Faculty of Science

Unit 2:
Atoms

CHEM 1503
Chemical Bonding and
Organic Chemistry

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Overview

Much of the material in this unit is historical. It deals with the discoveries made by scientists in the late nineteenth century and early twentieth century. Although this is not a history of science course, it is important that you understand these discoveries and experiments, and their importance in the development of a theory of atomic structure. Often, by reading a textbook, you are left with the impression that each successive discovery was a logical outcome of a set linear pattern. Yet this was not the way atomic theory developed. Rather, it was more the jigsaw puzzle approach. Various pieces of the puzzle would be turned over at different times. Sometimes these pieces would happen to fit together and at other times, new pieces would seem to belong to another puzzle entirely. Gradually, as more pieces were turned over, they began to fit together. By then, enough progress had been made so that new experiments could be directed towards completing parts of the puzzle.

Eventually, with enough pieces turned over and enough connections made, the overall picture became apparent. The whole jigsaw puzzle is not yet complete, but most of the major parts have been fitted together. As you work through this unit you should be trying to understand how the experiments, observations, and theories make one overall pattern. At first glance, there may seem to be little or no connection between the electrical particle (the electron) and the periodic table of the chemical elements. Yet there is indeed a connection and it is that connection and how it was deciphered that you will be studying in this unit.

Learning Outcomes

By the end of this unit you should be able to:

- Describe the observations and experiments that led to the theory of the nuclear atom and the atomic structure.

- Explain Bohr's theory of the hydrogen atom structure and its relationship to the atomic spectrum of hydrogen.

- Perform calculations involving wavelengths, velocities, frequencies, and energies of electromagnetic radiation in atomic spectroscopy.

- Explain terms such as quantum, Heisenberg uncertainty principle, wave nature of matter, Schrodinger wave equation, orbital, and probability as applied to atomic structure.

- Perform calculations using the de Broglie relationship and explain the significance of the answers.

- Use the quantum number rules to determine the allowable values of quantum numbers and hence relate these to the arrangement of electrons in atoms.

- Describe the correct electronic configurations and energy level diagrams for the first 36 elements and give "good guess" electronic configurations and energy level diagrams for the other elements.

- Describe periodic trends of ionization potential, electron affinity, and atomic and ionic size.

- Explain Mendeleev's contribution to the modern periodic table.

- Describe the modern periodic table and know the names given to the various groups, transition metals, and periods.

- Discuss trends in chemical and physical properties in the periodic table.

Development of the Atomic Theory

Review Section 2.1 in your textbook. You do not have to memorize this material which is aimed at giving you some historical background in the development of the theory of atomic structure. However, the four main assumptions of Dalton's atomic theory are important. You probably cannot remember when you first heard about atoms. Try to imagine how the introduction of a theory of the existence of atoms changed the outlook of the scientists of the time; there was finally a theoretical basis to explain observations. As well, the ability to make predictions, and to test these predictions by experiment, became possible. The scientific method could then develop.

Now review Section 2.2 in your textbook.

The Electron

The most important experiments on the electron, at least as far as the structure of the atom is concerned, are those of Thomson and Millikan. The important conclusions from Thomson's experiments are as follows.

- Cathode rays consist of *negatively charged particles* (later called *electrons*).

- Because the behaviour of cathode rays is independent of the cathode material, electrons can be considered to be *present in all matter*.

- The ratio of charge to mass (e/m) of an electron is -1.76×10^8 C/g.

- The e/m ratio for an electron is 1837 times that of the e/m ratio for the smallest ion. Since the value of the charge e is constant, the mass of the electron is 1837 times smaller than the mass of the hydrogen ion.

Thomson's experiments and conclusions also led to the modification of Dalton's first assumption. If electrons are common to all matter, then atoms are not the indivisible, featureless, tiny billiard balls postulated by Dalton. The electron was only the first subatomic particle discovered. Other subatomic particles were to be discovered and are still being discovered. Millikan's experiment measured the charge on the electron directly and so, through calculation, the mass of the electron.

X-rays and Radiation

If you are interested in the topics of radiation and radioactivity, you can read Chapter 23 of your textbook. Although CHEM 1503 does not cover the topic of nuclear chemistry, by the end of this unit you will have enough of a chemistry background to understand much of the material in Chapter 23. **Radioactivity** is the emission of radiant energy or particles by atomic nuclei. You should know the three types of rays emitted by radioactive elements. They are summarized in Table 2.1 of this unit.

The relationship of radiation to the structure of the atom should become clearer to you after you have read the next section.

Name and symbol of ray	Relative mass	Electric charge	Composition	Example of source of the radiation
alpha α	4	+2	particles with 2 protons and 2 neutrons, identical with helium atom nuclei, $\left(^{4}_{2}\text{He}\right)$	$^{238}_{92}\text{U} \longrightarrow {}^{4}_{2}\text{He} + {}^{234}_{90}\text{Th}$
beta β	$\frac{1}{1837}$	−1	a stream of electrons, $\left(^{0}_{-1}\text{e}\right)$	$^{234}_{90}\text{Th} \longrightarrow {}^{0}_{-1}\text{e} + {}^{234}_{91}\text{Pa}$
gamma γ	0	0	electromagnetic radiation of very short wavelength (high energy photons)	accompanies virtually all nuclear reactions

Table 2.1: Types of radiation from radioactive elements

The Nuclear Atom

Rutherford's scattering experiment led to the idea of an atomic nucleus. This postulation is the basis for the modern concept of the nuclear atom. It is extremely hard to imagine how small a nucleus is. It has been calculated that the density of a nucleus is of the order of 1.8×10^{14} g/cm^3. Lead, one of the densest metals, has a

density of 11.3 g/cm^3. A comparison of density using these values is probably not very meaningful to you. Another way of expressing density is to say that a nucleus is more than a million million times denser than lead. One tablespoon of nuclear matter would weigh about twenty billion tons! Matter having density of this order does actually exist in neutron stars. When a star with a mass slightly greater than that of the sun exhausts its fuel and collapses, the gravitational force is sufficient to squeeze the electrons into the nuclear protons, leaving a "neutron star" of only 10 to 20 miles in diameter.

You should memorize (if you do not already know) the following.

- The atomic number of an element (which determines its chemical name) equals the number of protons.

- The mass number (or atomic weight) of an element equals the total number of protons and neutrons.

- Isotopes of elements are atoms with the same number of protons but different numbers of neutrons.

Development of the Quantum Theory

The Interaction of Electromagnetic Radiation and Matter

Study Section 7.1 of your textbook.

At this point you may think that you have suddenly stumbled into a physics course. You have been reading about atoms, protons, neutrons, and electrons, and suddenly the textbook is discussing waves, wave motion, and light. But the relationship between matter and electromagnetic radiation, of which visible light is just a small part, is most important. So hang in here and learn the small amount of physics necessary. You must know the meaning of, and the symbols for, the terms *amplitude*, *wavelength*, *frequency*, and *velocity*. "Knowing" here means more than memorizing. You must understand these terms, how they are related, and how to do problems such as Example 7.1 and its practice exercise.

The speed of light in a vacuum is 3.00×10^8 m/s, a constant value. This value will always be given to you. However, it is a value used often enough that you will probably soon have memorized it.

Visible light is that part of the total electromagnetic spectrum that can be detected by the human eye. Study Figure 7.4 in your textbook, and Figures 2.1 and 2.2 in this unit—they show the expanded range of the electromagnetic radiation spectrum.
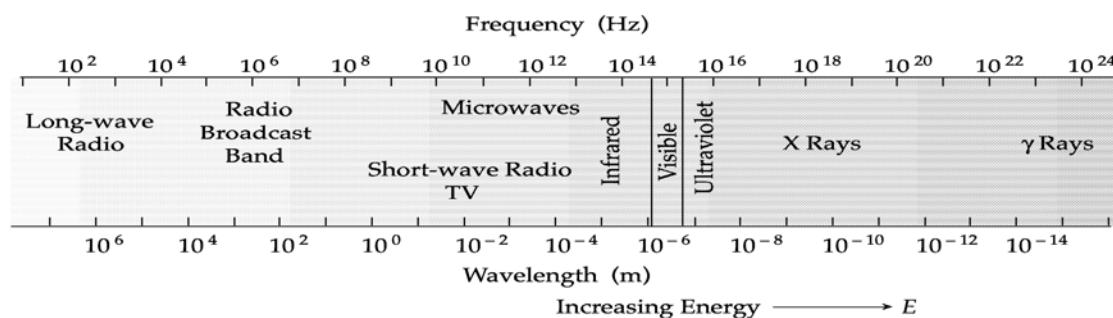

