Chapter Objectives:
• Understand the relationships between wavelength, frequency, and energy of light.
• Understand the origin of atomic line spectra.
• Learn how the quantum numbers are used to understand the arrangement of electrons in atoms.
• Learn how to predict trends in atomic radius, effective nuclear charge, ionic radius, ionization energy, and electron affinity, from the positions of the elements on the periodic table.

Quantum Mechanics: A Theory That Explains the Behavior of the Absolutely Small
• The distribution of electrons in atoms is explained in modern science using a branch of physics called quantum mechanics, which describes the behavior of things of extremely small things.
• Explaining the behavior of extremely small things, like electrons in atoms (whose arrangement gives rise to an element’s chemical properties) requires completely different ideas from the way that we model the behavior of larger objects.
• The quantum-mechanical model of the atom explains why the periodic table of the elements has the form that it does, and provides the basis of our understanding of how chemical bonds form.

A Brief History of Light
The Road to Quantum Mechanics is Paved with Good Intentions
• For many years, scientists debated about whether light was best understood as a stream of particles or as a wave phenomena.
  - Robert Hooke (1665) — light is a wave.
  - Isaac Newton (late 1600’s) — light is a stream of particles.
  - Thomas Young (1801) — explained diffraction using the wave theory of light.
  - James Clerk Maxwell (1864) — developed a mathematical description of EM radiation in terms of oscillating fields of electrical and magnetic waves, known as Maxwell’s equations:
    \[ \mathbf{E} \times \mathbf{A} = q \mathbf{E} \]
    \[ \mathbf{B} \times \mathbf{A} = 0 \]
    \[ \mathbf{E} \times \mathbf{H} = \frac{\partial \mathbf{B}}{\partial t} \]
    \[ \mathbf{B} \times \mathbf{H} = \mu_0 \mathbf{J} + \frac{\partial \mathbf{D}}{\partial t} \]

Light and Matter
• We now know that both light and electrons exhibit wave-particle duality — that is, some properties of each are best described with a wave model, and some properties are best described by a particle model.
• Quantum mechanics, which unifies the wave and particle models of light, arose from a combination of the attempts by physicists and chemists to understand both the structure of the atom, and their attempts to understand the behavior of light.
• Many basic clues to the structure of atoms came from the study of light. (This is because light is ultimately emitted by matter).

Electromagnetic Radiation
• Visible light, infrared radiation, ultraviolet light, radio waves, microwaves, X-rays, and gamma rays are types of electromagnetic (EM) radiation, which consist of energy propagated by electric and magnetic fields that are perpendicular to each other, and that alternately increase and decrease in intensity as they move through space. (movie)
Frequency, Wavelength, and Amplitude

- EM radiation traveling through a vacuum behaves in some ways like ocean waves traveling through water. The wave properties of EM radiation are described by three variables:
  - Wavelength ($\lambda$, lambda) — the distance from one wave peak to the next (or from one wave trough to the next) (units of length, m).
  - Amplitude — the height of the wave, measured from the center line between peak and trough; the intensity or brightness of the light is proportional to the square of the amplitude.
  - Frequency ($\nu$, nu) — the number of wave peaks that pass by a given point per unit of time (units of cycles per second, 1/second, s$^{-1}$, Hz [Hertz]).

The Speed of Light: Relating $\nu$ and $\lambda$

- In a vacuum, all EM radiation travels at the same speed: $2.99792458 \times 10^8$ m/s, known as $c$, the speed of light.
- Because the speed of light is a constant, frequency and wavelength are inversely proportional to each other:
  $$c = \lambda \nu = 3.00 \times 10^8 \text{ m s}^{-1}$$
- What’s different about each type of EM radiation is its wavelength and frequency (and also the energy of the radiation [later]).
- Visible light extends from wavelengths of 750 nm (red) to 400 nm (violet); “white light” is a combination of all of these wavelengths of radiation.

The Electromagnetic Spectrum

- The colors that we see around us results from an object absorbing some wavelengths of visible radiation and reflecting others back to our eyes.
- White light from the sun can be spread out with a prism to form a continuous spectrum, with no breaks in between the colors:
- Visible light represents only a small portion of the continuum of radiant energy known as the electromagnetic spectrum.
  - Higher frequency light includes ultraviolet (UV) rays, X-rays, and gamma rays.
  - Lower frequency light includes infrared (IR) radiation, microwaves, and radio waves.

Examples: Frequency and Wavelength

1. A dental hygienist uses x-rays ($\lambda = 1.00 \text{ Å}$ [Å = angstrom; 1 Å = $10^{-10}$ m]) to take a series of dental radiographs while the patient listens to a radio station ($\lambda = 325$ cm) and looks out the window at the blue sky ($\lambda = 473$ nm). What is the frequency (in s$^{-1}$) of the EM radiation from each source?

Answer: $3.00 \times 10^{18}$ s$^{-1}$, $9.23 \times 10^{7}$ s$^{-1}$, $6.34 \times 10^{14}$ s$^{-1}$
Examples: Frequency and Wavelength

2. What is the wavelength (in nm) of yellow light with a frequency of $5.22 \times 10^{14}$ Hz?

Answer: 575 nm

Properties of Waves — Interference

- Waves can interfere with each other constructively or destructively:
  - Wave amplitudes add
  - Wave amplitudes cancel

Properties of Waves — Diffraction

- A wave bends around an object that is comparable in size to its wavelength, producing a new set of waves in a process called diffraction:
  - A stream of particles, on the other hand, would either be blocked by the barrier, or sail through the opening without being diffracted:

Houston, We've Got A Problem

- In the late 19th and early 20th centuries, three newly discovered phenomena demonstrated that light not only has wave properties, but also particle properties:
  1. blackbody radiation
  2. the photoelectric effect
  3. atomic line spectra
- Ultimately, an entirely new way of looking at energy was required to understand these phenomena. This explanation — quantum mechanics — led to our modern understanding of the structure of the atom.

