Transitions in the Hydrogen Atom

- An electron can move to a higher energy state if energy is absorbed.
- Conversely, radiant energy is emitted when the electron falls to a lower energy state.



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Figure 7.11: Electron Transitions in the Hydrogen Atom

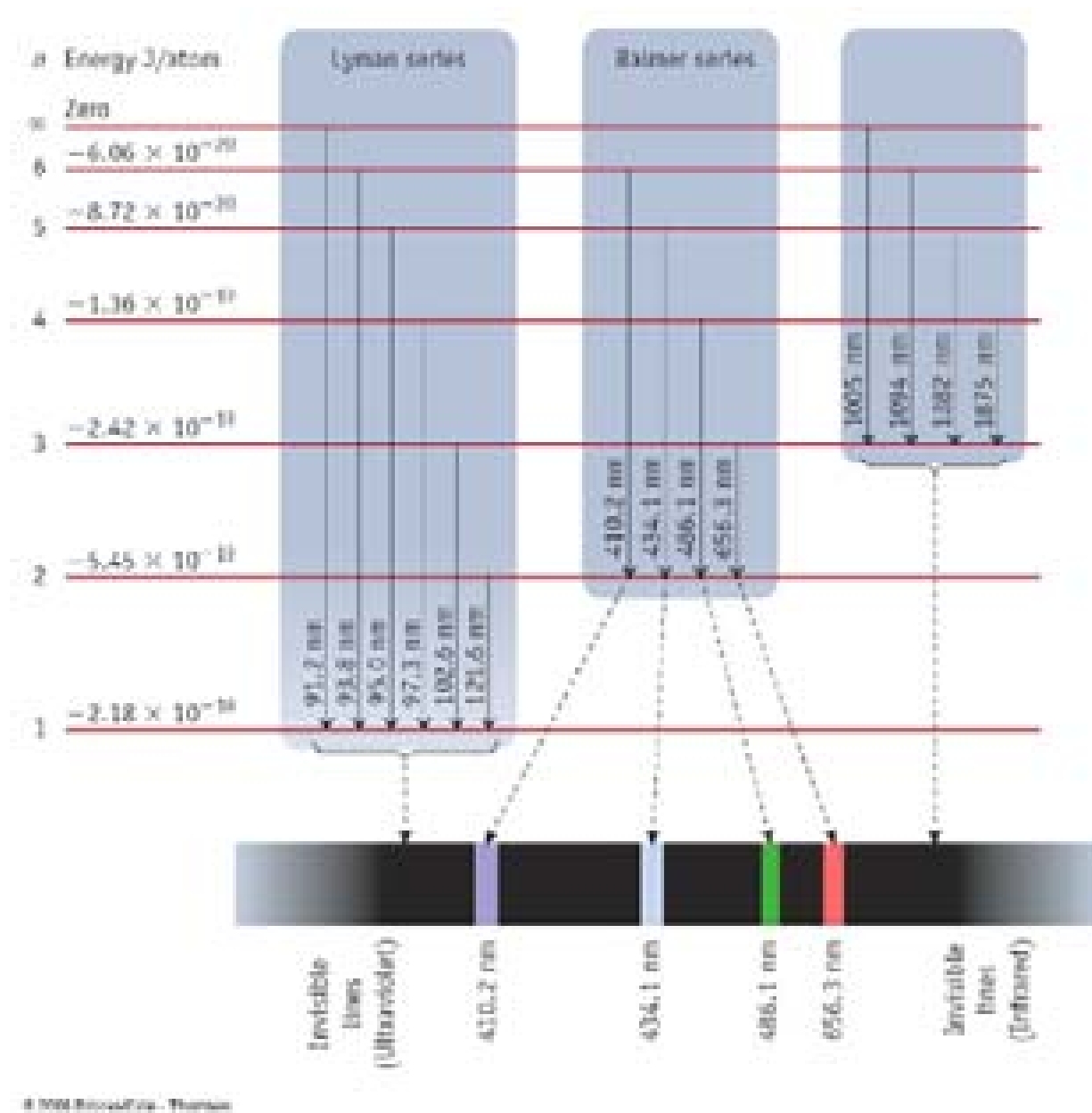


Figure 7.12: Paschen Series

- Notice that the energy is lowest (most negative) for $n = 1$.
- The energy difference between the *final* and *initial* states is given by the following equation:

$$\begin{aligned}
 \Delta E &= E_{\text{final}} - E_{\text{initial}} \\
 &= E_{\text{photon}} \\
 &= h\nu
 \end{aligned}
 \tag{7.4}$$