Figure 2.1: The electromagnetic spectrum. In this diagram, energy is increasing from left to right.
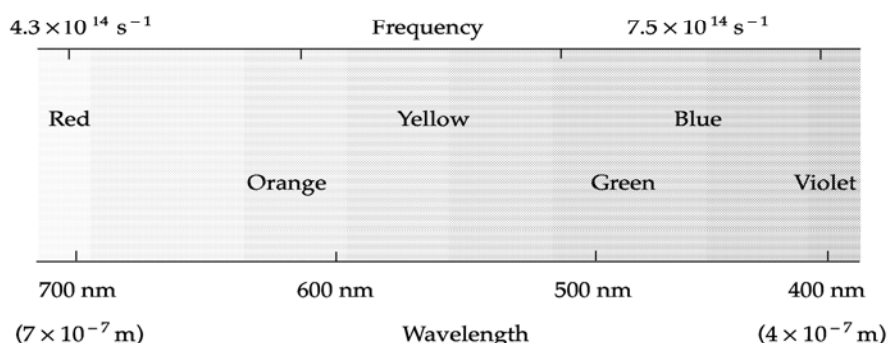

Figure 2.2: The visible light spectrum. An expanded portion of the electro-magnetic spectrum shows the wavelengths of visible light in nanometres (nm), one of the common units used for visible light.

Read in your textbook about the radiation emitted from heated solid bodies and its explanation in terms of Planck's quantum theory. There are two important pieces of information from Planck's theory that you will use. The first is the relationship

$$E = h\nu,$$

and the second is the concept of the quantum. As well as the examples given in your textbook, there are many examples of quantization in everyday life. If you go to a supermarket, you will often see many quantized products. The supermarket management has decided the sizes of the discrete, allowable items you may purchase. In the same way, energy comes in discrete allowable units. However, in the supermarket you can, at least theoretically, risk management displeasure and

open the plastic bag to buy two grapefruit, or open up a packet of butter to buy one stick. But the quantization of energy follows much stricter rules. Energy is not infinitely divisible—the size of the discrete units of energy are not set by humans. The quantum concept is the basis for understanding the structure of the atom. The quanta in radiant energy are known as **photons**.

Read about Einstein, the photoelectric effect, binding, and kinetic energy in Section 7.2 in your textbook then do Example 7.2 and its practice exercise. This should provide you with the further background information necessary for understanding modern atomic structure.

Your textbook does not go into any details on Einstein's theory of special relativity as a conceptual basis for the photon. While such details are not required in this course, Einstein's special relativity theory is generally regarded as the most profound and important scientific paper ever published. It is an important part of our scientific heritage and is worth considering here, although you are not required to memorize the details. What Einstein did was ask a simple question: why does a moving electric charge induce a magnetic field only if the charge is moving with respect to the earth? A stationary charge creates no field, but there is really no such thing as a stationary charge, since the earth itself is moving. Therefore, to what does velocity ultimately relate? This led Einstein to the answer that only the velocity of light is a constant. A beam of light from a moving object can move no faster than light from a stationary object. This, in turn, suggested that mass, as well as velocity (and hence also time), is relative. Further, the faster an object moves with respect to an observer, the greater its mass, and the harder it becomes to accelerate it to greater velocity. The velocity of light (c) is the limit, since an infinite amount of energy is required to accelerate an infinitely massive object. The additional mass of a moving object (relative to its rest mass) comes from the kinetic energy of the object, according to $E = mc^2$. Photons have zero rest mass, so only they can travel at velocity c. You can think of ordinary matter as "congealed energy," trapped by its possession of rest mass, whereas light is energy that has been liberated of its rest mass.

Special relativity does have consequences in chemistry. Chemists assume that the law of conservation of mass is absolute. In fact, it is approximate. During chemical reactions, mass can be converted to energy or energy converted to mass, but the mass amounts involved in these conversions are so small that they cannot be measured. Later in this unit you will be introduced to the Schrodinger equation, an attempt to describe an atom mathematically. Closer approximations to correct solutions of the Schrodinger equation can be obtained by using relativistic corrections.

By now you have turned up a number of the pieces of the jigsaw puzzle discussed in the overview of this unit. You will not yet have made the connections between all this experimental data and a theory of atomic structure. The rest of Chapter 7 in your textbook is devoted to making these connections, and to developing a picture of the structure of the atom. If you are to follow these readings, it is important that you are aware of the experimental facts mentioned below. You should also understand that any acceptable theory of atomic structure must be able to explain or account for such experimental results.

The Bohr Model of the Hydrogen Atom

Visible light and light from an incandescent solid, such as a filament of an ordinary light bulb, produce what is known as a **continuous spectrum**. A continuous spectrum is made up of all visible wavelengths. Discontinuous or **line spectra** are obtained by subjecting an atom to an intense electric field such as that found in an electric discharge. Familiar examples of line spectra from such sources are mercury and sodium vapour street lamps, and neon signs (Figure 7.8 in your textbook illustrates the emission spectra of these and other elements). The spectral lines obtained in this manner are each due to a discrete wavelength of light. Each element has its own pattern of these spectral lines. The existence of such atomic "fingerprints" has led to the development of an analytical instrument that makes use of emission spectroscopy to analyze for various elements.

Study Section 7.3 in your textbook. Although the Bohr theory is successful for only one electron species such as the hydrogen atom, the helium ion (He^+), or the deuterium atom (D), it is important that you know the postulates advanced by Bohr. You should also understand the relationship between Bohr's theory and the visible lines in the atomic spectrum of hydrogen. This relationship was later found to hold for a similar set of hydrogen spectral lines that exists in the infrared and ultraviolet regions of the spectrum. Go over Example 7.4 and its practice exercise.

You do not need to memorize the equations or formulas in this section because they will be given to you in an exam. But you should work through all of the derivations and make sure that you follow the arguments. These equations are not complicated mathematically. As you work through them, remember that they are just applications of the laws of physics and some algebraic manipulation.

Bohr's theory was a departure from the classical physics of the time and a beginning of the "nonclassical" or quantum theory. His postulates, which you should know, can be summarized as follows.

- Electrons exist in allowable energy states (quantization).

- Electrons require energy to jump to a higher energy level, and they emit energy when they jump to a lower energy level.

- The energy emitted when an electron jumps is related to the frequency of emitted radiation.

It is now known that the Bohr theory only partially explains the structure of atoms. However, the Bohr theory did go a long way in explaining the atomic spectrum of hydrogen, and it did predict the existence of a similar series of lines in the ultraviolet and infrared regions of the electromagnetic spectrum which were discovered later. A summary of the relationship between Bohr's theory and the atomic spectrum of hydrogen is given in Figures 2.3 to 2.5 in this unit.

That Bohr's theory is not applicable to multi-electron systems should not detract from the importance of his work to the development of the understanding of modern atomic structure. There is a brief, highly readable biography of this remarkable scientist available online at http://dwb.unl.edu/Teacher/NSF/C06/C06Links/207.138.35.143/nobel/macro/5000_79.html, or do an internet search for information on Niels Bohr.
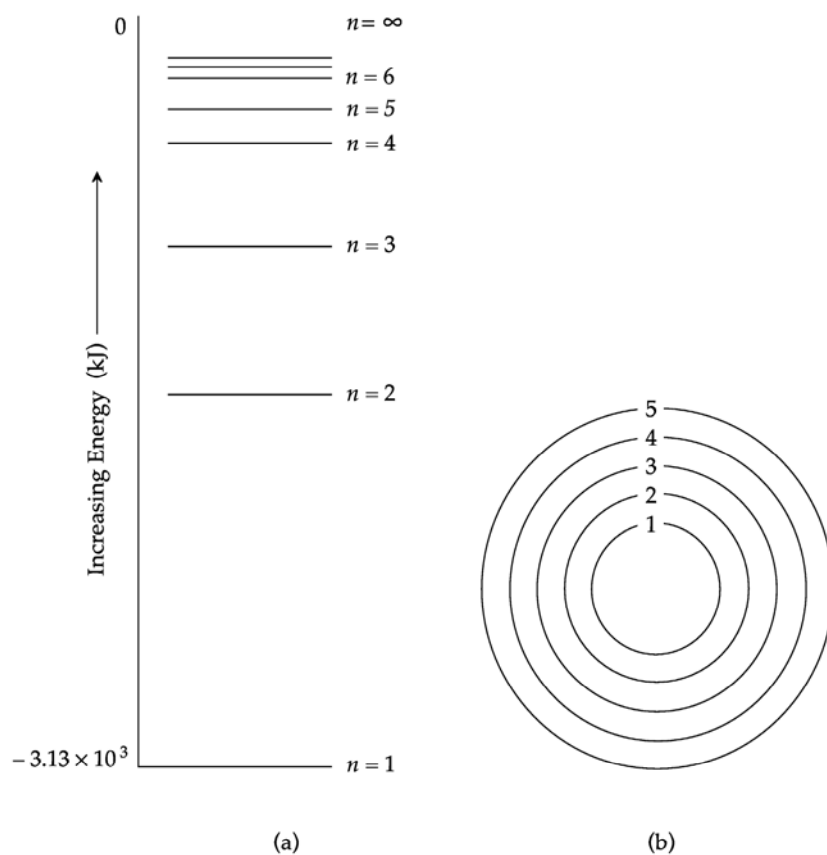
Figure 2.3: The Bohr atom and energy level diagram for hydrogen.

