2 THE STRUCTURE OF ATOMS

The remarkable advancement of science in the first half of the 20th century was characterized by parallel developments in theory and experiment. It is indeed exciting to follow that scientific advancement because we are able to see clearly several jumps in this development. Indeed the progression from the discovery of the electron, to the quantum theory of Planck, to the discovery of the atomic nucleus by Rutherford, to the Bohr theory, to the introduction of the quantum-mechanical theory stimulated intellectual excitement.

In chemistry, the establishment of the general ideas of orbitals and electron configurations has had particular significance. These ideas may be judged to be both the modernization and the completion of atomic theory.

2.1 Discovery of electrons

According to Dalton and scientists before him, the atom is the indivisible, ultimate microscopic component that constitutes matter. Thus, no scientist prior to the beginning of the 19th century considered that an atom might have a structure, in other words, that an atom is also constituted by smaller components.

The belief in the indivisibility of the atom began to waver because of the development of a deeper understanding of the relation between matter and electricity, not because scientists had become suspicious of its indivisibility. You can study the chronological progress in the understanding of the relation between matter and electricity.

Table 2.1 Progress of understanding the relation between matter and electricity

year	events
1800	discovery of the electric pile (Volta)
1807	isolation of Na and Ca by electrolysis (Davy)
1833	discovery of the law of electrolysis (Faraday)
1859	discovery of cathode rays (Plücker)
1874	naming the electron (Stoney)
1887	theory of ionization (Arrhenius)
1895	discovery of X rays (Röntgen)
1897	proof of the existence of the electron (Thomson)
1899	determination of *e*/*m* (Thomson)
1909-13	oil drop experiment (Millikan)

Faraday contributed significantly. He discovered that the amount of substance produced at the poles during electrolysis (the chemical change when electric current is passed through a solution of electrolytes) was proportional to the amount of electric current. He also found in 1833 that the amount of electricity required to produce 1 mole of substance at the electric poles is constant (96,500 C). These relations were summarized as **Faraday's law of electrolysis**.

Faraday himself had no intention to combine his law with the atomic theory. However, the Irish chemist George Johnstone Stoney (1826-1911) had the insight to notice the significance of Faraday's law for the structure of matter; he concluded that a fundamental unit of electricity exists, in other words, an atom of electricity. He dared to give the name **electron** to that hypothetical unit.

Then another interesting finding emerged due to vacuum discharge experiments. When cations hit the anode upon application of high voltage at low pressure (lower than 10^{-2} - 10^{-4} Torr[a)]), the gas in the tube, although it was an insulator, became conductive and emitted light. When the vacuum

[a)] Torr is a unit of the pressure that is often used to describe the degree of vacuum. 1 Torr = 133.3224 Pa)

was increased, the wall began to glitter, emitting fluorescent light (Fig. 2.1). The German physicist Julius Plücker (1801-1868) took interest in this phenomenon and interpreted it as follows: some particles are being emitted from the cathode. He gave the name **cathode ray** to these unidentified particles (1859).

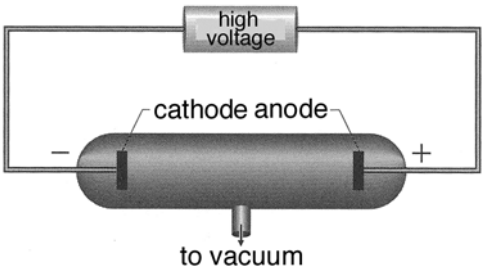


Fig. 2.1 Discovery of the cathode ray
The cathode ray generated in a vacuum tube when a high vacuum was applied provided very significant information on the structure of the atom.

This unidentified particle would, after being emitted from the cathode, fly straight toward the wall of the tube or to the anode. It was found that the particle was charged since its course of flight was curved when a magnetic field was applied. Furthermore, the properties of the ray did not depend on the type of metal used in the cathode tube, nor on the type of gas in the discharge tube. These facts suggested the possibility that the particle could be a fundamental constituent of matter.

The British physicist Joseph John Thomson (1856-1940) showed that the particle possessed negative charge. He further sought to determine the mass and the charge of the particle by estimating the effect of electric and magnetic fields on the motion of the particle. He obtained the ratio of the mass to the charge. To obtain their absolute values, one of the two had to be determined.

The American physicist Robert Andrew Millikan (1868-1953) successfully proved by an ingenious experiment the particulate nature of electricity. The experiment is called Millikan's **oil drop experiment**. Droplets of oil atomized in a chamber fall under the influence of gravity. If the oil droplet has an electric charge, its motion may be controlled by countering gravity with an electric attraction applied by an electric field. The combined motion can be analyzed by classical physics. Millikan demonstrated by these experiments that the charge of an oil drop is always an integral multiple of 1.6×10^{-19} C. This fact led to a neat explanation by attributing the charge of 1.6×10^{-19} C to the electron.

The charge/mass ratio of the charged particle so far known was *ca.* 1/1000 (C/g). The ratio Thomson obtained was much larger than that (the accurate value now accepted is as large as 1.76×10^{8} C/g), and that finding was not in the framework of the knowledge at that time. The particle should not be a kind of ion or molecule, but should be regarded as a part or fragment of an atom.

Sample Exercise 2.1 Calculation of the mass of an electron.

Calculate the mass of an electron using the experimental values obtained by Millikan and by Thomson.

Solution

You can obtain the solution by substituting the value obtained by Millikan for the relation: charge/mass = 1.76×10^{8} (C g^{-1}). Thus,

$m_e = e/(1.76 \times 10^{8}\ \mathrm{C\ g^{-1}}) = 1.6 \times 10^{-19}\ \mathrm{C}/(1.76 \times 10^{8}\mathrm{C\ g^{-1}}) = 9.1 \times 10^{-28}$ g

The electric charge possessed by an electron (the elementary electric charge) is one of the universal constants of nature and of great importance.

Sample Exercise 2.2 The ratio of the mass of an electron and that of a hydrogen atom.

Calculate the ratio of the mass of an electron and that of a hydrogen atom.

Solution

The mass m_H of a hydrogen atom is: $m_H = 1g/6 \times 10^{23} = 1.67 \times 10^{-24}g$. Hence, $m_e : m_H = 9.1 \times 10^{-28}g : 1.67 \times 10^{-24}g = 1 : 1.83 \times 10^3$

It is remarkable that the mass of the electron is extremely small. Even the lightest atom, hydrogen, is *ca.* 2000 times as heavy as an electron.

2.2 Atomic model

(a) The size of an atom

As mentioned in the previous section, the supposed indivisibility of the atom became gradually suspect. At the same time, concern as to the structure of an atom gradually became intense. If one considers the structure of an atom, its size should also be considered. It was already known that an approximation for the volume of an atom could be estimated by dividing the volume of 1 mol of solid by Avogadro's constant.

Sample Exercise 2.3 The volume of one molecule of water

Assuming that the water molecule is a cube, calculate the length of an edge of this cube. Using the value obtained, estimate the approximate size of an atom in terms of powers of ten.

Solution

The volume of 1 mole of water is approximately 18 cm^3. Thus, the volume of 1 molecule of water v is: $v = 18\ cm^3/6 \times 10^{23} = 3 \times 10^{-23}\ cm^3 = 30 \times 10^{-24}$ cm. The length of an edge is $\sqrt[3]{30} \times 10^{-8}$ cm $= 3.1 \times 10^{-8}$ cm. This indicates that the size of an atom is in the order of 10^{-8} cm.

Thomson assumed that an atom with such a dimension is a positively charged, uniform sphere and that negatively charged tiny electrons are scattered within the sphere. In this context, Thomson's model is called "the raisin bread model"; the raisins being the electrons and the atom the bread.

(b) Discovery of the atomic nucleus

After having made remarkable achievements in the study of radioactivity, the British physicist Ernest Rutherford (1871-1937) became interested in the structure of atoms from which radioactivity radiated. He bombarded a thin metallic foil (thickness of 10^4 atoms) with parallel streams of α particles (later it was found that the α particle is the atomic nucleus of He). He planned to determine the angles of scattered particles by counting the number of scintillations on a ZnS screen (Fig. 2.2). The results were extremely interesting. Most of the particles passed directly through the foil. Some particles rebounded. To explain this unexpected phenomenon, Rutherford proposed the idea of a nucleus.

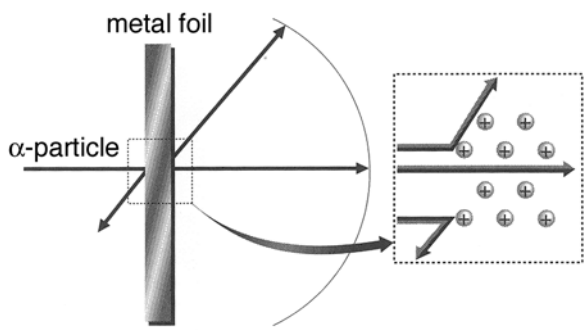


Fig. 2.2 Scattering experiment of α particles by Rutherford

It was very strange to find that some particles rebounded, and sometimes some even directly backward. He conceived that a particle must exist in the atom that has a mass large enough to repel an α particle possessing the mass of a helium atom, and which has an extremely small radius.

According to his idea, the positive charge of an atom is concentrated in a small central part (with a radius calculated to be *ca.* 10^{-12} cm) while the negative charge could be dispersed through the whole atom. The small particle at the center of the atom he named **nucleus**. All previous models of atoms as uniform spheres were thus denied.

However, the atomic model of Rutherford which consisted of a small nucleus with electrons dispersed around it could not explain all known phenomena. If the electrons did not move, they would join the nucleus by electrostatic attraction (Coulomb force). That was impossible because an atom is a stable entity. If the electrons circle the nucleus like planets under the influence of gravity, the electrons will undergo acceleration and lose energy through electromagnetic radiation. As a result, their orbits will diminish so that the electrons eventually fall into the nucleus. Meanwhile, the atom should emit a continuous spectrum. But again, the fact is that atoms are stable, and it was already known that atoms emit a group of line spectra (atomic spectrum; *cf* Ch. 2.3(a)) rather than a continuous spectrum. It was clear that a fundamental change in thought was necessary to explain all these experimental facts.

2.3 Foundation of classical quantum theory

(a) Atomic spectrum

If a metal or one of its compounds is heated in the flame of a burner, a color characteristic of the metal appears. This is the well-known **flame reaction**. If the colored light is separated by means of a prism, a few strong line spectra are observed, and the wavelength of each line is characteristic of the metal involved. For instance, the yellow flame reaction of Na corresponds to two yellow lines of its spectrum in the visible region, and the wavelengths of these two lines are 5.890 x 10^{-7} m and 5.896 x 10^{-7} m, respectively.

If a gas is sealed in a high vacuum tube, and a high voltage is applied, the gas discharges and emits light. Separation of this light by means of a prism will give a series of discontinuous line spectra. Since the wavelengths of this light are characteristic of the atom, the spectrum is called its **atomic spectrum.**

The Swiss physicist Johann Jakob Balmer (1825-1898) separated the light emitted during discharge from low-pressure hydrogen. He realized that the wavelength λ of a series of spectral lines could accurately be expressed by a simple equation (1885). The Swedish physicist Johannes Robert Rydberg (1854-1919) found that the wavenumber[a)] σ of a spectral line could be expressed by an equation as indicated below (1889).

$$\sigma = 1/\lambda = R\{(1/n_i^2) - (1/n_j^2)\}\text{cm}^{-1} \qquad (2.1)$$

where n_i and n_j are positive integer ($n_i < n_j$) and R is a constant characteristic of the given gas. For hydrogen it is 1.09678 x 10^7 m^{-1}.

Generally the wavenumbers of the spectral lines of hydrogen atom can be expressed by the difference of two terms, R/n^2. The spectra of atoms other than hydrogen are much more complicated, but their wavenumbers are also expressed by the difference of two terms.

(c) The Bohr theory

At the end of the 19th century, physicists had difficulty in understanding the relation between the wavelengh of radiation from a heated solid and its relative intensity. There was some disagreement between the prediction based on the theory of electromagnetism and the experimental results. The German physicist Max Karl Ludwig Planck (1858-1947) attempted to solve the problem, which had annoyed physicists of the day, by introducing a novel hypothesis which was later called the **quantum hypothesis** (1900).

According to his theory, a physical system cannot have arbitrary quantities of energy but is

[a)] The number of waves contained in a unit length (*e.g.,* per 1 cm)

allowed only to have discontinuous quantities. By thermal radiation, that is, the radiation of energy as electromagnetic waves from a substance, an electromagnetic wave with the frequency ν from the surface of solid is generated from an oscillator that oscillates at the surface of the solid with that frequency. According to Planck's hypothesis, the energy of this oscillator can only have discontinuous values as depicted by the following equation.

$$\varepsilon = nh\nu \ (n = 1, 2, 3, ...) \qquad (2.2)$$

where n is a positive integer and h is a constant, 6.626 x 10^{-34} J s, which is called **Planck's constant**.

The novel idea that energy is a discontinuous quantity was not easily accepted by the scientists of the day. Planck himself regarded what he proposed as a mere hypothesis only necessary for solving the problem of radiation from a solid. He had no intention to expand his hypothesis to a general principle.

The phenomenon of emission of electrons from the surface of a photo-irradiated metal is called the **photoelectric effect**. For a given metal, emission will take place only when the frequency of the irradiated light is above a certain value characteristic of that metal. The reason for this was not known at that time. Einstein was able to explain this phenomenon by applying the quantum hypothesis to the photoelectric effect (1905). Around that time, scientists began to believe that the quantum hypothesis was a general principle governing the microscopic world.

The Danish physicist Niels Hendrik David Bohr (1885-1962) attempted to combine Planck's quantum hypothesis with classical physics to explain the discontinuity of atomic spectra. Bohr made several assumptions as given below and in Fig. 2.3.

The Bohr theory

(i) Electrons in atoms are allowed to be in certain stationary states. Each stationary state is associated with a definite energy.
(ii) No energy emissions occur while an electron is in a stationary state. When it moves from a high-energy stationary state to a low-energy stationary state (a transition), an emission of energy takes place. The amount of energy, $h\nu$, is equal to the energy difference between the two stationary states.
(iii) In any stationary state, an electron moves in a circular orbit around the nucleus.
(iv) An electron is allowed to move with an angular momentum that is an integral multiple of $h/2\pi$, *i.e.*,

$$mvr = n(h/2\pi), \ n = 1, 2, 3, ... \qquad (2.3)$$

The energy of an electron belonging to a hydrogen atom can be calculated using these hypotheses. In classical mechanics, the electrostatic force exerted on an electron and the centrifugal force exerted on it are balanced. Hence,

$$e^2/4\pi\varepsilon_0 r^2 = mv^2/r \qquad (2.4)$$

in Eqs. 2.3 and 2.4, e, m and v are the electric charge, mass and velocity of the electron, respectively (the subscript e is omitted for simplicity), r is the distance between the electron and the nucleus, and ε_0 is the dielectric constant of a vacuum, 8.8542 x 10^{-2} C^2 N^{-1} m^2.

Sample Exercise 2.4 The radius of electron orbit in hydrogen

Derive an equation to determine the radius of orbit r for the electron in a hydrogen atom from Eqs. 2.3 and 2.4. Consider the meaning of the equation you derived.

Solution

$mvr = nh/2\pi$ may be changed to $v = nh/2\pi mr$. By substituting this into Eq. 2.4, you can obtain

the equation below.

$$e^2/4\pi\varepsilon_0 r^2 = mn^2h^2/4\pi^2m^2r^3$$

$$\therefore\ r = n^2\varepsilon_0 h^2/(2\pi)^2 me^2,\ n = 1, 2, 3,... \qquad (2.5)$$

Eq. 2.5 shows the restriction that only discontinuous values (quantization) are allowed for *r*-values. Here the value *n* is called the **quantum number**.

The radius *r* can be expressed as shown below.

$$r = n^2 a_B,\quad n = 1, 2, 3,... \qquad (2.6)$$

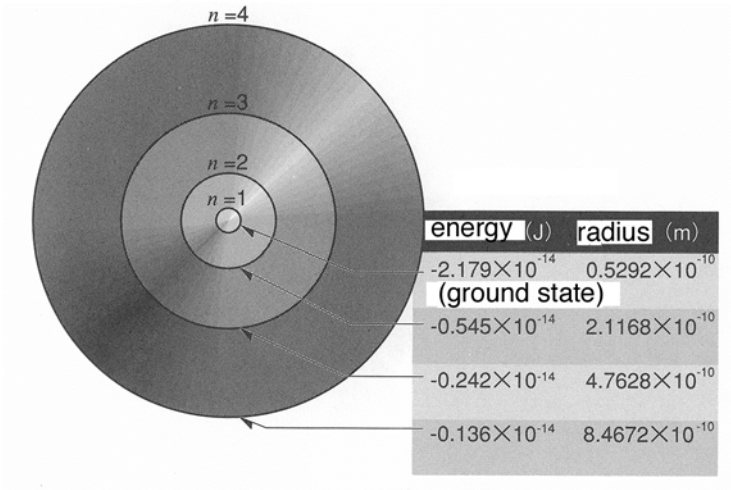


Fig. 2.3 The Bohr model.
Electrons are rotating in a circular orbit around the nucleus.
The values of the radius are discontinuous, and can be predicted by the Bohr theory

In this equation, a_B is the minimum radius when *n* is 1. This value, 5.2918 x 10^{-11} m, is called the **Bohr radius**.

The energy that the electron in a hydrogen atom possesses is the sum of its kinetic energy and potential energy. Thus,

$$E = mv^2/2 - e^2/4\pi\varepsilon_0 r \qquad (2.7)$$

Sample Exercise 2.5 Energy of the electron in a hydrogen atom.

Using Eqs. 2.3 and 2.4, derive an equation which does not contain *v* to express the energy of the electron in a hydrogen atom.

Solution

Eq. 2.4 can be converted into $mv^2 = e^2/4\pi\varepsilon_0 r$. By substituting this equation into Eq. 2.7, you can obtain the following equation after appropriate rearranging.

$$E = -me^4/8\varepsilon_0^2 n^2 h^2、\quad n = 1, 2, 3... \qquad (2.8)$$

Surely the energy of an electron can have only discontinuous values, each determined by the *n* value.

The reason why the *E* value is negative is as follows. The energy of the electron in an atom is lower than that of an electron that is not bound to a nucleus. Such electrons are called **free electrons**. The most stable stationary state of an electron corresponds to the state with *n* = 1. As *n* increases, the energy is decreases in absolute value and approaches zero.

(c) Atomic spectra of hydrogen

According to the Bohr theory, the energy of electromagnetic radiation emitted from the atom corresponds to the energy difference between two stationary states *i* and *j*. Thus,

$$\Delta E = h\nu = |E_j - E_j| = (2\pi^2 me^4/\varepsilon_0^2 h^2)\ [(1/n_i^2) - (1/n_j^2)] : \quad n_j > n_i \tag{2.9}$$

The wavenumber of electromagnetic radiation is given below:

$$\therefore \nu = me^4/8\varepsilon_0^2 n^2 h^3)\ [(1/n_i^2) - (1/n_j^2)] \tag{2.10}$$

The constant term calculated for the case of $n_j = 2$ and $n_i = 1$ is found to be identical with the value previously obtained by Rydberg for the hydrogen atom (*cf.* Eq. 2.1). The value theoretically obtained by Bohr (1.0973×10^{-7} m^{-1}) is called the **Rydberg constant** R_∞. A series of frequency values calculated by putting n_j = 1, 2, 3, … corresponds to the frequency of electromagnetic radiation emitted by an electron which returns from an excited state to three stationary states, n = 1, n =2 and n = 3, respectively. These values obtained by calculation were values already experimentally determined values from the atomic spectra of hydrogen. The three series were named the **Lyman series**, the **Balmer series** and the **Paschen series**, respectively. This indicates that the Bohr theory can perfectly predict the atomic spectra of hydrogen. The spectra are summarized in Fig. 2.4.

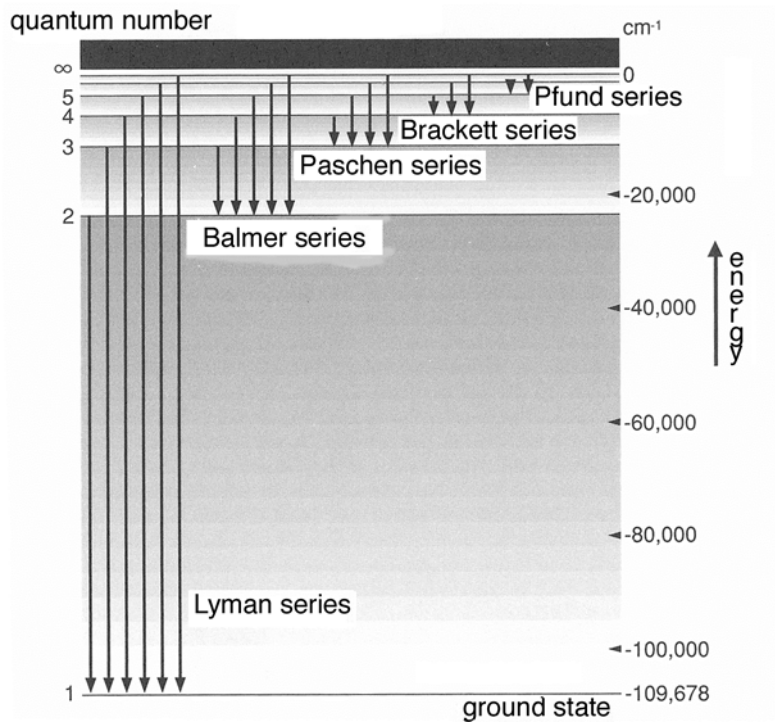


Figure 2.4 The atomic spectra of hydrogen.
The Bohr theory can explain the origin of all transitions.

(d) Moseley's law

The English physicist Henry Gwyn Jeffreys Moseley (1887-1915) found, by bombarding high-speed electrons on a metallic anode, that the frequencies of the emitted X-ray spectra were characteristic of the material of the anode. The spectra were called **characteristic X-rays**. He interpreted the results with the aid of the Bohr theory, and found that the wavelengths λ of the X-rays were related to the electric charge *Z* of the nucleus. According to him, there was the following relation between the two values (**Moseley's law;** 1912).

$$1/\lambda = c(Z - s)^2 \qquad (2.11)$$

where c and s are constants applicable to all elements, and Z is an integer.

When elements are arranged in line according to their position in the Periodic Table (*cf.* Ch. 5), the Z value of each element increases one by one. Moseley correctly interpreted that the Z values corresponded to the charge possessed by the nuclei. Z is none other than the **atomic number**.

Sample Exercise 2.6 Estimation of the atomic number (Moseley's law**)**

It was found that the characteristic X-ray of an unknown element was 0.14299 x 10^{-9} m. The wavelength of the same series of the characteristic X-ray of a known element Ir (Z = 77) is 0.13485 x 10^{-9} m. Assuming s = 7.4, estimate the atomic number of the unknown element.

Solution

First, estimate $\sqrt{c}$ from Eq. (2.1).

$$\sqrt{\frac{1}{0.13485\text{x}10^{-9}(\text{m})}} = \sqrt{c}(77 - 7.4) = 69.6\sqrt{c} \qquad \therefore\ \sqrt{c} = 1237.27$$

Then,

$$\sqrt{\frac{1}{0.14299\text{x}10^{-9}(\text{m})}} = 1222(z - 7.4) \qquad \therefore\ z = 75$$

Various elements were put in order by Moseley's law according to their atomic numbers. Thanks to Moseley's law, an old problem (how many elements are there in the world?) could be solved. This is another example of the outcome of the Bohr theory.

(e) Limitation of the Bohr theory

The success of the Bohr theory was magnificent. The Bohr theory vividly envisaged the structure of a hydrogen atom, with an electron rotating around the central nucleus in a circular orbit. It soon became clear that there was a limitation in the theory. After various improvements, the Bohr theory could manage to explain the atomic spectra of hydrogen-like atoms with one electron such as helium ion He^+. However, the atomic spectra of poly-electronic atoms could not be explained. In addition, no persuasive explanation for the chemical bond was obtained.

In other words, the Bohr theory was one step toward a theory of atomic structure that could be applicable to all atoms and chemical bonds. The significance of his theory should not be underestimated since it clearly demonstrated the necessity of quantum theory to understand atomic structure, and more generally, the structure of matter.

2.4 The birth of quantum mechanics

(a) The wave nature of particles

In the early half of the 20th century, it was noticed that electromagnetic waves, previously treated only as waves, seemed to behave sometimes as particles (photons). The French physicist Louis Victor De Broglie (1892-1987) assumed that the contrary might be true, in other words, that matter also can behave as a wave. Starting from Einstein's equation, $E = cp$ where p is the momentum of a photon, c the velocity of light and E is the energy, he obtained the following relation:

$$E = h\nu$$
$$\nu = c/\lambda\ ; \quad hc/\lambda = E$$
$$\therefore\ \ h/\lambda = p \qquad (2.12)$$

De Broglie conceived that each particle with a momentum $p = mv$ is accompanied by a wave (**material wave**) with the wavelengh λ as defined by equation (2.12) (1924). Table 2.2 gives some examples of the wavelength of material waves calculated by equation (2.12). As the size of the particle increases, the wavelength becomes shorter. Hence with macroscopic particles, it is impossible to observe diffraction and other phenomena associated with waves. For microscopic particles like an electron, the wavelength of the material wave is observable. In fact, the diffraction of electrons was observed (1927) and proved the theory of De Broglie.

Table 2.2 The wavelengths of material waves.

particle	mass (g)	velocity (cm s^{1})	wavelength (nm)
electron (300K)	9.1×10^{-28}	1.2×10^{7}	6.1
electron at 1 V	9.1×10^{-28}	5.9×10^{7}	0.12
electron at 100 V	9.1×10^{-28}	5.9×10^{8}	0.12
He atom at 300K	6.6×10^{-24}	1.4×10^{5}	0.071
Xe atom at 300K	2.2×10^{-22}	2.4×10^{4}	0.012

Sample Exercise 2.7 Wavelength of a material waves.

A 2 g bullet is moving at the velocity of 3×10^{2} m s^{-1}. Calculate the wavelength of the material wave associated with this bullet.

Solution

Using equation (2.12) and 1 J = 1 m^2 kg s^{-2},

$$\lambda = h/mv = 6.626 \times 10^{-24} \text{ (J s)} / 2.0 \times 10^{-3}\text{(kg)} \times 3\times10^{2}\text{(m s}^{-1}\text{)}$$
$$= 1.10 \times 10^{-30} \text{ (m}^2 \text{ kg s}^{-1}\text{)} / \text{(kg m s}^{-1}\text{)} = 1.10 \times 10^{-30} \text{ m}$$

Notice that the wavelength of the material wave associated with the moving bullet is much shorter than that of an X-ray or γ ray and hence unobservable.

(b) The uncertainty principle

From what we learned about the material wave, we can notice that care must be taken when a theory of the macroscopic world is applied to the microscopic world. The German physicist Werner Karl Heisenberg (1901-1976) thought that it was impossible to determine accurately the position and momentum of a minute particle such as an electron simultaneously. In order to observe the particle, one has to irradiate the particle with light. The collision between the particle and the photon will alter the position and momentum of the particle.

Heisenberg explained that the product of the uncertainty of position Δx and of the momentum Δp would be of the order of Planck's constant as shown below.

$$\Delta x \Delta p = h \qquad (2.13)$$

This relation is called Heisenberg's **uncertainty principle**.

Sample Exercise 2.8 Uncertainty of the position of an electron.

Suppose you want to determine the position of an electron to a precision of about 5×10^{-12} m. Estimate the uncertainty of velocity under this condition.

Solution

The uncertainty of momentum is estimated by Eq. (2.13).

$$\Delta p \fallingdotseq h/\Delta x = 6.626 \times 10^{-34} \text{ (J s)} / 5 \times 10^{-12} \text{ (m)} = 1.33 \times 10^{-22} \text{ (J s m}^{-1}\text{)}$$

Since the mass of an electron is 9.1065×10^{-31} kg, the uncertainty of the velocity Δv can be

estimated as follows.[a)]

$$\Delta v \fallingdotseq 1.33 \times 10^{-22} (\mathrm{J\ s\ m^{-1}}) / 9.10938 \times 10^{-31} (\mathrm{kg}) = 1.46 \times 10^{8} (\mathrm{m\ s^{-1}})$$

The estimated uncertainty of velocity amounts to nearly half of the velocity of light (2.998 x 10^8 m s^{-1}) indicating that it is clearly impossible to determine precisely the position of an electron. Thus, imaging a distinct circular orbit for an electron is not possible.

(c) Schrödinger's equation

The Austrian physicist Erwin Schrödinger (1887-1961) proposed an idea that the De Broglie equation could be applied not only to the free motion of particles, but also to the restricted motion of particles such as electrons in an atom. By extending this idea, he formulated the system of **wave mechanics**. At the same time, Heisenberg developed a system of **matrix mechanics**. Later these two were unified into **quantum mechanics**.

In the realm of quantum mechanics, the state of a system is described by a **wave function**. Schrödinger based his theory on the idea that the total energy of a system, E[b)] could be estimated by solving an equation. Since this equation has some similarity with the equation expressing a wave in classical physics, it was called Schrödinger's **wave equation**.

The wave equation of a particle (*e.g.*, an electron) moving in one direction (*e.g.*, x direction) is given below:

$$(-h^2/8\pi^2 m)(d^2\Psi/dx^2) + V\Psi = E\Psi \qquad (2.14)$$

where m is the mass of an electron, V is the potential energy of the system as a function of coordinates, and Ψ is the wave function.

One-dimensional square-well potential

The simplest example of Schrödinger's equation is the one for an electron in a one-dimensional square-well potential. Suppose the potential energy V of an electron confined in a box (the length is a) is 0 in the box ($0 < x < a$) and ∞ outside the box. The Schrödinger equation within the box is:

$$d^2\Psi/dx^2 = (-8\pi^2 mE/h^2)\Psi \qquad (2.15)$$

$$\Psi = 0 \text{ at } x = 0 \text{ and } x = a \qquad (2.16)$$

The following equation is obtained by solving the above equations.

$$\Psi(\mathrm{x}) = (\sqrt{2/a})\sin(n\pi x/a) \qquad (2.17)$$

Note that n arouse automatically.

The wave function Ψ itself does not have any physical meaning. The square of the absolute value of Ψ, Ψ^2, is, however, a mathematical indication of the possibility to find the electron in question at a given position, and hence very important because it is related to the electron density. If the possibility of existence of the electron existing at a certain position is integrated all over the active space, the result should be unity: *i.e.*,

$$\int \Psi^2 dx = 1$$

[a)] J(joule) is defined as kg m^2 s^{-2}.

[b)] The solution of Schrödinger equation (energy) is called the Eigenvalue (Eigen = a German word meaning "own")

The energy (Eigenvalue) is

$$E = n^2h^2/8ma^2;\ \mathrm{n} = 1, 2, 3... \tag{2.18}$$

It is clear that the energy value of the particle is discontinuous.

Hydrogen-like atom

It is possible to extend the method used in the one-dimensional square-well potential and to handle a hydrogen atom or hydrogen-like atoms in general. For this purpose, the one-dimensional equation (2.14) should be expanded to three-dimensions as shown below.

$$(-h^2/8\pi^2m)\Psi\ [(\partial^2/\partial x^2) + (\partial^2/\partial y^2) + (\partial^2/\partial z^2)]\ + V(x, y, z)\Psi\ = E\Psi \tag{2.19}$$

If we define ∇^2 as shown below;

$$(\partial^2/\partial x^2) + (\partial^2/\partial y^2) + (\partial^2/\partial z^2) = \nabla^2 \tag{2.20}$$

the three-dimensional Schrödinger's equation will become as below:

$$(-h^2/8\pi^2m)\nabla^2\Psi\ + V\Psi\ = E\Psi \tag{2.21}$$

or

$$\nabla^2\Psi\ + (8\pi^2m/h^2)(E - V)\Psi\ = 0 \tag{2.22}$$

The potential energy of a hydrogen-like atom is given below where Z is the electric charge.

$$V = -Ze^2/4\pi\varepsilon_0 r \tag{2.23}$$

If you substitute Eq. (2.23) into Eq. (2.22), you will obtain the following equation.

$$\nabla^2\Psi + (8\pi^2m/h^2)\ [E + (Ze^2/4\pi\varepsilon_0 r)]\ \Psi\ = 0 \tag{2.24}$$

To sum up, the solution of this equation for the energy of hydrogen-like atoms agrees with that obtained from the Bohr theory.

Quantum number

Since an electron moves in three-dimensions, three kinds of quantum numbers (Ch. 2.3(b)), **principal quantum number**, **azimuthal quantum number** and **magnetic quantum number**, are required to express one wave function. In Table 2.3, the notation and allowed numerical values for each quantum number are summarized. The 4th quantum number, **spin magnetic quantum number** is associated with the quantization of angular momentum of an electron caused by its spinning. The axial component of angular momentum is allowed to have only two values, $+1/2(h/2\pi)$ and $-1/2(h/2\pi)$. The spin magnetic quantum number is related to these values ($m_s = +1/2$ or $-1/2$). Only this quantum number is not an integer.

Table 2.3 Quantum numbers

Name (quantum number)	symbol	allowed values
principal	n	1, 2, 3,...
azimuthal	l	0, 1, 2, 3, ...n - 1

magnetic	$m(m_l)$	0, ±1, ±2,...±1
spin magnetic	m_s	+1/2, -1/2

Instead, symbols as shown in Table 2.4 are used for these. The energy of a hydrogen or hydrogen-like atom is determined by the principal quantum number alone, and the equation expressing the energy is identical with that derived from the Bohr theory.

Table 2.4 Symbols for azimuthal quantum number

value of *l*	0	1	2	3	4
symbol	s	p	d	f	g

(d) Orbital

A wave function for an electron is called an **orbital**. If the principal quantum number is $n = 1$, there is only one value for l, *i.e.*, 0. In this case there is only one orbital, and the set of quantum numbers for this orbital is ($n = 1$, $l = 0$). When $n = 2$, two values, 0 and 1, are allowed for l. In this case there are four orbitals which are defined by the following set of quantum numbers, ($n = 2$, $l = 0$), ($n = 2$, $l = 1$, $m = -1$), ($n = 2$, $l = 1$, $m = 0$), ($n = 2$, $l = 1$, $m = +1$).

Sample Exercise 2.9 Possible numbers of orbitals.

How many orbitals are possible when $n = 3$. Show the set of quantum numbers as was done above.

Solution

The same counting is possible for the set ($n = 3$, $l = 0$) and ($n = 3$, $l = 1$). In addition, there are five orbitals associated with ($n = 3$, $l = 2$). Thus, ($n = 3$, $l = 0$), ($n = 3$, $l = 1$, $m = -1$), ($n = 3$, $l = 1$, $m = 0$), ($n = 3$, $l = 1$, $m = +1$)、($n = 3$, $l = 2$, $m = -2$), ($n = 3$, $l = 2$, $m = -1$), ($n = 3$, $l = 2$, $m = 0$), ($n = 3$, $l = 2$, $m = +1$), ($n = 3$, $l = 2$, $m = +2$). Altogether there are 9 orbitals.

An abbreviation to describe orbitals by principal quantum numbers and symbols shown in Table 2.4 is widely used. For instance the orbital with a set of quantum numbers ($n = 1$, $l = 0$) is designated as 1s, and orbitals with a set of quantum number ($n = 2$, $l = 1$) to 2p regardless of the value of m.

It is difficult to express Ψ visually since it is a mathematical formula. However, Ψ^2 represents the probability of finding an electron within a definite distance around the nucleus. If the probability thus obtained is plotted, you can obtain Fig. 2.5. The spherical picture is called an **electron cloud**.

Figure 2.5 Electron cloud.
The probability of finding an electron will become smaller as the distance from the nucleus is larger. (a) 1s orbital of hydrogen. (b) 2s orbital of hydrogen.

If we give a boundary to the electron cloud so that the probability of finding an electron within

the boundary is, say, 95% confidence level, we can approximately visualize orbitals as shown in Figure 2.6.

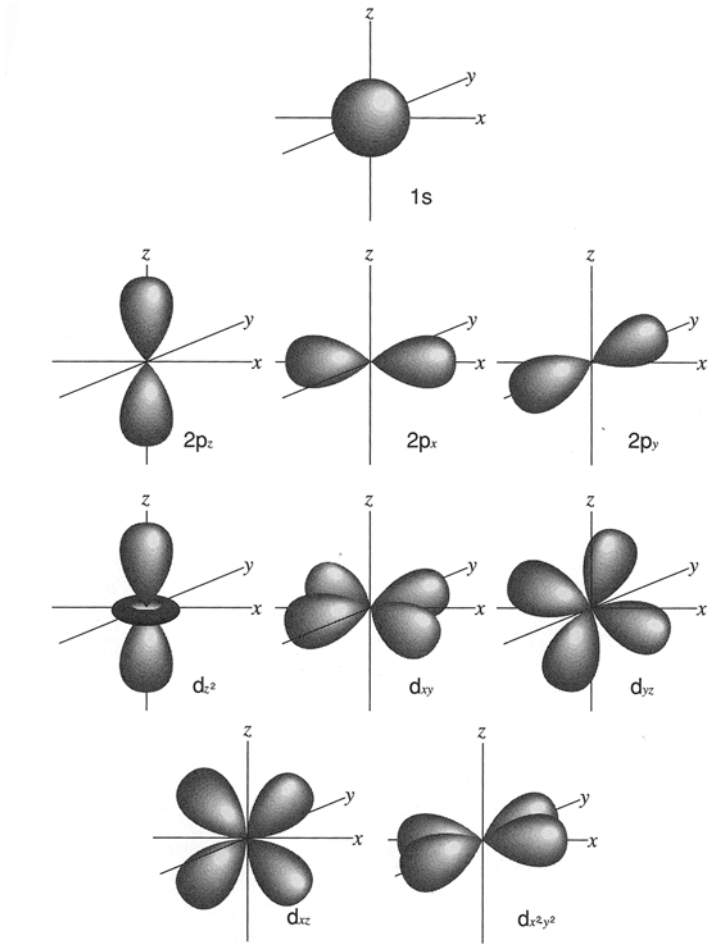


Figure 2.6 Visualization of orbitals.
The boundary of orbitals of hydrogen and hydrogen-like atoms can be drawn at any percentage of confidence you like.

Electron configuration of atoms

When an atom contains more than two electrons, interactions among the electrons should be taken into consideration, and it would be very difficult to solve the wave equation of such a complex system. If it is assumed that each electron in a poly-electronic atom will move in an averaged, spherically symmetric electric field, the orbital for each electron can be defined by three quantum numbers n, l and m plus spin magnetic quantum number m_s, as is the case with hydrogen-like atoms. The energy of hydrogen-like atoms is determined solely by the principal quantum number n, but that of poly-electronic atoms is mainly determined by n and l. If the atoms have the same n value, the larger that l is, the higher the energy.

Pauli's exclusion principle

According to the **Pauli's exclusion principle**, only one electron in the atom is allowed to occupy a state defined by a set of four quantum numbers, or, at most two electrons can occupy an orbital defined by three quantum numbers n, l and m. The two electrons should have different m_s *i.e.*, these are in **spin antiparallel** states, and such a pair of electrons is named an **electron pair**.

A group of electrons with the same n value is called a shell or an **electron shell**. The notation used in Table 2.5 will be used for electron shells.

Table 2.5 Symbols of electron shells.

n	1	2	3	4	5	6	7
symbol	K	L	M	N	O	P	Q

Table 2.6 summarizes the maximum number of electrons in each shell, from shell K to shell N. When an atom is in the most stable state, the **ground state**, its electrons will occupy an orbital with lower energy, following the Pauli principle.

Table 2.6 The maximum number of electrons occupying each shell.

n	shell	*l*	symbol	max. number of electron	
1	K	0	1s	2	($2 = 2x1^2$)
2	L	0	2s	2	($8 = 2x2^2$)
		1	2p	6	
3	M	0	3s	2	
		1	3p	6	($18 = 2x3^2$)
		2	3d	10	
4	N	0	4s	2	
		1	4p	6	($32 = 2x4^2$)
		2	4d	10	
		3	4f	14	

In Fig. 2.7, the energy level of each orbital is shown. With higher energy orbitals, the energy difference between orbitals is small, and sometimes, the order is reversed. The electron configuration of each atom in its ground state is shown in Table 5.4. The electron configuration of the outermost shell is clearly changed as the atomic number of the elements is changed. This is the theoretical basis for the Periodic Law, which will be discussed in detail in Ch. 5.

It must be added that, with the aid of the symbols given in Table 2.6, the electron configuration of an atom can be expressed. For instance, the hydrogen atom in the ground state has one electron in shell K and its electron configuration is ($1s^1$). A carbon atom has 2 electrons in the K shell and 4 electrons in the L shell. Its electron configuration is ($1s^2 2s^2 2p^2$).

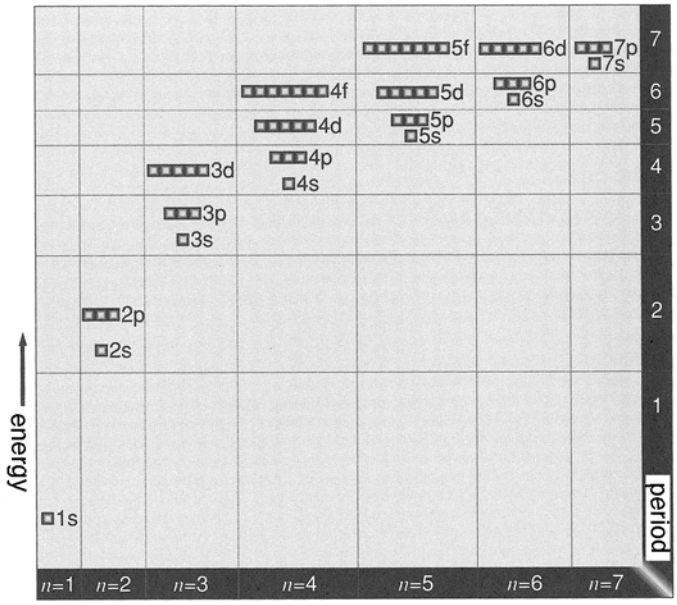


Figure 2.7 Energy level of electrons

The figures in the vertical columns correspond to the electron shells starting from K.
Two electrons are the maximum that can be accommodated in each box.

Exercise

2.1 The Bohr theory

Calculate the energy absorbed by an electron of a hydrogen atom when it is excited from the (n = 1) state to the (n = 3) state. Determine the wavelength of the relevant electromagnetic wave. Bohr's theory assumes the energy of an electron in the hydrogen atom is -2.718 x $10^{-18}/n^2$ (J)

2.1 Answer

The energy can be calculated with the aid of equation (2.9).

$$\Delta E = -2.178x10^{-18}\left[\frac{1}{3^2} - \frac{1}{1^2}\right] = +1.94x10^{-18}\ (J)$$

The relation between frequency and wavelength of electromagnetic wave is $\nu = c/\lambda$.

Hence, $\Delta E = hc/\lambda$, the wavelength can be obtained as below.

$$\lambda = \frac{6.626x10^{-34}(Js)x2.9979x10^{8}(ms^{-1})}{1.94x10^{-18}(J)} = 1.02x10^{-7}(m) = 102(nm)$$

2.2 The Bohr theory

What amount of energy is required in order to remove an electron of a hydrogen atom which is an excited (n – 2) state?

2.2 Answer

$$\Delta E = E_\infty - E_2 = |E_2| = \left|\frac{1}{4}E_1\right| = 5.45x10^{-19}\ (J)$$

2.3 De Broglie's equation

Calculate the wavelength of the material wave associated with an electron (m; 9.11 x 10^{-31} kg) moving with a velocity of 5.31x 10^6 m s^{-1}.

2.3 Answer

$$\lambda = \frac{h}{mv} = \frac{6.626x10^{-34}(Js)}{9.11x10^{-34}(kg)x5.31x10^{6}m\,s^{-1}} = \frac{6.626x10^{-34}(kg\,m^2\,s^{-2}\,s)}{9.11x10^{-34}(kg)x5.31x10^{6}m\,s^{-1}}$$

$$= 1.37x10^{-10}(m) = 0.137(nm)$$

2.4 One-dimensional square-well potential

An electron is confined in a one-dimensional square-well potential with the width of 0.3 nm. Determine its energy level. Calculate the frequency and wavelength of the electromagnetic wave when the electron moves from the (n = 2) state to the (n = 1) state.

2.4 Answer

$$E = \frac{n^2h^2}{8m_ea^2} = n^2\frac{\left(6.626x10^{34}\right)^2(J\,s)^2}{8(9.110x10^{-31}(kg)(0.3x10^{-9})^2\left(m^2\right)} = n^2\left(6.69x10^{-19}\right)(J)$$

The frequency and the wavelength of electron is:

$$\nu = \frac{\Delta E}{h} = \frac{(4-1)\left(6.69x10^{-19}\right)(J)}{6.626x10^{-34}(Js)} = 3.03x10^{15}s^{-1}$$

$$\lambda = \frac{c}{\nu} = \frac{3.00x10^{8}\ m\,s^{-1}}{3.03x10^{-15}\ s^{-1}} = 99x10^{-9}m = 99nm$$

2.5 Uncertainty principle

The position of an electron in an atom is to be determined to the precision of 0.02 nm. Estimate the uncertainty involved in the velocity of the electron.

