

CHAPTER 6

Atomic Structure

X-rays are produced when orbital electrons rearrange themselves in an atom to gain energy stability as discussed in Section 1.8. Likewise, gamma rays are produced when the nucleons rearrange themselves in a nucleus. On the other hand, bremsstrahlung radiation is produced when charged particles slow down near a nuclear field. The mechanisms leading to the production of radiation in an atom is the subject matter of this chapter. The materials in Chapters 6 to 10 are the required materials for the foundation of radiological physics. This chapter deals with atomic models while Chapters 7 to 10 shall examine nuclear structure, nuclear decay, and nuclear reactions. The development of the atomic models was based on Bohr's model leading to the formulation of energy levels in the hydrogen atom. As the atomic structure became complex for multi-electron atoms, additional quantum numbers were introduced to form the current atomic model. In this chapter, we shall also examine the energy-states and the transition of electrons in the atoms, the periodic table, and molecular bonding.

6.1 Matter, Element, and Atom

Matter is anything that constitutes a physical body and occupies space. The material substance called **mass** makes up the physical body and hence gives the body a shape and form. There exist three physical states of matter. In the solid state, matter has a definite volume and a definite shape. In the liquid state, it has a definite volume but the shape will assume that of the container it occupies. In the gaseous state, it does not have a definite volume and will fill as well as assume the shape of the container it occupies. **Plasma**, consisting of a collection of electrically charged particles of electrons and bare nuclei at very high temperatures (up to 10^8 K); may be considered the fourth state of matter. A system having a single physical state may show diversity. For example, a **mixture** of oil and water has the same physical state but is not chemically uniform. A homogeneous mixture is a **solution**. If a system is characterized as both physically and chemically uniform throughout, the

system is considered to be a single-phased system. A single phased system is considered a homogeneous system while a heterogeneous system has more than one phase present in it. As defined, a heterogeneous substance is a mixture while a homogeneous substance can be either a compound or an element. A **compound** is a homogeneous substance with a definite composition of elements. An **element** is a pure substance that cannot be produced by the combination of two or more substances.

As presented above, elements are individual entities that make up matter. Thus far, about 115 elements¹ have been identified and eighty-two of them are naturally occurring while the rest are produced artificially from high-energy particle accelerators. Each element is unique and can be distinguished from the others by its physical and chemical properties. All elements are composed of **atoms**. The atoms are the smallest particles of the element that preserve all identifiable properties of that element. In general, the atoms exhibit no electrical charge property and are said to be electrically neutral.

6.2 Concepts of the Atom

The Greek philosopher Democritus proposed the concept that matter was composed of the smallest invisible and indivisible particles called atoms. The word atom was derived from Greek to mean “indivisible”. However as we know today, atoms are composed of smaller particles such as electrons, protons, and neutrons. This concept of an atom was neglected for many centuries and through the Middle Ages. The accepted concept at that time was earth, air, fire, and water as the fundamental constituents of matter.

Evidence supporting the concept of atomic theory came in the eighteenth century. A number of experiments performed supported the law of definite proportions. The **law of definite proportions** states that when two or more elements combine to form a compound, they always combine in the same proportions by weight. For example, two grams of hydrogen must combine with sixteen grams of oxygen to form water. The work of John Dalton (1766–1844) showed that when two elements combined to form two or more compounds, the ratios of the combining weights of the elements in any two of the compounds were in proportion to two small integers. This fact is referred to as the **law of multiple proportions**. The law of multiple proportions alludes to the fact that when elements combine, they do not combine by weight but by unit number that has different weight for each element. For example, water is formed based on two parts of hydrogen and one part of oxygen. The work of Joseph Gay-Lussac (1778–1850) referred to as the **law of combining gas volumes** states that when gases combine, the volume of each type of gases used and the gas produced can be expressed in simple ratios. For example, a volume of nitrogen and a volume of oxygen when combined, form two volumes of nitrous oxide. In chemistry, this combination formula is written as,

¹ <http://ie.lbl.gov/education/info.htm> (Periodic table available).



where N is the symbol for nitrogen, O for oxygen, and NO for nitrous oxide. These experiments established that substances combine in specific ratios.

Around 1811, Amedeo Avogadro (1776–1856) postulated the existence of molecules. A molecule that is made up of two or more atoms is the smallest particle of a substance that can exist and has the same properties of larger masses of that substance. A molecule is also the smallest particle of a compound. For example, a molecule of sodium chloride consists of a sodium atom in combination with a chlorine atom. However, sodium and chlorine are examples of elements. In addition to the postulation of molecules, Avogadro's more notable contribution is his postulation that equal volumes of all gases have the same number of molecules under the same temperature and pressure. This postulation led to the calculation of **Avogadro's number** (6.022×10^{23} molecules/g-mol).

In 1869, a famous Russian chemist, Dmitri Ivanovich Mendeleev (1834–1907), published his observations on the relationship between the properties of elements and atomic weights. A periodic similarity of properties was discovered when all known elements were arranged in order of increasing atomic weight. This discovery led to the formation of the **periodic table**. This periodicity of properties was also discovered independently by the German chemist, Julius Lothar Meyer (1830–1895).

The existence of atoms was further supported by the work of the Swedish chemist, Svante August Arrhenius (1859–1927), when he dealt with the **theory of electrolytic dissociation**. According to this concept, when salt (sodium chloride) is dissolved in water, each molecule dissociates into positive sodium (Na^+) ion and negative chlorine (Cl^-) ion.

6.3 Atomic Models

In 1897, a British physicist Sir Joseph John Thomson (1856–1940) proved that cathode rays from a Crookes tube consisted of a stream of discrete negatively charged particles that were identical to the electrons. With this discovery, he visualized the atom as having electrons moving in constant motion inside a positively charged medium. Since atoms were electrically neutral, he supposed that the number of positive charges was the same as the number of negative charges from the electrons. With this supposition, the electron became the first **subatomic particle** to be discovered. Because of the similarity of the electrons to the raisin in plum pudding, this **Thomson model** of the atom was often referred to as the **plum pudding model**.

In 1911, Sir Ernest Rutherford (1871–1937) proposed that electrons revolved around a massive positively charged nucleus in an atom in a manner similar to that of the planets revolving around the sun in the solar system. This **Rutherford model** was derived from the experiment in which a thin gold foil was bombarded with high-energy alpha particles. Previously, Rutherford had established that the alpha particles from certain radioactive substances were

helium atoms without their electrons. The results from the experiment showed that the vast majority of the alpha particles were **unaffected by the gold foil**. This observation led to the deduction that there existed a large empty space in the atom. In addition, some of the alpha particles were scattered and a few were **reflected right back towards the source** inferring that there was a massive matter within the atom. This phenomenon cannot be explained using the Thomson model. To explain the forward and large angle backward scattering, Rutherford proposed an atomic model where all the positive charges and most of the masses were located centrally in a small volume with electrons orbiting around the mass like the planets orbiting around the sun in a vast empty space.

The planetary model proposed by Rutherford for a hydrogen atom is shown in Figure 6.1. If the electron moves at non-relativistic speed in a circular orbit having a radius r , the total energy of the hydrogen atom is given as

$$E = -\frac{ke^2}{2r} \quad (6.2)$$

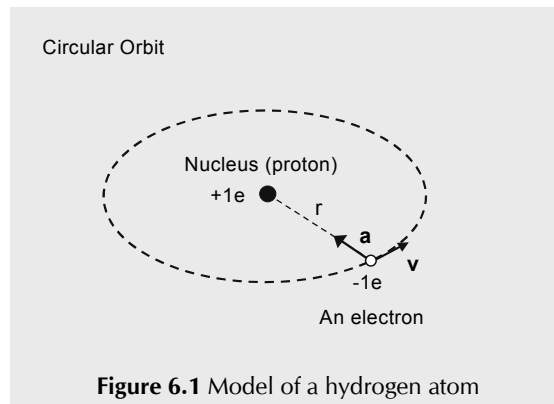


Figure 6.1 Model of a hydrogen atom

where $k = 1/(4\pi\epsilon_0) = 8.99 \times 10^9 \text{ N}\cdot\text{m}^2/\text{C}^2$ and e is the unit charge of the electron. The total energy of the hydrogen atom (excluding the rest energies of the electron and proton) is the sum of the electron's kinetic energy and the electric potential energy between the electron and the proton.

EXAMPLE 6.1 Derive equation (6.2) for the hydrogen atom using the planetary model.