- Substituting (7.3) into the above equation, while taking into account that (7.1), the

following results:

$$\begin{aligned}
 \Delta E &= h\nu \\
 &= \frac{hc}{\lambda} \\
 &= -2.18 \times 10^{-18} J \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right) \\
 &= 2.18 \times 10^{-18} J \left(\frac{1}{n_i^2} - \frac{1}{n_f^2} \right)
 \end{aligned} \tag{7.5}$$

- Another useful equation for directly calculating wavelength is as follows:

$$\frac{1}{\lambda} = R_H \left(\frac{1}{n_i^2} - \frac{1}{n_f^2} \right) \tag{7.6}$$

7.14 The Wave Behavior of Matter

- Louis de Broglie (1892-1987) suggested that a stream of particles should also exhibit properties of a wave.
- He proposed that the characteristic wavelength of a particle (e.g., an electron) depends on its mass (m) and velocity (v). The quantity mv is the **momentum** and h is simply **Planck's constant**.

$$\lambda = \frac{h}{mv} \tag{7.7}$$

- The equation provides sufficient wavelengths for particles of small mass (e.g., an electron) but not for ones for large mass. Due to the inverse relationship, as the mass gets very large, the corresponding wavelength becomes small and thus difficult to observe experimentally.

7.15 Heisenberg's Uncertainty Principle

- Werner Heisenberg (1901-1976). The **Heisenberg uncertainty principle** states that there is an inherent uncertainty in the precision with which we can simultaneously specify the position and momentum of extremely small particles, such as an electron.
- Mathematically:

$$\Delta x \cdot \Delta(mv) \geq \frac{h}{4\pi} \tag{7.8}$$

- where Δx is the uncertainty in the particle's position and $\Delta(mv)$ is the uncertainty in its momentum.

7.16 Quantum Mechanics and Atomic Orbitals

- Erwin Schrödinger (1887-1961), an Austrian physicist, developed an equation to describe both the wave- and particle-like behavior of the electron.
- Requires the use of complex calculus.
- Solving the Schrödinger equation provides a series of mathematical functions called **wave functions** that describe the electron in an atom.
- The wave functions are denoted by the lowercase Greek letter ψ (psi).
- ψ^2 is the probability or electron density. It relates to the probability of finding an electron in a certain region of space at a given instant.

7.17 Electron-Density Distribution in a Hydrogen Atom

- Diagram represents the probability of finding an electron in the ground state of a hydrogen atom.

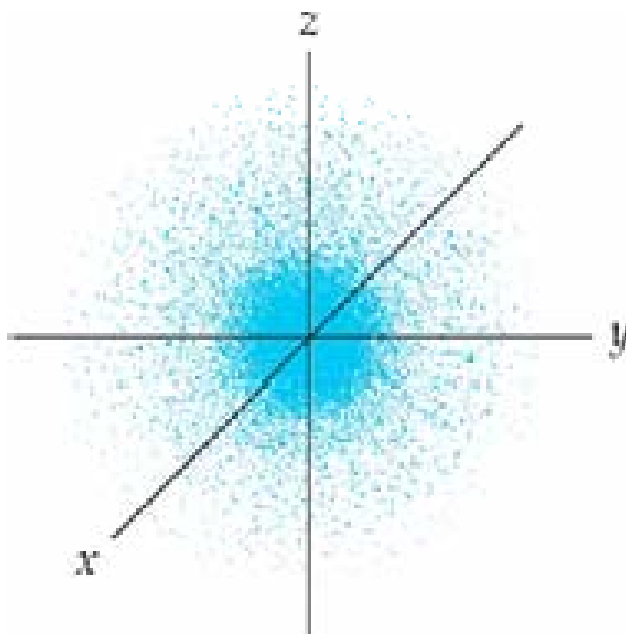


Figure 7.13: Electron-Density Distribution in a Hydrogen Atom

7.18 Orbitals and Quantum Numbers

- The wave function ψ depends on four quantum numbers (n , l , m_l , and m_s)
- Principal quantum number n** that can have integral values of 1, 2, 3, As n increases, the orbital becomes larger and the electron is further from the nucleus.

- Energy and size of the electron.