2.5 Answer

$$\Delta v = \frac{\Delta p}{m} = \frac{h}{m\Delta x} = \frac{6.626x10^{-34}(\text{Js})}{9.110x10^{-31}(kg)\ 0.02x10^{-9}(m)} = 3.58x10^{7}\,ms^{-1}$$

It will be interesting to compare the value with the velocity of light (3.0×10^{8} m s^{-1}).

2.6 Electron configuration of some atoms

Generally the energy of orbitals in poly-electronic atoms increases in the following order:

1s < 2s < 2p < 3s < 3p < 4s < 3d < 4p < 5s < 4d < 5p

Give the electron configuration of $_{26}$Fe, $_{40}$Zr, $_{52}$Te in the ground state. If you cannot now solve this problem, try again after you study Ch. 5.

2.6 Answer

$_{26}$Fe; $(1s)^2(2s)^2(2p)^6(3s)^2(3p)^6(3d)^6(4s)^2$

$_{40}$Zr; $(1s)^2(2s)^2(2p)^6(3s)^2(3p)^6(3d)^{10}(4s)^2(4p)^6(4d)^2(5s)^2$

$_{52}$Te; $(1s)^2(2s)^2(2p)^6(3s)^2(3p)^6(3d)^{10}(4s)^2(4p)^6(4d)^{10}(5s)^2(5p)^4$

that the noble gases are chemically inert and that the alkali metals are chemically reactive. We know that sodium tends to form $1+$ ions and that fluorine tends to form $1-$ ions. But we have not explored *why*. The quantum-mechanical model explains why. In doing so, it explains the modern periodic table and provides the basis for our understanding of chemical bonding.

7.2 The Nature of Light

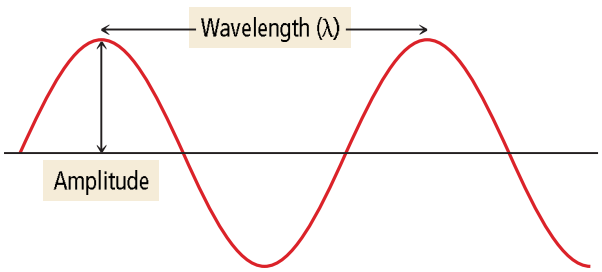
Before we explore electrons and their behavior within the atom, we must understand a few things about light. As quantum mechanics developed, light was (surprisingly) found to have many characteristics in common with electrons. Chief among these is the *wave–particle duality* of light. Certain properties of light are best described by thinking of it as a wave, while other properties are best described by thinking of it as a particle. In this chapter, we first explore the wave behavior of light, and then its particle behavior. We then turn to electrons to see how they display the same wave–particle duality.

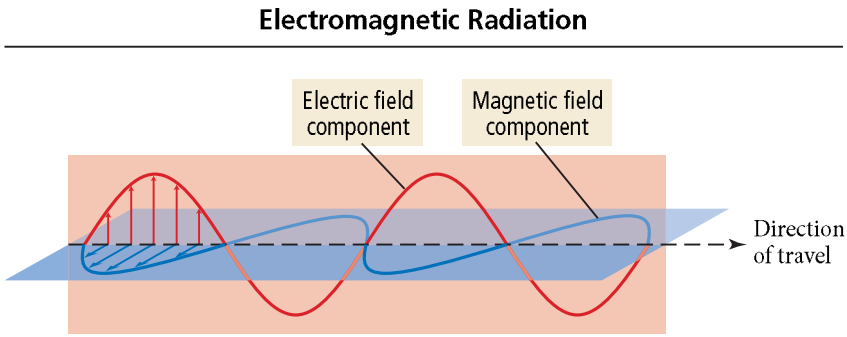
The Wave Nature of Light

Light is **electromagnetic radiation**, a type of energy embodied in oscillating electric and magnetic fields. A *magnetic field* is a region of space where a magnetic particle experiences a force (think of the space around a magnet). An *electric field* is a region of space where an electrically charged particle experiences a force. Electromagnetic radiation can be described as a wave composed of oscillating, mutually perpendicular electric and magnetic fields propagating through space, as shown in **Figure 7.1▼**. In a vacuum, these waves move at a constant speed of 3.00×10^8 m/s (186,000 mi/s)—fast enough to circle Earth in one-seventh of a second. This great speed explains the delay between the moment when you see a firework in the sky and the moment when you hear the sound of its explosion. The light from the exploding firework reaches your eye almost instantaneously. The sound, traveling much more slowly (340 m/s), takes longer. The same thing happens in a thunderstorm—you see the flash of the lightning immediately, but the sound of the thunder takes a few seconds to reach you.

An electromagnetic wave, like all waves, can be characterized by its *amplitude* and its *wavelength*. In the graphical representation shown below, the **amplitude** of the wave is the vertical height of a crest (or depth of a trough). The amplitude of the electric and magnetic field waves in light is related to the *intensity* or brightness of the light—the greater the amplitude, the greater the intensity. The **wavelength (λ)** of the wave is the distance in space between adjacent crests (or any two analogous points) and is measured in units of distance such as the meter, micrometer, or nanometer.

The symbol λ is the Greek letter lambda, pronounced "lamb-duh."





▶ FIGURE 7.1 Electromagnetic Radiation Electromagnetic radiation can be described as a wave composed of oscillating electric and magnetic fields. The fields oscillate in perpendicular planes.

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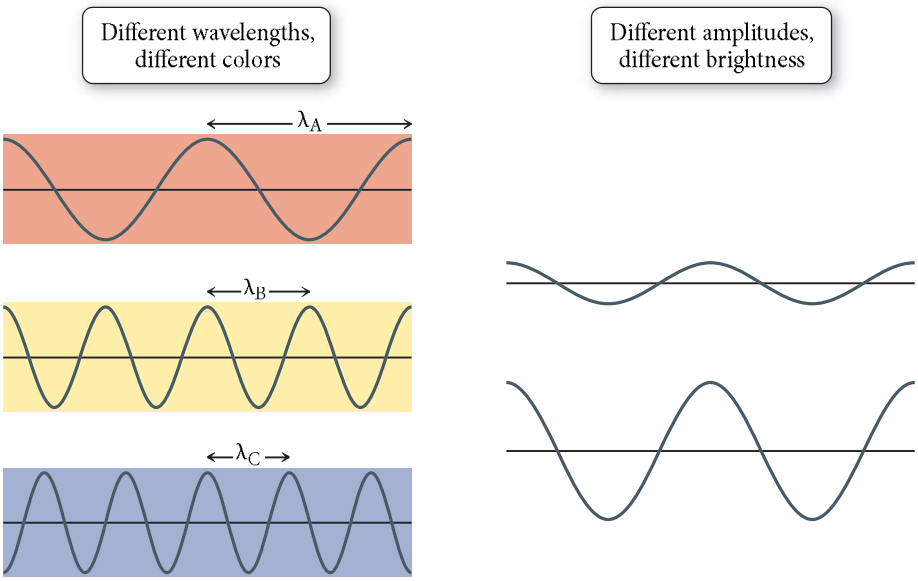

▲ **FIGURE 7.2 Wavelength and Amplitude** Wavelength and amplitude are independent properties. The wavelength of light determines its color. The amplitude, or intensity, determines its brightness.

Wavelength and amplitude are both related to the amount of energy carried by a wave. Imagine trying to swim out from a shore that is being pounded by waves. Greater amplitude (higher waves) or shorter wavelength (more closely spaced, and thus steeper, waves) make the swim more difficult. Notice also that amplitude and wavelength can vary independently of one another, as shown in **Figure 7.2▲**. A wave can have a large amplitude and a long wavelength, or a small amplitude and a short wavelength. The most energetic waves have large amplitudes and short wavelengths.

Like all waves, light is also characterized by its **frequency (ν)**, the number of cycles (or wave crests) that pass through a stationary point in a given period of time. The units of frequency are cycles per second (cycle/s) or simply s^{-1}. An equivalent unit of frequency is the hertz (Hz), defined as 1 cycle/s. The frequency of a wave is directly proportional to the speed at which the wave is traveling—the faster the wave, the more crests will pass a fixed location per unit time. Frequency is also *inversely* proportional to the wavelength (λ)—the farther apart the crests, the fewer that pass a fixed location per unit time. For light, therefore, we write

$$\nu = \frac{c}{\lambda} \qquad [7.1]$$

where the speed of light, c, and the wavelength, λ, are expressed using the same unit of distance. Therefore, wavelength and frequency represent different ways of specifying the same information—if we know one, we can readily calculate the other.

For *visible light*—light that can be seen by the human eye—wavelength (or, alternatively, frequency) determines color. White light, as produced by the sun or by a lightbulb, contains a spectrum of wavelengths and therefore a spectrum of colors. We see these colors—red, orange, yellow, green, blue, indigo, and violet—in a rainbow or when white light is passed through a prism (**Figure 7.3▶**). Red light, with a wavelength of about 750 nanometers (nm), has the longest wavelength of visible light; violet light, with a wavelength of about 400 nm, has the shortest. The presence of a variety of wavelengths in white light is responsible for the colors that we perceive. When a substance absorbs some colors while reflecting others, it appears colored. For example, a red shirt appears red because it reflects predominantly red light while absorbing most other colors (**Figure 7.4▶**). Our eyes see only the reflected light, making the shirt appear red.

▲ **FIGURE 7.3 Components of White Light** White light can be decomposed into its constituent colors, each with a different wavelength, by passing it through a prism. The array of colors makes up the spectrum of visible light.

The symbol ν is the Greek letter nu, pronounced "noo."

nano = 10^{-9}

▲ **FIGURE 7.4 The Color of an Object** A red shirt is red is because it reflects predominantly red light while absorbing most other colors.

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EXAMPLE 7.1 Wavelength and Frequency

Calculate the wavelength (in nm) of the red light emitted by a barcode scanner that has a frequency of $4.62 \times 10^{14}\,s^{-1}$.

SOLUTION

You are given the frequency of the light and asked to find its wavelength. Use Equation 7.1, which relates frequency to wavelength. You can convert the wavelength from meters to nanometers by using the conversion factor between the two (1 nm = 10^{-9} m).

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

$$\lambda = \frac{c}{\nu} = \frac{3.00 \times 10^{8}\,m/\cancel{s}}{4.62 \times 10^{14}\,1/\cancel{s}}$$

$$= 6.49 \times 10^{-7}\,m$$

$$= 6.49 \times 10^{-7}\,\cancel{m} \times \frac{1\,nm}{10^{-9}\,\cancel{m}} = 649\,nm$$

FOR PRACTICE 7.1

A laser used to dazzle the audience in a rock concert emits green light with a wavelength of 515 nm. Calculate the frequency of the light.

The Electromagnetic Spectrum

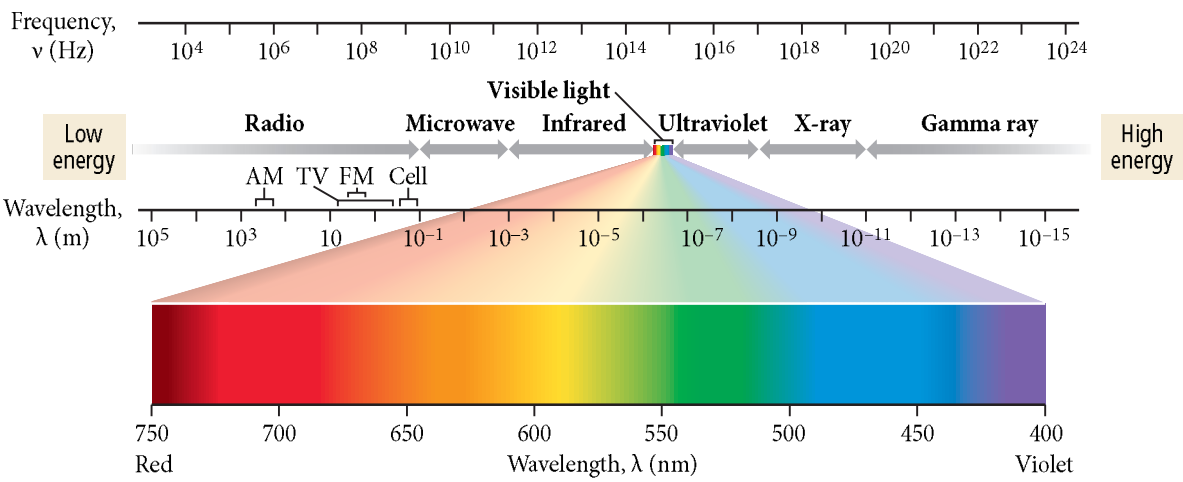
Visible light makes up only a tiny portion of the entire **electromagnetic spectrum**, which includes all known wavelengths of electromagnetic radiation. **Figure 7.5▼** shows the main regions of the electromagnetic spectrum, ranging in wavelength from 10^{-15} m (gamma rays) to 10^{5} m (radio waves).

As we noted previously, short-wavelength light inherently has greater energy than long-wavelength light. Therefore, the most energetic forms of electromagnetic radiation have the shortest wavelengths. The form of electromagnetic radiation with the shortest wavelength is the **gamma (γ) ray**. Gamma rays are produced by the sun, other stars, and certain unstable atomic nuclei on Earth. Human exposure to gamma rays is dangerous because the high energy of gamma rays can damage biological molecules.

Next on the electromagnetic spectrum, with longer wavelengths than gamma rays, are **X-rays**, familiar to us from their medical use. X-rays pass through many substances that block visible light and are therefore used to image bones and internal organs. Like gamma rays, X-rays are sufficiently energetic to damage biological molecules. While several yearly exposures to X-rays are relatively harmless, excessive exposure to X-rays increases cancer risk.

Sandwiched between X-rays and visible light in the electromagnetic spectrum is **ultraviolet (UV) radiation**, most familiar to us as the component of sunlight that produces a

The Electromagnetic Spectrum



▲ **FIGURE 7.5 The Electromagnetic Spectrum** The right side of the spectrum consists of high-energy, high-frequency, short-wavelength radiation. The left side consists of low-energy, low-frequency, long-wavelength radiation. Visible light constitutes a small segment in the middle.

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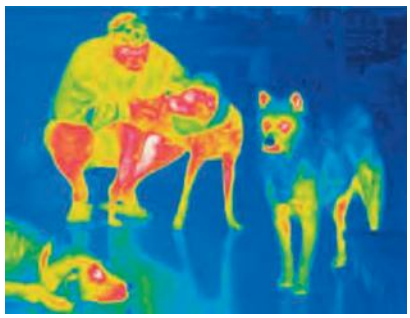
sunburn or suntan. While not as energetic as gamma rays or X-rays, ultraviolet light still carries enough energy to damage biological molecules. Excessive exposure to ultraviolet light increases the risk of skin cancer and cataracts and causes premature wrinkling of the skin.

Next on the spectrum is **visible light**, ranging from violet (shorter wavelength, higher energy) to red (longer wavelength, lower energy). Visible light—as long as the intensity is not too high—does not carry enough energy to damage biological molecules. It does, however, cause certain molecules in our eyes to change their shape, sending a signal to our brains that results in vision. Beyond visible light lies **infrared (IR) radiation**. The heat you feel when you place your hand near a hot object is infrared radiation. All warm objects, including human bodies, emit infrared light. Although infrared light is invisible to our eyes, infrared sensors can detect it and are used in night vision technology to "see" in the dark.

At longer wavelengths still, are **microwaves**, used for radar and in microwave ovens. Although microwave radiation has longer wavelengths and therefore lower energies than visible or infrared light, it is efficiently absorbed by water and can therefore heat substances that contain water. The longest wavelengths are those of **radio waves**, which are used to transmit the signals responsible for AM and FM radio, cellular telephones, television, and other forms of communication.

▲ Suntans and sunburns are produced by ultraviolet light from the sun.



▲ Warm objects emit infrared light, which is invisible to the eye but can be captured on film or by detectors to produce an infrared photograph.

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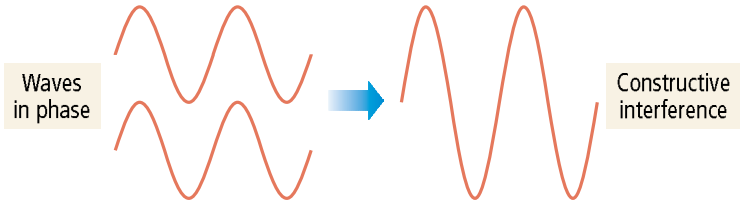
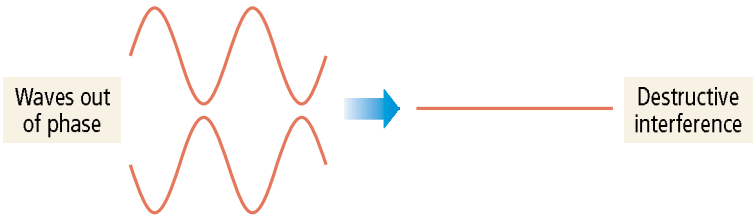
Interference and Diffraction

Waves, including electromagnetic waves, interact with each other in a characteristic way called **interference**: they can cancel each other out or build each other up, depending on their alignment upon interaction. For example, if waves of equal amplitude from two sources are *in phase* when they interact—that is, they align with overlapping crests—a wave with twice the amplitude results. This is called **constructive interference.**



On the other hand, if the waves are completely *out of phase*—that is, they align so that the crest from one source overlaps the trough from the other source—the waves cancel by **destructive interference.**



▲ When a reflected wave meets an incoming wave near the shore, the two waves interfere constructively for an instant, producing a large amplitude spike.

When a wave encounters an obstacle or a slit that is comparable in size to its wavelength, it bends around it—a phenomenon called **diffraction** (**Figure 7.6**▶). The diffraction of light through two slits separated by a distance comparable to the wavelength of the light results in an *interference pattern*, as shown in **Figure 7.7**▶. Each slit acts as a new wave source, and the two new waves interfere with each other. The resulting pattern consists of a series of bright and dark lines that can be viewed on a screen (or recorded on a film) placed at a short distance behind the slits. At the center of the screen, the two waves travel equal distances and interfere constructively to produce a bright line. However, a small distance away from the center in either direction, the two waves travel slightly different distances, so that they are out of phase. At the point where the difference in distance is one-half of a wavelength, the interference is destructive and a dark line appears on the screen. Moving a bit further away from the center produces constructive interference again because the difference between the paths is one whole wavelength. The end result is the interference pattern shown. Notice that interference results from the ability of a wave to diffract through the two slits—this is an inherent property of waves.

Understanding interference in waves is critical to understanding the wave nature of the electron, as we will soon see.

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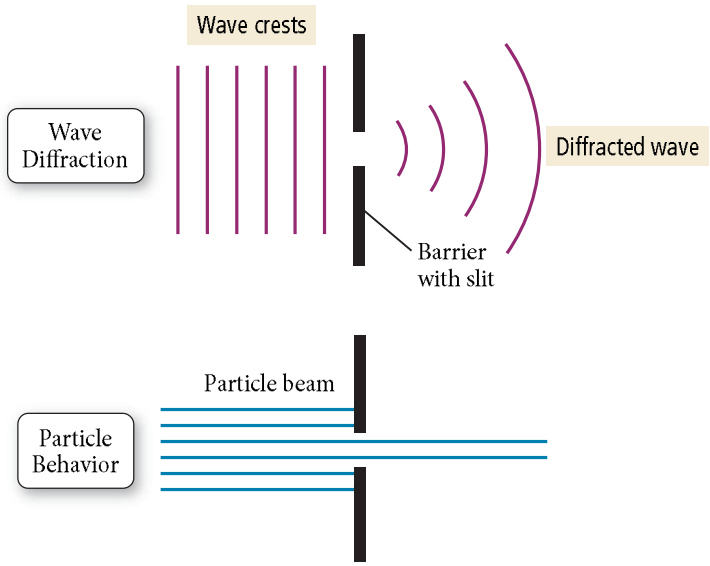
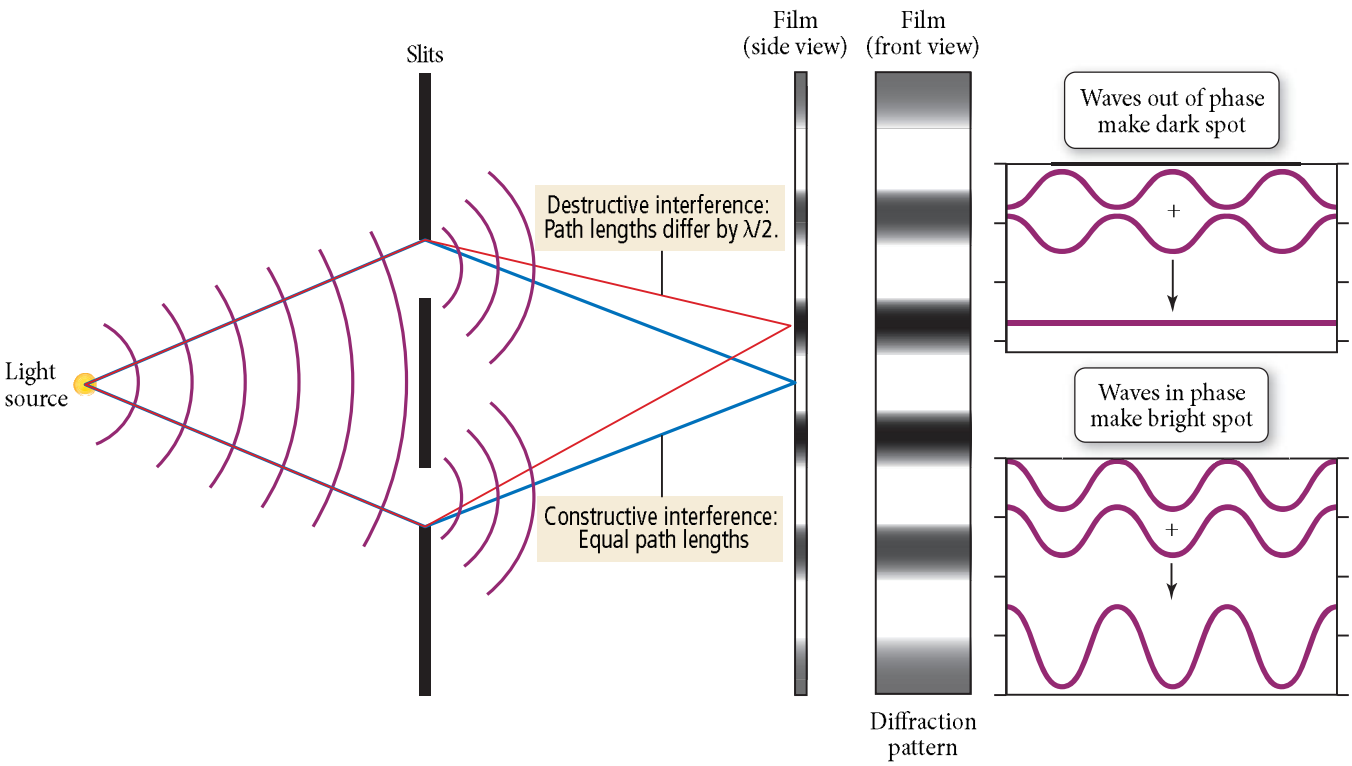
▶ **FIGURE 7.6 Diffraction** This view of waves from above shows how they are bent, or diffracted, when they encounter an obstacle or slit with a size comparable to their wavelength. When a wave passes through a small opening, it spreads out. Particles, by contrast, do not diffract; they simply pass through the opening.



Interference from Two Slits



▲ **FIGURE 7.7 Interference from Two Slits** When a beam of light passes through two small slits, the two resulting waves interfere with each other. Whether the interference is constructive or destructive at any given point depends on the difference in the path lengths traveled by the waves. The resulting interference pattern can be viewed as a series of bright and dark lines on a screen.

The Particle Nature of Light

The term *classical*, as in classical electromagnetic theory or classical mechanics, refers to descriptions of matter and energy before the advent of quantum mechanics.

Prior to the early 1900s, and especially after the discovery of the diffraction of light, light was thought to be purely a wave phenomenon. Its behavior was described adequately by classical electromagnetic theory, which treated the electric and magnetic fields that constitute light as waves propagating through space. However, a number of discoveries brought the classical view into question. Chief among those for light was the *photoelectric effect*.

The **photoelectric effect** was the observation that many metals eject electrons when light shines upon them, as shown in **Figure 7.8**▶. The light dislodges an electron from the metal when it shines on the metal, much like an ocean wave might dislodge a rock from a cliff when it breaks on a cliff. Classical electromagnetic theory attributed this effect to the

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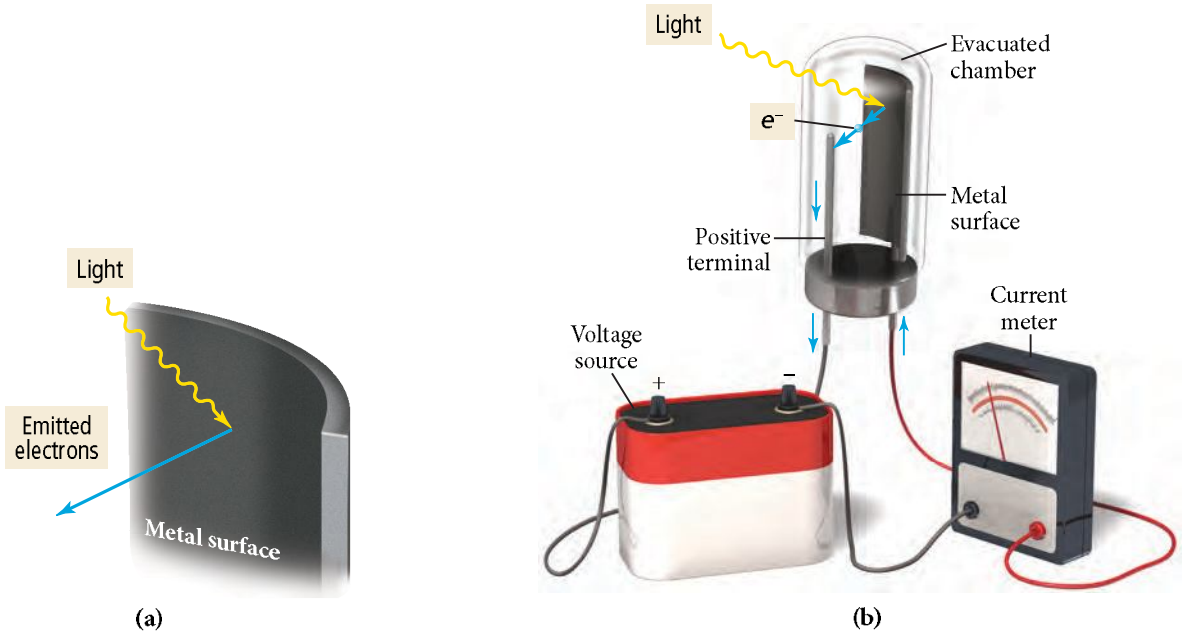
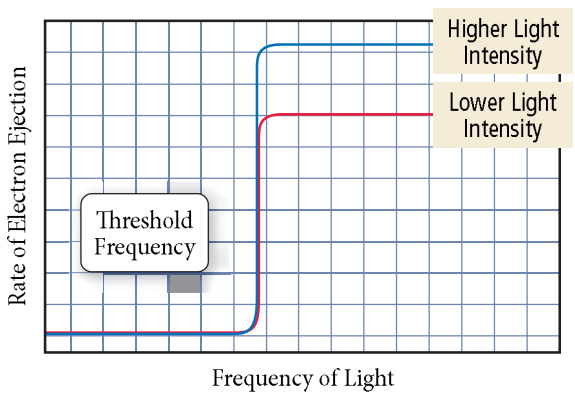
The Photoelectric Effect



▲ **FIGURE 7.8 The Photoelectric Effect** **(a)** When sufficiently energetic light shines on a metal surface, electrons are emitted. **(b)** The emitted electrons can be measured as an electrical current.

transfer of energy from the light to the electron in the metal, dislodging the electron. In this description, changing either the wavelength (color) or the amplitude (intensity) of the light should affect the ejection of electrons (just as changing the wavelength or intensity of the ocean wave would affect the dislodging of rocks from the cliff). In other words, according to the classical description, the rate at which electrons were ejected from a metal due to the photoelectric effect could be increased by using either light of shorter wavelength or light of higher intensity (brighter light). If a dim light were used, the classical description predicted that there would be a *lag time* between the initial shining of the light and the subsequent ejection of an electron. The lag time was the minimum amount of time required for the dim light to transfer sufficient energy to the electron to dislodge it (much as there would be a lag time for small waves to finally dislodge a rock from a cliff).

However, when observed in the laboratory, it was found that high-frequency, low-intensity light produced electrons without the predicted lag time. Furthermore, experiments showed that the light used to eject electrons in the photoelectric effect had a *threshold frequency*, below which no electrons were ejected from the metal, no matter how long or how brightly the light shone on the metal. In other words, low-frequency (long-wavelength) light would not eject electrons from a metal regardless of its intensity or its duration. But high-frequency (short-wavelength) light would eject electrons, even if its intensity were low. *This is like observing that long wavelength waves crashing on a cliff would not dislodge rocks even if their amplitude (wave height) was large, but that short wavelength waves crashing on the same cliff would dislodge rocks even if their amplitude was small.* **Figure 7.9▼** is a graph of the



◀ **FIGURE 7.9 The Photoelectric Effect** A plot of the electron ejection rate versus frequency of light for the photoelectric effect. Electrons are only ejected when the energy of a photon exceeds the energy with which an electron is held to the metal. The frequency at which this occurs is called the *threshold frequency*.

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rate of electron ejection from the metal versus the frequency of light used. Notice that increasing the intensity of the light does not change the threshold frequency. What could explain this odd behavior?

Einstein was not the first to suggest that energy was quantized. Max Planck used the idea in 1900 to account for certain characteristics of radiation from hot bodies. However, he did not suggest that light actually traveled in discrete packets.

In 1905, Albert Einstein proposed a bold explanation of this observation: *light energy must come in packets.* In other words, light was *not* like ocean waves, but more like particles. According to Einstein, the amount of energy (E) in a light packet depends on its frequency (ν) according to the equation:

The energy of a photon is directly proportional to its frequency.

$$E = h\nu \qquad [7.2]$$

where h, called *Planck's constant*, has the value $h = 6.626 \times 10^{-34}\,\text{J}\cdot\text{s}$. A *packet* of light is called a **photon** or a **quantum** of light. Since $\nu = c/\lambda$, the energy of a photon can also be expressed in terms of wavelength as follows:

The energy of a photon is inversely proportional to its wavelength.

$$E = \frac{hc}{\lambda} \qquad [7.3]$$

Unlike classical electromagnetic theory, in which light was viewed purely as a wave whose intensity was *continuously variable*, Einstein suggested that light was *lumpy*. From this perspective, a beam of light is *not* a wave propagating through space, but a shower of particles, each with energy $h\nu$.

EXAMPLE 7.2 Photon Energy

A nitrogen gas laser pulse with a wavelength of 337 nm contains 3.83 mJ of energy. How many photons does it contain?

SORT You are given the wavelength and total energy of a light pulse and asked to find the number of photons it contains.

GIVEN $E_{\text{pulse}} = 3.83\ \text{mJ}$
$\lambda = 337\ \text{nm}$

FIND number of photons

STRATEGIZE In the first part of the conceptual plan, calculate the energy of an individual photon from its wavelength.

In the second part, divide the total energy of the pulse by the energy of a photon to determine the number of photons in the pulse.

CONCEPTUAL PLAN

$$\lambda \xrightarrow{E = \frac{hc}{\lambda}} E_{\text{photon}}$$

$$\frac{E_{\text{pulse}}}{E_{\text{photon}}} = \text{number of photons}$$

RELATIONSHIPS USED $E = hc/\lambda$ (Equation 7.3)

SOLVE To execute the first part of the conceptual plan, convert the wavelength to meters and substitute it into the equation to calculate the energy of a 337-nm photon.

To execute the second part of the conceptual plan, convert the energy of the pulse from mJ to J. Then divide the energy of the pulse by the energy of a photon to obtain the number of photons.

SOLUTION

$$\lambda = 337\ \text{nm} \times \frac{10^{-9}\ \text{m}}{1\ \text{nm}} = 3.37 \times 10^{-7}\ \text{m}$$

$$E_{\text{photon}} = \frac{hc}{\lambda} = \frac{(6.626 \times 10^{-34}\ \text{J}\cdot\text{s})\left(3.00 \times 10^{8}\ \frac{\text{m}}{\text{s}}\right)}{3.37 \times 10^{-7}\ \text{m}}$$
$$= 5.8985 \times 10^{-19}\ \text{J}$$

$$3.83\ \text{mJ} \times \frac{10^{-3}\ \text{J}}{1\ \text{mJ}} = 3.83 \times 10^{-3}\ \text{J}$$

$$\text{number of photons} = \frac{E_{\text{pulse}}}{E_{\text{photon}}} = \frac{3.83 \times 10^{-3}\ \text{J}}{5.8985 \times 10^{-19}\ \text{J}}$$
$$= 6.49 \times 10^{15}\ \text{photons}$$

FOR PRACTICE 7.2

A 100-watt lightbulb radiates energy at a rate of 100 J/s. (The watt, a unit of power, or energy over time, is defined as 1 J/s.) If all of the light emitted has a wavelength of 525 nm, how many photons are emitted per second? (Assume three significant figures in this calculation.)

FOR MORE PRACTICE 7.2

The energy required to dislodge electrons from sodium metal via the photoelectric effect is 275 kJ/mol. What wavelength (in nm) of light has sufficient energy per photon to dislodge an electron from the surface of sodium?

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EXAMPLE 7.3 Wavelength, Energy, and Frequency

Arrange these three types of electromagnetic radiation—visible light, X-rays, and microwaves—in order of increasing:

(a) wavelength **(b)** frequency **(c)** energy per photon

SOLUTION

Examine Figure 7.5 and note that X-rays have the shortest wavelength, followed by visible light and then microwaves.	**(a)** wavelength X-rays < visible < microwaves
Since frequency and wavelength are inversely proportional—the longer the wavelength the shorter the frequency—the ordering with respect to frequency is the reverse order with respect to wavelength.	**(b)** frequency microwaves < visible < X-rays
Energy per photon decreases with increasing wavelength, but increases with increasing frequency; therefore, the ordering with respect to energy per photon is the same as for frequency.	**(c)** energy per photon microwaves < visible < X-rays

FOR PRACTICE 7.3

Arrange these colors of visible light—green, red, and blue—in order of increasing:

(a) wavelength **(b)** frequency **(c)** energy per photon

Einstein's idea that light was *quantized* elegantly explains the photoelectric effect. The emission of electrons from the metal depends on whether or not a single photon has sufficient energy (as given by $h\nu$) to dislodge a single electron. For an electron bound to the metal with binding energy ϕ, the threshold frequency is reached when the energy of the photon is equal to ϕ.

The symbol ϕ is the Greek letter phi, pronounced "fee."

Threshold frequency condition

$$h\nu = \phi$$

Energy of photon — Binding energy of emitted electron

Low-frequency light will not eject electrons because no single photon has the minimum energy necessary to dislodge the electron. Increasing the *intensity* of low-frequency light simply increases the number of low-energy photons, but does not produce any single photon with greater energy. In contrast, increasing the *frequency* of the light, even at low intensity, increases the energy of each photon, allowing the photons to dislodge electrons with no lag time.

As the frequency of the light is increased past the threshold frequency, the excess energy of the photon (beyond what is needed to dislodge the electron) is transferred to the electron in the form of kinetic energy. The kinetic energy (KE) of the ejected electron, therefore, is the difference between the energy of the photon ($h\nu$) and the binding energy of the electron, as given by the equation

$$\mathrm{KE} = h\nu - \phi$$

Although the quantization of light explained the photoelectric effect, the wave explanation of light continued to have explanatory power as well, depending on the circumstances of the particular observation. So the principle that slowly emerged (albeit with some measure of resistance) is what we now call the *wave–particle duality of light*. Sometimes light appears to behave like a wave, at other times like a particle. Which behavior you observe depends on the particular experiment performed.

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Conceptual Connection 7.1 The Photoelectric Effect

Light of three different wavelengths—325 nm, 455 nm, and 632 nm—was shone on a metal surface. The observations for each wavelength, labeled A, B, and C, were as follows:

Observation A: No photoelectrons were observed.

Observation B: Photoelectrons with a kinetic energy of 155 kJ/mol were observed.

Observation C: Photoelectrons with a kinetic energy of 51 kJ/mol were observed.

Which observation corresponds to which wavelength of light?

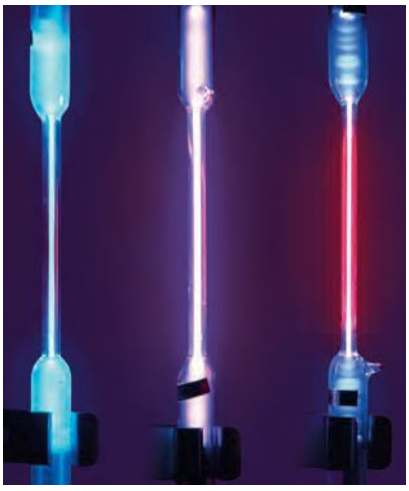
7.3 Atomic Spectroscopy and the Bohr Model

▲ The familiar red light from a neon sign is emitted by neon atoms that have absorbed electrical energy, which they reemit as visible radiation.

The discovery of the particle nature of light began to break down the division that existed in nineteenth-century physics between electromagnetic radiation, which was thought of as a wave phenomenon, and the small particles (protons, neutrons, and electrons) that compose atoms, which were thought to follow Newton's laws of motion (see Section 7.4). Just as the photoelectric effect suggested the particle nature of light, so certain observations of atoms began to suggest a wave nature for particles. The most important of these came from *atomic spectroscopy*, the study of the electromagnetic radiation absorbed and emitted by atoms.

When an atom absorbs energy—in the form of heat, light, or electricity—it often reemits that energy as light. For example, a neon sign is composed of one or more glass tubes filled with neon gas. When an electric current is passed through the tube, the neon atoms absorb some of the electrical energy and reemit it as the familiar red light of a neon sign. If the atoms in the tube are not neon atoms but those of a different gas, the emitted light is a different color. Atoms of each element emit light of a characteristic color. Mercury atoms, for example, emit light that appears blue, helium atoms emit light that appears violet, and hydrogen atoms emit light that appears reddish (**Figure 7.10**◀).

Remember that the color of visible light is determined by its wavelength.



▲ **FIGURE 7.10 Mercury, Helium, and Hydrogen** Each element emits a characteristic color.

Closer investigation of the light emitted by atoms reveals that it contains several distinct wavelengths. Just as the white light from a lightbulb can be separated into its constituent wavelengths by passing it through a prism, so can the light emitted by an element when it is heated, as shown in **Figure 7.11**▶. The result is a series of bright lines called an **emission spectrum**. The emission spectrum of a particular element is always the same—it consists of the same bright lines at the same characteristic wavelengths—and can be used to identify the element. For example, light arriving from a distant star contains the emission spectra of the elements that compose the star. Analysis of the light allows us to identify the elements present in the star.

Notice the differences between a white light spectrum and the emission spectra of hydrogen, helium, and barium. The white light spectrum is *continuous*; there are no sudden interruptions in the intensity of the light as a function of wavelength—it consists of light of all wavelengths. The emission spectra of hydrogen, helium, and barium, however, are not continuous—they consist of bright lines at specific wavelengths, with complete darkness in between. That is, only certain discrete wavelengths of light are present. Classical physics could not explain why these spectra consisted of discrete lines. In fact, according to classical physics, an atom composed of an electron orbiting a nucleus should emit a continuous white light spectrum. Even more problematic, the electron should lose energy as it emits the light, and spiral into the nucleus.

The Rydberg equation is $1/\lambda = R(1/m^2 - 1/n^2)$, where R is the Rydberg constant ($1.097 \times 10^7\ \text{m}^{-1}$) and m and n are integers.

Johannes Rydberg, a Swedish mathematician, analyzed many atomic spectra and developed an equation (shown in the margin) that predicted the wavelengths of the hydrogen emission spectrum. However, his equation gave little insight into *why* atomic spectra were discrete, *why* atoms were stable, or *why* his equation worked.

The Danish physicist Neils Bohr (1885–1962) attempted to develop a model for the atom that explained atomic spectra. In his model, electrons travel around the nucleus in circular orbits (similar to those of the planets around the sun). However, in

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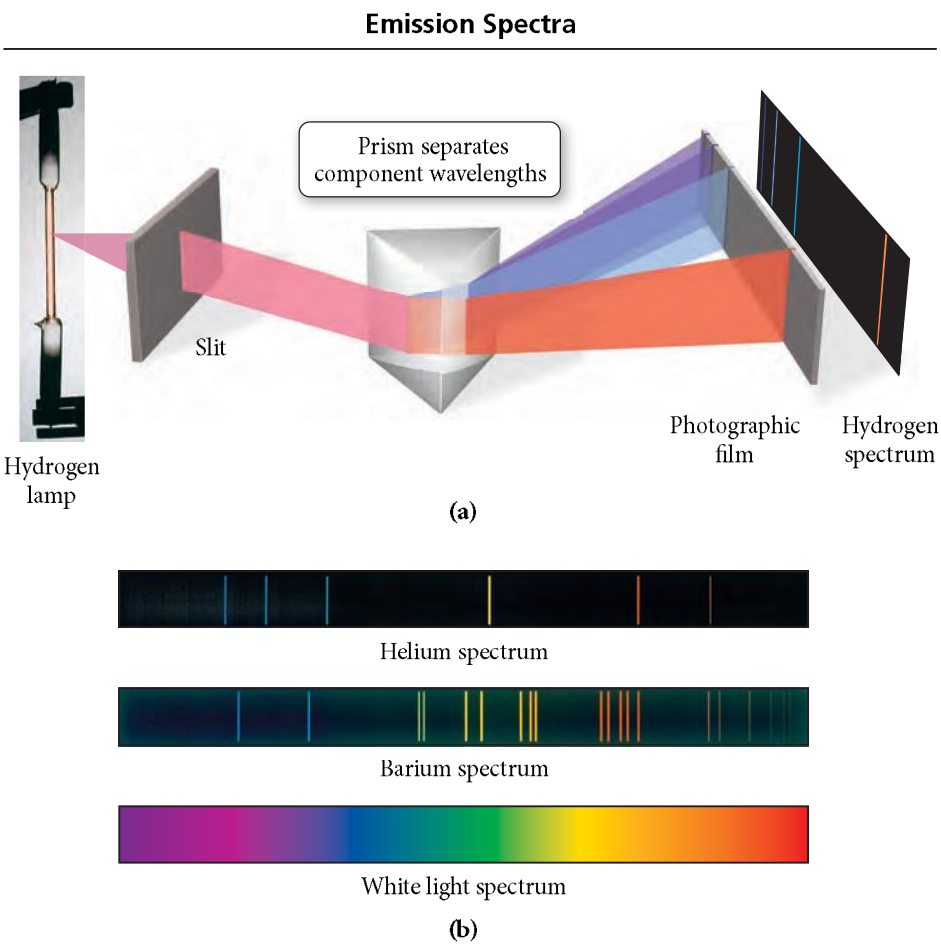

▲ **FIGURE 7.11 Emission Spectra** **(a)** The light emitted from a hydrogen, helium, or barium lamp consists of specific wavelengths, which can be separated by passing the light through a prism. **(b)** The resulting bright lines constitute an emission spectrum characteristic of the element that produced it.

contrast to planetary orbits—which can theoretically exist at any distance from the sun—Bohr's orbits could exist only at specific, fixed distances from the nucleus. The energy of each Bohr orbit was also fixed, or *quantized*. Bohr called these orbits *stationary states* and suggested that, although they obeyed the laws of classical mechanics, they also possessed "a peculiar, mechanically unexplainable, stability." We now know that the stationary states were really manifestations of the wave nature of the electron, which we expand upon shortly. Bohr further proposed that, in contradiction to classical electromagnetic theory, no radiation was emitted by an electron orbiting the nucleus in a stationary state. It was only when an electron jumped, or made a *transition*, from one stationary state to another that radiation was emitted or absorbed (**Figure 7.12**▶).

The transitions between stationary states in a hydrogen atom are quite unlike any transitions that you might imagine in the macroscopic world. The electron is *never observed between states*, only in one state or the next—the transition between states is instantaneous. The emission spectrum of an atom consists of discrete lines because the states exist only at specific, fixed energies. The energy of the photon created when an electron makes a transition from one stationary state to another is the energy difference between the two stationary states. Transitions between stationary states that are closer together, therefore, produce light of lower energy (longer wavelength) than transitions between stationary states that are farther apart.