(a) The allowed energy levels of the hydrogen atom are depicted on graphs of this kind, in which each horizontal line represents an allowed state. Only the lowest ($n = 1$) level is occupied in the ground state of the hydrogen atom. Although this diagram shows only 5 or 6 values for n, there is no limit to the number of values it can have. You should also notice that the energy scale is negative—at negative energies, the electron is bound to the nucleus.

(b) At the lowest allowed energy, the electron is in the innermost of the corresponding Bohr orbits depicted in (b). The attractive force of the nucleus is greatest at this innermost orbit and the electron is less tightly bound at the further out or higher energy orbits. An atom is considered to be "ionized" when the electron reaches the $n = \infty$ level. At this point, the electron is totally removed from the atom. The arbitrary assignment of zero energy to this $n = \infty$ level gives the negative energy scale to electrons with lower n values.
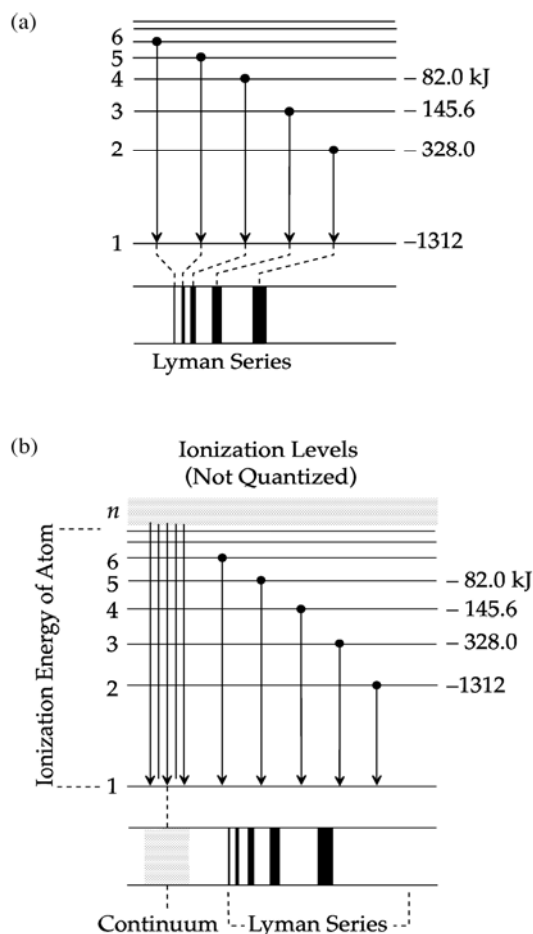
(a)

6
5
4 — 82.0 kJ
3 — 145.6
2 — 328.0

1 — −1312

Lyman Series

(b)

Ionization Levels
(Not Quantized)

Ionization Energy of Atom

n

6
5 — 82.0 kJ
4 — 145.6
3 — 328.0
2 — −1312

1

Continuum ┊--Lyman Series--┊

Figure 2.4: Energy levels and ultraviolet absorption spectra.

(a) When an electron of hydrogen, excited to various levels of energy, decays back
to the ground state, the resulting energy jumps give rise to a series of spectral
lines known as the Lyman series. These lines occur in the ultraviolet region of
the electromagnetic spectrum. In other words, an electron at a higher energy
level returns to a lower energy level, and energy is given out in the form of
radiant energy.

(b) If an atom absorbs so much energy that its electron is completely removed, then
that electron can have energy above this ionization level. If the electron is
eventually regained, the atom decays from a non-quantized energy level to the
ground state. This produces a continuous spectrum of radiant energy, not a
series of lines as in the quantized case. This continuous spectrum is known as a
continuum and its onset indicates the energy necessary to remove an electron
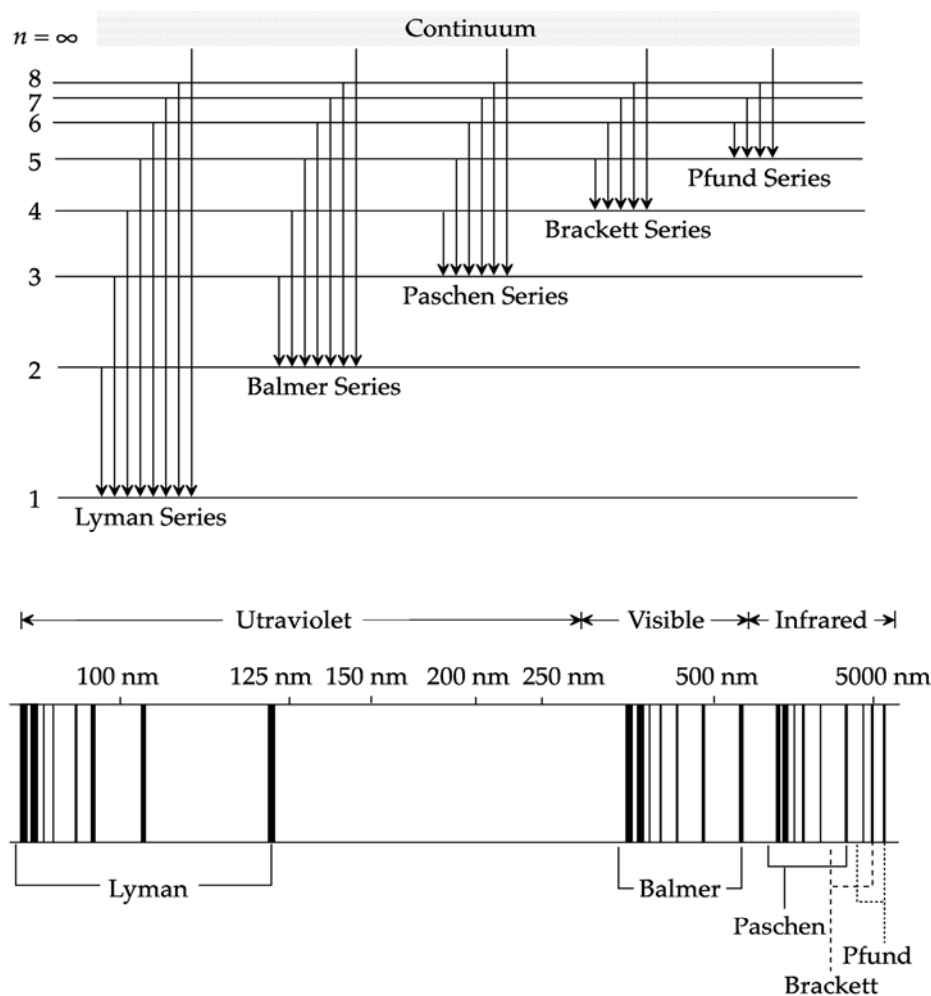(ionization energy).

Figure 2.5: Atomic spectrum of the hydrogen atom. In the upper graph, each set of arrows represents energy jumps of electrons from various upper energy levels to a common value of n. If an energy jump terminates at an n level greater than $n = 1$, then further jumps are permitted until the electron reaches the ground state. In an atomic spectrum of hydrogen, there are many hydrogen atoms and the electrons may be excited to higher energy levels and jump back to lower levels many times. Consequently, all possible lines can be seen. Those that correspond to jumps returning to the $n = 1$ level are seen in the ultraviolet portion of the spectrum (Lyman series). Those corresponding to jumps returning to the $n = 2$ level are the Balmer series found in the visible. The Paschen series corresponds to those jumps returning to the $n = 3$ level; these are found in the infrared. Many other series exist.

