

# CHAPTER 10: MODERN ATOMIC THEORY

## Enhanced Introductory College Chemistry

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## In this chapter, you will learn about

- The nature of electromagnetic energy/radiation
- The Bohr model of the atom, how atoms emit light, and how the emission spectrum of hydrogen supports the quantized nature of energy
- Wave nature of matter and the development of the quantum mechanical model
- Energy levels of electrons, shapes of orbitals, and development of the wave mechanical model
- The atomic structure of the first 18 elements and how principal energy levels fill with electrons in atoms beyond hydrogen
- Writing electron configurations according to an element's electron filling order
- Electron structures/configurations of atoms with atomic numbers greater than 18
- Understand and predict general trends in atomic properties in the periodic table

To better support your learning, you should be familiar with the following concepts before starting this chapter:

- Rutherford's nuclear model of the atom including its subatomic particles of an atom
- Structure of the hydrogen atom
- Use the periodic table to identify the number of electrons in neutral atoms for various elements
- Identify group/family names and numbers on the periodic table
- Review common trends in periodic table including physical and chemical properties of metals and non metals and ion formation



**Figure 10a:** The Crab Nebula consists of remnants of a supernova (the explosion of a star). NASA’s Hubble Space Telescope produced this composite image. Measurements of the emitted light wavelengths enabled astronomers to identify the elements in the nebula, determining that it contains specific ions including  $S^+$  (green filaments) and  $O^{2+}$  (red filaments). (credit: Crab Nebula by NASA, ESA, J. Hester and A. Loll (Arizona State University), PD).

In 1054, Chinese astronomers recorded the appearance of a “guest star” in the sky, visible even during the day, which then disappeared slowly over the next two years. The sudden appearance was due to a supernova explosion, which was much brighter than the original star. Even though this supernova was observed almost a millennium ago, the remaining Crab Nebula (Figure 10a) continues to release energy today. It emits not only visible light but also infrared light, X-rays, and other forms of electromagnetic radiation. The nebula emits both continuous spectra (the blue-white glow) and atomic emission spectra (the coloured filaments). In this chapter, we will discuss light and other forms of electromagnetic radiation and how they are related to the electronic structure of atoms. We will also see how this radiation can be used to identify elements, even from thousands of light years away.

## Attribution & References

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## References

Hester, J., & Loll, A. (2017, August). *The Crab Nebula*. NASA.

# 10.1 ELECTROMAGNETIC RADIATION

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## Learning Objectives

By the end of this section, you will be able to:

- Define the electromagnetic spectrum, and describe it in terms of wavelengths, frequencies, and energy
- Describe both the wave and particle nature of light
- Use appropriate equations to calculate related light-wave properties such as period, frequency, wavelength, and energy
- Describe and explain the differences and similarities of each section of the electromagnetic spectrum and the applications of radiation from those sections

The nature of light has been a subject of inquiry since antiquity. In the seventeenth century, Isaac Newton performed experiments with lenses and prisms and was able to demonstrate that white light consists of the individual colors of the rainbow combined together. Newton explained his optics findings in terms of a “corpuscular” view of light, in which light was composed of streams of extremely tiny particles travelling at high speeds according to Newton’s laws of motion. Others in the seventeenth century, such as Christiaan Huygens, had shown that optical phenomena such as reflection and refraction could be equally well explained in terms of light as waves travelling at high speed through a medium called “luminiferous aether” that was thought to permeate all space. Early in the nineteenth century, Thomas Young demonstrated that light passing through narrow, closely spaced slits produced interference patterns that could not be explained in terms of Newtonian particles but could be easily explained in terms of waves. Later in the nineteenth century, after James Clerk Maxwell developed his theory of **electromagnetic radiation** (EMR) and showed that light was the visible part of a vast spectrum of electromagnetic waves, the particle view of light became thoroughly discredited. By the end of the nineteenth century, scientists viewed the physical universe as roughly comprising two separate domains: matter composed of particles moving according to Newton’s laws of motion, and electromagnetic radiation consisting of waves governed by Maxwell’s equations. Today, these domains are referred to as classical mechanics and classical electrodynamics (or classical electromagnetism). Although there were a few physical phenomena that could not be explained within this framework, scientists

at that time were so confident of the overall soundness of this framework that they viewed these aberrations as puzzling paradoxes that would ultimately be resolved somehow within this framework. As we shall see, these paradoxes led to a contemporary framework that intimately connects particles and waves at a fundamental level called wave-particle duality, which has superseded the classical view.

Visible light and other forms of electromagnetic radiation play important roles in chemistry, since they can be used to infer the energies of electrons within atoms and molecules. Much of modern technology is based on electromagnetic radiation. For example, radio waves from a mobile phone, X-rays used by dentists, the energy used to cook food in your microwave, the radiant heat from red-hot objects, and the light from your television screen are forms of electromagnetic radiation that all exhibit wavelike behaviour.

**Watch the TED-Ed video *Light waves, visible and invisible* by Lucianne Walkowicz (5:56)**  
(<https://youtu.be/O0PawPSdk28>)

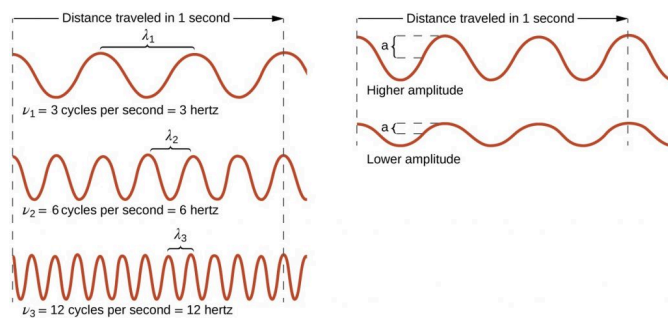
## Waves

A **wave** is an oscillation or periodic movement that can transport energy from one point in space to another. Common examples of waves are all around us. Shaking the end of a rope transfers energy from your hand to the other end of the rope, dropping a pebble into a pond causes waves to ripple outward along the water's surface, and the expansion of air that accompanies a lightning strike generates sound waves (thunder) that can travel outward for several miles. In each of these cases, kinetic energy is transferred through matter (the rope, water, or air) while the matter remains essentially in place. An insightful example of a wave occurs in sports stadiums when fans in a narrow region of seats rise simultaneously and stand with their arms raised up for a few seconds before sitting down again while the fans in neighbouring sections likewise stand up and sit down in sequence. While this wave can quickly encircle a large stadium in a few seconds, none of the fans actually travel with the wave—they all stay in or above their seats.

Waves need not be restricted to travel through matter. As Maxwell showed, electromagnetic waves consist of an electric field oscillating in step with a perpendicular magnetic field, both of which are perpendicular to the direction of travel. These waves can travel through a vacuum at a constant speed of  $2.998 \times 10^8$  m/s, the speed of light (denoted by  $c$ ).

All waves, including forms of electromagnetic radiation, are characterized by, a **wavelength** (denoted by  $\lambda$ , the lowercase Greek letter lambda), a **frequency** (denoted by  $\nu$ , the lowercase Greek letter nu), and an **amplitude**. As can be seen in Figure 10.1a, the wavelength is the distance between two consecutive peaks or troughs in a wave (measured in meters in the SI system). Electromagnetic waves have wavelengths that fall within an enormous range—wavelengths of kilometres ( $10^3$  m) to picometres ( $10^{-12}$  m) have been observed. The frequency is the number of wave cycles that pass a specified point in space in a specified amount of time (in the SI system, this is measured in seconds). A cycle corresponds to one complete wavelength. The unit for frequency, expressed as cycles per second [ $s^{-1}$ ], is the **hertz (Hz)**, so  $1 \text{ Hz} = 1 \text{ s}^{-1}$ . Common multiples of this unit are megahertz, ( $1 \text{ MHz} = 1 \times 10^6 \text{ Hz}$ ) and gigahertz ( $1 \text{ GHz} = 1 \times 10^9 \text{ Hz}$ ). The amplitude corresponds

to the magnitude of the wave's displacement and so, in Figure 10.1a, this corresponds to one-half the height between the peaks and troughs. The amplitude is related to the intensity of the wave, which for light is the brightness, and for sound is the loudness.



**Figure 10.1a:** Comparing Wavelength, Frequency, and Speed using Sinusoidal Waves: One-dimensional sinusoidal waves show the relationship among wavelength, frequency, and speed. The wave with the shortest wavelength has the highest frequency. Amplitude is one-half the height of the wave from peak to trough (credit: Chemistry (Open Stax), CC BY 4.0).

The product of a wave's wavelength ( $\lambda$ ) and its frequency ( $\nu$ ),  $\lambda\nu$ , is the speed of the wave. Thus, for electromagnetic radiation in a vacuum:

$$c = 2.998 \times 10^8 \text{ ms}^{-1} = \lambda\nu$$

In summary, the properties of a wave are determined by:

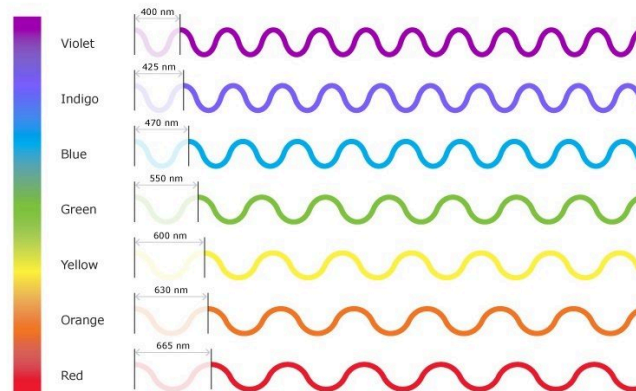
- wave speed; all electromagnetic waves move through space at the same, constant speed of  $2.99 \times 10^8 \text{ ms}^{-1}$ , which is the speed of light,  $c$ .
- height (amplitude)
- wavelength
- frequency

Electromagnetic radiation is also referred to as electromagnetic energy, which is a term used to describe the various energies that travel as wavelengths through space at the speed of light. Various types of electromagnetic radiation carry different amounts of energy. Wavelength is inversely proportional to its energy and frequency.

- Shorter wavelengths have higher frequency and have greater energy
- Longer wavelengths have lower frequency and less energy

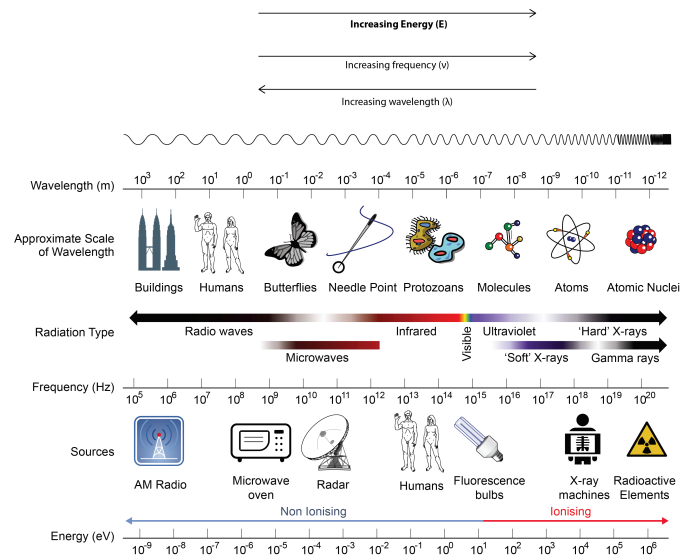
This inverse proportionality is illustrated in Figure 10.1b. Each component colour in the visible spectrum of light has different wavelengths, with corresponding frequencies and energy. The spectrum ranges from dark

red at 700 nm to violet at 400 nm. Longer wavelengths have lower frequency and carry less energy; shorter wavelengths have higher frequency and carry more energy.



**Figure 10.1b:** The Visible Light Spectrum of Electromagnetic Radiation: The Visual Spectrum of Electromagnetic Radiation: The visible spectrum is illustrated showing the wavelengths of each of the component colours. The spectrum ranges from dark red at 700 nm to violet at 400 nm. Longer wavelengths have lower frequency and carry less energy; Shorter wavelengths have higher frequency and carry more energy. (credit: Colours of Light by Science Learning Hub – Pokapū Akoranga Pūtaiao, University of Waikato, Educational Use.)

The inverse proportionality for a broader range of all types of electromagnetic energy is illustrated in Figure 10.1c. Each of the various colours of visible light has specific frequencies (energy amounts) and wavelengths associated with them, and you can see that visible light makes up only a small portion of the electromagnetic spectrum. Because the technologies developed to work in various parts of the electromagnetic spectrum are different, for reasons of convenience and historical legacies, different units are typically used for different parts of the spectrum. For example, radio waves are usually specified as frequencies (typically in units of MHz), while the visible region is usually specified in wavelengths (typically in units of nm or angstroms).



**Figure 10.1c:** The Electromagnetic Spectrum: Portions of the electromagnetic spectrum are shown in order of decreasing frequency and increasing wavelength. Examples of some applications for various wavelengths include positron emission tomography (PET) scans, X-ray imaging, remote controls, wireless Internet, cellular telephones, and radios. (credit: modification of work by Dinksbumf, Inductiveload, NASA, CC BY-SA 3.0. / Adapted by Revathi Mahadevan to include energy, frequency & wavelength trends).

### Example 10.1a

For the following example, reference Figure 10.1b.

Compare green light (550nm) and red light (665nm) from the visual light portion of the electromagnetic spectrum and answer the following questions:

1. Which colour of light, red or green, has a shorter wavelength?
2. Which colour of light, red or green, has a lower frequency?
3. Which colour of light, red or green, contains lower energy?

### Solution

1. Green light has a shorter wavelength than red light
2. Red light has lower frequency since it has a longer wavelength than green light
3. Red light contains less energy since it has a lower frequency compared to green light



## Exercise 10.1a

For the following exercises, reference Figure 10.1b.

Check Your Learning Exercise (Text Version)

Instructions: Answer the following questions related to Wavelength, Frequency, and Energy of Electromagnetic Radiation

1. True or False? Wavelength is inversely proportional to its energy and frequency
2. True or False? Longer wavelengths have lower frequency and less energy
3. True or False? Shorter wavelengths have higher frequency and have greater the energy
4. Review the word list provided which contains seven words or terms. Choose a word or phrase to fill in the (BLANK) to make the statements correct. Each word will be used once.  
WORD LIST: frequency ( $\nu$ ), wavelength ( $\lambda$ ), electromagnetic spectrum, greater, less, shorter, longer
  - a. [BLANK] wavelengths have higher frequency and [BLANK] energy
  - b. [BLANK] is the distance between two peaks or troughs in a wave of given amplitude(height).
  - c. [BLANK] is the number of waves (cycles) per second that pass a given point in space.
  - d. [BLANK] wavelengths have lower frequency and [BLANK] energy.
  - e. Visible light accounts for a very small portion of the [BLANK] of light.
5. Which of the following statements is true when you compare blue light (with a wavelength of 425nm) to orange light (with a wavelength of 620nm)
  - a. orange light has a higher frequency and more energy than blue light
  - b. blue light has a lower frequency than orange light
  - c. orange light has a lower frequency but higher energy than blue light
  - d. orange light has a lower frequency and less energy than blue light
  - e. blue light has less energy than orange light
6. True or False? The formula  $c=\lambda\nu$  can be used to solve for wavelength or frequency of electromagnetic radiation.

### Check Your Answer<sup>1</sup>

**Source:** "Exercise 10.1a" by Jackie MacDonald, CC BY-NC-SA 4.0

## Types of Electromagnetic Radiation (EMR)

We generally take light for granted, but it is a truly amazing and mysterious form of energy. Think about it: light travels to Earth across millions of kilometres of empty space. When it reaches us, it interacts with matter in various ways to generate almost all the energy needed to support life, provide heat, and cause weather patterns. Light is a form of electromagnetic radiation (EMR). The term light usually refers to visible light, but this is not the only form of EMR. As we will see, visible light occupies a narrow band in a broad range of types of electromagnetic radiation.

Take a few minutes to study the positions of the various types of radiation on the EM spectrum in Figure 10.1c. Sometimes all radiation with frequencies lower than those of visible light are referred to as infrared (IR) radiation. This includes radio waves, which overlap with the frequencies used for media broadcasts of TV and radio signals. The microwave radiation that you see on the diagram is the same radiation that is used in a microwave oven or cell phone. What we feel as radiant heat is also a form of low-frequency EMR.

All the high-frequency radiation to the right of visible light is sometimes referred to as ultraviolet (UV) radiation. This includes X-rays and gamma ( $\gamma$ ) rays. The narrow band that is visible light is a combination of the colours of the rainbow and extends from lower-frequency red light to higher-frequency violet light, thus the terms are infrared (below red) and ultraviolet (beyond violet). Electromagnetic Radiation is typically classified by its wavelength.

### TIPS for Success

Wavelengths of visible light are often given in nanometers, nm. One nm equals  $10^{-9}$  m.

$$1 \text{ nm} = 10^{-9} \text{ m}$$

For example, yellow light has a wavelength of about 600 nm, or  $6 \times 10^{-7}$  m.

Listed below are several forms of electromagnetic radiation and its wavelength, in order from lowest frequency and energy to highest frequency and energy:

- Radiowaves =  $\lambda > 0.01 \text{ m}$ .
- Microwaves =  $10^{-4} \text{ m} < \lambda < 10^{-2} \text{ m}$
- Infrared (IR) =  $8 \times 10^{-7} < \lambda < 10^{-5} \text{ m}$
- Visible =  $4 \times 10^{-7} < \lambda < 8 \times 10^{-7} \text{ m}$  (ROYGBIV – acronym for visible colour order)
- Ultraviolet (UV) =  $10^{-8} < \lambda < 4 \times 10^{-7} \text{ m}$
- X-rays =  $10^{-10} < \lambda < 10^{-8} \text{ m}$
- Gamma rays =  $\lambda < 10^{-10} \text{ m}$

### Example 10.1b

For the following example on types of electromagnetic radiation, reference Figure 10.1c.

Using the given five examples of electromagnetic radiation and its wavelength, arrange these in order of radiation that contains the most energy to least energy.

- Infrared  $\lambda = 900 \text{ nm}$
- Blue light = 450 nm
- Red light = 700nm
- Gamma rays  $\lambda = 0.01\text{nM}$
- Radio waves  $\lambda = 3000 \text{ m}$

### Solution

Since the wavelength of electromagnetic radiation is inversely proportional to its energy, they will be ordered from shortest wavelength to longest wavelength to show the order of radiation that contains most energy to least energy.

1. Gamma rays  $\lambda = 0.01\text{nM}$  – Contains the MOST ENERGY
2. Blue light = 450 nm
3. Red light = 700nm
4. Infrared  $\lambda = 900 \text{ nm}$
5. Radio waves  $\lambda = 3000 \text{ m}$  – Contains the LEAST ENERGY

**Source:** “Example 10.1b” created by Jackie MacDonald, CC BY-NC-SA 4.0

### Exercise 10.1b

For the following exercise, reference Figure 10.1c.

Using the given five examples of electromagnetic radiation and its wavelength, arrange these in order of radiation that has the lowest frequency to highest frequency.

- Microwaves = 300 cm
- Violet light = 400 nm

- Yellow light = 600nm
- X rays  $\lambda = 5 \text{ nm}$
- Infrared  $\lambda = 900 \text{ nm}$

**Check Your Answer<sup>2</sup> Source:** "Exercise 10.1b" created by Jackie MacDonald, CC BY-NC-SA 4.0

One can calculate the frequency or wavelength of electromagnetic radiation using the formula  $c = \lambda\nu$ , where  $c = 2.998 \times 10^8 \text{ ms}^{-1}$ .

### Example 10.1c

#### Calculations with Frequency and Wavelength of Electromagnetic Radiation

A sodium streetlight gives off yellow light that has a wavelength of 589 nm ( $1 \text{ nm} = 1 \times 10^{-9} \text{ m}$ ). What is the frequency of this light?

#### Solution

We can rearrange the equation  $c = \lambda\nu$  to solve for the frequency:

$$\nu = \frac{c}{\lambda}$$

Since  $c$  is expressed in meters per second, we must also convert 589 nm to meters.

$$\nu = \left( \frac{2.998 \times 10^8 \text{ ms}^{-1}}{589 \text{ nm}} \right) \left( \frac{1 \times 10^9 \text{ nm}}{1 \text{ m}} \right) = 5.09 \times 10^{14} \text{ s}^{-1}$$

## Exercise 10.1c

### Calculations with the Frequency and Wavelength of Electromagnetic Radiation

One of the frequencies used to transmit and receive cellular telephone signals in the United States is 850. MHz (3 significant figures). What is the wavelength in meters of these radio waves?

**Check Your Answer<sup>3</sup>**

## Particle-Wave Duality

We have long known that EM radiation is like a wave, capable of interference and diffraction. We now see that light can also be modelled as particles—massless photons of discrete energy and momentum. In 1905, Albert Einstein (1879-1955), developed a theory stating that light has a dual nature: Light acts not only as a wave, but also as a particle. As illustrated above when discussing visible light, each particle of light has a quantum of energy associated with it and is called a **photon**. We call this twofold nature the **particle-wave duality**, meaning that EM radiation has properties of both particles and waves. This may seem contradictory, since we ordinarily deal with large objects that never act like both waves and particles. An ocean wave, for example, looks nothing like a grain of sand. However, this so-called duality is simply a term for properties of the photon analogous to phenomena we can observe directly, on a macroscopic scale. If this term seems strange, it is because we do not ordinarily observe details on the quantum level directly, and our observations yield either particle-like or wave-like properties, but never both simultaneously.

**Watch Wave-Particle Duality and the Photoelectric Effect (3:55) (<https://youtu.be/MFPKwu5vugg>)**

## Exploring Specific Types of Electromagnetic Radiation

### Wireless Communication – Radio Waves

Wireless communication uses long radio waves to travel great distances to transmit their signals. Some forms of EMR that use radio waves (all with different wavelengths, frequencies and energy amounts) include, radio

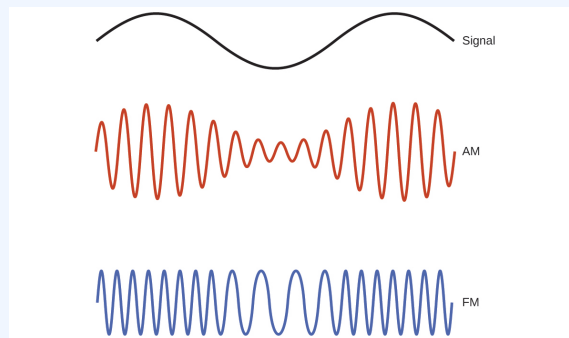
broadcasting, cellular networks, radar, satellite communication, remote controlled toys, and navigation and air traffic control (GPS).

## Wireless Communication



**Figure 10.1d:** Wireless communication: Radio and cell towers are typically used to transmit long-wavelength electromagnetic radiation. Increasingly, cell towers are designed to blend in with the landscape, as with the Tucson, Arizona, cell tower (right) disguised as a palm tree. (credit left: modification of work by Sir Mildred Pierce, CC BY 2.0; credit middle: modification of work by M.O. Stevens, CC BY 3.0; credit right: work by Gary Minnaert, PD)

Many valuable technologies operate in the radio (3 kHz-300 GHz) frequency region of the electromagnetic spectrum (Figure 10.1d). At the low frequency (low energy, long wavelength) end of this region are AM (amplitude modulation) radio signals (540-2830 kHz) that can travel long distances. FM (frequency modulation) radio signals are used at higher frequencies (87.5-108.0 MHz). In AM radio, the information is transmitted by varying the amplitude of the wave (Figure 10.1e). In FM radio, by contrast, the amplitude is constant and the instantaneous frequency varies.



**Figure 10.1e:** Schematic of AM and FM radio wave transmission: This schematic depicts how amplitude modulation (AM) and frequency modulation (FM) can be used to transmit a radio wave. (credit: *Chemistry (Open Stax)*, CC BY 4.0).

Other technologies also operate in the radio-wave portion of the electromagnetic spectrum. For example, 4G cellular telephone signals are approximately 880 MHz, while Global Positioning System (GPS) signals operate at 1.228 and 1.575 GHz, local area wireless technology (Wi-Fi) networks operate

at 2.4 to 5 GHz, and highway toll sensors operate at 5.8 GHz. The frequencies associated with these applications are convenient because such waves tend not to be absorbed much by common building materials. All are forms of radio waves.

## X-Rays

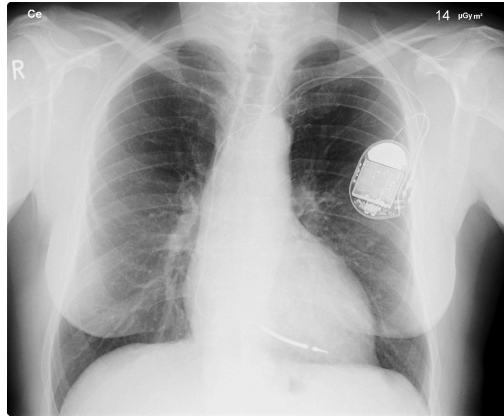
X-Rays are a form of electromagnetic radiation, invisible to the human eye. Unlike visible light, x-rays have higher energy, higher frequency (and shorter wavelengths), which can penetrate most matter, including the body. Medical x-rays are used to generate images of tissues and structures inside the body.

**Watch How Do X-rays Work? (1 min 28 s) ([https://www.youtube.com/watch?v=hTz\\_rGP4v9Y](https://www.youtube.com/watch?v=hTz_rGP4v9Y))**

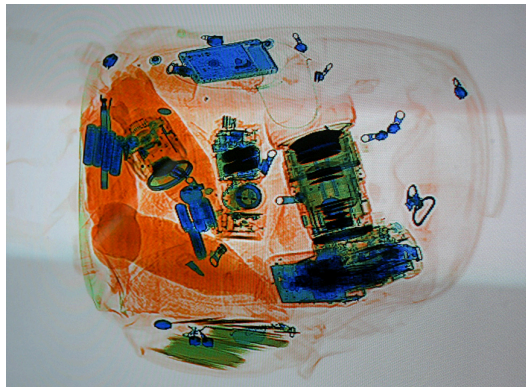
All of us can identify diagnostic uses of x-ray photons. Among these are the universal dental and medical x-rays that have become an essential part of medical diagnostics (Figure 10.1f and Figure 10.1g). X-rays are also used to inspect our luggage at airports, as shown in Figure 10.1h, and for early detection of cracks in crucial aircraft components. An x-ray is not only a noun meaning high-energy photon, it is also an image produced by x-rays, and it has been made into a familiar verb—to be x-rayed.