In spite of its initial success in explaining the line spectrum of hydrogen (including the correct wavelengths), the Bohr model left many unanswered questions. It did,

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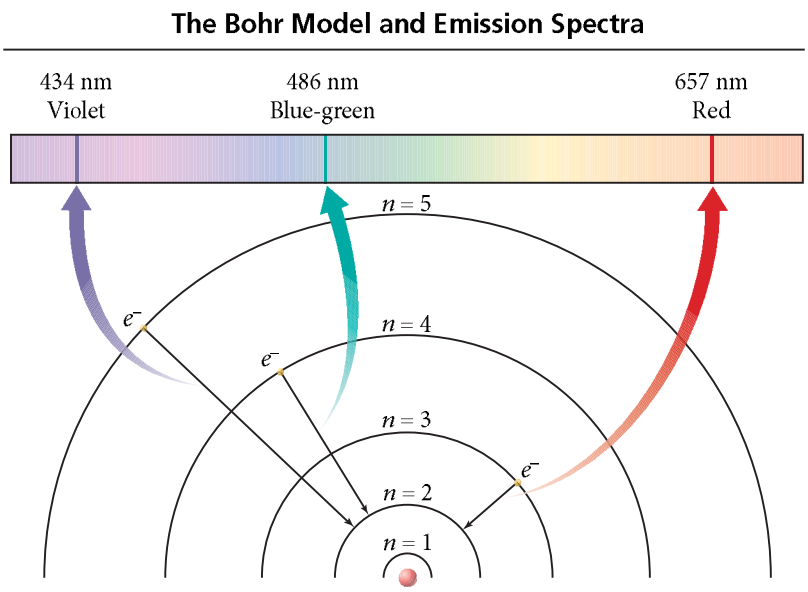

▲ **FIGURE 7.12 The Bohr Model and Emission Spectra** In the Bohr model, each spectral line is produced when an electron falls from one stable orbit, or stationary state, to another of lower energy.

however, serve as an intermediate model between a classical view of the electron and a fully quantum-mechanical view, and therefore has great historical and conceptual importance. Nonetheless, it was ultimately replaced by a more complete quantum-mechanical theory that fully incorporated the wave nature of the electron.

7.4 The Wave Nature of Matter: the de Broglie Wavelength, the Uncertainty Principle, and Indeterminacy

The heart of the quantum-mechanical theory that replaced Bohr's model is the wave nature of the electron, first proposed by Louis de Broglie (1892–1987) in 1924 and confirmed by experiments in 1927. It seemed incredible at the time, but electrons—which were thought of as particles and known to have mass—also have a wave nature. The wave nature of the electron is seen most clearly in its diffraction. If an electron beam is aimed at two closely spaced slits, and a series (or array) of detectors is arranged to detect the electrons after they pass through the slits, an interference pattern similar to that observed for light is recorded behind the slits (**Figure 7.13a▶**). The detectors at the center of the array (midway between the two slits) detect a large number of electrons—exactly the opposite of what you would expect for particles (**Figure 7.13b▶**). Moving outward from this center spot, the detectors alternately detect small numbers of electrons and then large numbers again and so on, forming an interference pattern characteristic of waves.

The first evidence of electron wave properties was provided by the Davisson-Germer experiment of 1927, in which electrons were observed to undergo diffraction by a metal crystal.

For interference to occur, the spacing of the slits has to be on the order of atomic dimensions.

It is critical to understand that the interference pattern described here is *not caused by pairs of electrons interfering with each other, but rather by single electrons interfering with themselves.* If the electron source is turned down to a very low level, so that electrons come out only one at a time, *the interference pattern remains.* In other words, we can design an experiment in which electrons come out of the source singly. We can then record where each electron strikes the detector after it has passed through the slits. If we record the positions of thousands of electrons over a long period of time, we find the same interference pattern shown in Figure 7.13(a). This leads us to an important conclusion: *The wave nature of the electron is an inherent property of individual electrons.* Recall from Section 7.1 that unobserved electrons can simultaneously occupy two different states. In this case, the unobserved electron goes through both slits—it exists in two states simultaneously, just like Schrödinger's cat—and interferes with itself. As it turns out, this wave nature is what explains the existence of stationary states (in the Bohr model)

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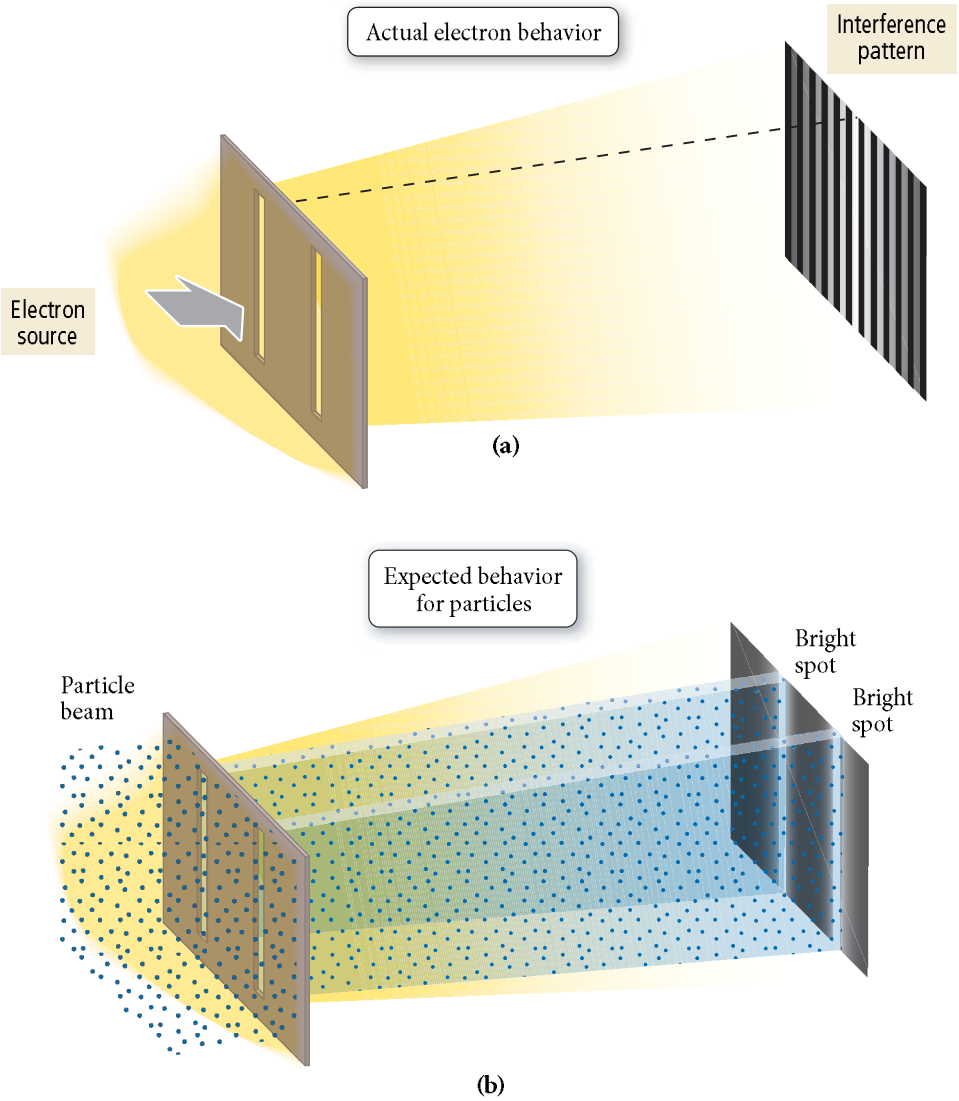

▲ **FIGURE 7.13 Electron Diffraction** When a beam of electrons goes through two closely spaced slits **(a)**, an interference pattern is created, as if the electrons were waves. By contrast, a beam of particles passing through two slits **(b)** should simply produce two smaller beams of particles. Notice that for particle beams, there is a dark line directly behind the center of the two slits, in contrast to wave behavior, which produces a bright line.

and prevents the electrons in an atom from crashing into the nucleus as they are predicted to do according to classical physics. We now turn to three important manifestations of the electron's wave nature: the de Broglie wavelength, the uncertainty principle, and indeterminacy.

The de Broglie Wavelength

As we have seen, a single electron traveling through space has a wave nature; its wavelength is related to its kinetic energy (the energy associated with its motion). The faster the electron is moving, the higher its kinetic energy and the shorter its wavelength. The wavelength (λ) of an electron of mass m moving at velocity v is given by the **de Broglie relation**:

$$\lambda = \frac{h}{mv} \qquad \text{de Broglie relation} \qquad [7.4]$$

The mass of an object (m) times its velocity (v) is its momentum. Therefore, the wavelength of an electron is inversely proportional to its momentum.

where h is Planck's constant. Notice that the velocity of a moving electron is related to its wavelength—knowing one is equivalent to knowing the other.

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EXAMPLE 7.4 De Broglie Wavelength

Calculate the wavelength of an electron traveling with a speed of 2.65×10^6 m/s.

SORT You are given the speed of an electron and asked to calculate its wavelength.	**GIVEN** $v = 2.65 \times 10^6$ m/s **FIND** λ
STRATEGIZE The conceptual plan shows how the de Broglie relation relates the wavelength of an electron to its mass and velocity.	**CONCEPTUAL PLAN** $v \longrightarrow \lambda$ $\lambda = \dfrac{h}{mv}$ **RELATIONSHIPS USED** $\lambda = h/mv$ (de Broglie relation, Equation 7.4)
SOLVE Substitute the velocity, Planck's constant, and the mass of an electron to calculate the electron's wavelength. To correctly cancel the units, break down the J in Planck's constant into its SI base units ($1\ \text{J} = 1\ \text{kg}\cdot\text{m}^2/\text{s}^2$).	**SOLUTION** $\lambda = \dfrac{h}{mv} = \dfrac{6.626 \times 10^{-34}\ \dfrac{\cancel{\text{kg}}\cdot\text{m}^2}{\text{s}^{\cancel{2}}}\ \cancel{\text{s}}}{(9.11 \times 10^{-31}\ \cancel{\text{kg}})\left(2.65 \times 10^6\ \dfrac{\text{m}}{\cancel{\text{s}}}\right)}$ $= 2.74 \times 10^{-10}$ m

CHECK The units of the answer (m) are correct. The magnitude of the answer is very small, as expected for the wavelength of an electron.

FOR PRACTICE 7.4

What is the velocity of an electron having a de Broglie wavelength that is approximately the length of a chemical bond? Assume this length to be 1.2×10^{-10} m.

Conceptual Connection 7.2 The de Broglie Wavelength of Macroscopic Objects

Since quantum-mechanical theory is universal, it applies to all objects, regardless of size. Therefore, according to the de Broglie relation, a thrown baseball should also exhibit wave properties. Why do we not observe such properties at the ballpark?

The Uncertainty Principle

The wave nature of the electron is difficult to reconcile with its particle nature. How can a single entity behave as both a wave and a particle? We can begin to answer this question by returning to the single-electron diffraction experiment. Specifically, we can ask the question: how does a single electron aimed at a double slit produce an interference pattern? We saw previously that the electron travels through both slits and interferes with itself. This idea is testable. We simply have to observe the single electron as it travels through both of the slits. If it travels through both slits simultaneously, our hypothesis is correct. But here is where nature gets tricky.

Any experiment designed to observe the electron as it travels through the slits results in the detection of an electron "particle" traveling through a single slit and no interference pattern. Recall from Section 7.1 that an *unobserved* electron can occupy two different states; however, the act of observation forces it into one state or the other. Similarly, the act of observing the electron as it travels through both slits forces it go through only one slit. The following electron diffraction experiment is designed to "watch" which slit the electron travels through by using a laser beam placed directly behind the slits.

An electron that crosses a laser beam produces a tiny "flash"—a single photon is scattered at the point of crossing. A flash behind a particular slit indicates an electron

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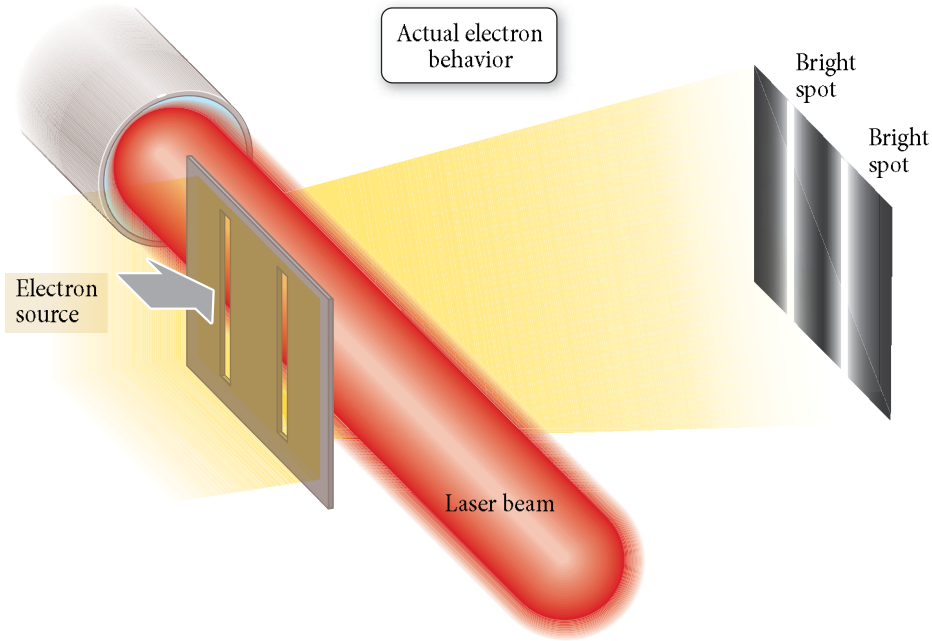

passing through that slit. However, when the experiment is performed, the flash always originates either from one slit *or* the other, but *never* from both at once. Futhermore, the interference pattern, which was present without the laser, is now absent. With the laser on, the electrons hit positions directly behind each slit, as if they were ordinary particles.

As it turns out, no matter how hard we try, or whatever method we set up, *we can never see the interference pattern and simultaneously determine which hole the electron goes through*. It has never been done, and most scientists agree that it never will. In the words of P. A. M. Dirac (1902–1984),

> There is a limit to the fineness of our powers of observation and the smallness of the accompanying disturbance—a limit which is inherent in the nature of things and can never be surpassed by improved technique or increased skill on the part of the observer.

The single electron diffraction experiment demonstrates that you cannot simultaneously observe both the wave nature and the particle nature of the electron. When you try to observe which hole the electron goes through (associated with the particle nature of the electron) you lose the interference pattern (associated with the wave nature of the electron). When you try to observe the interference pattern, you cannot determine which hole the electron goes through. The wave nature and particle nature of the electron are said to be **complementary properties**. Complementary properties exclude one another—the more you know about one, the less you know about the other. Which of two complementary properties you observe depends on the experiment you perform—in quantum mechanics, the observation of an event affects its outcome.

As we just saw in the de Broglie relation, the *velocity* of an electron is related to its *wave nature*. The *position* of an electron, however, is related to its *particle nature*. (Particles have well-defined positions, but waves do not.) Consequently, our inability to observe the electron simultaneously as both a particle and a wave means that we cannot simultaneously measure its position and its velocity. Werner Heisenberg formalized this idea with the equation:

$$\Delta x \times m\Delta v \geq \frac{h}{4\pi} \quad \text{Heisenberg's uncertainty principle} \qquad [7.5]$$

where Δx is the uncertainty in the position, Δv is the uncertainty in the velocity, m is the mass of the particle, and h is Planck's constant. **Heisenberg's uncertainty principle**

▲ Werner Heisenberg (1901–1976)

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states that the product of Δx and $m\Delta v$ must be greater than or equal to a finite number $(h/4\pi)$. In other words, the more accurately you know the position of an electron (the smaller Δx) the less accurately you can know its velocity (the bigger Δv) and vice versa. The complementarity of the wave nature and particle nature of the electron results in the complementarity of velocity and position.

Although Heisenberg's uncertainty principle may seem puzzling, it actually solves a great puzzle. Without the uncertainty principle, we are left with the question: how can something be *both* a particle and a wave? Saying that an object is both a particle and a wave is like saying that an object is both a circle and a square, a contradiction. Heisenberg solved the contradiction by introducing complementarity—an electron is observed as *either* a particle or a wave, but never both at once.

Indeterminacy and Probability Distribution Maps

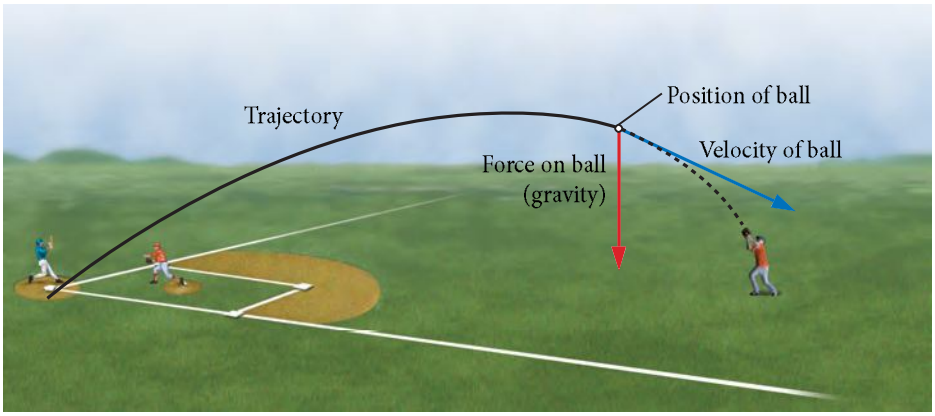
According to classical physics, and in particular Newton's laws of motion, particles move in a *trajectory* (or path) that is determined by the particle's velocity (the speed and direction of travel), its position, and the forces acting on it. Even if you are not familiar with Newton's laws, you probably have an intuitive sense of them. For example, when you chase a baseball in the outfield, you visually predict where the ball will land by observing its path. You do this by noting its initial position and velocity, watching how these are affected by the forces acting on it (gravity, air resistance, wind), and then inferring its trajectory, as shown in **Figure 7.14▼**. If you knew only the ball's velocity, or only its position (imagine a still photo of the baseball in the air), you could not predict its landing spot. In classical mechanics, both position and velocity are required to predict a trajectory.

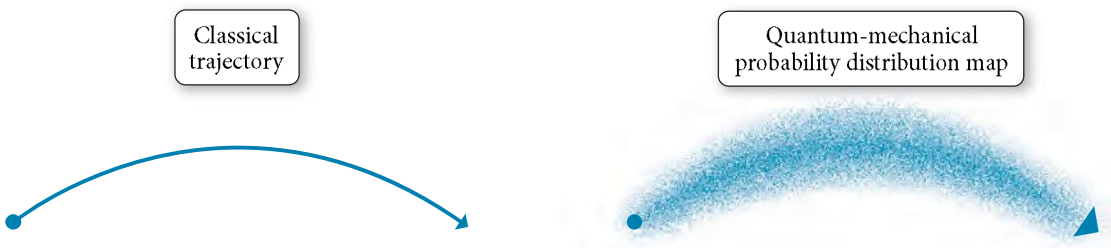
Remember that velocity includes speed as well as direction of travel.

Newton's laws of motion are **deterministic**—the present *determines* the future. This means that if two baseballs are hit consecutively with the same velocity from the same position under identical conditions, they will land in exactly the same place. The same is not true of electrons. We have just seen that we cannot simultaneously know the position and velocity of an electron; therefore, we cannot know its trajectory. In quantum mechanics, trajectories are replaced with *probability distribution maps*, as shown in **Figure 7.15▼**.

▶FIGURE 7.14 The Concept of Trajectory In classical mechanics, the position and velocity of a particle determine its future trajectory, or path. Thus, an outfielder can catch a baseball by observing its position and velocity, allowing for the effects of forces acting on it, such as gravity, and estimating its trajectory. (For simplicity, air resistance and wind are not shown.)

The Classical Concept of Trajectory





▲ FIGURE 7.15 Trajectory versus Probability In quantum mechanics, we cannot calculate deterministic trajectories. Instead, it is necessary to think in terms of probability maps: statistical pictures of where a quantum-mechanical particle, such as an electron, is most likely to be found. In this hypothetical map, darker shading indicates greater probability.

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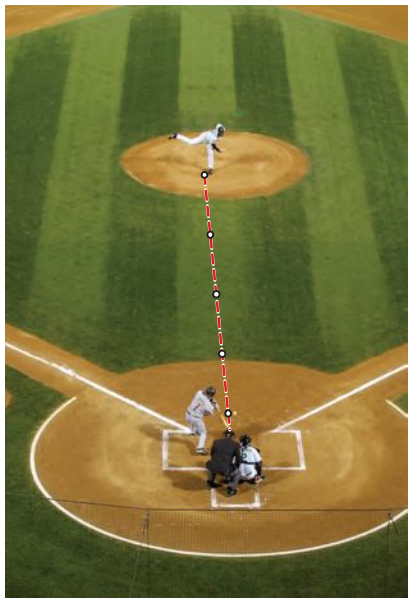
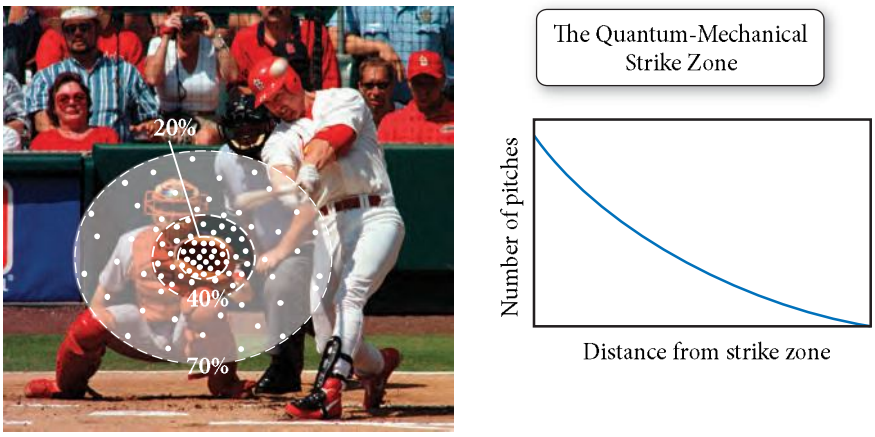
A probability distribution map is a statistical map that shows where an electron is likely to be found under a given set of conditions.

To understand the concept of a probability distribution map, let us return to baseball. Imagine a baseball thrown from the pitcher's mound to a catcher behind home plate (**Figure 7.16**▶). The catcher can watch the baseball's path, predict exactly where it will cross home plate, and place his mitt in the correct place to catch it. As we have seen, this would be impossible for an electron. If an electron were thrown from the pitcher's mound to home plate, it would generally land in a different place every time, even if it were thrown in exactly the same way. This behavior is called **indeterminacy**. Unlike a baseball, whose future path is *determined* by its position and velocity when it leaves the pitcher's hand, the future path of an electron is indeterminate, and can only be described statistically.

In the quantum-mechanical world of the electron, the catcher could not know exactly where the electron will cross the plate for any given throw. However, if he kept track of hundreds of identical electron throws, the catcher could observe a reproducible *statistical pattern* of where the electron crosses the plate. He could even draw a map of the strike zone showing the probability of an electron crossing a certain area, as shown in **Figure 7.17**▼. This would be a probability distribution map. In the sections that follow, we discuss quantum-mechanical electron *orbitals*, which are essentially probability distribution maps for electrons as they exist within atoms.



▲ **FIGURE 7.16 Trajectory of a Macroscopic Object** A baseball follows a well-defined trajectory from the hand of the pitcher to the mitt of the catcher.



▲ **FIGURE 7.17 The Quantum-Mechanical Strike Zone** An electron does not have a well-defined trajectory. However, we can construct a probability distribution map to show the relative probability of it crossing home plate at different points.

7.5 Quantum Mechanics and the Atom

As we have seen, the position and velocity of the electron are complementary properties—if we know one accurately, the other becomes indeterminate. Since velocity is directly related to energy (we have seen that kinetic energy equals $\frac{1}{2}mv^2$), position and *energy* are also complementary properties—the more you know about one, the less you know about the other. Many of the properties of an element, however, depend on the energies of its electrons. For example, whether an electron is transferred from one atom to another to form an ionic bond depends in part on the relative energies of the electron in the two atoms. In the following paragraphs, we describe the probability distribution maps for electron states in which the electron has well-defined energy, but not well-defined position. In other words, for each state, we can specify the *energy* of the electron precisely, but not its location at a given instant. Instead, the electron's position is described in terms of an **orbital**, a probability distribution map showing where the electron is likely to be found. Since chemical bonding often involves the sharing of electrons between atoms to form covalent bonds, the spatial distribution of atomic electrons is important to bonding.

These states are known as energy *eigenstates*.

The mathematical derivation of energies and orbitals for electrons in atoms comes from solving the Schrödinger equation for the atom of interest. The general form of the Schrödinger equation is:

$$H\psi = E\psi \qquad [7.6]$$

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An operator is different from a normal algebraic entity. In general, an operator transforms a mathematical function into another mathematical function. For example, d/dx is an operator that means "take the derivative of." When d/dx operates on a function (such as x^2) it returns another function ($2x$).

The symbol ψ is the Greek letter psi, pronounced "sigh."

The symbol H stands for the Hamiltonian operator, a set of mathematical operations that represent the total energy (kinetic and potential) of the electron within the atom. The symbol E is the actual energy of the electron. The symbol ψ is the **wave function**, a mathematical function that describes the wavelike nature of the electron. A plot of the wave function squared (ψ^2) represents an orbital, a position probability distribution map of the electron.

Solutions to the Schrödinger Equation for the Hydrogen Atom

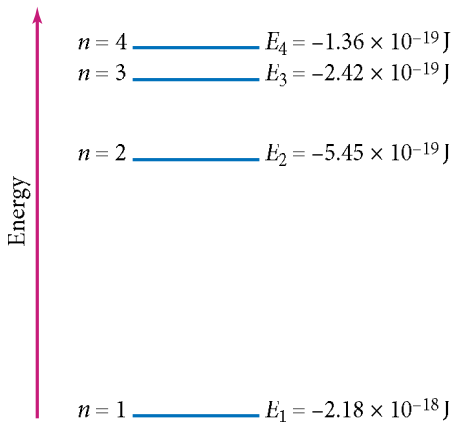
When the Schrödinger equation is solved, it yields many solutions—many possible wave functions. The wave functions themselves are fairly complicated mathematical functions, and we do not examine them in detail in this book. Instead, we introduce graphical representations (or plots) of the orbitals that correspond to the wave functions. Each orbital is specified by three interrelated **quantum numbers**: $\boldsymbol{n}$, the **principal quantum number**; $\boldsymbol{l}$, the **angular momentum quantum number** (sometimes called the *azimuthal quantum number*); and $\boldsymbol{m_l}$ the **magnetic quantum number**. These quantum numbers all have integer values, as had been hinted at by both the Rydberg equation and Bohr's model. A fourth quantum number, $\mathbf{m_s}$, the **spin quantum number**, specifies the orientation of the spin of the electron. We examine each of these quantum numbers individually.

The Principal Quantum Number (n)

The principal quantum number is an integer that determines the overall size and energy of an orbital. Its possible values are $n = 1, 2, 3, \ldots$ and so on. For the hydrogen atom, the energy of an electron in an orbital with quantum number n is given by

$$E_n = -2.18 \times 10^{-18}\,\text{J}\left(\frac{1}{n^2}\right) \qquad (n = 1, 2, 3, \ldots) \qquad [7.7]$$

The energy is negative because the energy of the electron in the atom is less than the energy of the electron when it is very far away from the atom (which is taken to be zero). Notice that orbitals with higher values of n have greater (less negative) energies, as shown in the energy level diagram below. Notice also that, as n increases, the spacing between the energy levels becomes smaller.



The Angular Momentum Quantum Number (l)

The angular momentum quantum number is an integer that determines the shape of the orbital. We consider these shapes in Section 7.6. The possible values of l are $0, 1, 2, \ldots, (n - 1)$. In other words, for a given value of n, l can be any integer (including 0) up to $n - 1$. For example, if $n = 1$, then the only possible value of l is 0; if $n = 2$, the possible values of l are 0 and 1. In order to avoid confusion between n and l, values of l are often assigned letters as follows:

The values of l beyond 3 are designated with letters in alphabetical order so that $l = 4$ is designated g, $l = 5$ is designated h, and so on.

Value of l	Letter Designation
$l = 0$	s
$l = 1$	p
$l = 2$	d
$l = 3$	f

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Conceptual Connection 7.3 The Relationship Between *n* and *l*

What is the full range of possible values of l for $n = 3$?

(a) 0 (or *s*) **(b)** 0 and 1 (or *s* and *p*) **(c)** 0, 1, and 2 (or *s*, *p*, and *d*) **(d)** 0, 1, 2, and 3 (or *s*, *p*, *d*, and *f*)

The Magnetic Quantum Number (m_l)

The magnetic quantum number is an integer that specifies the orientation of the orbital. We consider these orientations in Section 7.6. The possible values of m_l are the integer values (including zero) ranging from $-l$ to $+l$. For example, if $l = 0$, then the only possible value of m_l is 0; if $l = 1$, the possible values of m_l are -1, 0, and +1.

Conceptual Connection 7.4 The Relationship between *l* and m_l

What is the full range of possible values of m_l for $l = 2$?

(a) 0, 1, and 2 **(b)** 0 **(c)** -1, 0 and $+1$ **(d)** -2, -1, 0, $+1$, and $+2$

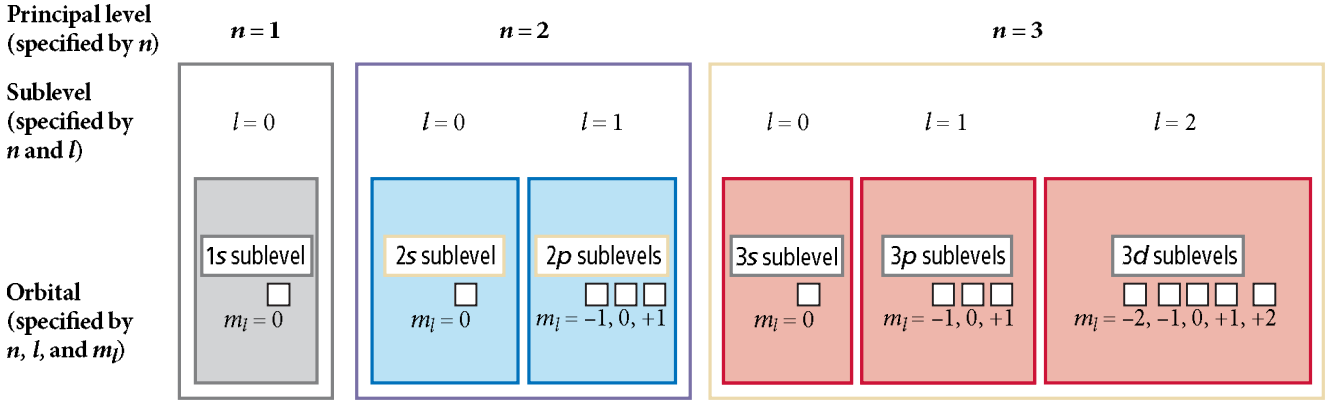
The Spin Quantum Number (m_s)

The spin quantum number specifies the orientation of the *spin* of the electron. **Electron spin** is a fundamental property of an electron (like its negative charge). One electron does not have more or less spin than another—all electrons have the same amount of spin. The orientation of the electron's spin is quantized, with only two possibilities that we can call spin up ($m_s = +1/2$) and spin down ($m_s = -1/2$). The spin quantum number becomes important when we begin to consider how electrons occupy orbitals (Section 8.3). For now, we will focus on the first three quantum numbers.

The idea of a "spinning" electron is something of a metaphor. A more correct way to express the same idea is to say that an electron has inherent angular momentum.

The Hydrogen Atom Orbitals

Each specific combination of the first three quantum numbers (n, l, and m_l) specifies one atomic orbital. For example, the orbital with $n = 1$, $l = 0$, and $m_l = 0$ is known as the 1*s* orbital. The 1 in 1*s* is the value of n and the *s* specifies that $l = 0$. There is only one 1*s* orbital in an atom, and its m_l value is zero. Orbitals with the same value of n are said to be in the same **principal level** (or **principal shell**). Orbitals with the same value of n and l are said to be in the same **sublevel** (or **subshell**). The following diagram shows all of the orbitals, each represented by a small square, in the first three principal levels.



For example, the $n = 2$ level contains the $l = 0$ and $l = 1$ sublevels. Within the $n = 2$ level, the $l = 0$ sublevel—called the 2*s* sublevel—contains only one orbital (the 2*s* orbital), with $m_l = 0$. The $l = 1$ sublevel—called the 2*p* sublevel—contains three 2*p* orbitals, with $m_l = -1, 0, +1$.

In general, notice the following:

- The number of sublevels in any level is equal to n, the principal quantum number. Therefore, the $n = 1$ level has one sublevel, the $n = 2$ level has two sublevels, etc.
- The number of orbitals in any sublevel is equal to $2l + 1$. Therefore, the *s* sublevel ($l = 0$) has one orbital, the *p* sublevel ($l = 1$) has three orbitals, the *d* sublevel ($l = 2$) has five orbitals, etc.
- The number of orbitals in a level is equal to n^2. Therefore, the $n = 1$ level has one orbital, the $n = 2$ level has four orbitals, the $n = 3$ level has nine orbitals, etc.

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EXAMPLE 7.5 Quantum Numbers I

What are the quantum numbers and names (for example, 2*s*, 2*p*) of the orbitals in the $n = 4$ principal level? How many $n = 4$ orbitals exist?

SOLUTION

You first determine the possible values of l (from the given value of n). You then determine the possible values of m_l for each possible value of l. For a given value of n, the possible values of l are $0, 1, 2, \ldots, (n - 1)$.	$n = 4$; therefore $l = 0, 1, 2$, and 3
For a given value of l, the possible values of m_l are the integer values including zero ranging from $-l$ to $+l$. The name of an orbital is its principal quantum number (n) followed by the letter corresponding to the value l. The total number of orbitals is given by n^2.	

l	Possible m_l Values	Orbital Name(s)
0	0	4*s* (1 orbital)
1	$-1, 0, +1$	4*p* (3 orbitals)
2	$-2, -1, 0, +1, +2$	4*d* (5 orbitals)
3	$-3, -2, -1, 0, +1, +2, +3$	4*f* (7 orbitals)
Total number of orbitals $= 4^2 = 16$		

FOR PRACTICE 7.5

List the quantum numbers associated with all of the 5*d* orbitals. How many 5*d* orbitals exist?

EXAMPLE 7.6 Quantum Numbers II

These sets of quantum numbers are each supposed to specify an orbital. One set, however, is erroneous. Which one and why?

(a) $n = 3; l = 0; m_l = 0$

(b) $n = 2; l = 1; m_l = -1$

(c) $n = 1; l = 0; m_l = 0$

(d) $n = 4; l = 1; m_l = -2$

SOLUTION

Choice **(d)** is erroneous because, for $l = 1$, the possible values of m_l are only $-1, 0$, and $+1$.

FOR PRACTICE 7.6

Each of the following sets of quantum numbers is supposed to specify an orbital. However, each set contains one quantum number that is not allowed. Replace the quantum number that is not allowed with one that is allowed.

(a) $n = 3; l = 3; m_l = +2$

(b) $n = 2; l = 1; m_l = -2$

(c) $n = 1; l = 1; m_l = 0$

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Atomic Spectroscopy Explained

Quantum theory explains the atomic spectra of atoms discussed in Section 7.3. Each wavelength in the emission spectrum of an atom corresponds to an electron *transition* between quantum-mechanical orbitals. When an atom absorbs energy, an electron in a lower energy level orbital is *excited* or promoted to a higher energy level orbital, as shown in **Figure 7.18**▼. In this new configuration, however, the atom is unstable, and the electron quickly falls back or *relaxes* to a lower energy orbital. As it does so, it releases a photon of light containing an amount of energy precisely equal to the energy difference between the two energy levels. We saw previously (see Equation 7.7) that the energy of an orbital with principal quantum number n is given by $E_n = -2.18 \times 10^{-18}\,\text{J}(1/n^2)$, where $n = 1, 2, 3, \ldots$. Therefore, the *difference* in energy between two levels n_{initial} and n_{final} is given by $\Delta E = E_{\text{final}} - E_{\text{initial}}$. If we substitute the expression for E_n into the expression for ΔE, we get the following important expression for the change in energy that occurs in an atom when an electron changes energy levels:

$$\begin{aligned}\Delta E &= E_{\text{final}} - E_{\text{initial}}\\ &= -2.18 \times 10^{-18}\,\text{J}\left(\frac{1}{n_f{}^2}\right) - \left[-2.18 \times 10^{-18}\,\text{J}\left(\frac{1}{n_i{}^2}\right)\right]\end{aligned}$$

$$\Delta E = -2.18 \times 10^{-18}\,\text{J}\left(\frac{1}{n_f{}^2} - \frac{1}{n_i{}^2}\right) \qquad [7.8]$$

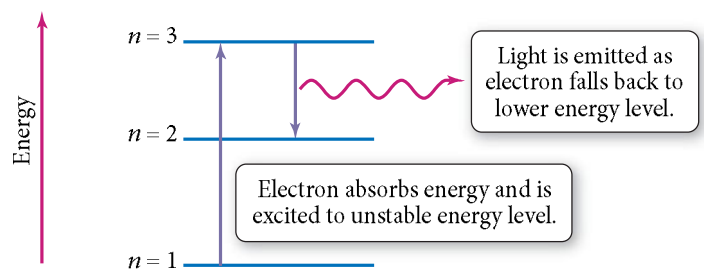
For example, suppose that an electron in a hydrogen atom relaxes from an orbital in the $n = 3$ level to an orbital in the $n = 2$ level. Recall that the energy of an orbital in the hydrogen atom depends only on n and is given by $E_n = -2.18 \times 10^{-18}\,\text{J}(1/n^2)$, where $n = 1, 2, 3, \ldots$. Therefore, ΔE, the energy difference corresponding to the transition from $n = 3$ to $n = 2$, is determined as follows:

$$\begin{aligned}\Delta E_{\text{atom}} &= E_2 - E_3\\ &= -2.18 \times 10^{-18}\,\text{J}\left(\frac{1}{2^2}\right) - \left[-2.18 \times 10^{-18}\,\text{J}\left(\frac{1}{3^2}\right)\right]\\ &= -2.18 \times 10^{-18}\,\text{J}\left(\frac{1}{2^2} - \frac{1}{3^2}\right)\\ &= -3.03 \times 10^{-19}\,\text{J}\end{aligned}$$

The energy carries a negative sign because the atom *emits* the energy as it relaxes from $n = 3$ to $n = 2$. Since energy must be conserved, the exact amount of energy emitted by the atom is carried away by the photon:

$$\Delta E_{\text{atom}} = -E_{\text{photon}}$$

Excitation and Radiation



▲ **FIGURE 7.18 Excitation and Radiation** When an atom absorbs energy, an electron can be excited from an orbital in a lower energy level to an orbital in a higher energy level. The electron in this "excited state" is unstable, however, and relaxes to a lower energy level, releasing energy in the form of electromagnetic radiation.

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This energy then determines the frequency and wavelength of the photon. Since the wavelength of the photon is related to its energy as $E = hc/\lambda$, we calculate the wavelength of the photon as follows:

$$\lambda = \frac{hc}{E}$$

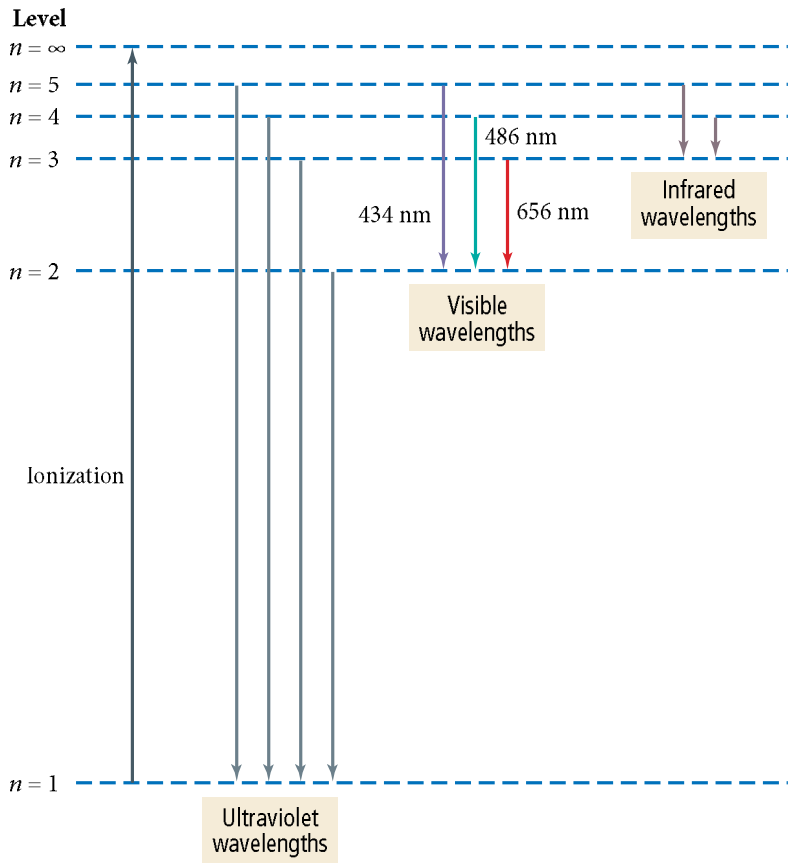
$$= \frac{(6.626 \times 10^{-34}\ \mathrm{J \cdot s})(3.00 \times 10^{8}\ \mathrm{m/s})}{3.03 \times 10^{-19}\ \mathrm{J}}$$

$$= 6.56 \times 10^{-7}\ \mathrm{m\ or\ 656\ nm}$$

The Rydberg equation, $1/\lambda = R(1/m^2 - 1/n^2)$, can be derived from the relationships just covered. We leave this derivation to an exercise (see Problem 7.62).

Consequently, the light emitted by an excited hydrogen atom as it relaxes from an orbital in the $n = 3$ level to an orbital in the $n = 2$ level has a wavelength of 656 nm (red). We can similarly calculate the light emitted due to a transition from $n = 4$ to $n = 2$ to be 486 nm (green). Notice that transitions between orbitals that are further apart in energy produce light that is higher in energy, and therefore shorter in wavelength, than transitions between orbitals that are closer together. **Figure 7.19▼** shows several of the transitions in the hydrogen atom and their corresponding wavelengths.

Hydrogen Energy Transitions and Radiation



▲ **FIGURE 7.19 Hydrogen Energy Transitions and Radiation** An atomic energy level diagram for hydrogen, showing some possible electron transitions between levels and the corresponding wavelengths of emitted light.

Conceptual Connection 7.5 Emission Spectra

Which transition will result in emitted light with the shortest wavelength?

(a) $n = 5 \rightarrow n = 4$
(b) $n = 4 \rightarrow n = 3$
(c) $n = 3 \rightarrow n = 2$

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EXAMPLE 7.7 Wavelength of Light for a Transition in the Hydrogen Atom

Determine the wavelength of light emitted when an electron in a hydrogen atom makes a transition from an orbital in $n = 6$ to an orbital in $n = 5$.

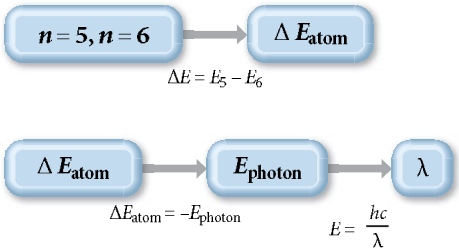
SORT You are given the energy levels of an atomic transition and asked to find the wavelength of emitted light.

GIVEN $n = 6 \rightarrow n = 5$
FIND λ

STRATEGIZE In the first part of the conceptual plan, calculate the energy of the electron in the $n = 6$ and $n = 5$ orbitals using Equation 7.7 and subtract to find ΔE_{atom}.

In the second part, find E_{photon} by taking the negative of ΔE_{atom}, and then calculate the wavelength corresponding to a photon of this energy using Equation 7.3. (The difference in sign between E_{photon} and ΔE_{atom} applies only to emission. *The energy of a photon must always be positive.*)

CONCEPTUAL PLAN



RELATIONSHIPS USED

$E_n = -2.18 \times 10^{-18}\,\text{J}(1/n^2)$

$E = hc/\lambda$

SOLVE Follow the conceptual plan. Begin by calculating ΔE_{atom}.

Calculate E_{photon} by changing the sign of ΔE_{atom}.

Solve the equation relating the energy of a photon to its wavelength for λ. Substitute the energy of the photon and calculate λ.

SOLUTION

$$\Delta E_{atom} = E_5 - E_6$$

$$= -2.18 \times 10^{-18}\,\text{J}\left(\frac{1}{5^2}\right) - \left[-2.18 \times 10^{-18}\,\text{J}\left(\frac{1}{6^2}\right)\right]$$

$$= -2.18 \times 10^{-18}\,\text{J}\left(\frac{1}{5^2} - \frac{1}{6^2}\right)$$

$$= -2.6\underline{6}44 \times 10^{-20}\,\text{J}$$

$$E_{photon} = -\Delta E_{atom} = +2.6\underline{6}44 \times 10^{-20}\,\text{J}$$

$$E = \frac{hc}{\lambda}$$

$$\lambda = \frac{hc}{E}$$

$$= \frac{(6.626 \times 10^{-34}\,\text{J}\cdot\text{s})(3.00 \times 10^{8}\,\text{m/s})}{2.6\underline{6}44 \times 10^{-20}\,\text{J}}$$

$$= 7.46 \times 10^{-6}\,\text{m}$$

CHECK The units of the answer (m) are correct for wavelength. The magnitude seems reasonable because 10^{-6} m is in the infrared region of the electromagnetic spectrum. We know that transitions from $n = 3$ or $n = 4$ to $n = 2$ lie in the visible region, so it makes sense that a transition between levels of higher n value (which are energetically closer to one another) would result in light of longer wavelength.