SOLUTION:

Assume that the mass of the electron is m and it moves with a speed of v . For the mass to move in a circular motion, Newton's centripetal force must be equal to the electrostatic force. The force equation is

$$\begin{aligned} F &= ma \\ \frac{ke^2}{r^2} &= \frac{mv^2}{r} \\ mv^2 &= \frac{ke^2}{r} \end{aligned}$$

The energy equation gives

$$E = E_k + E_p = \frac{1}{2}mv^2 + \left(\frac{-ke^2}{r}\right) = \frac{1}{2} \frac{ke^2}{r} - \frac{ke^2}{r} = -\frac{ke^2}{2r}$$

Equation (6.2) states that the total energy is negative, and as the radius of the orbit increases, the total energy approaches zero. The electron is most tightly bound to the nucleus when the radius is the smallest. Energy must be supplied to remove the bound electron in the hydrogen atom. If the electron

is at infinite distance where the total energy is zero, the electron is considered not bound and free to leave the hydrogen atom.

***EXERCISE 6.1** As a continuation of EXAMPLE 6.1, show that the orbital frequency, ν for the hydrogen atom is

$$\nu = \frac{1}{2\pi} \sqrt{\frac{ke^2}{mr^3}} \quad (6.3)$$

This Rutherford model of an atom contradicts previous experimental results showing that an accelerating electron radiates energy. The radiant energy should have a continuous range of frequencies but the observed spectra shows sets of discrete lines. Because the electron in the Rutherford model is constantly being accelerated, it should radiate energy and drop closer to the nucleus until the atom collapses based on the conservational law of energy. This process, if it occurs, is referred to as the **ultraviolet catastrophe** because the radiation emitted would have a wavelength in the ultraviolet region.

This inconsistency was resolved based on an atomic model proposed by a Danish Physicist, Niels Bohr (1885–1962) in 1913. Bohr postulated that **(a) electrons revolved around the nucleus in definite orbits corresponding to definite energy-states and (b) whenever an electron jumps from a higher energy-state to a lower energy-state, a photon with energy equal to the energy difference between the two energy-states will be emitted.** The word “definite” was used to stress that these orbits are not any orbits but certain discrete orbits with defined discrete energy values. So long as the electron is in one of these particular orbits, there is no radiation emitted. A transition of the electron from a higher energy-state to a lower energy-state is accompanied with the emission of radiation. Later, the Bohr model was found not to be able to explain the fine spectral lines (fine structure) from complex atoms. Refinement of the Bohr model continued until the formulation of the atomic model, which is presently adopted as the model of the atomic structure.

Under the present **atomic model**, electrons are described as revolving in definite orbits or shells through empty space around a centrally located massive positively charged nucleus. There are many definite orbits available for the electrons to occupy. These orbits are specified or identified using a set of parameters called **quantum numbers**. Quantum numbers are special numbers that had been derived based on quantum physics. The word “quantum” is used to describe the discrete nature instead of the continuous nature of the orbits. Each orbit is described by a unique set of quantum numbers. In addition to the quantum numbers, each orbit has an associated discrete radius and a discrete energy-state. How the electrons are distributed in these orbits will depend on the energy available to the atom. Typically the atom is in its lowest energy-state or stable state. This implies that orbits with the lowest energy are being filled first. The arrangement of electrons in an atomic structure will be discussed in Section 6.7.

The nucleus of an atom is composed of two subatomic particles, the protons and the neutrons. Rutherford discovered the proton in 1914 while Sir James Chadwick (1891–1972) discovered the neutron in 1932. Thus far, atoms are found to be composed of three subatomic particles: electrons, protons, and neutrons. An electron is a tiny particle, which possesses a charge of $-1e$ and a mass of about 9.109×10^{-31} kg. The proton carries a $+1e$ and is more massive, with a mass around 1.6726×10^{-27} kg. The neutron is electrically neutral and has a mass of about 1.6747×10^{-27} kg slightly heavier than a proton. Because an atom is electrically neutral, the number of protons equals the number of electrons. **The size of the atom is about 10^{-10} m whereas the size of the nucleus is about 10^{-15} m.** The number and the organization of the orbital electrons determine the properties of the atom.

6.4 Bohr's Model of the Hydrogen Atom

Bohr's postulations may have qualitatively explained why orbiting electrons do not radiate. However, incorporating such postulations in the description of the atomic structure can be a challenging task. For example, how is the definite orbit formed and what does the definite orbit look like? How do we identify each definite orbit? What mechanism should we use to describe electrons jumping from one orbit to another? What is the consequence of the electron transitions? In this section, we shall attempt to construct the structure of the hydrogen atom according to the Bohr model.

As we know, the hydrogen atom consists of a nucleus containing a proton and an orbiting electron. According to Niels Bohr's postulation, the electron revolves around the hydrogen nucleus in only certain discrete orbits. To create the discrete values, some form of quantization has to be introduced. Since we are dealing with rotational phenomena, the quantization is made on the angular momentum of the orbiting electron. The quantization requires the angular momentum to be divided into discrete multiple integral of \hbar (pronounced "h bar"). The value of \hbar is equal to $h/2\pi$ where h is Planck's constant (6.626×10^{-34} J·s) and $\pi = 3.1415\dots$. The angular momentum quantization can be mathematically expressed as

$$L = mvr = n\hbar \quad (6.4)$$

where L represents the angular momentum, m is the mass of the electron, v is the velocity of the electron, r is the radius of the orbit with the nucleus at the center, and $n = 1, 2, 3, \dots$ are positive integers. The angular momentum is the product of electron mass, velocity of the electron, and the radius of the orbit. The parameter n , called the **principal quantum number** can only have integer numbers starting from one. Using EXAMPLE 6.1 and equation (6.4), the radii of the many definite orbits can be derived and generalized into the simple equation of

$$r_n = r_1 n^2 \quad (6.5)$$

where $n = 1, 2, 3, \dots$, and r_1 is called the **Bohr radius**.

***EXERCISE 6.2** Using equation (6.4) and EXAMPLE 6.1, show that the Bohr's radius and the energy of the ground state of hydrogen atom are

$$r_1 = \frac{4\pi\epsilon_0\hbar^2}{me^2} = 0.53 \times 10^{-10} \text{ m} \quad (6.6)$$

and

$$E_1 = -\frac{me^4}{32\pi^2\epsilon_0^2\hbar^2} = -13.6 \text{ eV} \quad (6.7)$$

The only available quantized radii or orbits for the electron to occupy are defined by equation (6.5). These discrete orbits or shells are uniquely identified using quantum numbers. The smallest possible radius is obtained by setting $n = 1$ which is the **Bohr radius**. It is commonly denoted by r_0 and has a value of $0.53 \times 10^{-10} \text{ m}$ (see EXERCISE 6.2). According to equation (6.5), **the radius of definite orbit increases as the square of the quantum number, n** in multiple of Bohr radius as $4r_1, 9r_1, 16r_1, \dots$ so on. The schematic presentation of the orbits of a hydrogen atom is shown in Figure 6.2. Besides the radius of the orbit, the associated energy-state is also related to the quantum number n . The energy-states can be expressed in a generalized form as

$$E_n = -\frac{|E_1|}{n^2} \quad (6.8)$$

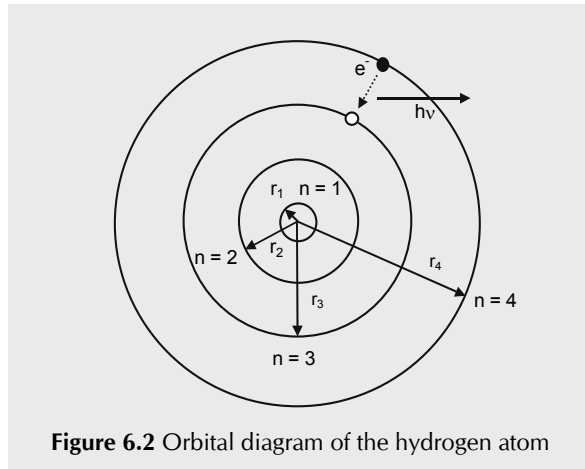


Figure 6.2 Orbital diagram of the hydrogen atom

where $|E_1|$ is the absolute value of E_1 . The energy value of E_1 is -13.6 eV for the hydrogen atom (see EXERCISE 6.2). The notation "eV" represents the electron volt, which is the unit of energy needed to accelerate an electron through a potential of 1 volt. The negative sign for E_n is explicitly written to indicate that the electron is bound to the atom. Conversely, a positive sign indicates positive energy implying that the electron is not bound to the atom. Based on equation (6.8), these are the only quantized energy-states available for the electron to occupy. However, **the energy of the energy-state decreases as the inverse square of the quantum numbers, n** . The lowest energy-state, called the **ground state**, is associated with the smallest quantum number, $n=1$. It has the lowest energy E_1 and the smallest orbital radius r_0 . This energy-state is the tightest bound

state and requires an energy of $|E_1|$ to eject the electron from its orbit. From equation (6.8), the energy of energy-states is expressed as fraction of E_1 as $E_1/4$, $E_1/9$, $E_1/16$... so on.