Angular momentum quantum number l can take on integral values from 0 to $n - 1$ for each defined value of n .

- Shape of the orbital

Magnetic quantum number m_l that can take values of $-l$ to $+l$, including 0.

- Orientation

Spin magnetic quantum number m_s are two possible values are $+\frac{1}{2}$ (spin pointing up) and $-\frac{1}{2}$ (spin pointing down).

7.19 Shells and Subshells

Electron Shell A collection of orbitals with the same value of n .

Subshell A set of orbitals that have the same n and l values.

Table 7.2: Value of l , Corresponding Letter Designation and Number of Orbitals in a Subshell

Value of l	Corresponding Subshell Label	Number of Orbitals in Subshell
0	s	1
1	p	3
2	d	5
3	f	7

Table 7.3: Relationship among n , l , and m_l values

n	Possible Values of l	Subshell Designation	Possible Values of m_l	Number of Orbitals in Subshell	Total Number of Orbitals in Shell
1	0	$1s$	0	1	1
2	0	$2s$	0	1	4
	1	$2p$	1, 0, -1	3	
3	0	$3s$	0	1	9
	1	$3p$	1, 0, -1	3	
	2	$3d$	2, 1, 0, -1, -2	5	
4	0	$4s$	0	1	16
	1	$4p$	1, 0, -1	3	
	2	$4d$	2, 1, 0, -1, -2	5	
	3	$4f$	3, 2, 1, 0, -1, -2, -3	7	