The Quantum Mechanical Description of Atoms

It is now accepted that atoms are best described using aspects of physics described as "nonclassical." With nonclassical physics, rules that apply to macroscopic objects do not necessarily apply to atomic-sized objects. This does not mean that there are two sets of rules. There is only one set of rules that applies to all matter, but many phenomena predicted by this set of rules become insignificant if you move from the atomic to the macroscopic scale. The nonclassical approach to the description of an atom is known as quantum mechanics.

Waves and Particles

Study Section 7.4 in your textbook.

The dual wave-particle nature of matter is very well explained in your textbook. You probably know that light (electromagnetic radiation) is now considered as both a wave and a particle phenomenon, but you are mainly familiar with the wave properties. The components that make up an atom are even called particles (i.e., the subatomic particles such as electrons, protons, and neutrons). Although you may have always thought of these as being particles, we now know that we can just as correctly consider them waves. This may seem a bit odd, but two examples of the application of the **de Broglie equation** ($\lambda = h/mu$) that follow may help you decide that the dual wave-particle nature of matter is no more difficult to accept than the dual nature of light.

Problem: Calculate the de Broglie wavelength associated with a 400. g baseball travelling at 40.0 m/s.

Solution: Use

$$\lambda \quad = \frac{h}{mu} \; = \; \frac{6.63 \times 10^{-34} \;\text{J s}}{400 \;\text{g} \times 40.0 \;\text{m s}^{-1}}$$

The SI definition of a joule is $1 \text{ J} = 1 \text{ kg m}^2 \text{ s}^{-2}$, so

$$\lambda \quad = \frac{6.63 \times 10^{-34} \;\text{kg m}^2 \text{ s}^{-2}\text{ s}}{0.400 \;\text{kg} \times 40.0 \;\text{m s}^{-1}}$$

$$= 4.14 \times 10^{-35} \text{ m}$$

You should note two things about this solution. First, converting a unit such as a joule into its base SI units of kg m^2 s^{-2} makes unit cancellation easy. You end up with a value in metres, the correct unit for wavelength. Second, 10^{-35} metres is an exceedingly small wavelength. The size of an atom is of the order of 10^{-10} metres. γ rays can have a wavelength as small as 10^{-16} metres, but there is no way of measuring a wavelength of 10^{-35} metres. There is no electromagnetic radiation that has a wavelength anywhere near as small as this. Thus, a baseball is very much more a particle than a wave! An example of where a de Broglie wavelength could be measured is shown in the next problem.

Problem: Calculate the de Broglie wavelength associated with one electron travelling at 4.00×10^4 m/s. The mass of an electron is 9.10×10^{-31} kg.

Solution: Use

$$\lambda = \frac{h}{mu} = \frac{6.63 \times 10^{-34} \text{ kg m}^2 \text{ s}^{-2} \text{ s}}{4.00 \times 10^4 \text{ m s}^{-1} \times 9.10 \times 10^{-31} \text{ kg}}$$

$$= 1.82 \times 10^{-8} \text{ m}$$

Since 1 nm = 10^{-9} m,

$$\lambda = 1.82 \times 10^{-8} \text{ m} \times \frac{\text{nm}}{10^{-9}\text{ m}} = 18 \text{ nm}.$$

A wavelength of 18 nm is in the detectable range. A beam of electrons travelling at 4.00×10^4 m s^{-1} is diffracted by diffraction gratings about 18 nm apart. A crystal of nickel, where the layers of atoms are 22 nm apart, will diffract such a beam of electrons. In fact, this was the first experimental evidence supporting the de Broglie hypotheses.

Now try Example 7.5 from your textbook and its practice exercise.

Quantum Mechanics and the Hydrogen Atom

Study Section 7.5 of your textbook. The discussion of the consequences of the **Heisenberg uncertainty principle** gives a good explanation of why this principle is very important at the subatomic level. The uncertainty principle can be used to give a general answer to the question, "Why does the electron not exist in the nucleus?" The uncertainty principle says that you cannot find the precise location of an object with a specified momentum. Since the nucleus is a precise location, you cannot specify that a known electron is in that position. You may come across the Heisenberg uncertainty principle expressed in a number of informal ways—for example, "the more you know about one thing, the less you know about the other." A favourite bumper sticker among physicists reads "Heisenberg MAY have slept here!"

You are not expected to memorize or use the Schrodinger equation, but you should understand what is meant by the term "orbital." You can think of an orbital as being the region of space in which the probability of finding the electron is high. Specific energy levels of electrons correspond to specific orbitals. If you say that an electron occupies a certain orbital, you are not saying exactly where the electron is, but that there is a very good chance that the electron is within a certain region of space.

Quantum Numbers and Atomic Orbitals

Study Sections 7.6 and 7.7 in your textbook. This is a very important section of the material on atomic structure. While you are not expected to solve the Schrodinger equation, you should realize that the first three quantum numbers described here come from solutions of the Schrodinger equation. The fourth, or spin, quantum number comes from experiments showing that electrons spin. You should know (i.e., memorize and understand) the information on the quantum numbers that is summarized for you in Table 2.2 in this unit. If you have never encountered quantum numbers before, and if Section 7.6 in your textbook seems totally unrelated to chemistry, don't get too upset. You have to work through this material before it starts fitting in with your previous chemical knowledge. And it will! The beauty of quantum mechanics (or wave mechanics, as it is sometimes called) is that it provides a theoretical basis for a vast number of chemical facts, including the shape of the periodic table. Each electron can be assigned values of n, ℓ, m_ℓ, and m_s; the relations between these are determined by the rules shown in the fourth column of Table 2.2 in this unit (and which you are expected to memorize).

Table 2.2: Summary of information about quantum numbers

Quantum number	Symbol	Name (or names) of quantum number	Allowed values	What the quantum number tells you
1st	n	Principal quantum number	$n = 1, 2, 3, \ldots \infty$	total energy of electron in the orbital (*size*)
2nd	ℓ	Angular momentum or azimuthal quantum number	$\ell = 0, 1, 2, \ldots, (n-1)$	*shape* of the orbital
3rd	m_ℓ	Magnetic quantum number	$m_\ell = 0, \pm 1, \pm 2, \ldots, \pm \ell$	*direction* of the orbital
4th	m_s	Spin quantum number	$m_s = +\frac{1}{2}$ or $-\frac{1}{2}$	electron *spin*, maximum number of electrons in an orbital is two

Problem: Which of the following sets of quantum numbers are allowed?

a. $n = 1$ $\ell = 1$ $m_\ell = 0$ $m_s = +\frac{1}{2}$

b. $n = 3$ $\ell = 1$ $m_\ell = 0$ $m_s = -1$

c. $n = 3$ $\ell = 2$ $m_\ell = +3$ $m_s = -\frac{1}{2}$

d. $n = 3$ $\ell = 2$ $m_\ell = -2$ $m_s = +\frac{1}{2}$

e. $n = -3$ $\ell = 1$ $m_\ell = 0$ $m_s = +\frac{1}{2}$

Solution: (d) is the only allowable set. In

a. If $n = 1$, the maximum value that ℓ can have is 0 [using the rule $\ell = 0, 1, 2, \ldots, (n-1)$];

b. n, ℓ, and m_ℓ fit the rules, but the value for m_s is restricted to $+\frac{1}{2}$ or $-\frac{1}{2}$;

c. If $\ell = 2$, the only values m_ℓ can have are $0, +1, -1, +2, -2$ using the rule $m_\ell = 0, \pm 1, \pm 2, \ldots, \pm\ell$;

e. The only values n can have are positive integers to ∞.

The relationship between quantum numbers and atomic orbitals allows you to designate "names" to orbitals. You might think of these designations as a shorthand way of describing an orbital. The first quantum number is given as the integer and the second quantum number is given using

s for $\ell = 0$

p for $\ell = 1$

d for $\ell = 2$

f for $\ell = 3$

So where $n = 2$ and $\ell = 0$ the orbital is designated $2s$. Other examples are

$n = 4$ $\ell = 3$ the orbital is known as $4f$

$n = 1$ $\ell = 0$ the orbital is known as $1s$

$n = 2$ $\ell = 1$ the orbital is known as $2p$

$n = 3$ $\ell = 2$ the orbital is known as $3d$

$2s$ is not that much shorter than $n = 2$, $\ell = 0$, but the $2s$, $4f$, $3p$, and so forth, designations are really used for historical reasons rather than because they are shorter. Any given orbital is distinguished by the three quantum numbers: n, ℓ, and m_ℓ.