Blackbody Radiation

- Blackbody radiation is the visible glow that solid objects give off when heated, as a result of the vibration of electrons within the solid (e.g., the heating element of a metal stovetop, the hot metal filament in a light bulb).
- When iron is heated, it first glows a dull red color, becomes orange as the temperature increases, then a blinding white glare, and eventually a dull blue.
  - The longer wavelengths (red) have a lower intensity, and the shorter wavelengths (white, blue) have a higher intensity.
  - If this trend were to continue, the intensity would be even higher in the UV range; instead, the intensity reaches a maximum, and then falls off with shorter wavelengths.
Blackbody Radiation

- Classical physics was unable to explain the variation in radiation emitted at different temperatures.
- In 1900, Max Planck (Nobel Prize, 1918) concluded that the energy radiated by a heated object can’t be continuously variable; instead the energy is emitted only in discrete amounts, or quanta (singular, quantum). [Think stairs instead of ramps.]
- Each change in the energy of the atoms in a heated substance results from the gain or loss of these “packets” of energy. The amount of energy, $E$, associated with each quantum of energy is given by the Planck equation:

$$ E = h \nu $$

$h = $ Planck’s constant $= 6.626 \times 10^{-34}$ J s

The Photoelectric Effect

- The photoelectric effect occurs when light shines on a metal, causing it to emit electrons. [movie]
  - If the frequency of light is below a specific threshold frequency, $\nu_0$, no electrons are emitted, no matter how bright the light is.
  - If the frequency is above $\nu_0$, the number of electrons emitted increases with the intensity of the light. The kinetic energy of the electrons increases with the frequency.

Examples: Energy of a Photon

3. (a) What is the energy of a photon of radar radiation with $\nu = 3.35 \times 10^8$ Hz? (b) What is the energy of a mole of these photons?

Answer: (a) $2.22 \times 10^{-25}$ J; (b) 0.134 J/mol

4. (a) What is the energy (in kJ/mol) of blue light with a wavelength of 432 nm? (b) If a single pulse of this light delivers 5.00 mJ of energy, how many photons does it contain?

Answer: (a) 277 kJ/mol; (b) $1.09 \times 10^{16}$ photons

Examples: Energy of a Photon

5. The biological effects of EM radiation become more serious as the energy of the radiation increases: Infrared radiation has a pleasant warming effect; ultraviolet radiation causes skin to tan or sunburn; and X rays and gamma rays (“ionizing radiation”) can knock electrons from molecules, which can seriously damage large biological molecules.

What energies (in kJ/mol) are associated with the following wavelengths: infrared radiation (IR) with $\lambda = 1.55 \mu$m; ultraviolet (UV) light with $\lambda = 250$ nm, X rays with $\lambda = 5.49$ nm, and gamma rays with $\lambda = 0.0255$ pm?

Answer: IR 77.2 kJ/mol; UV 479 kJ/mol; X-ray 2180 kJ/mol; $\gamma$-ray $4.69 \times 10^9$ kJ/mol
Chapter 7 A Quantum Model of Atoms

So, Is Light A Wave Or A Particle? . . .

Light as a wave

Light as a stream of particles (photons)

. . . It’s Both! (?????)

• In classical electromagnetic theory, light was pictured as purely a wave phenomenon, with an energy that was continuously variable.
  – The wave model explains phenomena such as refraction, diffraction, etc., that don’t make sense by treating light as a particle.
• Now, we are suddenly picturing light as a shower of particles, each having an energy of \( h \).
  – The particle model explains blackbody radiation and the photoelectric effect, that don’t make sense by treating light as a wave.
• It is now known that in addition to behaving as waves, light can also behave as small particles.

The Wavelike Properties of Matter

• So now we have light having properties of waves and of particles. Louis de Broglie (1924, Nobel Prize, 1929) further blurred the distinction between matter and radiant energy by suggesting that if light can have particle-like properties, then matter can have wave-like properties.
• By combining the equation for the energy of a photon and Einstein’s equation for the relationship of mass and energy, and replacing the speed of light \( c \) with the speed of a particle \( v \), we can calculate the wavelength of a particle of matter:
  \[
  E = hv = h\frac{c}{\lambda}, \quad E = mc^2
  \]
  \[
  \lambda = \frac{h}{mv} \quad \text{the de Broglie relation}
  \]

Examples: de Broglie Wavelength

1. Calculate the de Broglie wavelength in nm of:
   a. an electron with a speed of \( 2.2 \times 10^6 \) m/s, \( m_e = 9.11 \times 10^{-31} \) kg) and
   b. a two ton car (909 kg) moving at 55.0 mi/hr (24.5 m/s).

   Answer: (a) 0.331 nm; (b) \( 2.96 \times 10^{-29} \) nm

Electron “Waves”

• Electrons are particles, and have a mass associated with them. However, they can diffract just like light does, and produce interference patterns, which means they have wave properties. [movie]
  – In 1927, Clinton Davission and George Thomson demonstrated electron diffraction by scattering electrons off a nickel crystal (Nobel Prize, 1937). [Thomson was the son of J. J. Thomson, who won a Nobel Prize for the discovery of the electron.]
Wave-Particle Duality

- Thus, both light and matter exhibit **wave-particle** duality: they are both wave-like and particle-like.
  - For matter with large masses (like baseballs or people) the de Broglie wavelength is so small that wave-like properties are negligible, and they behave “entirely” like particles.
  - For matter with small masses (like electrons or protons) the de Broglie wavelength is large enough to be measurable, and the wave properties of these particles become important.
- In order to model how electrons are arranged inside atoms, we have to take into account both their particle properties and their wave properties.