7.20 The p Orbitals

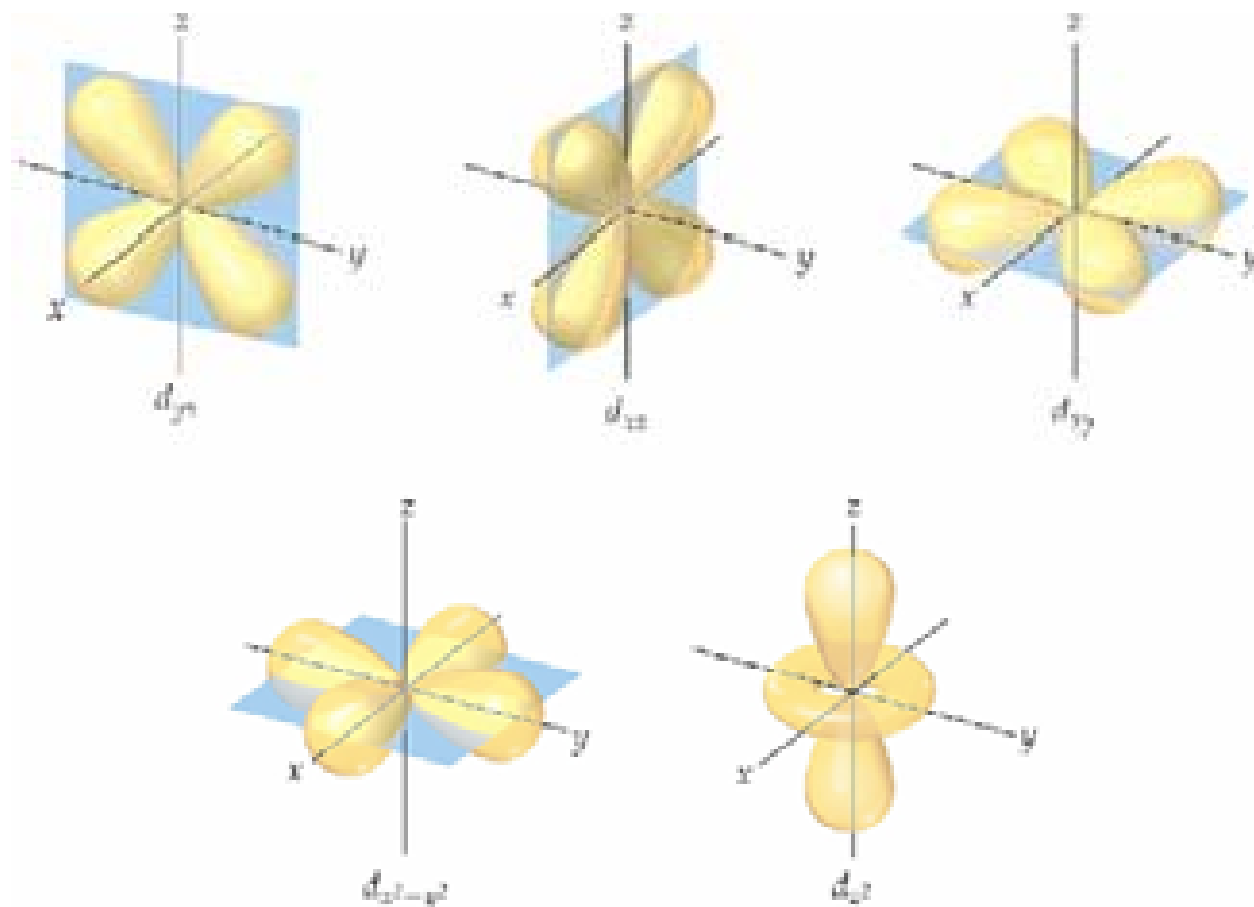


Figure 7.14: The p Orbitals

Note the three different orientations ($m_l : -1, 0, 1$) on a Cartesian coordinate axis system! In each orbital, there are two lobes that are separated by a nodal plane (a point at which the electron density is zero).

7.21 The d orbitals

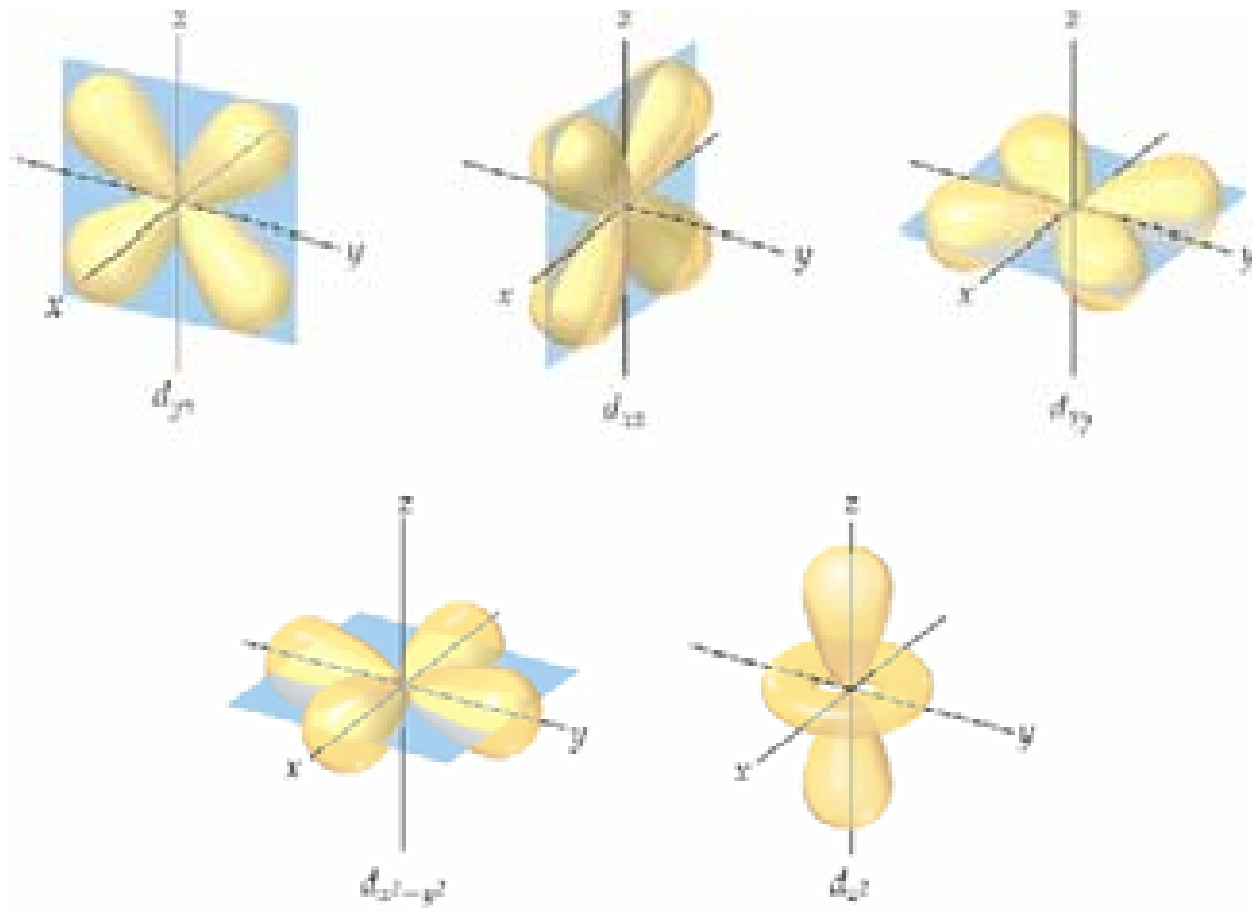


Figure 7.15: The d Orbitals

These are the representations of the five d orbitals ($m_l : -2, -1, 0, 1, 2$)