It is important that you also learn the shape of the s and p orbitals. s orbitals are spheres (hollow) with $3s$ larger than $2s$, $4s$ larger than $3s$, and so on. A sphere is nondirectional so there is only one possible m_ℓ value for an s orbital, and that is $m_\ell = 0$.

Figure 2.6 in this unit shows how to graph the probability of finding an electron against its distance from the nucleus. Such a graph results in the spherical shape for an *s* orbital.
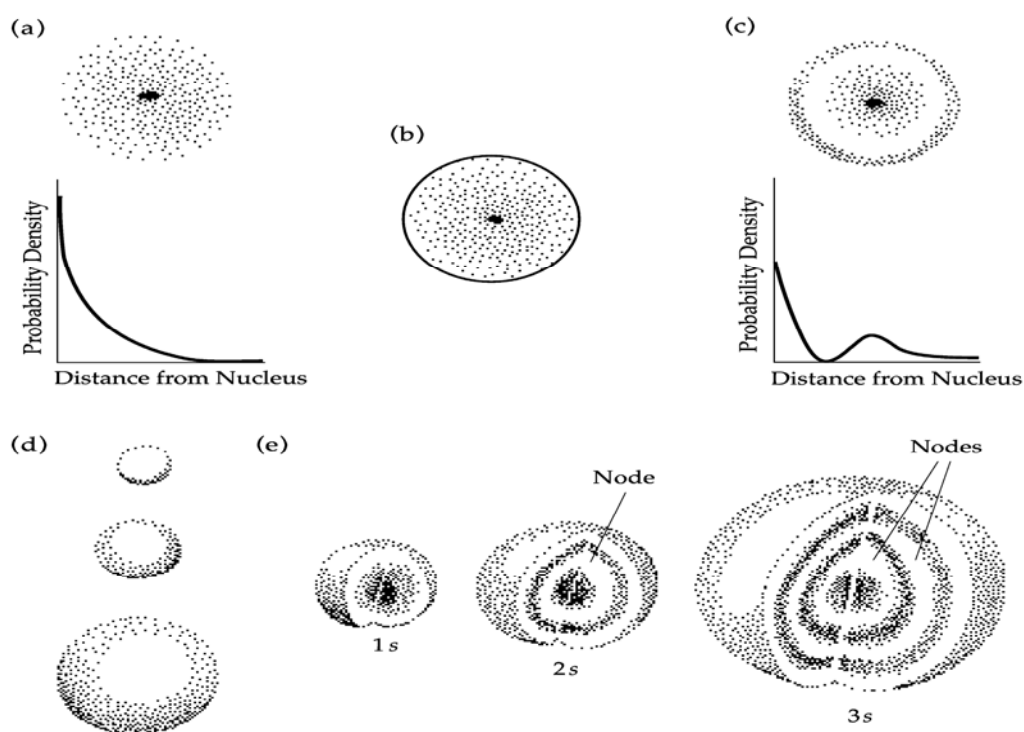
Figure 2.6: Probability diagrams for *s* orbitals.

(a) Plot of probability of locating an electron per unit volume in the hydrogen 1*s* orbital, as a function of distance away from the nucleus. Note that the probability density falls off rapidly as the distance from the nucleus increases.

(b) Boundary surface diagram of the hydrogen 1*s* orbital. A boundary surface diagram shows the region that contains most (about 90%) of the electron density in an orbital.

(c) Plot of probability of finding an electron per unit volume in the 2*s* hydrogen orbital versus distance from the nucleus. A node is a point at which the probability of finding the electron is zero.

(d) Boundary surface diagrams of the hydrogen 1*s*, 2*s*, and 3*s* orbitals. Each sphere contains within it about 90% of the total electron density. All *s* orbitals are spherical in shape, but their size increases roughly as the square of *n* (i.e., as n^2) where *n* is the principal quantum number.

(e) A combined and cutaway representation of the electron density distribution in the 1s, 2s, and 3s orbitals of an atom. Note the position of the nodes. Remember that the average distance between the electron and the nucleus is the same for all values of ℓ and m_ℓ for a given value of n.

p orbitals have the angular momentum quantum number $\ell = 1$. Therefore, there are three possible magnetic quantum numbers, $m_\ell = 0$, $m_\ell = 1$, and $m_\ell = -1$. The three p orbitals are often called p_x, p_y, and p_z, but you should note that x, y, and z do not correspond to any particular value of m_ℓ.

Figure 2.7 below gives probability density graphs for $2p$ and $3p$ orbitals and shows a combined boundary surface diagram of the p_x, p_y, and p_z orbitals.
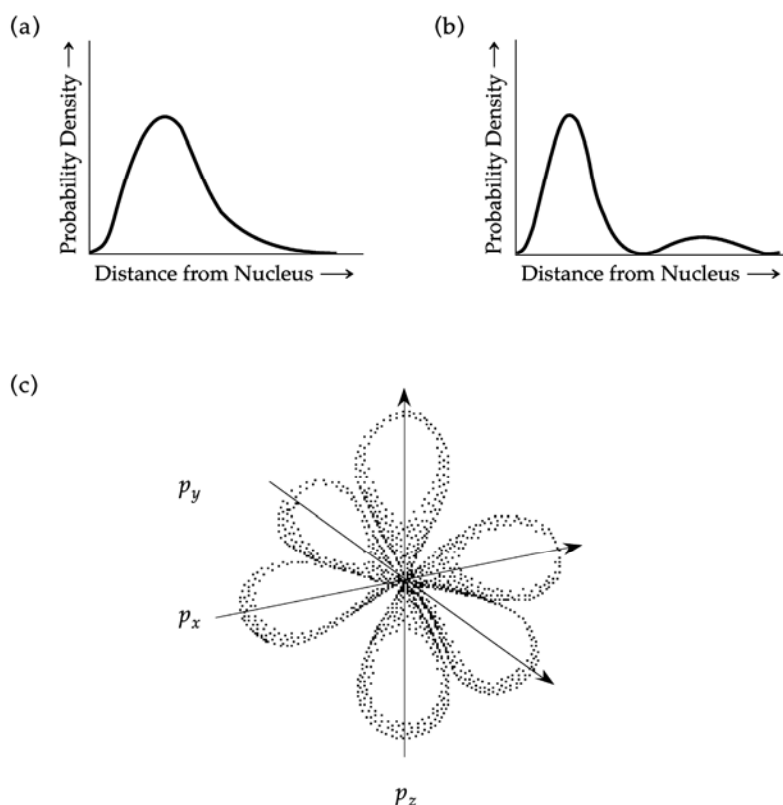

Figure 2.7: Probability diagrams for p orbitals.

(a) Plot of probability of locating an electron per unit volume in the hydrogen $2p$ orbital as a function of distance away from the nucleus.

(b) Plot of probability of locating an electron per unit volume in the hydrogen $3p$ orbital as a function of the distance away from the nucleus.

(c) Boundary surface diagram of the combined p_x, p_y, and p_z orbitals.

For d orbitals, $\ell = 2$ and therefore $m_\ell = 0, +1, -1, +2$, or -2. There are always five d orbitals. At this stage, you do not need to memorize the shapes or the names of these d_{xy}, d_{yz}, d_{zx}, $d_{x^2-y^2}$, and d_{z^2} orbitals. In later units you may be referred back to these shapes. You do not have to memorize the shapes of the probability graphs.

Now try Examples 7.7 and 7.8 from your textbook and their practice exercises.

Electronic Configurations and the Aufbau Principle

Study Sections 7.8 and 7.9 in your textbook. The same set of rules that governed allowable quantum numbers for a one-electron atom can now be used for multi-electron atoms. You may need to read through these sections a number of times in order to understand the material. Make sure that you understand the difference between one-electron and multi-electron atoms. In **one-electron atoms**, all orbitals having the same n value have the same energy (see text Figure 7.22). In **multi-electron atoms**, the electron clouds are negative and tend to repel each other. This repulsion (and, thus, the energy) depends on the shapes of the orbitals and therefore on the value of ℓ. Hence, the s, p, d, and f orbitals now have different energies (see text Figure 7.23). Table 2.3 in this unit summarizes the Aufbau process for you. To follow Table 2.3, you must know the following basic principles or facts.

- The lowest energy arrangement of the electrons (ground state) is obtained by putting the electrons in the lowest energy orbital available (**Aufbau principle**).