EXAMPLE 6.2 What is the radius and energy of the $n=4$ state in the hydrogen atom?

SOLUTION:

a) Using equation (6.5) and $n=4$, the radius is

$$r_4 = 4^2 r_1 = 16 r_1 = (16)(0.53 \times 10^{-10} \text{ m}) = 8.48 \times 10^{-10} \text{ m}$$

b) Using equation (6.8) and $n=4$, the energy of the orbit is

$$E_4 = \frac{E_1}{4^2} = \frac{-13.6 \text{ eV}}{16} = -0.85 \text{ eV}$$

Any energy-state above the ground state is called an **excited state**. The spread of energy-states on the energy level diagram is shown in Figure 6.3. As the quantum number increases, the spacing between the energy-states gets smaller. This negative energy state for an atom is interpreted as a bound system between the electron and the atom. Positive energy indicates that the electron is not bound and free from the influence of the atom.

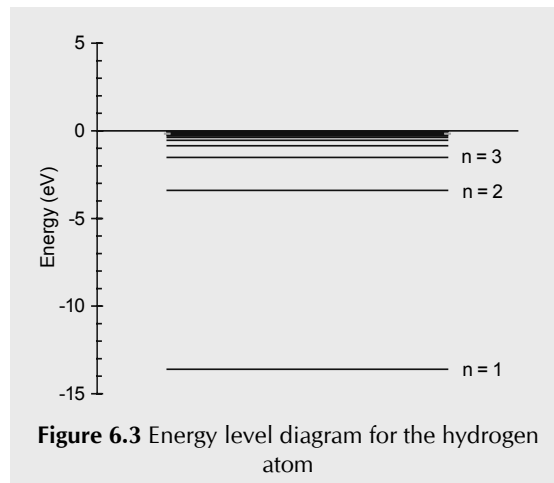


Figure 6.3 Energy level diagram for the hydrogen atom

When a hydrogen atom makes a transition from one orbit to another, energy is either absorbed or emitted by the atom. If the initial energy-state labeled i has a higher energy than the final energy-state labeled f , a photon is emitted as illustrated in Figure 6.4. The energy of the photon emitted is equal to the energy difference between the two energy-states according to Bohr's postulation. The wavelength, λ , of the light emitted from the hydrogen atom is given as

$$E_f - E_i = hv = -E_1 \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right) \quad (6.9)$$

or in terms of wavelength is

$$\frac{1}{\lambda} = R \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right) \quad (6.10)$$

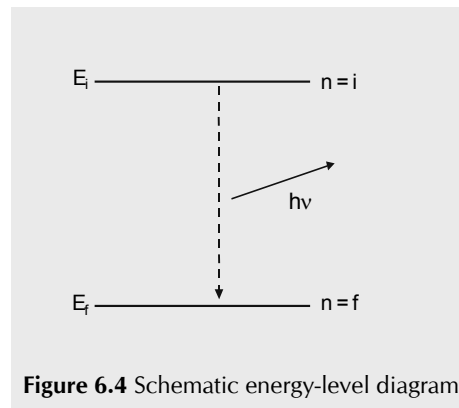


Figure 6.4 Schematic energy-level diagram

where $R = 1.0974 \times 10^7 \text{ m}^{-1}$ is the Rydberg constant calculated from equation (6.11).

***EXERCISE 6.3** Derive the Rydberg constant using the Bohr formulation for electron transition.

$$R = \frac{me^4}{64\pi^3 \hbar^3 \epsilon_0^2 c} \quad (6.11)$$

The wavelength λ is related to frequency via the light equation ($\lambda\nu = c = 3 \times 10^8 \text{ m/s}$).

EXAMPLE 6.3 What is the energy of the photon emitted when the electron in the hydrogen atom de-excites from $n=4$ energy-state to the ground state? What is the wavelength of the photon?

SOLUTION:

According to equation (6.9), the energy of emitted photon is

$$E_x = -E_1 \left(\frac{1}{4^2} - \frac{1}{1^2} \right) = -E_1 \left(\frac{1-16}{16} \right) = 13.6 \text{ eV} \left(\frac{15}{16} \right) = 12.75 \text{ eV}$$

The wavelength can be determined as

$$\lambda = \frac{hc}{E_x} = \frac{(6.62 \times 10^{-34} \text{ J} \cdot \text{s})(2.9979 \times 10^8 \text{ m/s})}{(12.75 \text{ eV})(1.6022 \times 10^{-19} \text{ J/eV})} = 0.972 \times 10^{-7} \text{ m}$$

The relationship between the wavelength and energy given in equation (1.4) can be expressed in different units as

$$\lambda(\text{m}) = \frac{1.24 \times 10^{-6}}{E(\text{eV})} \quad (6.12)$$

provided E is expressed in electron volts and λ is expressed in meters.

***EXERCISE 6.4** Derive equation (6.12).

6.5 Atomic Spectra

Light emitted from an electrical discharge through a tube containing a monoatomic gas at low pressure exhibits a series of very distinct lines when analyzed using a prism spectrometer. The series of distinct lines is unique to the particular gas. With these characteristics, atomic spectra have been used as a means of identifying different types of gases by spectroscopists.

The line spectrum of hydrogen in the visible range is called **Balmer series** after J.J Balmer who discovered it in 1885. This series represents the transition from higher energy-state to the $n = 2$ energy-state, that is

$$\frac{1}{\lambda} = R \left(\frac{1}{2^2} - \frac{1}{n_i^2} \right) \quad (6.13)$$

and n_i is the initial energy-state as shown in Figure 6.5. The thick solid lines in the figure represent multiple transitions from higher energy-states. The other line spectrum series for transitions to the ground state $n_f = 1$ is named the **Lyman series**; to the $n_f = 3$ energy-state is named the **Paschen series**; to the $n_f = 4$ energy-state is named the **Brackett series**; and to the $n_f = 5$

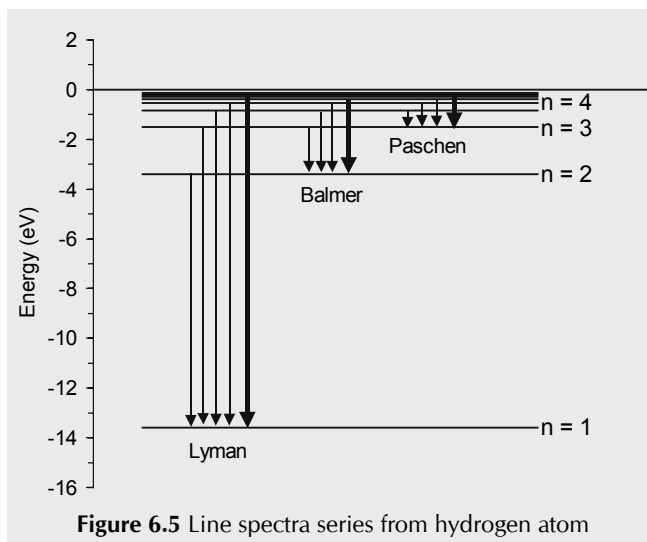


Figure 6.5 Line spectra series from hydrogen atom

energy-state is named the **Pfund series** after their discoverers. These spectroscopy works confirm the discrete nature of energy-states in atoms.

6.6 Shell Structure of Electrons

Bohr's model, which is extended to hydrogen-like atoms, is very successful in explaining simple atomic systems like the hydrogen atom. It explains why atoms are stable and how light is absorbed and emitted by an atom at discrete wavelengths. The wavelengths of line spectra and ionization energy of the hydrogen atom that are predicted are in excellent agreement with the experiment. However, there are also important limitations to Bohr's model. The line spectra for a complex atom having more than two electrons cannot be predicted using Bohr's model. Nor can it explain the fine structure. It also cannot explain why some spectral lines are brighter than the others and also the bonding of atoms in molecules or in liquids and solids. In addition to its limitation, the model is criticized as a mixture of classical and quantum ideas. This model does not resolve the wave-particle duality of light. During this time period in the early 1920, there was also increasing evidence that a new and more comprehensive model was needed.

Erwin Schrodinger (1887–1961) and Werner Heisenberg (1901–1976) independently developed a new theory called **quantum mechanics**. This theory unifies the wave-particle duality into a single consistent concept. It has been successful in dealing with the spectra emitted by complex atoms, even the fine structure. It explains the relative brightness of the spectral lines and

how atoms form molecules. The theory of quantum mechanics has successfully explained a wide range of natural phenomena and from its predictions have led to many new inventions. Quantum mechanics has been so successful that it has been widely accepted by physicists as the fundamental theory describing the behavior of small size particles.