Applications of Quantum Mechanics

- Quantum mechanics may seem really abstract, and not connected to the everyday world, but there are a lot of things that we use every day that depend on the principles of QM:

Atomic Line Spectra

- At the same time that physicists were struggling to understand light, chemists were trying to understand the structure of matter from the atomic standpoint.
- One of the earliest clues to the arrangement of electrons inside the atom came from the discovery of **line spectra**.
- When an electric current is passed through a sample of an element in the gas phase, the sample emits light (e.g., neon or fluorescent lights). If this light is passed through a prism, we see a **line spectrum** (atomic emission spectrum), consisting of a series of discrete lines separated by blank areas. 

Atomic Fingerprints

- Each element has its own set of wavelengths of radiation that it emits when energetically excited; these spectral lines can be used as a “fingerprint” for identifying that element.
Chapter 7 A Quantum Model of Atoms

Flame Tests and Fireworks

• The colors of a flame can be used to identify what metal ions are present in a solution (flame test).

• Metal salts are used in fireworks to produce different colors.

• The element helium was first identified in the Sun, before it was ever isolated on Earth, from its pattern of lines in the solar spectrum.

Emission and Absorption Spectra

• Elements absorb the same wavelengths of light that they radiate when they are heated. By passing white light through a sample and observing what wavelengths of light are subtracted from it, an absorption spectrum is produced.

The Balmer-Rydberg Equation

• The Balmer-Rydberg equation is an empirically derived equation that allows us to predict the position and wavelength of any of the lines in a given series for the hydrogen atom:

\[ \frac{1}{\lambda} = R_n \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \]

where \( R_n = \text{Rydberg constant} = 1.097 \times 10^{-2} \text{ nm}^{-1} \)

• Unfortunately, there was nothing to explain why this equation worked, or why the hydrogen atom produced line spectra as opposed to a continuous spectrum.

Examples: The Balmer-Rydberg Equation

1. What are the two longest-wavelength lines (in nm) in the Lyman series (\( n_1 = 1 \)) of the hydrogen spectrum?

\[ \frac{1}{\lambda} = (1.097 \times 10^{-2} \text{ nm}^{-1}) \left( \frac{1}{1^2} - \frac{1}{2^2} \right) = 8.228 \times 10^{-3} \text{ nm}^{-1} \]

\[ \lambda = 121.5 \text{ nm} \]

\[ \frac{1}{\lambda} = (1.097 \times 10^{-2} \text{ nm}^{-1}) \left( \frac{1}{1^2} - \frac{1}{3^2} \right) = 9.751 \times 10^{-4} \text{ nm}^{-1} \]

\[ \lambda = 102.5 \text{ nm} \]

Why Are There Atomic Line Spectra?

• The existence of line spectra implies that only certain energies are allowed for an electron inside an atom — the energy levels in atoms are quantized, just like the energy of photons.

• The existence of line spectra is related to the structure of the atom. To understand line spectra, we need a model for how electrons are arranged in atoms, and the energy that the electrons possess.

• This led to the development of the Bohr model of the atom, and then to quantum mechanics.
Chapter 7 A Quantum Model of Atoms

**The Bohr Model of the Atom**

- Ernest Rutherford, after discovering the nucleus (1911, Nobel Prize in Chemistry, 1908), proposed that the atom looked like a miniature solar system, with electrons orbiting the nucleus just like planets orbiting the Sun. This was known as the Rutherford Model of the atom.

- However, moving charges emit EM radiation, and would continuously lose energy; in this model an electron would crash into the nucleus in about $10^{-10}$ s.

- Since atoms are obviously more stable than this, this model is still not right.

**The Bohr Model of the Hydrogen Atom**

- In 1913, Neils Bohr (Nobel Prize, 1922) suggested a model for the H atom that explained line spectra.

- In this model, the energy levels in atoms are quantized, having only certain allowed energy levels associated with fixed electron orbits called stationary states.

$$E = -\frac{2\pi^2 m e^2 Z^2}{h^2 n^2}$$

$$= -\left(2.178 \times 10^{-18} J \right) \left(\frac{Z^2}{n^2}\right)$$

**Energy Absorption in the Bohr Model**

- When an atom absorbs an amount of energy equal to the energy difference between two fixed orbits ($E_1$), an electron jumps from the low energy orbit (the ground state) to a higher-energy orbit (an excited state).

**Energy Emission in the Bohr Model**

- When an atom releases energy, the electron falls back down to the ground state, releasing a photon of light which corresponds exactly to the energy difference ($E_i$) between orbits.

- In this model, line spectra arise because the atom’s energy has only certain allowed orbits, and atoms can absorb or emit energy only in these “chunks.”
Limitations of the Bohr Model

• The Bohr model rationalized the existence of line spectra, and mathematically predicted the wavelengths of radiation emitted by the hydrogen atom in its line spectrum:

\[ \Delta E = -2.178 \times 10^{-18} \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \]

• Unfortunately, the Bohr model couldn’t explain where these fixed electron orbits came from, and failed to predict the location of line spectra for elements with more than one electron.

• Ultimately, the ideas behind the Bohr model became incorporated into quantum mechanics.

The Quantum Mechanical Model of the Atom

• The wave and particle descriptions of matter and energy were combined independently by Erwin Schrödinger in 1926 (Nobel Prize, 1933) and Werner Heisenberg in 1927 (Nobel Prize, 1932) in the quantum mechanical model of the atom.

  – Quantum mechanics is the branch of physics which describes the properties of light and matter at the atomic scale.

  – Quantum mechanics unifies the particle and wave models into a single description of reality.

• In quantum mechanics, we abandon the notion of an electron as a small particle moving around the nucleus in a defined path and concentrate on its wave-like properties.

Standing Waves

• Schrödinger used the mathematics of standing waves to model electrons inside atoms.

• Standing waves are fixed on either end, and vibrate up and down (the wave itself does not move, hence the name).

• There is a limitation on the number of “half-wavelengths” that are allowed in a standing wave; anything other than a whole number of half-waves produces destructive interference, and cancels out.

Standing Waves in Atoms

• If an electron in an H atom is modeled as a standing wave, only circular orbits with a whole number of wavelengths “fit” the size of the atom.