**Figure 10.1f:** X-Ray of Human Mouth: An x-ray image reveals fillings in a person's teeth and can be used to detect cavities or other oral hygiene concerns. (credit: work by Dmitry G, PD)



**Figure 10.1g:** Medical Diagnostic Use of X-Ray: This x-ray image of a person's chest shows many details, including an artificial pacemaker. (credit: work by Sunzi99, CC BY 3.0)



**Figure 10.1h:** X-Ray Imaging for Security: This x-ray image shows the contents of a piece of luggage. The denser the material, the darker the shadow. (credit: work by IDuke, CC BY 2.5)

The most common x-ray images are simple shadows. Since x-ray photons have high energies, they penetrate materials that are opaque to visible light. The more energy an x-ray photon has, the more material it will penetrate. So an x-ray tube may be operated at 50.0 kV for a chest x-ray, whereas it may need to be operated at 100 kV to examine a broken leg in a cast. The depth of penetration is related to the density of the material as well as to the energy of the photon. The denser the material, the fewer x-ray photons get through and the darker the shadow. Thus x-rays excel at detecting breaks in bones and in imaging other physiological structures, such as some tumours, that differ in density from surrounding material. Because of their high photon energy, x-rays produce significant ionization in materials and damage cells in biological organisms. Modern uses minimize exposure to the patient and eliminate exposure to others.




## Scientists in Action: Dorothy Hodgkin, PhD.

Because the wavelengths of X-rays (10-10,000 picometres [pm]) are comparable to the size of atoms, X-rays can be used to determine the structure of molecules. When a beam of X-rays is passed through molecules packed together in a crystal, the X-rays collide with the electrons and scatter. Constructive and destructive interference of these scattered X-rays creates a specific diffraction pattern. Calculating backward from this pattern, the positions of each of the atoms in the molecule can be determined very precisely. One of the pioneers who helped create this technology was Dorothy Crowfoot Hodgkin.

### TODAY IN CHEMISTRY HISTORY


12<sup>TH</sup> MAY – DOROTHY HODGKIN'S BIRTHDAY



**DOROTHY HODGKIN**


**BORN**  
12 May 1910

**DIED**  
29 July 1994



**1964**

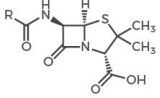
Hodgkin used X-ray crystallography to determine the structure of vitamin B<sub>12</sub>, for which she won a Nobel Prize. She went on to determine the structure of insulin.



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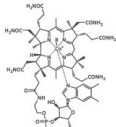
KEY STRUCTURES DETERMINED BY HODGKIN

**PENICILLIN (1945)**



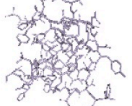
Hodgkin confirmed the structure of penicillin – the first time the structure of a whole molecule had been calculated using X-ray data.

**VITAMIN B<sub>12</sub> (1955)**




Vitamin B<sub>12</sub> was, at the time, the most complex molecule tackled by X-ray crystallography. Its structure took Hodgkin eight years to solve.

**INSULIN (1969)**



Hodgkin first grew crystals of insulin in 1935, but it was another 34 years before she determined its three-dimensional structure.

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 Image: National Portrait Gallery, CC-BY-NC-ND licence.



**Infographic 10.1a:** Noble Prize Winner, Dorothy-Hodgkin Read more about “This Day in Chemistry May 12 – Dorothy Hodgkin (<https://www.compoundchem.com/2019/05/12/hodgkin/>)” by Andy Brunning / Compound Interest, CC BY-NC-ND or access a text-based summary of infographic 10.1a [New tab].

She was born in Cairo, Egypt, in 1910, where her British parents were studying archeology. Even as a young girl, she was fascinated with minerals and crystals. When she was a student at Oxford University, she began researching how X-ray crystallography could be used to determine the structure of biomolecules. She invented new techniques that allowed her and her students to determine the structures of vitamin B<sub>12</sub>, penicillin, and many other important molecules. Diabetes, a disease that affects 382 million people worldwide, involves the hormone insulin. Hodgkin began studying the structure of insulin in 1934, but it required several decades of advances in the field

before she finally reported the structure in 1969. Understanding the structure has led to better understanding of the disease and treatment options (Bunning, 2019).

## Key Equations

$$c = \lambda\nu$$

## Attribution & References

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## References

Bunning, A. (2019). This Day in Chemistry May 12 – Dorothy Hodgkin. *Compound Interest*. CC BY-NC-ND 4.0

Science Learning Hub – Pokapū Akoranga Pūtaiao, University of Waikato. (April 24, 2019). *Colours of Light*.

## Notes

- (1) True; (2) True; (3) True (4a) shorter, less; (4b) wavelength ( $\lambda$ ); (4c) frequency ( $\nu$ ); (4d) longer, greater; (4e) electromagnetic spectrum; (5) d; (6) True
- Since the wavelength of electromagnetic radiation is inversely proportional to its frequency, they will be ordered from longest wavelength to shortest wavelength to show the order of radiation that contains lowest frequency to highest frequency.
  - Microwaves = 300 cm - LOWEST FREQUENCY
  - Infrared  $\lambda = 900$  nm
  - Yellow light = 600nm
  - Violet light = 400 nm
  - X rays  $\lambda = 5$  nm - HIGHEST FREQUENCY
- We can rearrange the equation  $c = \lambda\nu$  to solve for the frequency:

$$\lambda = \frac{c}{\nu}$$

Since  $c$  is expressed in meters per second ( $\text{ms}^{-1}$ ), we must also convert 850. MHz to  $\text{s}^{-1}$ . Recall,  $1 \text{ MHz} = 1.0 \times 10^6 \text{ Hz} = 1.0 \times 10^6 \text{ s}^{-1}$

So  $850. \text{ MHz} = 8.50 \times 10^8 \text{ s}^{-1}$

SOLVE:

$$\lambda = \frac{2.99 \times 10^8 \text{ ms}^{-1}}{8.50 \times 10^8 \text{ s}^{-1}}$$

$\lambda = 0.3527 \text{ m}$  (round final answer to 3 significant figures)

$$\lambda = 0.353 \text{ m}$$

## 10.2 THE BOHR ATOM

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### Learning Objectives

By the end of this section, you will be able to:

- Explain the difference between the absorption spectrum and the emission spectrum of radiation emitted by atoms
- Describe the Bohr model of the hydrogen atom
- Summarize how Bohr's quantum model of the hydrogen atom explains the radiation spectrum of atomic hydrogen
- Review key equations used to calculate energies of light emitted or absorbed by hydrogen atoms

Our view of objects in the sky at night, the warm radiance of sunshine, the sting of sunburn, neon signs around us, our cell phone conversations, and the X-rays revealing a broken bone—all are brought to us by electromagnetic waves. It would be hard to overstate the practical importance of electromagnetic waves, through their role in vision, through countless technological applications, and through their ability to transport the energy from the Sun through space to sustain life and almost all of its activities on Earth.

Theory predicted the general phenomenon of electromagnetic waves before anyone realized that light is a form of an electromagnetic wave. In the mid-nineteenth century, James Clerk Maxwell formulated a single theory combining all the electric and magnetic effects known at that time. Maxwell's equations, summarizing this theory, predicted the existence of electromagnetic waves that travel at the speed of light. His theory also predicted how these waves behave, and how they carry both energy and momentum. These discoveries contributed to the emergence of the modern atomic theory.

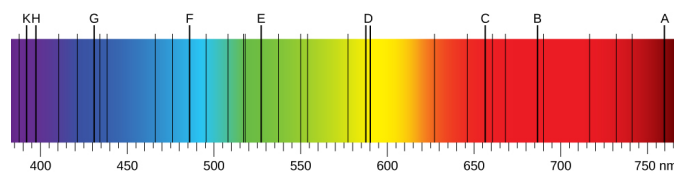
Scientists continued to perform experiments to investigate the properties of electromagnetic radiation. Evidence supported that atoms could give off light. Following the work of Ernest Rutherford and his colleagues in the early twentieth century, the picture of atoms consisting of tiny dense nuclei surrounded by lighter and even tinier electrons continually moving about the nucleus was well established. This theory was called the planetary model since it pictured the atom as a miniature “solar system” with the electrons orbiting the nucleus like planets orbiting the sun. Rutherford's model for atoms had one serious problem. Maxwell's

theory of electromagnetic radiation says that when electrons change either speed or the direction of motion, they must emit energy. Science had proved that orbiting electrons constantly change their direction of motion, so they should, in theory, emit a constant stream of energy. Applying Maxwell's theory to Rutherford's model, all electrons should spiral into the nucleus of the atom as they lose energy, and this collapse should happen very quickly—in about  $10^{-16}$  seconds. However, experimental results were not supporting such findings. Scientists concluded the atom's structure and how electrons move around the nucleus must be different than originally theorized. It was Danish physicist, Niels Bohr (1885–1962), who proposed an updated theory of how electrons remain in orbit.

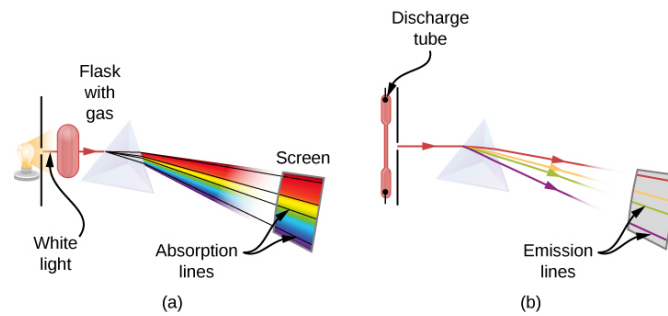
## Emission and Absorption Spectra

To understand the specifics of Bohr's model, we must first review the nineteenth-century discoveries regarding line spectra that prompted its formulation.

When we use a prism to analyze white light coming from the sun, several dark lines in the solar spectrum are observed (Figure 10.2a). Solar absorption lines are called Fraunhofer lines after Joseph von Fraunhofer, who accurately measured their wavelengths. During 1854–1861, Gustav Kirchhoff and Robert Bunsen discovered that for the various chemical elements, the line emission spectrum of an element exactly matches its line absorption spectrum. The difference between the absorption spectrum and the emission spectrum is explained in Figure 10.2b. An absorption spectrum is observed when light passes through a gas. This spectrum appears as black lines that occur only at certain wavelengths on the background of the continuous spectrum of white light (Figure 10.2b). The missing wavelengths tell us which wavelengths of the radiation are absorbed by the gas. The emission spectrum is observed when light is emitted by a gas. This spectrum is seen as colourful lines on the black background (Figure 10.2c and Figure 10.2d). Positions of the emission lines tell us which wavelengths of the radiation are emitted by the gas. Over time it was observed and concluded that each chemical element has its own characteristic emission spectrum. For each element, the positions of its emission lines are exactly the same as the positions of its absorption lines. This means that atoms of a specific element absorb radiation only at specific wavelengths and radiation that does not have these wavelengths is not absorbed by the element at all. This also means that the radiation emitted by atoms of each element has exactly the same wavelengths as the radiation they absorb.



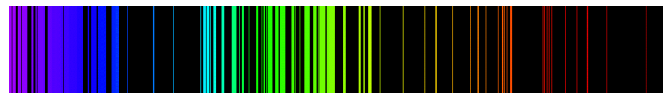
**Figure 10.2a:** Absorption spectra: in the solar emission spectrum in the visible range from 380 nm to 710 nm, Fraunhofer lines are observed as vertical black lines at specific spectral positions in the continuous spectrum. Highly sensitive modern instruments observe thousands of such lines. (credit: *University Physics Volume 3 (Open Stax)*, CC BY 4.0).



**Figure 10.2b:** Observation of line spectra: (a) setup to observe absorption lines; (b) setup to observe emission lines. (a) White light passes through a cold gas that is contained in a glass flask. A prism is used to separate wavelengths of the passed light. In the spectrum of the passed light, some wavelengths are missing, which are seen as black absorption lines in the continuous spectrum on the viewing screen. (b) A gas is contained in a glass discharge tube that has electrodes at its ends. At a high potential difference between the electrodes, the gas glows and the light emitted from the gas passes through the prism that separates its wavelengths. In the spectrum of the emitted light, only specific wavelengths are present, which are seen as colourful emission lines on the screen. (credit: *University Physics Volume 3 (Open Stax)*, CC BY 4.0.)



**Figure 10.2c:** The emission spectrum of atomic hydrogen: the spectral positions of emission lines are characteristic for hydrogen atoms. (credit: work by JKasd, CC BY 3.0)



**Figure 10.2d:** The emission spectrum of atomic iron: the spectral positions of emission lines are characteristic for iron atoms. (credit: *University Physics Volume 3 (Open Stax)*, CC BY 4.0.)

Emission spectra of the elements have complex structures; they become even more complex for elements with higher atomic numbers. The simplest spectrum, the emission spectrum of atomic hydrogen (Figure 10.2c), belongs to the hydrogen atom. Only four lines are visible to the human eye. As you read the emission spectrum of hydrogen from right to left, these lines are: red (656 nm), aqua (486 nm), blue (434 nm), and violet (410 nm). The lines with wavelengths shorter than 400 nm appear in the ultraviolet part of the spectrum and are invisible to the human eye. There are infinitely many invisible spectral lines in the series for hydrogen. Hydrogen's emission spectrum is much different than that of iron, which is shown in Figure 10.2d. It was determined that each element has a unique set of spectral lines that is characteristic of that element.

**Watch Emission and Absorption Spectra (5:17)** (<https://youtu.be/1uPyq63aRvg>)

## The Bohr Atom

It was Niels Bohr who solved the mystery of how electrons remain in orbit. Historically, Bohr's model of the hydrogen atom is the very first model of atomic structure that correctly explained the specific radiation emittance spectra of atomic hydrogen. He applied the concept of energy quanta, proposed by German physicist, Max Planck (1858-1947), which stated that energy is never emitted continuously, but in small, discrete packages of energy called quanta. With this in mind, Bohr suggested that the spectrum of hydrogen can be understood if we assume that orbits of only certain sizes and specific distances from the atom's nucleus are possible for the electron to exist in. Bohr further assumed that as long as the electron moves in only one of these allowed orbits, it radiates no energy. Its energy would change only if it moved from one orbit to another. At the microscopic level of the atom, experiment after experiment has confirmed the validity of Bohr's strange idea. Bohr's suggestions became one of the foundations of the new (and much more sophisticated) model of the subatomic world called quantum mechanics.

In Bohr's model, if the electron moves from one orbit to another closer to the atomic nucleus, it must give up some energy in the form of electromagnetic radiation. If the electron goes from an inner orbit to one farther from the nucleus, however, it requires some additional energy. One way to obtain the necessary energy is to absorb electromagnetic radiation that may be streaming past the atom from an outside source.

A key feature of Bohr's model is that each of the permitted electrons that orbit around a given atom have a certain energy value; we, therefore, can think of each orbit as an energy level. Furthermore, all elements have the same set of energy levels. Lower energy levels are closer to the nucleus and higher energy levels are farther from the nucleus of an atom. To move from one orbit to another either up or down (which will have its own specific energy value) requires a change in the electron's energy—a change determined by the difference between the two energy values. Here we have one of the situations where it is easier to think of electromagnetic radiation as particles (photons) rather than as waves since each jump (or transition) to a different level has a fixed and definite energy change associated with it. Bohr concluded the following:

1. The atom must first receive a quantum amount of energy from an outside source for an electron to move to a higher orbit level and enters an **excited state** (an atom with excess energy).
2. When the excited electron moves to a lower energy level or its **ground state** (lowest possible state), the energy difference is released as a photon of light. The energy of the photon corresponds exactly to the energy change experienced by the emitting atom, which correlates with the colour of light specific to that energy amount.

A crude analogy for this situation might be life in a tower of luxury apartments where the rent is determined by the quality of the view. Such a building has certain, definite numbered levels or floors on which apartments are located. No one can live on floor 5.37 or 22.5. In addition, the rent gets higher as you go up to higher floors. If you want to exchange an apartment on the twentieth floor for one on the second floor, you will not

owe as much rent. However, if you want to move from the third floor to the twenty-fifth floor, your rent will increase. In an atom, too, the “cheapest” place for an electron to live is the lowest possible level, and energy is required to move to a higher level.

The photon and wave perspectives must be equivalent: light is light, no matter how we look at it. Thus, each photon carries a certain amount of energy that is proportional to the frequency ( $f$ ) of the wave it represents. The value of its energy ( $E$ ) is given by the formula

$$E=hf$$

where the constant of proportionality,  $h$ , is called Planck’s constant.

The constant is named for Max Planck, who was one of the originators of the quantum theory. If metric units are used (that is, if energy is measured in joules and frequency in hertz), then Planck’s constant has the value  $h = 6.626 \times 10^{-34}$  joule-seconds (J-s). As mentioned in the previous section, higher-energy photons correspond to higher-frequency waves (which have a shorter wavelengths); lower-energy photons are waves of lower frequency (which have longer wavelengths).

For a summary about the Bohr model of the atom, **watch the video The Bohr Atom (6:20)** (<https://youtu.be/GhAn8xZQ-d8>)

## The Mathematics and Physics Involved in the Evolution of the Bohr Atom

Niels Bohr attempted to resolve the atomic paradox by ignoring classical electromagnetism’s prediction that the orbiting electron in hydrogen would continuously emit light. Instead, he incorporated into the classical mechanics description of the atom, Planck’s ideas of quantization and Albert Einstein’s finding that light consists of photons whose energy is proportional to their frequency. Bohr assumed that the electron orbiting the nucleus would not normally emit any radiation (the stationary state hypothesis), but it would emit or absorb a photon if it moved to a different orbit. The energy absorbed or emitted would reflect differences in the orbital energies according to this equation:

$$|\Delta E| = |E_f - E_i| = h\nu = \frac{hc}{\lambda}$$

In this equation,  $h$  is Planck’s constant and  $E_i$  and  $E_f$  are the initial and final orbital energies, respectively. The absolute value of the energy difference is used, since frequencies and wavelengths are always positive. Instead of allowing for continuous values for the angular momentum, energy, and orbit radius, Bohr assumed that only discrete values for these could occur (actually, quantizing any one of these would imply that the other two are also quantized). Bohr’s expression for the quantized energies is:



$$E_n = -\frac{k}{n^2}, n = 1, 2, 3, \dots$$

In this expression,  $k$  is a constant comprising fundamental constants such as the electron mass and charge and Planck's constant. Inserting the expression for the orbit energies into the equation for  $\Delta E$  gives

$$\Delta E = k\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) = \frac{hc}{\lambda}$$

or

$$\frac{1}{\lambda} = \frac{k}{hc} \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

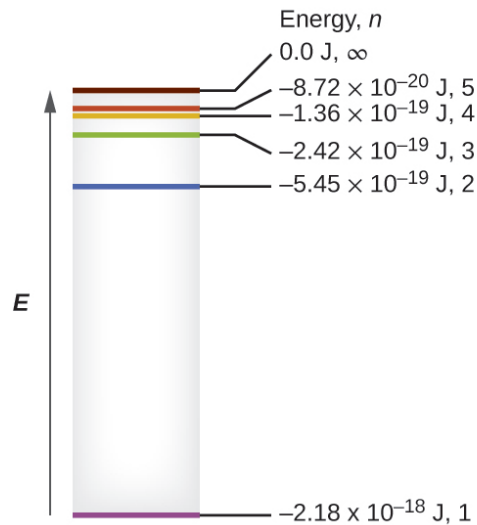
which is identical to the Rydberg equation for  $R_\infty = \frac{k}{hc}$ . Johannes Rydberg developed an empirical formula that predicted all of hydrogen's emission lines, not just those restricted to the visible range, where,  $n_1$  and  $n_2$  are integers,  $n_1 < n_2$ , and  $R_\infty$  is the Rydberg constant ( $1.097 \times 10^7 \text{ m}^{-1}$ ).

$$\frac{1}{\lambda} = R_\infty \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

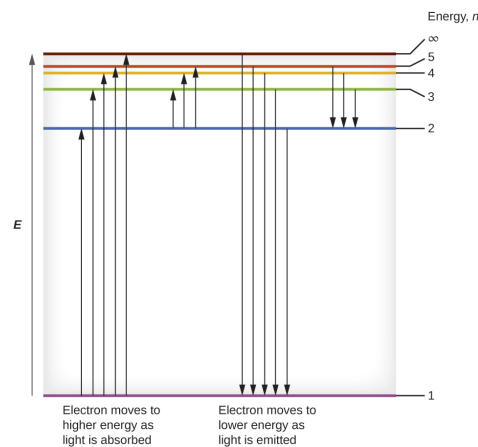
When Bohr calculated his theoretical value for the Rydberg constant  $R_\infty$ , and compared it with the experimentally accepted value, he got excellent agreement. Since the Rydberg constant was one of the most precisely measured constants at that time, this level of agreement was astonishing and meant that **Bohr's model** was taken seriously, despite the many assumptions that Bohr needed to derive it.

One of the fundamental laws of physics is that matter is most stable with electrons filling the lowest possible energy levels, which are designated by the letter  $n$ , where  $n$  is a positive integer. The lowest principal energy level is  $n = 1$  and increase in increments of 1 for each successive higher energy level. Thus, the electron in a hydrogen atom usually moves in the  $n = 1$  orbit, the lowest energy orbit and is said to be in its ground electronic state (or simply ground state). If the atom receives energy from an outside source, it is possible for the electron to move to an orbit with a higher  $n$  value and the atom is now in an excited electronic state (or simply an excited state) with a higher energy. When an electron transitions from an excited state (higher energy orbit) to a less excited state, or ground state, the difference in energy is emitted as a photon. The lowest few energy levels are shown in Figure 10.2e. We can relate the energy of electrons in atoms to what we learned previously about energy. The law of conservation of energy says that we can neither create nor destroy energy. Thus, if a certain amount of external energy is required to excite an electron from one energy level to another, that same amount of energy will be liberated when the electron returns to its initial state (Figure 10.2f). In effect, an atom can "store" energy by using it to promote an electron to a state with a higher energy and release it when the electron returns to a lower state. The energy can be released as one quantum of

energy, as the electron returns to its ground state (say, from  $n = 5$  to  $n = 1$ ), or it can be released as two or more smaller quanta as the electron falls to an intermediate state, then to the ground state (say, from  $n = 5$  to  $n = 4$ , emitting one quantum, then to  $n = 1$ , emitting a second quantum).



**Figure 10.2e:** Quantum numbers and energy levels in a hydrogen atom: the more negative the calculated value, the lower the energy. (credit: *Chemistry (Open Stax)*, CC BY 4.0)



**Figure 10.2f:** Relative energy of orbits in the Bohr model of the hydrogen atom: The horizontal lines show the relative energy of orbits in the Bohr model of the hydrogen atom, and the vertical arrows depict the energy of photons absorbed (left) or emitted (right) as electrons move between these orbits. (credit: *Chemistry (Open Stax)*, CC BY 4.0)

Since Bohr's model involved only a single electron, it could also be applied to the single electron ions  $\text{He}^+$ ,  $\text{Li}^{2+}$ ,  $\text{Be}^{3+}$ , and so forth, which differ from hydrogen only in their nuclear charges, and so one-electron atoms and ions are collectively referred to as hydrogen-like atoms. The energy expression for

hydrogen-like atoms is a generalization of the hydrogen atom energy, in which  $Z$  is the nuclear charge (+1 for hydrogen, +2 for He, +3 for Li, and so on) and  $k$  has a value of  $2.179 \times 10^{-18}$  J.

$$E_n = -\frac{kZ^2}{n^2}$$

The sizes of the circular orbits for hydrogen-like atoms are given in terms of their radii by the following expression, in which  $a_0$  is a constant called the Bohr radius, with a value of  $5.292 \times 10^{-11}$  m:

$$r = \frac{n^2}{Z} a_0$$

The equation also shows us that as the electron's energy increases (as  $n$  increases), the electron is found at greater distances from the nucleus. This is implied by the inverse dependence on  $r$  in the Coulomb potential, since, as the electron moves away from the nucleus, the electrostatic attraction between it and the nucleus decreases, and it is held less tightly in the atom. Note that as  $n$  gets larger and the orbits get larger, their energies get closer to zero, and so the limits  $n \rightarrow \infty$ , and  $r \rightarrow \infty$  imply that  $E = 0$  corresponds to the ionization (energy) limit where the electron is completely removed from the nucleus. Thus, for hydrogen in the ground state  $n = 1$ , the ionization energy would be:

$$\Delta E = E_{n \rightarrow \infty} - E_1 = 0 + k = k$$

With three extremely puzzling paradoxes now solved (blackbody radiation, the photoelectric effect, and the hydrogen atom), and all involving Planck's constant in a fundamental manner, it became clear to most physicists at that time that the classical theories that worked so well in the macroscopic world were fundamentally flawed and could not be extended down into the microscopic domain of atoms and molecules. Unfortunately, despite Bohr's remarkable achievement in deriving a theoretical expression for the Rydberg constant, he was unable to extend his theory to the next simplest atom, He, which only has two electrons. Bohr's model was severely flawed, since it was still based on the classical mechanics notion of precise orbits, a concept that was later found to be untenable in the microscopic domain, when a proper model of quantum mechanics was developed to supersede classical mechanics.

For examples and exercises on applying these equations, visit section 6.2 – the Bohr Model In *Chemistry 2e*.

**Watch Bohr Model of the Hydrogen Atom (4min 49s). (<https://youtu.be/au2HCVn9IJI>)**

## Exercise 10.2a

### Check Your Learning Exercise (Text Version)

Part 1 Instructions: Review the scientist name list below. Match each of the nine scientists with their key discovery by filling in the [blank] with the correct scientist's name.

Scientist Name List (includes 9 names):

James Clerk Maxwell, Ernst Rutherford, Joseph von Fraunhofer, Gustav Kirchhoff, Robert Bunsen, Albert Einstein, Max Planck, Niels Bohr, Johannes Rydberg

Part 1 QUESTIONS:

1. [BLANK] accurately measured the wavelengths of solar absorption lines; these lines are named after the scientist who measured them.
2. [BLANK] developed an empirical formula that predicted all of hydrogen's emission lines, not just those restricted to the visible range.
3. [BLANK] predicted the existence of electromagnetic waves that travel at the speed of light. His theory also predicted how these waves behave, and how they carry both energy and momentum.
4. [BLANK] theorized that electrons can move from one discrete energy level (orbit) to another by absorbing or emitting quantized energy.
5. [BLANK] is known as the originator of the quantum theory. Energy is never emitted continuously from an atom, but in small, discrete quantities only. The smallest amount of energy that can be emitted or absorbed in the form of electromagnetic radiation is known as quantum.
6. [BLANK] and [BLANK] discovered that for the various chemical elements, the line emission spectrum of an element exactly matches its line absorption spectrum.
7. [BLANK] developed the planetary model of the nuclear atom since it pictured the atom as a miniature "solar system" with the electrons orbiting the nucleus (protons and neutrons) like planets orbiting the sun.
8. [BLANK] determined that light consists of photons whose energy is proportional to their frequency.