Quantum mechanics requires four different quantum numbers to specify an energy-state in an atom. The four quantum numbers are the **principal quantum number** n , the **orbital quantum number** ℓ , the **magnetic quantum number** m , and the **spin quantum number** s . The principal quantum number whose integer values vary from $n=1$ to ∞ , is the same as the quantum number in the Bohr Model. The orbital quantum number also called the **angular momentum or azimuthal quantum number** is related to the quantization of the angular momentum of the electron. The integer values of ℓ are restricted by the principal quantum number. For a particular value of n , ℓ can only have integer values between 0 and $n-1$, e.g. 0, 1, 2, 3, ... $n-1$. In the case where $n=1$, ℓ can only have a zero value or no angular momentum. This condition is interpreted as the electron moving in circular orbit in two-dimensional space or a spherical symmetric orbit in three-dimensional space. The orbital shape would deviate from spherical symmetry if ℓ carries a non-zero value. The ℓ quantum number has no effect on the energy-state of the Bohr's hydrogen atom. The energy-state depends on both n and ℓ for atoms with two or more electrons. The magnetic quantum number is related to the quantization of the direction of the electron's angular momentum and takes on integer values from $-\ell$ to $+\ell$. For example if $\ell=2$, m can have the possible values of $-2, -1, 0, 1, 2$. In general, for any value ℓ , m can only have $2\ell+1$ possible values. The name 'magnetic quantum number' was derived from an experimental work where a beam from a gas-discharge tube passed through an external magnetic field. The external magnetic field causes spectral lines to split into several closely spaced lines known as the **Zeeman effect**. The splitting of the energy levels implies that the energy-state in an atom depends not only on the principal quantum number, n but also on the magnetic quantum number, m . The fourth quantum number is the spin quantum number. In 1925, S. A. Goudsmit and G. E. Uhlenbeck proposed that an electron has intrinsic spin as a result of Paul Adrian Maurice Dirac's (1902–1984) relativistic quantum treatment of the electron. The existence of the spin quantum number was experimentally verified in the study of fine structure in atomic spectra. The **fine structure** refers to the tiny splitting of energy levels seen using high precision spectrograph as two or more very closely spaced lines in the absence of an external magnetic field. Since there is no external magnetic field, the extra spectral lines cannot be due to the Zeeman effect. The spatial quantization of the spin produces only two possible values of $+\frac{1}{2}$ or $-\frac{1}{2}$ spin quantum numbers. This phenomenon can be conceived as clockwise and anti-clockwise spin of the particle.

Thus, quantum mechanics introduces four quantum numbers to specify an energy-state. Associated with these quantum numbers are their imposed restrictions as summarized below:

$$\begin{aligned}
 n &= 1, 2, 3 \dots \\
 \ell &= 0, 1, 2 \dots n-1 \\
 m &= -\ell, -\ell+1, \dots 0 \dots, +\ell-1, +\ell \\
 s &= +\frac{1}{2} \text{ or } -\frac{1}{2}
 \end{aligned}$$

The assignment of various quantum numbers to a one-electron atom is quite simple but to a multi-electron atom can be very difficult. This classification of electrons became clear when Wolfgang Pauli (1900–1958) formulated the Pauli exclusion principle. **The Pauli exclusion principle states, “No two electrons in the same atom can have identical sets of quantum numbers”.**

6.7 Arrangement of Electrons in an Atom

The quantum mechanical rules and the Pauli exclusion principle govern the arrangement of electrons in an atom. The stable state of an atom is obtained by first filling the lowest energy orbits. This means that electrons will be placed in the lowest quantum number first starting from the $n=1$ shell followed by the $n=2$ shell and the $n=3$ shell, and so on. The first shell with **the smallest radius is called the K shell**, followed by the L shell, M shell, N shell, and so on.

The number of electrons that can occupy a shell according to the Pauli exclusion principle is presented in Table 6.1. For the $n=1$ shell, the quantum numbers are restricted to $\ell=0$ and hence limits m to zero. The only quantum number that can be different is the spin quantum number. The spin quantum number has two possible values of $+\frac{1}{2}$ or $-\frac{1}{2}$; two electrons can occupy the $n=1$ shell consistent with the Pauli exclusion principle. For the $n=2$ shell, the quantum numbers are restricted to $\ell=0, \pm 1$. In the case of $\ell = \pm 1$, m can have 0, +1, and -1. From Table 6.1, we see that 8 electrons can occupy the $n=2$ shell.

Table 6.1 Maximum number of electrons occupying a shell.

shell	n	ℓ	m	s	# of e ⁻	total		
K	1	0	0	$\pm \frac{1}{2}$	2	2		
L	2	0	0	$\pm \frac{1}{2}$	2	8		
				1	-1		$\pm \frac{1}{2}$	2
					0		$\pm \frac{1}{2}$	2
					+1		$\pm \frac{1}{2}$	2
M	3	0	0	$\pm \frac{1}{2}$	2	18		
				1	-1		$\pm \frac{1}{2}$	2
					0		$\pm \frac{1}{2}$	2
		2	+1	$\pm \frac{1}{2}$	2			
			-2	$\pm \frac{1}{2}$	2			
			-1	$\pm \frac{1}{2}$	2			
			0	$\pm \frac{1}{2}$	2			
			+1	$\pm \frac{1}{2}$	2			
			+2	$\pm \frac{1}{2}$	2		2n ²	

EXAMPLE 6.4 Determine the electronic structure for a helium atom.

SOLUTION:

	n	ℓ	m	s
Electron 1	1	0	0	$+\frac{1}{2}$
Electron 2	1	0	0	$-\frac{1}{2}$

The helium atom has two electrons. The placement of these electrons starts with $n=1$ shell. Two electrons can occupy this shell as shown in the table to the right. Each electron has its own unique quantum numbers.

The number of electrons that can occupy a shell can be deduced to be $2n^2$ as demonstrated in Table 6.1. The formula shows that a maximum of 2 electrons can occupy the K shell, 8 electrons in the L shell, and 18 electrons in the M shell. In addition, the number of electrons that can occupy a sub-shell defined by the orbital angular momentum can also be deduced to be $2(2\ell + 1)$.

EXAMPLE 6.5 Determine the maximum number of electrons that can occupy the L shell and each sub-shell using the n and the ℓ restriction rule.

SOLUTION:

L shell ($n=2$): $2n^2 = 2(2)^2 = 8$ electrons.

Sub-shells for $n=2$ are $\ell = 0$ and $\ell = 1$.

$\ell = 0$ sub-shell, is $2(2\ell + 1) = 2(1) = 2$ electrons and

$\ell = 1$ sub-shell, is $2(2\ell + 1) = 2(3) = 6$ electrons

The configuration of electrons in an atom is typically denoted using spectroscopic notations as $n\ell^x$. Numerical value is used for the principal quantum number while the spectroscopic designation of orbital quantum numbers is based on letters as follows,

$$\ell = 0, 1, 2, 3, 4, 5, \dots$$

$$s, p, d, f, g, h, \dots$$

The designation "s" is for sharp, "p" for principal, "d" for diffused, and "f" for fundamental of the spectral lines as interpreted by spectroscopists. These letters have been retained for historical reasons while other designations that follow are in alphabetical order. The letter x in the spectroscopic notation represents the number of electrons in that sub-shell. For example, a helium atom having two electrons in the lowest energy-state is designated as $1s^2$. In general, the lowest energy shell designated by the lowest principal quantum number will be filled first.

EXAMPLE 6.6 Write the electronic configuration for chlorine (Cl-17).

SOLUTION:

Chlorine has 17 electrons to fill its orbits. According to the Pauli's exclusion principle, orbits with the smallest quantum numbers are to be filled first. The shell structure in accordance with increasing energy would be $1s, 2s, 2p, 3s, 3p$, and so on....

Configuration for Cl-17		
Shell	No. of e^- in a shell	Total Electrons
1s	2	2
2s	2	4
2p	6	10
3s	2	12
3p	5	17

Therefore the electronic configuration for Cl-17 is $1s^2 2s^2 2p^6 3s^2 3p^5$.

The correspondence of the lowest energy shell to the lowest quantum number is not true for heavy atoms. In some atoms, some sub-shells of the shells with higher principal quantum numbers actually have lower energy than the upper sub-shells with a lower principal quantum number, and hence get filled first.