- Any one orbital can have a maximum of two electrons, each spinning in opposite directions (**Pauli exclusion principle**).

- The filling order for the subshells for the first 36 elements is ls, 2s, 2p, 3s, 3p, 4s, 3d, and 4p.

- If there is more than one orbital at the same energy level, you should put one electron in each of these available orbitals before you pair up the electrons in one orbital (**Hund's rule**).

You are expected to know the electronic configuration of, and be able to draw an energy level diagram for, any element up to and including Kr, number 36. Do not memorize the electronic configurations as such; rather, learn the filling order from $1s$ to $4p$ and know how to derive the electronic configuration and energy level diagram using the four statements above. You should also know that there are two exceptions to the filling order rule in the first thirty-six elements—namely Cr and Cu. The electronic configurations to expect are

$$\text{Cr:} \quad [\text{Ar}]\, 4s^2\, 3d^4 \quad \text{and} \quad \text{Cu:} \quad [\text{Ar}]\, 4s^2\, 3d^9,$$

but experimental evidence indicates that these are actually

$$\text{Cr:} \quad [\text{Ar}]\, 4s^1\, 3d^5 \quad \text{and} \quad \text{Cu:} \quad [\text{Ar}]\, 4s^1\, 3d^{10}.$$

Table 2.3: Applications of the Aufbau principle for the first thirteen elements

Atom	Number of electrons	Energy level diagram	Full electronic configuration	Condensed form of electronic configuration
H	1		$1s^1$	$1s^1$
He	2		$1s^2$	[He]
Li	3		$1s^2\,2s^1$	[He] $2s^1$
Be	4		$1s^2\,2s^2$	[He] $2s^2$
B	5		$1s^2\,2s^2\,2p^1$	[He] $2s^2\,2p^1$
C	6		$1s^2\,2s^2\,2p^2$	[He] $2s^2\,2p^2$
N	7		$1s^2\,2s^2\,2p^3$	[He] $2s^2\,2p^3$
O	8		$1s^2\,2s^2\,2p^4$	[He] $2s^2\,2p^4$
F	9		$1s^2\,2s^2\,2p^5$	[He] $2s^2\,2p^5$
Ne	10		$1s^2\,2s^2\,2p^6$	[Ne]
Na	11		$1s^2\,2s^2\,2p^6\,3s^1$	[Ne] $3s^1$
Mg	12		$1s^2\,2s^2\,2p^6\,3s^2$	[Ne] $3s^2$
Al	13		$1s^2\,2s^2\,2p^6\,3s^2\,3p^1$	[Ne] $3s^2\,3p^1$

The reason for these exceptions is that the increased stability of a half-filled (d^5) or completely filled (d^{10}) d subshell more than compensates for creating the half-filled (s^1) s subshell. Be sure to learn these exceptions so that you can accurately give electronic configurations for any element up to number 36. Table 2.3 in this unit follows the Aufbau principle through the first thirteen elements. Now make your own continuation of Table 2.3 for the elements 14 through 36, and then check your results against Table 7.3 in your textbook. The following diagram shows what to do for all the elements from number 19 to number 36.

Ti (22 electrons)	energy level diagram	electronic configuration
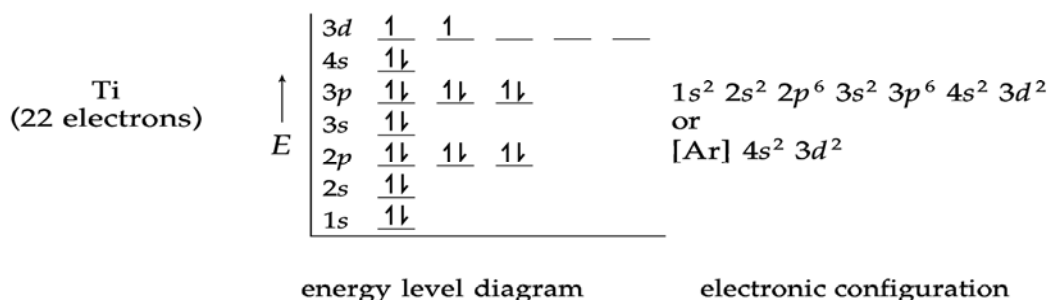
Note that titanium is element number 22. It has 22 electrons, there are 22 electrons shown in the energy level diagram, and the sum of the superscripts, $2 + 2 + 6 + 2 + 6 + 2 + 2$, also equals 22.

You are not expected to give absolutely correct electronic configurations or energy level diagrams for elements above number 36. As the atomic weight of the element increases, there are more and more exceptions to the filling order, and the electronic configuration cannot always be predicted accurately. One reason for this lack of predictability is that, at higher energies, the orbitals crowd together and even small changes in the chemical environment of an atom can cause one orbital to move above or below another in energy. If you take a good look at Table 7.3 in your textbook, you will be able to see this. Elements of atomic number 41 through 47 are good examples of the unpredictability of the higher electronic configurations.

In this course, you should be able to make a "good guess" as to the electronic configuration of elements greater than number 36. Figure 2.8 in this unit can be used effectively for this purpose. If you were given element number 78, platinum, you could use Figure 2.8 and a normal periodic table to identify that platinum was in the $5d$ row, eight spaces along. This means that you could make a "good guess" that platinum has an electronic configuration of [Xe] $6s^2\, 4f^{14}\, 5d^8$. If you check in Table 7.3 of your textbook, you will find that Pt actually is [Xe] $6s^1\, 4f^{14}\, 5d^9$. You had no way of predicting the true electronic configuration was an "exemption" and your "good guess" is acceptable. In many cases, a "good guess" does give you the correct answer. Element number 52, tellurium, is four spaces along in the $5p$ row.

Your "good guess" system gives an electronic configuration for Te of [Kr] $5s^2\, 4d^{10}$ $5p^4$—the true configuration given in your textbook.
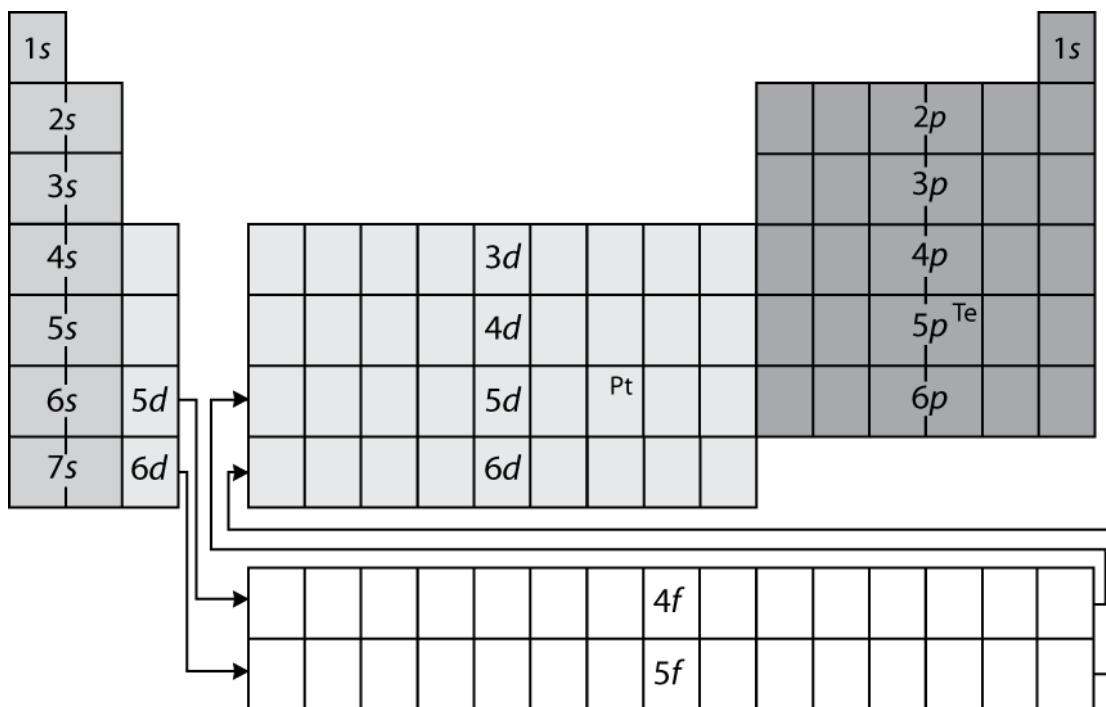
Figure 2.8: Electronic configuration and the periodic table. This diagram shows the relationship between the arrangement of the electrons and the resulting position on the periodic table.