FOR PRACTICE 7.7

Determine the wavelength of the light absorbed when an electron in a hydrogen atom makes a transition from an orbital in $n = 2$ to an orbital in $n = 7$.

FOR MORE PRACTICE 7.7

An electron in the $n = 6$ level of the hydrogen atom relaxes to a lower energy level, emitting light of $\lambda = 93.8$ nm. Find the principal level to which the electron relaxed.

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7.6 The Shapes of Atomic Orbitals

As we noted previously, the shapes of atomic orbitals are important because covalent chemical bonds depend on the sharing of the electrons that occupy these orbitals. In one model of chemical bonding, for example, a bond consists of the overlap of atomic orbitals on adjacent atoms. Therefore the shapes of the overlapping orbitals determine the shape of the molecule. Although we limit ourselves in this chapter to the orbitals of the hydrogen atom, we will see in Chapter 8 that the orbitals of all atoms can be approximated as being hydrogen-like and therefore have very similar shapes to those of hydrogen.

The shape of an atomic orbital is determined primarily by l, the angular momentum quantum number. Recall that each value of l is assigned a letter that therefore corresponds to particular orbitals. For example, the orbitals with $l = 0$ are s orbitals; those with $l = 1$, p orbitals; those with $l = 2$, d orbitals, etc. We now examine the shape of each of these orbitals.

s Orbitals ($l = 0$)

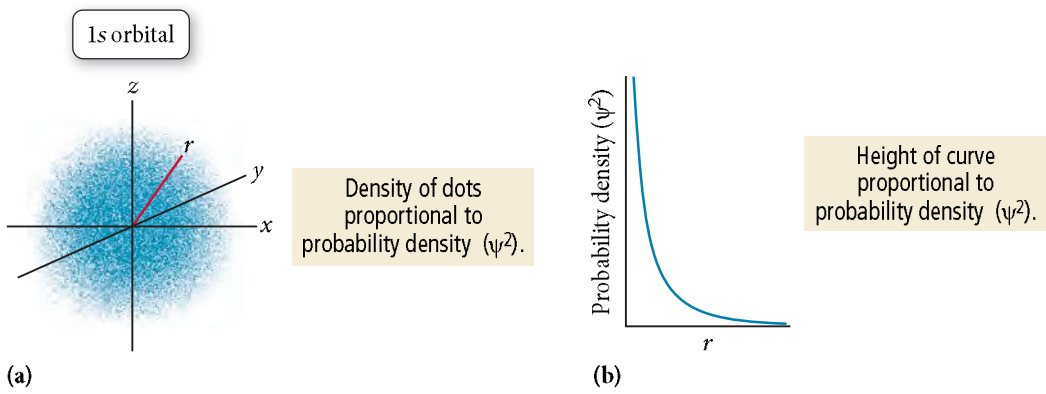
The lowest energy orbital is the spherically symmetrical 1s orbital shown in **Figure 7.20a▼.** This image is actually a three-dimensional plot of the wave function squared (ψ^2), which represents **probability density**, the probability (per unit volume) of finding the electron at a point in space.

$$\psi^2 = \text{probability density} = \frac{\text{probability}}{\text{unit volume}}$$

The magnitude of ψ^2 in this plot is proportional to the density of the dots shown in the image. The high dot density near the nucleus indicates a higher probability density for the electron there. As you move away from the nucleus, the probability density decreases. **Figure 7.20(b)▼** shows a plot of probability density (ψ^2) versus r, the distance from the nucleus. This is essentially a slice through the three-dimensional plot of ψ^2 and shows how the probability density decreases as r increases.

We can understand probability density with the help of a thought experiment. Imagine an electron in the 1s orbital located within the volume surrounding the nucleus. Imagine also taking a photograph of the electron every second for 10 or 15 minutes. In one photograph, the electron is very close to the nucleus, in another it is farther away, and so on. Each photo has a dot showing the electron's position relative to the nucleus when the photo was taken. Remember that you can never predict where the electron will be for any one photo. However, if you took hundreds of photos and superimposed all of them, you would have a plot similar to Figure 7.20(a)—a statistical representation of how likely the electron is to be found at each point.

An atomic orbital can also be represented by a geometrical shape that encompasses the volume where the electron is likely to be found most frequently—typically, 90% of



▲ **FIGURE 7.20 The 1s Orbital: Two Representations** In **(a)** the dot density is proportional to the electron probability density. In **(b),** the height of the curve is proportional to the electron probability density. The x-axis is r, the distance from the nucleus.

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the time. For example, the 1*s* orbital can be represented as the three-dimensional sphere shown in **Figure 7.21**▶. If we were to superimpose the dot-density representation of the 1*s* orbital on the shape representation, 90% of the dots would be within the sphere, meaning that when the electron is in the 1*s* orbital it has a 90% chance of being found within the sphere.

The plots we have just seen represent probability *density*. However, they are a bit misleading because they seem to imply that the electron is most likely to be found *at the nucleus*. To get a better idea of where the electron is most likely to be found, we can use a plot called the **radial distribution function**, shown in **Figure 7.22**▶ for the 1*s* orbital. The radial distribution function represents the *total probability of finding the electron within a thin spherical shell at a distance r from the nucleus.*

$$\text{Total radial probability (at a given } r) = \frac{\text{probability}}{\text{unit volume}} \times \text{volume of shell at } r$$

The radial distribution function represents, not *probability density at a point r*, but *total probability at a radius r*. In contrast to probability density, which has a maximum at the nucleus, the radial distribution function has a value of *zero* at the nucleus. It increases to a maximum at 52.9 pm and then decreases again with increasing *r*.

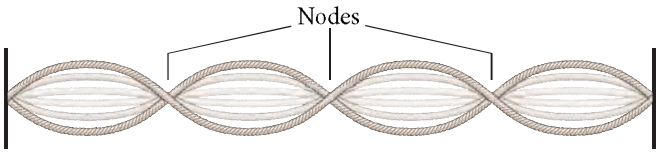
The shape of the radial distribution function is the result of multiplying together two functions with opposite trends in *r*:

1. the probability density function (ψ^2), which is the probability per unit volume, has a maximum at the nucleus, and decreases with increasing *r*
2. the volume of the thin shell, which is zero at the nucleus and increases with increasing *r*.

At the nucleus ($r = 0$) the probability *density* is at a maximum; however, the volume of a thin spherical shell is zero, so the radial distribution function is zero. As *r* increases, the volume of the thin spherical shell increases. We can see this by analogy to an onion. A spherical shell at a distance *r* from the nucleus is like a layer in an onion at a distance *r* from its center. If the layers of the onion all have the same thickness, then the volume of any one layer—think of this as the total amount of onion in the layer—is greater as *r* increases. Similarly, the volume of any one spherical shell in the radial distribution function increases with increasing distance from the nucleus, resulting in a greater total probability of finding the electron within that shell. Close to the nucleus, this increase in volume with increasing *r* outpaces the decrease in probability density, producing a maximum at 52.9 pm. Farther out, however, the density falls off faster than the volume increases.

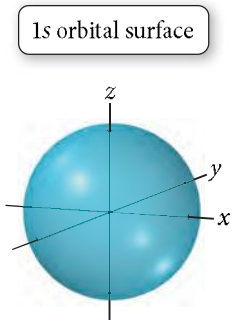
The maximum in the radial distribution function, 52.9 pm, turns out to be the very same radius that Bohr had predicted for the innermost orbit of the hydrogen atom. However, there is a significant conceptual difference between the two radii. In the Bohr model, every time you probe the atom (in its lowest energy state), you would find the electron at a radius of 52.9 pm. In the quantum-mechanical model, you would generally find the electron at various radii, with 52.9 pm having the greatest probability.

The probability densities and radial distribution functions for the 2*s* and 3*s* orbitals are shown in **Figure 7.23**▶. Like the 1*s* orbital, these orbitals are spherically symmetric. These orbitals are larger in size, however, than the 1*s* orbital, and, unlike the 1*s* orbital, they contain *nodes*. A **node** is a point where the wave function (ψ), and therefore the probability density (ψ^2) and radial distribution function, all go through zero. A node in a wave function is much like a node in a standing wave on a vibrating string. We can see nodes in an orbital most clearly by actually looking at a slice through the orbital. Plots of probability density and the radial distribution function as a function of *r* both reveal the presence of nodes. The probability of finding the electron at a node is zero.

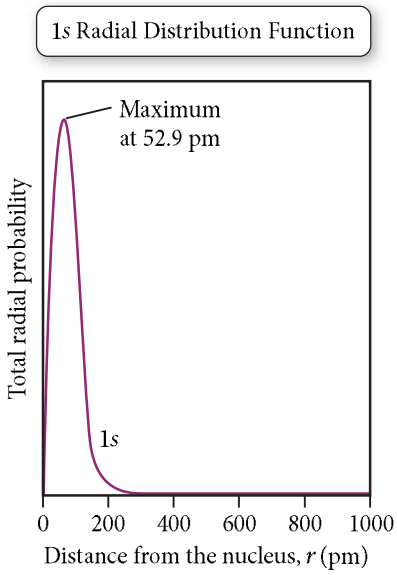


▲ The nodes in quantum-mechanical atomic orbitals are three-dimensional analogs of the nodes we find on a vibrating string.

When an orbital is represented as shown below, the surface shown is one of constant probability. The probability of finding the electron at any point on the surface is the same.



▲ **FIGURE 7.21 The 1s Orbital Surface** In this representation, the surface of the sphere encompasses the volume where the electron is found 90% of the time when the electron is in the 1*s* orbital.



▲ **FIGURE 7.22 The Radial Distribution Function for the 1s Orbital** The curve shows the total probability of finding the electron within a thin shell at a distance *r* from the nucleus.

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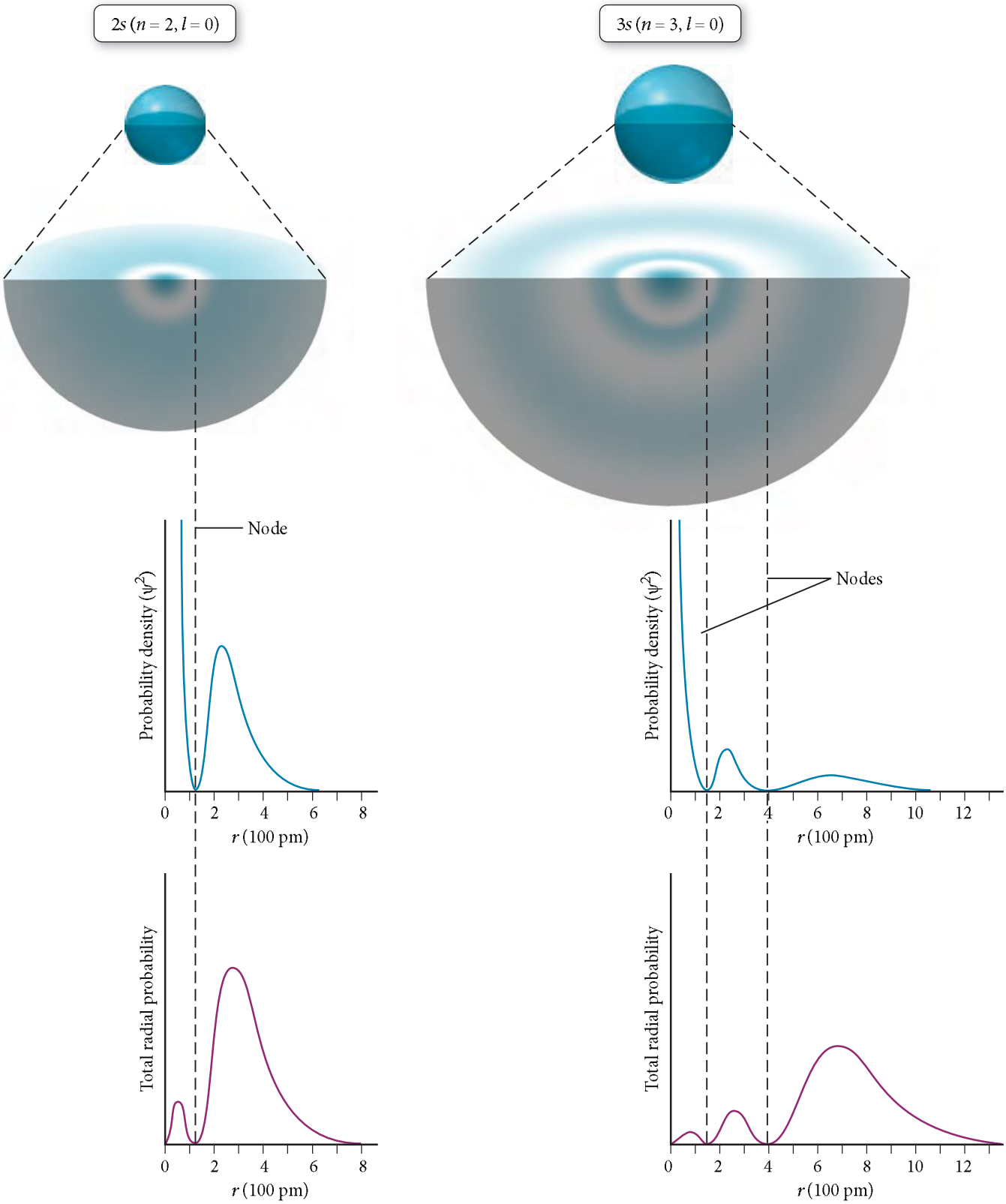
The 2*s* and 3*s* Orbitals



▲ **FIGURE 7.23 Probability Densities and Radial Distribution Functions for the 2s and 3s Orbitals**

A nodal plane is a plane where the electron probability density is zero. For example, in the d_{xy} orbitals, the nodal planes lie in the *xz* and *yz* planes.

p Orbitals ($l = 1$)

Each principal level with $n = 2$ or greater contains three *p* orbitals ($m_l = -1, 0, +1$). The three 2*p* orbitals and their radial distribution functions are shown in **Figure 7.24**▶. The *p* orbitals are not spherically symmetric like the *s* orbitals, but have two *lobes* of electron density on

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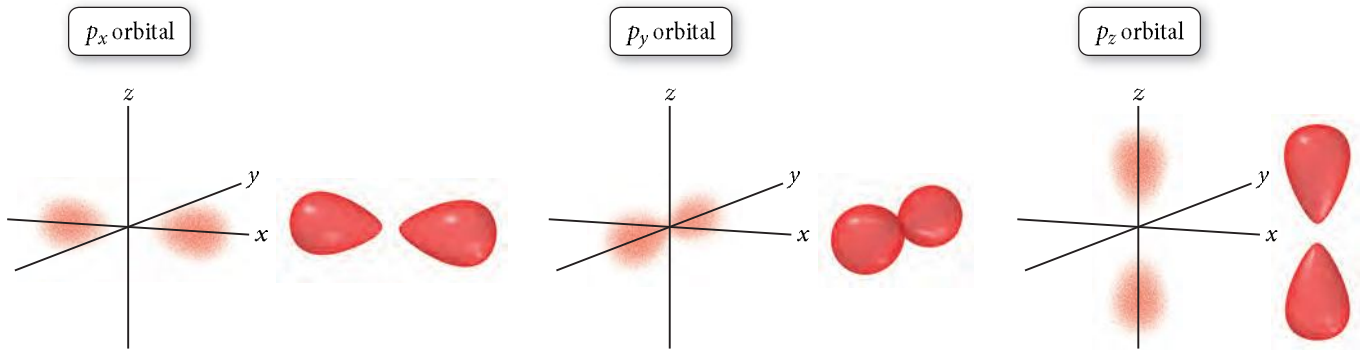
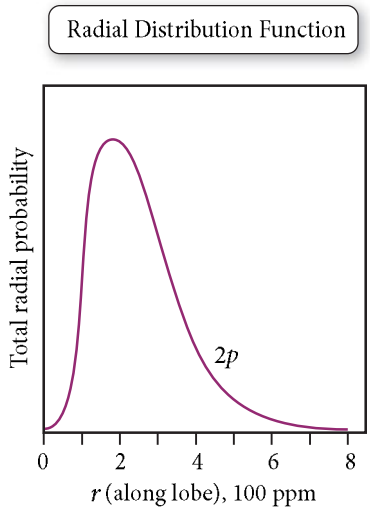


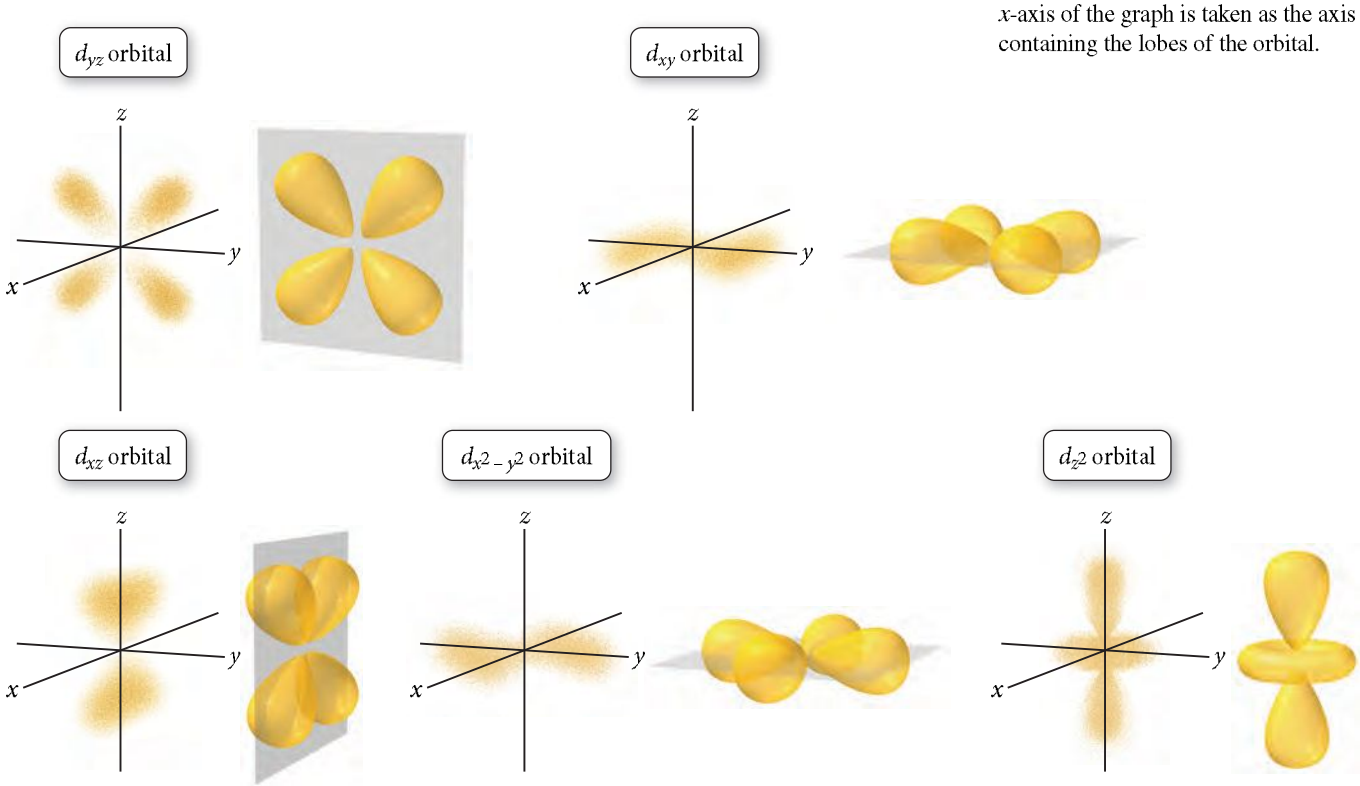
either side of the nucleus and a node located at the nucleus. The three p orbitals differ only in their orientation and are orthogonal (mutually perpendicular) to one another. It is convenient to define an x-, y-, and z-axis system and then label each p orbital as p_x, p_y, and p_z. The $3p$, $4p$, $5p$, and higher p orbitals are all similar in shape to the $2p$ orbitals, but they contain additional nodes (like the higher s orbitals) and are progressively larger in size.



▲ **FIGURE 7.24 The 2*p* Orbitals and Their Radial Distribution Function** The radial distribution function is the same for all three $2p$ orbitals when the x-axis of the graph is taken as the axis containing the lobes of the orbital.

d Orbitals ($l = 2$)

Each principal level with $n = 3$ or greater contains five d orbitals ($m_l = -2, -1, 0, +1, +2$). The five $3d$ orbitals are shown in **Figure 7.25▼**. Four of these orbitals have a cloverleaf shape, with four lobes of electron density around the nucleus and two perpendicular nodal planes. The d_{xy}, d_{xz}, and d_{yz} orbitals are oriented along the xy, xz, and yz planes, respectively, and their lobes are oriented *between* the corresponding axes. The four lobes of the $d_{x^2-y^2}$ orbital are oriented along the x- and y-axes. The d_{z^2} orbital is different in shape from the other four, having two lobes oriented along the z-axis and a donut-shaped ring along the xy plane. The $4d$, $5d$, $6d$, etc., orbitals are all similar in shape to the $3d$ orbitals, but they contain additional nodes and are progressively larger in size.



▲ **FIGURE 7.25 The 3*d* Orbitals**

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f Orbitals ($l = 3$)

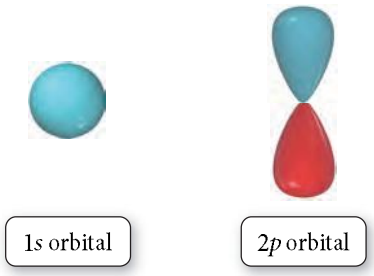
Each principal level with $n = 4$ or greater contains seven *f* orbitals ($m_l = -3, -2, -1, 0, +1, +2, +3$). These orbitals have more lobes and nodes than *d* orbitals.

The Phase of Orbitals

The orbitals we have just seen are three-dimensional waves. We can understand an important property of these orbitals by analogy to one-dimensional waves. Consider the one-dimensional waves shown here:

The wave on the left has a positive amplitude over its entire length, while the wave on the right has a positive amplitude over half of its length and a negative amplitude over the other half. The sign of the amplitude of a wave—positive or negative—is known as its **phase**. In these images, blue indicates positive phase and red indicates negative phase. The phase of a wave determines how it interferes with another wave as we saw in Section 7.2.

Just as a one-dimensional wave has a phase, so does a three-dimensional wave. We often represent the phase of a quantum mechanical orbital with color. For example, we can represent the phase of a 1s and 2p orbital as follows:



In these depictions, blue represents positive phase and red represents negative phase. The 1s orbital is all one phase, while the 2p orbital exhibits two different phases. The phase of quantum mechanical orbitals is important in bonding, as we shall see in Chapter 10.

▲ **FIGURE 7.26 Why Atoms Are Spherical** Atoms are depicted as roughly spherical because all the orbitals together make up roughly spherical shape.

The Shapes of Atoms

If some orbitals are shaped like dumbbells and three-dimensional cloverleafs, and if most of the volume of an atom is empty space diffusely occupied by electrons in these orbitals, then why do we often depict atoms as spheres?

Atoms are usually drawn as spheres because most atoms contain many electrons occupying a number of different orbitals. Therefore, the shape of an atom is obtained by superimposing all of its orbitals. If we superimpose the *s*, *p*, and *d* orbitals we get a spherical shape, as shown in **Figure 7.26**◀.

CHAPTER IN REVIEW

Key Terms

Section 7.1
quantum-mechanical model (253)

Section 7.2
electromagnetic radiation (254)
amplitude (254)
wavelength (λ) (254)
frequency (ν) (255)
electromagnetic spectrum (256)
gamma rays (256)
X-rays (256)
ultraviolet (UV) radiation (256)
visible light (257)
infrared (IR) radiation (257)
microwaves (257)
radio waves (257)
interference (257)
constructive interference (257)
destructive interference (257)
diffraction (257)
photoelectric effect (258)
photon (quantum) (260)

Section 7.3
emission spectrum (262)

Section 7.4
de Broglie relation (265)
complementary properties (267)
Heisenberg's uncertainty principle (267)
deterministic (268)
indeterminacy (269)

Section 7.5
orbital (269)
wave function (270)
quantum number (270)

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5 PERIODIC PROPERTIES OF ELEMENTS

One of the greatest intellectual achievement in chemistry is the periodic table of the elements. The periodic table can be printed on a single sheet of paper, but what it contains and can teach us is enormous and beyond measure.

The periodic table is the outcome of continuous effort, beginning in ancient Greece, to understand the true nature of matter. It can rightly be called the Bible of chemistry. The value of the periodic table is not only in its organization of known information, but also in its ability to predict unknown properties. The true greatness of the periodic table lies in that ability.

5.1 Periodic table

(a) Proposals before Mendeleev

The concept of elements is very old, dating back to ancient Greece. According to the Greek philosophers, matter was made up of four elements: earth, water, fire and air. That view gradually declined, and in the 17th century, the definition of elements by the British chemist Robert Boyle (1627-1691) replaced it. Boyle stated that **element**s are substances that cannot be decomposed into simpler substances.

Lavoisier proposed a list of elements in his principal work "*Traite Elementire de Chemie*". Though he included light and heat in the list, the other members of the list were what we accept as elements today. In addition, he added to the list some elements that had not yet been detected but whose existence he presumed. For instance, chlorine had not yet been isolated, but he added it to the list as the radical of muriatic acid[a)]. Similarly, sodium and potassium were listed.

In the early 19th century, these elements were isolated by means of electrolysis, and the list of elements gradually expanded. In the middle of the 19th century, spectroscopic analysis, a new method of detecting elements was introduced and accelerated the expansion of the list. Although welcomed by chemists, new problems arose. One was the question "Is there any limitation on the number of elements?" and the other was "Should we expect any kind of regularity in the properties of elements?"

The discovery of new elements catalysed such discussions. When iodine was discovered in 1826, the German chemist Johann Wolfgang Döbereiner (1780-1849) noticed the similarity between this new element and the already known elements chlorine and bromine. He also detected other trios of similar elements. This is the "**triad**" theory of Döbereiner.

Table 5.1 Triads by Döbereiner

lithium (Li)	calcium (Ca)	chlorine (Cl)	sulfur (S)	manganese (Mn)
sodium (Na)	strontium (Sr)	bromine (Br)	selenium (Se)	chromium (Cr)
potassium (K)	barium (Ba)	iodine (I)	tellurium (Te)	iron (Fe)

(b) Predictions by Mendeleev and their fulfillment

Many other ideas were proposed but nonesatisfied the scholarly world of that day. However, the theory proposed by the Russian chemist Dmitrij Ivanovich Mendeleev (1834-1907), and independently by the German chemist Julius Lothar Meyer (1830-1895) differed from other theories and was more persuasive. Their common viewpoint is stated below.

The viewpoint of Mendeleev and Meyer

(1) The list of elements known at that time is not necessarily complete.
(2) It is expected that the properties of elements vary systematically. Hence the properties of unknown elementscan be predicted.

[a)] the old name of hydrochloric acid

Initially the theory of Mendeleev failed to attract much attention. In 1875, however, it was shown that a new element gallium discovered by the French chemist Paul Emile Lecoq de Boisbaudran (1838-1912) was none other than *eka*-aluminum whose existence and properties had been predicted by Mendeleev. Thus, the significance of the theory of Mendeleev and Meyer was gradually accepted. Table 5.2 gives the properties predicted by Mendeleev for the unknown element *eka*-silicon and those for germanium discovered by the German chemist Clemens Alexander Winkler (1838-1904).

Table 5.2 Predictions of properties by Mendeleev and comparison with actual results

property	eka-silicon	germanium
atomic weight	72	72.32
specific gravity	5.5	5.47
atomic volume	13	13.22
valence	4	4
specific heat	0.073	0.076
specific gravity of dioxide	4.7	4.703
boiling point of tetrachloride (°C)	<100	86

Mendeleev published a table that might be regarded as the origin of the modern periodic table. In preparing the table, Mendeleev initially arranged the elements in the order of their atomic weights, as his predecessors had. However, he pointed out the periodicity of properties, and sometimes rearranged the elements, thus reversing the order based on atomic weights.

Furthermore, the situation was complicated because the procedure for determining the atomic weights had not yet been standardized, and sometimes chemists might use different atomic weights for one and the same element. This troublesome dilemma was gradually improved after the 1st International Chemical Congress[a)] which Mendeleev attended, yet difficulties still remained.

By depending on valence in determining atomic weights, Mendeleev circumvented the problem to some extent (Table 5.3).

Table 5.3 Early periodic table by Mendeleev (1869)

			K = 39	Rb = 85	Cs = 133	—	—
			Ca = 40	Sr = 87	Ba = 137	—	—
			—	?Yt = 88?	?Di = 138?	Er = 178?	—
			Ti = 48?	Zr = 90	Ce = 140?	?La = 180?	Th = 231
			V = 51	Nb = 94	—	Ta = 182	—
			Cr = 52	Mo = 96	—	W = 184	U = 240
			Mn = 55	—	—	—	—
			Fe = 56	Ru = 104	—	Os = 195?	—
Typische Elemente			Co = 59	Rh = 104	—	Ir = 197	—
			Ni = 59	Pd = 106	—	Pt = 198?	—
H = 1	Li = 7	Na = 23	Cu = 63	Ag = 108	—	Au = 199?	—
	Be = 9,4	Mg = 24	Zn = 65	Cd = 112	—	Hg = 200	—
	B = 11	Al = 27,3	—	In = 113	—	Tl = 204	—
	C = 12	Si = 28	—	Sn = 118	—	Pb = 207	—
	N = 14	P = 31	As = 75	Sb = 122	—	Bi = 208	—
	O = 16	S = 32	Se = 78	Te = 125?	—	—	—
	F = 19	Cl = 35,5	Br = 80	J = 127	—	—	—

(c) Periodic table and electron configuration

The periodic table continuously expanded after the proposal of Mendeleev. Meanwhile

[a)] The Congress was held in 1860 at Karlsruhe, Germany. The purpose of the Congress was to discuss the problem of the unification of atomic weight. On this occasion Cannizzaro introduced the theory of Avogadro.

Table 5.4a Electron configuration of atoms ($_1$H-$_{54}$Xe)

period	element	K	L		M			N				O			
		1s	2s	2p	3s	3p	3d	4s	4p	4d	4f	5s	5p	5d	5f
1	1 H	1													
	2 He	2													
2	3 Li	2	1												
	4 Be	2	2												
	5 B	2	2	1											
	6 C	2	2	2											
	7 N	2	2	3											
	8 O	2	2	4											
	9 F	2	2	5											
	10 Ne	2	2	6											
3	11 Na	2	2	6	1										
	12 Mg	2	2	6	2										
	13 Al	2	2	6	2	1									
	14 Si	2	2	6	2	2									
	15 P	2	2	6	2	3									
	16 S	2	2	6	2	4									
	17 Cl	2	2	6	2	5									
	18 Ar	2	2	6	2	6									
4	19 K	2	2	6	2	6		1							
	20 Ca	2	2	6	2	6		2							
	21 Sc	2	2	6	2	6	1	2							
	22 Ti	2	2	6	2	6	2	2							
	23 V	2	2	6	2	6	3	2							
	24 Cr	2	2	6	2	6	5	1							
	25 Mn	2	2	6	2	6	5	2							
	26 Fe	2	2	6	2	6	6	2							
	27 Co	2	2	6	2	6	7	2							
	28 Ni	2	2	6	2	6	8	2							
	29 Cu	2	2	6	2	6	10	1							
	30 Zn	2	2	6	2	6	10	2							
	31 Ga	2	2	6	2	6	10	2	1						
	32 Ge	2	2	6	2	6	10	2	2						
	33 As	2	2	6	2	6	10	2	3						
	34 Se	2	2	6	2	6	10	2	4						
	35 Br	2	2	6	2	6	10	2	5						
	36 Kr	2	2	6	2	6	10	2	6						
5	37 Rb	2	2	6	2	6	10	2	6			1			
	38 Sr	2	2	6	2	6	10	2	6			2			
	39 Y	2	2	6	2	6	10	2	6	1		2			
	40 Zr	2	2	6	2	6	10	2	6	2		2			
	41 Nb	2	2	6	2	6	10	2	6	4		1			
	42 Mo	2	2	6	2	6	10	2	6	5		1			
	43 Tc	2	2	6	2	6	10	2	6	6		1			
	44 Ru	2	2	6	2	6	10	2	6	7		1			
	45 Rh	2	2	6	2	6	10	2	6	8		1			
	46 Pd	2	2	6	2	6	10	2	6	10					
	47 Ag	2	2	6	2	6	10	2	6	10		1			
	48 Cd	2	2	6	2	6	10	2	6	10		2			
	49 In	2	2	6	2	6	10	2	6	10		2	1		
	50 Sn	2	2	6	2	6	10	2	6	10		2	2		
	51 Sb	2	2	6	2	6	10	2	6	10		2	3		
	52 Te	2	2	6	2	6	10	2	6	10		2	4		
	53 I	2	2	6	2	6	10	2	6	10		2	5		
	54 Xe	2	2	6	2	6	10	2	6	10		2	6		

several problems arose. One important problem was how to deal with rare gases, transition elements and **rare earth elements**. All these problems were nicely solved and made the periodic table more valuable. The periodic table, being the Bible of chemistry, should be consulted frequently.

The new entry for the unreactive rare gases was conveniently inserted between the very reactive positive elements, the alkaline metals (group 1) and the very reactive negative elements, halogens (group 7).

Transition metal elements were accommodated in the periodic table by introducing the **long period** though the rationale was not quite clear. The real problem was the lanthanoids. They were treated as “extra” elements and were placed marginally out of the main body of the periodic table. However, in fact that procedure did not solve the main problem. First of all, why such extra elements existed was not clear at all; even more puzzling was the question: as to whether there was any limitation on the number of elements? Since very similar elements existed, it was very difficult to judge how many elements could exist.

The Bohr thoey and experiments by Moseley yieldede theoretical solution of these problems. The explanation of the periodic table from the 1st period to the 3rd period could be explained by the theory of electron configuration described in Ch. 4. The 1st period ($_1$H and $_2$He) corresponds to the

process in which electrons are going to occupy the 1s orbital. Similarly the 2nd period (from $_{3}$Li to $_{10}$Ne)

Table 5.4b Electron configuration of atoms ($_{55}$Cs-$_{103}$Lr)

period	element	K	L		M			N				O				P			Q
		1s	2s	2p	3s	3p	3d	4s	4p	4d	4f	5s	5p	5d	5f	6s	6p	6d	7s
6	55 Cs	2	2	6	2	6	10	2	6	10		2	6			1			
	56 Ba	2	2	6	2	6	10	2	6	10		2	6			2			
	57 La	2	2	6	2	6	10	2	6	10		2	6	1		2			
	58 Ce	2	2	6	2	6	10	2	6	10	1	2	6	1		2			
	59 Pr	2	2	6	2	6	10	2	6	10	3	2	6			2			
	60 Nd	2	2	6	2	6	10	2	6	10	4	2	6			2			
	61 Pm	2	2	6	2	6	10	2	6	10	5	2	6			2			
	62 Sm	2	2	6	2	6	10	2	6	10	6	2	6			2			
	63 Eu	2	2	6	2	6	10	2	6	10	7	2	6			2			
	64 Gd	2	2	6	2	6	10	2	6	10	7	2	6	1		2			
	65 Tb	2	2	6	2	6	10	2	6	10	9	2	6			2			
	66 Dy	2	2	6	2	6	10	2	6	10	10	2	6			2			
	67 Ho	2	2	6	2	6	10	2	6	10	11	2	6			2			
	68 Er	2	2	6	2	6	10	2	6	10	12	2	6			2			
	69 Tm	2	2	6	2	6	10	2	6	10	13	2	6			2			
	70 Yb	2	2	6	2	6	10	2	6	10	14	2	6			2			
	71 Lu	2	2	6	2	6	10	2	6	10	14	2	6	1		2			
	72 Hf	2	2	6	2	6	10	2	6	10	14	2	6	2		2			
	73 Ta	2	2	6	2	6	10	2	6	10	14	2	6	3		2			
	74 W	2	2	6	2	6	10	2	6	10	14	2	6	4		2			
	75 Re	2	2	6	2	6	10	2	6	10	14	2	6	5		2			
	76 Os	2	2	6	2	6	10	2	6	10	14	2	6	6		2			
	77 Ir	2	2	6	2	6	10	2	6	10	14	2	6	7		2			
	78 Pt	2	2	6	2	6	10	2	6	10	14	2	6	9		1			
	79 Au	2	2	6	2	6	10	2	6	10	14	2	6	10		1			
	80 Hg	2	2	6	2	6	10	2	6	10	14	2	6	10		2			
	81 Tl	2	2	6	2	6	10	2	6	10	14	2	6	10		2	1		
	82 Pb	2	2	6	2	6	10	2	6	10	14	2	6	10		2	2		
	83 Bi	2	2	6	2	6	10	2	6	10	14	2	6	10		2	3		
	84 Po	2	2	6	2	6	10	2	6	10	14	2	6	10		2	4		
	85 At	2	2	6	2	6	10	2	6	10	14	2	6	10		2	5		
	86 Rn	2	2	6	2	6	10	2	6	10	14	2	6	10		2	6		
7	87 Fr	2	2	6	2	6	10	2	6	10	14	2	6	10		2	6		1
	88 Ra	2	2	6	2	6	10	2	6	10	14	2	6	10		2	6		2
	89 Ac	2	2	6	2	6	10	2	6	10	14	2	6	10		2	6	1	2
	90 Th	2	2	6	2	6	10	2	6	10	14	2	6	10		2	6	2	2
	91 Pa	2	2	6	2	6	10	2	6	10	14	2	6	10	2	2	6	1	2
	92 U	2	2	6	2	6	10	2	6	10	14	2	6	10	3	2	6	1	2
	93 Np	2	2	6	2	6	10	2	6	10	14	2	6	10	4	2	6	1	2
	94 Pu	2	2	6	2	6	10	2	6	10	14	2	6	10	6	2	6		2
	95 Am	2	2	6	2	6	10	2	6	10	14	2	6	10	7	2	6		2
	96 Cm	2	2	6	2	6	10	2	6	10	14	2	6	10	7	2	6	1	2
	97 Bk	2	2	6	2	6	10	2	6	10	14	2	6	10	8	2	6	1	2
	98 Cf	2	2	6	2	6	10	2	6	10	14	2	6	10	9	2	6	1	2
	99 Es	2	2	6	2	6	10	2	6	10	14	2	6	10	10	2	6	1	2
	100 Fm	2	2	6	2	6	10	2	6	10	14	2	6	10	11	2	6	1	2
	101 Md	2	2	6	2	6	10	2	6	10	14	2	6	10	12	2	6	1	2
	102 No	2	2	6	2	6	10	2	6	10	14	2	6	10	13	2	6	1	2
	103 Lr	2	2	6	2	6	10	2	6	10	14	2	6	10	14	2	6	1	2

corresponds to the occupation of the 1s, 2s and 2p orbitals by electrons, and the 3rd period (from $_{11}$Na to $_{18}$Ar) to the occupation of the 1s, 2s, 2p, 3s and 3p orbitals.

The long period begins with the 4th period. The explanation for it is that the shape of d orbitals differ greatly from a circle, and hence the energy of 3d electrons is even higher than that of 4s electrons. As a result, in the 4th period, electrons will occupy the 4s orbital ($_{19}$K and $_{20}$Ca) immediately after occupying the 3s and 3p orbitals, skipping over the 3d orbital. Then electrons begin to occupy the five 3d orbitals. This process corresponds to the ten elements from $_{21}$Sc to $_{30}$Zn. The process of the occupation of the 4p orbitals that then ensued corresponds to the six elements from $_{31}$Ga to $_{36}$Kr. This is the reason why the 4th period contains eighteen elements rather than eight. The energy of electrons in the 4f orbitals is much higher than that in 4d orbitals and hence 4f electrons do not play any role in the 4th period.

The 5th period resembles the 4th period. The electrons will occupy the 5s, 4d and 5p orbitals in that order. Consequently the 5th period will have eighteen elements. The 4f orbitals are not involved yet and this is the reason why the number of elements in the 5th period is eighteen.

The number of elements included in the 6th period is now thirty-two because the 7x2 = 14 elements corresponding to the occupation of the 4f orbitals are included. At first electrons occupy the 6s orbital ($_{55}$Cs and $_{56}$Ba). Though there is some exception, the elements from $_{57}$La to $_{80}$Hg

correspond to the occupation of the 4f and then the 5d orbitals. The **lanthanoid** (to $_{71}$Lu) series of rare earth elements correspond to the occupation of the 4f orbitals. After this process, six main group elements ($_{81}$Tl to $_{86}$Rn) follow which corresponds to the occupation of the 6p orbitals.

The 7th period starts from the occupation of the 7s orbital ($_{87}$Fr and $_{88}$Ra) followed by the filling of the 5f orbitals to yield the **actinoid** series of rare earth elements (from $_{89}$Ac to element no. 103). The world of elements is going to expand a little further, but among naturally occurring elements, the element with the largest atomic number is $_{92}$U. Elements beyond $_{92}$U are artificial elements with very short half-lives. It is not easy to foretell the extent of the list of such elements, but it is most likely that new elements will have very short half-lives.

In Table 5.5, the relation between the periodic table and electron configuration is summarized.

Table 5.5 Electron configuration of each period

period	orbitals filled	number of elements
1 (short)	1s	2
2 (short)	2s, 2p	2 + 6 = 8
3 (short)	3s, 3p	2 + 6 = 8
4 (long)	3d, 4s, 4p	2 + 6 + 10 = 18
5 (long)	4d, 5s, 5p	2 + 6 + 10 = 18
6 (long)	4f, 5d, 6s, 6p	2 + 6 + 10 + 14 = 32

Sample exercise 5.1 Electron configuration of lawrencium

The electron configuration of $_{89}$Ac is $_{86}$Rn.6d^{1}7s^2. Propose the electron configuration of lawrencium $_{103}$Lr.

Answer

Lawrencium has fourteen more electrons as compared with actinium. Since these electrons will occupy the 5f orbitals, the electron configuration of $_{103}$Lr is $_{86}$Rn. 5f^{14}6d^{1}7s^2.

As previously described, Moseley's law states that there is the following relation between the wavelength λ of the characteristic X-ray of the element and the electric charge of its nucleus *Z* (*i.e.*, atomic number):

$$1/\lambda = c(Z - s)^2 \tag{2.11}$$

Thanks to Moseley's law, the elements can now be roll-called by atomic number. We are now able to know the exact number of elements in nature.

5.2 Periodic nature of the properties of simple bodies

(1) First ionization energy

When the elements were arranged according to their atomic weights, the properties of simple bodies or compounds exhibited some periodicity, and this observation led to the discovery of the periodic law. The electron configuration of elements influences not only the chemical properties of elements but also their physical properties. The periodicity is clearly demonstrated because the ionization energy of atoms is directly governed by the electron configuration. The **ionization energy** is defined as the heat of reaction required to remove an electron from a neutral atom, for example, sodium:

$$Na(g) \rightarrow Na^+(g) + e^- \tag{5.1}$$

The **1st ionization energy**, the energy required to remove the 1st electron, shows a remarkable periodicity as is clearly shown in Fig. 5.1. For any period, the ionization energy increases as the

atomic number increases to reach the maximum value that for the rare gas. In the same group, the ionization energy decreases as the atomic number increases. Such tendencies can be explained in terms of the number of valence electrons, the nuclear charge, and the number of inner shell electrons.

The 2nd and 3rd ionization energies are defined as the energies required to remove the 2nd and 3rd electrons.

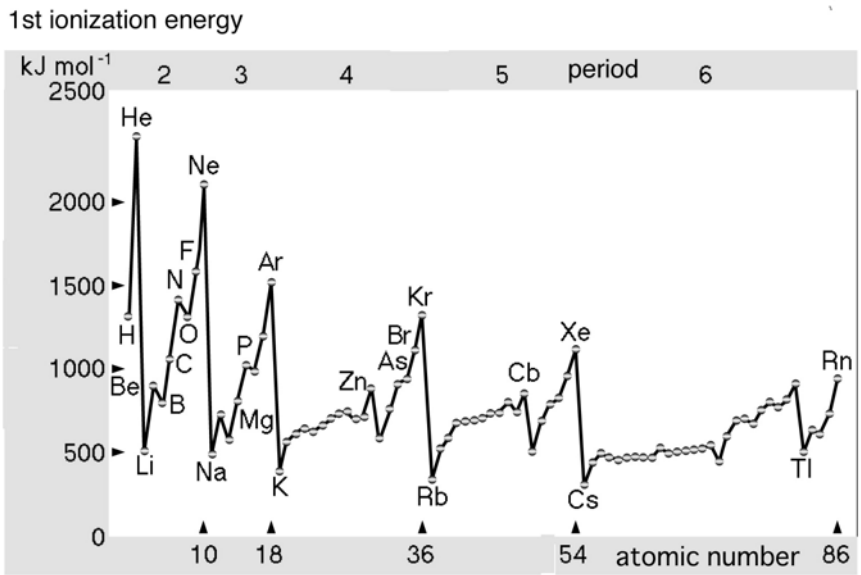


Figure 5.1 First ionization energy of atoms

For every period, the energy is a minimum for the alkaline metal, and a maximum for the rare gases.

Sample Exercise 5.2 Ionization energy

Three atoms have the electron configurations shown below.