In addition to the principal quantum number, the energy-state in a multi-electron atom is also influenced by the orbital quantum number. The orbital quantum number causes certain sub-shells such as the d, f, and g sub-shell to have higher energy than the s sub-shell of the next quantum number. As such, the s sub-shell of the next quantum number is filled first. In potassium, for example, the 4s sub-shell is filled first before 3d sub-shell after completing the 3s and 3p sub-shells. The order of filling energy levels starting from the lowest energy in a multi-electron atom is as follows:

$$1s < 2s < 2p < 3s < 3p < 4s < 3d < \dots$$

A method of memorizing the order of energies of the subshells is shown in Figure 6.6 following the direction of the arrow. Starting from the bottom up, the 1s sub-shell is initially filled followed by 2s. Following the direction of the arrow, the next sub-shell to be filled is 2p, and then 3s. The next level starts with the 3p sub-shell, and then 4s sub-shell. One can then deduce that the order of filling is slanted starting from the lowest energy and then moving upwards.

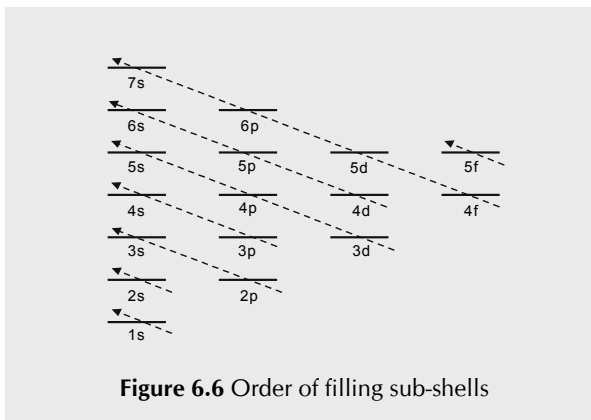


Figure 6.6 Order of filling sub-shells

6.8 Periodic Table

In 1869, D. Mendeleev constructed a periodic table to emphasize the periodicity of the elements. Although elements such as rare earths did not fit well into the scheme, he was able to develop a somewhat successful periodic table of elements. The periodic table was not complete until the discoveries of many missing elements and the development of the exclusion principle. The current periodic table is shown in Figure 6.7.² The periodic table is arranged in order of increasing mass and elements with similar chemical properties are placed in the same column. The eight columns are periods showing the transition from chemically active metals to inert gases. The elements are divided into eight groups or columns indicating **that there are no more than eight electrons in the outer shell.**

As discussed in Section 6.7, the arrangement of electrons does not strictly follow the principal quantum number but altered by the orbital quantum number. Certain sub-shells such as the d, f, and g sub-shells have higher energy than the s sub-shell of the next quantum number. Therefore, the s sub-shell of the next quantum number is filled first. The first column represents an electron outside a closed shell.

² <http://physics.nist.gov/PhysRefData/IonEnergy/periodic-table.pdf>

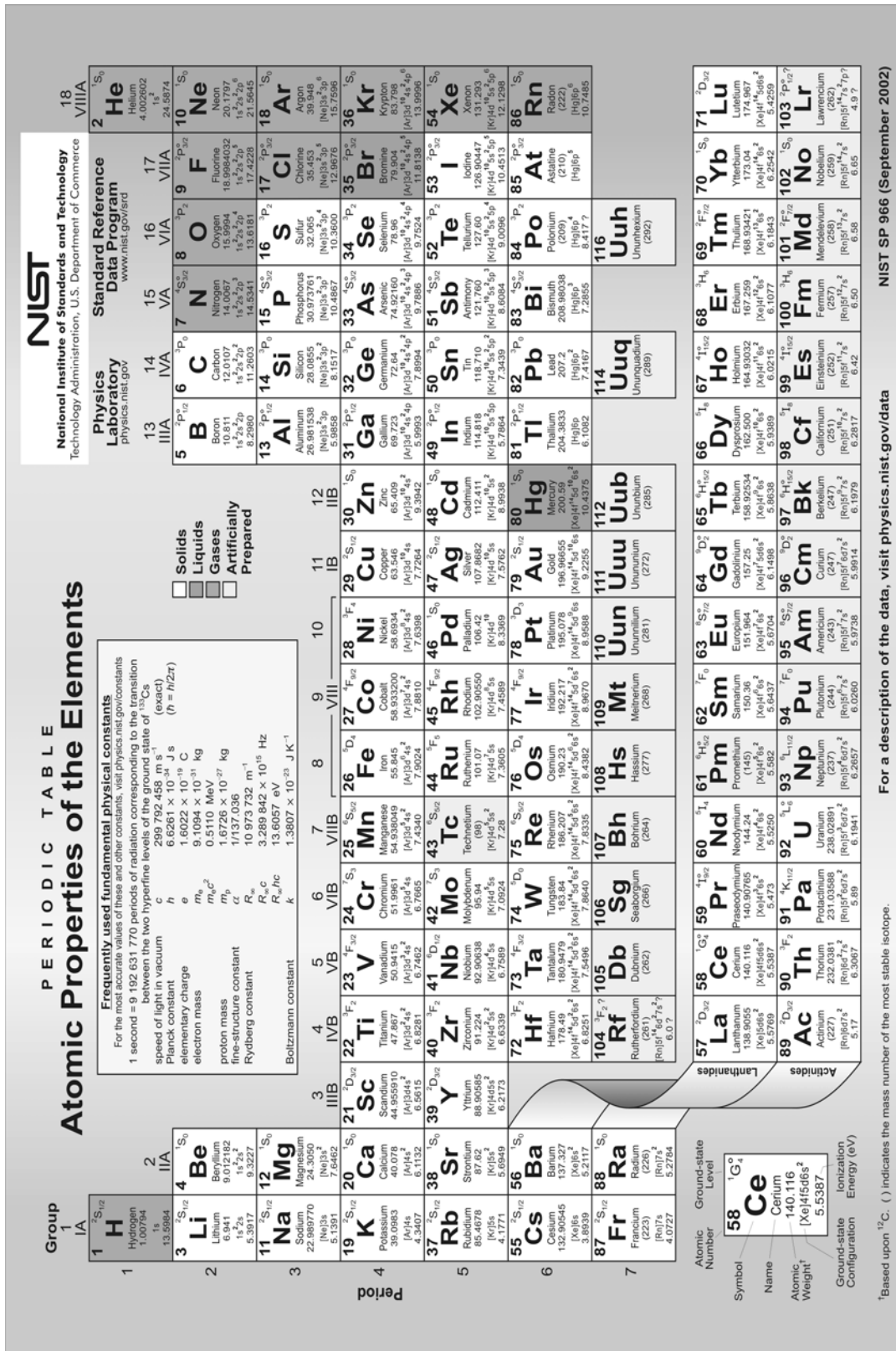


Figure 6.7 Periodic Table of the elements³

³ Dragoset, R.A.; Musgrove, A.; Clark, C.W.; and Martin, W.C. *Periodic Table: Atomic Properties of the Elements*. Version 3, NIST SP 966 handbook. Gaithersburg, MD: National Institute of Standards and Technology; 2002.

The next column represents two extra electrons outside the closed shell. Alternatively, the eighth or last column represents a completely filled shell or sub-shell.

The next to last column represents the elements that need one more electron to completely fill the shells or sub-shells. The last column of the periodic table consists of noble gases having elements with completely filled shells or sub-shells. With a completely filled shell or sub-shell, the noble gases are chemically inactive, hence are called **inert gases**. For helium and neon, the K and L shells are completely filled with electrons. For argon, the first two sub-shells of $n=3$ are full. The third sub-shell of $n=3$ and the second sub-shell of $n=4$ are filled for krypton. For xenon, the third sub-shell of $n=4$, and second sub-shell of $n=5$ are filled. The fourth sub-shell of $n=5$ and the second sub-shell of $n=6$ are filled for radon. The next to the last column contains the **halogens**, which are reactive elements. Each element needs an additional electron to completely fill its shells or sub-shells. Conversely, elements in the first column are alkali metals that have an extra electron in its outer shell. The extra electron is far from the nucleus and is shielded from the nuclear charge by the inner electrons. As such, it is easily removed and hence is highly reactive.

The transitional elements at the central bottom of the periodic table are the lanthanides and actinides. They have incompletely filled inner shells. After filling the s sub-shell of the next quantum number, the lower sub-shell is then filled followed by the p sub-shell. The transition elements deal with the filling of the 3d and 4d sub-shells while lanthanides with the 5d and 4f sub-shells. Similarly, the actinides and transuranic elements deal with the filling of the 6d and 5f sub-shells.