Part 2 Instructions: Read the following statements about the Bohr atom and determine whether the statement is True OR False.

9. Bohr suggested that the spectrum of hydrogen can be understood if one assumes that orbits

of only certain sizes and specific distances from the atom's nucleus are possible for the electron to exist in.

10. All electrons in an atom spiral into the nucleus of the atom as they lose energy.
11. Each element has a unique set of spectral lines that is characteristic of that element.
12. Lower energy levels are closer to the nucleus and higher energy levels are farther from the nucleus of an atom.
13. For an electron to move from a higher energy level to a lower energy level, it must absorb a discrete amount of energy from an outside source.
14. When an atom receives a quantum amount of energy from an outside source, it jumps to a higher orbit level and enters an excited state.
15. Matter is least stable when electrons fill the lowest possible energy levels.
16. The lowest principal energy level is  $n = 1$  and increase in increments of 1 for each successive higher energy level.
17. When an electron transitions from an excited state to its ground state, the difference in energy is emitted as a photon.

### Check Your Answer<sup>1</sup>

**Source:** "Exercise 10.2a" by Jackie MacDonald, licensed under CC BY-NC-SA 4.0

Bohr's model of the hydrogen atom provides insight into the behaviour of matter at the microscopic level, but it does not account for electron–electron interactions in atoms with more than one electron. It does introduce several important features of all models used to describe the distribution of electrons in an atom. These features include the following:

- The energies of electrons (energy levels) in an atom are quantized, described by **quantum numbers**: integer numbers having only specific allowed value and used to characterize the arrangement of electrons in an atom.
- An electron's energy increases (becomes less stable) with increasing distance from the nucleus.
- The discrete energies (lines) in the spectra of the elements result from quantized electronic energies.

Of these features, the most important is the postulate of quantized energy levels for an electron in an atom. As a consequence, the model laid the foundation for the quantum mechanical model of the atom. Bohr won a Nobel Prize in Physics for his contributions to our understanding of the structure of atoms and how that is related to line spectra emissions.

## Attribution & References

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## Notes

- |    |                                        |            |
|----|----------------------------------------|------------|
| 1. | 1. Joseph von Fraunhofer;              | 10. False; |
|    | 2. Johannes Rydberg;                   | 11. True;  |
|    | 3. James Clerk Maxwell;                | 12. True;  |
|    | 4. Niels Boh;                          | 13. False; |
|    | 5. Max Planck;                         | 14. True;  |
|    | 6. Gustav Kirchhoff and Robert Bunsen; | 15. False; |
|    | 7. Ernst Rutherford;                   | 16. True;  |
|    | 8. Albert Einstein;                    | 17. True   |
|    | 9. True                                |            |

## 10.3 WAVE NATURE OF MATTER

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### Learning Objectives

By the end of this section, you will be able to:

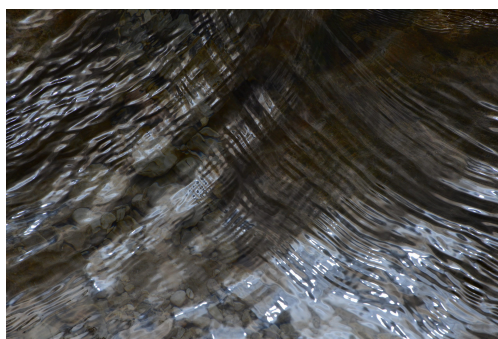
- Extend the concept of wave–particle duality that was observed in electromagnetic radiation to matter as well

Bohr’s model explained the experimental data for the hydrogen atom and was widely accepted, but it also raised many questions. Why did electrons orbit at only fixed distances defined by a single quantum number  $n = 1, 2, 3$ , and so on, but never in between? Why did the model work so well describing hydrogen and one-electron ions, but could not correctly predict the emission spectrum for helium or any larger atoms? To answer these questions, scientists needed to completely revise the way they thought about matter.

### Wave Behaviour of Matter from a Microscopic Perspective

We know how matter behaves in the macroscopic world – objects that are large enough to be seen by the naked eye follow the rules of classical physics. A billiard ball moving on a table will behave like a particle: It will continue in a straight line unless it collides with another ball or the table cushion, or is acted on by some other force (such as friction). The ball has a well-defined position and velocity (or a well-defined momentum,  $p = mv$ , defined by mass  $m$  and velocity  $v$ ) at any given moment. In other words, the ball is moving in a classical trajectory. This is the typical behaviour of a classical object.

When waves interact with each other, they show interference patterns that are not displayed by macroscopic particles such as the billiard ball. For example, interacting waves on the surface of water can produce interference patterns similar to those shown on Figure 10.3a. This is a case of wave behaviour on the macroscopic scale, and it is clear that particles and waves are very different phenomena in the macroscopic realm.



**Figure 10.3a:** Interference patterns on water surface: an interference pattern on the water surface is formed by interacting waves. The waves are caused by the reflection of water from the rocks. (credit: work by Daniela\_deGol, CC BY 4.0)

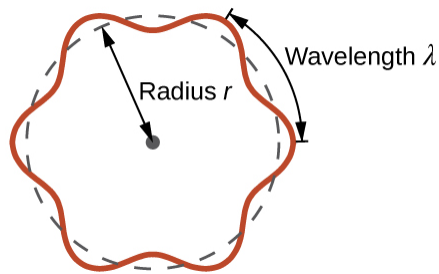
As technological improvements allowed scientists to probe the microscopic world in greater detail, it became increasingly clear by the 1920s that very small pieces of matter follow a different set of rules from those we observe for large objects. The unquestionable separation of waves and particles was no longer the case for the microscopic world.

One of the first people to pay attention to the special behaviour of the microscopic world was Louis de Broglie. He asked the question: If electromagnetic radiation can have particle-like character, can electrons and other submicroscopic particles exhibit wavelike character? In his 1925 doctoral dissertation, de Broglie extended the wave–particle duality of light that Einstein used to resolve the photoelectric-effect paradox to material particles. He predicted that a particle with mass  $m$  and velocity  $v$  (that is, with linear momentum  $p$ ) should also exhibit the behaviour of a wave with a wavelength value  $\lambda$ , given by this expression in which  $h$  is the familiar Planck’s constant:

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

This is called the *de Broglie wavelength*. Unlike the other values of  $\lambda$  discussed in this chapter, the de Broglie wavelength is a characteristic of particles and other bodies, not electromagnetic radiation (note that this equation involves velocity [ $v$ , m/s], not frequency [ $\nu$ , Hz]. Although these two symbols are identical, they mean very different things). Where Bohr had postulated the electron as being a particle orbiting the nucleus in quantized orbits, de Broglie argued that Bohr’s assumption of quantization can be explained if the electron is considered not as a particle, but rather as a circular standing wave such that only an integer number of wavelengths could fit exactly within the orbit (Figure 10.3b).





**Figure 10.3b:** de Broglie's electron circulating standing wave theory: if an electron is viewed as a wave circling around the nucleus, an integer number of wavelengths must fit into the orbit for this standing wave behaviour to be possible (credit: *Chemistry (OpenStax)*, CC BY 4.0).

For a circular orbit of radius  $r$ , the circumference is  $2\pi r$ , and so de Broglie's condition is:

$$2\pi r = n\lambda, n = 1, 2, 3, \dots$$

Since the de Broglie expression relates the wavelength to the momentum and, hence, velocity, this implies:

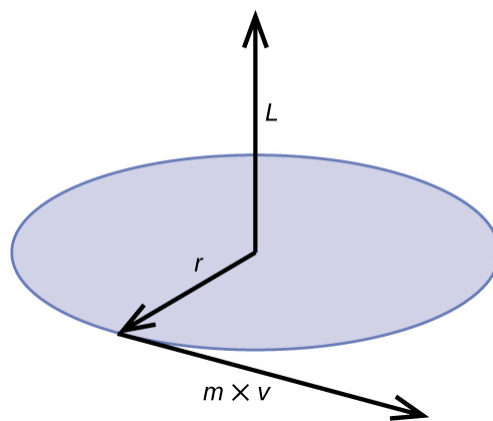
$$2\pi r = n\lambda = \frac{nh}{p} = \frac{nh}{mv} = \frac{nh}{mvr} = \frac{nh}{L}$$

This expression can be rearranged to give Bohr's formula for the quantization of the angular momentum:

$$L = \frac{nh}{2\pi} = n\hbar$$

Classical angular momentum  $L$  for a circular motion is equal to the product of the radius of the circle and the momentum of the moving particle  $p$  (Figure 10.3c).

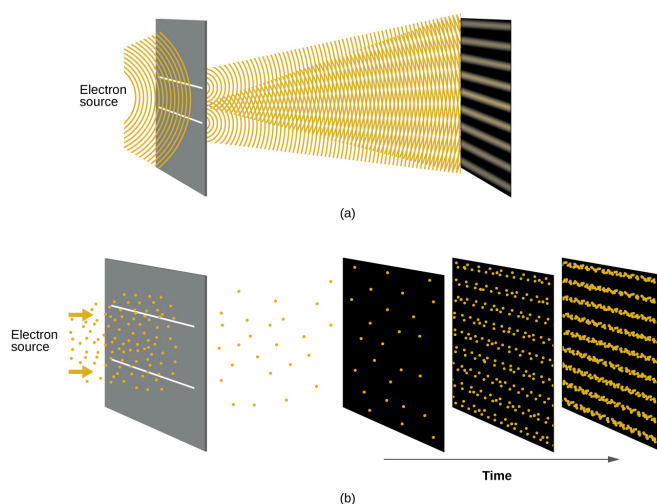
$$L = rp = rmv \text{ (for a circular motion)}$$



**Figure 10.3c:** Angular momentum for circular motion: the diagram shows angular momentum for a circular motion.  $L = rp = rmv$  (credit: *Chemistry (OpenStax)*, CC BY 4.0).

Shortly after de Broglie proposed the wave nature of matter, two scientists at Bell Laboratories, C. J. Davisson

and L. H. Germer, demonstrated experimentally that electrons can exhibit wavelike behaviour by showing an interference pattern for electrons travelling through a regular atomic pattern in a crystal. The regularly spaced atomic layers served as slits, as used in other interference experiments. Since the spacing between the layers serving as slits needs to be similar in size to the wavelength of the tested wave for an interference pattern to form, Davisson and Germer used a crystalline nickel target for their “slits,” since the spacing of the atoms within the lattice was approximately the same as the de Broglie wavelengths of the electrons that they used. Figure 10.3d shows an interference pattern.



**Figure 10.3d:** Experiments showing interference pattern for electrons: (a) The interference pattern for electrons passing through very closely spaced slits demonstrates that quantum particles such as electrons can exhibit wavelike behaviour. (b) The experimental results illustrated here demonstrate the wave–particle duality in electrons. The electrons pass through very closely spaced slits, forming an interference pattern, with increasing numbers of electrons being recorded from the left image to the right. With only a few electrons recorded, it is clear that the electrons arrive as individual localized “particles,” but in a seemingly random pattern. As more electrons arrive, a wavelike interference pattern begins to emerge. Note that the probability of the final electron location is still governed by the wave-type distribution, even for a single electron, but it can be observed more easily if many electron collisions have been recorded (credit: *Chemistry (OpenStax)*, CC BY 4.0).

The wave–particle duality of matter can be seen in Figure 10.3d by observing what happens if electron collisions are recorded over a long period of time. Initially, when only a few electrons have been recorded, they show clear particle-like behaviour, having arrived in small localized packets that appear to be random. As more and more electrons arrived and were recorded, a clear interference pattern that is the hallmark of wavelike behaviour emerged. Thus, it appears that while electrons are small localized particles, their motion does not follow the equations of motion implied by classical mechanics, but instead it is governed by some type of a wave equation that governs a probability distribution even for a single electron’s motion. Thus the wave–particle duality first observed with photons is actually a fundamental behaviour intrinsic to all quantum particles.

**Watch Dr. Quantum – Double Slit Experiment (5min 12s) (<https://youtu.be/Q1YqgPAzho>)**

### Example 10.3a

#### Calculating the Wavelength of a Particle

If an electron travels at a velocity of  $1.000 \times 10^7 \text{ m s}^{-1}$  and has a mass of  $9.109 \times 10^{-28} \text{ g}$ , what is its wavelength?

#### Solution

We can use de Broglie's equation to solve this problem, but we first must do a unit conversion of Planck's constant. You learned earlier that  $1 \text{ J} = 1 \text{ kg m}^2/\text{s}^2$ . Thus, we can write  $h = 6.626 \times 10^{-34} \text{ J s}$  as  $6.626 \times 10^{-34} \text{ kg m}^2/\text{s}$ .

$$\begin{aligned}\lambda &= \frac{h}{mv} \\ &= \frac{6.626 \times 10^{-34} \text{ kg m}^2/\text{s}}{(9.190 \times 10^{-31} \text{ kg})(1.000 \times 10^7 \text{ m/s})} \\ &= 7.274 \times 10^{-11} \text{ m}\end{aligned}$$

This is a small value, but it is significantly larger than the size of an electron in the classical (particle) view. This size is the same order of magnitude as the size of an atom. This means that electron wavelike behaviour is going to be noticeable in an atom.

### Exercise 10.3a

Calculate the wavelength of a softball with a mass of 100 g traveling at a velocity of  $35 \text{ m s}^{-1}$ , assuming that it can be modelled as a single particle.

#### Check Your Answer<sup>1</sup>

We never think of a thrown softball having a wavelength, since this wavelength is so small it is impossible for our senses or any known instrument to detect (strictly speaking, the wavelength of a real baseball would correspond to the wavelengths of its constituent atoms and molecules, which, while much larger than this

value, would still be microscopically tiny). The de Broglie wavelength is only appreciable for matter that has a very small mass and/or a very high velocity.

Werner Heisenberg considered the limits of how accurately we can measure properties of an electron or other microscopic particles. He determined that there is a fundamental limit to how accurately one can measure both a particle's position and its momentum simultaneously. The more accurately we measure the momentum of a particle, the less accurately we can determine its position at that time, and vice versa. This is summed up in what we now call the **Heisenberg uncertainty principle**: *It is fundamentally impossible to determine simultaneously and exactly both the momentum and the position of a particle.* For a particle of mass  $m$  moving with velocity  $v_x$  in the  $x$  direction (or equivalently with momentum  $p_x$ ), the product of the uncertainty in the position,  $\Delta x$ , and the uncertainty in the momentum,  $\Delta p_x$ , must be greater than or equal to  $\frac{\hbar}{2}$  (recall that  $\hbar = \frac{h}{2\pi}$ , the value of Planck's constant divided by  $2\pi$ ).

$$\Delta x \times \Delta p_x = (\Delta x)(m\Delta v) \geq \frac{\hbar}{2}$$

This equation allows us to calculate the limit to how precisely we can know both the simultaneous position of an object and its momentum. For example, if we improve our measurement of an electron's position so that the uncertainty in the position ( $\Delta x$ ) has a value of, say, 1 pm ( $10^{-12}$  m, about 1% of the diameter of a hydrogen atom), then our determination of its momentum must have an uncertainty with a value of at least

$$[\Delta p = m\Delta v = \frac{h}{(2\Delta x)}] = \frac{(1.055 \times 10^{-34} \text{ kg m}^2/\text{s})}{(2 \times 1 \times 10^{-12} \text{ m})} = 5 \times 10^{-23} \text{ kg m/s}$$

The value of  $\hbar$  is not large, so the uncertainty in the position or momentum of a macroscopic object like a baseball is too insignificant to observe. However, the mass of a microscopic object such as an electron is small enough that the uncertainty can be large and significant.

It should be noted that Heisenberg's uncertainty principle is not just limited to uncertainties in position and momentum, but it also links other dynamical variables. For example, when an atom absorbs a photon and makes a transition from one energy state to another, the uncertainty in the energy and the uncertainty in the time required for the transition are similarly related, as  $\Delta E \Delta t \geq \frac{\hbar}{2}$ . Even the vector components of angular momentum cannot all be specified exactly simultaneously.

**Watch The Basics of Quantum Mechanics: What is the Heisenberg Uncertainty Principle? (4min 43s).** (<https://youtu.be/TQKELOE9eY4>)

Heisenberg's principle imposes ultimate limits on what is knowable in science. The uncertainty principle can be shown to be a consequence of wave-particle duality, which lies at the heart of what distinguishes modern quantum theory from classical mechanics. Recall that the equations of motion obtained from classical mechanics are trajectories where, at any given instant in time, both the position and the momentum of a particle can be determined exactly. Heisenberg's uncertainty principle implies that such a view is untenable in

the microscopic domain and that there are fundamental limitations governing the motion of quantum particles. This does not mean that microscopic particles do not move in trajectories, it is just that measurements of trajectories are limited in their precision. In the realm of quantum mechanics, measurements introduce changes into the system that is being observed.

The modern model for the electronic structure of the atom is based on recognizing that an electron possesses particle and wave properties, the so-called wave–particle duality.

## Attribution & References

Except where otherwise noted, this page is adapted by Jackie MacDonald from:

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## Notes

1.  $1.9 \times 10^{-34}$  m

# 10.4 QUANTUM MECHANICAL MODEL OF THE ATOM

## Learning Objectives

By the end of this section, you will be able to:

- Understand the general idea of the quantum mechanical description of electrons in orbitals
- Relate the 3D shape of an orbital and how electrons are arranged within the atom to the radial distribution function
- List and describe traits of the four quantum numbers that describe orbitals and specify the location of an electron in an atom

Shortly after de Broglie published his ideas that the electron in a hydrogen atom could be better thought of as being a circular standing wave instead of a particle moving in quantized circular orbits, as Bohr had argued, Erwin Schrödinger extended de Broglie's work by incorporating the de Broglie relation into a wave equation, deriving what is today known as the Schrödinger equation. When Schrödinger applied his equation to hydrogen-like atoms, he was able to reproduce Bohr's expression for the energy and, thus, the Rydberg formula governing hydrogen spectra, and he did so without having to invoke Bohr's assumptions of stationary states and quantized orbits, angular momenta, and energies. Quantization in Schrödinger's theory was a natural consequence of the underlying mathematics of the wave equation. Like de Broglie, Schrödinger initially viewed the electron in hydrogen as being a physical wave instead of a particle, but where de Broglie thought of the electron in terms of circular stationary waves, Schrödinger properly thought in terms of three-dimensional stationary waves, or wavefunctions, represented by the Greek letter psi,  $\psi$ . A few years later, Max Born proposed an interpretation of the wavefunction  $\psi$  that is still accepted today: Electrons are still particles, and so the waves represented by  $\psi$  are not physical waves but, instead, are complex probability amplitudes. The square of the magnitude of a wavefunction  $|\psi|^2$  describes the probability of the quantum particle being present near a certain location in space. This means that wavefunctions can be used to determine the distribution of the electron's density with respect to the nucleus in an atom. In the most general form, the Schrödinger equation can be written as:

$$\hat{H}\psi = E\psi$$

$\hat{H}$  is the Hamiltonian operator, a set of mathematical operations representing the total energy of the quantum particle (such as an electron in an atom),  $\psi$  is the wavefunction of this particle that can be used to find the special distribution of the probability of finding the particle, and  $E$  is the actual value of the total energy of the particle.

Schrödinger's work, as well as that of Heisenberg and many other scientists following in their footsteps, is generally referred to as **quantum mechanics**.

**Watch The Basics of Quantum Mechanics – What can Schrödinger's Cat Teach us about Quantum Mechanics? (5min 23sec).** (<https://youtu.be/z1GCnycbMeA>)

**Watch The uncertain location of electrons (3:46 min)** (<https://youtu.be/8ROHpZ0A70I?>)

**Video Source:** TED-Ed. (2013, October 14). *The uncertain location of electrons – George Zaidan and Charles Morton* [Video]. YouTube.

## Understanding Quantum Theory of Electrons in Atoms

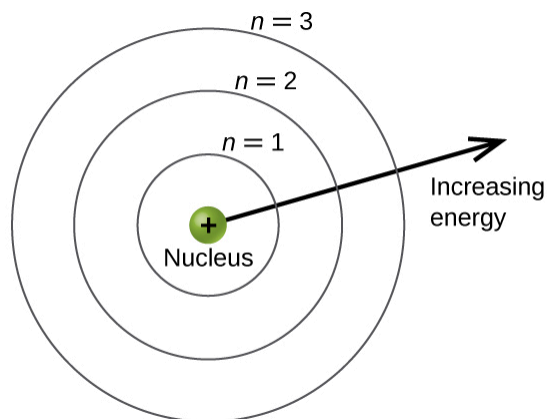
Key discoveries about electron orbitals (location of electrons in atoms), their different energies, and other quantum properties led to our modern day understanding of atomic theory. The use of quantum theory provides the best understanding to these topics and provides the foundation to understanding why and how elements combine to form molecules through chemical bonding.

As was described previously, electrons in atoms can exist only on discrete energy levels but not between them. It is said that the energy of an electron in an atom is quantized, that is, it can be equal only to certain specific values and can jump from one energy level to another but not transition smoothly or stay between these levels. In atoms, an electron's location around the nucleus of an atom can be defined by four quantum numbers: the **principal quantum number** ( $n$ ), the orbital **angular momentum quantum number** ( $l$ ), the **magnetic quantum number** ( $m_l$ ), and the electron spin quantum number ( $m_s$ ).

### Principal Quantum Number

The principal energy levels are labeled with an  $n$  value, where  $n = 1, 2, 3, \dots$ . Generally speaking, the energy of an electron in an atom is greater for greater values of  $n$  and as the  $n$  value increases, so does the distance from the nucleus of the atom. This number,  $n$ , is referred to as the principal quantum number. The principal quantum number defines the location of the energy level and is essentially the same concept as the  $n$  in the Bohr atom description. Another name for the principal quantum number is the shell number. The **spin quantum numbers** shells of an atom can be thought of as concentric circles radiating out from the nucleus. The electrons that belong to a specific shell are most likely to be found within the corresponding circular area. The

further we proceed from the nucleus, the higher the shell number, and so the higher the energy level (Figure 10.4a). The positively charged protons in the nucleus stabilize the electronic orbitals by electrostatic attraction between the positive charges of the protons and the negative charges of the electrons. So the further away the electron is from the nucleus, the greater the energy it has.



**Figure 10.4a:** Principal energy level schematic: different shells are numbered by principal quantum numbers (credit: *Chemistry (OpenStax)*, CC BY 4.0).

This quantum mechanical model for where electrons reside in an atom can be used to look at electronic transitions, the events when an electron moves from one energy level to another. As postulated by Bohr, if the transition is to a higher energy level, energy is absorbed, and the energy change has a positive value. To obtain the amount of energy necessary for the transition to a higher energy level, a photon of light is absorbed by the atom. A transition to a lower energy level involves a release of energy, and the discrete energy change is negative. This process is accompanied by emission of a photon by the atom. The following equation summarizes these relationships and is based on the hydrogen atom:

$$\Delta E = E_{\text{final}} - E_{\text{initial}} = -2.18 \times 10^{-18} \left( \frac{1}{n_{\text{f}}^2} - \frac{1}{n_{\text{i}}^2} \right) \text{ J}$$

The values  $n_{\text{f}}$  and  $n_{\text{i}}$  are the final and initial energy states of the electron. To review calculations of such energy changes, see examples provided in *Chapter 10.2 – The Bohr Atom*.

The principal quantum number is one of three quantum numbers used to characterize an orbital. An **atomic orbital**, however, is distinct from Bohr's *orbit* analogy where the electron was thought to move around the nucleus in circular, defined orbits. Instead, an atomic orbital is a general region in an atom within which an electron is most probable to reside or be found in a given instant. The quantum mechanical model specifies the probability of finding an electron in the three-dimensional space around the nucleus and is based on solutions of the Schrödinger equation. It does not provide the precise path taken by an electron. In addition, the principal quantum number defines the energy of an electron in a hydrogen or hydrogen-like



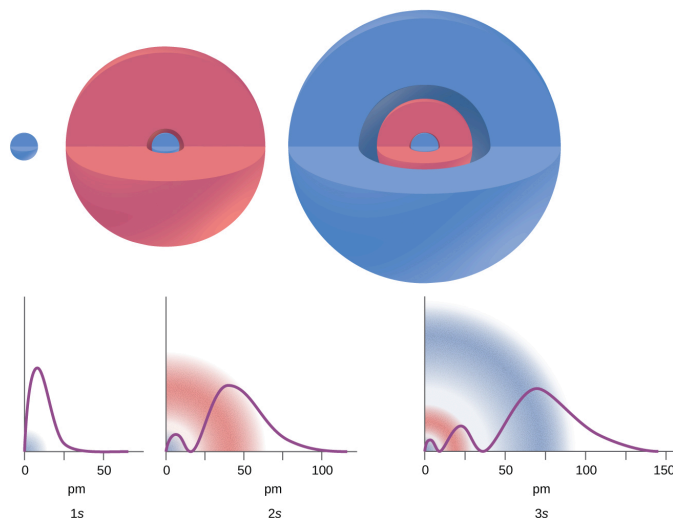
atom or an ion (an atom or an ion with only one electron) and the general region in which discrete energy levels of electrons in a multi-electron atoms and ions are located.

## Angular Momentum Quantum Number

Another quantum number is  $l$ , the angular momentum quantum number. It is an integer that defines the shape of the orbital, and takes on the values,  $l = 0, 1, 2, \dots, n - 1$ . This means that an orbital with  $n = 1$  can have only one value of  $l$ ,  $l = 0$  (one orbital shape), whereas  $n = 2$  permits  $l = 0$  and  $l = 1$  (two orbital shapes) and so on. The principal quantum number defines the general size and energy of the orbital. The  $l$  value specifies the shape of the orbital. Orbitals with the same value of  $l$  form a **subshell**. In addition, the greater the angular momentum quantum number, the greater is the angular momentum of an electron at this orbital.

Orbitals with  $l = 0$  are called **s orbitals** (or the  $s$  subshells). The value  $l = 1$  corresponds to the  $p$  orbitals. For a given  $n$ , **p orbitals** constitute a  $p$  subshell (e.g.,  $3p$  if  $n = 3$ ). The orbitals with  $l = 2$  are called the **d orbitals**, followed by the  $l = 3$ , called the  $f$  orbitals. There are higher values we will not consider, as introductory chemistry courses typically focus on  $s$ ,  $p$ ,  $d$  and sometimes  $f$  orbitals.