  • All other orbits produce destructive interference, and are not allowed.
**The Schrödinger Wave Equation**

- The quantum mechanical model is framed in the form of the Schrödinger wave equation.

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

- The solutions to the wave equation are called wave functions, or orbitals, represented by the Greek letter \( \psi \) (psi). These are equations that encode what’s known about a particle with a given energy.

- The Schrödinger equation can be solved exactly only for the hydrogen atom (one proton and one electron), but very good approximate solutions for multi-electron atoms can be found starting with the basic functions for the hydrogen atom.

**The Meaning of the Uncertainty Principle**

- What the uncertainty principle implies is that we can never know both the position and the velocity of an electron beyond a certain level of precision.
  - If we know the velocity with a high degree of certainty, the position must be uncertain.
  - If we know the position exactly, we can’t know the velocity.
  - We cannot know the exact path an electron takes as it moves around the nucleus. All we can compute is the probability that an electron is in a certain location at a certain time.

- Essentially, we observe either the particle or the wave behavior, but not both at the same time.

**Electrons and Probability**

- The probability of finding an electron within a certain region of space in an atom is given by \( \psi^2 \).

\[ \int_{-\infty}^{\infty} \psi^2 \, dx \, dy \, dz = 1 \]

**The Heisenberg Uncertainty Principle**

- Heisenberg showed that it is impossible to know simultaneously the exact position and velocity of a particle. This is known as the Heisenberg Uncertainty Principle.

\[ (\Delta x)(m \Delta v) \geq \frac{\hbar}{4\pi} \]

\( \Delta x \) = uncertainty in position along the x-axis

\( m \) = mass of object

\( \Delta v \) = uncertainty in velocity

- Position and velocity are said to be complementary properties: the more you know about one, the less you know about the other.

**Quantum Quotes**

*Anyone who is not shocked by quantum mechanics has not understood it.*  
Niels Bohr

*If someone says that he can think about quantum physics without becoming dizzy, that shows only that he has not understood anything whatever about it.*  
Niels Bohr

*Can nature possibly be as absurd as it seems?*  
Werner Heisenberg

*The theory of quantum electrodynamics describes nature as absurd from the point of view of common sense. And it agrees fully with experiment. So I hope you can accept nature as she is — absurd.*  
Richard Feynman
Quantum Numbers

 quantum model of atoms

Quantum Numbers and Atomic Orbitals

- A wave function for an electron in an atom is called an atomic orbital; this atomic orbital describes a region of space in which there is a high probability of finding the electron.
- Each electron in an atom is described by four different quantum numbers.
  - Principal quantum number, \( n \): energy and size.
  - Angular momentum quantum number, \( l \): shape.
  - Magnetic quantum number, \( m_l \): orientation in space.
  - Spin quantum number, \( m_s \): orientation of spin axis.
- The first three (\( n, l, m_l \)) specify the particular orbital of interest, and the fourth (\( m_s \)) specifies how many electrons can occupy that orbital.

Principal Quantum Number, \( n \)

- The Principal Quantum Number, \( n \) is an integer that can range from 1 to infinity: \( n = 1, 2, 3, ..., \infty \).
- It specifies the size and energy level of an orbital.
  - For one-electron atoms, such as H, the energy depends only on \( n \); for atoms with more than one electron, the energy depends on both \( n \) and \( l \).
  - As \( n \) increases, the number of allowed orbitals increases and the size of those orbitals increases, allowing an electron to be farther from the nucleus; this requires it to be higher in energy.
- All orbitals that have the same value of \( n \) are said to be in the same shell (level).
- The total number of orbitals for a given \( n \) value is \( n^2 \).

Angular Momentum Quantum Number, \( l \)

- The Angular-Momentum Quantum Number (a.k.a. secondary or azimuthal), \( l \), is an integer that ranges from 0 to \( n-1 \): \( l = 0, ..., n-1 \).
- It specifies the shape of an orbital with a particular value of \( n \).
- The angular-momentum quantum number divides the shells into smaller groups of orbitals called subshells (sublevels).
- Usually, a letter code is used to identify \( l \) to avoid confusion with \( n \):
  \[
  l \quad 0 \quad 1 \quad 2 \quad 3 \quad 4 \quad 5 \quad ... \\
  Letter \quad s \quad p \quad d \quad f \quad g \quad h \quad ... 
  \]

Magnetic Quantum Number, \( m_l \)

- The Magnetic Quantum Number, \( m_l \), is an integer which runs from \(-l\) to \(+l\):
  \[
  m_l = -l, ..., 0, ..., +l. 
  \]
- It specifies the orientation in space of an orbital of a given energy (\( n \)) and shape (\( l \)).
- This number divides the subshell into individual orbitals which hold the electrons. There are \( 2l+1 \) orbitals in each subshell, and \( n^2 \) orbitals in each shell.
- Thus the \( s \) subshell has only one orbital, the \( p \) subshell has three orbitals, and so on.
The First Three Quantum Numbers

- This table summarizes the available orbitals in the shells from \( n = 1 \) to \( n = 4 \):

<table>
<thead>
<tr>
<th>Value of ( n )</th>
<th>Allowed Value of ( l )</th>
<th>Subshell Label</th>
<th>Allowed Values of ( m_l )</th>
<th>Subshell</th>
<th>Shell</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>( s )</td>
<td>0</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>2</td>
<td>0</td>
<td>( s )</td>
<td>0</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>1</td>
<td>( \pm 1 )</td>
<td>( \pm 1 )</td>
<td>3</td>
<td>3</td>
<td>4</td>
</tr>
<tr>
<td>3</td>
<td>0</td>
<td>( s )</td>
<td>0</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>1</td>
<td>( \pm 1 )</td>
<td>( \pm 1 )</td>
<td>3</td>
<td>3</td>
<td>4</td>
</tr>
<tr>
<td>2</td>
<td>( \pm 2 )</td>
<td>( \pm 2 )</td>
<td>5</td>
<td>5</td>
<td>9</td>
</tr>
<tr>
<td>4</td>
<td>0</td>
<td>( s )</td>
<td>0</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>1</td>
<td>( \pm 1 )</td>
<td>( \pm 1 )</td>
<td>3</td>
<td>3</td>
<td>4</td>
</tr>
<tr>
<td>2</td>
<td>( \pm 2 )</td>
<td>( \pm 2 )</td>
<td>5</td>
<td>5</td>
<td>9</td>
</tr>
</tbody>
</table>