6.9 Binding Energies of Electrons

The **binding energy** of an electron is the energy needed to remove an electron from a shell of an atom. Hence, the energy of this shell is the negative of the binding energy of the electron. This binding energy is the result of the Coulomb interactions between the positively charged nucleus and the negatively charged electrons. The closer the electron is to the nucleus, the higher is the binding energy. Since the electron in the K-shell is the most tightly bound electron, it requires the most energy to remove it. The larger the positive charge is on the nucleus, the greater is the attractive force on the inner shell electrons. The outer shell electrons, however, also feel a repulsive force from the inner shell electrons, in a sense are screened from the nucleus and therefore are less affected. This phenomenon is often referred to as the **electron screening effect**. The binding energies for electrons in the atom are listed in Table 6.2. In cases where there is a difference in binding energy for different sub-shells, the largest number has been listed. Within a multi-shell atom like radon, the K-shell electrons are much more tightly bound than the L-

shell electrons, which in turn are more tightly bound than the M-shell electrons. For the outer shells, however, the inner orbit within the higher energy sub-shells may have lower energy than the outer orbit of the lower energy sub-shells.

Ionization refers to the process in which an electron is ejected from an atom. To be ejected, the electron must gain sufficient energy to overcome the binding energy. After the electron is ejected, the ionized atom, which is now charged, is called an **ion**. The ion carries a charge equal in magnitude to the difference between the number of protons and electrons. The **ionization potential** is the amount of energy needed to remove a valence electron from an atom. The valence electrons occupy the outer orbit and are responsible for chemical reaction. From Table 6.3, the ionization potential is shown to increase as the shell is being filled. The ionization potential is the largest for a completely filled shell or sub-shell such as the noble gases. The process in which an elemental change occurs such as the addition or subtraction of a proton is not considered as ionization but nuclear transformation. This will be discussed later in Chapter 8.

Table 6.2 Binding energies for electrons in various shells

Shell	n	H	C	Cu	W	Pb
K	1	13.6 eV	284 eV	8.98 keV	69.5 keV	88.0 keV
L	2		6.4 eV	1.10 keV	12.1 keV	15.9 keV
M	3			0.12 keV	2.8 keV	3.9 keV
N	4				59.5 eV	894 eV
O	5				7 eV	147 eV

Table 6.3 Filling of electronic shells in atoms

Element	n	ℓ	m	s	Ionization Potential (eV)
hydrogen	1	0	0	+½	13.6
helium	1	0	0	-½	24.6
lithium	2	0	0	+½	5.4
beryllium	2	0	0	-½	9.3
boron	2	1	-1	+½	8.3
carbon	2	1	-1	-½	11.3
nitrogen	2	1	0	+½	14.5
oxygen	2	1	0	-½	13.6
fluorine	2	1	+1	+½	17.4
neon	2	1	+1	-½	21.6
sodium	3	0	0	+½	5.1
magnesium	3	0	0	-½	7.6
aluminum	3	1	-1	+½	6.0
silicon	3	1	-1	-½	8.2
phosphorus	3	1	0	+½	10.6
sulfur	3	1	0	-½	10.4
chlorine	3	1	+1	+½	13.0
argon	3	1	+1	-½	15.8

6.10 Transitions between Energy-States

A transition in an atom is said to occur when an electron jumps from one energy-state to another energy-state. During this process a photon with energy equal to the energy difference between the two energy-states can either be emitted or absorbed by the atom. If a photon is absorbed, the process is called an **excitation** process, which produces an **excited atom**. Conversely, in the **de-excitation** process, the electron jumps from a higher energy-state to a lower energy-state resulting in a more stable atom with the emission of a photon. The photon emitted is called **characteristic radiation**. A group of these characteristic x-rays uniquely identifies the species of the atom. The excitation and de-excitation processes are different from the ionization process in the sense that the latter process expects the electron to be ejected from the

atom. In more complex atoms, the transition may correspond to an electron moving from one shell to another. De-excitation is possible only if there is a vacancy in the inner orbit. The vacancy can be created when an incident particle collides with an inner orbit electron or via the emission of Auger electrons to be discussed in Section 6.11.

The electron transition obeys the quantum mechanical rules. A photon is emitted when the principal quantum number of an electron changes by one or more units. Energy must be added to the atom to increase the principal quantum number of an electron by one or more units. There is the similar rule for the angular momentum quantum number. Transition involving no change in ℓ is forbidden. The reason is that the photon carries off one unit of angular momentum. Transition in which the change in momentum is one ($\Delta\ell = 1$) is allowed, and takes place in around 10^{-8} sec. Transition in which $\Delta\ell > 1$ is forbidden, although it can happen and proceeds very slowly with a long half-life.

EXAMPLE 6.7 Assume that a tungsten ion has a missing electron in the K-shell. (a) What is the energy of photon emitted if a free electron drops into this orbit? (b) What is the energy of the photon emitted if an electron from the L-shell drops into this vacancy? Subsequently, an electron in the M-shell drops to the L-shell, what is the energy of the emitted photon?

SOLUTION:

(a) The binding energy of the electron in the K-shell is 69.5 keV. The photon emitted will have this energy, i.e.,

$$\Delta E = E_{\infty} - E_K = 0 - (-69.5 \text{ keV}) = 69.5 \text{ keV}$$

(b) In this case, the photon energy is equal to the difference between the energies of the L-shell and K-shell states, e.g.,

$$\Delta E = E_L - E_K = (-12.1 \text{ keV}) - (-69.5 \text{ keV}) = 57.4 \text{ keV}$$

A similar calculation can be made for the transition from the M-shell to L-shell. The photon energy emitted is 9.3 keV

6.11 Auger Electrons

In some cases, an atom may de-excite by emitting an **Auger electron** itself or accompanied by a reduced energy photon instead of a characteristic radiation. The ejection of an Auger electron is explained as a two-step process. In the first step, the energy needed to eject the Auger electron comes from the de-excitation of other electron jumping from an outer orbit to an inner orbit. This de-excitation energy is transferred to another electron in the atom. Next, if the energy is greater than the binding energy of this particular electron, the electron referred to as Auger electron is ejected. As such, an Auger electron must have a minimum energy equal to its binding energy in order for it to leave the atom. Excess energy is transformed into kinetic energy for the Auger electron if it is not accompanied by a reduced energy photon. This energy description can be written as

$$KE = \frac{1}{2}mv^2 = E - E_B \quad (6.14)$$

where E_B is the binding energy of the Auger electron and E is the transitional energy of the de-excited electron.

EXAMPLE 6.8 Assume that a lead ion with K-shell vacancy is filled by an L-shell electron. Instead of emitting a photon, the atom ejects an L-shell electron. What is the kinetic energy of the ejected electron?

SOLUTION:

The binding energy of the electron in the K-shell and L-shell are 88.0 keV and 15.9 keV, respectively. The energy available to the L-shell electron is

$$\Delta E = E_L - E_K = (-15.9 \text{ keV}) - (-88.0 \text{ keV}) = 72.1 \text{ keV}$$

This energy is greater than the binding energy of the L-shell electron and hence one of the other electrons in this orbit can be ejected. The difference between the energy available and the binding energy is the kinetic energy, described as

$$KE = 72.1 \text{ keV} - 15.9 \text{ keV} = 56.2 \text{ keV}$$

Characteristic x-rays and Auger electron emissions are competing processes for an excited atom to release its excess energy. Either of these processes may occur, but the occurrence of each process is unpredictable. The probability of occurrence of emission of characteristic x-rays from an n-shell is termed the fluorescent yield. The **fluorescent yield**, ω_n , is defined as the ratio of the number of characteristic x-rays emitted from the n-shell to the number of electron shell vacancies; and mathematically represented as

$$\omega_n = \frac{\text{No. of characteristic x-rays}}{\text{No. of n-shell vacancies}} \quad (6.15)$$

Conversely, $(1 - \omega_n)$ represents the Auger electron yield for that particular n-shell. Note that the fluorescent yield is discussed relative to a particular shell. Suppose that we are interested in the K-shell, we state that the fluorescent yield, ω_K increases with increasing atomic number for K-shell. In general, fluorescent yield is high for high atomic number and Auger electrons are favored for low atomic number. Fluorescent yield data is important in nuclear medicine. If the fluorescent yield is low, the atoms are not suitable for nuclear imaging since Auger electrons merely increase the dose to patients and do not improve the quality of imaging in the study.

6.12 Molecules

The chemical combination of two or more atoms forms a molecule. The molecule can be composed of atoms of the same or different types. An example of the same types of atoms is the nitrogen molecule, N_2 formed

through the combination of two nitrogen atoms. An example of the different types of atoms is the water molecule (H_2O), which is the combination of two hydrogen atoms with one oxygen atom. The molecule formed by combining different types of atoms is called a **compound**. The chemical combination or bond to form a molecule is based on the idea that atoms having completely filled shells are stable. Hence, a molecule is formed via the interaction of the valence electrons of an atom since the inner shells are generally filled. The valence electrons can combine in various ways to form a molecule.