There are certain distances from the nucleus at which the probability density of finding an electron located at a particular orbital is zero. In other words, the value of the wave function  $\psi$  is zero at this distance for this orbital. Such a value of radius  $r$  is called a radial node, which is the spherical surface region where the probability of finding an electron is zero. The number of radial nodes in an orbital is  $n - l - 1$ .

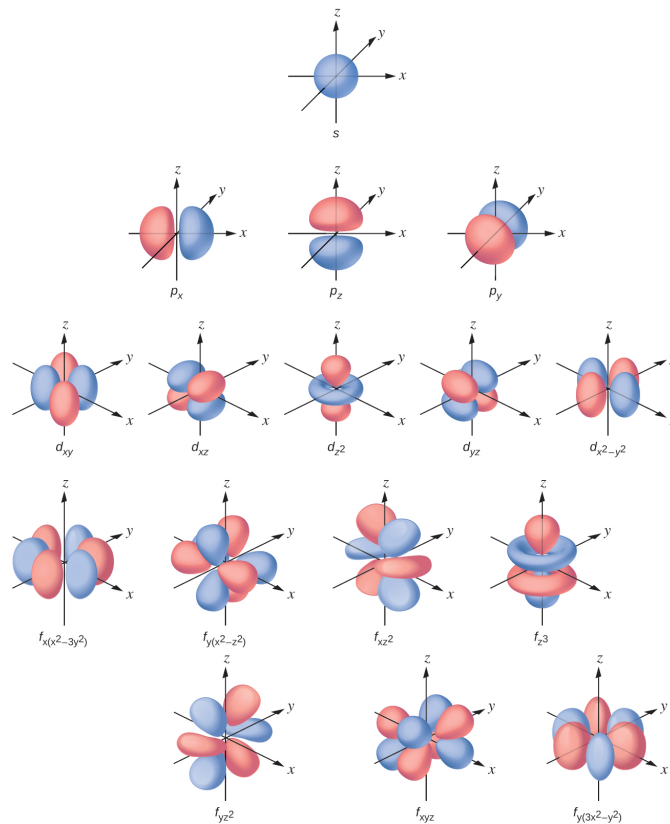


**Figure 10.4b:** Probability of finding an electron vs distance from nucleus: the graphs show the probability (y axis) of finding an electron for the 1s, 2s, 3s orbitals as a function of distance from the nucleus (credit: Chemistry (OpenStax), CC BY 4.0).

Consider the examples in Figure 10.4b. The orbitals depicted are of the  $s$  type (which were determined to be sphere shaped probability orbital shapes), thus  $l = 0$  for all of them. It can be seen from the graphs of the

probability densities that for  $1s$  ( $n = 1$ ) there are  $1 - 0 - 1 = 0$  places where the density is zero (nodes). For  $2s$  ( $n = 2$ ) there are  $2 - 0 - 1 = 1$  node, and for the  $3s$  orbitals ( $n = 3$ ) there are  $3 - 0 - 1 = 2$  nodes.

It was determined that the  $s$  subshell electron density distribution is spherical and the  $p$  subshell has a dumbbell shape. The  $d$  and  $f$  orbitals are more complex. These shapes represent the three-dimensional regions within which the electron is likely to be found (Figure 10.4c).



**Figure 10.4c:** The shapes of orbitals: shapes of  $s$ ,  $p$ ,  $d$ , and  $f$  orbitals (credit: *Chemistry (OpenStax)*, CC BY 4.0).

If an electron has an angular momentum ( $l \neq 0$ ), (as it will in  $p$ ,  $d$ ,  $f$  orbitals), then this vector can point in different directions. In addition, the  $z$  component of the angular momentum can have more than one value. This means that if a magnetic field is applied in the  $z$  direction, orbitals with different values of the  $z$  component of the angular momentum will have different energies resulting from interacting with the field. This provides the third quantum numbers, the magnetic quantum number, called  $m_l$ ,

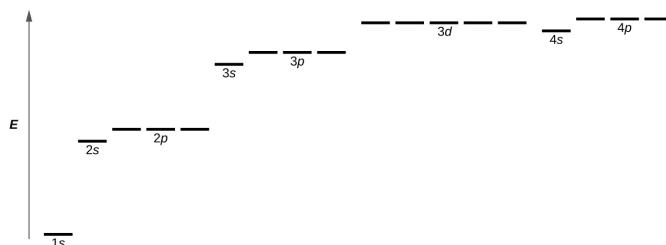
## Magnetic Quantum Number

The magnetic quantum number ( $m_l$ ) specifies the  $z$  component of the angular momentum for a particular orbital. For example, for an  $s$  orbital,  $l = 0$ , and the only value of  $m_l$  is zero. For  $p$  orbitals,  $l = 1$ , and  $m_l$  can be equal to  $-1$ ,  $0$ , or  $+1$ . Generally speaking,  $m_l$  can be equal to  $-l$ ,  $-(l - 1)$ , ...,  $-1$ ,  $0$ ,  $+1$ , ...,  $(l - 1)$ ,  $l$ . The total

number of possible orbitals with the same value of  $l$  (a subshell) is  $2l + 1$ . Thus, there is one  $s$ -orbital for  $m_l = 0$ , there are three  $p$ -orbitals for  $m_l = 1$ , five  $d$ -orbitals for  $m_l = 2$ , seven  $f$ -orbitals for  $m_l = 3$ , and so forth.

In summary, the principal quantum number defines the general value of the electronic energy, the angular momentum quantum number determines the shape of the orbital, and the magnetic quantum number specifies number of orientations of the orbital in space, as can be seen in Figure 10.4c.

Figure 10.4d illustrates the energy levels for various orbitals. The number before the orbital name (such as  $2s$ ,  $3p$ , and so forth) stands for the principal quantum number,  $n$ . The letter in the orbital name defines the subshell with a specific angular momentum quantum number  $l = 0$  for  $s$  orbitals, 1 for  $p$  orbitals, 2 for  $d$  orbitals. Finally, there are more than one possible orbitals for  $l \geq 1$  ( $p$ ,  $d$ , and  $f$  orbitals), each corresponding to a specific orientation, value of  $m_l$ . Figure 10.4d illustrates the concept of **degeneracy**, electron orbitals having the same energy levels. In the case of a hydrogen atom or a one-electron ion (such as  $\text{He}^+$ ,  $\text{Li}^{2+}$ , and so on), energies of all the orbitals with the same  $n$  are the same. In this case, the energy levels for the same principle quantum number,  $n$ , are called degenerate energy levels. However, in atoms with more than one electron, this degeneracy is eliminated by the electron–electron interactions, and orbitals that belong to different subshells in the same energy level have different energies, as shown on Figure 10.4d. For instance, an electron in the  $2s$  orbital has lower energy than one in any of the three  $2p$  orbitals. Orbitals of the same subshell ( $l$  value) are still degenerate and have the same energy (for example any of the three  $2p$  subshells will have the same energy).



**Figure 10.4d:** Energy levels of electron orbitals: the chart shows the energies of electron orbitals in a multi-electron atom (credit: *Chemistry (OpenStax)*, CC BY 4.0).

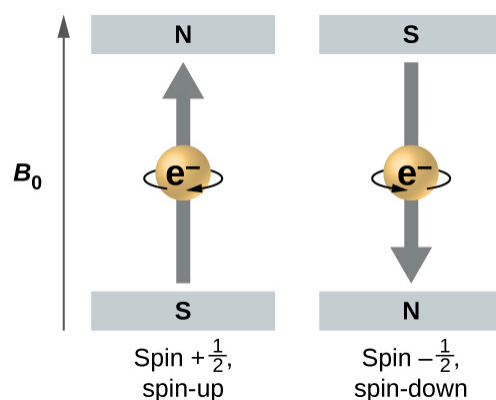
## Spin Quantum Number

While the three quantum numbers discussed in the previous paragraphs work well for describing electron orbitals, some experiments showed that they were not sufficient to explain all observed results. It was demonstrated in the 1920s that when hydrogen-line spectra are examined at extremely high resolution, some lines are actually not single peaks but, rather, pairs of closely spaced lines. This is the so-called fine structure of the spectrum, and it implies that there are additional small differences in energies of electrons even when they are located in the same orbital. These observations led Samuel Goudsmit and George Uhlenbeck to propose that electrons have a fourth quantum number. They called this the spin quantum number, or  $m_s$ .

The other three quantum numbers,  $n$ ,  $l$ , and  $m_l$ , are properties of specific atomic orbitals that also define in what part of the space an electron is most likely to be located. Orbitals are a result of solving the Schrödinger

equation for electrons in atoms. The electron spin is a different kind of property. It is a completely quantum phenomenon with no analogues in the classical realm. In addition, it cannot be derived from solving the Schrödinger equation and is not related to the normal spatial coordinates (such as the Cartesian  $x$ ,  $y$ , and  $z$ ). Electron spin describes an intrinsic electron “rotation” or “spinning.” Each electron acts as a tiny magnet or a tiny rotating object with an angular momentum, even though this rotation cannot be observed in terms of the spatial coordinates.

The magnitude of the overall electron spin can only have one value, and an electron can only “spin” in one of two quantized states. One is termed the  $\alpha$  state, with the  $z$  component of the spin being in the positive direction of the  $z$  axis. This corresponds to the spin quantum number  $m_s = \frac{1}{2}$ . The other is called the  $\beta$  state, with the  $z$  component of the spin being negative and  $m_s = -\frac{1}{2}$ . Any electron, regardless of the atomic orbital it is located in, can only have one of those two values of the spin quantum number. The energies of electrons having  $m_s = -\frac{1}{2}$  and  $m_s = \frac{1}{2}$  are different if an external magnetic field is applied.



**Figure 10.4e:** The spin quantum number ( $m_s$ ): electrons with two possible spin values  $\pm 1/2$  in an external magnetic field (credit: *Chemistry (OpenStax)*, CC BY 4.0).

Figure 10.4e illustrates this phenomenon. An electron acts like a tiny magnet. Its moment is directed up (in the positive direction of the  $z$  axis) for the  $\frac{1}{2}$  spin quantum number and down (in the negative  $z$  direction) for the spin quantum number of  $-\frac{1}{2}$ . A magnet has a lower energy if its magnetic moment is aligned with the external magnetic field (the left electron on Figure 10.4e) and a higher energy for the magnetic moment being opposite to the applied field. This is why an electron with  $m_s = \frac{1}{2}$  has a slightly lower energy in an external field in the positive  $z$  direction, and an electron with  $m_s = -\frac{1}{2}$  has a slightly higher energy in the same field. This is true even for an electron occupying the same orbital in an atom. A spectral line

corresponding to a transition for electrons from the same orbital but with different spin quantum numbers has two possible values of energy; thus, the line in the spectrum will show a fine structure splitting.

## The Pauli Exclusion Principle

An electron in an atom is completely described by four quantum numbers:  $n$ ,  $l$ ,  $m_l$ , and  $m_s$ . The first three quantum numbers define the orbital and the fourth quantum number describes the intrinsic electron property called spin. An Austrian physicist Wolfgang Pauli formulated a general principle that gives the last piece of information that we need to understand the general behaviour of electrons in atoms. The **Pauli exclusion principle** can be formulated as follows: No two electrons in the same atom can have exactly the same set of all the four quantum numbers. What this means is that electrons can share the same orbital (the same set of the quantum numbers  $n$ ,  $l$ , and  $m_l$ ), but only if their spin quantum numbers,  $m_s$ , have different values. Since the spin quantum number can only have two values ( $\pm \frac{1}{2}$ ), no more than two electrons can occupy the same orbital (and if two electrons are located in the same orbital, they must have opposite spins). Therefore, any atomic orbital can be populated by only zero, one, or two electrons.

The properties and meaning of the quantum numbers of electrons in atoms are briefly summarized in Table 10.4a.

**Table 10.4a: Quantum Numbers, Their Properties, and Significance**

Name	Symbol	Allowed values	Physical meaning
principal quantum number	$n$	1, 2, 3, 4, ...	shell, the general region for the value of energy for an electron on the orbital; principal energy level
angular momentum or azimuthal quantum number	$l$	$0 \leq l \leq n - 1$	subshell, the shape of the orbital ( $s, p, d, f, \dots$ )
magnetic quantum number	$m_l$	$-l \leq m_l \leq l$	orientation of the orbital
spin quantum number	$m_s$	$\frac{1}{2}, -\frac{1}{2}$	direction of the intrinsic quantum “spinning” of the electron

The quantum (wave) mechanical model of the atom was devised. Electrons occupy orbitals, which are probability fields or spaces around the nucleus of an atom where an electron is likely to be found. Important criteria was established in developing this modern atomic theory:

1. Atoms have a series of energy levels called principal energy levels, which are designated by whole numbers ( $n = 1, 2, 3, \dots$ ).
2. The energy of the level increases as the value of  $n$  increases.

- Each principal energy level contains one or more types of orbitals, called subshells.
- The number of subshells present in a given principal energy level equals  $n$ . For example: Principal energy level 4 ( $n = 4$ ) has 4 subshells including  $s$ ,  $p$ ,  $d$  and  $f$
- The  $n$  value is always used to label the orbitals of a given principal level and is followed by a letter that indicates the type (shape) of the orbital (For example:  $1s$ ,  $2p$ ,  $3d$  ...).
- An orbital can be empty or it can contain one or two electrons, but never more than two. If two electrons occupy the same orbital, they must have opposite spins.
- The shape of an orbital does not indicate the specific details of electron movement (how it moves in a given orbital). It gives the probability distribution for where an electron is most likely to be found in that orbital.
- The total number of orbitals in a given shell (principal energy level) is  $2n$  and the maximum number of electrons in each shell (principal energy level) is  $2n^2$ .

The properties of the principal energy levels ( $n = 1-4$ ), subshells, and capacity of electrons in each subshell and energy level is summarized in Table 10.4b.

**Table 10.4b: Types of Orbitals and Electron Capacities of the First Four Principal Energy Levels**

Principal Energy Level ( $n$ )	Type of Subshell ( $l$ )	Number of Orbitals per Type of Subshell ( $m_l$ )	Orbital Name	Maximum Number of Electrons in each Subshell	Maximum Number of Electrons in each Principal Energy Level ( $2n^2$ )
1	$s(0)$	1 (0)	$1s$	2	2
2	$s(0)$	1 (0)	$2s$	2	8
2	$p(1)$	3 (-1, 0, +1)	$2p$	6	
3	$s(0)$	1 (0)	$3s$	2	18
3	$p(1)$	3 (-1, 0, +1)	$3p$	6	
3	$d(2)$	5 (-2, -1, 0, +1, +2)	$3d$	10	
4	$s(0)$	1 (0)	$4s$	2	32
4	$p(1)$	3 (-1, 0, +1)	$4p$	6	
4	$d(2)$	5 (-2, -1, 0, +1, +2)	$4d$	10	
4	$f(3)$	7 (-3, -2, -1, 0, +1, +2, +3)	$4f$	14	

**Source:** “Table 10.4b” by Jackie MacDonald is licensed under CC BY-NC-SA 4.0.

For a video summary on quantum numbers and atomic orbitals as well as an introduction to electron orbital filling watch **Quantum Numbers, Atomic Orbitals, and Electron Configurations (8min 41s)** (<https://youtu.be/Aoi4j8es4gQ>)

## Example 10.4a

### Working with Shells and Subshells

Indicate the number of subshells, the number of orbitals in each subshell, and the values of  $l$  and  $m_l$  for the orbitals in the  $n = 4$  shell of an atom. How many total orbitals are in principal energy level four ( $n = 4$ )

### Solution

For  $n = 4$ ,  $l$  can have values of 0, 1, 2, and 3. Thus,  $s$ ,  $p$ ,  $d$ , and  $f$  subshells are found in the  $n = 4$  shell of an atom.

For  $l = 0$  (the  $s$  subshell),  $m_l$  can only be 0. Thus, there is only one  $4s$  orbital.

For  $l = 1$  ( $p$ -type orbitals),  $m_l$  can have values of  $-1$ ,  $0$ ,  $+1$ , so we find three  $4p$  orbitals.

For  $l = 2$  ( $d$ -type orbitals),  $m_l$  can have values of  $-2$ ,  $-1$ ,  $0$ ,  $+1$ ,  $+2$ , so we have five  $4d$  orbitals.

When  $l = 3$  ( $f$ -type orbitals),  $m_l$  can have values of  $-3$ ,  $-2$ ,  $-1$ ,  $0$ ,  $+1$ ,  $+2$ ,  $+3$ , and we can have seven  $4f$  orbitals.

Thus, we find a total of  $(1+3+5+7)$  16 orbitals in the  $n = 4$  shell of an atom.

## Exercise 10.4a

### Working with Shells and Subshells

Identify the subshell in which electrons with the following quantum numbers are found: (a)  $n = 3, l = 1$ ; (b)  $n = 4, l = 3$ ; (c)  $n = 2, l = 0$ ; (d)  $n = 5, l = 0$ ; (e)  $n = 3, l = 2$

### Check Your Answer<sup>1</sup>

## Example 10.4b

### Maximum Number of Electrons – Electron Capacity

Calculate the maximum number of electrons that can occupy a shell with (a)  $n = 2$ , (b)  $n = 4$ , and (c)  $n$  as a variable. Note you are only looking at the orbitals with the specified  $n$  value, not those at lower energies.

### Solution

(a) When  $n = 2$ , there are four orbitals (a single  $2s$  orbital, and three orbitals labeled  $2p$ ). Since a maximum of two electrons can occupy the same orbital, these four orbitals can contain eight electrons. (4 orbitals  $\times$  2 electrons in each orbital = 8 electrons).

(b) When  $n = 4$ , there are four subshells of orbitals that we need to sum:

1 orbital labeled  $4s$

3 orbitals labeled  $4p$

5 orbitals labeled  $4d$

7 orbitals labeled  $4f$

---

16 orbitals total



Again, each orbital holds two electrons, so 32 electrons can fit in this  $n = 4$  shell (32 electrons can fit in the fourth energy level)

Alternatively, one could use the formula  $2n^2 = 2(4)^2 = 2(16) = 32$  electrons.

(c) The number of orbitals in any shell  $n$  will equal  $n^2$ . There can be up to two electrons in each orbital, so the maximum number of electrons will be  $2 \times n^2$

## Exercise 10.4b

### Electron Capacity

Calculate the maximum number of electrons that can occupy a shell with

- $n = 1$
- $n = 5$

### Check Your Answer<sup>2</sup>

## Exercise 10.4c

### Electron Capacity

If a shell contains a maximum of 32 electrons, what is the principal quantum number,  $n$ ?

### Check Your Answer<sup>3</sup>

## Example 10.4c

### Working with Quantum Numbers

Complete the following table for atomic orbitals using the following rules:

- The orbital designation is  $nl$ , where  $l = 0, 1, 2, 3, 4, \dots$  is mapped to the letter sequence  $s, p, d, f, g, \dots$ ,
- The  $m_l$  degeneracy is the number of orbitals within an  $l$  subshell, and so is  $2l + 1$  (there is one  $s$  orbital, three  $p$  orbitals, five  $d$  orbitals, seven  $f$  orbitals, and so forth).

- The number of radial nodes is equal to  $n - l - 1$ .

**Table 10.4c: Working with Quantum Numbers Exercise 10.4c** (Fill the spaces marked with blank in each column)

Orbital	$n$	$l$	$m_l$ degeneracy	Radial nodes (no.)
$4f$	[blank]	[blank]	[blank]	[blank]
[blank]	4	1	[blank]	[blank]
[blank]	7	[blank]	7	3
$5d$	[blank]	[blank]	[blank]	[blank]

## Solution

**Table 10.4d: Answers to Exercise 10.4c – Working with Quantum Numbers**

Orbital	$n$	$l$	$m_l$ degeneracy	Radial nodes (no.)
$4f$	4	3	7	0
$4p$	4	1	3	2
$7f$	7	3	7	3
$5d$	5	2	5	2

## Exercise 10.4d

How many orbitals have  $l = 2$  and  $n = 3$ ?

**Check Your Answer<sup>4</sup>**

## Attribution & References

Except where otherwise noted, this page is adapted by Jackie MacDonald from:

- “6.3 Development of Quantum Theory (<https://openstax.org/books/chemistry-2e/pages/6-3-development-of-quantum-theory>)” In *Chemistry 2e (Open Stax)* by Paul Flowers, Klaus Theopold,

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- “3.3 Development of Quantum Theory (<https://boisestate.pressbooks.pub/chemistry/chapter/3-3-development-of-quantum-theory/>)” In *General Chemistry 1 & 2* by Rice University, a derivative of *Chemistry (Open Stax)* by Paul Flowers, Klaus Theopold, Richard Langley & William R. Robinson and is licensed under CC BY 4.0. Access for free at *Chemistry (OpenStax)* (<https://openstax.org/books/chemistry/pages/1-introduction>)

## Notes

- $n = 3$  is the third energy level,  $l = 1$  represents  $p$  orbital ANSWER is  $3p$ ;
  - $n = 4$  is the fourth energy level,  $l = 3$  represents  $f$  orbital ANSWER is  $4f$ ;
  - $n = 2$  is the second energy level,  $l = 0$  represents  $s$  orbital ANSWER is  $2s$ ;
  - $n = 5$  is the fifth energy level,  $l = 0$  represents  $s$  orbital ANSWER is  $5s$ ;
  - $n = 3$  is the third energy level,  $l = 2$  represents  $d$  orbital ANSWER is  $3d$
- $2n^2 = 2(1)^2 = 2$  electrons fill the first principal energy level (shell,  $n = 1$ );
  - $2n^2 = 2(5)^2 = 50$  electrons fill the fifth principal energy level (shell,  $n = 5$ )
  - ANSWER  $n = 4$  follow these steps to solve:  $2n^2 = 32$  (divide each side by two)  $n^2 = 16$  (take the root of each side)  $n = 4$ ; the fourth shell can has a capacity to fit 32 electrons
  - the five degenerate  $3d$  orbitals

# 10.5 ATOMIC STRUCTURES OF THE FIRST 20 ELEMENTS

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## Learning Objectives

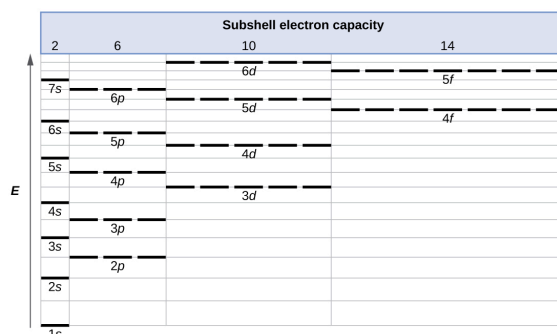
By the end of this section, you will be able to:

- Derive the predicted ground-state electron configurations of atoms
- Identify and explain exceptions to predicted electron configurations for atoms and ions
- Relate electron configurations to element classifications in the periodic table

Having introduced the basics of atomic structure and quantum mechanics, we can use our understanding of quantum numbers to determine how atomic orbitals relate to one another. This allows us to determine which orbitals are occupied by electrons in each atom. The specific arrangement of electrons in orbitals of an atom determines many of the chemical properties of that atom.

## Orbital Energies and Atomic Structure

The energy of atomic orbitals increases as the principal quantum number,  $n$ , increases. In any atom with two or more electrons, the repulsion between the electrons makes energies of subshells with different values of  $l$  differ so that the energy of the orbitals increases within a shell in the order  $s < p < d < f$ . Figure 10.5a depicts how these two trends in increasing energy relate. The  $1s$  orbital at the bottom of the diagram is the orbital with electrons of lowest energy. The energy increases as we move up to the  $2s$  and then  $2p$ ,  $3s$ , and  $3p$  orbitals, showing that the increasing  $n$  value has more influence on energy than the increasing  $l$  value for small atoms. However, this pattern does not hold for larger atoms with more electrons. The  $3d$  orbital is higher in energy than the  $4s$  orbital. Such overlaps continue to occur frequently as we move up the chart.



**Figure 10.5a:** Generalized energy-level diagram: generalized energy-level diagram for atomic orbitals in an atom with two or more electrons (not to scale) (credit: *Chemistry (OpenStax)*, CC BY 4.0).

Electrons in successive atoms on the periodic table tend to fill low-energy orbitals first. Thus, many students find it confusing that, for example, the  $5p$  orbitals fill immediately after the  $4d$ , and immediately before the  $6s$ . The filling order is based on observed experimental results, and has been confirmed by theoretical calculations. As the principal quantum number,  $n$ , increases, the size of the orbital increases and the electrons spend more time farther from the nucleus. Thus, the attraction to the nucleus is weaker and the energy associated with the orbital is higher (less stabilized), consistent with Coulomb's Law. But this is not the only effect we have to take into account. Within each shell, as the value of  $l$  increases, the electrons are less penetrating (meaning there is less electron density found close to the nucleus), in the order  $s > p > d > f$ . Electrons that are closer to the nucleus slightly repel electrons that are farther out, offsetting the more dominant electron–nucleus attractions slightly (recall that all electrons have  $-1$  charges, but nuclei have  $+Z$  charges). This phenomenon is called shielding. Electrons in orbitals that experience more shielding are less stabilized and thus higher in energy. For small orbitals ( $1s$  through  $3p$ ), the increase in energy due to  $n$  is more significant than the increase due to  $l$ ; however, for larger orbitals the two trends are comparable and cannot be simply predicted. We will discuss methods for remembering the observed order.

The arrangement of electrons in the orbitals of an atom is commonly represented using two methods: **orbital diagrams** and **electron configurations** of an atom. Both methods will be introduced in this section. It is important to apply the electron capacity rules for each type of subshell ( $l$ ):

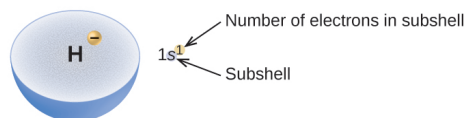
- electron capacity for subshell  $s$  is 2
- electron capacity for subshell  $p$  is 6
- electron capacity for subshell  $d$  is 10
- electron capacity for subshell  $f$  is 14

We write an electron configuration with a symbol that contains three pieces of information (Figure 10.5b):

1. The number of the principal energy level (shell),  $n$ ,
2. The letter that designates the orbital type (the subshell,  $l$ ), and

3. A superscript number that designates the number of electrons in that particular subshell.

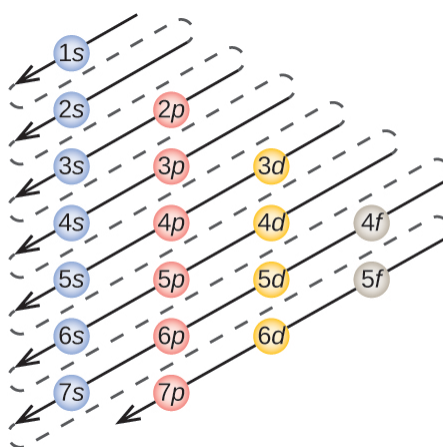
For example, the notation  $2p^4$  (read “two-p-four”) indicates four electrons in a  $p$  subshell ( $l = 1$ ) with a principal quantum number ( $n$ ) of 2. The notation  $3d^8$  (read “three-d-eight”) indicates eight electrons in the  $d$  subshell (i.e.,  $l = 2$ ) of the principal shell for which  $n = 3$ .