(1) $1s^2 2s^2 2p^6$

(2) $1s^2 2s^2 2p^6 3s^1$

(3) $1s^2 2s^2 2p^6 3s^2$

Which of the three atoms has the highest 1st ionization energy? Propose which atom may have the highest 2nd ionization energy?

Answer

Atom (1) has the closed electron shell, and should have the highest ionization energy. Atoms (2) and (3) are sodium and magnesium, respectively. The second electron to be removed is a 2p electron for Na but a 3s electron for Mg. You can surmise that the outer electron is easer to remove as compared with the inner electron.

(b) Electron affinity and electronegativity

Electron affinity is defined as the heat of reaction in which an electron is added to a gaseous neutral atom, *e.g.*,

$$F(g) + e^- \rightarrow F^-(g) \qquad (5.2)$$

A positive value indicates an exothermic reaction, a negative value an endothermic reaction. Since there are not many atoms, that can add an electron in the gas phase, the available data is limited as compared with that for ionization energies. Table 5.6 indicates that the electron affinity is in general larger for nonmetals than for metals.

Table 5.6 Electron affinity of atoms

H 72.4	C 122.5	F 322.3
Li 59.	O 141.8	Cl 348.3
Na 54.0	P 72.4	Br 324.2
K 48.2	S 200.7	I 295.2

The magnitude of (electron) negativity is defined by **electronegativity** (Table 5.7), which is a measure of an atom's ability to hold electrons. The American chemist Robert Sanderson Mulliken (1896-1986) defined **electronegativity** as proportional to the arithmetic mean of the ionization energy and the electron affinity.

Table 5.7 Electronegativity of main group elements (Pauling)

H 2.1						
Li 0.97	Be 1.5	B 2.0	C 2.5	N 3.1	O 3.5	F 4.1
Na 1.0	Mg 1.2	Al 1.5	Si 1.7	P 2.1	S 2.4	Cl 2.8
K 0.90	Ca 1.0	Ga 1.8	Ge 2.0	As 2.2	Se 2.5	Br 2.7
Rb 0.89	Sr 1.0	In 1.5	Sn 1.72	Sb 1.82	Te 2.0	I 2.2
Cs 0.86	Ba 0.97	Tl 1.4	Pb 1.5	Bi 1.7	Po 1.8	At 1.9

Pauling defined the difference of electronegativity between two atoms A and B as the difference in bond energies of the diatomic molecules AB, AA and BB. Suppose D(A-B), D(A-A) and D(B-B) are the bond energies for AB, AA and BB, respectively. D(A-B) is larger than the geometric mean of both D(A-A) and D(B-B). This is because hetero-diatomic molecules are in general more stable than homo-diatomic molecules due to the contribution of ionic structure. Consequently, Δ(A-B), as defined below, is positive.

$$\Delta(\text{A-B}) = D(\text{A-B}) - \sqrt{D(\text{A-A})D(\text{B-B})} > 0 \qquad (5.3)$$

Δ(A-B) will be larger as the ionic character of the bond is larger. Using these values, Pauling defined the electronegativity x as a measure of an atom's ability to attract electrons.

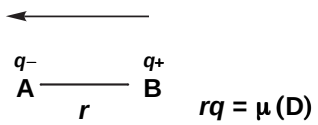
$$|x_A - x_B| = \sqrt{D(\text{A-B})} \qquad (5.4)$$

where x_A and x_B are the electronegativities of atoms A and B, respectively.

Regardless of which of two electronegativity scale one chooses, it is clear that the electronegativity increases going from left to right across a period and decreases going down the group for the main group elements. Electronegativity is very useful in understanding the chemical properties of the elements.

Much more useful information can be drawn from Table 5.7. The difference between the electronegativity of two bonding atoms can be, though only semi-quantitatively, correlated with such properties of chemical bonds as the dipole moment or the bond energy.

Suppose there is an unequal charge distribution in the A-B bond ($x_A > x_B$). Pairs of positive and negative charges $\pm q$ separated by distance r form, (electric) **dipoles**.



The direction of the dipole can be represented by an arrow pointing towards the negative charge center with the tail of the arrow at the positive center of the charge. The magnitude of the dipole, *rq*, is called the **dipole moment**. The dipole moment is a vector with the magnitude μ and a direction. The magnitude can be determined by experiment but the direction cannot.

The dipole moment of a molecule (**molecular dipole moment**) is the vector sum of the dipole moment of each bond (**bond dipole moment**). If there is symmetry in the molecule, large bond dipole moments may cancel each other so that the molecular dipole moment will be small or even zero.

Sample Exercise 5.3 Bond dipole moment and molecular dipole moment

(a) Answer the following questions on hydrogen chloride HCl and carbon tetrachloride CCl_4. Show the direction of the bond dipole moment for each compound. Propose whether these have molecular dipole moments or not.

(a) Carbon dioxide CO_2 and sulfur trioxide SO_3 do not have molecular dipole moments. Propose the molecular structures of these compounds based on these observations.

Answer

(a) The direction of the bond dipole moment is shown below. HCl should have a molecular dipole moment while CCl_4 should not because the bond dipole moments cancel each other.

(a) Both compounds should have symmetry in order that the large C-O and S-O bond dipole moments cancel each other. Hence, CO_2 is linear while SO_3 is a triangle.

(c) The oxidation number of atoms

There is a clear relation between the **oxidation number** (or **oxidation state**) of each atom and its position in the periodic table. Oxidation numbers of the atoms in a covalent compound are defined as the imaginary charges the atoms would have if the shared electrons were divided equally between identical atoms bonded to each other or, for different atoms, were all assigned to the atom in each bond that has the greater attraction for electrons.

(1) Main group elements

For main group elements, the oxidation numbers are in most cases the number of electrons the atom will lose or gain to attain the closed shell state, ns^2np^6 (except in the 1st period) or nd^{10} electron configuration (Fig. 5.2).

This is clear for the low period elements belonging to the 1st, 2nd and 13th-18th groups. For high period elements, these tend to have oxidation numbers corresponding to the electron configuration in which ns electrons are retained but np electrons are lost. For instance, tin Sn and lead Pb, both group 14 elements, have the oxidation number +2 by loosing np^2 electrons but retaining ns^2 electrons, in addition to the oxidation number +4. The same reason is applied for the fact that phosphorous P and bismuth Bi, both group 15 elements with ns^2np^3 electron configuration, have the oxidation numbers +3 and +5.

Generally speaking, the importance of the oxidation state in which ns^2 electrons are retained will become more and more important for the higher period elements. For nitrogen and phosphorus compounds, the oxidation number of +5 is important, while for bismuth the oxidation number of +3

is dominant, and that of +5 is rather rare.

Metals and semimetal elements (silicon Si or germanium Ge) seldom have negative values, but these are common for nonmetal elements. In hydrides of nitrogen and phosphorus, NH_3 and PH_3, the oxidation number of N and P are –3 for each. The higher period elements lose this property and bismuth Bi does not have any negative oxidation number. Among group 16 elements, the oxidation number of –2 is important as is the case with oxygen O. This tendency again gradually decreases among higher period elements. For instance oxygen has only negative oxidation numbers but sulfur S has positive oxidation numbers such as +4 and +6 which are significant.

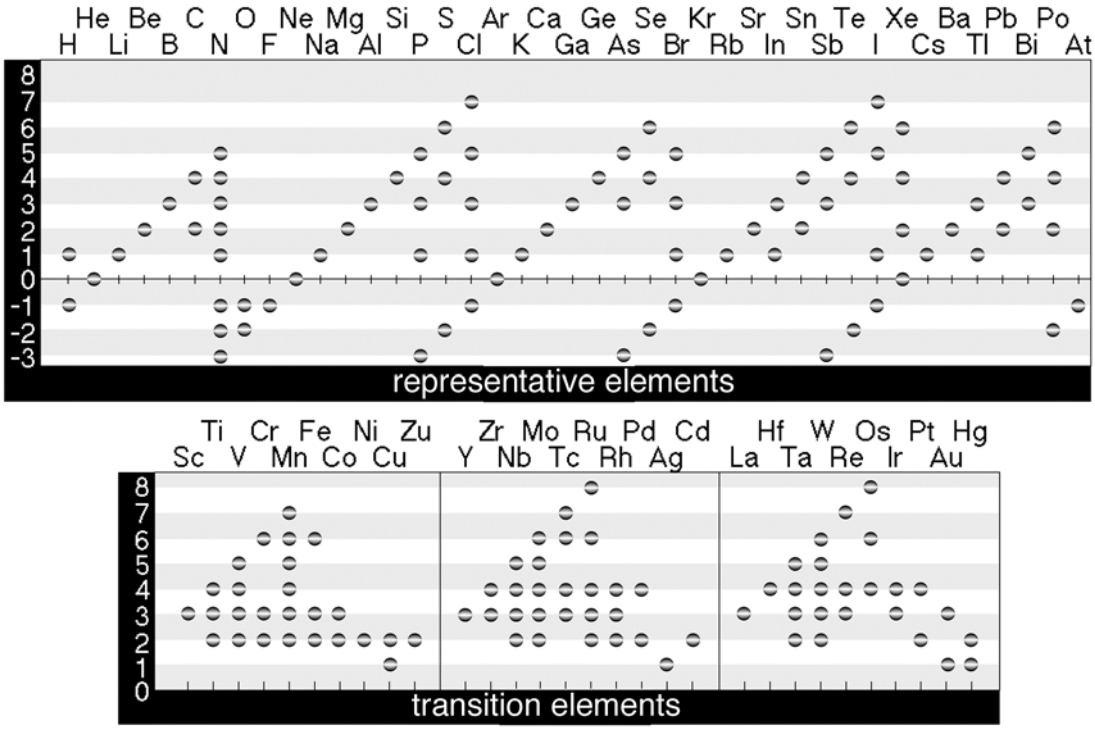


Figure 5.2 Oxidation numbers of elements
The number and values of oxidation number an element can have are various, but the highest oxidation number does exhibit periodicity.

Sample Exercise 5.4 Oxidation numbers of atoms

Find the oxidation numbers of the elements indicated below.

(1) $MnSO_4$, Mn_2O_3, MnO_2, MnO_4^-, MnO_4^{2-} (Mn)

(2) As_2O_3, AsO_2^-, AsO_4^{3-}, AsH_3 (As)

(3) I^-, IO^-, IO_3^-, I_2, ICl_3, ICl_2^- (I)

Answer

(1) +2, +3, +4, +7, +6

(2) +3, +3, +5, -3

(3) -1, +1, +5, 0, +3 (electronegativity of Cl is larger than that of I)

(2) Transition elements

Though transition elements have several oxidation numbers, a regularity can be recognized. The highest oxidation number of atoms which have five electrons as a maximum in the d orbital corresponds to the state where all of these d electrons (in addition to an s electron) are lost. Thus, in the case of scandium which has an electron configuration of $(n–1)d^1ns^2$, the highest oxidation number is 3. Manganese has an electron configuration of $(n–1)d^5ns^2$, and hence the highest oxidation number is +7.

If the number of d electrons exceeds 5, the situation is changed. For iron Fe with the electron

configuration of $(n-1)d^6ns^2$, the principal oxidation numbers are +2 and +3. Very rarely is the oxidation number +6. The highest oxidation number of important transition elements such as cobalt Co, Nickel Ni, cupper Cu and zinc Zn is lower than the oxidation number of atoms which has lost all of their (n–1)d and ns electrons. Among the elements belonging to the same group, the higher oxidation number is more important for the elements belonging to the higher period.

(d) The size of atoms and ions

When Meyer plotted the **atomic volume** defined as the volume of 1 mole of the given element (atomic weight/density) against the atomic number he obtained a saw-toothed plot. This is clear evidence that the atomic volume shows a periodicity. Since it is rather difficult to determine the atomic volume of all elements with an identical standard, this correlation has to remain more or less qualitative. However, Meyer's contribution in attracting attention to the periodicity of atomic size is noteworthy.

There remains necessarily some ambiguity if you want to determine the size of an atom itself because the electron cloud does not have a distinct boundary. For the size of a metal atom, we can determine its **atomic radius** by dividing the interatomic distance measured by X-ray crystallographic analysis by two. It must be pointed out that the value thus obtained depends on the crystal form (*e.g.*, simple cubic lattice or face-centered cubic lattice, *etc.*) and this will cause some ambiguity. The same problem remains in the determination of the **ionic radius** as determined by the X-ray crystallographic analysis of ionic crystals.

The general periodicity is evident as is shown in Fig. 5.3 which shows the atomic and ionic radii of main atoms and ions. For example, ionic radii of cations belonging to the same group decrease as the atomic number increases. This is reasonable since a larger nuclear charge will attract electrons more strongly. As for the ionic radii, the higher the period, the larger is the ionic radius.

Sample Exercise 5.5 The size of atoms and ions

Choose the smallest one from each group of atoms or ions.

(1) Li, Na, K (2) P, Sb, As (3) S, Cl, Ar (4) O^+, O, O^-

Answer

(1) Li (2) P (3) Cl (4) O^+

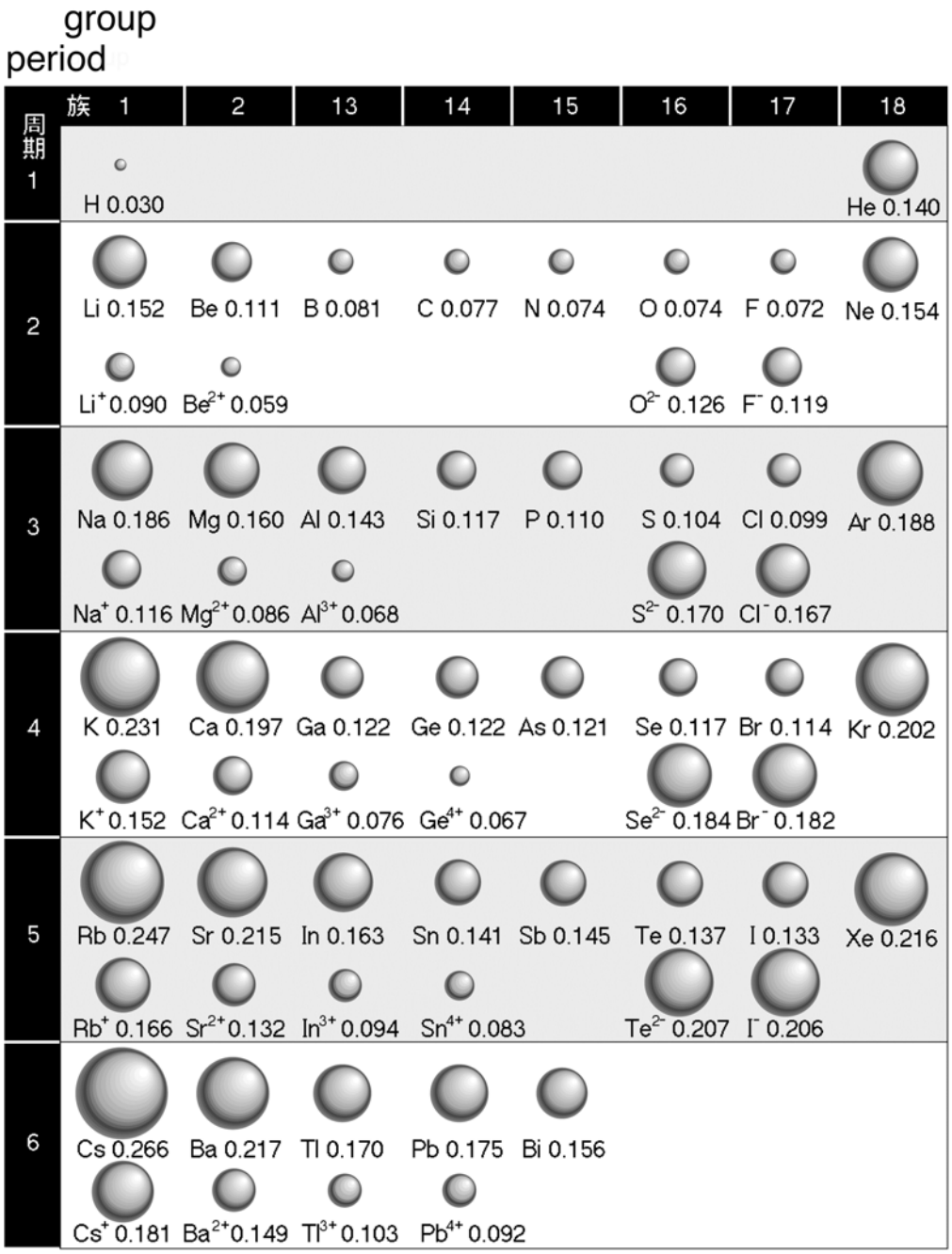


Figure 5.3 Atomic and ionic radii of main atoms and ions
Because of transition elements, the change between the 3rd and 4th periods is rather large.

5.3 Periodicity of the properties of simple compounds

(a) Periodicity of the properties of oxides

Oxygen can form compounds (oxides) with almost all elements except a few of the rare gases. This is the reason why oxygen was once used as the standard for atomic weights. When the procedure for determining the atomic weight had not yet fully established, it was convenient and dependable to use "equivalent", that is, the quantity of a substance that is just enough to react with a given amount of oxygen. Even today, comparing the properties of oxides is important as a measure for comparing the properties of elements.

Most heats of formation of oxides, that is, the heat of reaction in which a simple body reacts with oxygen, are large and negative. This indicates that there is at least one stable oxide. There are only a few oxides, such as those of the halogens or rare gases, that have a positive value of the heat

of formation.

In order to ascertain whether or not these values show periodicity, the heat of reaction in which the element reacts with a given amount (*e.g.*, 8 g) of oxygen should be considered rather than the heat of reaction per mole. The schematic representation of these values is given in Fig. 5.4. In all periods, the absolute value of the heat of formation tends to decrease as the atomic number increases.

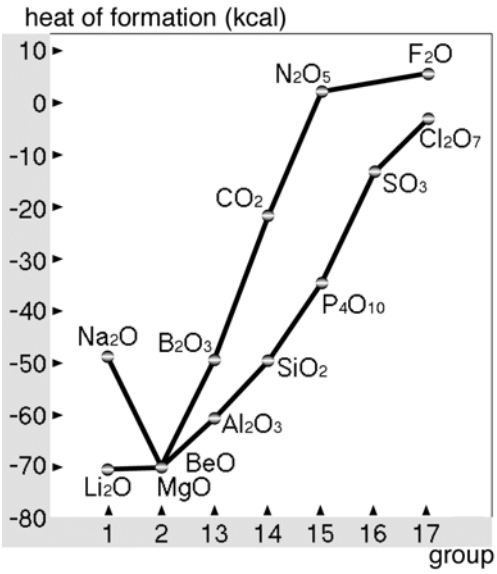


Figure 5.4 Heat of formation obtained from a reaction with a given quantity of oxygen.
Periodicity is evident except for the alkaline metals.

It is convenient to classify oxides according to their acidity or basicity since almost all oxides are either acidic or basic. This will also help in understanding Ch. 9 where acidity and basicity are treated.

The reaction products between oxides and water generally have a hydroxy group. As will be discussed later, many oxides are acidic even if these do not have any hydrogen. In the case of the reaction product between an **acidic oxide** and water, the hydrogen of a hydroxy group tends to be dissociated as a proton. Thus, an acid in which acidic hydrogen is bonded to oxygen is called **oxoacid**. On the other hand, the reaction product between a basic oxide and water is named a hydroxide in which the hydroxy group tends to be dissociated as the hydroxide ion OH^-.

Oxides of alkaline metals and alkaline earth metals are more or less soluble in water and exhibit basicity. Sodium oxide Na_2O is a typical basic oxide. Thus,

$$Na_2O(s) + H_2O \rightarrow 2Na^+(aq) + 2OH^-(aq) \tag{5.5}$$

where (aq) indicates an aqueous solution. Even if barely soluble in water, an oxide is a basic oxide if it can react with an acid.

The oxides of group 13 elements are reactive to both an acid and a base and are named **amphoteric oxides**. A well-known example is aluminum oxide Al_2O_3.

$$Al_2O_3 + 6HCl \rightarrow 2AlCl_3 + 3H_2O \tag{5.6}$$

$$Al_2O_3 + 2NaOH + 3H_2O \rightarrow 2Na[Al(OH)_4]_2 \tag{5.7}$$

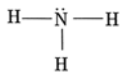
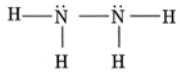
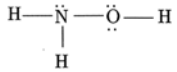
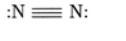
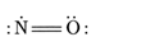
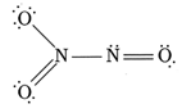
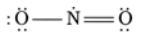
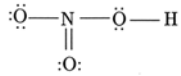
Most of the oxides of nonmetal elements are acidic. Their strength as acids increases going from left to right across a period of the periodic table. In other words, the acidity is stronger as the nonmetal property increases. As for group 14 elements, carbon has two oxides, CO and CO_2, and the

acidity of CO_2 is weak (H_2CO_3 is a weak acid). Oxides of carbon are gaseous but oxides of silicon and of elements below silicon are solid. SiO_2 is not soluble in water, but it is an acidic oxide since it reacts with a base.

$$SiO_2 + 2NaOH \rightarrow Na_2SiO_3 + H_2O \qquad (5.8)$$

In contrast, many oxides of group 15 and 16 elements are soluble in water. SO_3 and P_4O_{10} are acidic oxides since these react with water to give protons. For these elements, there are several oxides corresponding to different oxidation numbers. There are two oxides of sulfur with the oxidation numbers of +4 and +6. A typical example would be the oxides of nitrogen. In Table 5.8, a series of oxides of nitrogen and its hydride are listed. They will be discussed later.

Table 5.8 Oxidation numbers of various nitrogen compounds

oxidation number of nirogen	compound	molecular formula	Lewis structure
−3	ammonia	NH_3	
−2	hydrazine	N_2H_4	
−1	hydroxylamine	NH_2OH	
0	nitrogen	N_2	
+1	dinitrogen oxide	N_2O	
+2	nitrogen oxide	NO	
+3	dinitrogen trioxide	N_2O_3	
+4	nitrogen dioxide	NO_2	
+5	nitric acid	HNO_3	

When an element has more than one oxide, the oxides with higher oxidation numbers have larger acidities than those with lower oxidation numbers. For sulfur, SO_2 (oxoacid; H_2SO_3) is a weak acid but SO_3 (H_2SO_4) is a strong acid. The acidities of oxides of chlorine increase in the order shown below.

$$Cl_2O\ (HClO) < Cl_2O_3\ (HClO_2) < Cl2O_5\ (HClO_3) < Cl_2O_7\ (HClO_4)$$

The acidity of Cl_2O (HClO) is very weak while Cl_2O_7 ($HClO_4$) is one of the strong acids.

Table 5.9 gives the oxides with the highest oxidation number among main group elements and the periodicity of their acidity/basicity. Note that the amphoteric oxides are located from the upper left-hand corner to the lower right-hand corner of the table.

b) Periodicity of properties of hydrides

Most of main group elements produce hydrides by reacting with hydrogen, but the stability of hydrides depends on the location of the element in the periodic table. Hydride of electropositive group 1 and 2 elements and electronegative group 16 and 17 elements are stable, while some of the

Table 5.9 Acidity and basicity of oxides of main group elements

Li_2O	BeO	B_2O_3	CO_2	N_2O_5		F_2O
Na_2O	MgO	Al_2O_3	SiO_2	P_4O_{10}	SO_3	Cl_2O_7
K_2O	CaO	Ga_2O_3	GeO_2	As_2O_5	SeO_3	Br_2O
Rb_2O	SrO	In_2O_3	SnO_2	Sb_2O_5	TeO_3	I_2O_5
Cs_2O	BaO	Tl_2O_3	PbO_2	Bi_2O_5		

basicity increases ↓

acidity increases →

hydrides of group 13, 14 and 15 heavy metal elements are sometimes difficult to prepare.

Hydrides of the alkaline and alkaline earth metal elements are colorless crystals, and by molten salt electrolysis these give hydrogen at the anode. This fact suggests in such metal hydrides, for instance in sodium hydride, it exists as Na^+H^-, *i.e.*, as a salt-like crystal. All of these hydrides are strong bases.

Some group 13 and 14 elements have more than one hydride. For instance, for the hydrides of carbon, there are not only methane CH_4, but also carbene CH_2, although it is difficult to isolate CH_2 because of excessive instability. All hydrides of group 14 elements including methane are covalent molecules. In going from left to right on the periodic table, the covalent character of hydrides decreases and the ionic character increases. The O-H bond of water and the Cl-H bond of hydrogen chloride, for example, are considerably polar, and dissociate to some degree in water to produce H^+. In constrast, the acidity of methane is essentially negligible.

In general the hydrides of main group elements are molecules; they have distinct boiling and melting points, and exhibit periodicity. However, hydrides of 2nd period elements behave less so. For example, the boiling points are much higher than those of 3rd period elements (Fig. 5.5).

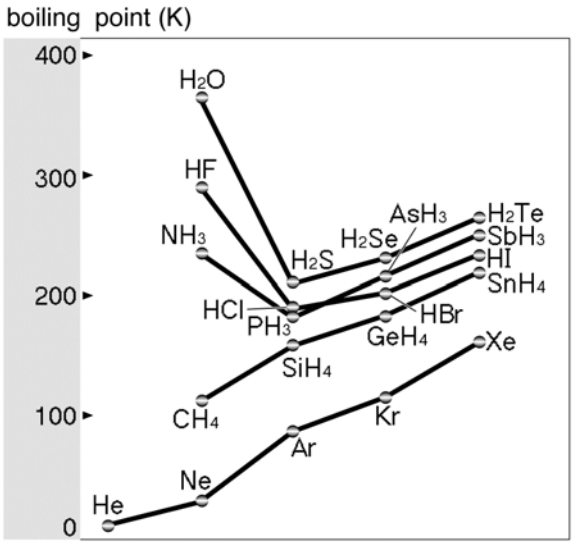


Figure 5.5 Boiling points of hydrides of main group elements.
The periodicity observed for the rare gases and the hydrides of group 14 elements is not evident for hydrides of group 15, 16 and 17 elements.

Since the boiling points of the hydrides of 3rd period elements, and thereafter, continue to become higher, and show vivid periodicity, it is clear that the behavior of the hydrides of 2nd period elements is exceptional. It is well known that the reason for this is the characteristic formation of hydrogen bonds in the hydrides of 2nd period elements.

Hydrogen bonds take place in the compounds which have a bond between hydrogen and electronegative elements. The H-X bond polarizes into H^+-X^-. The attractive interaction between the dipoles thus formed is the driving force of hydrogen bonds.

Physical properties of elements such as boiling and melting points show periodicity to some extent. Among the elements belonging to the same group, this periodicity is sometimes clear. For instance, among halogens, the element changes from the gaseous state to liquid, and from liquid to solid. The change is not necessarily uniform. Nitrogen is a gas, but phosphorus and other atoms are all solid. Some discontinuity is evident.

Exercise

5.1 Electron configuration of atoms

Without consulting the periodic table, write down the electron configuration and the group number in the periodic table for the elements with the atomic numbers shown below.

3, 8, 14, 17, 32, 37, 56

Answer

Check your answers with the aid of the periodic table.

5.2 Energy levels of atomic orbitals

Choose the orbital from each pair that has the higher energy.

(a) 3d, 4s (b) 4p, 5s (c) 4s, 4p

Answer

(a) 3d (b) 5s (c) 4p

5.3 Electron affinity

From each set of three chemical species, choose the one with the maximum electron affinity and the one with the minimum electron affinity.

(a) Ge, Si, C (b) Cl, Cl^-, Cl^+

Answer

(a) C, Ge (b) Cl^+, Cl^-

5.4 Ionization energy

The 2nd ionization energies are defined as the energy required to remove the second electron from the atom. The 3rd and 4th ionization energy is defined in a similar manner. Select from among elements X, Y and Z the one that will most clearly exhibit the properties (a), (b) and (c) given below.

(a) to form a monovalent ionic compound with chlorine

(b) to form a covalent bond with chlorine.

(c) To have the oxidation number of +2 in most cases.

Atom/ionization energy	1st	2nd	3rd	4th
X	738	1450	7730	10550
Y	800	2427	3658	25024
Z	495	4563	6912	9540

Answer

X belongs probably to an alkaline metal group since both 1st and 2nd ionization energies are small. You can surmize Y is a group 13 element and Z a group 1 element.

(a) Z (b) Y (c) X

5.5 The size of atoms and ions

Arrange each of the following quartet of four chemical species in the order of increasing the radius.

(a) Ar, Cl^-, K^+, S^{2-} (b) C, Al, F, Si (c) Na, Mg, Ar, P (d) I^-, Ba^{2+}, Cs^+, Xe

Answer

(a) $K^+ < Cl^- < S^{2-} < Ar$ (b) F < C < Si < Al (c) P < Mg < Na < Ar (d) $Ba^{2+} < Cs^+ < I^- < Xe$

Coffee-break

An unrecognized pioneer

There were quite a few chemists who were interested in the periodicity of the properties of elements. The British chemist John Alexandere Reina Newlands (1837-1898) was one of them. Around 1865, he arranged in the order of atomic weight some 60 elements known at that time, and put these in a table with eight rows and six columns. To his surprise, he noticed that the 1st element and the 8th element and moreover, the 8th element and the 15th element had similar properties. In other words, an element with similar properties appears at every eighth position in the table. This appearance at every eighth position was very similar to that of musical notes. He announced his findings at a scientific meeting, and called his rule the **law of octaves**. British scientists at that time made fun of him, asking what would happen if one arranges the elements in an alphabetical order.

For many years Newlands was ignored. Finally in 1887, more than ten years after the achievement of Mendeleev was recognized, the Chemical Society (of England) awarded him a prize.

John Newlands (1837-1898)

Chapter 2: Atomic Structure and Chemical Bonding

- Materials → Molecules → Atoms
- Atoms = protons (p) + neutrons (n) + electrons (e)
- Protons and neutrons are made of quarks
- Quantitative measurements need units: *metric* or *S.I.* (Systeme International) or *mks* (meter-kilogram-second) units

meter	(m)	for length
cubic meter	(m^3)	for volume
kilogram	(kg)	for mass
Kelvin	(K)	for temperature
second	(s)	for time
mole	(mol)	for amount of substance

Typical parameters: atoms are small

	Mass (kg)	Charge (coulomb)
Proton	1.673×10^{-27}	$+1.602 \times 10^{-19}$
Neutron	1.675×10^{-27}	0
Electron	9.109×10^{-31}	-1.602×10^{-19}

- Nuclear radius is measured in 10^{-15}m = fm
- Electron radii measured in Å = 0.1 nm = 10^{-10} m
- Fundamental charge = e = -1.602×10^{-19} C

2.1 The Structure of Atoms

- Atomic number **Z**

In neutral atom:

# of protons = # of electrons = atomic number **Z**

Value of Z is different for each element H (Z = 1), O (Z = 8), Fe (Z = 26)

- Isotopes

Mass number → A X ← *Element*

Atomic number → Z

Same element (same Z) might have different # of neutrons (**N**)

Same chemistry (same # of electron)

Hydrogen: "protium" H-1; ${}^{1}_{1}H$ "deutiruim" H-2 or D ${}^{2}_{1}H$ "tritium" H-3 or T ${}^{3}_{1}H$

- Atomic mass unit (amu): 1/12 of C-12 (<1% of C-13, isotopically pure)
- Atomic mass **A** **A ≈ Z + N**
- Atomic weight (periodic table) – weighted average of all isotopes

2.2 Periodic Table of Elements

Metal

Nonmetal

Intermediate

Key: 29 Cu 63.54 — Atomic number, Symbol, Atomic weight

IA	IIA	IIIB	IVB	VB	VIB	VIIB	VIII			IB	IIB	IIIA	IVA	VA	VIA	VIIA	0
1 H 1.0080																	2 He 4.0026
3 Li 6.939	4 Be 9.0122											5 B 10.811	6 C 12.011	7 N 14.007	8 O 15.999	9 F 18.998	10 Ne 20.183
11 Na 22.990	12 Mg 24.312											13 Al 26.982	14 Si 28.086	15 P 30.974	16 S 32.064	17 Cl 35.453	18 Ar 39.948
19 K 39.102	20 Ca 40.08	21 Sc 44.956	22 Ti 47.90	23 V 50.942	24 Cr 51.996	25 Mn 54.938	26 Fe 55.847	27 Co 58.933	28 Ni 58.71	29 Cu 63.54	30 Zn 65.37	31 Ga 69.72	32 Ge 72.59	33 As 74.922	34 Se 78.96	35 Br 79.91	36 Kr 83.80
37 Rb 85.47	38 Sr 87.62	39 Y 88.91	40 Zr 91.22	41 Nb 92.91	42 Mo 95.94	43 Tc (99)	44 Ru 101.07	45 Rh 102.91	46 Pd 106.4	47 Ag 107.87	48 Cd 112.40	49 In 114.82	50 Sn 118.69	51 Sb 121.75	52 Te 127.60	53 I 126.90	54 Xe 131.30
55 Cs 132.91	56 Ba 137.34	Rare earth series	72 Hf 178.49	73 Ta 180.95	74 W 183.85	75 Re 186.2	76 Os 190.2	77 Ir 192.2	78 Pt 195.09	79 Au 196.97	80 Hg 200.59	81 Tl 204.37	82 Pb 207.19	83 Bi 208.98	84 Po (210)	85 At (210)	86 Rn (222)
87 Fr (223)	88 Ra (226)	Acti-nide series															

Rare earth series	57 La 138.91	58 Ce 140.12	59 Pr 140.91	60 Nd 144.24	61 Pm (145)	62 Sm 150.35	63 Eu 151.96	64 Gd 157.25	65 Tb 158.92	66 Dy 162.50	67 Ho 164.93	68 Er 167.26	69 Tm 168.93	70 Yb 173.04	71 Lu 174.97
Actinide series	89 Ac (227)	90 Th 232.04	91 Pa (231)	92 U 238.03	93 Np (237)	94 Pu (242)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (249)	99 Es (254)	100 Fm (253)	101 Md (256)	102 No (254)	103 Lw (257)

2.3 Electrons in Atoms

- One of the first models: Bohr atom

Bohr assumed that electrons orbited the nucleus due to Coulomb forces
Electrons could only be in one of infinitely many discrete states
Explained spectra of H, He^+, Li^{2+}

- Not working for atoms with >1 electron
- Need a quantum mechanics approach → Will summarize main points

1. **Particles can have wave-like properties**

de Broglie suggested that any particles with momentum p(=m×V, non-relativistically) displays wave-like properties:

$$\lambda = h/p$$

2. **Wave can have particle-like properties**

Light as a propagating wave of electric and magnetic fields
Wavelength determines the colour
Einstein showed that light is divided into packets of E (so called "photons")

$$E = h f$$

The Heisenberg Uncertainty Principle

3. We can no longer describe a particle as having a **precise position x and momentum p**
4. **The Heisenberg Uncertainty Principle**

We cannot know both x and p simultaneously with arbitrary precision
There is a limit ! $\delta x\, \delta p \geq h/ 2\Pi \equiv \hbar$
We do know exactly where an electron is, we can't know how fast it is moving

5. **Electrons in atoms can only be in certain "states"**

The energy is "quantized" – only certain levels are permitted
The level can change, but only if exactly the correct energy is emitted or absorbed

6. **4 quantum numbers:** The state of an electron in an atom is described by a set of 4 quantum numbers

principle	quantum number	n =	1, 2, 3, …n
subsidiary or azimuthal	number	L =	0, 1, 2, … n-1
magnetic	quantum number	m_L=	0, ±1, ±2, … ±n-1
spin	quantum number	m_S =	±½

7. **The Pauli Exclusion Principle:** Two electrons in an atom can never have exactly the same set of all 4 quantum numbers (n, L, m_L, m_S)

Possible electron states

- So … what are the possible combinations of states?
- Notation

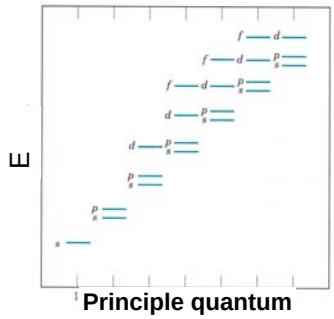
n		L	
1	K	0	s
2	L	1	p
3	M	2	d
4	N	3	f

- We can describe an electron state as 1s or 3p or 5f

Energy levels of the electron states

- the energy of an electron is determined by its state
- If there is only **one** electron in the atom, the energy depends on n alone
- If there are more electrons, they interact (repel each other), and so different states have different energies

Shell and Subshell Energies



Schematic representation of the relative energies of the electrons for various shells and subshells (adopted from Callister, Figure 2.4)

Valence electrons

- The electrons in the outer shell (largest n) are called valence electrons
- Very important for chemical reactions and holding matter together
- If the outer shell is filled, the atom is inert
- If not, there is a tendency for the outer shell to become filled

Electronegative – if it is almost full, the atom has a tendency to gain enough electrons to fill the shell

Electropositive – if it is almost empty, it easily losses the electrons in the outer shell

Periodic Table of Elements

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Electropositive – if it is almost empty, it easily losses the electrons in the outer shell

Electronegativity

Electronegativity is a degree to which an atom attracts electron to itself

													H 2.1			
Li 1.0	Be 1.5											B 2.0	C 2.5	N 3.1	O 3.5	F 4.1
Na 1.0	Mg 1.3											Al 1.5	Si 1.8	P 2.1	S 2.4	Cl 2.9
K 0.9	Ca 1.1	Sc 1.2	Ti 1.3	V 1.5	Cr 1.6	Mn 1.6	Fe 1.7	Co 1.7	Ni 1.8	Cu 1.8	Zn 1.7	Ga 1.8	Ge 2.0	As 2.2	Se 2.5	Br 2.8
Rb 0.9	Sr 1.0	Y 1.1	Zr 1.2	Nb 1.3	Mo 1.3	Tc 1.4	Ru 1.4	Rh 1.5	Pd 1.4	Ag 1.4	Cd 1.5	In 1.5	Sn 1.7	Sb 1.8	Te 2.0	I 2.2
Cs 0.9	Ba 0.9	La 1.1	Hf 1.2	Ta 1.4	W 1.4	Re 1.5	Os 1.5	Ir 1.6	Pt 1.5	Au 1.4	Hg 1.5	Tl 1.5	Pb 1.6	Bi 1.7	Po 1.8	At 2.0
Fr 0.9	Ra 0.9	Ac 1.0	Lanthanides: 1.0–1.2 Actinides: 1.0–1.2													

The electronegativity of the elements, adapted from Smith&Hashemi

Chemical reactivity: valence e-s

Noble gases: s^2p^6 configuration

Ne: $1s^22s^2p^6$

Electronegative – if it is almost full, the atom has a tendency to gain enough electrons to fill the shell

Cl: $1s^22s^2p^63s^2p^5$ or [Ne] $3s^2p^5$

Cl + 1e = Cl^- negative ion (anion)

Electropositive – if it is almost empty, it easily losses the electrons in the outer shell (typically metals)

K: $1s^22s^2p^63s^2p^64s^1$ or [Ar] 4s

K – 1e = K^+ positive ion (cation)

Oxidation number or oxidation state - not all allowed!!!

Periodic Table of Elements

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2.4 Types of atomic and molecular bonds

- Primary atomic bonds

1. Ionic (large interatomic forces, nondirectional, electron transfer, coulombic forces)
2. Covalent (large interatomic forces, localized (directional), electron sharing)
3. Metallic (large interatomic forces) nondirectional

- Secondary atomic and molecular bonds

1. Permanent dipole bonds
2. Fluctuating dipole bonds

Examples and characteristics of 5 types of bonds

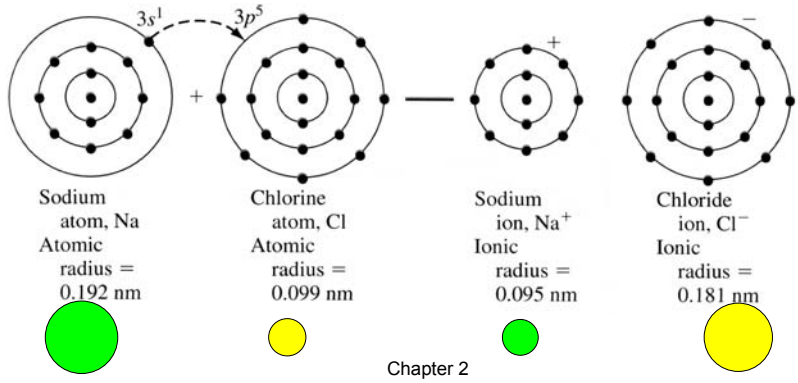
Bond type	Examples	Typical energies, eV/atom	Distinct characteristics
Ionic	**LiF, NaCl, CsCl**	**5-10**	**Nondirected bonding, giving structures of high coordination; no electrical conductivity at low temperature**
Covalent	**Diamond, Si, Ge**	**3-8**	**Spatially directed bonds, structures with low coordination; low conductivity at low temperature for pure crystals**
Metallic	**Li, Na, Cu, Ta**	**0.7-1.6**	**Nondirected bond, structures of very high coordination and density; high electrical conductivity; ductility**
Fluctuating or permanent dipole	Ne, Ar,Kr, Xe, $CHCl_3$	0.05-0.2	Low melting and boiling points
Hydrogen	H_2O, HF	0.25-0.6	Increase in bonding energy over similar molecules without hydrogen bonds

2.5 Ionic bonding

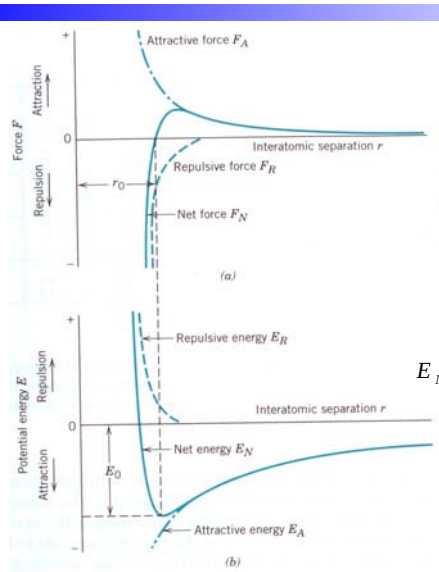
Typically between highly electropositive (metallic) and electronegative (nonmetallic) elements

NaCl Na $1s^2 2s^2 p^6 3s$ Cl $1s^2 2s^2 p^6 3s^2 p^5$

Na^+ $1s^2 2s^2 p^6$ Cl^- $1s^2 2s^2 p^6 3s^2 p^6$



Force and Energy Diagram



$F_{net} = F_{attactive} + F_{repulvise}$

The **interionic energy** can be defined as the energy needed to rip a compound into its components placed ∞ far apart ($E_{NET}(\infty) = 0$)

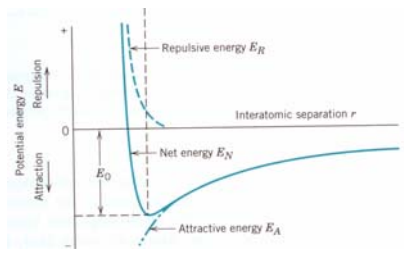
$$E_{NET} = E_{attractive} + E_{repulsive} = +\frac{Z_1 Z_2 e^2}{4\pi\varepsilon_o a} + \frac{b}{a^n}$$

- Q.: Calculate attractive force between Na^+ and Cl^- ion at equilibrium interionic separation distance

Interionic Energies

- the energy needed to rip a compound into its components placed ∞ far apart ($E_{net}(\infty) = 0$

$$E_{net} = E_{attraction} + E_{repulsion} = +\frac{Z_1 Z_2 e^2}{4\Pi\varepsilon_o a} + \frac{b}{a^n}$$



- Q2.: Calculate the net potential energy of a simple Na^+ Cl^- ion pair in equilibrium (using the equation above) and assuming that n = 9

Bonding Energies in Ionic Solids

- Typically large lattice energies (Table 2.6)
  600-3000 kJ/mol
- High melting temperatures
  801°C for NaCl

For NaCl: $E_{Na+Cl-} = -7.42 \times 10^{-19}$J = 4.63eV (2.315 per ion)
Compare to 3.3eV (elsewhere): big difference…!