Ionic bonding refers to the use of valence electrons in one atom to fill the vacancy in the shell of another atom. An example of ionic bonding is sodium chloride where the extra electron in the sodium atom is used to fill the vacancy in the chlorine atom. The sodium atom has 11 protons and 11 electrons. The atomic configuration requires one electron to be in its outer shell. When this electron leaves the atom, the result is an overall positively charged atom, called a sodium ion. On the other hand, a chlorine atom has 17 protons and 17 electrons with 7 electrons in its outer shell. By accepting an additional electron, the atomic configuration achieves a filled shell. This results in an overall negatively charged atom, called a chloride (Cl^-) ion. This atomic rearrangement creates a positively charged sodium atom and a negatively charged chlorine atom, which attract each other to form the ionic bonding. In general, a positively charged ion is called a **cation** while a negatively charged ion is called an **anion**.

Another type of chemical bond, called **covalent bond**, is formed when the available electron pairs are shared between the two atoms. In covalent bonding, no atom loses or gains electrons. For example in the hydrogen (H_2) molecule, the two atoms share both electrons. Each hydrogen atom has its own electron and the electron from the other atom to complete its shell. As a result, no atom loses or gains an electron. These two electrons circulate through both nuclei. If one electron pair is used in the bond, the bond is called **single covalent bond**. If two electron pairs are used, the bond is called **double covalent bond**, like the oxygen (O_2) molecule. Likewise, triple covalent bond indicates that three electron pairs are used in the formation of the molecule, like the nitrogen (N_2) molecule.

The third type of bond is called the **hydrogen bond**. When a hydrogen atom bonds to another atom with a stable valence orbit, such as oxygen or nitrogen, it causes a polarizing effect on the hydrogen atoms. The partially positive hydrogen atom will attract or polarize unpaired electrons from a nearby atom in another molecule to form a chemical bond called the hydrogen bond. Hydrogen bonds are weak, about 5% the strength of a covalent bond and as such do not bind atoms into molecules. The bond serves as a bridge between different molecules or between various parts of the same molecules. The weak bond is broken easily. This property accounts for the temporary bonding between certain atoms within large complex molecules such as proteins and nucleic acids. The stability and strength of these large molecules are attributed to many hydrogen bonds even though each of these bonds is weak.

Chemical reactions are essentially the process of forming and breaking bonds. Thus, a chemical reaction involves only the electrons and not the nucleus. These reactions occur continually in all the cells in our body. These reaction processes allow our body structures to build new and destroy old tissues, as well as carry out the various body functions.

The number of molecules in a gram of a substance is determined using Avogadro's number. The molecular weight of a substance, for example H₂O with 16 mass units of oxygen and 2 mass units of hydrogen yields a total mass of 18. Avogadro's number states that there are 6.022×10^{23} molecules in one mole or 18 g of water.

EXAMPLE 6.9 Compute the number of sodium atoms in 1 gram of salt.

SOLUTION:

The mass unit or molecular weight of NaCl is (22.989 g + 35.453 g) 58.442 g.

The number of molecules in 1 gram of salt is

$$N = \frac{6.022 \times 10^{23} \text{ molecules}}{58.442 \text{ g}} = 1.03 \times 10^{22} \text{ molecules/g}$$

Since there is one sodium atom in one salt molecule, the number of sodium in one gram of salt is

$$N_{\text{Na}} = 1.03 \times 10^{22} \text{ molecules/g}$$

Note the number of sodium atoms in salt is identical to chlorine. However the fractional weight of sodium (22.989 g/58.442 g) is only 39.33%.

6.13 Lasers

The medical applications of lasers have been discussed in Section 1.1. A laser device produces a very narrow and intense beam of monochromatic coherent light. The principle of operations of lasers is based on the quantum theory that states the existence of unique metastable states in molecular or other systems. Since metastable states have long half-lives, transitions from these metastable states are very slow. Hence, it is possible to excite most of the valence electrons to these metastable states and leave the ground states virtually empty. This technique is called **population inversion**. To perform population inversion, energy must be added or pumped into the system. This process is referred to as **optical pumping**. For the ruby laser, green light whose wavelength is 550 nm (and energy is 2.2 eV) is used to excite the chromium ions in the ruby crystal to the 2.2 eV excited energy-state. The atoms quickly de-excite and return to either the ground state or the 1.8 eV metastable energy-state (half-life of 3×10^{-3} s). However, most of these ions are trapped in the metastable states, which eventually lead to a population inversion. Another characteristic of the laser is the stimulated instantaneous depopulation. If a photon with exactly the same energy of the excited state interacts with the atom, the interaction will stimulate the metastable state to de-excite and emit a photon that will travel in the same direction as the incident photon. If this process is repeated many times, a collection of

monoenergetic photons will emerge and hence generating a coherent intense laser beam.

6.14 Heisenberg Uncertainty Principles

In 1925, Schrodinger and Heisenberg independently introduced quantum mechanics, which is now considered to be the fundamental theory applicable at the atomic level. It is a statistical theory rather than a deterministic one.

An important aspect of quantum mechanics is the **Heisenberg uncertainty principle**. It results from the wave-particle duality concerns and the unavoidable interaction between the observed object and the observer. One form of the uncertainty principle states that the position x and momentum p of an object cannot be measured precisely at the same time. The product of their uncertainties, $(\Delta x)(\Delta p)$ cannot be less than \hbar ($h/2\pi$):

$$(\Delta x)(\Delta p) \geq \hbar \quad (6.16)$$

The uncertainty principle related to energy states that the energy could be uncertain or non-conserved by an amount ΔE for a time Δt :

$$(\Delta E)(\Delta t) \geq \hbar \quad (6.17)$$

In the quantum mechanical viewpoint of the atoms, the electrons do not have well-defined orbits but instead exist as a “cloud”. The precise position of the electrons cannot be measured. Hence, the locations of electrons are represented as clouds. Electron clouds can be interpreted as an electron wave spread out in space or a probability distribution of position for electrons.

Summary

- 6.1 Matter is anything that makes up a physical body and occupies space. Mass is the substance of matter. Elements are individual entities that make up matter. An atom is the smallest particle of an element that preserves all identifiable properties of the element. Two or more elements combine to form a compound. The smallest compound is the molecule.
- 6.2 An atom is made up of a massive core called the nucleus, surrounded by a cloud of orbiting electrons. The radius of an atom is about 10^{-10} m, whereas the nuclear radius is about 10^{-15} m.
- 6.3 According to the plum pudding model, an atom consists of negatively charged electrons moving in a constant motion within a positively charged medium.
- 6.4 According to the Rutherford model, an atom consists of largely empty space with electrons orbiting around the nucleus like a planetary model. The Rutherford model was formulated based on the bombardment of alpha particles on gold foil. The

observed unaffected alpha particles implied that the atom constituted largely of empty space, and the existence of backscattered alpha particles implied that the atom had a massive center.

- 6.5 Niels Bohr postulated that an electron revolved around a nucleus only in stable orbits with quantized angular momentum. If the electron jumps from a higher energy-state to a lower energy-state, a photon with energy equal to the energy difference between the two energy-states is emitted. Likewise, an electron gains energy through transitions to a higher energy-state of the atom.
- 6.6 According to the quantum theory, an atom is completely described using four quantum numbers, namely the principal quantum number n , the orbital quantum number ℓ , the magnetic quantum number m , and the spin quantum number s . These quantum numbers are restricted as

$$\begin{aligned} n &= 1, 2, 3 \dots \\ \ell &= 0, 1, 2 \dots n-1 \\ m &= -\ell, -\ell+1, \dots 0 \dots, +\ell-1, +\ell \\ s &= +\frac{1}{2} \text{ or } -\frac{1}{2} \end{aligned}$$

- 6.7 Orbital shells of an atom are filled with electrons according to the Pauli exclusion principle, which states that no two electrons can have the same quantum number.
- 6.8 The maximum number of electrons that can completely occupy a shell is $2n^2$. The maximum number of electrons that can occupy a sub-shell is given as $2(2\ell+1)$.
- 6.9 The periodic table indicates that the preferential arrangement of the electrons results in filling no more than eight electrons in the outer shell of an atom.
- 6.10 The binding energy of an electron increases as the atomic number (Z) increases. For example, the K-shell binding energy is 13.6 eV for hydrogen atom while for tungsten atom the binding energy is 69.5 keV.
- 6.11 The transitions between energy-states result in the absorption or emission of photons. The emitted photons are called characteristic x-rays, which are unique to each element.
- 6.12 During de-excitation of an atom, the emission of characteristic x-rays competes with Auger electrons. The fluorescent yield refers to the ratio of the number of characteristic x-rays emitted to the number of shell vacancies.
- 6.13 The different types of chemical bonds are the ionic bond, covalent bond, and hydrogen bond. The ionic bonds are based on the filling of a vacant shell with electrons from another atom while covalent bonds share electron pairs between atoms. Hydrogen bond is the weakest bond formed by sharing its electron with one oxygen atom or a nitrogen atom while bonding covalently to either oxygen or a nitrogen atom. The bonding energies are around 2–5 eV for strong bonds, and 0.04–0.3 eV for weak bonds.
- 6.15 The principle operation of laser is based on the existence of metastable states in molecules. Energy is initially pumped into the system to excite ions into the metastable state, causing a population inversion. When a photon with the precise energy is directed at these molecules, it stimulates de-excitation to emit an intense laser beam.