Spin Quantum Number, \( m_s \)

- The Spin Quantum Number, \( m_s \), has only two possible values:
  \( m_s = \pm \frac{1}{2} \) (\( \uparrow \), spin up) or \( \pm \frac{1}{2} \) (\( \downarrow \), spin down)
- It specifies the orientation of the spin axis of an electron.
- Because an electron spins either clockwise or counter-clockwise, it creates a tiny magnetic field, which can be oriented either up or down.
- \( m_s \) tells us how many electrons can occupy a particular orbital.

The Pauli Exclusion Principle

- The Pauli exclusion principle (Wolfgang Pauli, 1925, Nobel Prize 1945) states that no two electrons in an atom can have the same values for all four of the quantum numbers. This means that:
  - Since two electrons in the same orbital have three of the same quantum numbers (\( n, l, \) and \( m_l \)), they must have opposite spins (the spins are paired).
  - An orbital can hold at most two electrons.
- Substances in which all electrons are paired are diamagnetic — they are not attracted to magnets.
- Atoms with more electrons that spin in one direction than another contain unpaired electrons. These substances are paramagnetic — they are weakly attracted to magnets.

Examples: Quantum Numbers

1. Each of the following sets of quantum numbers is supposed to specify an orbital. However, each set contains one quantum number that is not allowed. Replace the quantum number that is not allowed with one that is allowed.
   a. \( n = 3, l = 3, m_l = +2 \)
   b. \( n = 2, l = 1, m_l = -2 \)
   c. \( n = 1, l = 1, m_l = 0 \)
   d. Is there any such thing as a 3f orbital?
   e. What are the allowed subshells when \( n = 7 \)?
Quantum Mechanics and Line Spectra

- In the quantum mechanical model of the atom, each wavelength in a line spectrum corresponds to an energy transition between orbitals.
  - When an atom in its ground state absorbs energy, an electron in a lower energy level is promoted to a higher-energy orbital in an excited state.
  - The energetically excited atom is unstable, and goes back to the ground state by emitting this excess energy as a photon of EM radiation.

The energy difference between the excited state and the ground state corresponds to the energy of the photon ($h\nu$) which is emitted.

The frequencies of light in line spectra correspond to the energy differences between the orbitals in the atom. [movie]

$l = 0$: the s orbital

- All s orbitals are spherical; since there is only one “direction” for a sphere to point in, the only allowed value for $m_l$ is 0, and there is only one s orbital per shell (1s, 2s, 3s, 4s, etc.)
- The graph below is the probability density of finding an electron in a region of space around the nucleus.
  - The maximum probability of finding an electron in an H atom occurs at a distance of 52.9 pm from the nucleus.

At higher values of $n$, the s orbitals have more spherical regions of high probability of finding an electron, separated by surfaces of zero probability called nodes, where there is zero probability of finding an electron.
  - A node corresponds to a zero-amplitude part of a standing wave or a vibrating string (like a guitar string). [Figure 7.24]
**Chapter 7 A Quantum Model of Atoms**

### $l = 0$: the $s$ orbital
- A $2s$ orbital is larger than a $1s$ orbital, and has two high-probability regions for finding electrons, separated by one node.
- A $3s$ orbital is even larger, and has three high-probability regions separated by two nodes.

### $l = 1$: the $p$ orbitals
- When $l = 1$, $m_l = -1, 0, +1$. There are three $p$ orbitals at each energy level (except for $n=1$).
- The $p$ orbitals are dumbbell-shaped, with their electron distributions concentrated in identical lobes on opposite sides of the nucleus, separated by a nodal plane. The $p$ orbitals are all perpendicular to each other, aligned along the $x, y,$ and $z$ axes.

### $l = 2$: the $d$ orbitals
- When $l = 2$, $m_l = -2, -1, 0, +1,$ or $+2$. There are five $d$ orbitals at each energy level (except for $n=1$ and 2).

### $l = 3$: the $f$ orbitals

### Why Atoms are Spherical
- If all of the orbitals are superimposed on each other, a roughly spherical shape emerges.
Electron Configurations of Atoms and Ions

Energy Levels of One-Electron Atoms
- In one-electron atoms (H, He⁺, etc.) the energy of the orbital depends only on \( n \). The 2\( s \) and 2\( p \) orbitals have the same energy, the 3\( s \), 3\( p \), and 3\( d \) orbitals all have the same energy, etc. (Orbitals having the same energy are degenerate.)

Energy Levels of Multi-Electron Atoms
- In multi-electron atoms, for various complicated reasons, the orbital energy depends on \( n \) and \( l \) \((s < p < d < f)\), so there are differences in energy between the subshells.

Putting Everything Together
- Knowing the relative energies of the various orbitals allows us to predict the electron configuration for any atom or ion — a list of how the electrons in that atom are distributed among its orbitals.
- Each successive electron added to an atom occupies the lowest-energy orbital available, resulting in the ground-state configuration of the atom.
- A set of rules called the aufbau principle (German, building-up) guides the order in which orbitals are filled.

The Aufbau Principle
- Lower-energy orbitals fill before higher-energy orbitals. The order in which the orbitals are filled is:
  \[ 1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s, 4d, 5p, 6s, 4f, 5d, 6p, 7s, 5f \]
- An orbital can hold only two electrons, which must have opposite spins (Pauli exclusion principle).
- Hund’s Rule: If two or more degenerate orbitals (orbital at the same energy level) are available, one electron goes into each orbital (spin up) until all are half-full; only then does a second electron fill one of the orbitals. (This is a consequence of the mutual repulsion between like charged-electrons.)