Ionic Packing

•X-ray crystallography tells us most of ionic compounds (NaCl, CsCl, LiF, etc) are crystals

• Ionic radii of selected ions are listed in the table below (note increase in size, as their principle quantum number increases)

• No preferred orientation (nondirectional character of the ionic bond)

• Geometrical arrangements (coordination) and neutrality is maintained

Cation	Ionic radius (nm)	Anion	Ionic radius (nm)
Li+	0.060	F-	0.136
Na+	0.095	Cl-	0.181
K+	0.133	Br-	0.195
Rb+	0.148	I-	0.216
Cs+	0.169		

Coordination and neutrality in ionic crystals

CsCl:

8 Cl^- ions can pack around Cs^+

$R(Cs^+)/R(Cl^-)$=

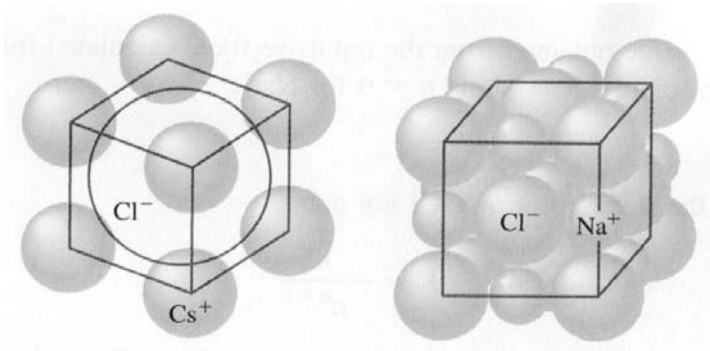
= 0.169 / 0.181 = 0.934

NaCl:

6 Cl^- ions can pack around Na^+

$R(Na^+)/R(Cl^-)$=

= 0.095 / 0.181 = 0.525



Evaluation of the Madelung Constant

1. Consider a cube of 8 ions

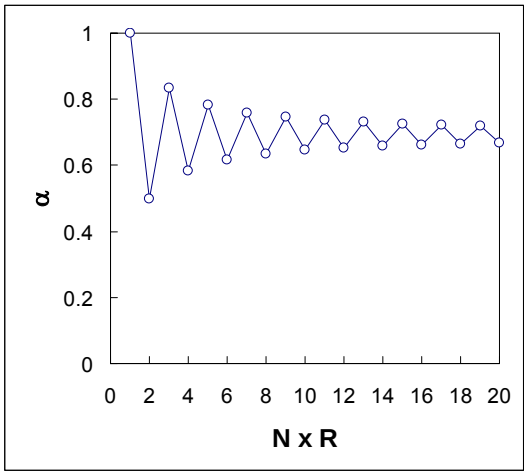
2. Consider a line of alternating in sign ions, with distance R between ions

3. Consider a lattice: lattice sum calculation can be used to estimate Madelung constant, α

$$\alpha = \sum_j \frac{\pm}{R_{ij}}$$

Structure	α
NaCl	1.7475
CsCl	1.7626
ZnS	1.6381

Madelung constant for line of ions



Electronegativity

																H 2.1
Li 1.0	Be 1.5											B 2.0	C 2.5	N 3.1	O 3.5	F 4.1
Na 1.0	Mg 1.3											Al 1.5	Si 1.8	P 2.1	S 2.4	Cl 2.9
K 0.9	Ca 1.1	Sc 1.2	Ti 1.3	V 1.5	Cr 1.6	Mn 1.6	Fe 1.7	Co 1.7	Ni 1.8	Cu 1.8	Zn 1.7	Ga 1.8	Ge 2.0	As 2.2	Se 2.5	Br 2.8
Rb 0.9	Sr 1.0	Y 1.1	Zr 1.2	Nb 1.3	Mo 1.3	Tc 1.4	Ru 1.4	Rh 1.5	Pd 1.4	Ag 1.4	Cd 1.5	In 1.5	Sn 1.7	Sb 1.8	Te 2.0	I 2.2
Cs 0.9	Ba 0.9	La 1.1	Hf 1.2	Ta 1.4	W 1.4	Re 1.5	Os 1.5	Ir 1.6	Pt 1.5	Au 1.4	Hg 1.5	Tl 1.5	Pb 1.6	Bi 1.7	Po 1.8	At 2.0
Fr 0.9	Ra 0.9	Ac 1.0	Lanthanides: 1.0–1.2 Actinides: 1.0–1.2													

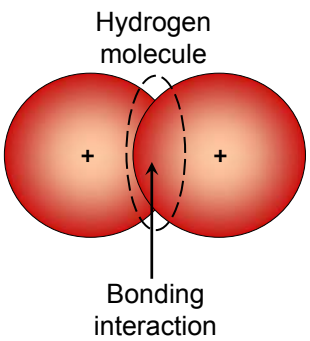
2.6 Covalent bonding

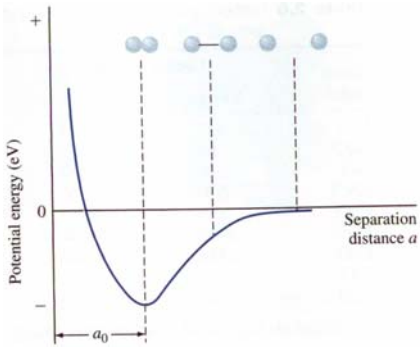
- Takes place between elements with small difference in electronegativity
  - F, O, N, Cl, H, C, Si…
- *s* and *p* electrons are commonly shared to attain noble-gas electron configuration
- Multiple bonds can be formed by one atom

Hydrogen molecule

2 H: 1s → H_2 $1s^2$

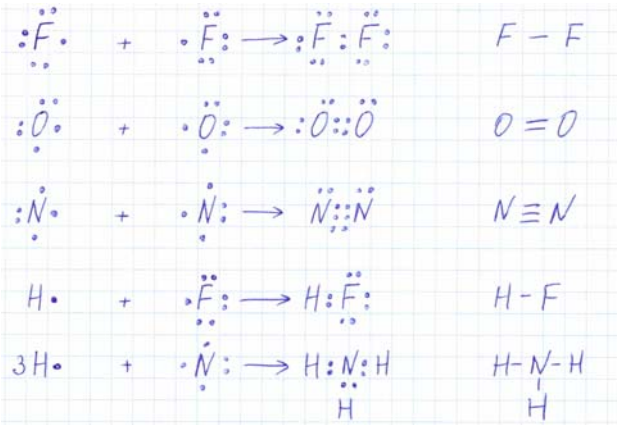
H· + H· →H : H (electron –pair covalent bond)





Other Covalent Molecules

- F $2s^22p^5$
- O $2s^22p^4$
- N $2s^22p^3$

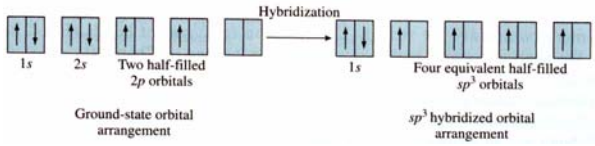


Bond energies and bond lengths of selected covalent bonds

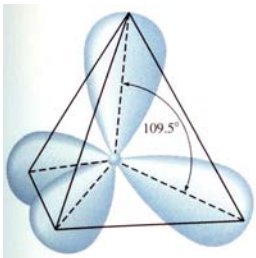
150 - 890 kJ/mol (or ~1.5-9.1eV) 0.074nm (H_2) – 0.18nm (C-Cl)

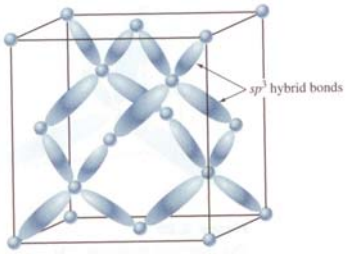
Covalent bonding by carbon

- C $1s^2 2s^2 2p^2$
- Formation of 4 equal covalent bond: hybridization
- *sp³* hybridization



- other hybridizations..? $\rightarrow$ sp^2, sp





29

Carbon-containing molecules

- C and H: *hydrocarbons*
- Structural formulas: CH_4 (methane), C_2H_6 (ethane), and C_4H_{10} (normal butane)

- Saturated C_nH_{2n+2}

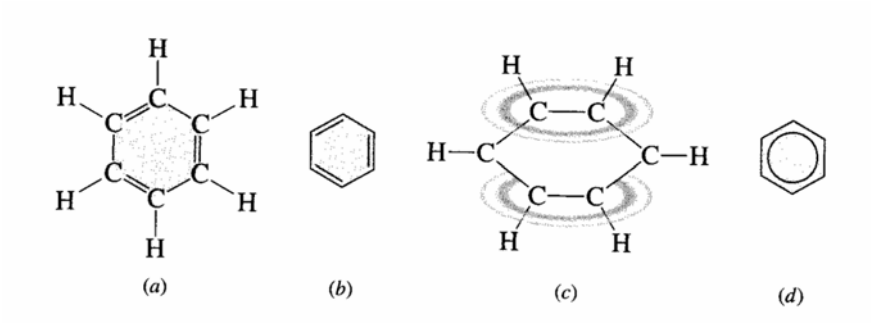
- strong bonds inside molecule, weak between molecules

- Unsaturated C_nH_{2n}, C_nH_{2n-2}

- generally more reactive

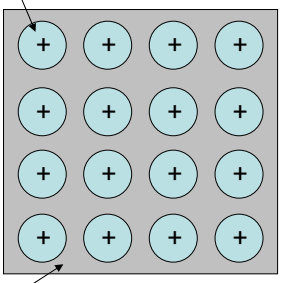
Benzene (C_6H_6)

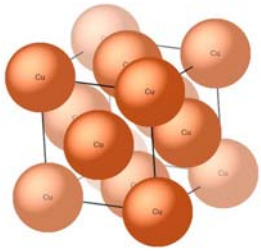
important for some polymeric materials



2.7 Metallic Bonding

- Consider Na metal: what holds it together?
- In solid state metal atoms are packed in a systematic pattern or crystal structure
- The valence electrons are weakly bonded to the positive-ion cores and can readily move as “free electrons”





Nonlocalized behavior of electrons in metals

- **High electrical conductivity**

- electrons move easily when E-field applied

- **High thermal conductivity**

- the electrons can carry energy through metal

- **High density**

- outer shell removed from atoms, so can be packed together

- **High ductility**

- if metal distorted, bent, electrons can quickly move to compensate

- metal bond is not directional

2.8. Secondary Bonding

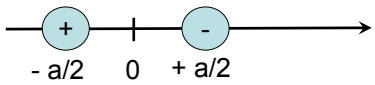
- Fluctuating or permanent dipoles (also called ***physical bonds, or van der Waals bonds or forces)***

- weak relatively to the primary bonding (2-5eV/atom or ion)
  ~ 0.1eV/atom or ~ 10 kJ/mol

- always present, but overwhelmed by other interaction
  most easily observed in inert gases

- dipoles to be considered…

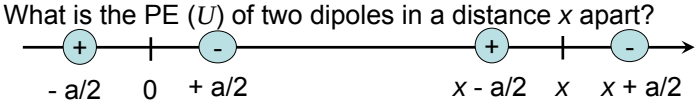
Electric dipole



consider a "+" and "-" charge (e) separated by a distance $\boldsymbol{a}$

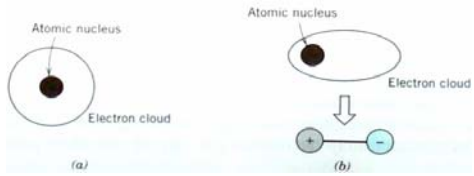
Dipole moment [debye]: $\mu = e \times a$

What is the PE (U) of two dipoles in a distance x apart?

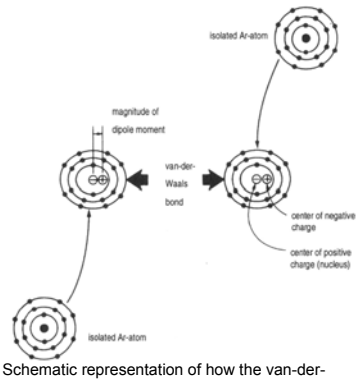


$$U = -\frac{ke^2}{x-a} + 2\frac{ke^2}{x} - \frac{ke^2}{x+a}$$

Fluctuation Dipole

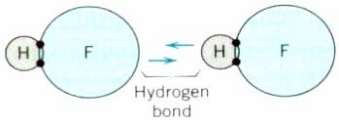


- Noble-gas elements: s^2p^6
- Stronger effect for larger electron shells → Boiling temperature increases as a function of Z



Schematic representation of how the van-der-Waals bond is formed by interaction of induced dipoles.

Permanent Dipoles



• When a covalent molecule has permanent dipole? Depends on geometry of the molecule…

• CH_4 ? CH_3Cl ? H_2O ?

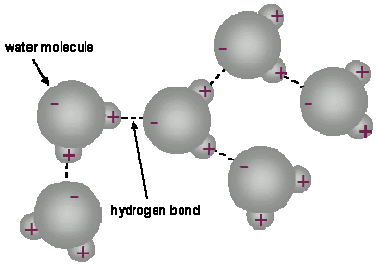
Q.: Calculate the dipole moment associated with the ionic model of the water molecule. The length of the O-H bond is 0.097nm and the angle between the bonds is 104.5°.

• Hydrogen bond: permanent dipole-dipole interaction for the molecules with a hydrogen atoms bonded to a highly electronegative element (F, Cl, O, N)

e.g.: H_2O, polymeric materials

Permanent dipole bond: a secondary bond created by the attraction of molecules that have permanent dipoles

Q.: Calculate the dipole moment associated with the ionic model of the water molecule. The length of the O-H bond is 0.097nm and the angle between the H-O-H bonds is 104.5°.



2.9 Mixed Bonding

• Ionic - Covalent Mixed Bonding

AB: $$\%_ionic_character = 100\% \times \left(1 - e^{\left(-\frac{1}{4}\right)(X_A - X_B)^2}\right)$$

where X_A and X_B are the electronegativity of the atoms A and B (Table above) e.g. ZnSe, GaAs

• Metallic - Ionic Mixed Bonding

Typical for intermetallic compounds between elements with significant difference in electronegative

e.g.: $NaZn_{13}$

Summary

- Primary atomic bonds

1. Ionic (large interatomic forces, nondirectional, electron transfer, coulombic forces)

$$E_{net} = E_{attraction} + E_{repulsion} = +\frac{Z_1 Z_2 e^2}{4\Pi\varepsilon_o a} + \frac{b}{a^n}$$

2. Covalent (large interatomic forces, localized (directional), electron sharing)
3. Metallic (large interatomic forces, nondirectional)

- Secondary atomic and molecular bonds

Dipole moment [debye]: $\mu = e \times a$

1. Permanent dipole bonds
2. Fluctuating dipole bonds

Periodic Table of Elements

Key: 29 Cu 63.54 — Atomic number, Symbol, Atomic weight

Metal | Nonmetal | Intermediate

IA	IIA	IIIB	IVB	VB	VIB	VIIB	VIII			IB	IIB	IIIA	IVA	VA	VIA	VIIA	0
1 H 1.0080																	2 He 4.0026
3 Li 6.939	4 Be 9.0122											5 B 10.811	6 C 12.011	7 N 14.007	8 O 15.999	9 F 18.998	10 Ne 20.183
11 Na 22.990	12 Mg 24.312											13 Al 26.982	14 Si 28.086	15 P 30.974	16 S 32.064	17 Cl 35.453	18 Ar 39.948
19 K 39.102	20 Ca 40.08	21 Sc 44.956	22 Ti 47.90	23 V 50.942	24 Cr 51.996	25 Mn 54.938	26 Fe 55.847	27 Co 58.933	28 Ni 58.71	29 Cu 63.54	30 Zn 65.37	31 Ga 69.72	32 Ge 72.59	33 As 74.922	34 Se 78.96	35 Br 79.91	36 Kr 83.80
37 Rb 85.47	38 Sr 87.62	39 Y 88.91	40 Zr 91.22	41 Nb 92.91	42 Mo 95.94	43 Tc (99)	44 Ru 101.07	45 Rh 102.91	46 Pd 106.4	47 Ag 107.87	48 Cd 112.40	49 In 114.82	50 Sn 118.69	51 Sb 121.75	52 Te 127.60	53 I 126.90	54 Xe 131.30
55 Cs 132.91	56 Ba 137.34	Rare earth series	72 Hf 178.49	73 Ta 180.95	74 W 183.85	75 Re 186.2	76 Os 190.2	77 Ir 192.2	78 Pt 195.09	79 Au 196.97	80 Hg 200.59	81 Tl 204.37	82 Pb 207.19	83 Bi 208.98	84 Po (210)	85 At (210)	86 Rn (222)
87 Fr (223)	88 Ra (226)	Acti-nide series															

Rare earth series	57 La 138.91	58 Ce 140.12	59 Pr 140.91	60 Nd 144.24	61 Pm (145)	62 Sm 150.35	63 Eu 151.96	64 Gd 157.25	65 Tb 158.92	66 Dy 162.50	67 Ho 164.93	68 Er 167.26	69 Tm 168.93	70 Yb 173.04	71 Lu 174.97
Actinide series	89 Ac (227)	90 Th 232.04	91 Pa (231)	92 U 238.03	93 Np (237)	94 Pu (242)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (249)	99 Es (254)	100 Fm (253)	101 Md (256)	102 No (254)	103 Lw (257)

Problems

2.1 How many atoms are there in 1 g of copper?

2.2. What is the mass in grams of one atom of copper?

2.3 The first Canadian pennies were made in 1858 and had a diameter of 25.4 mm and weight of 4.54 grams. Composition of the penny was 95% copper, 4% tin, 1% zinc (weight %) alloy.

(a) What are the atomic percentages of Cu, Sn and Zn in this alloy?

(b) Imagine that you found 1234 such pennies in your backyard. The current scrap copper value is ~ $3.4/kg (Cu). How much will you gain, if you give "this treasure" away as a scrap copper metal?

2.4 What is the chemical formula of an intermetallic compound that consists of 15.68wt% Mg and 84.32wt % Al?

2.5 Calculate the energy in joules and electron volts of the photon whose wavelength is 303.4nm.

2.6 A hydrogen atom exists with its electron in the n = 6 state. The electron undergoes a transition to the n = 2 state. Calculate (*a*) the energy of the photon emitted, (*b*) its frequency, and (*c*) its wavelength in nanometers.

2.7 Write the electron configuration of the following ions using the spdf notation

(a) Mn^{2+}, Mn^{3+}, Mn^{7+}; (b) S^{4+}, S^{6+}, S^{2-}; (c) Mo^{3+}, Mo^{4+}, Mo^{6+}.

2.8 Carbon tetrachloride (CCl_4) has a zero dipole moment. What does this tell us about the C-Cl bonding arrangement in this molecule?

5

CHEMICAL BONDING

In lesson 1 you have learnt about the structure of atom while in the lesson 2 you studied about the classification of elements and the variation in atomic properties. You know that molecules are obtained by the combination of two or more than two atoms of the same or different elements. In this lesson you will study

- Why do atoms combine?
- What are the different ways in which the atoms can combine?, and
- What are the shapes of different molecules?

The answers to these questions are of fundamental importance to the study of chemistry, as you would discover while studying the later parts of this course.

Objectives

After reading this lesson you will be able to

- explain the formation of bond in terms of potential energy diagram and octet rule;
- list different types of bonds;
- define ionic bond and cite some examples;
- write Lewis structures of some simple molecules;
- llst the characteristics of ionic compounds;
- define covalent bond and cite some examples;
- list the characteristics of covalent compounds;
- state valence shell electron pair repulsion (VSEPR) theory;
- predict the geometry of molecules with the help of VSEPR theory;
- explain the hybridisation of atomic orbitals involving s, p and d orbitals and illustrate with examples;

- tabulate the geometry of some molecules showing sp, sp^2, sp^3, dsp^2, and dsp^3 hybridisation;
- explain the formation of % and $ bonds in CH_4, C_2H_4 and C_2H_2 ;
- explain molecular orbital theory;
- write the molecular orbital configuration of H_2, N_2, O_2 and F_2 molecules;
- define bond length and bond order and relate them and
- explain hydrogen bonding with the help of examples.

5.1 What is a Chemical Bond

When two atoms of same or different elements approach each other, the energy of the combination of the atoms becomes less than the sum of the energies of the two separate atoms at a large distance. We say that the two atoms have combined or a bond is formed between the two. The bond is called a **chemical bond.** Thus *a chemical bond may be visualised as an effect that leads to the decrease in the energy*. The combination of atoms leads to the formation of a molecule that has distinct properties different from that of the constituent atoms.

A question arises, " How do atoms achieve the decrease in energy to form the bond". The answer lies in the electronic configuration. As you are aware, the noble gases do not react with other elements to form compounds. This is due to their stable electronic configuration with eight electrons (two in case of helium) in their outermost shells. The formation of a bond between two atoms may be visualised in terms of their acquiring stable electronic configurations. That is when two atoms (other than that of noble gases) combine they will do so in such a way that they attain an electronic configuration of the nearest noble gas.

The stable electronic configuration of the noble gases can be achieved in a number of ways; by losing, gaining or sharing of electrons. Accordingly, there are different types of chemical bonds, like,

- Ionic or electrovalent bond
- Covalent bond
- Co-ordinate covalent bond

In addition to these we have a special kind of bond called hydrogen bond. Let us discuss about different types of bonds, their formation and the properties of the compounds so formed.

5.2 Ionic or Electovalent Bond

According to Kossel's theory, in the process of formation of ionic bond the atoms acquire the noble gas electronic configuration by the gain or loss of electrons. Let us consider the formation of NaCl in terms of Kossel's Theory.

The electronic configuration of sodium atom (atomic number 11) is 2,8,1. Since it is highly electropositive, it readily loses an electron to attain the stable configuration of the nearest noble gas (neon) atom. It becomes a positively charged sodium cation (Na^+) in the process

$$\underset{2,8,1}{Na} \;(\;(\&\; \underset{2,8}{Na^+} + e^- \;; \qquad "H = 493.8 \text{ kJ mol}^{-1}$$

(ΔH is enthalpy change)

On the other hand, a chlorine atom (electronic configuration: 2,8,7) requires one electron to acquire the stable electronic arrangement of an argon atom. It becomes a negatively charged chloride anion (Cl^-) in the process.

$$\underset{2,8,7}{Cl} + \underset{2,8,8}{e^-} \;(\;(\&\; Cl^- \;; \qquad "H = -379.5 \text{ kJ mol}^{-1}$$

According to **Kossel's** theory, there is a **transfer** of one electron from sodium atom to chlorine atom and both the atoms attain noble gas configuration.

$$\underset{2,8,1}{Na} + \underset{2,8,7}{Cl} \;(\;(\&\; \underset{2,8}{Na^+} + \underset{2,8,8}{Cl^-}$$

The positively charged sodium ion and the negatively charged chloride ion are held together by electrostatic attractions. The bond so formed is called an **electrovalent** or an **ionic bond**. Thus *the ionic bond can be visualised as the electrostatic force of attraction that holds the cation and anion together*. The compounds so formed are termed as ionic or electrovalent compounds.

5.2.1 Energetics of Ionic Compound Formation

We have just described the formation of an ionic compound (NaCl) as a result of transfer of electrons as proposed by Kossel. You may raise a question here that when **more energy is required** (ionisation energy) to form a sodium ion from sodium atom, **than that released** (electron affinity) in the formation of chloride ion from chlorine atom then how do we say that the formation of NaCl is accompanied by a decrease in energy? Your question is quite justified but let us assure you that there is no anomaly. Let us look at the whole process somewhat closely to clarify your doubts.

The formation of NaCl from sodium and chlorine can be broken down into a number of steps as :

a) **Sublimation** of solid sodium to gaseous sodium atoms.

$$Na(s) \;(\;(\&\; Na(g) \;; \qquad "H = 108.7 \text{ kJ mol}^{-1}$$

b) **Ionization** of gaseous sodium atom to give sodium ion.

$$Na(g) \;(\;(\&\; Na^+(g) + e^- \;; \qquad "H = 493.8 \text{ kJ mol}^{-1}$$

c) **Dissociation** of gaseous chlorine molecule into chlorine atoms

$$\frac{1}{2}Cl_2(g) \;(\;(\&\; Cl(g) \;; \qquad "H = -120.9 \text{ kJ mol}^{-1}$$

d) Conversion of gaseous chlorine atom to chloride ion **(addition of electron)**

$$Cl(g) + e^- \;(\;(\&\; Cl^-(g) \;; \qquad "H = -379.5 \text{ kJ mol}^{-1}$$

e) Formation of NaCl from sodium and chloride ions.(**Crystal or lattice formation**).

$$Na^+(g) + Cl^-(g) \quad (\quad (\& \quad Na^+Cl^-(s); \qquad "H = -754.8 \text{ kJ mol}^{-1}$$

The energy released in this step is **lattice energy**.

The net reaction would be

$$Na(s) + \frac{1}{2}Cl_2(g) \quad (\quad (\& \quad Na^+Cl^-(s); \qquad "H = -410.9 \text{ kJ mol}^{-1}$$

The overall energy change can be computed by taking the sum of all the energy changes:

$$"H = (180.7 + 493.8 + 120.9 - 379.5 - 754.8) = -410.9 \text{ kJ mol}^{-1}$$

Thus we see that the net process of formation of NaCl from sodium and chlorine is accompanied by a large decrease in the energy. The approach we have just followed is based on the law of conservation of energy and is known as **Born-Haber cycle**.

Of the five different types of energies involved, two (sublimation and dissociation energies) are generally have low values than the rest. Therefore, the three energy terms i.e., ionization energy, electron affinity and lattice energy are important in determining the formation of an ionic compound. On the basis of the above discussion we can say that the formation of an ionic compound is favoured by

i. Low ionisation energy of the metal,

ii. High electron affinity of the other element (non-metal), and

iii. High lattice energy

5.2.2 Characteristic Properties of Ionic Compounds

' These exist as crystalline solids in which the ions are arranged in a regular three dimensional structure. The ionic compounds are generally hard and brittle in nature.

' These compounds have high melting and boiling points due to strong electrostatic interactions between the ions.

' These are generally soluble in water and less soluble in non-polar solvents like ether, alcohol, etc.

' These conduct electricity when in molten state or in aqueous solutions.

Kossel's theory explains bonding quite well but only for a small class of solids composed of electropositive elements of Group 1 and 2 with highly electronegative elements. Secondly, this theory is incapable of explaining the formation of compounds like, SO_2 or O_2, etc. For example in case of O_2, there is no reason to expect that one atom of oxygen would lose two electrons while the other accepts them. The problem was solved by Lewis theory of covalent bonding.

5.3 Covalent Bond

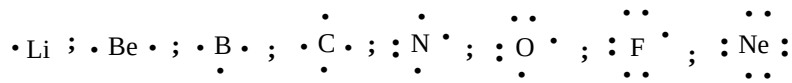
Like Kossel, Lewis also assumed that atoms attain noble gas electronic configuration in the process of bond formation. However, the way the noble gas electronic configuration

is achieved, is different. Lewis proposed that this is achieved by "sharing of a pair of electrons" between the two atoms. Both the atoms contribute an electron each to this pair. For example, two hydrogen atoms form a molecule by sharing a pair of electrons. If electrons are indicated as dots, formation of hydrogen molecule can be shown as

H. .H ((& H : H ((& H — H

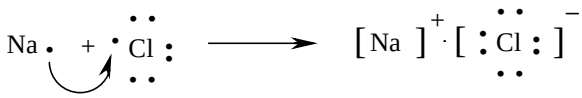
This shared pair of electrons contributes towards the stability of both the atoms and is said to be responsible for 'bonding' between the two atoms. Such a bond is called **covalent bond** and the compounds so obtained are called covalent compounds. In the process of suggesting the process of chemical bonding Lewis provided a very convenient way of representing bonding in simple molecules. This is called **Lewis electron-dot structures** or simply **Lewis structures**.

In Lewis structure each element is represented by a **Lewis symbol**. This symbol consists of the normal chemical symbol of the element surrounded by number of dots representing the electrons in the valence shell. Since the electrons are represented by dots, these are called electron-dot structures. The Lewis symbols of some elements are as:

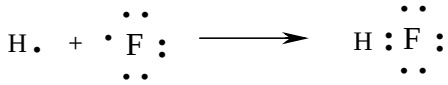


You may note here that while writing the Lewis symbols, single dots are placed first on each side of the chemical symbol then they are paired up. The Lewis structure of a molecule is written in terms of these symbols

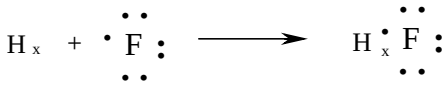
In terms of Lewis symbols the ionic bond formation in NaCl can be represented as



and the covalent bond formation in HCl is represented as

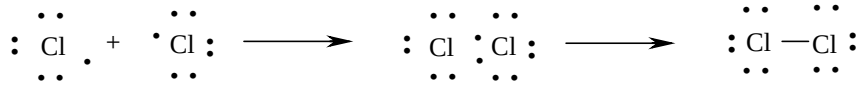


Sometimes the electrons contributed by different atoms are represented by different symbols. For example, formation of HF may also be shown as

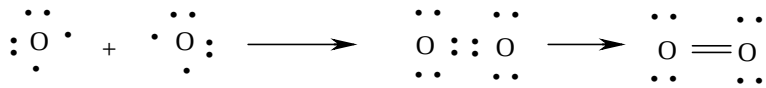


In this case the hydrogen electron is shown as a cross while the electrons of fluorine are represented by dots. There is no difference between electrons; it is just a presentation for the sake of convenience.

In terms of Lewis structures the formation of a chlorine molecule from two chlorine atoms may be represented as



Here each chlorine atom with seven valence electrons, contributes one electron to the shared pair. In the process of bond formation both the chlorine atoms acquire the electronic configuration of argon. In the same way, the formation of oxygen molecule involves sharing of two pairs of electrons between the two oxygen atoms. In this case both the atoms contribute two electrons each and acquire eight electrons or an octet in their valence shell.

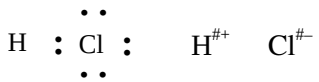


You may have noticed that in the process of bond formation, the elements of second period acquire eight electrons in their valence shell. This is called '**Octet rule'**. You may also note that in case of H_2 and Cl_2 the atoms are linked by a single line while in case of O_2 the atoms are linked by two lines. These lines represent bonds. When two atoms are bound by sharing a single pair of electron, they are said to be joined by a single bond. And when, two pairs of electrons are shared (as in case of O_2), the two atoms are said to be bound by a double bond. In nitrogen (N_2) the two atoms are joined by a triple bond as they share three pairs of electrons.

In a Lewis representation the electrons shown to be involved in the bond formation are called bonding electrons; the pair of electrons is called *'bond pair'* and the pairs of electrons not involved in the bonding process are called *'lone pairs'*. The nature of the electron pair plays an important role in determining the shapes of the molecules. This aspect is discussed later in Section 5.4.

5.3.1 Polar Covalent Bond

In a chemical bond the shared electron pair is attracted by the nuclei of both the atoms. When we write the electron dot formula for a given molecule this shared electron pair is generally shown in the middle of the two atoms indicating that the two atoms attract it equally. However, actually different kinds of atoms exert different degrees of attraction on the shared pair of electrons. A more electronegative atom has greater attraction for the shared pair of electrons in a molecule. As a consequence in most cases the sharing is not equal and the shared electron pair lies more towards the atom with a higher electronegativity. For example, in HCl, the shared pair of electron is attracted more towards more electronegative chlorine atom. As a result of this unequal sharing of the electron pair , the bond acquires polarity or partial ionic character.

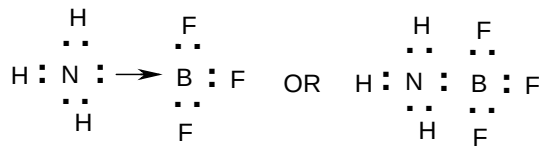


In an extreme case, the difference in the electronegativity may be so high that the electron pair is practically under the influence of a single atom. In other words the polarization of the bond is complete i.e., we have a case of ionic bonding. Thus , though the Lewis theory talks about covalent bonding it can account for the formation of ionic compounds also.

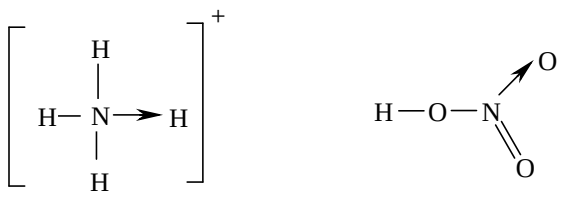
5.3.2 Coordinate Covalent Bond

You have learnt that in the formation of a covalent bond between the atoms, each atom contributes one electron to the shared electron pair, However, in some cases both the electrons of the shared pair are contributed by only one species (atom, molecule or ion) A

common example is the formation of a bond between boron trifluoride (BF_3) and ammonia (NH_3). BF_3 is an electron deficient molecule and can accept a pair of electrons. The molecule of ammonia on the other hand is electron rich. It has a lone pair of electron on the nitrogen atom and that can be donated. Electron rich ammonia donates a pair of electron to electron deficient BF_3. Such electron donor-acceptor bonds are called **coordinate covalent** or **dative bonds**.



A coordinate bond is normally represented by an arrow pointing from a donor atom to the acceptor atom. A coordinate bond is identical to a covalent bond in terms of its polarity and strength. The two are different only in the way they are formed. We cannot distinguish between covalent and coordinate covalent bond, once these are formed. HNO_3 and NH_4^+ ion are some more common examples of formation of a coordinate bond.



Intext Question 5.1

1. Define electrovalent bond.

   .....

2. Show the formation of a nitrogen molecule from two nitrogen atoms in terms of Lewis theory.

   .....

3. What do you understand by a polar covalent bond? Give two examples.

   .....

4. What is a coordinate covalent bond ? How is it different from a covalent bond?

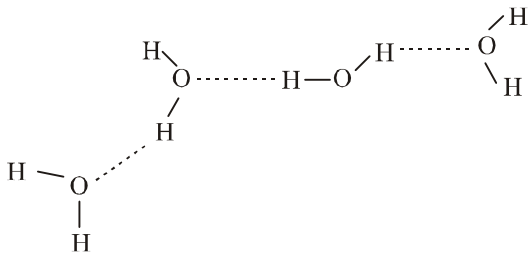
   .....

5.3.3 Characteristic properties of Covalent Compounds

- The covalent compounds have low melting and boiling points due to weak forces of interaction between the molecules.
- The covalent compounds are poor conductors of electricity as these lack ionic species.
- The covalent compounds are generally insoluble in water and dissolve in nonpolar solvents like benzene, carbon tetrachloride etc.

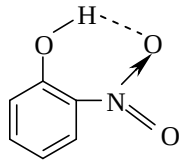
5.3.4 Hydrogen Bonding

It is a special type of attraction between a hydrogen atom bonded to a strongly electronegative atom (like nitrogen, oxygen or fluorine) and the unshared pair of electrons on another electronegative atom. Hydrogen bond is a weak bond, the strength being just about 4-25 kJ mol^{-1}. It is quite small as compared to the covalent bond, which needs a few hundreds of kJ mol^{-1} of energy to break. However, it is strong enough to be responsible for the high boiling points of H_2O and HF etc. In fact it is due to hydrogen bonding only that water exists as a liquid. The low density of ice also can be explained in terms of hydrogen bonding.

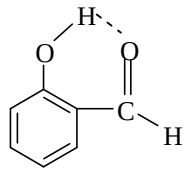


H—F ····· H—F ····· H—F ·····H—F

Due to the difference in the electronegativity between hydrogen and the other electronegative atom, the bond connecting them becomes polar. The hydrogen atom acquires a positive charge while the electronegative atom bears the negative charge. Hydrogen bonding results from the electrostatic interaction between the positively charged hydrogen atom and the negatively charged electronegative atom. The second electronegative atom may be a part of the same molecule or it may belong to a different molecule. Accordingly, there are two types of hydrogen bonds. If the hydrogen bond is formed between two different molecules it is called **intermolecular hydrogen bond**. When the hydrogen bond exists within the same molecule, it is called **intramolecular hydrogen bonding.** Salicyldehyde ad o-nitrophenol are two common examples of the molecules showing intramolecular hydrogen bonding whereas in water, intermolecular hydrogen bonding exists.



o-nitrophenol



Salicyldehyde

Hydrogen bonding plays an important role in the structure and function of many biomolecules like proteins and nucleic acids.

5.4 Valence Shell Electron Pair Repulsion (VSEPR) Theory

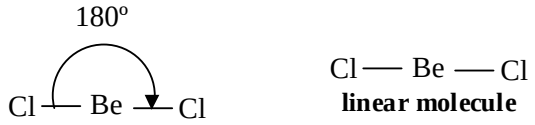
In a molecule the constituent atoms have definite positions relative to one another i.e., the molecules have a definite shape. The theories of bonding that we have discussed so far do not say anything about the shape of the molecules. A simple theory called VSEPR theory

was put forth by Sidgwick and Powell in 1940 to explain the shapes of molecules. It was later refined and extended by Nyholm and Gillespie in1957. This theory focuses on the electron pairs present in the valence shell of the central atom of the molecule and can be stated in terms of two postulates:

POSTULATE 1

The electron pairs (both bonding and non-bonding) around the central atom in a molecule arrange themselves in space in such a way that they minimize their mutual repulsion. In other words, the chemical bonds in the molecule will be energetically most stable when they are as far apart from each other as possible. Let us take up some examples.

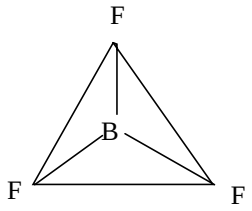
$BeCl_2$ is one of the simple triatomic molecules. In this molecule, the central atom, beryllium has an electronic configuration of $1s^2\ 2s^2$. That is it has two electrons in its valence shell. In the process of covalent bond formation with two chlorine atoms two more electrons are contributed (one by each chlorine atom) to the valence shell. Thus there are a total of 4 valence electrons or two pairs of valence electrons. According to the postulate given above, these electron pairs would try to keep as far away as possible. It makes the two electron pairs to be at an angle of 180° which gives the molecule a linear shape.



linear molecule

Other molecules of this type would also have a similar shape.

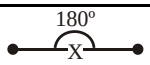
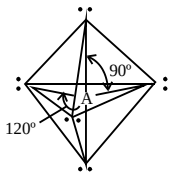
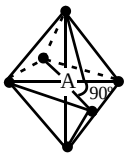
BF_3 : In boron trifluoride, the central atom, boron has an electronic configuration of $1s^2\ 2s^2\ 2p^1$. That is, it has three electrons in its valence shell. In the process of covalent bond formation with three fluorine atoms three more electrons are contributed (one by each fluorine atom) to the valence shell. Thus there are a total of 6 valence electrons or three pairs of valence electrons. According to the VSEPR postulate, these electron pairs would try to keep as far apart as possible. It makes the three electron pairs to be located at an angle of 120° which gives the molecule a planar trigonal shape.



Planar trigonal shape

Thus different molecules would have different shapes depending on the number of valence shell electrons involved. The geometric shapes associated with various numbers of electron pairs surrounding the central atom are given in Table 5.1.

Table 5.1: Geometric arrangements of electron pairs around central atom.

Molecule Type	Number of electron pairs	Predicted geometry	Representative structure	Examples
AX_2	2	Linear		$HgCl_2$, BeH_2
AX_3	3	Planer trigonal		BF_3, BCl_3
AX_4	4	Tetrahedral		CCl_4, CH_4, $SiCl_4$
AX_5	5	Trigonal bipyramidal		PCl_5, PF_5
AX_6	6	Octahedral		SF_6, PF_6^-

POSTULATE 2

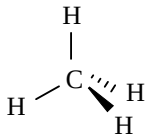
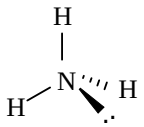
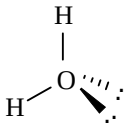
The repulsion of a lone pair of electrons for another lone pair is greater than that between a bond pair and a lone pair which in turn is greater than that between two bond pairs The order of repulsive force between different possibilities is as under.

lone pair - lone pair > lone pair - bond pair > bond pair - bond pair

The shapes of the molecules given in Table 5.1. correspond to the molecules containing only bond pair electrons. The shapes of molecules containing a combination of lone pairs and bond pairs would be distorted from the above mentioned shapes.

Let us take an example of three molecules namely, methane, ammonia and water. All the three contain a total of 4 electron pairs around their central atom. But the nature of these is different in the three cases. In methane molecule the central carbon atom has 4 valence electrons and it shares 4 electrons with four hydrogen atoms. So there are a total of 4 bond pairs and according to Table 5.1 it should have a tetrahedral shape. In case of ammonia also there are four pairs of electrons but their nature is different. Three of these are bond pairs while one is a lone pair. Similarly, in case of water again there are four pairs of electrons ; two are bond pairs while two are lone pairs. Due to the differences in the mutual repulsion between bond pair - bond pair and lone pair - bond pair the molecular shape would be slightly distorted from the expected tetrahedral shape. The number and nature of electron pairs and the geometries of these three molecules are given in Table 5.2.

Table 5.2: Molecular geometries of molecules with 4 electron pairs with different combinations of lone pairs and bond pairs.

Molecule	Number of bond pairs	Number of lone pairs	Molecular geometry	Molecular Shape	Bond angle (in degrees)
CH_4	4	0	tetrahedral		109.5
NH_3	3	1	trigonal pyramidal		107
H_2O	2	2	angular or bent		104.5

We have so far learnt that a chemical bond formation between two atoms can occur by transfer (ionic bonding) or sharing (covalent bonding) of electrons. The processes of bond formation and the bonding in simple molecules can be conveniently represented in terms of electron – dot structures. Further, the VSEPR theory provides a good idea of the shapes of the molecules. But! have you noticed that we have been representing electrons as well defined dots i.e., localized particles. This is in contradiction with the probabilistic (orbital) representation of the electron that you have learnt in lesson 3. Let us learn how do we explain the process of bond formation in terms of modern theories that incorporate the wave mechanical representation of atom.

Intext Question 5.2

1. What are the basic postulates of VSEPR theory?

   .....

2. Predict the shape of methane (CH_4) on the basis of VSEPR theory.

   .....

5.5 Modern Theories of Chemical Bonding

The theories of chemical bonding proposed (in 1916) by Kossel and Lewis are called as classical theories of bonding. These do not take into account the wave mechanical or quantum mechanical principles. After the development of quantum mechanical description of atomic structure two more theories were proposed to explain the bonding between atoms. These are called modern theories of chemical bonding. These are Valence Bond Theory (VBT) and Molecular Orbital Theory (MOT). Let us discuss these theories in brief.

5.5.1 Valence Bond Theory

Valence bond theory was proposed by Heitler and London in 1927, to describe the formation of hydrogen molecule from its atoms. Linus Pauling and others further developed it. In this approach the process of chemical bond formation can be visualised as the overlapping of atomic orbitals of the two atoms as they approach each other. The strength of the bond depends on the effectiveness or extent of the overlapping. Greater the overlapping of the orbitals, stronger is the bond formed. Let us take the example of bonding in hydrogen molecule to understand the VB approach.

Suppose that the two hydrogen atoms are at infinite distance from each other. Their electrons are in their respective 1*s* orbitals and are under the influence of the corresponding nuclei. As the two atoms approach each other their 1s orbitals begin to overlap which lead to decrease in energy, Fig.5.1. At a distance equal to the bond length the overlapping is maximum and the energy is minimum. The overlapping can be equated to the sharing of electrons between the atoms. The electrons occupying the shared region of orbitals are under the influence of both the nuclei.

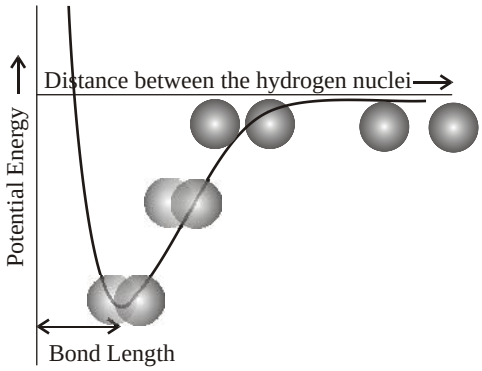
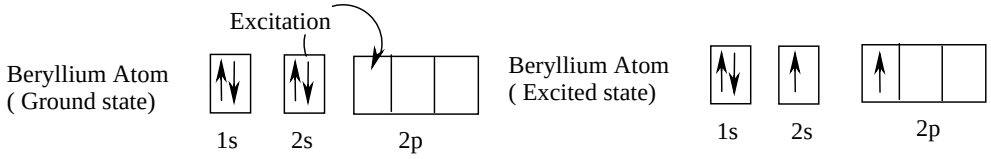


Fig. 5.1 : *Formation of hydrogen molecule from overlapping of two hydrogen atoms*

This simple approach can be used to explain the bonding in simple diatomic molecules like HF,F_2 etc.. However, to explain bonding in molecules containing more than two atoms some additional concepts like excitation and hybridisation need to be used.

5.5.1.1 Hybridisation

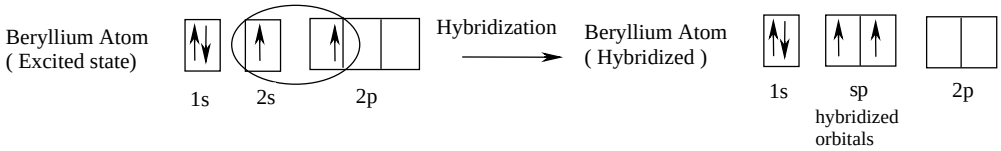
Let us take up the example of bonding in a triatomic molecule; say beryllium hydride (BeH_2) to understand the concept of hybridisation of orbitals and the need for the same. The atomic number of beryllium is 4. Its electronic configuration is $1s^2\ 2s^2$. In order to form bonds with two hydrogen atoms the valence electrons ($2s^2$) of beryllium atom must overlap with the 1s electrons of the two hydrogen atoms. Since the valence shell of beryllium atom contains both the electrons in the same orbital (i.e., 2s) it cannot overlap with the 1s orbital of hydrogen atoms containing one electron.[You know that an orbital can contain a maximum of two electrons with opposite spin]. Pauling got over this problem by suggesting that in the process of bond formation an electron from the 2s orbital of beryllium atom gets momentarily excited to the empty 2p orbital as shown below.



Now the two valence electrons are in two singly occupied orbitals which can overlap with the 1s orbitals of the two hydrogen atoms and form two bonds. The problem is still not over. The two bonds formed by these overlaps would be of different nature. One of these would involve overlapping of 2*s* orbital of beryllium with 1*s* orbital of hydrogen while the other would involve overlapping of 2*p* orbital of beryllium with 1*s* orbital of hydrogen. However, experimentally the two bonds are found to be equivalent.