**Figure 10.5b:** Diagram of an electron configuration for hydrogen: the diagram of an electron configuration specifies the subshell ( $n$  and  $l$  value, with letter symbol) and superscript number of electrons (credit: Chemistry (OpenStax), CC BY 4.0).

## The Aufbau Principle

To determine the electron configuration (electron filling order) for any particular atom, we can “build” the structures in the order of atomic numbers. Beginning with hydrogen, and continuing across the periods of the periodic table, we add one proton at a time to the nucleus and one electron to the proper subshell until we have described the electron configurations of all the elements. This procedure is called the **Aufbau principle**, from the German word *Aufbau* (“to build up”). Each added electron occupies the subshell of lowest energy available (in the order shown in Figure 10.5a), subject to the limitations imposed by the allowed quantum numbers according to the Pauli exclusion principle. Electrons enter higher-energy subshells only after lower-energy subshells have been filled to capacity. Figure 10.5c illustrates the traditional way to remember the filling order for atomic orbitals. It is a helpful schematic to use when writing electron configurations or drawing orbital diagrams.



**Figure 10.5c:** Using the Aufbau principle to determine appropriate filling order for electron configurations: the arrow leads through each subshell in the appropriate filling order for electron configurations. This chart is straightforward to construct. Simply make a column for all the  $s$  orbitals with each  $n$  shell on a separate row. Repeat for  $p$ ,  $d$ , and  $f$ . Be sure to only include orbitals allowed by the quantum numbers (no  $1p$  or  $2d$ , and so forth). Finally, draw diagonal lines from top to bottom as shown (credit: *Chemistry (OpenStax)*, CC BY 4.0).

For an introduction on how to use the Orbital Filling Diagram and Aufbau's principle to write electron configurations watch **Using the Electron Configuration Chart (3min 32s)** (<https://youtu.be/TjVrcw2sZLs>)

## Electron Configuration Arrangement using the Periodic Table

Since the arrangement of the periodic table is based on the electron configurations, the periodic table can be converted to an electron configuration table to map out electron filling order. Figure 10.5d illustrates this method for determining the electron configuration. The filling order simply begins at hydrogen and includes each subshell as you proceed in increasing  $Z$  order. For example, after filling the  $3p$  block up to Argon (Ar), we see the next orbital to be filled with electrons will be  $4s$  (for potassium (K) and calcium (Ca)), followed by the  $3d$  orbitals.



Electron Configuration Table

Period	Group	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	1	H																	He
2	1	Li	Be											B	C	N	O	F	Ne
3	1	Na	Mg											Al	Si	P	S	Cl	Ar
4	1	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
5	1	Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
6	1	Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
7	1	Fr	Ra	Ac	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn	Uut	Fl	Uup	Lv	Uus	Uuo
				Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu		
				Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr		

Name → **H** ← Electrons  
 ← Subshell

**Figure 10.5d:** Using the periodic table to predict electron configuration for each subshell: this periodic table shows the electron configuration for each subshell. By “building up” from hydrogen, this table can be used to determine the electron configuration for any atom on the periodic table. Review the Periodic Table of the Elements in other formats in Appendix A (credit: *Chemistry (OpenStax)*, CC BY 4.0).

When filling electrons to create electron configurations and orbital diagrams, remember the number of electrons increases by one as the atomic number increases by one.

For an introduction on how to use the periodic table to write electron configurations, **watch Writing Electron Configurations Using Only the Periodic Table (4min 51s)**. (<https://youtu.be/ououF9nHUhk>)

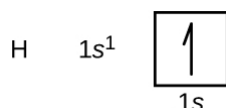
## Writing Electron Configuration and Orbital Diagrams of Elements

We will now construct the ground-state electron configuration and orbital diagram for a selection of atoms in the first and second periods of the periodic table. You can use the orbital filling diagram or your periodic table as tools to determine correct filling order. Orbital diagrams are pictorial representations of the electron configuration, showing the individual orbitals and the pairing arrangement of electrons. Boxes are drawn to represent each orbital (which can only contain zero, one, or two electrons). The orbitals’  $n$  value and  $l$  value are written under the box. Small arrows are used to indicate electrons. If two electrons share the same orbital, the first is drawn pointing in the up direction and the other in the down direction; this illustrates that the two electrons have opposite spins.

When reading orbital diagrams, you may notice two different version of arrows drawn: A full arrow head or “half” arrow head. Either is appropriate to use when drawing orbital diagrams, as both

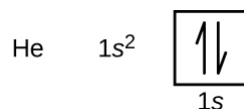
represent an electron. In this textbook, orbital diagrams will use both options interchangeably in examples, exercises, and answers.

We start with a single hydrogen atom (atomic number 1), which consists of one proton and one electron. Referring to Figure 10.5c or Figure 10.5d, we would expect to find the electron in the 1s orbital. By convention, the  $m_s = +\frac{1}{2}$  value is usually filled first. The symbol for hydrogen, its electron configuration, and its orbital diagram, respectively, are:



**Figure 10.5e:** Electron configuration and orbital diagram for hydrogen (credit: *Chemistry (OpenStax)*, CC BY 4.0).

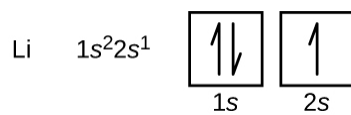
Following hydrogen is the noble gas helium, which has an atomic number of 2. The helium atom contains two protons and two electrons. The first electron has the same four quantum numbers as the hydrogen atom electron ( $n = 1, l = 0, m_l = 0, m_s = +\frac{1}{2}$ ). The second electron also goes into the 1s orbital and fills that orbital. The second electron has the same  $n, l,$  and  $m_l$  quantum numbers, but must have the opposite spin quantum number,  $m_s = -\frac{1}{2}$ . This is in accordance with the Pauli exclusion principle: No two electrons in the same atom can have the same set of four quantum numbers. For orbital diagrams, this means two arrows go in each box (representing two electrons in each orbital) and the arrows must point in opposite directions (representing paired spins). The electron configuration and orbital diagram of helium are:



**Figure 10.5f:** Electron configuration and orbital diagram for helium (credit: *Chemistry (OpenStax)*, CC BY 4.0).

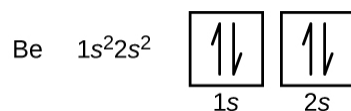
The  $n = 1$  shell is completely filled in a helium atom.

The next atom is the alkali metal lithium, with an atomic number of 3, which means it has three electrons to fill. The first two electrons in lithium fill the 1s orbital and have the same sets of four quantum numbers as the two electrons in helium. The remaining electron must occupy the orbital of next lowest energy, the 2s orbital (Figure 10.5c or Figure 10.5d). Thus, the electron configuration and orbital diagram of lithium are:



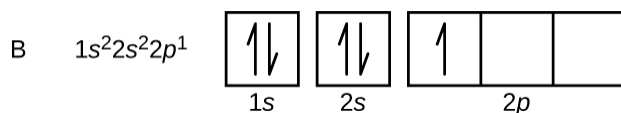
**Figure 10.5g:** Electron configuration and orbital diagram for lithium (credit: *Chemistry (OpenStax)*, CC BY 4.0).

An atom of the alkaline earth metal beryllium, with an atomic number of 4, contains four protons in the nucleus and four electrons surrounding the nucleus. The fourth electron fills the remaining space in the 2s orbital.



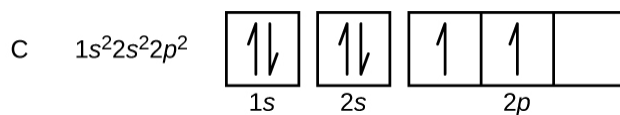
**Figure 10.5h:** Electron configuration and orbital diagram for beryllium (credit: *Chemistry (OpenStax)*, CC BY 4.0).

An atom of boron (atomic number 5) contains five electrons. The  $n = 1$  shell is filled with two electrons and three electrons will occupy the  $n = 2$  shell. Because any  $s$  subshell can contain only two electrons, the fifth electron must occupy the next energy level, which will be a  $2p$  orbital. There are three degenerate  $2p$  orbitals ( $m_l = -1, 0, +1$ ) and the electron can occupy any one of these  $p$  orbitals. When drawing orbital diagrams, we include empty boxes to depict any empty orbitals in the same subshell that we are filling.



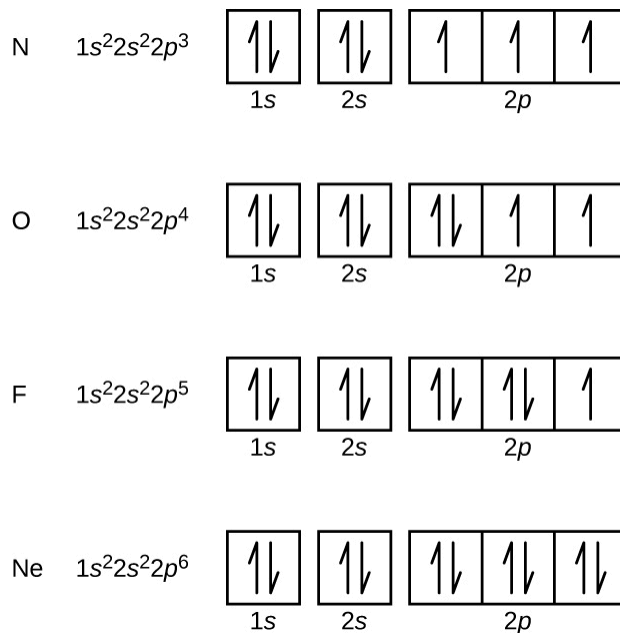
**Figure 10.5i:** Electron configuration and orbital diagram for boron (credit: *Chemistry (OpenStax)*, CC BY 4.0).

Carbon (atomic number 6) has six electrons. Four of them fill the 1s and 2s orbitals. The remaining two electrons occupy the 2p subshell. We now have a choice of filling one of the 2p orbitals and pairing the electrons or of leaving the electrons unpaired in two different, but degenerate, p orbitals. The orbitals are filled as described by **Hund's rule**: the lowest-energy configuration for an atom with electrons within a set of degenerate orbitals is that having the maximum number of unpaired electrons. Thus, the two electrons in the carbon 2p orbitals have identical  $n$ ,  $l$ , and  $m_s$  quantum numbers and differ in their  $m_l$  quantum number (in accord with the Pauli exclusion principle). The electron configuration and orbital diagram for carbon are:



**Figure 10.5j:** Electron configuration and orbital diagram for carbon (credit: *Chemistry (OpenStax)*, CC BY 4.0).

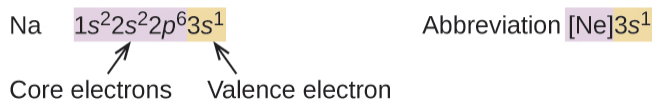
Nitrogen (atomic number 7) fills the  $1s$  and  $2s$  subshells and has one electron in each of the three  $2p$  orbitals, in accordance with Hund's rule (electrons fill each orbital first, then double up). These three electrons have unpaired spins. Oxygen (atomic number 8) has a pair of electrons in any one of the  $2p$  orbitals (the electrons have opposite spins) and a single electron in each of the other two. Fluorine (atomic number 9) has only one  $2p$  orbital containing an unpaired electron. All of the electrons in the noble gas neon (atomic number 10) are paired, and all of the orbitals in the  $n = 1$  and the  $n = 2$  shells are filled. The electron configurations and orbital diagrams of these four elements are:



**Figure 10.5k:** Electron configuration and orbital diagram for nitrogen, oxygen, fluorine, and neon (credit: *Chemistry (OpenStax)*, CC BY 4.0).

The alkali metal sodium (atomic number 11) has one more electron than the neon atom. This electron must go into the next lowest-energy subshell available, the  $3s$  orbital, giving a  $1s^2 2s^2 2p^6 3s^1$  configuration. The electrons occupying the outermost shell orbital(s) (highest value of  $n$ ) are called **valence electrons**, and those occupying the inner shell orbitals are called **core electrons** (Figure 10.5l). Since the core electron shells correspond to noble gas electron configurations, we can abbreviate and shorten electron configurations by writing the noble gas that matches the core electron configuration, along with the valence electrons in a condensed format. This is often referred to as the noble gas electron configuration of a given element. For our

sodium example, the symbol [Ne] represents core electrons, ( $1s^2 2s^2 2p^6$ ) and our abbreviated or condensed configuration is  $[\text{Ne}]3s^1$ .



**Figure 10.5l:** Identifying core electrons and valence electrons in electron configurations: a core-abbreviated electron configuration (right) replaces the core electrons with the noble gas symbol whose configuration matches the core electron configuration of the other element. The abbreviated notation represents the element's noble gas electron configuration (credit: *Chemistry (OpenStax)*, CC BY 4.0).

Similarly, the abbreviated configuration of lithium can be represented as  $[\text{He}]2s^1$ , where  $[\text{He}]$  represents the configuration of the helium atom, which is identical to that of the filled inner shell of lithium. Writing the configurations in this way emphasizes the similarity of the configurations of lithium and sodium. Both atoms, which are in the alkali metal family, have only one electron in a valence  $s$  subshell outside a filled set of inner shells.



The alkaline earth metal magnesium (atomic number 12), with its 12 electrons in a  $[\text{Ne}]3s^2$  configuration, is analogous to its family member beryllium,  $[\text{He}]2s^2$ . Both atoms have a filled  $s$  subshell outside their filled inner shells. Aluminum (atomic number 13), with 13 electrons and the electron configuration  $[\text{Ne}]3s^2 3p^1$ , is analogous to its family member boron,  $[\text{He}]2s^2 2p^1$ .

The electron configurations of silicon (14 electrons), phosphorus (15 electrons), sulfur (16 electrons), chlorine (17 electrons), and argon (18 electrons) are analogous in the electron configurations of their outer shells to their corresponding family members carbon, nitrogen, oxygen, fluorine, and neon, respectively, except that the principal quantum number of the outer shell of the heavier elements has increased by one to  $n = 3$ . Figure 10.5m shows the lowest energy, or ground-state, electron configuration for these elements as well as that for atoms of each of the known elements.

Electron Configuration Table

Period	Group	Element																				
1	1	H																18	2	He		
2	1	Li		Be												13	14	15	16	17	18	Ne
3	1	Na		Mg												31	32	33	34	35	36	Ar
4	1	K		Ca		Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr	
5	1	Rb		Sr		Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe	
6	1	Cs		Ba		La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn	
7	1	Fr		Ra		Ac	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn	Uut	Fl	Uup	Lv	Uus	Uuo	

Atomic number	1	Name	H
Outer electron configuration	1s <sup>1</sup>		

**Figure 10.5m:** The periodic table showing the outer-shell electron configuration of each element: this version of the periodic table shows the outer-shell electron configuration of each element. Note that down each group, the configuration is often similar. Review the Periodic Table of the Elements in other formats in Appendix A (credit: *Chemistry (OpenStax)*, CC BY 4.0).

When we come to the next element in the periodic table we move down to period 4, group 1, the alkali metal potassium (atomic number 19). We might expect that we would begin to add electrons to the  $3d$  subshell. However, all available chemical and physical evidence indicates that potassium is like lithium and sodium, and that the next electron is not added to the  $3d$  level but is, instead, added to the  $4s$  level since it is the next lowest energy level (Figure 10.5m). As discussed previously, the  $3d$  orbital with no radial nodes is higher in energy because it is less penetrating and more shielded from the nucleus than the  $4s$ , which has three radial nodes. Thus, potassium has an electron configuration of  $[\text{Ar}]4s^1$ . Hence, potassium corresponds to its group 1 members, Li and Na in its valence shell configuration. The next element to consider is calcium. One electron is added to complete the  $4s$  subshell and calcium has a

- complete electron configuration of  $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$  and
- noble gas electron configuration of  $[\text{Ar}]4s^2$

This gives calcium an outer-shell electron configuration corresponding to other elements in group 2 including beryllium and magnesium.

Beginning with the transition metal scandium (atomic number 21), additional electrons are added successively to the  $3d$  subshell. This subshell is filled to its capacity with 10 electrons (remember that for  $l = 2$  [ $d$  orbitals], there are  $2l + 1 = 5$  values of  $m_l$ , meaning that there are five  $d$  orbitals that have a combined capacity of 10 electrons). The  $4p$  subshell fills next. Note that for three series of elements, scandium (Sc) through copper (Cu), yttrium (Y) through silver (Ag), and lutetium (Lu) through gold (Au), a total of 10  $d$  electrons are successively added to the  $(n - 1)$  shell next to the  $n$  shell to bring that  $(n - 1)$  shell from 8 to 18

electrons. For two series, lanthanum (La) through lutetium (Lu) and actinium (Ac) through lawrencium (Lr), 14  $f$  electrons ( $l = 3$ ,  $2l + 1 = 7 m_l$  values; thus, seven orbitals with a combined capacity of 14 electrons) are successively added to the  $(n - 2)$  shell to bring that shell from 18 electrons to a total of 32 electrons.

For a summary on electron configurations and orbital filling diagrams **watch Electron Configuration (10min 16s)**. (<https://youtu.be/2AFPfg0Como>)

## Example 10.5a

### Quantum Numbers and Electron Configurations

What is the electron configuration and orbital diagram for a phosphorus atom? What are the four quantum numbers for the last electron added?

#### Solution

The atomic number of phosphorus is 15. Thus, a phosphorus atom contains 15 electrons. The order of filling of the energy levels is  $1s$ ,  $2s$ ,  $2p$ ,  $3s$ ,  $3p$ ,  $4s$ , ... The 15 electrons of the phosphorus atom will fill up to the  $3p$  orbital, which will contain three electrons:



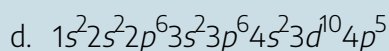
The last electron added is a  $3p$  electron. Therefore,  $n = 3$  and, for a  $p$ -type orbital,  $l = 1$ . The  $m_l$  value could be  $-1$ ,  $0$ , or  $+1$ . The three  $p$  orbitals are degenerate, so any of these  $m_l$  values is correct. For unpaired electrons, convention assigns the value of  $+\frac{1}{2}$  for the spin quantum number; thus,

$$m_s = +\frac{1}{2}.$$

## Exercise 10.5a

Identify the atoms from the electron configurations given:

- $[\text{Ar}]4s^2 3d^5$
- $[\text{Kr}]5s^2 4d^{10} 5p^6$
- $1s^2 2s^2 2p^3$



### Check Your Answer<sup>1</sup>

## Exceptions to Orbital Electron Filling Order

As mentioned previously in this section, the periodic table can be a powerful tool in predicting the electron configuration of an element. However, we do find exceptions to the order of filling of orbitals that are shown in Figure 10.5c or Figure 10.5d. For instance, the electron configurations (shown in Figure 10.5m) of the transition metals chromium (Cr; atomic number 24) and copper (Cu; atomic number 29), among others, are not those we would expect. In general, such exceptions involve subshells with very similar energy, and small effects can lead to changes in the order of filling.

In the case of Cr and Cu, we find that half-filled and completely filled subshells apparently represent conditions of preferred stability. This stability is such that an electron shifts from the  $4s$  into the  $3d$  orbital to gain the extra stability of a half-filled  $3d$  subshell (in Cr) or a filled  $3d$  subshell (in Cu). Other exceptions also occur. For example, niobium (Nb, atomic number 41) is predicted to have the electron configuration  $[\text{Kr}]5s^2 4d^3$ . Experimentally, we observe that its ground-state electron configuration is actually  $[\text{Kr}]5s^1 4d^4$ . We can rationalize this observation by saying that the electron–electron repulsions experienced by pairing the electrons in the  $5s$  orbital are larger than the gap in energy between the  $5s$  and  $4d$  orbitals. There is no simple method to predict the exceptions for atoms where the magnitude of the repulsions between electrons is greater than the small differences in energy between subshells.

## More about Electron Configurations and the Periodic Table

As described earlier, the periodic table arranges atoms based on increasing atomic number so that elements with the same chemical properties recur periodically. When their electron configurations are added to the table (Figure 10.5m), we also see a periodic recurrence of similar electron configurations in the outer shells of these elements. Because they are in the outer shells of an atom, valence electrons play the most important role in chemical reactions. The outer electrons have the highest energy of the electrons in an atom and are more easily lost or shared than the core electrons. Valence electrons are also the determining factor in some physical properties of the elements.

Elements in any one group (or column) have the same number of valence electrons; the alkali metals lithium and sodium each have only one valence electron, the alkaline earth metals beryllium and magnesium each have two, and the halogens fluorine and chlorine each have seven valence electrons. The similarity in



chemical properties among elements of the same group occurs because they have the same number of valence electrons. It is the loss, gain, or sharing of valence electrons that defines how elements react.

It is important to remember that the periodic table was developed on the basis of the chemical behaviour of the elements, well before any idea of their atomic structure was available. Now we can understand why the periodic table has the arrangement it has—the arrangement puts elements whose atoms have the same number of valence electrons in the same group. This arrangement is emphasized in Figure 10.5m, which shows in periodic table form the electron configuration of the last subshell to be filled by the Aufbau principle. The coloured sections of Figure 10.5m show the three categories of elements classified by the orbitals being filled: main group, transition, and inner transition elements. These classifications determine which orbitals are counted in the valence shell, or highest energy level orbitals of an atom.

1. Main group elements (sometimes called representative elements) are those in which the last electron added enters an  $s$  or a  $p$  orbital in the outermost shell, shown in blue and red in Figure 10.5m. This category includes all the nonmetallic elements, as well as many metals and the intermediate semi-metallic elements. The valence electrons for main group elements are those with the highest  $n$  level. For example, gallium (Ga, atomic number 31) has the electron configuration  $[\text{Ar}]4s^23d^{10}4p^1$ , which contains three valence electrons (underlined –  $4s^2, 4p^1$ ). The completely filled  $d$  orbitals count as core, not valence, electrons.
2. Transition elements or transition metals. These are metallic elements in which the last electron added enters a  $d$  orbital. The valence electrons (those added after the last noble gas configuration) in these elements include the  $ns$  and  $(n - 1)d$  electrons. The official IUPAC definition of transition elements specifies those with partially filled  $d$  orbitals. Thus, the elements with completely filled orbitals (Zn, Cd, Hg, as well as Cu, Ag, and Au in Figure 10.5m) are not technically transition elements. However, the term is frequently used to refer to the entire  $d$  block (coloured yellow in Figure 10.5m), and we will adopt this usage in this textbook.
3. Inner transition elements are metallic elements in which the last electron added occupies an  $f$  orbital. They are shown in green in Figure 10.5m. The valence shells of the inner transition elements consist of the  $(n - 2)f$ , the  $(n - 1)d$ , and the  $ns$  subshells. There are two inner transition series:
  1. The lanthanide series: lanthanide (La) through lutetium (Lu)
  2. The actinide series: actinide (Ac) through lawrencium (Lr)

Lanthanum and actinium, because of their similarities to the other members of the series, are included and used to name the series, even though they are transition metals with no  $f$  electrons.

## Electron Configurations of Ions

We have seen that ions are formed when atoms gain or lose electrons. A cation (positively charged ion) forms

when one or more electrons are removed from a parent (neutral) atom. For main group elements, the valence electrons that were added last are the first electrons removed. For transition metals and inner transition metals, however, valence electrons in the  $s$  orbital are easier to remove than the  $d$  or  $f$  electrons, and so the highest  $ns$  electrons are lost, and then the  $(n - 1)d$  or  $(n - 2)f$  electrons are removed. An anion (negatively charged ion) forms when one or more electrons are added to the valence shell of a parent atom. The added electrons fill in the order predicted by the Aufbau principle. Generally speaking:

- Metals forming simple cations typically lose valence electrons to achieve a stable electron configuration of their closest noble gas.
- Non-metals forming simple anions typically gain electrons to fill their outer valence shell to achieve a stable electron configuration of their closest noble gas.

## Exercise 10.5b

Watch and Participate in this interactive video lesson (5min 11sec) to learn more about writing electron configurations of ions.

Check Your Learning Exercise (Text Version)

Question 1 (49 sec): For the two statements provided, fill in the [BLANK] with the correct key terms.

Key Terms:

1. gain; 2. lose; 3. cation; 4. Anion

Statements:

- a. A positive ion is called a(n) [BLANK]. Atoms [BLANK] electrons to form this type of ion.
- b. A negative ion is called a(n) [BLANK]. Atoms [BLANK] electrons to form this type of ion.

Question 2 (2min 8sec): Which of the following statements about calcium are true?

- a. The electron configuration for neutral calcium atom is  $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$
- b. Calcium forms a  $\text{Ca}^{2+}$  cation by losing 2 electrons.
- c. The electron configuration for a calcium  $2+$  ion is  $1s^2 2s^2 2p^6 3s^2 3p^6$
- d. a calcium  $2+$  ion has the same electron configuration as its closest noble gas, argon.
- e. All these options are correct statements.

Questions 3 (2min 54sec) is a statement that reads, “This Lewis dot diagram is introducing concepts in ionic bonding of simple ions and is discussed in more detail in chemical bonding units”

Question 4 (3min 42sec) is a statement that reads, “The electron configuration of Al is incorrectly written in the video. The correct electron configuration of Al is  $1s^2 2s^2 2p^6 3s^2 3p^1$ .”

Question 5 (4min 7sec) is a statement that reads, “The three valence electrons lost from the aluminum atom were from  $3s^2 3p^1$ .”

### Check Your Answer<sup>2</sup>

**Activity Source:** “Exercise 10.5b” by Jackie MacDonald is licensed under CC-BY-NC-SA 4.0, based on video source: Breslyn, W. (2020, October 1). *How to write the electron configuration for ions* (<https://www.youtube.com/watch?v=-N7a7OfIxFE&t=5s>) [Video]. YouTube.