7.22 Many-Electron Atoms - Relative Orbital Energy Levels

The energies follow the order:

$$ns < np < nd < nf$$

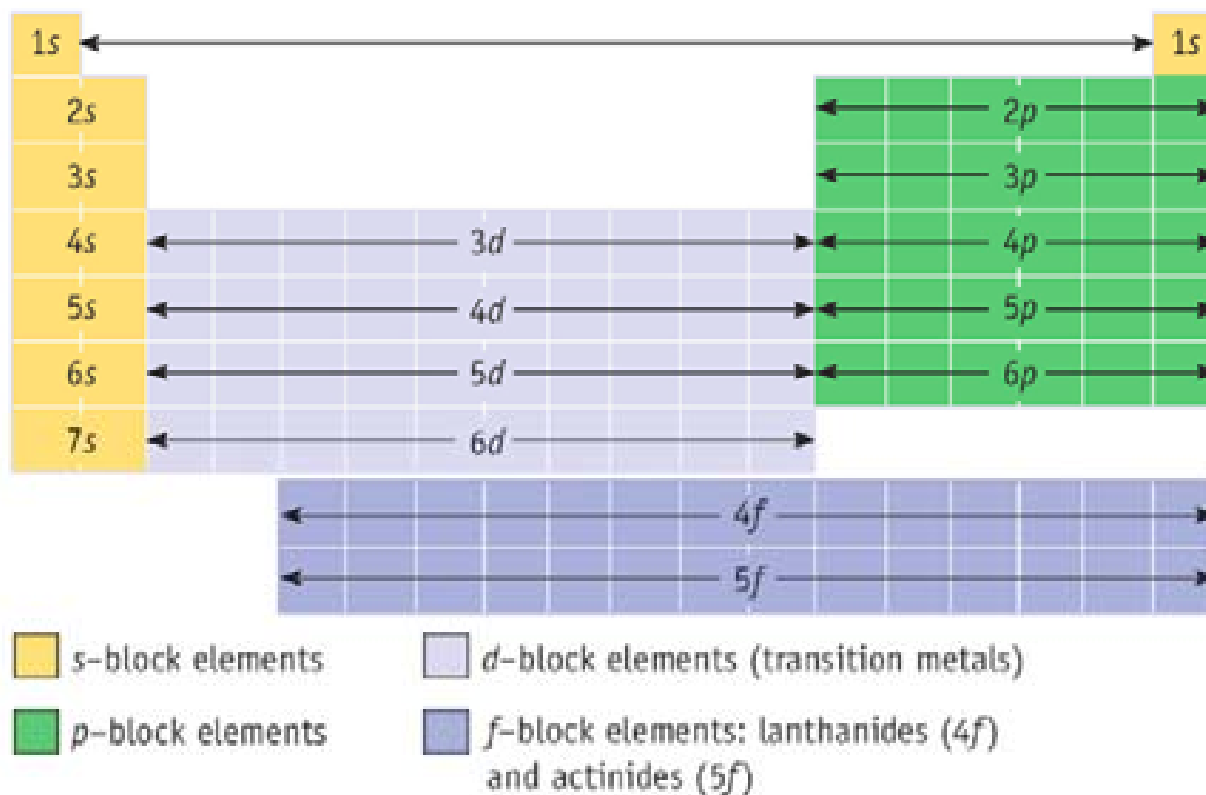
e.g., $3s < 3p < 3d$

7.23 Electron Configurations

- We use the **Aufbau Principle** for filling electrons from bottom to top.
- **Pauli Exclusion Principle** – a maximum of two electrons can be placed in an orbital and must have opposite spin.

- **Hunds Rule** – for degenerate orbitals, the lowest energy is attained when the number of electrons with the same spin is maximized.

7.24 Subshell Filling Order



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Figure 7.16: Periodic Table Levels