This problem is solved with the help of a concept called **hybridisation** of orbitals. According to this two or more than two non equivalent orbitals (having different energies and shapes) of comparable energies mix or hybridize and give rise to an equal number of equivalent (same energies and shapes) hybrid orbitals.

In case of $BeCl_2$ the two singly occupied orbitals (2s and 2p) hybridize to give two sp-hybrid orbitals. This is called **sp- hybridisation**. These hybrid orbitals lie along the *z*-direction and point in opposite directions.



These hybrid orbitals can now overlap with the 1s orbitals of hydrogen atoms to give the linear molecule of $BeCl_2$ as shown below, Fig. 5.2 .

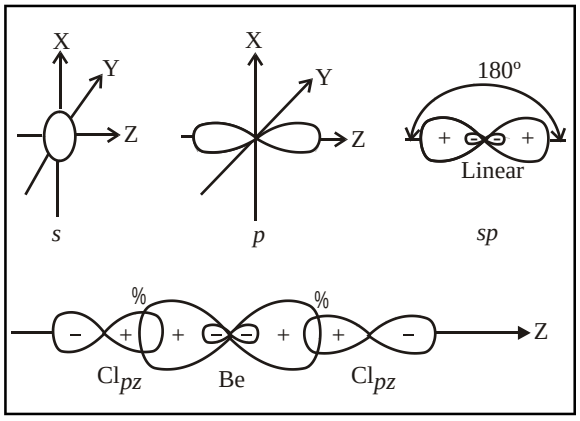
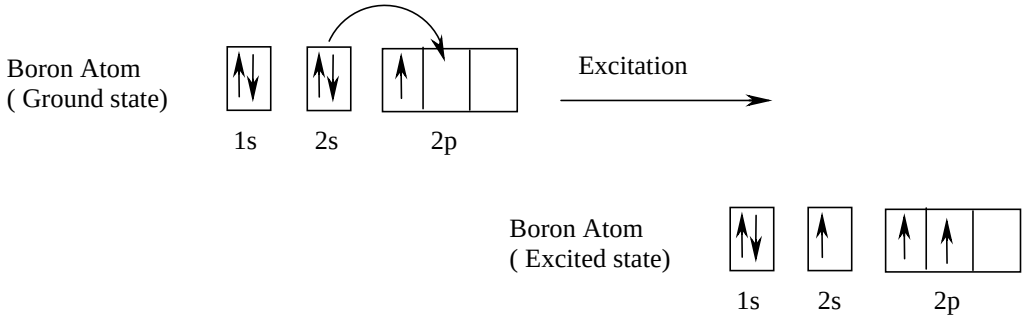


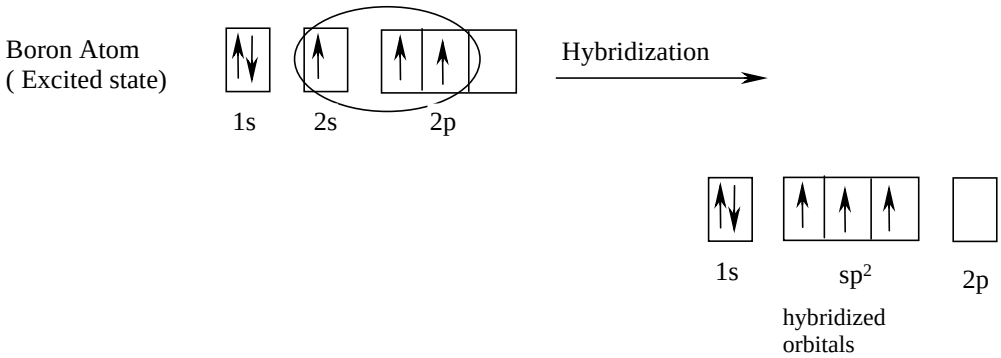
Fig. 5.2 : *Formation of $BeCl_2$; sp hybridisation*

The concept of hybridisation as illustrated above can be used to describe the bonding and shapes of different molecules by considering hybridisation of suitable orbitals. Let us take up some more cases involving hybridisation of *s* and *p* orbitals.

Boron trichloride (*sp*^{2} hybridisation) : In boron there are five electrons and the electronic configuration is $1s^2$, $2s^2$,$2p^1$. There are three electrons in the valence shell of boron atom. In order to form bonds with three chlorine atoms one of the electrons from the 2s orbital of boron atom is excited to its 2p orbital.



One 2s orbital and two 2p orbitals hybridise to give three sp^2 hybridized orbitals. This is called **sp^2 - hybridisation**.



The three hybridized orbitals are coplanar and directed towards the corners of an equilateral ..... **hybrid** orbitals then form bonds with the p –orbitals of chlorine atoms as shown below, fig. 5.3.

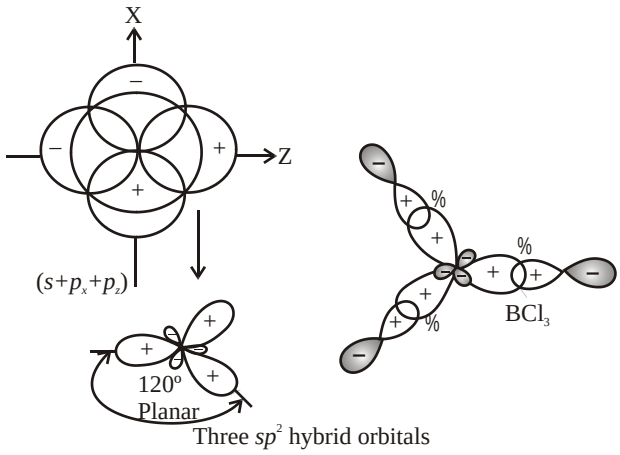
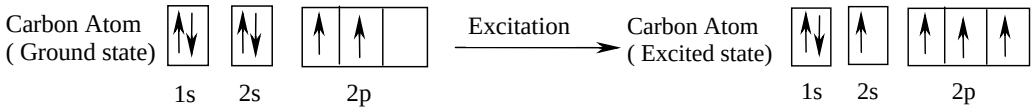
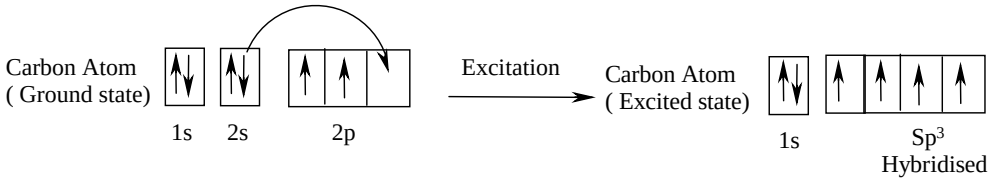


Fig. 5.3 : *Formation of BCl_3 ; sp^2 hybridisation.*

Bonding in Methane (sp^3 hybridisation) : In case of methane the central atom, carbon, has an electronic configuration of $1s^2$, $2s^2$,$2p^2$. In order to form bonds with four hydrogen atoms one of the electrons from the 2s orbital of carbon atom is excited to the 2p orbital.



One 2s orbital and three 2p orbitals of the carbon atom then hybridize to give four sp^3 hybridized orbitals. This is called **sp^3- hybridisation.**



These four sp^3 hybrid orbitals are directed towards the corners of a regular tetrahedron. These **hybrid** orbitals then form bonds with the 1s orbitals of hydrogen atoms to give a methane molecule as shown below, Fig. 5.4.

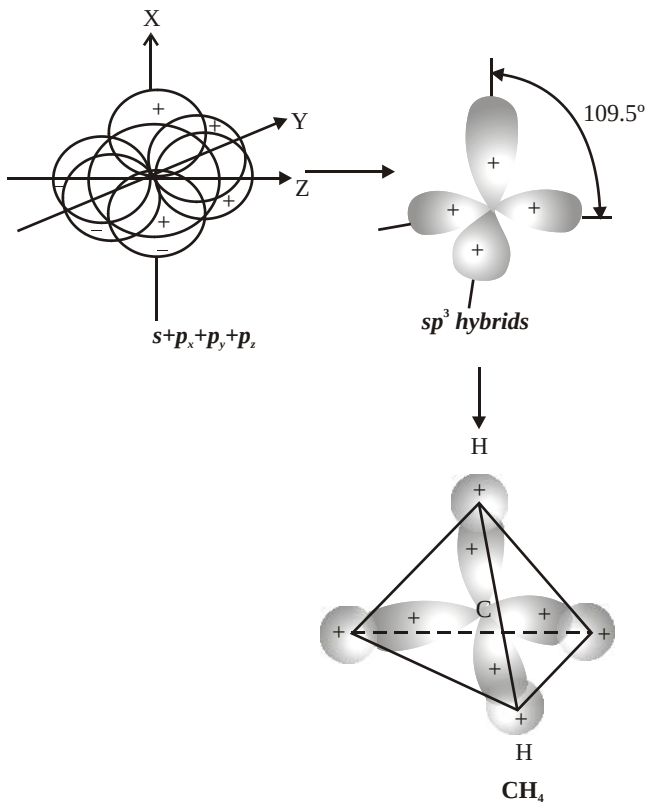


Fig. 5.4 : *Formation of CH_4 ; sp^3 hybridisation.*

Phosphorus pentachloride (sp^3d hybridisation):

P (ground state)

P (excited state)

sp^3d hybridisation

Five sp^3d hybrid orbitals are formed which are directed towards the corners of a trigonal bipyramidal (Fig. 5.5a). These orbitals overlap with singly filled *p*-orbitals of five chlorine atoms and five % bonds are formed. Thus PCl_5 molecule has a trigonal bipyramidal geometry. Three P–Cl bonds (equatorial) make an angle of 120º with each other and lie in one plane. The other two P–Cl bonds (axial) are at 90º to the equatorial plane, one lying above and the other lying below the plane.

SF_6 (sp^3d^2 hybridisation):

P (ground state)

P (excited state)

sp^3d^2 hybridisation

Six sp^3d^2 hybrid orbitals are formed which are directed towards the corners of a regular octahedron. These orbitals overlap with singly filled orbitals of six F atoms and form % bonds giving a regular octahedral geometry (Fig. 5.5 b)

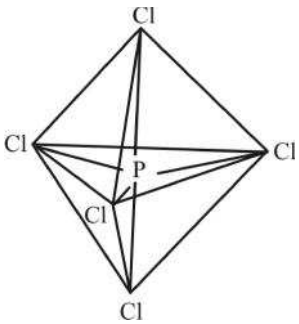


Fig. 5.5 (a) : *Trigonal bipyramidal geometry of PCl_5 molecule.*

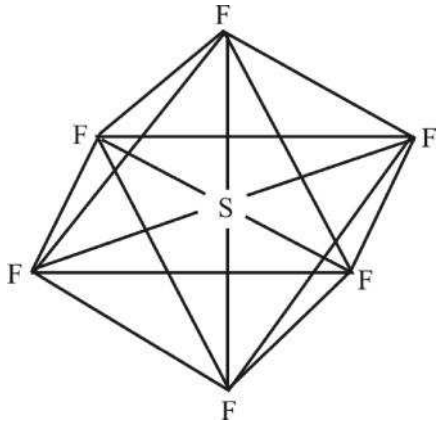


Fig. 5.5 (b) : *Octahedral geometry of SF_6 molecule*

5.5.1.2 Hybridisation and Multiple Bonds

So far we have discussed the bonding in those molecules in which the orbitals on a single central atom are hybridized. Let us see how does the concept of hybridisation help us in understanding bonding between pairs of such atoms. In the case of bonding in ethane (C_2H_6), two carbon atoms are bonded to each other and each carbon atom is bonded to three hydrogen atoms. You would recall that in the case of methane the valence orbitals of carbon atom undergo sp^3 hybridisation. In ethane each carbon atom undergoes sp^3 hybridisation to give four sp^3 hybridized orbitals. The two carbon atoms form a carbon – carbon bond by sp^3 - sp^3 overlapping. The remaining six sp^3 *hybridized* orbitals overlap with 1*s* orbitals of hydrogen atoms to give a molecule of *ethane*, C_2H_6 as shown in fig. 5.6. The C-C bond so formed is along the internuclear axis. Such a bond is called a **bond.**

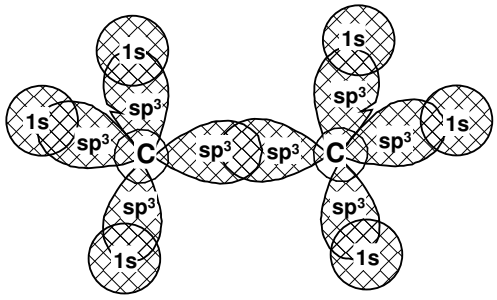


Fig. 5.6 : *Formation of ethane molecule*

Bonding in ethene: In case of ethene, the relevant orbitals of the carbon atoms undergo sp^2 hybridisation. Here, only two of the three *p* orbitals of the carbon atoms hybridize with the *2s* orbital to form three sp^2 hybrid orbitals each. The remaining p-orbitals (one on each carbon atom) do not take part in hybridisation. A carbon – carbon bond is formed by overlapping of sp^2 orbital on the two carbon atoms [Fig 5.7(a)]. The remaining four sp^2 hybridized orbitals overlap with the 1*s* orbitals of hydrogen atoms to give the basic skeleton

of the molecule. This leaves an un-hybridized *p* orbital each on both the carbon atoms[Fig 5.7(b)]. These are perpendicular to the molecular plane and undergo sideways overlap to give an electron cloud in the plane above and below the molecule [Fig 5.7(b and c)]. This is called a $- **bond**. In ethene there are two bonds between the carbon atoms (one sigma and one pi bond).

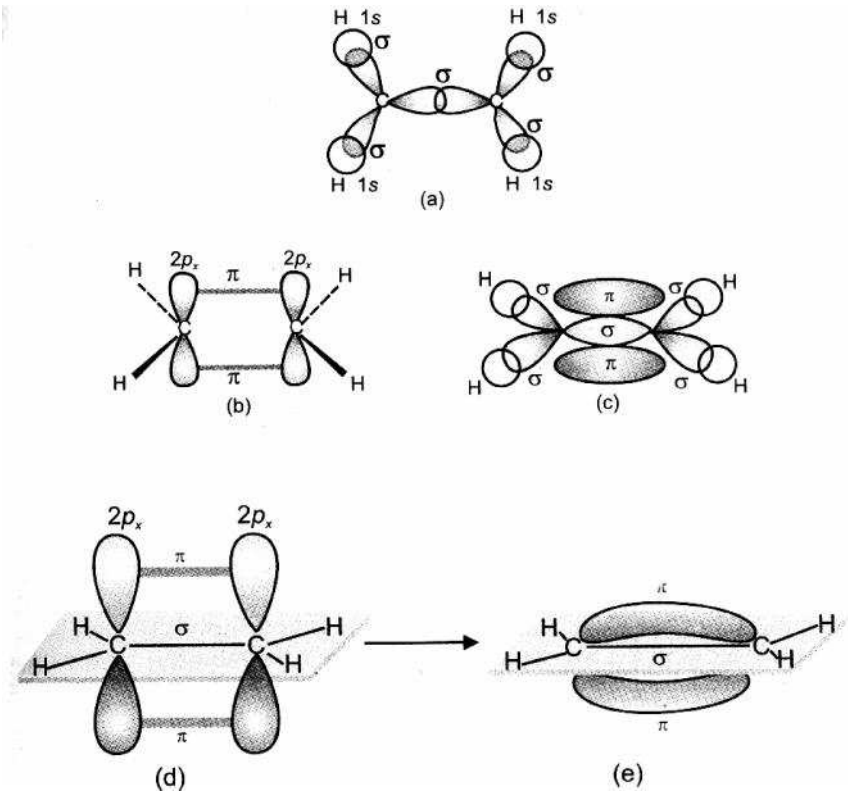


Fig. 5.7 : *Formation of ethylene molecule: a) formation of the basic skeleton of the molecule b) sideways overlapping of the un-hybridized p orbitals and c) a π- bond (d) and (e) complete picture of ethylene molecule.*

Bonding in ethyne (acetylene): In case of acetylene the bonding can be explained in terms of sp-hybridisation in carbon atoms. One 2s and one 2p orbitals hybridize to give two sp-hybridized orbitals. This leaves two mutually perpendicular unhybridised *p* orbitals each on both the carbon atoms. The carbon – carbon bond is formed by sp - sp overlapping with each other. The remaining sp orbital on each carbon overlaps with the 1s orbital of hydrogen to give C-H bonds (Fig. 5.8). The unhybridised *p* orbital each on both the carbon atoms overlap sideways to give two $-bonds.

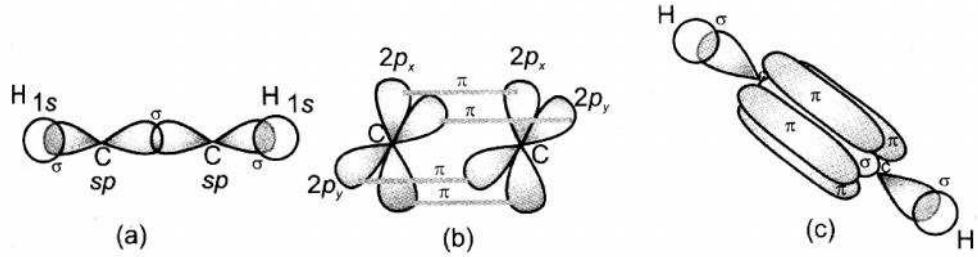


Fig. 5.8 : *Formation of acetylene molecule : a) formation of the basic skeleton of the molecule b) sideways overlapping of two pairs of un-hybridized p orbitals and c) two mutually perpendicular π- bonds.*

Intext Question 5.3

1. What do you understand by the term, 'hybridisation'?

   .....

2. How would you explain the shape of ammonia molecule on the basis of hybridisation?

   .....

5.5.2 Molecular Orbital Theory

You have just learnt about valence bond theory. It describes bond formation as a result of overlapping of the atomic orbitals belonging to the constituent atoms. The overlapping region responsible for bonding is situated between the two atoms i.e., it is localised. Molecular orbital theory(MOT) developed by F.Hund and R.S.Mulliken in 1932, is based on the wave mechanical model of atom. In contrast to the localized bonding in VBT, the molecular orbital theory visualises the bonding to be delocalised in nature i.e., spread over the whole molecule. According to MOT, in the process of bond formation

- **The atomic orbitals of the constituent atoms combine to generate new types of orbitals (called molecular orbitals).** These are spread over the whole molecule i.e., they are delocalised. In other words these new orbitals, do not "belong" to any one atom but extend over the entire region of the bonded atoms.
- These molecular orbitals are created by Linear Combination of Atomic Orbitals **(LCAO)** approach in which, **the atomic orbitals of comparable energies and of suitable symmetry combine to give rise to an equal number of molecular orbitals.**
- The available **electrons then fill these orbitals in the order of increasing energy as in the Aufbau principle** used in the electron configurations of atoms.

Let us take the example of hydrogen molecule to understand the molecular orbital approach to chemical bonding. The two hydrogen atoms have an electron each in their respective 1s orbitals. In the process of bond formation the atomic orbitals of two hydrogen atoms can combine in two possible ways. In one, the MO wavefunction is obtained by addition of the two atomic wave functions whereas in the other the MO is obtained by subtraction of the atomic orbitals. The combination of the 1s orbitals on the two hydrogen atoms are shown in fig. 5.9.

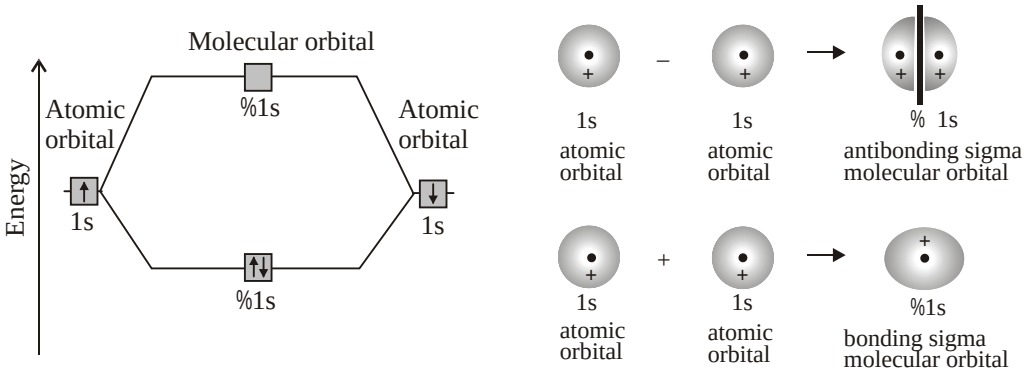
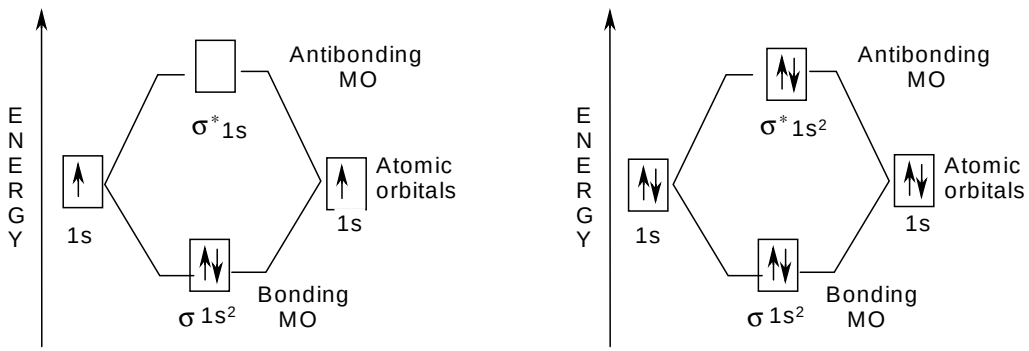


Fig. 5.9 : *Formation of bonding (σ) and anti bonding (σ*) molecular orbitals*

The molecular orbital obtained by the addition of atomic orbitals is of lower energy than that of the atomic orbitals and is called a **bonding orbital.** On the other hand, the orbital obtained by subtraction of atomic orbitals is of higher energy and is called an **anti-bonding orbital.** You can note here that the molecular orbitals obtained here are symmetric around the bond axis (the line joining the two nuclei). Such molecular orbitals are called **sigma (%)** molecular orbitals. The bonding orbital obtained above is denoted as %1s while the anti- bonding orbital is denoted as %*1s. Here % indicates the type of molecular orbital; 1s tells about the atomic orbital involved and * is indicative of the anti-bonding nature of the MO. There are a total of 2 electrons in a hydrogen molecule, according to Aufbau principle these are filled into $\%_{1s}$ orbital. Since the $\%_{1s}$ orbital is a bonding orbital, its getting filled leads to stability or the bond formation.

Like electronic configuration of atoms we write MO electronic configuration for molecules. The MO configuration of hydrogen molecule is given as $(\%1s)^2$. The molecular orbital energy level diagram are given in Fig. 5.10(a and b)



(a) (b)

Fig. 5.10 : *Molecular orbital energy level diagram for a) H_2 and b) He_2 molecules*

Bond Order: we may define a new parameter called bond order as

Bond order = (b.o.) = $\frac{1}{2}(n_b - n_a)$

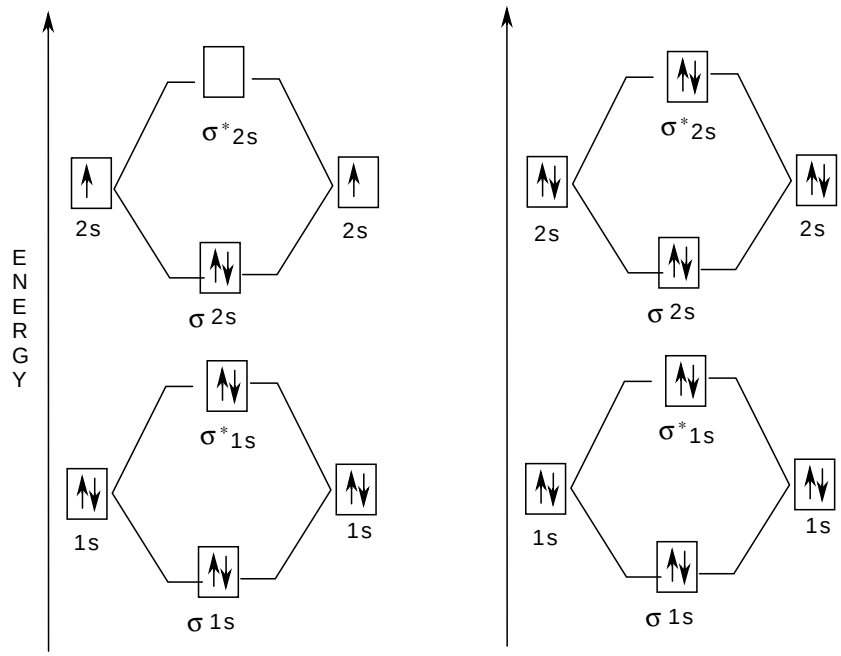
Where, n_b and n_a refer to the number of electrons present in bonding and antibonding molecular orbitals respectively. For hydrogen molecule the bond order will be ½(2–0) = 1, i.e., there is a single bond between two hydrogen atoms.

Helium (He_2) molecule

In case of He_2, also there will be linear combination of 1s orbitals leading to the formation of %1s and %*1s orbitals. The four electrons would be distributed as per the MO electronic configuration : $(\%1s)^2 (\%^*1s)^2$. The molecular orbital energy level diagram is given in fig. 3.10 (b) .This gives a bond order of ½(2–2) = 0, that is there is no bond between two helium atoms. In other words He_2 molecule does not exist.

Li_2 and Be_2 molecules

The bonding in Li_2 and Be_2 can be explained by combining the 1s and 2s orbitals to give appropriate MO's. The molecular orbital diagrams for Li_2 and Be_2 are given in Fig. 5.11.



(a) **(b)**

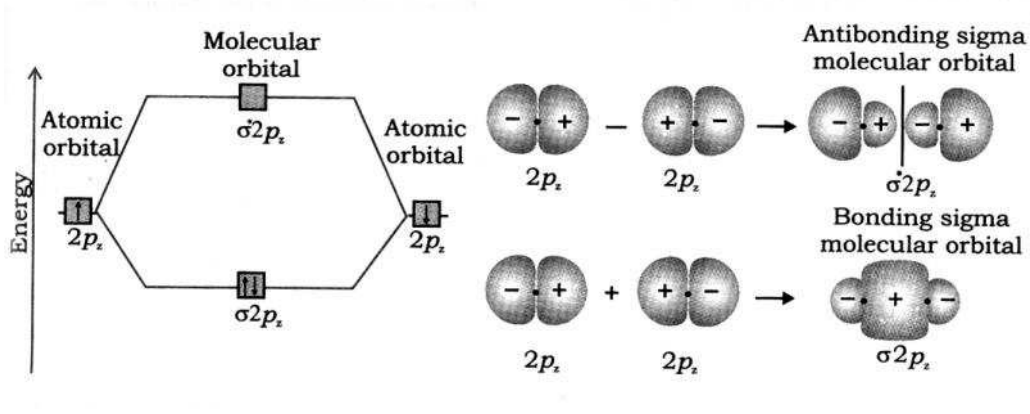
Fig. 5.11: *Molecular orbital energy level diagram for a) Li_2 and b) Be_2 molecules*

5.5.2.1 Molecular Orbital Bonding in Diatomic Molecules of Second Period

So far we have talked about bonding in the elements in which the MO's were obtained from the linear combination of s orbitals. In case of the atoms of second period (beyond Be) elements both *s* and *p* orbitals are involved in the formation of molecular orbitals. In such a case a number of different molecular orbitals are obtained depending on the type and symmetry of the atomic orbitals involved in the process. Let us try to understand the nature of MO's obtained in this case.

Here also the 1s and 2s orbitals of the two atoms would combine to give corresponding bonding and anti-bonding molecular orbital as shown in Fig.5.11 (b). Let us learn about the formation of MO's from the combination of p orbitals

As mentioned above, in LCAO, the atomic orbitals of **comparable energies** and of **suitable symmetry** combine to give molecular orbitals. A suitable symmetry means that the combining orbitals should have same symmetry about the molecular axis. It is nomally assumed that the bond formation takes place along the z-direction. You have learnt in the first unit that the three *p* orbitals are directed towards three mutually perpendicular directions namely the x, y and z directions. Therefore the p_z orbitals of the two atoms would combine along the bond axis to give two molecular orbitals as shown below fig. 5.12. Since these molecular orbitals are symmetric around the molecular axis these are called % orbitals. The designation of the orbitals would be $\%_{2pz}$ and $\%^*_{2pz}$.



(a) (b)

Fig.5.12: *Overlapping of two $2p_z$ orbitals to give molecular orbitals*

Combination of a p_z-orbital with either a p_x or a p_y orbital would not lead to any bonding. On the other hand a p_x orbital will combine with a p_x and the p_y with a p_y as shown in fig. 5.13.

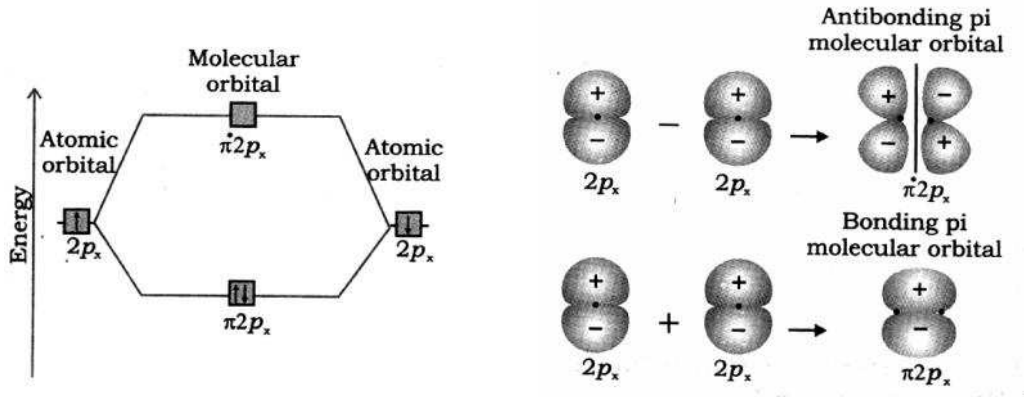


Fig 5.13 : *Formation of molecular orbitals from two $2p_x$ atomic orbtials.*

You may note here that these orbitals combine in a lateral fashion and the resulting molecular orbitals are not symmetric around the bond axis. These MO's are called $- molecular orbitals. These have large electron density above and below the internuclear axis. The anti-bonding $ orbital, $* $2p_x$ (or $* $2p_y$) have a node (a region of zero electron density) between the nuclei.

The molecular orbitals obtained as a result of combination of respective AO's of two atoms can be represented in the form of following energy level diagram, Fig 5.14(a) . The MO's obtained from the combination of 1s orbitals are not shown.(these belong to the inner core and are completely filled) The electrons in these molecular orbitals are filled in accordance with Aufbau principle and Hund's rule.

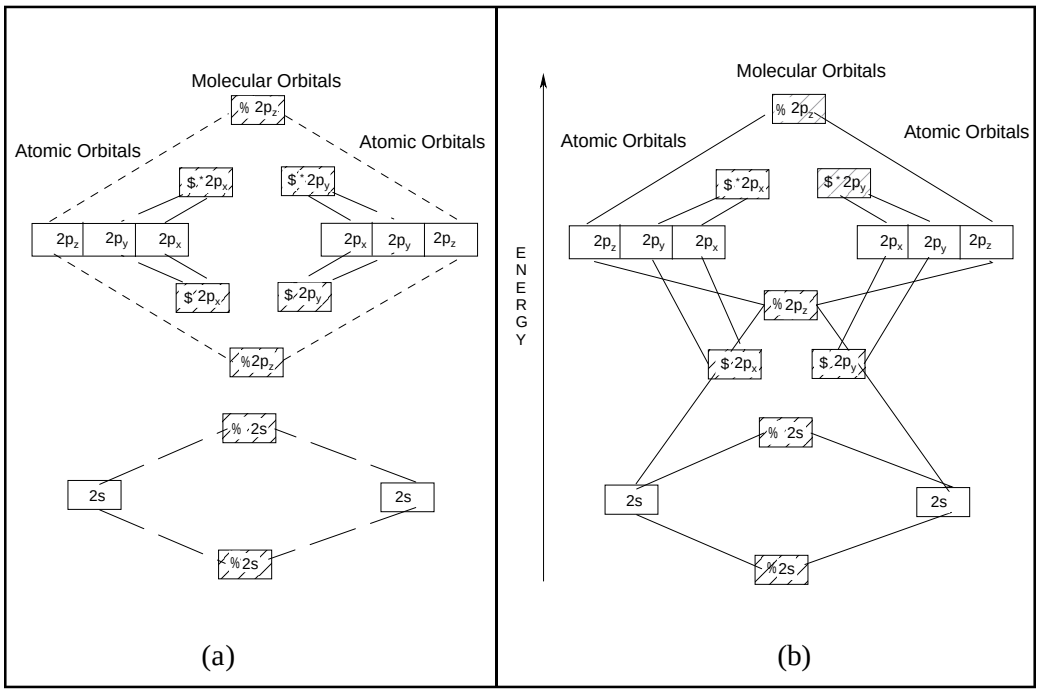


Fig.5.14: *Molecular orbital energy level diagrams a) for O_2 and F_2 and b) for diatomic orbitals of lighter elements Li, Be, B, C and N*

However, this energy level diagram is valid for the diatomic molecules O_2 and F_2 only; For the diatomic molecules of the lighter elements like, B, C and N this energy level diagram is somewhat modified. It is so because in case of lighter elements the difference in the energy of 2s and 2p orbitals is very low and *s* and *p* orbitals on the two atoms get mixed up. In place of normal pure 2*s*-2*s* or 2*p*-2*p* combinations we may have s-p combinations; for example 2*s* orbital of first atom can have a reasonable overlapping with $2p_z$, orbital of the second atom and vice versa. The modified energy level diagram is given in Fig 5.14 (b).

5.5.2.2 MO Electronic Configuration and Properties of the Molecule

The MO energy level diagram discussed above can be used to find out the MO electronic configuration of the molecule. This in turn provides the information about some properties of the molecule. Let us take the example of nitrogen molecule. An atom of nitrogen has five valence electrons; since there are two atoms, we have a total of ten valence electrons that need to be filled in the MO's. Using Fig.5.14 , the MO electronic configuration can be written as $\%2s^2$, $\%^*2s^2$, $\$\ 2p_x^2$, $\$\ 2p_y^2$, $\%2p_z^2$

Bond order : ½ [n_b ! n_a] = ½ [8 ! 2] = ½ [6]= 3 ; this means that in nitrogen molecule, a triple bond exists between the two nitrogen atoms.

Magnetic nature: molecules show magnetic behaviour depending on their MO electronic configuration. If all the MO's are **doubly occupied** the substance shows **diamagnetic** behaviour. In case one or more MO's are **singly occupied,** the substance shows **paramagnetic** behaviour. The MO electronic configuration of O_2 (with 12 valence electrons) is $\%2s^2$, $\%^*2s^2$, $\%2p_z^2$, , $\$\ 2p_x^2$, $\$\ 2p_y^2$, $\$^*\ 2p_x^1$, $\$^*\ 2p_y^1$; Since it contains

unpaired electrons, oxygen shows paramagnetic behaviour. This has been found to be so experimentally also. In fact, the explanation of the paramagnetic behaviour of oxygen is an achievement of MOT.

The bond order and the magnetic behaviour of the molecular cations and anions can also be obtained in the same way. In such cases we add one electron for every negative charge and for every +ve charge we subtract an electron. For example, O_2^{2}!(oxygen molecule dianion) would have a total of 14 valence electrons (12 + 2) while oxygen molecule cation O_2^{+} would have 12!1 = 11 valence electrons.

Intext Question 5.4

1. What is the basic difference between the valence bond and molecular orbital theories?

   .....

2. Calculate the bond orders for Li_2 and Be_2 molecules using the molecular orbital diagrams given in Fig. 5.12.

   .....

3. Predict the magnetic behaviour of O_2 .

   .....

What You Have Learnt

- A chemical bond may be visualised as an effect that leads to the decrease in the energy of the combination of two atoms when they come closer.
- The atoms combine in such a way so as to attain stable electronic configuration of noble gases.
- According to Kossel, transfer of an electron from one atom to the other achieves the stable configuration. This leads to formation of ions, which are held together by electrostatic interactions called ionic bond.
- According to Lewis, the stable configuration is achieved by sharing of electron pairs between the bonding atoms. This leads to the formation of a covalent bond.
- Bonding in simple molecules can be conveniently represented in terms of Lewis electron-dot structures.
- In some covalently bound atoms the shared pair of electron is more towards the atom with greater electronegativity and leads to partial ionic character in the molecule.
- Valence shell electron pair repulsion (VSEPR) theory is very helpful in predicting the shapes of simple molecules. It is based on the interactions between the electron pairs around the central atom in the molecule.
- Valence bond theory (VBT) and Molecular orbital theory (MOT) are two modern theories of chemical bonding. These are based on the wave mechanical model of atom.

- According to the valence bond theory the process of chemical bond formation can be visualised as the overlapping of atomic orbitals of the two atoms as they approach each other. The overlap increases the electron charge density in the inter-nuclear region.
- In order to explain bonding in molecules containing more than two atoms, Pauling proposed the concept of hybridisation. In hybridisation, the atomic orbitals of the valence shell of the central atom ' hybridise' or merge and give newer orbitals with proper orientations, which explain the shape of the molecule.
- According to the Molecular orbital theory the atomic orbitals of comparable energies and of suitable symmetry combine to give rise to an equal number of molecular orbitals. These molecular orbitals extend over the entire region of the molecule i.e., these are delocalised over the whole molecule.
- When two atomic orbitals combine it gives a pair of molecular orbitals; one is called bonding molecular orbital of lower energy and the other of higher energy is called anti-bonding orbital.
- The electrons present in the molecule are filled in these orbitals in the order of increasing energy (Aufbau principle) to give the MO electronic configuration.
- The number of bonds between the two atoms is called bond order and is defined as Bond order = b.o. = $\frac{1}{2}(n_b - n_a)$
- The MO electronic configuration can be used to predict the magnetic nature of the molecule. If all the MO's are doubly occupied the substance shows diamagnetic behaviour and if one or more MO's are singly occupied the substance shows paramagnetic behaviour.

Terminal Exercise

1. What do you understand by a chemical bond?
2. Explain the process of bond formation as a decrease in energy.
3. What do you understand by the term, 'bond length' ?
4. Describe the two possible ways in which the noble gas electronic configuration is achieved in the process of bond formation.
5. What are Lewis electron-dot symbols ? Show the formation of $MgCl_2$ in terms of Lewis symbols.
6. Define a coordinate bond and give some examples.
7. What is VSEPR theory ? predict the shape of SF_6 molecule using this theory.
8. Why do we need the concept of hybridisation ? How does it help in explaining the shape of methane ?
9. Give the salient features of molecular orbital theory.
10. Be_2 molecule does not exist. Explain on the basis of molecular orbital theory.

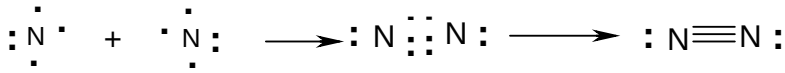
11. Write down the molecular orbital electronic configuration of the following species and compute their bond orders.

O_2 ; O_2^+ ; $O_2^!$; $O_2^{2!}$

Answers to Intext Questions

5.1

1. An electrovalent bond is formed when one or more electrons are transferred from one atom to another atom or atoms.

2. 

3. In a covalent bond the shared pair of electrons is closer to the more electronegative atom. This leads to charge separation in the molecule and the bond becomes polar

4. A bond in which both the bonding electrons are contributed by one atom only.

5.2

1. The two postulates of VSEPR theory are

i) The electron pairs (both bonding and non-bonding) around the central atom in a molecule arrange themselves in space in such a way that they minimize their mutual repulsion

ii) The repulsion of a lone pair of electrons for another lone pair is greater than that between a bond pair and a lone pair which in turn is stronger than that between two bond pairs The order of repulsive force between different possibilities is as under.

lone pair - lone pair > lone pair - bond pair > bond pair - bond pair

2. In methane the central carbon atom would have four pairs of electrons in its valence shell. According to VSEPR theory these would be placed tetrahedrally around the carbon atom. Hence the methane molecule would have a tetrahedral shape.

5.3

1. Hybridisation is a concept which is quite useful in explaining the shapes of molecules. According to this two or more than two non equivalent orbitals with comparable energies and different shapes mix and give rise to an equal number of equivalent hybrid orbitals. The hybrid orbitals have identical energies and shapes.

2. In ammonia the 2s and three 2p orbitals hybridize to give four sp^3 hybridized orbitals. Three of these overlap with the 1s orbitals of hydrogen and one remains nonbonding containing a lone pair. The sp^3 hybridized orbitals are directed towards the corners of a regular tetrahedron. But due to the difference in the repulsion between lone pair - bond pair and bond pair - bond pair the ammonia molecule has a distorted tetrahedral shape which is some what like a trigonal pyramid.

5.4

1. Valence bond theory visualises the bond formation to be localized whereas according to MOT it is delocalised.

2. Bond order = b.o. = ½(n_b - n_a)
   for Li_2 ; Bond order = ½ [4-2] = ½ [2] = 1
   for Be_2 ; Bond order = ½ [4-4] = ½ [0] = 0

3. MO configuration of O_2 is % $2s^2$, %* $2s^2$, %$2p_z^2$, \$$2p_x^2$ = \$ $2p_y^2$
   \$* $2p^1_x$ = \$* $2p^1_y$
   Due to 2 unpaired electrons O_2 molecule is paramagnetic.

Ab initio Calculation of the Potential Energy Curve of H_2

Introduction

The hydrogen molecule (H_2) is the simplest polyelectronic molecular system, involving only 2 nuclei and 2 electrons. This makes it the best place to start learning about how theoretical molecular energy calculations can be performed. For more complex systems, molecular energy calculations require a large number of electron wavefunctions and significant amounts of computing power to create a good approximation to the true molecular wavefunction. However, performing qualitatively good calculations on H_2 is possible on an ordinary laptop, although the mathematical calculations are still fairly involved. As such, my project over the course of the UTRIP program was to derive the potential energy curve of H_2 from first principles.

Basis Set

The spatial atomic orbitals of a hydrogen atom are known exactly, and they have the form $\varphi(\underline{r})=\exp[-a|\underline{r}-\underline{R}|]$, where $\underline{r}$ is the position vector of the electron and $\underline{R}$ the position of the hydrogen nucleus. However, functions of this type (Slater orbitals) are mathematically difficult to manipulate, so it is common to use functions of Gaussian form, $\varphi(\underline{r})=\exp[-a(\underline{r}-\underline{R})^2]$. As a result, one Gaussian type orbital on each hydrogen atom was taken as the basis set in this approximation. Although this is a tiny basis set and a poor approximation to the real orbitals, it is not only good enough to give an initial insight into how molecular energies can be calculated, but also to give a qualitatively adequate potential energy curve.

Molecular Wavefunction

Due to the high mass ratio between electrons and nuclei, it is a good approximation to assume that the nuclei are fixed relative to the electronic movement (Born-Oppenheimer approximation), so this was done to calculate the energy at various internuclear distances. For the overall electronic wavefunction, a Slater determinant of 1-electron orbitals was used in order to satisfy the Pauli Principle that the wavefunction must be antisymmetric with respect to electron exchange. This gives the electronic wavefunction as:

$$\Psi = \frac{1}{\mathrm{sqrt}(2)} \begin{vmatrix} \psi(1)\alpha(1) & \psi(1)\beta(1) \\ \psi(2)\alpha(2) & \psi(2)\beta(2) \end{vmatrix}$$

The one electron spatial orbitals, $\psi(i)$, are linear combinations of the spatial atomic orbitals given above, so $\psi = N\{\exp[-a(\underline{r}-\underline{R}_A)^2] + \exp[-a(\underline{r}-\underline{R}_B)^2]\}$ where N is the normalisation constant and $\underline{R}_I$ is the position of nucleus I. This linear combination is good near the equilibrium bond length. However, in the dissociation limit it predicts that each electron will still spend equal time on each H atom, when in reality each electron becomes localised onto one nucleus. This causes some problems with energy calculations in the dissociation limit.

Molecular Integral Calculation

The main body of this task involved the calculation of molecular integrals. Although computer programs are available to do these quickly for Gaussian type orbitals, it was decided that for a first molecular energy calculation it would be instructive to perform the integrals by hand, to understand how they are solved and also to gain an appreciation of the need for computer programs to solve them more efficiently.

Molecular integrals arise because the energy of the system is given by $\langle\Psi|\hat{H}|\Psi\rangle$. When the expression for Ψ in terms of atomic orbitals is substituted in, and the 7 terms of the Hamiltonian (4 electron-nuclear attractions, 2 electron kinetic energies and 1 electron-electron repulsion term) are considered, this expands to give 448 separate energy integrals, even for this very simple system. Fortunately, half of these are 0 due to spin orthogonality, and many of the other integrals are also equal due to the symmetry of the wavefunction, meaning there are in fact many fewer integrals to

calculate.
These energy integrals fall into 3 categories depending on which part of the Hamiltonian they arise from. These categories are kinetic energy integrals (of the form $<i|-d^2/d\underline{r}^2|j>$), electron-nucleus attraction integrals (of the form $<i|-1/(\underline{r}-\underline{R}_K)|j>$) and electron-electron repulsion integrals (of the form $<ij|1/(\underline{r}_1-\underline{r}_2)|kl>$).