6.16 A summary of formulas:

$$\text{Bohr radii of hydrogen: } r_n = (0.53 \times 10^{-10} \text{ m}) n^2$$

$$\text{Energy levels of hydrogen: } E_n = -\frac{13.6 \text{ eV}}{n^2}$$

$$\text{Photon wavelength: } \lambda = \frac{1.24 \times 10^{-6}}{E}$$

$$\text{Fluorescent yield: } \omega_n = \frac{\text{No. of characteristic x-rays}}{\text{No. of } n\text{-shell vacancies}}$$

Study Guide

- 6.1 In your own words, define the following terms:
- | | |
|---------------------------|-------------------------------|
| (a) matter | (b) substance |
| (c) mixture | (d) compound |
| (e) element | (f) atom |
| (g) subatomic particle | (h) Bohr radius |
| (i) quantum mechanics | (j) Zeeman effect |
| (k) atomic fine structure | (l) inert gas |
| (m) halogens | (n) ionization potential |
| (o) binding energy | (p) excitation |
| (q) de-excitation | (r) Characteristics radiation |
| (s) Auger electrons | |
- 6.2 Name the three physical states of matter.
- 6.3 Identify the contributions of (a) Dalton, (b) Avogadro, (c) Mendeleev, and (d) Arrhenius to the development of the concept of the atom.
- 6.4 Identify evidences used to support the proposal of the (a) Thomson model and (b) Bohr model.
- 6.5 Identify the experimental evidence that supports Rutherford's thinking that an atom consists of electrons revolving around a massive center just like the planetary system.
- 6.6 State the Bohr postulations.
- 6.7 Give the approximate size of an atom and a nucleus.
- 6.8 Compare the masses and charges of a proton and a neutron to an electron.
- 6.9 Review the energy level diagram for a hydrogen atom as shown in Figure 6.3. Locate the zero energy position, $n = 1$ state, and $n = 100$ state on the energy level diagram. Is there any energy state above the zero energy level?
- 6.10 Identify the spectral line series and its associated final state transitions, e.g., Balmer ... spectral lines.
- 6.11 List the four quantum numbers used to describe the atomic structure. What are the restrictions imposed on these quantum numbers?

- 6.12 State the Pauli's exclusion principle and its relationship to the organization of the electrons in the shell structure.
- 6.13 Discuss the arrangement of elements in the periodic table based on orbital shells.
- 6.14 Explain why the noble gases are chemically inactive.
- 6.15 What is the binding energy of a K-shell electron in a (a) hydrogen atom, (b) tungsten atom, and (c) lead atom?
- 6.16 Why is the binding energy larger for a high Z atom compared to the hydrogen atom?
- 6.17 Define and differentiate between anions and cations.
- *6.18 The wave aspects of matter called **De Broglie wave or matter wave** was postulated by De Broglie. This postulation makes it possible to explain the quantization of angular momentum postulated by Niels Bohr. Explain what it means.

Problems

- 6.1 Compute the radii of the $n=2$ and $n=10$ orbits in the hydrogen atom.
- 6.2 Compute the energies of the $n=2$ and $n=10$ energy-states in the hydrogen atom.
- 6.3 Compute the wavelength of the photon emitted during the transition from the $n=10$ to $n=2$ energy-states of the hydrogen atom.
- 6.4 Determine the energy that must be absorbed by a hydrogen atom for an electron in the $n=2$ shell to be ionized.
- 6.5 How many electrons can fill the $n=3$ shell? Of these electrons, how many are used to fill the $\ell=0$, $\ell=1$, and $\ell=2$ sub-shells?
- 6.6 Write the electronic configuration for phosphorus-32, which has 15 electrons using the appropriate s, p, d, and f notations.
- 6.7 An unusual atom has three energy states: K-shell = -69 keV; L-shell = -12 keV; and M-shell = -3 keV. Identify the entire possible characteristic x-rays emitted during de-excitation. Can a photon with 72 keV come from this atom?
- 6.8 An Auger electron is ejected when an electron makes the transition from the $n=3$ shell to $n=2$ shell of an atom. Can this Auger electron come from the $n=1$ shell?
- 6.9 Assume that an electron drops from the $n=5$ shell to the $n=1$ shell of a hydrogen atom. What is the kinetic energy of an Auger electron (if available) ejected from the $n=10$ shell due to the excess energy?
- *6.10 Derive equation (6.4) using de Broglie wave for an electron. The motion of an electron in the Bohr's orbit of an atom must be equal to multiples of the de Broglie wavelength λ , e.g. $2\pi r = n\lambda$, where $n = 1, 2, 3, \dots$ so on.
- *6.11 Show that the energy levels of hydrogen-like atoms (i.e., 1 orbiting electron) with atomic number Z' are given as

$$E_n = \frac{E}{n^2} (Z')^2 \text{ eV}; \quad n = 1, 2, 3, \dots$$

and its associated radius is

$$r_n = 0.53 \times 10^{-8} \frac{n^2}{Z'} \text{ cm}; \quad n = 1, 2, 3, \dots$$

Multiple Choice Questions

Select the one correct answer.

- 6.1 The radius of the Bohr's orbit is 0.53×10^{-10} m. What is the radius of the $n = 5$ orbit of a hydrogen atom?
- 0.106×10^{-10} m
 - 0.53×10^{-10} m
 - 2.65×10^{-10} m
 - 13.25×10^{-10} m
 - none of the above
- 6.2 The energy level of the Bohr's orbit is -13.6 eV. What is the $n = 5$ energy level in a hydrogen atom?
- -0.544 eV
 - -2.72 eV
 - -13.6 eV
 - -68.0 eV
 - none of the above
- 6.3 In his experiment involving the bombardment of alpha particles onto gold foils, Rutherford observed that
- a vast majority of the alpha particles were unaffected by the gold foil.
 - an alpha particle is actually a helium atom.
 - an atom has a large empty space.
 - an atom has a massive center.
 - none of the above.
- 6.4 Which of the following statements is NOT consistent with the Bohr Model?
- Electrons revolve around the nucleus in definite orbits.
 - Whenever an electron jumps from a higher energy-state to a lower energy-state, a photon with energy equal to the energy difference between the two states is emitted.
 - So long as the electrons revolve in definite orbits around a nucleus there is no radiation.
 - Energy absorption occurs when an electron jumps from a lower energy-state to a higher energy-state of an atom.
 - none of the above.
- 6.5 Which of the following is not an appropriate electronic configuration of an atom?
- $1s^2 2s^2$
 - $1s^2 2s^2 2p^4$
 - $1s^2 2s^2 2p^3 3s^2$
 - $1s^2 2s^2 2p^6 3s^2 3p^6$
 - none of the above

- 6.6 A line spectrum series resulting from the transitions to the final state of $n=1$ in a hydrogen atom is called
- Lyman series.
 - Balmer series.
 - Paschen series.
 - Brackett series.
 - none of the above.
- 6.7 Noble gases are chemically inactive because
- they have an extra electron in their outer shell.
 - they have two extra electrons in their outer shell.
 - they have completely filled shells and sub-shells.
 - they have partially filled shells.
 - none of the above.
- 6.8 The amount of energy required to remove a valence electron is called
- ionization potential.
 - binding energy.
 - excitation energy.
 - de-excitation energy.
 - transitional energy.
- 6.9 A sample has two types of atoms with the following binding energies:
- Atom A: $K=-30$ eV; $L=-5$ eV; $M=-0.5$ eV
Atom B: $K=-35$ eV; $L=-5$ eV; $M=-1.5$ eV
- Two characteristic x-rays with energies of 33.5 eV and 3.7 eV from the sample were detected using an energy detector: Which of the following relationship is true?
- both x-rays belong to atom A
 - both x-rays belong to atom B
 - both x-rays are not from atoms A or B
 - one of the x-rays is from atom A
 - one of the x-rays is from atom B
- 6.10 Calculate the wavelength of the emitted photon during the transition from the $n=3$ to $n=1$ energy-state in a hydrogen atom.
- 1.023×10^{-7} m
 - 1.023×10^{-8} m
 - 1.023×10^{-9} m
 - 1.023×10^{-10} m
 - none of the above