## Example 10.5b

### Predicting Electron Configurations of Ions

Write the electron configuration and orbital diagram of the following ions:

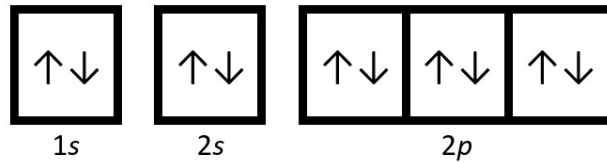
- $O^{2-}$
- $Na^+$
- $P^{3-}$
- $Al^{2+}$
- $Fe^{2+}$

### Solution

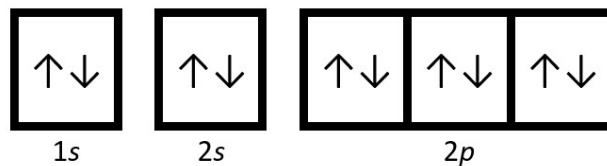
First, write out the electron configuration for each parent atom. We have shown full, unabbreviated configurations to provide more practice for students who want it, but listing the core-abbreviated electron configurations is also acceptable.

Next, determine whether an electron is gained or lost. Remember electrons are negatively charged, so ions with a positive charge have *lost* an electron. For main group elements, the last orbital gains or loses the electron. For transition metals, the last *s* orbital loses an electron before the *d* orbitals.

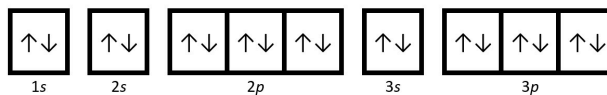
(a) O:  $1s^2 2s^2 2p^4$ . Oxygen anion gains two electrons in valence shell (*2p* shell), so  $O^{2-}$ :  $1s^2 2s^2 2p^6$ .

Orbital Diagram of  $O^{2-}$ 

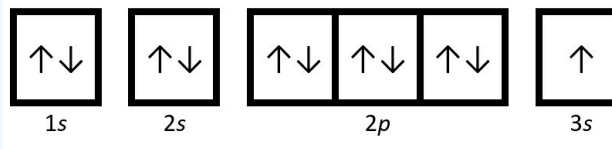
(b) Na:  $1s^2 2s^2 2p^6 3s^1$ . Sodium cation loses one electron from valence shell (3s shell), so  $Na^+$ :  $1s^2 2s^2 2p^6$ . To review a video showing the solution to this question watch  $Na^+$  Electron Configuration (Sodium Ion) (2min 17s) (<https://youtu.be/pkv44EVdUAs>)

Orbital Diagram of  $Na^+$ 

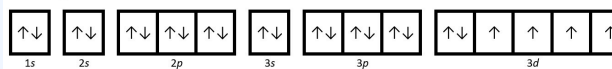
(c) P:  $1s^2 2s^2 2p^6 3s^2 3p^3$ . Phosphorus trianion gains three electrons (3 electrons are added to the valence shell, 3p) to form  $P^{3-}$ :  $1s^2 2s^2 2p^6 3s^2 3p^6$ .

Orbital Diagram of  $P^{3-}$ 

(d) Al:  $1s^2 2s^2 2p^6 3s^2 3p^1$ . Aluminum dication loses two electrons (from outer valence shells; one from 3p and the other from 3s) to form  $Al^{2+}$ :  $1s^2 2s^2 2p^6 3s^1$ .

Orbital Diagram of  $Al^{2+}$ 

(e) Fe:  $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^6$ . Iron(II) loses two electrons and, since it is a transition metal, they are removed from the 4s orbital:  $Fe^{2+}$ :  $1s^2 2s^2 2p^6 3s^2 3p^6 3d^6$ .

Orbital Diagram of  $Fe^{2+}$ 

## Exercise 10.5c

### Predicting Electron Configurations of Ions

- Write the electron configuration and orbital diagram of the following ions:
  - $\text{Mg}^{2+}$
  - $\text{Cl}^-$
  - $\text{Zn}^{2+}$
- Which ion with a +2 charge has the electron configuration  $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^5$ ?  
Which ion with a +3 charge has this configuration?

### Check Your Answer<sup>3</sup>

## Links to Interactive Learning Tools

Explore The Dynamic Periodic Table of Elements (<https://ptabla.com/>) from Ptabla to reference noble gas electron configurations of elements.

Practice Electron configuration order (<https://h5pstudio.ecampusontario.ca/content/8519>) from eCampusOntario H5P Studio. (<https://h5pstudio.ecampusontario.ca/>)

Explore the It's Elementary section of The Interactive Periodic Table (<https://www.learner.org/series/interactive-the-periodic-table/>) from Annenberg Learner. (<https://www.learner.org/>)

Practice Electron Configurations (<https://www.physicsclassroom.com/Concept-Builders/Chemistry/Electron-Configuration>) from the Physics Classroom (<https://www.physicsclassroom.com/>).

## Attribution & References

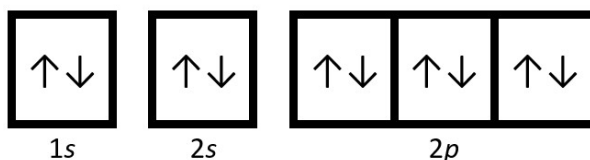
Except where otherwise noted, this page is adapted by Jackie MacDonald from:

- “3.4 Electronic Structure of Atoms (Electron Configurations) (<https://boisestate.pressbooks.pub/chemistry/chapter/3-4-electronic-structure-of-atoms-electron-configurations/>)” In *General Chemistry 1 & 2* by Rice University, a derivative of *Chemistry (Open Stax)* by Paul Flowers, Klaus Theopold, Richard Langley & William R. Robinson and is licensed under CC BY 4.0. Access for free at *Chemistry (OpenStax)* (<https://openstax.org/books/chemistry/pages/1-introduction>) AND
- “6.4 Electronic Structure of Atoms (Electron Configurations) (<https://openstax.org/books/chemistry-2e/pages/6-4-electronic-structure-of-atoms-electron-configurations/>)” In *Chemistry 2e (Open Stax)* by Paul Flowers, Klaus Theopold, Richard Langley & William R. Robinson is licensed under CC BY 4.0. Access for free at *Chemistry 2e (Open Stax)* (<https://openstax.org/details/books/chemistry-2e>). / Adaptations to content and addition of examples and exercises to optimize student comprehension.
- Orbital Diagrams of:  $O^{2-}$  ion, Sodium Ion ( $Na^+$ ), Phosphorus 3- ion, Aluminum two plus ion ( $Al^{2+}$ ), Iron two plus ion ( $Fe^{2+}$ ) by Jackie MacDonald, licensed under the CC BY-NC-SA (Attribution NonCommercial ShareAlike) license

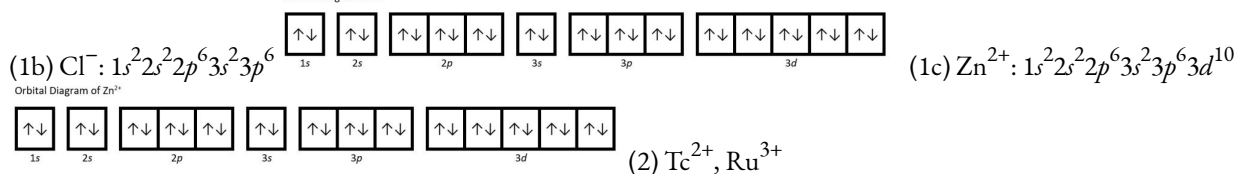
## Notes

- Mn;
  - Xe;
  - N;
  - Br
- Question 1: (a) cation, lose; (b) anion, gain
- (1a)  $Mg^{2+}$ :  $1s^2 2s^2 2p^6$

Orbital Diagram of  $Mg^{2+}$



Orbital Diagram of  $Zn^{2+}$



# 10.6 ATOMIC PROPERTIES AND PERIODIC TABLE TRENDS

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## Learning Objectives

By the end of this section, you will be able to:

- Describe and explain the observed trends in atomic size, ionization energy, and electron affinity of the elements

The elements in groups (vertical columns) of the periodic table exhibit similar chemical behaviour. This similarity occurs because the members of a group have the same number and distribution of electrons in their valence shells. However, there are also other patterns in chemical properties on the periodic table. For example, as we move down a group, the metallic character of the atoms increases. Oxygen, at the top of group 16 (6A), is a colourless gas; in the middle of the group, selenium is a semiconducting solid; and, toward the bottom, polonium is a silver-grey solid that conducts electricity.

As we go across a period from left to right, we add a proton to the nucleus and an electron to the valence shell with each successive element. As we go down the elements in a group, the number of electrons in the valence shell remains constant, but the principal quantum number increases by one each time. An understanding of the electronic structure of the elements allows us to examine some of the properties that govern their chemical behaviour. These properties vary periodically as the electronic structure of the elements changes. They are (1) size (radius) of atoms and ions, (2) ionization energies, and (3) electron affinities.

## Variation in Covalent Radius

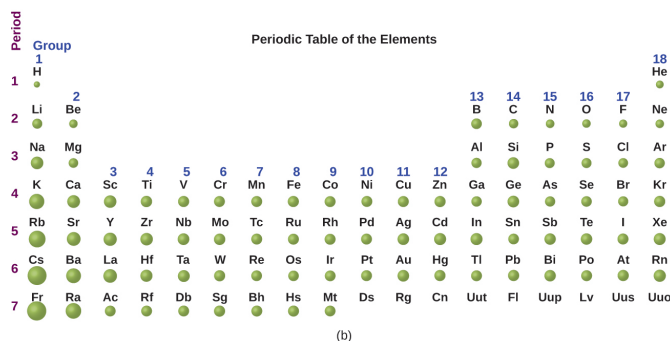
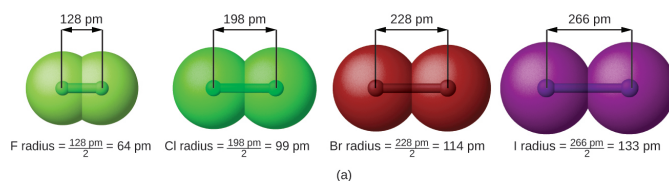
The quantum mechanical picture makes it difficult to establish a definite size of an atom. However, there are several practical ways to define the radius of atoms and, thus, to determine their relative sizes that give roughly similar values. We will use the **covalent radius** (Table 10.6a), which is defined as one-half the distance between the nuclei of two identical atoms when they are joined by a covalent bond (this measurement is

possible because atoms within molecules still retain much of their atomic identity). We know that as we scan down a group, the principal quantum number,  $n$ , increases by one for each element. Thus, the electrons are being added to a region of space that is increasingly distant from the nucleus. Consequently, the size of the atom (and its covalent radius) must increase as we increase the distance of the outermost electrons from the nucleus. This trend is illustrated for the covalent radii of the halogens in Table 10.6a and Figure 10.6a. The trends for the entire periodic table can be seen in Figure 10.6b.

**Table 10.6a: Covalent Radii of the Halogen Group Elements**

Atom	Covalent radius (pm)	Nuclear charge
F	64	+9
Cl	99	+17
Br	114	+35
I	133	+53
At	148	+85

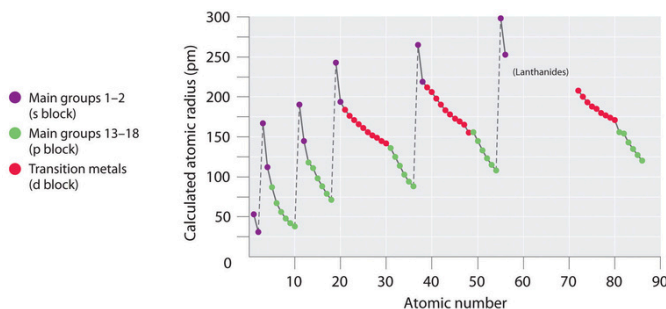
As shown in Figure 10.6b, we see the general trend for atomic radii:



**Figure 10.6a:** Trends in atomic radii using the periodic table: (a) The radius of an atom is defined as one-half the distance between the nuclei in a molecule consisting of two identical atoms joined by a covalent bond. In (a) The atomic radius for the halogens increases down the group as  $n$  increases. (b) Covalent radii of the elements are shown to scale. The general trend is that radii increase down a group and decrease across a period. Review the Periodic Table of the Elements in other formats in Appendix A (credit: Chemistry (OpenStax), CC BY 4.0).



As we move across a period from left to right, atomic radius decreases; as we move down a group the atomic radius increases.



**Figure 10.6b:** A Plot of periodic variation of atomic radius for the first six rows of the periodic table: the intrinsic sizes of all the elements and clearly show that atomic size varies in a periodic fashion. Atomic number is listed in ascending order on the x-axis. The calculated atomic radius (pm) is plotted on the y-axis. The main groups 1 and 2 (s Blocks) are shown in purple dots; the main groups 13-18 (p block) is shown in green dots; the transition metals (d block) are shown in red. The general trend shows that atomic radii decrease from left to right across a row and increase from top to bottom down a column. Because of these two trends, the largest atoms are found in the lower left corner of the periodic table, and the smallest are found in the upper right corner. (credit: “7.3 Sizes of Atoms and Ions” by Joshua Halpern/LibreTexts, CC BY-NC-SA 4.0)

This might seem counterintuitive because it implies that atoms with more electrons have a smaller atomic radius. This can be explained with the concept of **effective nuclear charge,  $Z_{\text{eff}}$** . This is the pull exerted on a specific electron by the nucleus, taking into account any electron-electron repulsions. For hydrogen, there is only one electron and so the nuclear charge ( $Z$ ) and the effective nuclear charge ( $Z_{\text{eff}}$ ) are equal. For all other atoms, the inner electrons partially *shield* the outer electrons from the pull of the nucleus, and thus:

$$Z_{\text{eff}} = Z - \text{shielding}$$

Shielding is determined by the probability of another electron being between the electron of interest and the nucleus, as well as by the electron-electron repulsions the electron of interest encounters. Core electrons are adept at shielding, while electrons in the same valence shell do not block the nuclear attraction experienced by each other as efficiently. Thus, each time we move from one element to the next across a period,  $Z$  increases by one, but the shielding increases only slightly. Thus,  $Z_{\text{eff}}$  increases as we move from left to right across a period. The stronger pull (higher effective nuclear charge) experienced by electrons on the right side of the periodic table draws them closer to the nucleus, making the covalent radii smaller.

Thus, as we would expect, the outermost or valence electrons are easiest to remove because they have the highest energies, are shielded more, and are farthest from the nucleus. As a general rule, when the representative elements form cations, they do so by the loss of the  $ns$  or  $np$  electrons that were added last in the Aufbau process. The transition elements, on the other hand, lose the  $ns$  electrons before they begin to lose the  $(n - 1)d$  electrons, even though the  $ns$  electrons are added first, according to the Aufbau principle.

## Example 10.6a

### Sorting Atomic Radii using Periodic Table Trends

Predict the order of increasing covalent radius for Ge, Pb, Br, Kr.

#### Solution

Order of increasing covalent radius means ordering elements in order of smallest to largest Radii. Here, the radius increases as we move down a group, so  $\text{Ge} < \text{Pb}$ . Radius decreases as we move across a period, so  $\text{Kr} < \text{Br} < \text{Ge}$ . Putting the trends together, we obtain  $\text{Kr} < \text{Br} < \text{Ge} < \text{Pb}$ .

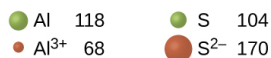
## Exercise 10.6a

1. Give an example of an atom in group 2 whose size is larger than boron (B).
2. Predict the order of decreasing covalent radius for Mg, Fr, Cs, Na, Ca

### Check Your Answer<sup>1</sup>

## Variation in Ionic Radii

Ionic radius is the measure used to describe the size of an ion. A cation always has fewer electrons and the same number of protons as the parent atom; it is smaller than the atom from which it is derived (Figure 10.6c). For example, the covalent radius of an aluminum atom ( $1s^2 2s^2 2p^6 3s^2 3p^1$ ) is 118 pm, whereas the ionic radius of an  $\text{Al}^{3+}$  ( $1s^2 2s^2 2p^6$ ) is 68 pm. As electrons are removed from the outer valence shell, the remaining core electrons occupying smaller shells experience a greater effective nuclear charge  $Z_{\text{eff}}$  (as discussed) and are drawn even closer to the nucleus and the cation is smaller than the parent atom.



**Figure 10.6c:** Comparing atomic radius of a cation to its parent atom: the radius for a cation is smaller than the parent atom (Al), due to the lost electrons; the radius for an anion is larger than the parent (S), due to the gained electrons.

Cations with larger charges are smaller than cations with smaller charges (e.g.,  $V^{2+}$  has an ionic radius of 79 pm, while that of  $V^{3+}$  is 64 pm). Proceeding down the groups of the periodic table, we find that cations of successive elements with the same charge generally have larger radii, corresponding to an increase in the principal quantum number,  $n$ .

An anion (negative ion) is formed by the addition of one or more electrons to the valence shell of an atom. This results in a greater repulsion among the electrons and a decrease in  $Z_{\text{eff}}$  per electron. Both effects (the increased number of electrons and the decreased  $Z_{\text{eff}}$ ) cause the radius of an anion to be larger than that of the parent atom (Figure 10.6c). For example, a sulfur atom ( $[\text{Ne}]3s^23p^4$ ) has a covalent radius of 104 pm; whereas, the ionic radius of the sulfide anion ( $[\text{Ne}]3s^23p^6$ ) is 170 pm. For consecutive elements proceeding down any group, anions have larger principal quantum numbers and, thus, larger radii.

Atoms and ions that have the same electron configuration are said to be **isoelectronic**. Examples of isoelectronic species are  $N^{3-}$ ,  $O^{2-}$ ,  $F^-$ , Ne,  $Na^+$ ,  $Mg^{2+}$ , and  $Al^{3+}$ , which all have an electron configuration  $1s^22s^22p^6$ . Another isoelectronic series is  $P^{3-}$ ,  $S^{2-}$ ,  $Cl^-$ , Ar,  $K^+$ ,  $Ca^{2+}$ , and  $Sc^{3+}$ , which all have an electron configuration ( $[\text{Ne}]3s^23p^6$ ). For atoms or ions that are isoelectronic, the number of protons determines the size. The greater the nuclear charge, the smaller the radius in a series of isoelectronic ions and atoms.

## Example 10.6b

### Sorting Ionic Radii and Parent Atoms using Periodic Table Trends

Predict the order of increasing radius when comparing the following ions and parent atoms:

1.  $Mg^{2+}$  and Mg
2.  $N^{3-}$  and N
3.  $I^-$  and I
4.  $Cs^+$  and Cs

### Solution

Cations have smaller atomic radii than their parent atom; whereas, anions have larger atomic radii than their parent atom. We were asked to order by increasing radii, so smaller radii followed by larger radius.

1.  $Mg > Mg^{2+}$
2.  $N^{3-} > N$
3.  $I^- > I$
4.  $Cs > Cs^+$

## Example 10.6c

### Sorting Ionic Radii and Parent Atoms using Periodic Table Trends

Predict the order of decreasing atomic radius when comparing the following ions/atoms:

1.  $\text{K}^+$ ,  $\text{Ba}^{2+}$ ,  $\text{F}^-$ ,  $\text{K}$ ,  $\text{Ba}$ ,  $\text{F}$
2.  $\text{Se}^{2-}$ ,  $\text{Br}^-$ ,  $\text{Kr}$ ,  $\text{Rb}^+$ ,  $\text{Sr}^{2+}$

### Solution

Cations have smaller atomic radii than their parent atom; whereas, anions have larger atomic radii than their parent atom. We were asked to order by decreasing radii, so in order of largest radius to smallest radius.

1.  $\text{Ba} > \text{Ba}^{2+} > \text{K} > \text{K}^+ > \text{F}^- > \text{F}$
2. These ions all have the same electron configuration  $[\text{Ar}]4s^23d^{10}4p^6$  (the configuration of the noble gas Kr,  $[\text{Kr}]$ ), and are said to be isoelectronic. For atoms or ions that are isoelectronic, the number of protons determines the size. The greater the nuclear charge (# of protons), the smaller the radius in a series of isoelectronic ions and atoms. Therefore, largest to smallest we have:  $\text{Se}^{2-} > \text{Br}^- > \text{Kr} > \text{Rb}^+ > \text{Sr}^{2+}$

## Exercise 10.6b

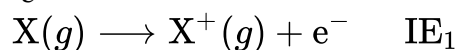
Predict the order of increasing atomic radius when comparing the following ions / atoms:

1.  $\text{K}^+$ ,  $\text{Cs}^{2+}$ ,  $\text{O}^{2-}$ ,  $\text{K}$ ,  $\text{Fr}$ ,  $\text{F}^-$
2.  $\text{F}^-$ ,  $\text{O}^{2-}$ ,  $\text{Ne}$ ,  $\text{Al}^{3+}$ ,  $\text{Mg}^{2+}$

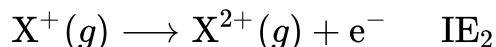
**Check Your Answer<sup>2</sup>**

## Variation in Ionization Energies

The amount of energy required to remove the most loosely bound electron from a gaseous atom in its ground state is called its first **ionization energy** ( $\text{IE}_1$ ). The first ionization energy for an element,  $\text{X}$ , is the energy required to form a cation with +1 charge:



The energy required to remove the second most loosely bound electron is called the second ionization energy ( $\text{IE}_2$ ).



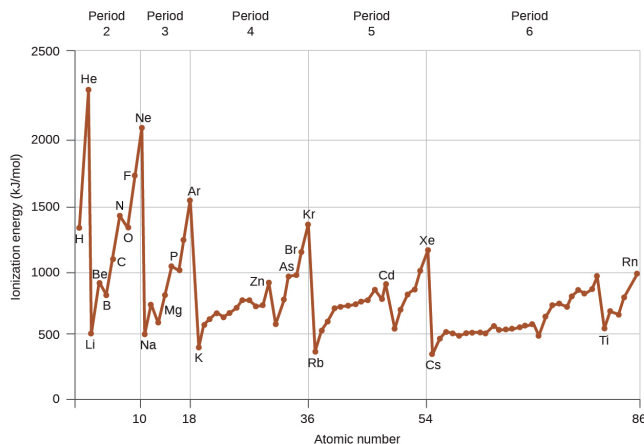
The energy required to remove the third electron is the third ionization energy, and so on. Energy is always required to remove electrons from atoms or ions, so ionization processes are endothermic and IE values are always positive. For larger atoms, the most loosely bound electron is located farther from the nucleus and so is easier to remove.

Thus, as size (atomic radius) increases, the ionization energy should decrease.

Relating this logic to what we have just learned about radii, we would expect first ionization energies to decrease down a group and to increase across a period. Generally speaking, atomic radius and ionization energy are inversely proportional to one another.

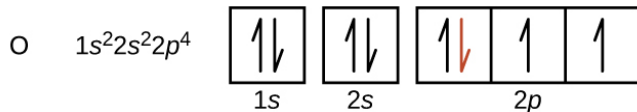
Figure 10.6d graphs the relationship between the first ionization energy and the atomic number of several elements. The values of first ionization energy for the elements are given in Figure 10.6d. Within a period, the  $\text{IE}_1$  generally increases with increasing  $Z$ . Down a group, the  $\text{IE}_1$  value generally decreases with increasing  $Z$ . There are some systematic deviations from this trend, however. Note that the ionization energy of boron

(atomic number 5) is less than that of beryllium (atomic number 4) even though the nuclear charge of boron is greater by one proton. This can be explained because the energy of the subshells increases as  $l$  increases, due to penetration and shielding (as discussed previously). Within any one shell, the  $s$  electrons are lower in energy than the  $p$  electrons. This means that an  $s$  electron is harder to remove from an atom than a  $p$  electron in the same shell. The electron removed during the ionization of beryllium ( $[\text{He}]2s^2$ ) is an  $s$  electron, whereas the electron removed during the ionization of boron ( $[\text{He}]2s^22p^1$ ) is a  $p$  electron; this results in a lower first ionization energy for boron, even though its nuclear charge is greater by one proton. Thus, we see a small deviation from the predicted trend occurring each time a new subshell begins.



**Figure 10.6d:** First ionization energies of some elements: the first ionization energy of the elements in the first five periods are plotted against their atomic number (credit: *Chemistry (OpenStax)*, CC BY 4.0).

Another deviation occurs as orbitals become more than one-half filled. The first ionization energy for oxygen is slightly less than that for nitrogen, despite the trend in increasing  $IE_1$  values across a period. Looking at the orbital diagram of oxygen, we can see that removing one electron will eliminate the electron-electron repulsion caused by pairing the electrons in the  $2p$  orbital and will result in a half-filled orbital (which is energetically favourable).



Analogous changes occur in succeeding periods (note the dip for sulfur after phosphorus in Figure 10.6e).

First Ionization Energies of Some Elements (kJ/mol)

Period	Group																																								
1	1	H																	18	He																					
		1310																		2370																					
2	1	Li	2	Be														13	B	14	C	15	N	16	O	17	F	18	Ne												
		520		900														800	1090	1400	1310	1680	2080																		
3	1	Na	2	Mg	3	Al	4	Si	5	P	6	S	7	Cl	8	Ar																									
		490		730		580		780		1060		1000		1250		1520																									
4	1	K	2	Ca	3	Sc	4	Ti	5	V	6	Cr	7	Mn	8	Fe	9	Co	10	Ni	11	Cu	12	Zn	13	Ga	14	Ge	15	As	16	Se	17	Br	18	Kr					
		420		590		630		660		650		660		710		760		760		730		740		910		580		780		960		950		1140		1350					
5	1	Rb	2	Sr	3	Y	4	Zr	5	Nb	6	Mo	7	Tc	8	Ru	9	Rh	10	Pd	11	Ag	12	Cd	13	In	14	Sn	15	Sb	16	Te	17	I	18	Xe					
		400		550		620		660		670		680		710		720		800		870		870		560		700		830		870		1010		1170							
6	1	Cs	2	Ba	3	La	4	Hf	5	Ta	6	W	7	Re	8	Os	9	Ir	10	Pt	11	Au	12	Hg	13	Tl	14	Pb	15	Bi	16	Po	17	At	18	Rn					
		380		500		540		700		760		770		760		840		890		870		890		1000		590		710		800		810		...		1030					
7	1	Fr	2	Ra																																					
		...		510																																					

**Figure 10.6e:** Ionization energies of elements shown in the periodic table: this version of the periodic table shows the first ionization energy of ( $IE_1$ ), in kJ/mol, of selected elements. Review the Periodic Table of the Elements in other formats in Appendix A (credit: Chemistry (OpenStax), CC BY 4.0).