Writing Electron Configurations
- To write an element’s electron configuration, write in the orbitals that are occupied by electrons, followed by a superscript to indicate how many electrons are in the set of orbitals (e.g., H \( 1s^1 \)).
- Another way to show the placement of electrons is an orbital diagram, in which each orbital is represented by a circle (or a line, or a square), and the electrons as arrows pointing up (↑) or down (↓) (indicating the electron spin).


**Examples: Electron Configurations**

1. Using the diagram on the next page, write the electron configuration and orbital diagram for the following elements, and state whether they are diamagnetic or paramagnetic.

   - Li
   - Be
   - B
   - C
   - N
   - O
   - F
   - Ne

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**Abbreviated Electron Configurations**

- For atoms following neon, the full electron configuration can be extremely cumbersome to write:

  Ba: 1s\(^2\) 2s\(^2\) 2p\(^6\) 3s\(^2\) 3p\(^6\) 4s\(^2\) 4p\(^6\) 5s\(^2\) 4d\(^10\) 5p\(^6\) 6s\(^2\)

- Since everything up to the 5p\(^6\) is exactly the same electron configuration as the noble gas xenon (Xe), this configuration can be abbreviated as:

  Ba: \([\text{Xe}]\) 6s\(^2\)

- *Abbreviated electron configurations* are always based on the nearest preceding noble gas.

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**Electron Configurations and the Periodic Table**

- It is not necessary to memorize the orbital order in the aufbau scheme, because this sequence can be read from the periodic table in the following fashion:

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**Examples: Electron Configurations**

2. For the following elements, provide the abbreviated electron configuration, orbital diagram, and state whether the element is diamagnetic or paramagnetic.

   - Na
   - Mg
   - Al
   - S
   - Ar
   - Fe
   - Sn
   - Pb
   - I
   - Hf
   - Ra
   - Gd
Valence Electrons

- **Valence electrons** are the electrons in the outermost shell (with the highest value of \( n \)). All the elements in the same group on the periodic table have similar electron configurations for their valence shells, and therefore have similar chemical properties.

- **Core electrons** are those in complete principal energy levels, and do not participate in bonding.

Some Anomalous Electron Configurations

- Half-filled and filled subshells have special stability, leading to some unexpected electron configurations:
  - Cr [Ar] 4s\(^2\) 3d\(^{10}\) actual: [Ar] 4s\(^1\) 3d\(^{10}\)
  - Cu [Ar] 4s\(^2\) 3d\(^{10}\) actual: [Ar] 4s\(^1\) 3d\(^{10}\)
  - Ag [Kr] 5s\(^2\) 4d\(^{10}\) actual: [Kr] 5s\(^1\) 4d\(^{10}\)
  - Au [Xe] 6s\(^2\) 5f\(^{14}\) 6d\(^{10}\) actual: [Xe] 6s\(^1\) 5f\(^{14}\) 6d\(^{10}\)

- Most of the anomalous electron configurations occur in elements with atomic numbers greater than \( Z = 40 \), where the energy differences between subshells are very small. In all of these cases, the transfer of an electron from one subshell to another lowers the total energy of the atom because of a decrease in electron-electron repulsion.

The Octet Rule

- The electrons in the valence shell have the highest energies, and are on average the farthest away from the nucleus, and so are the ones which are most exposed to other atoms.
- For main-group metals, the electrons lost in forming cations are taken from the valence shell.
- For main-group nonmetals, the electrons gained in forming anions are added to the valence shell.
- The inner, core electrons (inner shell) do not usually play a role in chemical bonding.

Group 1A-3A Cations

- Elements with similar outer shell configurations form similar ions.
- The alkali metals form ions with a +1 charge; the valence \( s^1 \) electron is the one that’s lost:
  1A Li 1s\(^2\) 2s\(^1\)  \( \text{Li}^+ 1s^2 \)
  1A Na 1s\(^2\) 2s\(^2\) 2p\(^6\) 3s\(^1\) \( \text{Na}^+ 1s^2 2s^2 2p^6 \)
  1A K 1s\(^2\) 2s\(^2\) 2p\(^6\) 3s\(^2\) 3p\(^6\) 4s\(^1\) \( \text{K}^+ 1s^2 2s^2 2p^6 3s^2 3p^6 \)
- The Group 2A and 3A metals also tend to lose all of their valence electrons to form cations:
  2A Be 1s\(^2\) 2s\(^2\)  \( \text{Be}^{2+} 1s^2 \)
  2A Mg 1s\(^2\) 2s\(^2\) 2p\(^6\) 3s\(^2\) \( \text{Mg}^{2+} 1s^2 2s^2 2p^6 \)
  3A Al 1s\(^2\) 2s\(^2\) 2p\(^6\) 3s\(^2\) 3p\(^1\) \( \text{Al}^{3+} 1s^2 2s^2 2p^6 \)

Group 4A and 5A Cations

- The Group IV and V metals can lose either the electrons from the \( p \) subshell only, or from both the \( s \) and \( p \) subshells, producing a pseudo-noble gas configuration.
  4A Sn [Kr] 5s\(^2\) 4d\(^{10}\) 5p\(^2\)  \( \text{Sn}^{2+} [\text{Kr}] 5s^2 4d^{10} \)
  4A Pb [Xe] 6s\(^2\) 4f\(^{14}\) 5d\(^{10}\) 6p\(^2\)  \( \text{Pb}^{2+} [\text{Xe}] 6s^2 4f^{14} 5d^{10} \)
  5A Bi [Xe] 6s\(^2\) 4f\(^{14}\) 5d\(^{10}\) 6p\(^3\)  \( \text{Bi}^{3+} [\text{Xe}] 6s^2 4f^{14} 5d^{10} \)
  5A Po [Xe] 6s\(^2\) 4f\(^{14}\) 5d\(^{10}\) 6p\(^4\)
**Transition Metal Cations**

- Transition metals lose their $ns^x$ electrons before the $(n-1)d$ electrons, usually forming 2+ charges. Some can also lose electrons from their highest $d$ levels.