By now you should see the connection between the quantum number allowable values and real chemistry. The rules specify the maximum number of electrons in each shell (2, 8, 8, 18, 18, 32…). Remember that after $n = 2$, a "shell" does not correspond to a principal quantum number. When $n = 3$, there are three types of orbitals: the s, p, and d orbitals. Only $3s$ and $3p$ are found in the argon subshell. The $3d$ orbitals are found with the $4s$ and $4p$ orbitals in the krypton subshells. Figure 2.8 in this unit shows the relationship between the orbitals and the periodic table of the elements. *The periodic table is not an arrangement created by chemists. It is the natural outcome of the application of the quantum number rules.*

Go over Examples 7.9 to 7.12 in your textbook and their practice exercises. There are two other useful facts you need to know at this stage.

- Electrons with higher principal quantum numbers experience two opposing forces. They are attracted by the nucleus, but they are also repelled by the inner electrons and by each other. The effect of this repulsion is to weaken the "effective nuclear charge" experienced by the outer electrons. This effect is sometimes called "shielding" or "screening," and its net result is that outer electrons are held less tightly and are thus more active chemically than they would otherwise be.

- The electrons that lie outside the highest completed noble gas shell primarily govern the chemical behaviour of the element. They are known as **valence electrons**.

Use the summary at the end of Chapter 7 in your textbook to ensure that you have covered all the relevant aspects of the structure of the atom.

Periodicity

Development of the Periodic Table

Study Section 8.1 of your textbook. You do not need to memorize exact details of Mendeleev's periodic table, however, you should be able to explain why it was accepted as valid by the scientists of the time. First, Mendeleev did not assign elements to a position on his periodic table solely by atomic weight. If he had, then iodine (modern atomic weight 126.9) would occur before tellurium (modern atomic weight 127.6). Mendeleev avoided such incongruous placements by considering chemical properties. Iodine obviously belongs in Group 7A. Mendeleev's reasons were wrong; he thought that the atomic weights of these elements would be found to be incorrect. However, his overall assumption about placement was correct. The second reason that Mendeleev's periodic table "worked" was that he left gaps in the table for as yet undiscovered elements. This allowed elements such as titanium to be placed in Group 4B, by leaving a gap for element number 21 preceding Ti. Mendeleev predicted the properties of a number of undiscovered elements, and his predictions were later found to be remarkably accurate.

Periodic Classification of the Elements

Study Section 8.2 of your textbook and become familiar with terms such as lanthanides, actinides, noble gas, transition metals, and representative elements. Figure 2.9 in this unit shows how the periodic table would look if the lanthanides and actinides were not listed separately but were included in the body of the table. You can easily see what an impractical shape the periodic table would then take. Almost all chemistry textbooks have a periodic table on the inside front cover. If the periodic table of Figure 2.9 were routinely used, your textbook might end up being peculiarly wide and short.

Work through Example 8.1 in your textbook and its practice exercise.

1A	2A	3B	4B	5B	6B	7B	8B	8B	8B	1B	2B	3A	4A	5A	6A	7A	8A
H 1																	He 2
Li 3	Be 4											B 5	C 6	N 7	O 8	F 9	Ne 10
Na 11	Mg 12											Al 13	Si 14	P 15	S 16	Cl 17	Ar 18
K 19	Ca 20	Sc 21	Ti 22	V 23	Cr 24	Mn 25	Fe 26	Co 27	Ni 28	Cu 29	Zn 30	Ga 31	Ge 32	As 33	Se 34	Br 35	Kr 36
Rb 37	Sr 38	Y 39	Zr 40	Nb 41	Mo 42	Tc 43	Ru 44	Rh 45	Pd 46	Ag 47	Cd 48	In 49	Sn 50	Sb 51	Te 52	I 53	Xe 54
Cs 55	Ba 56	La 57	Hf 72	Ta 73	W 74	Re 75	Os 76	Ir 77	Pt 78	Au 79	Hg 80	Tl 81	Pb 82	Bi 83	Po 84	At 85	Rn 86
Fr 87	Ra 88	Ac 89	104	105													

Ce 58	Pr 59	Nd 60	Pm 61	Sm 62	Eu 63	Gd 64	Tb 65	Dy 66	Ho 67	Er 68	Tm 69	Yb 70	Lu 71
Th 90	Pa 91	U 92	Np 93	Pu 94	Am 95	Cm 96	Bk 97	Cf 98	Es 99	Fm 100	Md 101	No 102	Lr 103

Figure 2.9 Modified version of the periodic table with the inner transition elements (i.e., the lanthanides and the actinides) included within the body of the table. Note the unworkable width of the table and the loss of detail compared to that normally found in a periodic table.

Periodic Trends

Physical Properties

Study Section 8.3 in your textbook, which explains the general trend to decreasing atomic size across a period in the periodic table. This trend is sometimes referred to as a **periodic contraction**. You should be able to explain why atomic size decreases across a period and increases down a group. You should also know why a cation is smaller than its corresponding atom, while an anion is larger than its corresponding atom. Try the following example, in which you apply these ideas.

Problem: Arrange each of the following sets in order of increasing size.

    a.   Li, Na, K

    b.   P, Cl, S

    c. O^+, O^-, O

    d.   Ar, K^+, Cl^-, Ca^{2+}, S^{2-}

Solution:

    a.   Li < Na < K because K has a greater number of shells ($n = 4$) than Na ($n = 3$) than Li ($n = 2$).

    b.   Cl < S < P because of periodic contraction—Cl has a more effective nuclear charge than S and than P, therefore its outer electrons are more tightly held.

    c. $O^+ < O < O^-$ because all have 8 protons, but O^- has 9 electrons (O has 8, O^+ has 7) and therefore a less effective nuclear charge.

    d. $Ca^{2+} < K^+ < Ar < Cl^- < S^{2-}$ because all are **isoelectronic** (have the same number of electrons, namely 18) but Ca^{2+} has 20 protons pulling on the outer electrons and, therefore, has the most effective nuclear charge.

Now try Examples 8.2 and 8.3 from your textbook, and their practice exercises.

Ionization Energy

Study Section 8.4 of your textbook. Ionization energy is an important property of an atom. You should understand what it is and how it varies as you go across the periods, and also down the groups, in the periodic table. Figure 2.10 in this unit expands part of Figure 8.11 in your textbook and gives a simple explanation of the periodic trend of ionization potential. This simple explanation depends mainly on stability of filled and half-filled subshells. Like most simple explanations, it is not complete. However, it will give you a straightforward method of understanding the periodicity of ionization potential and the relationship of ionization energies to chemical properties. The difference between a transition metal and a nontransition metal can now be explained in terms of ionization energy. The first ionization of a transition metal always removes a $4s$ electron for the elements Sc through Zn (it would be a $5s$ electron for Y through Cd, etc.). Since it is always one of the s electrons removed in the first ionization of these elements, the first ionization energies and, hence, the chemical properties are similar.

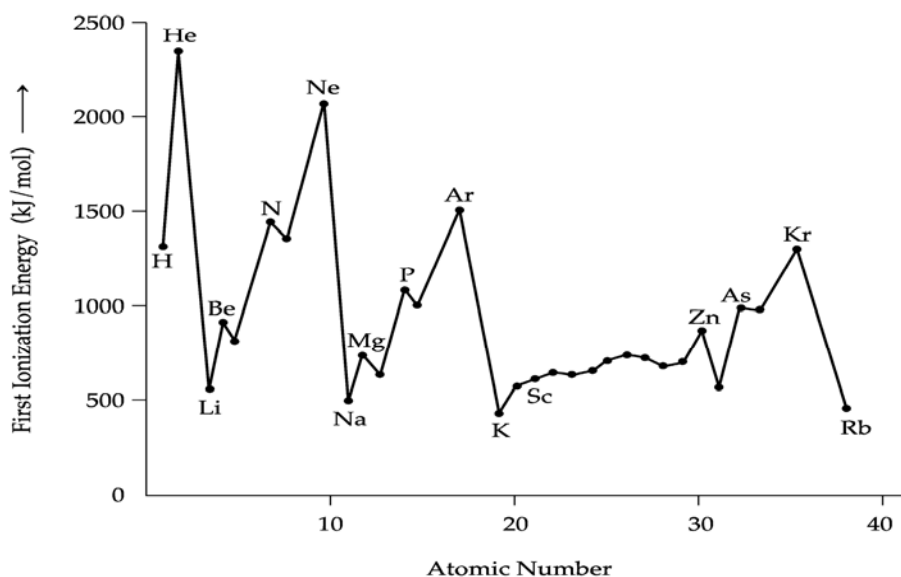Now do Example 8.4 in your textbook and its practice exercise.