Removing an electron from a cation is more difficult than removing an electron from a neutral atom because of the greater electrostatic attraction to the cation. Likewise, removing an electron from a cation with a higher positive charge is more difficult than removing an electron from an ion with a lower charge. Thus, successive ionization energies for one element always increase. As seen in Table 10.6b, there is a large increase in the ionization energies (colour change) for each element. This jump corresponds to removal of the core electrons, which are harder to remove than the valence electrons. For example, Sc and Ga both have three valence electrons, so the rapid increase in ionization energy occurs after the third ionization.

**Table 10.6b: Successive Ionization Energies for Selected Elements (kJ/mol)**

Element	$IE_1$	$IE_2$	$IE_3$	$IE_4$	$IE_5$	$IE_6$	$IE_7$
K	418.8	3051.8	4419.6	5876.9	7975.5	9590.6	11343
Ca	589.8	1145.4	4912.4	6490.6	8153.0	10495.7	12272.9
Sc	633.1	1235.0	2388.7	7090.6	8842.9	10679.0	13315.0
Ga	578.8	1979.4	2964.6	6180	8298.7	10873.9	13594.8
Ge	762.2	1537.5	3302.1	4410.6	9021.4	Not available	Not available
As	944.5	1793.6	2735.5	4836.8	6042.9	12311.5	Not available

## Example 10.6d

### Ranking Ionization Energies

Predict the order of increasing energy for the following processes:  $IE_1$  for Al,  $IE_1$  for Tl,  $IE_2$  for Na,  $IE_3$  for Al.

## Solution

Removing the  $6p^1$  electron from Tl is easier than removing the  $3p^1$  electron from Al because the higher  $n$  orbital is farther from the nucleus, so  $IE_1(\text{Tl}) < IE_1(\text{Al})$ . Ionizing the third electron from Al ( $\text{Al}^{2+} \rightarrow \text{Al}^{3+} + e^-$ ) requires more energy because the cation  $\text{Al}^{2+}$  exerts a stronger pull on the electron than the neutral Al atom, so  $IE_1(\text{Al}) < IE_3(\text{Al})$ . The second ionization energy for sodium removes a core electron, which is a much higher energy process than removing valence electrons. Putting this all together, we obtain:  $IE_1(\text{Tl}) < IE_1(\text{Al}) < IE_3(\text{Al}) < IE_2(\text{Na})$ .

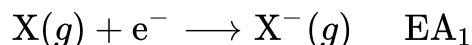
## Exercise 10.6c

Which has the lowest value for  $IE_1$ : O, Po, Pb, or Ba?

**Check Your Answer<sup>3</sup>**

## Variation in Electron Affinities

The **electron affinity** [EA] is the energy change for the process of adding an electron to a gaseous atom to form an anion (negative ion).



This process can be either endothermic (requiring energy) or exothermic (releasing energy), depending on the element. The EA of some of the elements is given in Figure 10.6f. You can see that some elements have negative values, whereas, other have positive values:

- Elements having negative values of EA tells us energy is released when the gaseous atom accepts an electron.
- Elements having positive values of EA means energy is required for the atom to become negatively charged.



Electron Affinity Values for Selected Elements (kJ/mol)

Period	Group 1		Group 2												Group 13	Group 14	Group 15	Group 16	Group 17	Group 18																
1	H	-72																			He	+20*														
2	Li	-60	Be	+240*											B	-23	C	-123	N	0	O	-141	F	-322	Ne	-30										
3	Na	-53	Mg	+230*											Al	-44	Si	-120	P	-74	S	-20	Cl	-348	Ar	+35*										
4	K	-48	Ca	+150*	Sc		Ti		V		Cr		Mn		Fe		Co		Ni		Cu		Zn		Ga	-40*	Ge	-115	As	-7	Se	-195	Br	-324	Kr	+40*
5	Rb	-46	Sr	+160*	Y		Zr		Nb		Mo		Tc		Ru		Rh		Pd		Ag		Cd		In	-40*	Sn	-121	Sb	-101	Te	-190	I	-295	Xe	+40*
6	Cs	-45	Ba	+50*	La		Hf		Ta		W		Re		Os		Ir		Pt		Au		Hg		Tl	-50	Pb	-101	Bi	-101	Po	-170	At	-270*	Rn	+40*
7	Fr		Ra																																	

\* Calculated value

**Figure 10.6f:** Electron affinities shown in a periodic table: this version of the periodic table displays the electron affinity values (in kJ/mol) for selected elements. Review the Periodic Table of the Elements in other formats in Appendix A (credit: *Chemistry (OpenStax)*, CC BY 4.0).

Just as with ionization energy, subsequent EA values are associated with forming ions with more charge. The second EA is the energy associated with adding an electron to an anion to form a  $-2$  ion, and so on.

As we might predict, it becomes easier to add an electron across a series of atoms as the effective nuclear charge of the atoms increases. We find, as we go from left to right across a period, EAs tend to become more negative. The exceptions found among the elements of group 2 (2A), group 15 (5A), and group 18 (8A) can be understood based on the electronic structure of these groups. The noble gases, group 18 (8A), have a completely filled shell and the incoming electron must be added to a higher  $n$  level, which is more difficult to do. Group 2 (2A) has a filled  $ns$  subshell, and so the next electron added goes into the higher energy  $np$ , so, again, the observed EA value is not as the trend would predict. Finally, group 15 (5A) has a half-filled  $np$  subshell and the next electron must be paired with an existing  $np$  electron. In all of these cases, the initial relative stability of the electron configuration disrupts the trend in EA.

We also might expect the atom at the top of each group to have the largest EA; their first ionization potentials suggest that these atoms have the largest effective nuclear charges. However, as we move down a group, we see that the second element in the group most often has the greatest EA. The reduction of the EA of the first member can be attributed to the small size of the  $n = 2$  shell and the resulting large electron-electron repulsions. For example, chlorine, with an EA value of  $-348$  kJ/mol, has the highest value of any element in the periodic table. The EA of fluorine is  $-322$  kJ/mol. When we add an electron to a fluorine atom to form a fluoride anion ( $F^-$ ), we add an electron to the  $n = 2$  shell. The electron is attracted to the nucleus, but there is also significant repulsion from the other electrons already present in this small valence shell. The chlorine atom has the same electron configuration in the valence shell, but because the entering electron is going into the  $n = 3$  shell, it occupies a considerably larger region of space and the electron-electron repulsions are reduced. The entering electron does not experience as much repulsion and the chlorine atom accepts an additional electron more readily.

In summary, the electron affinity (EA) of an element is the energy change that occurs when an electron is

added to a gaseous atom to give an anion. In general, elements with the most negative electron affinities (the highest affinity for an added electron) are those with the smallest size and highest ionization energies and are found in the upper right corner of the periodic table. With some exceptions to the rule, electron affinities become more negative across a row of the periodic table, which means they have a higher affinity for an electron. As you go down a group in the periodic table, atomic radius increases, ionization energy (affinity for their own valence electrons) decreases, and an atom's electron affinity for an added electron also decreases. Generally speaking,

Electron affinity increases as you go up a group and from left to right across periods of the periodic table.

The properties discussed in this section (size of atoms and ions, effective nuclear charge, ionization energies, and electron affinities) are central to understanding chemical reactivity. For example, because fluorine has an energetically favourable EA and a large energy barrier to ionization (IE), it is much easier to form fluorine anions than cations. Metallic properties including conductivity and malleability (the ability to be formed into sheets) depend on having electrons that can be removed easily. Thus, metallic character increases as we move down a group and decreases across a period is the same trend observed for atomic size because it is easier to remove an electron that is farther away from the nucleus. For both IE and electron affinity data, there are exceptions to the trends when dealing with completely filled or half-filled subshells.

For a summary on periodic table trends, **watch [The Periodic Table: Atomic Radius, Ionization Energy, and Electronegativity \(7 min 52 sec\)](https://youtu.be/hePb00CqvP0)**. (<https://youtu.be/hePb00CqvP0>)

## Links to Interactive Learning Tools

Explore Periodictable.com (<https://periodictable.com/Properties/A/AtomicNumber.st.html>)'s visualizations of the periodic trends discussed in this section (and many more trends). With just a few clicks, you can create three-dimensional versions of the periodic table showing atomic size or graphs of ionization energies from all measured elements.

Practice Periodic Trends (<https://www.physicsclassroom.com/Concept-Builders/Chemistry/Periodic-Trends>) from the Physics Classroom (<https://www.physicsclassroom.com/>).

## Attribution & References

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## Notes

- possible answers include Be, Li
  - Order of decreasing covalent radius means ordering elements in order of Largest to smallest Radii. Here, the radius increases as we move down a group, so  $\text{Fr} > \text{Cs}$ . Next determine which is the next largest radii by comparing Na, Mg and Ca. Radius decreases as we move across a period, so  $\text{Mg} > \text{Na}$ . Since radius increases as we move down a group  $\text{Ca} > \text{Mg}$ . Putting the trends together, we obtain  $\text{Fr} > \text{Cs} > \text{Ca} > \text{Mg} > \text{Na}$ .
- $\text{F}^- < \text{O}^{2-} < \text{K}^+ < \text{K} < \text{Cs}^{2+} < \text{Fr}$ ;
  - $\text{Al}^{3+} < \text{Mg}^{2+} < \text{Ne} < \text{F}^- < \text{O}^{2-}$
- Ba has the lowest value for  $1E_1$

# CHAPTER 10 - SUMMARY

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## 10.1 Electromagnetic Radiation

Light and other forms of electromagnetic radiation move through a vacuum with a constant speed,  $c$ , of  $2.998 \times 10^8 \text{ m s}^{-1}$ . This radiation shows wavelike behaviour, which can be characterized by a frequency ( $\nu$ ) and a wavelength ( $\lambda$ ) such that  $c = \lambda\nu$ . Each particle of EMR spectrum has a quantum of energy associated with it and is called a photon. The energy of a photon is proportional to its frequency, and inversely proportional to its wavelength. Light demonstrates both wavelike and particle-like behaviour is known as wave-particle duality. All forms of electromagnetic radiation share these properties, although various forms including X-rays, visible light, microwaves, and radio waves interact differently with matter and have very different practical applications.

## 10.2 The Bohr Atom

Bohr incorporated Planck's and Einstein's quantization ideas into a model of the hydrogen atom that resolved the paradox of atom stability and discrete spectra. The Bohr model of the hydrogen atom explains the connection between the quantization of photons and the quantized emission from atoms. Bohr described the hydrogen atom in terms of an electron moving in a circular orbit about a nucleus. He postulated that the electron was restricted to certain orbits characterized by discrete energies. Transitions between these allowed orbits result in the absorption or emission of photons. When an electron moves from a higher-energy orbit to a more stable one, energy is emitted in the form of a photon. The colour of photon emitted will be specific to that photon's energy, frequency, and wavelength. To move an electron from a stable orbit to a more excited one, a photon of energy must be absorbed. Using the Bohr model, we can calculate the energy of an electron and the radius of its orbit in any one-electron system.

## 10.3 Wave Nature of Matter

An electron possesses both particle and wave properties. The modern model for the electronic structure of the atom is based on recognizing that an electron possesses particle and wave properties, the so-called wave-particle duality. Louis de Broglie showed that the wavelength of particle is equal to Planck's constant divided by the mass times the velocity of the particle. He argued that Bohr's assumption of quantization can be explained if the electron is considered not as a particle, but rather as a circular standing wave such that only

an integer number of wavelengths could fit exactly within the orbit. Thus, it appears that while electrons are small localized particles, their motion does not follow the equations of motion implied by classical mechanics, but instead it is governed by some type of a wave equation that governs a probability distribution even for a single electron's motion. Thus the wave-particle duality first observed with photons is actually a fundamental behaviour intrinsic to all quantum particles.

Werner Heisenberg considered the limits of how accurately we can measure properties of an electron or other microscopic particles. He determined that there is a fundamental limit to how accurately one can measure both a particle's position and its momentum simultaneously. The more accurately we measure the momentum of a particle, the less accurately we can determine its position at that time, and vice versa. This is summed up in what we now call the Heisenberg uncertainty principle: *It is fundamentally impossible to determine simultaneously and exactly both the momentum and the position of a particle.*

## 10.4 Quantum-Mechanical Model of the Atom

Macroscopic objects act as particles. Microscopic objects (such as electrons) have properties of both a particle and a wave. Their exact trajectories cannot be determined. The quantum mechanical model of atoms describes the three-dimensional position of the electron in a *probabilistic* manner according to a mathematical function called a wavefunction, often denoted as  $\psi$ . Atomic wavefunctions are also called orbitals. The squared magnitude of the wavefunction describes the distribution of the probability of finding the electron in a particular region in space. Therefore, atomic orbitals describe the areas in an atom where electrons are most likely to be found.

An atomic orbital is characterized by three quantum numbers. The principal quantum number,  $n$ , can be any positive integer. The general region for value of energy of the orbital and the average distance of an electron from the nucleus are related to  $n$ . Orbitals having the same value of  $n$  are said to be in the same shell. The angular momentum quantum number,  $l$ , can have any integer value from 0 to  $n - 1$ . This quantum number describes the shape or type of the orbital. Orbitals with the same principle quantum number and the same  $l$  value belong to the same subshell. The magnetic quantum number,  $m_l$ , with  $2l + 1$  values ranging from  $-l$  to  $+l$ , describes the orientation of the orbital in space. The fourth quantum number is spin quantum number. Each electron has a spin quantum number,  $m_s$ , that can be equal to  $(\pm \frac{1}{2})$ . No two electrons in the same atom can have the same set of values for all the four quantum numbers. An orbital can be empty or it can contain one or two electrons, but never more than two. If two electrons occupy the same orbital, they must have opposite spins.

In summary, electrons occupy orbitals, which are probability fields or spaces around the nucleus of an atom where an electron is likely to be found. Important criteria was established in defining the modern atomic theory:

1. Atoms have a series of energy levels called principal energy levels, which are designated by whole numbers ( $n = 1, 2, 3, \dots$ ).
2. The energy of the level increases as the value of  $n$  increases.
3. Each principal energy level contains one or more types of orbitals, called subshells.
4. The number of subshells present in a given principal energy level equals  $n$ .
  1. For example: Principal energy level 4 ( $n = 4$ ) has 4 subshells including  $s, p, d$  and  $f$
5. The  $n$  value is always used to label the orbitals of a given principal level and is followed by a letter that indicates the type (shape) of the orbital (For example:  $1s, 2p, 3d \dots$ ).
6. An orbital can be empty or it can contain one or two electrons, but never more than two. If two electrons occupy the same orbital, they must have opposite spins.
7. The shape of an orbital does not indicate the specific details of electron movement (how it moves in a given orbital). It gives the probability distribution for where an electron is most likely to be found in that orbital.
8. The total number of orbitals in a given shell (principal energy level) is  $2n$  and the maximum number of electrons in each shell (principal energy level) is  $2n^2$ .

## 10.5 Atomic Structures of the First 20 Elements and the Periodic Table

The relative energy of the subshells determine the order in which atomic orbitals are filled ( $1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p$ , and so on). Electron configurations and orbital diagrams can be determined by applying the Pauli exclusion principle (no two electrons can have the same set of four quantum numbers) and Hund's rule (whenever possible, electrons retain unpaired spins in degenerate orbitals). The orbital filling diagram and the periodic table can be used as tools to help determine the electron filling order when writing electron configurations and orbital diagrams. Full electron configuration or noble gas configurations can be used to represent the number of electrons in a parent atom. For ions, electron configurations and orbital diagrams can also be used to illustrate the electrons in an ion.

Electrons in the outermost orbitals, called valence electrons, are responsible for most of the chemical behaviour of elements. In the periodic table, elements with analogous valence electron configurations usually occur within the same group. There are some exceptions to the predicted filling order, particularly when half-filled or completely filled orbitals can be formed. The periodic table can be divided into three categories based on the orbital in which the last electron to be added is placed: main group elements ( $s$  and  $p$  orbitals), transition elements ( $d$  orbitals), and inner transition elements ( $f$  orbitals).

## 10.6 Atomic Properties and Periodic Table Trends

Electron configurations allow us to understand many periodic trends. Covalent radius increases as we move down a group because the  $n$  level (orbital size) increases. Covalent radius mostly decreases as we move left to right across a period because the effective nuclear charge experienced by the electrons increases, and the electrons are pulled in tighter to the nucleus. Anionic radii are larger than the parent atom, while cationic radii are smaller, because the number of valence electrons has changed while the nuclear charge has remained constant. Ionization energy (the energy associated with forming a cation) decreases down a group and mostly increases across a period because it is easier to remove an electron from a larger, higher-energy orbital. Electron affinity (the energy associated with forming an anion) is more favourable (exothermic) when electrons are placed into lower energy orbitals, closer to the nucleus. Therefore, electron affinity becomes increasingly negative as we move left to right across the periodic table and decreases as we move down a group. For both IE and electron affinity data, there are exceptions to the trends when dealing with completely filled or half-filled subshells.

### Attribution & References

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# CHAPTER 10 - REVIEW

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## 10.1 Electromagnetic Radiation & 10.2 The Bohr Atom

1. The light produced by a red neon sign is due to the emission of light by excited neon atoms. Qualitatively describe the spectrum produced by passing light from a neon lamp through a prism.  
**Check Answer:** <sup>1</sup>
2. The laser on a Blu-ray player has a wavelength of 405 nm. In what region of the electromagnetic spectrum is this radiation? What is its frequency?  
**Check Answer:** <sup>2</sup>
3. CKUN-FM is a First Nations/community radio station broadcasting at 101.3 FM dial in Christian Island, Ontario, Canada broadcasts at a frequency of  $1.013 \times 10^8 \text{ s}^{-1}$  (101.3 MHz) (Wikipedia, 2022). What is the wavelength of these radio waves in meters?  
**Check Answer:** <sup>3</sup>
4. FM-95, an FM radio station, broadcasts at a frequency of  $9.51 \times 10^7 \text{ s}^{-1}$  (95.1 MHz). What is the wavelength of these radio waves in meters?  
**Check Answer:** <sup>4</sup>
5. A bright violet line occurs at 435.8 nm in the emission spectrum of mercury vapour. What amount of energy, in joules, must be released by an electron in a mercury atom to produce a photon of this light?  
**Check Answer:** <sup>5</sup>
6. Light with a wavelength of 614.5 nm looks orange. What is the energy, in joules, per photon of this orange light? What is the energy in eV ( $1 \text{ eV} = 1.602 \times 10^{-19} \text{ J}$ )?  
**Check Answer:** <sup>6</sup>
7. Heated lithium atoms emit photons of light with an energy of  $2.961 \times 10^{-19} \text{ J}$ . Calculate the frequency and wavelength of one of these photons. What is the total energy in 1 mole of these photons? What is the colour of the emitted light?  
**Check Answer:** <sup>7</sup>
8. A photon of light produced by a surgical laser has an energy of  $3.027 \times 10^{-19} \text{ J}$ . Calculate the frequency and wavelength of the photon. What is the total energy in 1 mole of photons? What is the colour of the emitted light?  
**Check Answer:** <sup>8</sup>
9. When rubidium ions are heated to a high temperature, two lines are observed in its line spectrum at wavelengths (a)  $7.9 \times 10^{-7} \text{ m}$  and (b)  $4.2 \times 10^{-7} \text{ m}$ . What are the frequencies of the two lines? What colour do we see when we heat a rubidium compound?



**Check Answer:**<sup>9</sup>

10. The emission spectrum of cesium contains two lines whose frequencies are (a)  $3.45 \times 10^{14}$  Hz and (b)  $6.53 \times 10^{14}$  Hz. What are the wavelengths and energies per photon of the two lines? What colour are the lines?

**Check Answer:**<sup>10</sup>

11. One of the radiographic devices used in a dentist's office emits an X-ray of wavelength  $2.090 \times 10^{-11}$  m. What is the energy, in joules, and frequency of this X-ray? **Check Answer:**<sup>11</sup>
12. The eyes of certain reptiles pass a single visual signal to the brain when the visual receptors are struck by photons of a wavelength of 850 nm. If a total energy of  $3.15 \times 10^{-14}$  J is required to trip the signal, what is the minimum number of photons that must strike the receptor?

**Check Answer:**<sup>12</sup>

13. RGB colour television and computer displays use cathode ray tubes that produce colours by mixing red, green, and blue light. If we look at the screen with a magnifying glass, we can see individual dots turn on and off as the colours change. Using a spectrum of visible light, determine the approximate wavelength of each of these colours. What is the frequency and energy of a photon of each of these colours?

**Check Answer:**<sup>13</sup>

14. Why is the electron in a Bohr hydrogen atom bound less tightly when it has a quantum number of  $n = 3$  than when it has a quantum number of  $n = 1$ ?

**Check Answer:**<sup>14</sup>

15. What does it mean to say that the energy of the electrons in an atom is quantized?

**Check Answer:**<sup>15</sup>

16. Using the Bohr model, determine the energy, in joules, necessary to ionize a ground-state hydrogen atom. Use formula  $E_n = -\frac{kZ^2}{n^2}$  where  $Z$  is the nuclear charge (+1 for hydrogen) and  $k$  has a value of  $2.179 \times 10^{-18}$  J. Show your calculations.

**Check Answer:**<sup>16</sup>

17. The electron volt (eV) is a convenient unit of energy for expressing atomic-scale energies. It is the amount of energy that an electron gains when subjected to a potential of 1 volt;  $1 \text{ eV} = 1.602 \times 10^{-19}$  J. Using the Bohr model, determine the energy, in electron volts, of the photon produced when an electron in a hydrogen atom moves from the orbit with  $n = 5$  to the orbit with  $n = 2$ . Use formula

$$\Delta E = k \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \text{ and } k \text{ has a value of } 2.179 \times 10^{-18} \text{ J. Show your calculations.}$$

**Check Answer:**<sup>17</sup>

18. Consider a large number of hydrogen atoms with electrons randomly distributed in the  $n = 1, 2, 3,$  and  $4$  orbits.

**Check Answer:**<sup>18</sup>

- a. How many different wavelengths of light are emitted by these atoms as the electrons fall into lower-

energy orbitals?

- b. Calculate the lowest and highest energies of light produced by the transitions described in part (a).

Use formula  $\Delta E = k\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$  and  $k$  has a value of  $2.179 \times 10^{-18}$  J.

- c. Calculate the frequencies and wavelengths of the light produced by the transitions described in part (b). Using **Figure 10.1c: The Electromagnetic Spectrum** as a reference, specify the type of electromagnetic radiation emitted in each energy jump in part (b). Use  $E=hf$  to calculate frequency, where the constant of proportionality,  $h$ , is called Planck's constant  $h = 6.626 \times 10^{-34}$  joule-seconds (J-s). Use equation  $c = \lambda\nu$  to solve for the wavelength:  $\lambda = \frac{c}{\nu}$

19. How are the Bohr model and the Rutherford model of the atom similar? How are they different?

**Check Answer:**<sup>19</sup>

20. The spectra of hydrogen and of iron are shown in **Figures 10.2c and 10.2d Comparing Emission Line Spectra of White Light and Light from Various Elements**. When referencing these figures, recall that 1 angstrom = 0.1 nm =  $1 \times 10^{-10}$  m. Answer the following questions: (a) What causes the lines in these spectra? (b) Why are the colours of the lines different? (c) Suggest a reason for the observation that the spectrum of iron is more complicated than the spectrum of hydrogen.

**Check Answer:**<sup>20</sup>

## 10.3 Wave Nature of Matter & 10.4 Quantum Mechanical Model of the Atom

1. How are the Bohr model and the quantum mechanical model of the hydrogen atom similar? How are they different?

**Check Answer:**<sup>21</sup>

2. Summarize the allowed values for each of the four quantum numbers:  $n$ ,  $l$ ,  $m_l$ , and  $m_s$ ?

**Check Answer:**<sup>22</sup>

3. Describe the properties of an electron associated with each of the following four quantum numbers:  $n$ ,  $l$ ,  $m_l$ , and  $m_s$ .

**Check Answer:**<sup>23</sup>

4. Identify the subshell in which electrons with the following quantum numbers are found:

**Check Answer:**<sup>24</sup>

- $n = 2, l = 1$
- $n = 4, l = 2$
- $n = 6, l = 0$

5. Which of the subshells described in the previous question contain degenerate orbitals? How many degenerate orbitals are in each?

**Check Answer:**<sup>25</sup>

6. Identify the subshell in which electrons with the following quantum numbers are found:

**Check Answer:**<sup>26</sup>

a.  $n = 3, l = 2$

b.  $n = 1, l = 0$

c.  $n = 4, l = 3$

7. Which of the subshells described in the previous question contain degenerate orbitals? How many degenerate orbitals are in each?

**Check Answer:**<sup>27</sup>

8. (a) How many different types of orbitals are found in principal energy level 2? Provide the letter name for these subshells. (b) How many different types of orbitals are found in principal energy level 4? Provide the letter name for these subshells.

**Check Answer:**<sup>28</sup>

9. What is the smallest possible  $n$  value for an  $s$  orbital?  $p$  orbital?  $d$  orbital?  $f$  orbital?

**Check Answer:**<sup>29</sup>

10. Write the maximum number of electrons allowed in the indicated sublevels:  $s$  sublevel?  $p$  sublevel?  $d$  sublevel?  $f$  sublevel?

**Check Answer:**<sup>30</sup>

11. (a) What is the maximum number of electrons that can occupy (a) the first principal energy level? (b) the second principal energy level? (c) the third principal energy level? (d) the fourth principal energy level?