<table>
<thead>
<tr>
<th>Element</th>
<th>Configuration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>[Ar] 4s$^2$ 3d$^6$</td>
</tr>
<tr>
<td>Fe$^{3+}$</td>
<td>[Ar] 3d$^6$</td>
</tr>
<tr>
<td>Fe$^{3+}$</td>
<td>[Ar] 3d$^5$</td>
</tr>
<tr>
<td>Zn</td>
<td>[Ar] 4s$^2$ 3d$^{10}$</td>
</tr>
<tr>
<td>Zn$^{2+}$</td>
<td>[Ar] 3d$^{10}$</td>
</tr>
<tr>
<td>Ag</td>
<td>[Kr] 5s$^1$ 4d$^{10}$ [anomalous configuration]</td>
</tr>
<tr>
<td>Ag$^+$</td>
<td>[Kr] 4d$^{10}$</td>
</tr>
</tbody>
</table>

**Nonmetal Anions and Noble Gases**

- The Group 4A - 7A nonmetals gain electrons until their valence shells are full (8 electrons).

<table>
<thead>
<tr>
<th>Element</th>
<th>Configuration</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>[He] 2s$^2$ 2p$^2$</td>
</tr>
<tr>
<td>C$^+$</td>
<td>[He] 2s$^2$ 2p$^4$</td>
</tr>
<tr>
<td>N</td>
<td>[He] 2s$^2$ 2p$^3$</td>
</tr>
<tr>
<td>N$^+$</td>
<td>[He] 2s$^2$ 2p$^5$</td>
</tr>
<tr>
<td>O</td>
<td>[He] 2s$^2$ 2p$^4$</td>
</tr>
<tr>
<td>O$^-$</td>
<td>[He] 2s$^2$ 2p$^6$</td>
</tr>
<tr>
<td>F</td>
<td>[He] 2s$^2$ 2p$^5$</td>
</tr>
<tr>
<td>F$^-$</td>
<td>[He] 2s$^2$ 2p$^6$</td>
</tr>
</tbody>
</table>

- The Group 8A noble gases already possess a full outer shell, so they have no tendency to form ions.

<table>
<thead>
<tr>
<th>Element</th>
<th>Configuration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ne</td>
<td>1s$^2$ 2s$^2$ 2p$^6$</td>
</tr>
<tr>
<td>Ar</td>
<td>1s$^2$ 2s$^2$ 2p$^6$ 3s$^2$ 3p$^6$</td>
</tr>
</tbody>
</table>

**Examples: Predicting Ion Configurations**

3. Predict the ground-state electron configuration for each of the following ions.

a. Ba$^{2+}$
b. La$^{2+}$, La$^{3+}$
c. Mn$^{2+}$, Mn$^{3+}$
d. Ni$^{2+}$
e. Ti$^{2+}$, Ti$^{4+}$
f. P$^-$
g. Cl$^-$
h. Se$^{2-}$

**Examples: Predicting Ion Configurations**

4. What 2+ ion has the ground-state electron configuration 1s$^2$2s$^2$2p$^6$3s$^2$3p$^6$? 

**Examples: Predicting Ion Configurations**

5. Write the electron configurations of the ions in CsF, MgCl$_2$, CaO, and Na$_2$S. What noble gas are each of these ions isoelectronic (having the same number of electrons) with?

**The Explanatory Power of the QM Model**

- The chemical properties of elements are largely determined by the number of valence electrons they contain.
  - The Group 8A elements are inert because their valence shells are already full.
  - The Group 1A elements ($ns^1$) can attain a noble gas configuration by losing their single valence electrons, forming 1+ charges.
  - The Group 2A elements ($ns^2$) lose their two valence electrons to form 2+ charges.
  - The Group 7A elements ($ns^5np^1$) gain one electron to complete their valence shells.
Periodic Properties

A number of element and ion properties vary in a periodic, predictable way across the periodic table. These include:

- atomic radius
- effective nuclear charge
- ionic radius
- ionization energy
- electron affinity
- metallic character
- electronegativity (Ch. 8)

Atomic Radius

- The atomic radius of an atom can be measured by taking one-half of the distance between atoms in an atomic solid (the metallic radius), or by taking one half of the distance between two identical bonded nuclei or between atoms in a metallic crystal (the covalent radius). The ionic radius is derived from the distances between the centers in ionic crystals.

Trends in Atomic Radii

- When the atomic radius is graphed against atomic number, there is a pattern to the radii across a group:

Atomic Radius: Top to Bottom

- As we add larger valence shells (larger values of n), the size of the atom increases. Therefore, atomic size increases as we move from top to bottom in a group.

Effective Nuclear Charge

- The net nuclear charge actually felt by an outer-shell electron, called the effective nuclear charge \( Z_{\text{eff}} \), is often substantially lower than the actual nuclear charge \( Z \), because the core electrons “shield” the outer electrons from the full effect of the nuclear charge:

\[
Z_{\text{eff}} = Z_{\text{actual}} - \text{Electron shielding}
\]
### Atomic Radius: Left to Right

- As we move to the right in a period, there are more protons in the nucleus, but no increase in shielding (the number of inner electrons isn’t changing, and valence electrons don’t shield each other). $Z_{\text{eff}}$ increases from left to right across a period.

- An increasing $Z_{\text{eff}}$ means there is a stronger attraction between the nucleus and the valence electrons. Therefore, atomic radius decreases from left to right in a period.

### Effective Nuclear Charge and Atomic Radius

![Graph showing atomic radius and effective nuclear charge versus atomic number](image)

### Trends in Atomic Radii

#### Examples: Atomic Radii and the Size of Atoms

1a. Which atom is larger, C or N?

1b. Which atom is larger, Si or Ge?