Figure 2.10: First ionization energies (ionization potentials) of the first thirty-seven elements. If you remember that filled and half-filled subshells are particularly stable, you should be able to interpret this graph. The greatest ionization energies are required to remove an electron from one of the noble gases (He, Ne, Ar, and Kr) which have full subshells and full shells. The least ionization energy is required to remove an electron from an alkali metal (Li, Na, K, Rb) where loss of the s^1 electron leads to

the stable noble gas configuration. Within each period, there is an increase of ionization energy as atomic number increases. The exceptions to this increase are for those elements with filled or half-filled subshells (e.g., Be with $2s^2$ and N with $2p^3$). The extra stability of filled or half-filled subshells means that slightly more energy is required to remove the electron. The same exceptions show up in the next short period with Mg and P ($3s^2$ and $3p^3$). The transition metals, Sc to Zn, show a similar but more gradual increase in ionization energy. That is, their atomic number increases and they exhibit the same type of exceptions as do elements that possess filled or half-filled subshells. Therefore, they have slightly greater stability.

Electron Affinity

Study Section 8.5 in your textbook. The definition given states that electron affinity is the energy change when a gaseous atom accepts an electron.
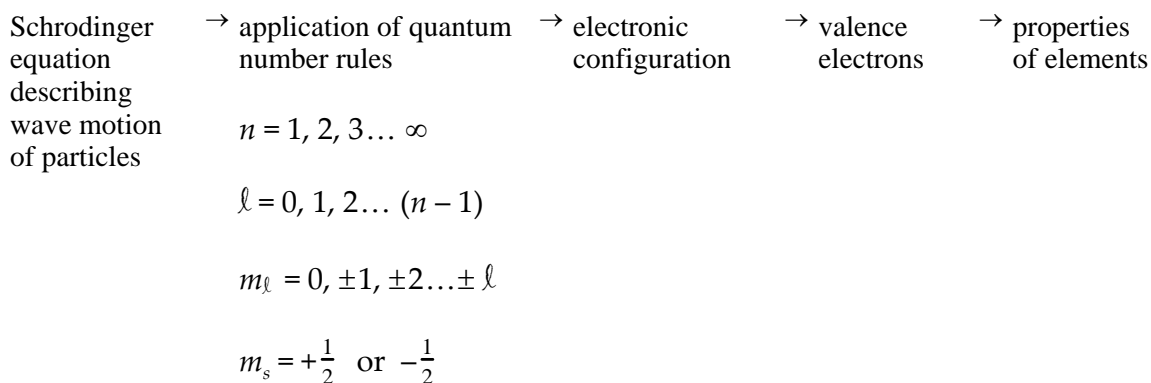
$$\text{X}(g) + e^- \longrightarrow \text{X}^-(g)$$
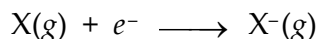
Read the explanation carefully and note that when change in enthalpy (ΔH, or heat energy) for the process is negative (energy released), the electron affinity is *defined* as positive. Also note the trends in electron affinities as shown in Table 8.3 in your textbook; especially the very low values for the alkali earth metals and noble gases compared to the halogens. This is easily explained by the halogen atoms releasing large amounts of heat energy when they accept an electron and complete their outer shell (a favourable exothermic process, *negative* ΔH and *positive* electron affinity). In contrast, the most alkaline earth metals and noble gases require energy to place the added electron in a higher orbital (*positive* ΔH and *negative* electron affinity).

Try Example 8.5 from your textbook and its practice exercise.

Chemical Properties

Read Section 8.6 in your textbook. This section addresses the correlation between properties of compounds and elements with the position of their elements in the periodic table. The correlation is important, and it is a continuation of the relationship between electronic configuration and the periodic table. However, at this stage you do not need to remember all the details of the chemistry of these elements.

This unit explains the relationship between atomic structure and properties of an element. Atomic structure, or at least the way the electrons are arranged in the atomic structure, can be derived by application of the rules for allowable values of the quantum numbers. These rules themselves result from solutions of the **Schrodinger equation**. This equation describes the wave properties of electrons bound by a positive nucleus. You might find the following diagram useful in understanding how properties of elements can be considered the end result of the application of quantum mechanics.

Schrodinger equation describing wave motion of particles $\rightarrow$ application of quantum number rules $\rightarrow$ electronic configuration $\rightarrow$ valence electrons $\rightarrow$ properties of elements

$$n = 1, 2, 3 \ldots \infty$$

$$\ell = 0, 1, 2 \ldots (n - 1)$$

$$m_\ell = 0, \pm 1, \pm 2 \ldots \pm \ell$$

$$m_s = +\frac{1}{2} \quad \text{or} \quad -\frac{1}{2}$$

Use the summary at the end of Chapter 8 to ensure that you know the basic concepts explained there.

Self-Assessment

Having reached the end of Unit 2, you should be able to:

- Describe the observations and experiments that led to the theory of the nuclear atom and the atomic structure.

- Explain Bohr's theory of the hydrogen atom structure and its relationship to the atomic spectrum of hydrogen.

- Perform calculations involving wavelengths, velocities, frequencies, and energies of electromagnetic radiation in atomic spectroscopy.

- Explain terms such as quantum, Heisenberg uncertainty principle, wave nature of matter, Schrodinger wave equation, orbital, and probability as applied to atomic structure.

- Perform calculations using the de Broglie relationship and explain the significance of the answers.

- Use the quantum number rules to determine the allowable values of quantum numbers and hence relate these to the arrangement of electrons in atoms.

- Describe the correct electronic configurations and energy level diagrams for the first 36 elements and give "good guess" electronic configurations and energy level diagrams for the other elements.

- Describe periodic trends of ionization potential, electron affinity, and atomic and ionic size.

- Explain Mendeleev's contribution to the modern periodic table.

- Describe the modern periodic table and know the names given to the various groups, transition metals, and periods.

- Discuss trends in chemical and physical properties in the periodic table.

Practice Exercise 2

Finish working through Unit 2 before starting this practice exercise which is found listed under the Practice Exercises section of course. The material in Unit 2 is integrated throughout the practice exercise. The solutions to these problems will be provided once you have completed this practice exercise.

You may want to first try some of the supplementary exercises suggested under the next heading. However, if you feel that you have a reasonable understanding of the material, you can begin the practice exercise immediately. If you have no difficulties with this practice exercise, begin Assignment 2. If you feel that you need more practice, go to the Suggested Supplementary Exercises that follow.

You should make a serious attempt to solve the practice exercise problems by yourself, using as a guide similar examples given in the textbook and in this unit. If your attempt is serious, you will learn a lot more from the worked solutions in the Solutions to Practice Exercise 2 section of the Course Units.

Suggested Supplementary Exercises

At the end of each chapter in your textbook are further exercises on the material covered. We suggest that you do as many of these exercises as necessary. Doing such problems helps you understand and apply the principles involved in the concepts discussed. Fully worked solutions for all even-numbered problems are given in the *Student Solutions Manual*, by B. J. Cruickshank and Raymond Chang. Some of the even-numbered exercises at the end of the chapter have their answers in the back of the textbook. If you decide to try the odd-numbered problems and need help, consult your Open Learning Faculty Member.

Important: You should make a serious attempt to solve a problem by yourself before looking at a worked solution.

From Chapter 7:

7.8, 7.12, 7.16, 7.20, 7.28, 7.30, 7.32, 7.34, 7.40, 7.54, 7.56, 7.58, 7.60, 7.62, 7.64, 7.68, 7.76, 7.78, 7.84, 7.86, 7.88, 7.90, 7.98, 7.120, 7.130

From Chapter 8:

8.20, 8.22, 8.24, 8.26, 8.28, 8.30, 8.32, 8.38, 8.42, 8.44, 8.46, 8.48, 8.52, 8.54, 8.56, 8.62, 8.64, 8.68, , 8.82, 8.84, 8.86, 8.88, 8.90, 8.92, 8.110, 8.120

Assignment 2

Now refer to your *Assignments* and complete Assignment 2. Consult your Course Guide for the week this assignment is due.

You may send the assignment to your Open Learning Faculty Member using the assignment tool in Blackboard or by mail with a Marked Assignment Form.

Be sure to keep a copy of the assignment—it will be useful if you wish to discuss your work with your Open Learning Faculty Member.