**Check Answer:**<sup>31</sup>

12. State the Heisenberg uncertainty principle. Describe briefly what the principle implies.

**Check Answer:**<sup>32</sup>

13. Write a set of quantum numbers for each of the electrons with an  $n$  of 4 in a Se atom.

**Check Answer:**<sup>33</sup>

## 10.5 Atomic Structures Of The First 20 Elements.

- 100% pure Canadian maple syrup disguises nutrients in a sweet natural taste. One 30 ml (2 Tablespoons) serving of pure maple syrup contains 35% of the Daily Value of Manganese. It is also a source of calcium and potassium. (Source: Quebec Maple Syrup Producers (QMSP), 2021). Write the complete electron configurations and noble gas configurations for manganese, calcium, and potassium. **Check Answer:**<sup>34</sup>
- Water and electrolyte balance is important in maintaining homeostasis in the human body. The main electrolytes (ions) in the body that we get from the food we eat and fluids we drink include sodium, calcium, potassium, chloride, and magnesium. (a) Write the complete electron configurations for the following ions: sodium, magnesium, and chloride. (b) What do you notice about these ions? **Check Answer:**<sup>35</sup>

3. Using complete subshell notation (not abbreviations,  $1s^2 2s^2 2p^6$ , and so forth), predict the electron configuration of each of the following atoms: **Check Answer:**<sup>36</sup>
- C ( $z = 6$ )
  - P ( $z = 15$ )
  - V ( $z = 23$ )
  - Sb ( $z = 51$ )
  - Sm ( $z = 62$ )
4. Using complete subshell notation ( $1s^2 2s^2 2p^6$ , and so forth), predict the electron configuration of each of the following atoms: **Check Answer:**<sup>37</sup>
- N
  - Si
  - Fe
  - Te
  - Tb
5. Draw the orbital diagram for the valence shell of each of the following atoms: **Check Answer:**<sup>38</sup>
- C
  - P
  - V
  - Sb
6. Use an orbital diagram to describe the electron configuration of the valence shell of each of the following atoms:  
**Check Answer:**<sup>39</sup>
- N
  - Si
  - Fe
  - Te
7. Using complete subshell notation ( $1s^2 2s^2 2p^6$ , and so forth), predict the electron configurations of the following ions.  
**Check Answer:**<sup>40</sup>
- $N^{3-}$
  - $Ca^{2+}$
  - $S^-$
  - $Cs^{2+}$
  - $Fe^{3+}$
  - $Cd^{2+}$
8. Which atom has the electron configuration  $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^2$ ?  
**Check Answer:**<sup>41</sup>

9. Which atom has the electron configuration  $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^7$ ?  
**Check Answer:** <sup>42</sup>
10. Which ion with a +1 charge has the electron configuration  $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6$ ? Which ion with a -2 charge has this configuration?  
**Check Answer:** <sup>43</sup>
11. Which of the following atoms has only two unpaired electrons?  
**Check Answer:** <sup>44</sup>
- Mg
  - Si
  - S
  - Ge
12. Which atom would be expected to have a half-filled  $6p$  subshell?  
**Check Answer:** <sup>45</sup>
13. Which atom would be expected to have a half-filled  $4s$  subshell?  
**Check Answer:** <sup>46</sup>
14. In one area of Australia, the cattle did not thrive despite the presence of suitable forage. An investigation showed the cause to be the absence of sufficient cobalt in the soil. Cobalt forms cations in two oxidation states,  $\text{Co}^{2+}$  and  $\text{Co}^{3+}$ . Write the electron structure of the two cations.  
**Check Answer:** <sup>47</sup>
15. Thallium ( $Z = 81$ ) was used as a poison in the Agatha Christie mystery story “The Pale Horse.” Thallium has two possible cationic forms, +1 and +3. The +1 compounds are the more stable. Write the electron structure of the +1 cation of thallium.  
**Check Answer:** <sup>48</sup>
16. Cobalt-60 and iodine-131 are radioactive isotopes commonly used in nuclear medicine. How many protons, neutrons, and electrons are in atoms of these isotopes? Write the complete electron configuration for each isotope.  
**Check Answer:** <sup>49</sup>

## 10.6 Atomic Properties And Periodic Table Trends

- Based on their positions in the periodic table, predict which has the smallest atomic radius: Mg, Sr, Si, Cl, I.  
**Check Answer:** <sup>50</sup>
- Based on their positions in the periodic table, predict which has the largest atomic radius: Li, Rb, N, F, I.  
**Check Answer:** <sup>51</sup>
- Based on their positions in the periodic table, predict which has the largest first ionization energy: Mg, Ba, B, O, Te.

**Check Answer:** <sup>52</sup>

4. Based on their positions in the periodic table, predict which has the smallest first ionization energy: Li, Cs, N, F, I.

**Check Answer:** <sup>53</sup>

5. Based on their positions in the periodic table, rank the following atoms in order of increasing first ionization energy: F, Li, N, Rb.

**Check Answer:** <sup>54</sup>

6. Based on their positions in the periodic table, rank the following atoms or compounds in order of increasing first ionization energy: Mg, O, S, Si.

**Check Answer:** <sup>55</sup>

7. Atoms of which group in the periodic table have a valence shell electron configuration of  $ns^2np^3$ ?

**Check Answer:** <sup>56</sup>

8. Atoms of which group in the periodic table have a valence shell electron configuration of  $ns^2$ ?

**Check Answer:** <sup>57</sup>

9. Based on their positions in the periodic table, list the following atoms in order of increasing radius: Mg, Ca, Rb, Cs.

**Check Answer:** <sup>58</sup>

10. Based on their positions in the periodic table, list the following atoms in order of increasing radius: Sr, Ca, Si, Cl.

**Check Answer:** <sup>59</sup>

11. Based on their positions in the periodic table, list the following ions in order of increasing radius:  $K^+$ ,  $Ca^{2+}$ ,  $Al^{3+}$ ,  $Si^{4+}$ .

**Check Answer:** <sup>60</sup>

12. List the following ions in order of increasing radius:  $Li^+$ ,  $Mg^{2+}$ ,  $Br^-$ ,  $Te^{2-}$ .

**Check Answer:** <sup>61</sup>

13. Which atom and/or ion is/are isoelectronic with  $Br^+$ :  $Se^{2+}$ , Se,  $As^-$ , Kr,  $Ga^{3+}$ ,  $Cl^-$ ?

**Check Answer:** <sup>62</sup>

14. Which of the following atoms and ions is/are isoelectronic with  $S^{2+}$ :  $Si^{4+}$ ,  $Cl^{3+}$ , Ar,  $As^{3+}$ , Si,  $Al^{3+}$ ?

**Check Answer:** <sup>63</sup>

15. Compare both the numbers of protons and electrons present in each to rank the following ions in order of increasing radius:  $As^{3-}$ ,  $Br^-$ ,  $K^+$ ,  $Rb^+$ ,  $Mg^{2+}$ .

**Check Answer:** <sup>64</sup>

16. The ionic radii of the ions  $S^{2-}$ ,  $Cl^-$ , and  $K^+$  are 184, 181, 138 pm respectively. Explain why these ions have different sizes even though they contain the same number of electrons.

**Check Answer:** <sup>65</sup>

17. Which main group atom would be expected to have the lowest second ionization energy?

**Check Answer:** <sup>66</sup>

18. Explain why Al is a member of group 13 rather than group 3.

**Check Answer:** <sup>67</sup>

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## Notes

1. The spectrum consists of coloured lines, at least one of which (probably the brightest) is red.
2. Visible light spectrum;  $v = 6.7 \times 10^{14} \text{ s}^{-1}$  or Hz
3.  $\lambda = 2.960 \text{ m}$
4. 3.15 m
5.  $4.558 \times 10^{-19} \text{ J}$ ; Watch "6.4 | A bright violet line occurs at 435.8 nm in the emission spectrum of mercury vapor (<https://youtu.be/ook67jveHTg>)" for an explanation of the solution to this question
6.  $3.233 \times 10^{-19} \text{ J}$ ; 2.018 eV; Watch "6.5 | Light with a wavelength of 614.5 nm looks orange ([https://youtu.be/R2\\_cJbj0WVI](https://youtu.be/R2_cJbj0WVI))" for an explanation of the solution to this question
7.  $v = 4.469 \times 10^{14} \text{ s}^{-1}$ ;  $\lambda = 6.708 \times 10^{-7} \text{ m}$  or 670.8 nm; Total Energy in 1 mole of photons =  $1.783 \times 10^5 \text{ J/mol}$  or  $\text{J mol}^{-1}$ ; Colour of light = Red; Watch "6.6 | Heated lithium atoms emit photons of light with an energy of 2.961 ×

$10^{-19}$  J (<https://youtu.be/mlF5zZdL9CU>)." for an explanation of the solution to this question.

8.  $\nu = 4.568 \times 10^{14} \text{ s}^{-1}$ ;  $\lambda = 6.563 \times 10^{-7} \text{ m}$  or 656.3 nm; Total Energy in 1 mole of photons =  $1.823 \times 10^5 \text{ J mol}^{-1}$ ; Colour of light = red
9. (a)  $\nu = 3.8 \times 10^{14} \text{ s}^{-1}$  or Hz; (b)  $\nu = 7.1 \times 10^{14} \text{ s}^{-1}$  or Hz; The colour of (a) is red since wavelength is 790 nm; (b) is purple/violet/ deep blue since wavelength is 420 nm; Watch "6.8 | When rubidium ions are heated to a high temperature (<https://youtu.be/xU7LiRz4VP4>)" for an explanation of solution to this question.
10. (a)  $\lambda = 8.69 \times 10^{-7} \text{ m}$ ;  $E = 2.29 \times 10^{-19} \text{ J}$ ; (b)  $\lambda = 4.59 \times 10^{-7} \text{ m}$ ;  $E = 4.33 \times 10^{-19} \text{ J}$ ; The colour of (a) is red since wavelength is 869 nm; (b) is blue since wavelength is 459 nm; Watch "6.9 | The emission spectrum of cesium contains two lines (<https://youtu.be/WfO7FP0vJso>)" for an explanation of solution to this question.
11.  $E = 9.502 \times 10^{-15} \text{ J}$ ;  $\nu = 1.434 \times 10^{19} \text{ s}^{-1}$  or Hz; Watch "6.11 | One of the radiographic devices used in a dentist's office (<https://youtu.be/wUMIN6SbkrE>)" for an explanation of solution to this question.
12. Minimum number of photons required =  $1.4 \times 10^5$  photons; Watch "6.12 | The eyes of certain reptiles (<https://youtu.be/Uymjf9vHsEo>)" for an explanation of solution to this question.
13. If use wavelength of 680 nm for Red:  $\nu = 4.4 \times 10^{14} \text{ s}^{-1}$  or Hz and  $E = 2.9 \times 10^{-19} \text{ J}$ . If use wavelength of 520 nm for Green:  $\nu = 5.8 \times 10^{14} \text{ s}^{-1}$  or Hz and  $E = 3.8 \times 10^{-19} \text{ J}$ . If use wavelength of 440nm for Blue:  $\nu = 6.8 \times 10^{14} \text{ s}^{-1}$  or Hz and  $E = 4.5 \times 10^{-19} \text{ J}$ . Somewhat different numbers are also possible if you chose different wavelengths for each colour. Watch "6.13 | RGB color television and computer displays (<https://youtu.be/3rJ40tfFBUI>)" for an explanation of solution to this question.
14. An  $n$  of 3 indicates that an electron in the hydrogen atom is in the third energy level, which is further from the nucleus than the first energy level ( $n=1$ ). The Bohr model uses the theory of electrostatic attraction between the positively charged nucleus and the negatively charge electron in its orbital. The closer an electron is to the nucleus the more closely it is held by the nucleus. The farther an electron is from the nucleus ( in higher shells or energy levels), the less the electrostatic attraction of an electron to the nucleus due to the shielding effect; hence, an electron in energy level 3 will be bound less tightly than an electron in energy level 1.
15. Quantized energy means that the electrons can possess only certain discrete energy values; values between those quantized values are not permitted.
16.  $E_n = -2.179 \times 10^{-18} \text{ J}$
- 17.

$$E \quad E_2 - E_5 = 2.179 \times 10^{-18} \left( \frac{1}{n_2^2} - \frac{1}{n_5^2} \right) \text{ J}$$

18.  $2.179 \times 10^{-18} \left( \frac{1}{2^2} - \frac{1}{5^2} \right) = 4.576 \times 10^{-19} \text{ J}$  Watch "6.19 | The electron volt (eV) is a convenient unit of

$$\frac{4.576 \times 10^{-19} \text{ J}}{1.602 \times 10^{-19} \text{ J eV}^{-1}} = 2.856 \text{ eV}$$

energy (<https://youtu.be/VaAO1XMZ4IY>)" for an explanation of solution to this question.

19. (a) 6 different wavelengths. (b) Lowest energy would be a jump from  $n = 4$  to  $n = 3$ , and the change in energy is  $-1.06 \times 10^{-19} \text{ J}$ ; the highest energy would be a jump from  $n = 4$  to  $n = 1$ , and the change in energy is  $-2.04 \times 10^{-18} \text{ J}$ . Recall that a negative energy value means that energy is being released. (c) For the lowest energy jump ( $n = 4$  to  $n = 3$ ),  $\nu = 1.60 \times 10^{14} \text{ s}^{-1}$  and  $\lambda = 1.87 \times 10^{-6} \text{ m}$ , which is indicative of infrared radiation (1870 nm); for the highest energy jump ( $n = 4$  to  $n = 1$ ),  $\nu = 3.08 \times 10^{15} \text{ s}^{-1}$  and  $\lambda = 9.73 \times 10^{-8} \text{ m}$ , which is indicative of UV radiation (97.3 nm). Watch "6.28 | Consider a large number of hydrogen atoms with electrons (<https://youtu.be/gD6UgC9jDn0>)" for an explanation of solution to this question.
20. Both involve a relatively heavy nucleus with electrons moving around it, although strictly speaking, the Bohr model works only for one-electron atoms or ions. According to classical mechanics, the Rutherford model predicts a miniature "solar system" with electrons moving about the nucleus in circular or elliptical orbits that are confined to planes. If the requirements of classical electromagnetic theory that electrons in such orbits would emit electromagnetic



radiation are ignored, such atoms would be stable, having constant energy and angular momentum, but would not emit any visible light (contrary to observation). If classical electromagnetic theory is applied, then the Rutherford atom would emit electromagnetic radiation of continually increasing frequency (contrary to the observed discrete spectra), thereby losing energy until the atom collapsed in an absurdly short time (contrary to the observed long-term stability of atoms). The Bohr model retains the classical mechanics view of circular orbits confined to planes having constant energy and angular momentum, but restricts these to quantized values dependent on a single quantum number,  $n$ . The orbiting electron in Bohr's model is assumed not to emit any electromagnetic radiation while moving about the nucleus in its stationary orbits, but the atom can emit or absorb electromagnetic radiation when the electron changes from one orbit to another. Because of the quantized orbits, such "quantum jumps" will produce discrete spectra, in agreement with observations.

21. (a) Every line represents a specific wavelength of discrete energies that is emitted when electrons transition from a higher energy shell to a lower energy shell. The emitted light corresponds to energies of the specific electrons. (b) The colours of the lines are different because different wavelengths equate to different discrete energies that represent a specific colour. (c) The line spectrum of iron is more complicated than hydrogen (which only has four lines). Hydrogen (atomic number = 1) only has 1 electron, where iron (atomic number = 26) has 26 electrons. As a result, iron has more energy shell transition possibilities for its electrons and will have a more complicated emission line spectra than hydrogen.
22. Both models have a central positively charged nucleus with electrons moving about the nucleus in accordance with the Coulomb electrostatic potential. The Bohr model *assumes* that the electrons move in circular orbits that have quantized energies, angular momentum, and radii that are specified by a single quantum number,  $n = 1, 2, 3, \dots$ , but this quantization is an ad hoc assumption made by Bohr to incorporate quantization into an essentially classical mechanics description of the atom. Bohr also assumed that electrons orbiting the nucleus normally do not emit or absorb electromagnetic radiation, but do so when the electron switches to a different orbit. In the quantum mechanical model, the electrons do not move in precise orbits (such orbits violate the Heisenberg uncertainty principle) and, instead, a probabilistic interpretation of the electron's position at any given instant is used, with a mathematical function  $\psi$  called a wavefunction that can be used to determine the electron's spatial probability distribution. These wavefunctions, or orbitals, are three-dimensional stationary waves that can be specified by three quantum numbers that arise naturally from their underlying mathematics (no ad hoc assumptions required): the principal quantum number,  $n$  (the same one used by Bohr), which specifies shells such that orbitals having the same  $n$  all have the same energy and approximately the same spatial extent; the angular momentum quantum number  $l$ , which is a measure of the orbital's angular momentum and corresponds to the orbitals' general shapes, as well as specifying subshells such that orbitals having the same  $l$  (and  $n$ ) all have the same energy; and the orientation quantum number  $m$ , which is a measure of the  $z$  component of the angular momentum and corresponds to the orientations of the orbitals. The Bohr model gives the same expression for the energy as the quantum mechanical expression and, hence, both properly account for hydrogen's discrete spectrum (an example of getting the right answers for the wrong reasons, something that many chemistry students can sympathize with), but gives the wrong expression for the angular momentum (Bohr orbits necessarily all have non-zero angular momentum, but some quantum orbitals [ $s$  orbitals] can have zero angular momentum). (**Answer Source:** Answer to this question was retrieved from Problem 2.3.7 in General Chemistry II (Addie Clark). LibreTexts. licensed under CC BY-NC-SA 3.0)
23. The principal quantum number ( $n$ ) values are 1, 2, 3, 4, and so on. The angular momentum quantum number ( $l$ ) can be any integer between 0 and  $n - 1$ . It specifies the type of subshell, specifically the 3D shape of an orbital ( $0 = s$ ;  $1 = p$ ;  $2 = d$ ;  $3 = f$ ; and so on. If  $n = 3$ , for example,  $l$  can be either 0, 1, or 2. The third energy level can have electrons occupying  $s$ ,  $p$  or  $d$  orbitals. The magnetic quantum number ( $m_l$ ) can be any integer between  $-l$  and  $+l$ . This number divides the subshell into individual orbitals which hold two electrons per orbital; there are  $2l+1$  orbitals in each subshell. If  $l = 2$ ,  $m_l$  can be either -2, -1, 0, +1, or +2 (a  $d$  subshell has 5 orbitals, each can contain 2 electrons). Spin quantum number ( $m_s$ ) specifies the orientation of the spin axis of an electron. An electron can only spin one of two ways where  $m_s = \frac{1}{2}$  (up) or  $-\frac{1}{2}$  (down). If two electrons share the same orbital, they must have opposite spins.

24.  $n$  determines the general range for the value of energy (principal energy level) and the probable distances that the electron can be from the nucleus.  $l$  determines the shape of the orbital.  $m_l$  determines the orientation of the orbitals of the same  $l$  value with respect to one another; it divides subshell into individual orbitals, which hold two electrons per orbital (there are  $2l+1$  orbitals in each subshell).  $m_s$  determines the spin of an electron.
25. (a)  $2p$ ; (b)  $4d$ ; (c)  $6s$
26. The orbitals which have the same energy [belong to the same subshell and shell (energy level,  $n$ )] are called degenerate orbitals. Therefore,  $2p$  contains 3 degenerate orbitals;  $4d$  contains 5 degenerate orbitals;  $6s$  is not degenerate.
27. (a)  $3d$ ; (b)  $1s$  (c)  $4f$
28. The orbitals which have the same energy [belong to the same subshell and shell (energy level,  $n$ )] are called degenerate orbitals. Therefore,  $3d$  contains 5 degenerate orbitals;  $1s$  is not degenerate;  $4f$  contains 7 degenerate orbitals.
29.  $n = 2$  has two possible subshells  $s$  and  $p$ ;  $n = 4$  has four possible subshells  $s$ ,  $p$ ,  $d$  and  $f$ .
30. The smallest possible  $n$  value for an  $s$  orbital is  $1s$ ,  $p$  orbital is  $2p$ ,  $d$  orbital is  $3d$ ,  $f$  orbital is  $4f$ .
31.  $s$  sublevel electron capacity is 2 electrons;  $p$  sublevel electron capacity is 6 electrons;  $d$  sublevel electron capacity is 10 electrons;  $f$  sublevel electron capacity is 14 electrons
32. Use electron capacity for a given energy level (shell) =  $2n^2$  (a) the first principal energy level can fit  $2(1)^2 = 2$  electrons; (b) the second principal energy level can fit  $2(2)^2 = 8$  electrons; (c) the third principal energy level can fit  $2(3)^2 = 18$  electrons; (d) the fourth principal energy level can fit  $2(4)^2 = 32$  electrons
33. Heisenberg's uncertainty principle states that for particles exhibiting both particle and wave nature, It is fundamentally impossible to accurately determine both the position and velocity (momentum of a particle at the same time. The more precise our measurement of position is, the less accurate will be our momentum measurement and vice-versa

	$n$	$l$	$m_l$	$s$
34.	4	0	0	$+\frac{1}{2}$
	4	0	0	$-\frac{1}{2}$
	4	1	-1	$+\frac{1}{2}$
	4	1	0	$+\frac{1}{2}$
	4	1	+1	$+\frac{1}{2}$
	4	1	-1	$-\frac{1}{2}$

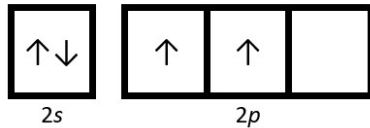
NOTE: Selenium (Se) has 34 electrons, 6 of which are valence electrons in the fourth principal energy level. The quantum numbers for these 6 valence electrons are shown in the Table. Two electrons are found in the  $4s$  orbital, the other four are found dispersed amongst the three  $4p$  orbitals.

35. manganese -  $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^5$ , [Ar] $4s^2 3d^5$ ; calcium -  $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$ , [Ar] $4s^2$ ; potassium -  $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$ , [Ar] $4s^1$
36. (a) sodium ion ( $\text{Na}^+$ ) -  $1s^2 2s^2 2p^6$ ; magnesium ( $\text{Mg}^{2+}$ ) -  $1s^2 2s^2 2p^6$ ; chlorine ( $\text{Cl}$ ) -  $1s^2 2s^2 2p^6 3s^2 3p^6$ ; (b) Both the sodium

ion and magnesium ion have the same electron configurations as their closest noble gas, neon (Ne), which all have 10 electrons. A chlorine ion has the same electron configuration as its closest noble gas, argon (Ar), with 18 electrons.

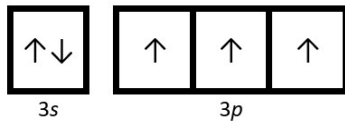
37. (a) C -  $1s^2 2s^2 2p^2$ ; P -  $1s^2 2s^2 2p^6 3s^2 3p^3$ ; V -  $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^3$ ; Sb -  $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^3$ ; Sm -  $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 6s^2 4f^6$
38. (a)  $1s^2 2s^2 2p^3$ ; (b)  $1s^2 2s^2 2p^6 3s^2 3p^2$ ; (c)  $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^6$ ; (d)  $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^4$ ; (e)  $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 6s^2 4f^9$

Orbital Diagram of the Valence Electrons in a Carbon Atom



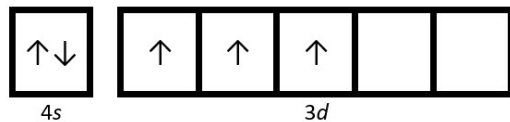
39. (a) C (b) P

Orbital Diagram of the Valence Electrons in a Phosphorus Atom



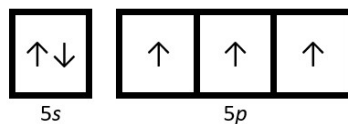
(c) V

Orbital Diagram of the Valence Electrons in a Vanadium Atom

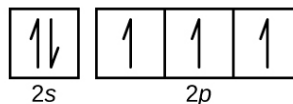


(d) Sb

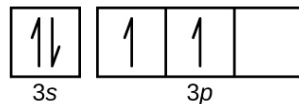
Orbital Diagram of the Valence Electrons in an Antimony Atom



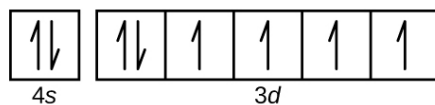
40. (a) N



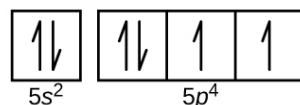
(b) Si



(c) Fe



(d) Te



41. (a)  $1s^2 2s^2 2p^6$ ; (b)  $1s^2 2s^2 2p^6 3s^2 3p^6$ ; (c)  $1s^2 2s^2 2p^6 3s^2 3p^5$ ; (d)  $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^5$ ; (e)  $1s^2 2s^2 2p^6 3s^2 3p^6 3d^5$ ; (f)  $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 4d^{10}$
42. Zr, Zirconium
43. Co, Cobalt

44.  $\text{Rb}^{+1}$  (Rubidium ion);  $\text{Se}^{2-}$  (Selenium Ion)
45. answer (b) and (d) are correct. Silicon and Germanium both have only 2 unpaired electrons.
46. Bi, Bismuth
47. K, Potassium
48.  $\text{Co}^{2+} - 1s^2 2s^2 2p^6 3s^2 3p^6 3d^7$ ;  $\text{Co}^{3+} - 1s^2 2s^2 2p^6 3s^2 3p^6 3d^6$
49.  $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^6 6s^2 4f^{14} 5d^{10}$
50. Cobalt (Co) has 27 protons, 27 electrons, and 33 neutrons:  $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^7$ . Iodine (I) has 53 protons, 53 electrons, and 78 neutrons:  $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^5$
51. Cl
52. Rb
53. O
54. Cs
55.  $\text{Rb} < \text{Li} < \text{N} < \text{F}$
56.  $\text{Mg} < \text{Si} < \text{S} < \text{O}$
57. 15 (5A)
58. 2 (2A) Alkaline Earth Metals
59.  $\text{Mg} < \text{Ca} < \text{Rb} < \text{Cs}$
60.  $\text{Cl} < \text{Si} < \text{Ca} < \text{Sr}$
61.  $\text{Si}^{4+} < \text{Al}^{3+} < \text{Ca}^{2+} < \text{K}^{+}$
62.  $\text{Li}^{+}, \text{Mg}^{2+}, \text{Br}^{-}, \text{Te}^{2-}$
63. Se,  $\text{As}^{-}$  (all have 34 electrons)
64.  $\text{Cl}^{3+}, \text{Si}$  (all have 14 electrons)
65.  $\text{Mg}^{2+} < \text{K}^{+} < \text{Rb}^{+} < \text{Br}^{-} < \text{As}^{3-}$
66. Even though all these options have the same number of electrons, they have different numbers of protons, which determines their size. An increase in protons, increases the positive charge inside the nucleus of the atom, which has a greater attraction and pull of those electrons. When comparing atoms with the same number of electrons, the greater the atomic number, the smaller the radius.
67. Ra; Watch "6.85 | Which main group atom would be expected to have the lowest second ionization energy? (<https://www.youtube.com/watch?v=IEwJAULjLMU>)" for an explanation of the solution to the math portion of this question visit
68. The periodic table is arranged in accordance with increasing atomic number (increasing number of protons and electrons). The groups are arranged according to their chemical behaviours, which is dictated by the number of valence electrons typical for that neutral element. Based on the rules of orbital filling of electrons, aluminum has 13 electrons to fill its orbitals. Al is a p-block element, and electrons must fill 3p block before 4s or 3d. The group 3 elements are d-block elements, which are also known as transition elements. This is why Al does not have any properties like d-block elements; rather, Al has similar properties of elements found in group 13 (3A).