1c. Which atom is larger, Mg or Ba?

1d. Which atom is larger, Al or Ge?

1e. Arrange the following elements in order of increasing size: Cs, Rb, Sr, Ca.

### Periodic Properties of Ions — Ionic Radius

- **Cations** are smaller than their parent atoms, since electrons are being removed from the valence shell.
- **Anions** are larger than their parent atoms, since e⁻-e⁻ repulsions increase when electrons are added.
- The greater the positive charge, the smaller the ionic radius (e.g., Fe³⁺ < Fe²⁺).
- Trends in ion size are the same as for neutral atoms:
  - Ionic radius increases down a group.
  - Ionic radius decreases for cations across a period.
  - Ionic radius decreases for anions across a period.
- Isoelectronic ions decrease in radius as the number of protons increases.
Examples: Predicting Ionic Radii

2a. Arrange the following ions in order of increasing size: $\text{O}^{2-}$, $\text{P}^{3-}$, $\text{S}^{2-}$, $\text{As}^{3-}$.

2b. Which species is larger, Na or Na$^{+}$?

2c. Which species is larger, Br or Br$^{-}$?

2d. Which species is larger, Sn$^{2+}$ or Sn$^{4+}$?

2e. Which species is larger, Rb$^{+}$ or Br$^{-}$?

2f. Arrange the following in order of increasing size: Ca$^{2+}$, $\text{S}^{2-}$, Ar, K$^{+}$, Cl$^{-}$.

Ionization Energy

- Ionization Energy (IE) — the amount of energy needed to remove an electron from a mole of neutral atoms in the gas phase:
  $$\text{M(g)} \rightarrow \text{M}^{+}(\text{g}) + e^{-}(\text{g}) ; \Delta H^\circ = \text{IE}$$ (always $> 0$)

- Ionization energy is a positive energy value; energy must be provided in order to remove an electron from an atom.

- The energy required to remove the first electron is the first ionization energy (IE$_1$).

Trends in First Ionization Energy

- As we move down a group, atomic size increases, so the outermost electrons become easier to remove, since they are farther from the nucleus. Therefore, ionization energy decreases as we move down a group.

- As we move left-to-right across a period, $Z_{\text{eff}}$ increases and atomic size decreases. As a result, the outer electrons are held more tightly, and are harder to remove. Therefore, ionization energy increases as we move from left to right across a period.

- Atoms with low ionization energies (metals) tend to form cations; those with high ionization energies (nonmetals) tend to form anions.
Exceptions to Trends in First Ionization Energy

- There are some variations in the general trends; these variations result from the ionization of atoms which have either one electron in a p subshell (B, Al), or are one electron away from being half-filled (O, S).

Higher Ionization Energies

- Of course, it is possible to form more than just 1+ cations:
  - \( M(g) \rightarrow M^+(g) + e^-(g) \)  
    first ionization energy (IE)
  - \( M^+(g) \rightarrow M^{2+}(g) + e^-(g) \)  
    second ionization energy (IE)
  - \( M^{2+}(g) \rightarrow M^{3+}(g) + e^-(g) \)  
    third ionization energy (IE)

- More energy is required for each successive ionization step (IE > IE > IE) because it is harder to remove an electron from a positively charged ion.
- Large jumps in ionization energy occur when we are trying to remove electrons from filled shells.

Higher Ionization Energies

- Why is the third ionization energy of Be so much higher than the second and first?

Electron Affinity

- Electron Affinity (\( E_{ea} \)) — the energy change accompanying the addition of electrons to 1 mole of atoms in the gas phase:
  - \( \Delta H^f = E_{ea} \) (usually < 0)
- Electron affinity is usually a negative energy value; energy is usually released when an electron is added to a neutral atom.
- The more negative the electron affinity, the greater the tendency of the atom to accept an electron and the more stable the resulting anion will be.
- In general, electron affinity decreases as we move down a group, and increases from left to right, but the trend is not as smooth as for ionization energy and size.

<table>
<thead>
<tr>
<th>( Z )</th>
<th>( E_{ea} ) (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>7193</td>
</tr>
<tr>
<td>2</td>
<td>1519</td>
</tr>
<tr>
<td>3</td>
<td>136.1</td>
</tr>
<tr>
<td>4</td>
<td>867.7</td>
</tr>
<tr>
<td>5</td>
<td>1096</td>
</tr>
<tr>
<td>6</td>
<td>1820</td>
</tr>
<tr>
<td>7</td>
<td>4560</td>
</tr>
<tr>
<td>8</td>
<td>6910</td>
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</tr>
<tr>
<td>10</td>
<td>496</td>
</tr>
<tr>
<td>11</td>
<td>1450</td>
</tr>
<tr>
<td>12</td>
<td>738</td>
</tr>
</tbody>
</table>

*All values in kilojoules per mole of atoms.
Trends in Metallic Character

- Metals are good conductors of heat and electricity, they are malleable and ductile, are often shiny, and easily lose electrons in chemical reactions.
- Nonmetals are poor conductors of heat and electricity, their physical states vary from solid to gas, and they tend to gain electrons in chemical reactions.
- Moving from left to right across a period, ionization energy increases and electron affinity becomes more negative. Therefore, metallic character decreases as we move from left to right across a period.
- As we move down a group, ionization energy decreases, making electrons more likely to be lost. Therefore, metallic character increases as we move down a group.

Summary of the Periodic Trends

Examples: Predicting Periodic Trends

3a. Which atom has the larger IE: Al or S?

3b. Which atom has the larger IE: As or Sb?

3c. Which atom has the larger IE: N or Si

3d. Which atom has the larger IE: O or Cl?

3e. Which atom has the largest IE: Na, Sr, Be, Rb?
Examples: Predicting Periodic Trends

3f. Arrange the following in order of increasing IE: F, S, Cl.

3g. Which has the larger electron affinity, O or F?

3h. Which element is more metallic: Sn or Te?

3i. Which element is more metallic: Ge or In?