Calculating the Total Energy

The total electronic energy of the system is given by summing these molecular integrals (after multiplying by the correct coefficients). However, to obtain the total energy, the internuclear repulsion (which is $1/[\underline{R}_A-\underline{R}_B]$) must also be added. Also, the true energy of 2 free H atoms has been subtracted, in order to obtain the binding energy of the approximate wavefunctions. This means that the energy should tend to 0 as the bond length increases.
To find the molecular energy at a large number of internuclear distances it made sense to create a computer program to do many calculations quickly. This could also be used to optimise the exponential coefficients in the wavefunction, to obtain the best possible energy – optimisation of the atomic orbitals leads to a value of $a=0.26au^{-2}$ in the Gaussian exponentials, and this is the value used throughout this text. As H_2 is a homonuclear diatomic, the symmetry of the system means it is not necessary to perform any self-consistent field calculations, making the calculations of the potential energy curve very rapid.

Results

As explained above, the electronic energy of the system can be split into 3 categories with definite classical analogues. Below is a graph of each of these, as calculated by the Fortran computer code:

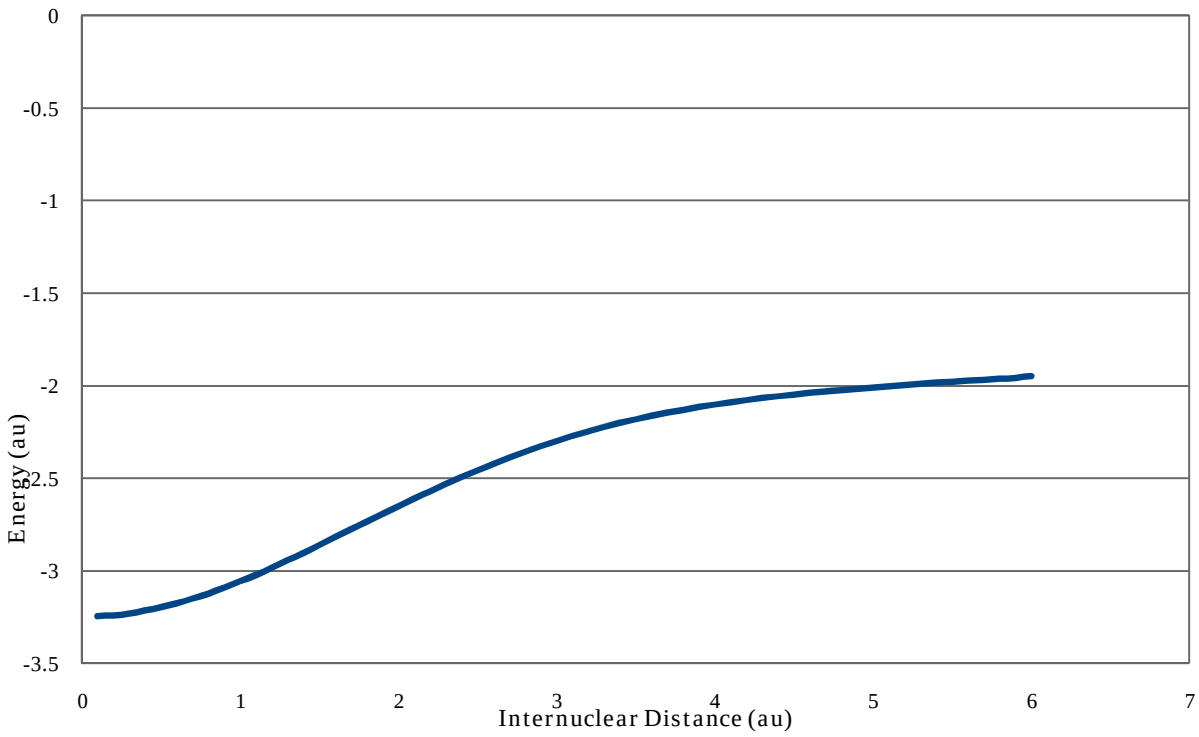


Fig. 1. Electron-nucleus attraction energy in H_2 as a function of internuclear distance ($a=0.26au^{-2}$)

The attraction of the electrons for the nucleus is the most significant term for binding in the molecule. In fact, it is the only negative term in this approximation, so is solely responsible for bonding. From Fig. 1 it can be seen that as the nuclei get further apart the attraction energy becomes less negative. This is because at large internuclear distances an electron will only ever be close to one nucleus. However, when the nuclei are close together an electron can be close to both nuclei

simultaneously, lowering the energy of the system at these distances.

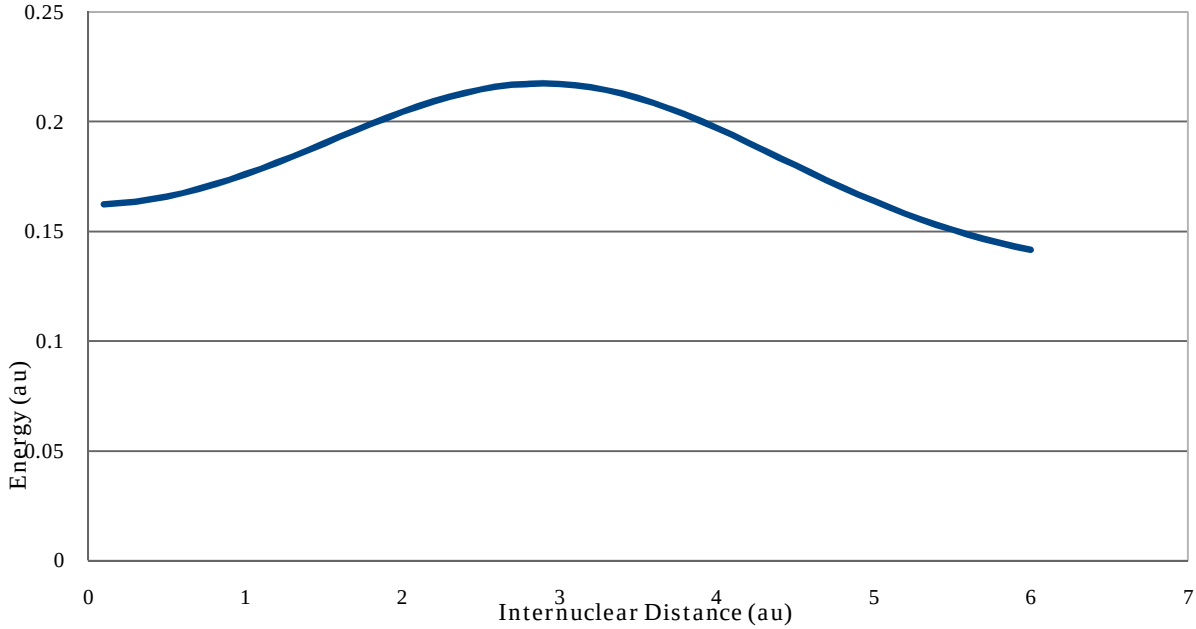


Fig. 2. Electron kinetic energy in H_2 as a function of internuclear distance ($a=0.26au^{-2}$)

Electron kinetic energy is closely related to the size of the orbital it is in, as kinetic energy is given by the second spatial derivative which will generally decrease as the orbital size increases. As a result, we expect the kinetic energy to increase with internuclear distance as the electrons become localised onto one atom, rather than being spread over both. From Fig. 2 we can see that this is not true in this case. This is because the wavefunction that has been used is incorrect in the dissociation limit as it assumes that the electrons are always equally likely to be located on each hydrogen. This results in the electron orbitals increasing in size as the bond length increases, rather than decreasing as we would expect.

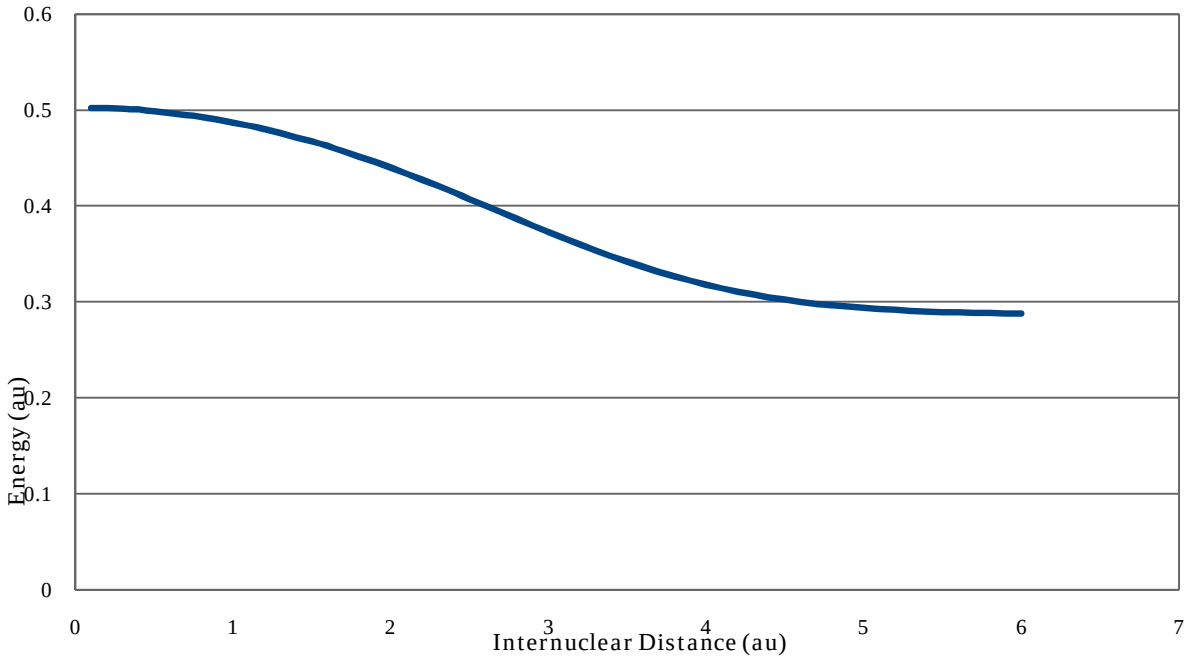


Fig. 3. Electron-electron repulsion energy in H_2 as a function of internuclear distance ($a=0.26au^{-2}$)

The electron-electron repulsion is related to the internuclear distance, as the increasing distance between nuclei means the electrons will on average be further apart. In reality, however, the electron-electron repulsion should tend to 0 at large internuclear distances as the electrons will be localised on separate nuclei at a far distance. This doesn't occur with the simple wavefunction used here, as there is a finite probability of the electrons being on the same hydrogen, even at infinite bond length. This means that about half the electron-electron repulsion remains in this limit.

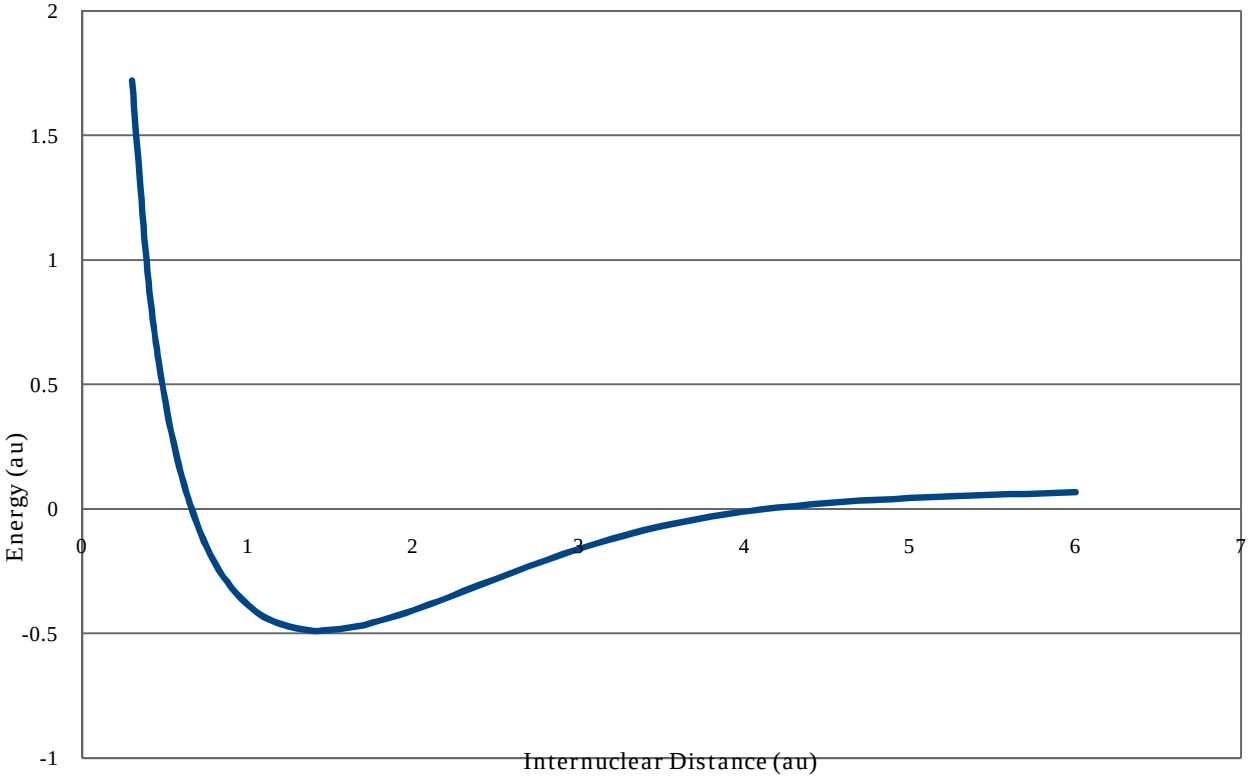


Fig. 4. The potential energy curve of H_2 as calculated using the simple model described in the main text ($a=0.26au^{-2}$)

The calculated potential energy curve of H_2 is in good qualitative agreement with the true curve – there is a lot of repulsion at very short distances as the nuclear repulsion becomes large, there is a bound region where the total energy is less than 0 (meaning H_2 is a stable molecule) and the energy tends to a constant value at large bond lengths. Also, there is even good quantitative agreement of the calculated bond length with experimental data – the energy minimum occurs at a bond length of 1.388 au compared with the actual equilibrium bond length of 1.401 au.
The value of the energy is less good – the calculated value is only 45% of the true value. However, this is to be expected given the simplicity of the basis set used to create this model.

<u>Improvements</u>
As the wavefunction that has been used is so simple there are obviously some significant improvements that can be made.
Firstly, the atomic orbital basis set that has been used could be improved. There are two main ways this could be done – firstly, the exact Slater orbitals, with optimised coefficients, could be used to calculate a good approximation. However, it will be computationally much more difficult to use Slater orbitals, so a better approach may be to use a linear combination of Gaussian functions as the atomic orbitals, to more closely approximate the Slater-type orbital. In general, a combination of 3 Gaussian functions is a good approximation, although occasionally more are used.
Another improvement would be to solve the problems that arise in the dissociation limit. This could be achieved by including a variable in the 1-electron wavefunctions to allow for the localisation of

the electrons onto one hydrogen each at dissociation. For example, we set $\psi = N\{\exp[-a(\underline{r}-\underline{R}_A)^2] + \zeta\exp[-a(\underline{r}-\underline{R}_B)^2]\}$ where ζ is a function of bond length (tending to 0 or ∞ at large bond lengths)
Inclusion of other orbitals (2s, 2p, etc.) will slightly improve the energy we calculate, but the effect of this will be minimal as there is such a large energy gap between the 1s and 2s orbitals of hydrogen.

Conclusion

Although the energy calculated is significantly wrong, the techniques used to calculate it can be applied to much more complicated systems, using more accurate wavefunctions to represent the electrons. Also, even though the approximation to the wavefunctions was so simple, it was still good enough to be in qualitative agreement with the experimental results, meaning there may be situations where using a model this simple is appropriate in order to gain a basic insight into complex problems.

M.Sc. Chemistry

Paper – I : INORGANIC CHEMISTRY

VSEPR Theory

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UNIT-1 STEREO CHEMISTRY IN MAIN GROUP COMPOUNDS

Structure:

1. Introduction
2. Objectives
3. Valence Shell Electron Pair Repulsion (VSEPR)
   - 3.1. Gillespie Laws
   - 3.2. Applications
   - 3.3. Comparison of CH_4, NH_3, H_2O and H_3O^+
   - 3.4. Comparison of PF_5, SF_4 and $[ICl_2^-]$
4. Walsh Diagrams
   - 4.1. Application to triatomic molecules.
   - 4.2. Application to penta atomic molecules.
5. dπ - pπ Bonds.
   - 5.1. Phosphorous Group Elements.
   - 5.2. Oxygen Group Elements.
6. Bent's rule and Energetic of hybridisation.
   - 6.1. III and IV groups halides.
   - 6.2. V and VI groups Hydrides halides.
   - 6.3. Isovalent hybridisation.
   - 6.4. Apicophilicity.
7. Some simple reactions of covalently bonded molecules.
   - 7.1. Atomic invevsion.
   - 7.2. Berrypseudo rotation.
   - 7.3. Nucleophillic substitution.
8. Let Us Sum Up.
9. Check Your Progress: The key.

1. INTRODUCTION

The concept of molecular shape is of the greatest importance in inorganic chemistry for not only does it affect the physical properties of the molecule, but it provides hints about how some reactions might occur. Pauling and Slater (1931) in their Valence Bond Theory (VBT) proposed the use of hybrid orbital, by the central atom of the molecule, during bond formation. Thus, with the knowledge of the hybridisation used by the central atom of the molecule, one can predict the shape and also the angles between the bonds of a molecule. However, since then more advanced theories have come into existence. In this chapter we explore some of the consequences of molecular shape in terms of VSEPR theory and refine that concept into the powerful concept of molecular symmetry and the language of group theory, using Walsh diagrams and Bent's Theory, towards the end of the unit.

You may recall what you have already studied about the directional property of a covalent bond and the concept of hybridisation of orbital to predict molecular geometry.

2. OBJECTIVES

The main aim of this Unit is to study stereochemistry in main group compounds. After going through this unit you should be able to:

- discuss absolute shapes of various molecules;
- explain anomalies in bond angles present in some molecules;
- describe stability of molecular shapes in terms of energetics, and
- discuss simple reactions of covalently bonded molecules on the basis of the principles studied in this unit;

2. VSEPR THEORY (VALENCE SHELL ELECTRON PAIR REPULSION THEORY)

In order to predict the geometry of covalent molecules, Valence Shell Electron Pair Repulsion Theory is used. This theory was given by Gillespie and Nyholm. According to this theory the geometry of a molecule depends upon the number of bonding and non-bonding electron pairs in the central atom. These arrange themselves in such a way that there is a minimum repulsion between them so that the molecule has minimum energy (i.e. maximum stability).

2.1. Gillespie Laws

The following rules have been reported by Gillespie to explain the shape of some covalent molecules:

1. If the central atom of a molecule is surrounded only by bonding electron pairs and not by non-bonding electron pairs (lone pairs), the geometry of the molecule will be regular.

   In other words we can say that the shape of covalent molecule will be linear for 2 bonding electron pairs, triangular for 3 bonding electron pairs. tetrahedral for 4 bonding electron pairs, trigonal bipyramidal for 5 bonding electron pairs:

Name of Compound	Bonding Electron Pairs	Shape
$BeCl_2$	2	Linear
$BeCl_3$	3	Triangular Planar
$SnCl_4$	4	Regular Tetrahedral
PCl_5	5	Trigonal bipyramidal
SF_6	6	Regular Octahedral

2. When the central atom in a molecule is surrounded by both, bonding electron pairs as well as by lone pairs, then molecule will not have a regular shape. The geometry of the molecule will be disturbed. This alteration or distortion in shape is due to the alteration in bond angles which arises due to the presence of lone pairs on the central atom. How the presence of lone pairs causes an alteration in bond angles can be explained as follows:

At a fixed angle the closer the electric-pairs to the central atom, the greater is the repulsion between them. Since the lone-pair electrons are under the influence of only one positive centre (i.e. nucleus), they are expected to have a greater electron density than the bond-pair electrons which are under the influence of two positive centres. Thus lone pair is much closer to the central atom than the bond pair. Hence it is believed that lone pair will exert more repulsion on any adjacent electron pair than a bond pair will do on the same adjacent electron pair.

$$(lp - lp) > (lp - bp) \quad \text{.....(i)}$$

(lp = lone pair and bp = bond pair)

If the adjacent electron pair is a bond pair, then repulsive force between lone pair and bond pair will be greater than repulsive force between two bond pairs.

$$(lp - bp) > (bp - bp) \quad \text{.....(ii)}$$

On combining relations (i) and (ii) we get

$$(lp - lp) > (lp - bp) > (bp - bp)$$

Thus the repulsion between two lone pairs is maximum in magnitude, that between a bp and lp is intermediate while that between two bond pairs is the minimum.

The more the numbers of lone pairs on a central metal atom, the greater is the contraction caused in the angle between the bonding pairs. This fact is clear when we compare the bond angles in CH_4, NH_3 and H_2O molecules. (Table 1.1)

Table 1.1

Molecules	**No. of Lone pairs on central atom**	**Bond Angle**	**Contraction in bond angle w.r.t. CH_4**
CH_4	0	109.5^o	0
NH_3	1	107.5^o	2°
H_2O	2	105.5^o	4°

3. B-A-B bond angle decreases with the increase in electro negativity of atom B in AB_2 molecule where A is the central atom.

   Example: Pl_3 (102°) > P Br_3 (101.5^o) > PCl_3 (100°)

4. Bond angles involving multiple bonds are generally larger than those involving only single bonds. However, the multiple bonds do not affect the geometry of the molecule.

5. Repulsion between electron pairs in filled shells are larger than the repulsion between electron pairs in incompletely filled shells.
   Examples: H_2O (105.5^o) < H_2S (92.2^o)

2.2. Applications of Gillespie Laws

Let us take some examples in support of these laws:

(a) AX_2 molecule, which has only two bond-pairs, will be linear:

X___A___X

Examples in this groups will be $BeCl_2$, $CaCl_2$, CO_2 etc.

(b) If the molecule is AX_3 (I) or AX_2 with a lone pair of electrons on the central atom A, i.e. AX_2E (II), then the molecule will be triangular (Fig 1.1):

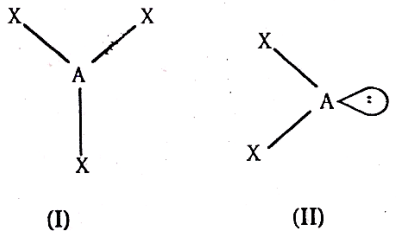


Fig 1.1 : (I) = BCl_3, BF_3 etc.

(II) = SO_2, $SnCl_2$ etc.

(c) If the molecule is AX_4 (III) or AX_3E (IV) or AX_2E_2, then AX_4 will be tetrahedral; AX_3E will be pyramidal and AX_2E_2 will be angular. (Fig. 1.2):

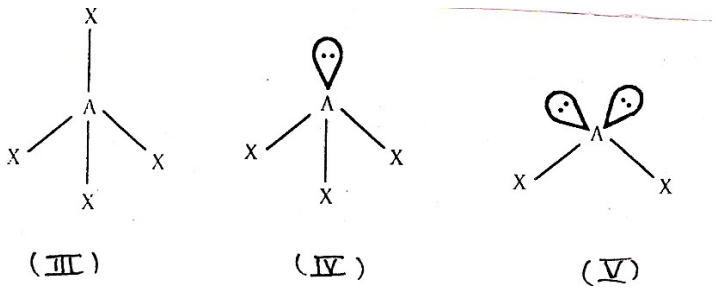
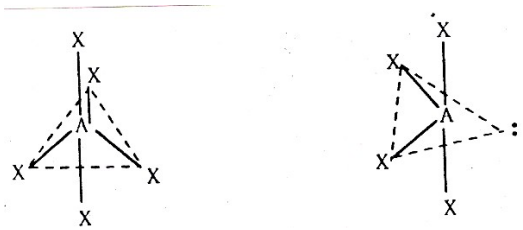


Fig 1.2 : (III) = CCl_4, CH_4, $SiCl_4$, $GeCl_4$ etc.

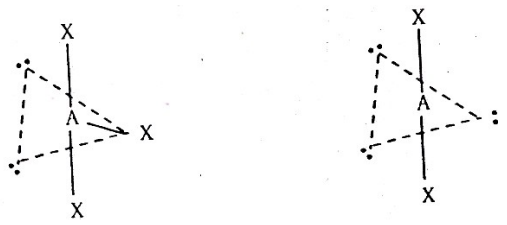
(IV) =NH_3, PCl_3, As_2O_3 etc.

(V) = H_2O, $SeCl_2$, etc.

(d) If the molecule is AX_5 (VI) or AX_4E (VII) or AX_3E_2 (VIII) or AX_2E_3 (IX) then AX_5 will be triangular bi pyramidal; AX_4E will irregular tetrahedral; AX_3E_2 will be T-shaped,; and AX_2E_3 will be linear. (Fig. 1.3)



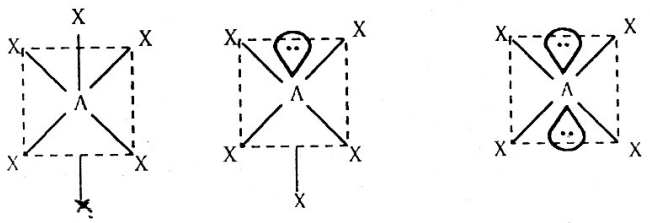
(VI) (IX)



(VIII) (IX)

Fig 1.3 : (VI) = PCl_5; (VII) SF_4, $TeCl_4$ etc.
(VIII) = ClF_3, BrF_3 etc.
(IX) = X_eF_2, ICl_2^-, or I_3^- etc.

(e) If the molecule is AX_6 (X) or AX_5E (XI) or AX_4E_2 (XII) then AX_6 will be octahedral, AX_5E will be square pyramidal; and AX_4E_2 will be square planar. (Fig. 1.4)



(X) (XI) (XII)

Fig 1.4 : (X) = SF_6, WF_6, etc.
(XI) = BrF_5, IF_5 etc.
(XII) = ICl_4^-, X_eF^- etc.

2.3. Comparison of CH_4, NH_3, H_2O and H_3O^+

In table 1.1 bond angles in CH_4, NH_3 and H_2O molecules are given. In all these molecules, the central atom (C, N and O respectively) is sp^3 hybridised. But they differ in the number of lone pair (s) present on the central atom, being zero in CH_4, one in NH_3 and two in case of H_2O. Thus the repulsive force between electron pairs gradually increases in these molecules from CH_4 to H_2O, resulting in the change of geometry and the bond angles. This CH_4 (Four bond pairs) is tetrahedral with the

characteristic bond angle of 109.5°. NH_3 is pyramidal (Three bond pairs and one lone pair) and has a bond angle of 107°. While H_2O is angular (Two bond-pairs and two lone-pairs) and has bond angle of 105°. The increasing lp-lp repulsion decreases the bond angles from 109.5° to ~107° in NH_3 and ~105.5° in H_2O. On comparing H_3O^+ with these molecules, we notice that, it resembles with NH_3 molecule. As the central atom of H_3O^+ on (Oxygen) is also sp^3 hybridised and has 3bp+1 lp. Thus H_3O^+ will also be pyramidal with a bond angle of ~107°. (Fig 1.5)

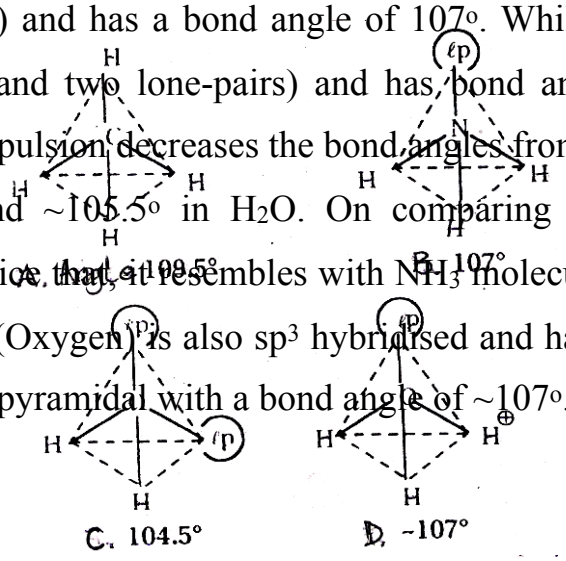


Fig 1.5 :A- CH_4, Tetrahedral, bond angle 109.5°
B- NH_4, Pyramidal, bond angle ~107°
C- H_2O, Angular, bond angle ~105°
D- H_3O^+, Pyramidal, bond angle ~107°

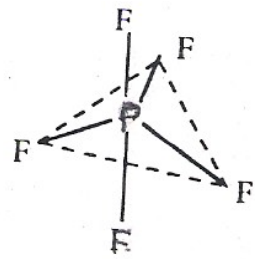
2.4. Comparison of PF_5, SF_4, ClF_3 and $[ICl_2^-]$

A comparison of PF_5, SF_4, ClF_3 and $[ICl_2]^-$ species clearly indicates that each of these molecules have 10 electrons in the valence shell of the central atom, being P, S, Cl and I respectively. In addition to this, the central atom in each case is sp^3d hybridised, and has 0, 1, 2 and 3 lone pairs (lp) respectively. In PF_5, all the five electron pairs (= 10 electrons) are bond pairs and are housed in the five sp^3d hybrid orbital; resulting in the trigonal bipyramidal geometry of the molecule. (Fig 1.6 (a)).

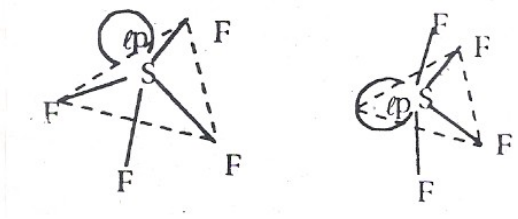
SF_4 molecule has 4 bond-pairs and one lone pair on the central S atom. The lp in this molecule has two options- it can sit in a axial or in an equatorial orbital. In the axial position (Fig. 1.6 (b))i)) it has three bps at 90° and one bp directly opposite to itself. While in equatorial position (Fig. 1.6 (b)(ii)) it has two bps at 90° and two bps at 120°. As in the equatorial position lp-bp repulsion is less and expansion is easy the lp prefers the equatorial position and the molecule is therefore irregular tetrahedral.

In ClF_3., the two lps may be axial-axial (Fig 1.6(c)(i)), or axial-equatorial (Fig 1.6(c)(ii)), or equatorial-equatorial (Fig 1.6(c)(iii)) positions. As the axial position will result in maximum repulsion hence the axial position for the lp is ruled out. Thus the molecule will have T. shaped geometry, according to the Fig. 1.6(c)(ii).

Similarly, due to reduced lp-lp repulsions and a larger volume that a lp can occupy at equatorial positions, the $[ICl_2]^-$ ion will be linear. The three lps occupy the three equatorial positions, leaving the axial positions for the Cl atoms (Fig. 1.6(d)).

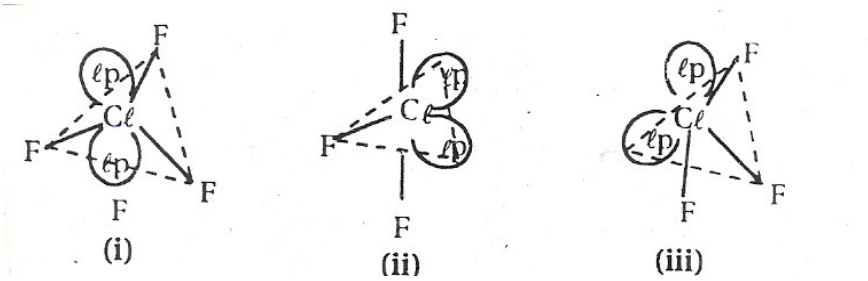


(a) PF_5, Trigonal bipyamidal

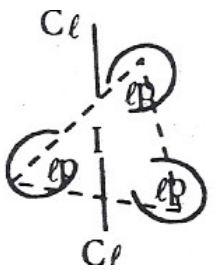


(I) (II)

(b) SF_4, Irregular tetrahedral



(c) ClF_3, T-Shaped



(d) $[ICl_2]^-$, Linear

Fig. 1.6 : Structures of PF_5, SF_4, ClF_3 and $[ICl_2]^-$

Limitations of VSEPR Theory

1. This theory is not able to predict the shapes of certain transition element complexes.

2. This theory is unable to explain the shapes of certain molecules with an inert pair of electrons.

3. This theory is unable to explain the shapes of molecules having extensive delocalised π-electron system.

4. This theory can not explain the shapes of molecules which have highly polar bonds.

Check Your Progress-1

Notes: (i) Write your answers in the space given below;

(ii) Compare your answers with those given at the end of the unit.

(a) Identify and write the shapes of the following molecules.

(i) $BeCl_2$ .....(iv)

ClF_3..... (ii)

PCl_3 .....(v)

XeF_2.....

(iii) SF_4 .....(vi)

BrF_5..... (b) Arrange the following species in the order of increasing bond-angle, considering the repulsive forces due to lone pair:

$^{\oplus}NO_2$, NO_2 and $^{\ominus}NO_2$

>_____>_____>_____

3. WALSH DIAGRAMS

We know all the systems want to be in a stable state, and the stable state is one in which it has the minimum possible energy. Same is true for the stereochemistry or the geometry of a molecule. The VSEPR theory considered that the most stable configuration of a molecule is one in which repulsive forces between the valence electron-pairs is minimum. In contrast, the molecular orbital theory (MOT) considers that the stable geometry of a molecule can be determined on the basis of the energy of molecular orbitals formed as a result of linear combination of atomic orbitals (LCAO). In 1953 A.D.Walsh proposed a simple pictoral-approach to determine the geometry of a molecule considering and calculating the energies of molecular orbitals of the molecule.

The basic approach is to calculate the energies of molecular orbitals for two limiting structures, say linear or bent to 90° for an AB_2 molecule, and draw a diagram showing how the orbitals of one configuration correlate with those of the other. Then depending on which orbitals are occupied, one or the other structure can be seen to be preferred. By means of approximate MO Theory implemented by digital computers, this approach has been extended and generalized in recent years.

Walsh's approach to the discussion of the shape of an AB_2 triatomic molecule (such as BeH_2 and H_2O) is illustrated in Fig. 1.8. The illustration shows an example of a Walsh diagram, a graph of the dependence of orbital energy on molecular geometry. A Walsh diagram for an B_2A or AB_2 molecule is constructed by considering how the composition and energy of each molecular orbital changes as the bond angle changes from 90° to 180°. The diagram is in fact just a more elaborate version of the correlation diagram.

3.1. Application to Triatomic Molecules

The coordinate system for the AB_2 molecule is shown in Figure 1.8. The AB_2 molecule has C_{2v} symmetry when it is bent and, when linear D_2h symmetry. To simplify notations, however, the linear configuration is considered to be simply an extremum of the C_{2v} symmetry. Therefore the labels given to the orbitals through the range $90^o \leq \theta < 180^o$ are retained even when $\theta = 180^o$. The symbols used to label the orbitals are derived from the orbital symmetry properties in a systematic way, but a detailed explanation is not given here. For present purposes, these designations may be treated simply as labels. (Fig. 1.7).

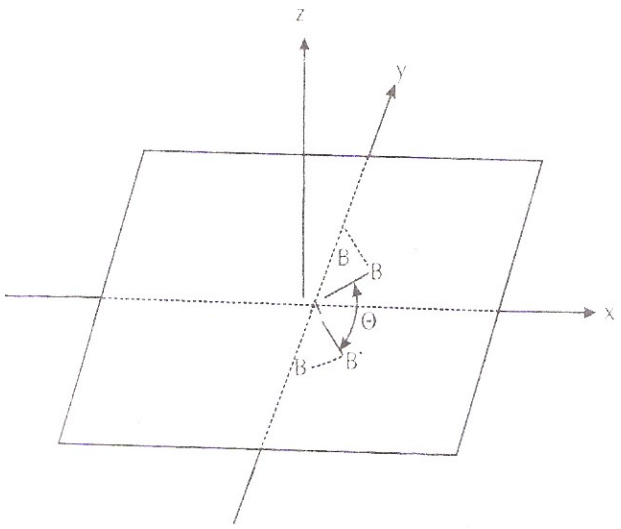
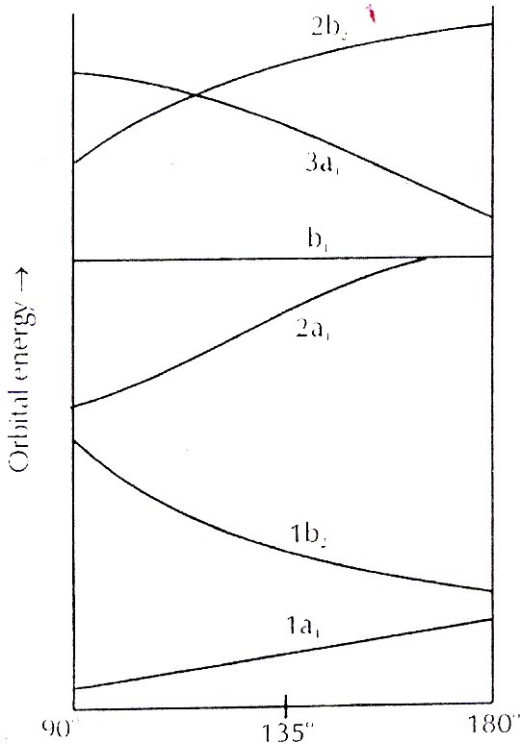


Fig. 1.7

The A atom of AB_2 molecule will be assumed to have only s, px, py and pz orbitals in its valence shell, whereas each of the B atoms is allowed only a single orbital oriented to form a σ bond to A. In the linear configuration $P^A{}_X$ and $P^A{}_Z$ are equivalent non-bonding orbitals labelled 2a, and b_1 respectively. The orbitals S^A and $P^A{}_Y$ interact with $\sigma_1{}^B$ and $\sigma_2{}^B$, σ orbitals on the B atoms, to form one very strongly bonding orbital, 1a, one less strongly bonding orbital, $1b_2$, one less strongly bonding $3a_1$ and $3b_2$. The ordering of these orbitals and in more detail, the approximate values of their energies can be estimated by an MO calculation. Similarly, for the bent molecule the MO energies may be estimated. Here only $p_z{}^A$ is non bonding, spacing and even the order of the other orbitals is function of the angle of bending θ. The complete pattern of orbital energies, over a range of θ, is obtained with typical input parameters. This is shown in the figure 1.8. Calculations in the Huckel approximation are simple to perform and give the correct general features of the diagram but for certain cases (e.g. AB_2E_2) very exact computations are needed for an unambiguous prediction of structure.



(Angle θ)

Figure 1.8 Orbital Correlation Diagram For AB_2 Triatomic Molecules Where A uses only s and p orbitals

Form the approximate diagram (Fig. 1.8) it is seen that an AB_2 molecule (one with no lone pairs) is more stable when linear then when bent. The $1b_2$ orbital drops steadily in energy form $\theta = 90^o$ to 180°; while the energy of the $1a_1$ orbitals is fairly insensitive to angle.

For an AB_2E molecule the results are ambiguous, because the trend in the energy of the $2a_1$ orbital approximately offsets that of the $1b_2$ orbiral.

For AB_2E_2 molecules, the result should be the same as for AB_2E. Since the energy of b_1 orbirtal is independent of the angle. Thus it is not clear in this approach that AB_2E_2 molecules should necessarily be bent, but all known ones are.

The H_2O Molecule:

Because of its unique importance, this molecule has been subjected to more detailed study than any other AB_2E_2 molecule. A correlation diagram calculated specially for H_2O is shown in the figure. Although it differs in detail for the general AB_2E_2 shown in the figure it is encouraging to see that the important qualitative features are the same. The general purpose diagram pertains to a situation in which there is only a small energy difference between the ns and np orbitals of the central atom. As stated in discussing that general purpose diagram, it is not clear whether an AB_2E_2 molecule ought necessarily to be bent.

In the diagram calculated expressly for H_2O the lowest level's is practically pure 2s and its energy is essentially constant for all angles. It can be determined from this diagram that the energy is minimized at an angle of 106°, essentially in accord with the experimental value of 104.5°. (Fig. 1.9).

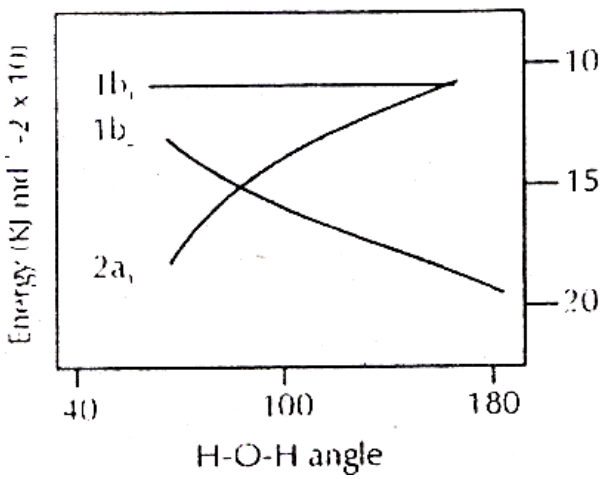


Fig. 1.9

BeH_2 - Molecule

The simplest AB_2 molecule in Period 2 is the transient gas-phase BeH_2 molecule (BeH_2 normally exists as a polymeric solid), in which there are four valence electrons. These four electrons occupy the lowest two molecular orbitals. If the lowest energy is achieved with the molecule angular, then that will be its shape. We can decide whether the molecule is likely to be angular by accommodating the electrons in the lowest two orbitals corresponding to an arbitrary bond angle in Fig. 1.7. We then note that the HOMO decreases in energy on going to the right of the diagram and that the lowest total energy is obtained when the molecules is linear. Hence, BeH_2 is predicted to be linear and to have configuration $1\sigma_g^2 2\sigma_u^2$. In CH_2, which has two more electrons than BEH_2, three of the molecular orbital must be occupied. In this case, the lowest energy is achieved if the molecule is angular and has configuration $1a_1^2 2a_1^2 1b_2^2$.

The principal feature that determines whether or not the molecule is angular is whether the $2a_1$ orbital is occupied. This is the orbital that has considerable A-2s character in the angular molecule but not in the linear molecule.

3.2. Application to Penta Atomic Molecules

For peta-atomic molecules examples of CH_4 and SF_4 may be taken for consideration. For these molecules, two geometries are possible: one a symmetrical tetrahedral and the other, a distorted tetrahedral geometry (or a tetragonal geometry of relatively lower symmetry).

CH_4 - Molecule

Methane, CH_4, has eight valence electrons. During bonding, for orbitals [a_1g (2s) and t_{1u} (2p)] of carbon, and one [a_{1g} (1s)] orbital of each

four hydrogen atoms take part. Overlapping of these eight orbitals, eight molecular orbitals are formed, the four bonding (2σg or $2a_1$ and 2tσ or $2t_1$) and the four antibonding (2σg* and 2t*σ). The eight valency electrons of CH_4 molecule are distributed in the four bonding molecular orbitals (Electronic Configuration, $2\alpha_1^2 2t_1^b$). In the tetrahedral geometry due to overlapping with the orbitals of hydrogen atom the energy of $2a_1g$ and $2t_{1u}$ orbitals is considerably reduced. In contrast, in the distorted geometry, comparatively less overlapping of t_{1u} orbitals with the hydrogen orbitals (as compared to that in the tetrahedral geometry) the energy of $2t_1$ molecular orbitals increases. Thus the geometry of CH_4 molecule is symmetrical tetrahedral, rather than a distorted tetrahedral.

SF_4 - Molecule

In the valence shall of sulphur atom, in SF_4 molecule, in addition to 3s (α_{1g}) and 3p (t_{1u}) orbitals, 3d (t_{2g} and eg) orbitals are also present. During the bonding, $2p_z$ orbital of each of the four fluoring atoms take part. As a result for bonding ($2a_1$ and $2t_1$) and four antibonding ($2\alpha_1^* 2t_1^*$) molecular orbitals formed; while the d-orbitals [$\alpha_1(dz^2)$, $b_1(dx^2 - y^2)$ and t_2 (d_{xy}, d_{xz}, d_{yz})] are present as non-bonding molecular orbitals. Ten valency electrons of SF_4 molecule remain distributed in the four bonding and one non-bonding molecular orbitals, resulting in $2\alpha_1^2, 2t_1^b. 3a_1^2$ configuration. As in the distorted geometry, overlapping of $2t_1$ orbitals is comparatively greater (thus reducing their energy) and the filling in $3\alpha_1$ orbital considerably reduce the energy of the system as compared to that in the regular tetrahedral structure. Hence SF_4 molecule has a distorted tetrahedral geometry, rather than a regular tetrahedral structure.

Thus we can say 'Walsh Diagrams' are complementary to the VSEPR concept.

Check Your Progress 2

Notes:1. Write your answers in the space given below.

2. Compare your answers with those given at the end of this unit.

(a). Predict the shape of an H_2O molecule on the basis of a Walsh Diagram for an AB_2 molecule.

(b) Is any AB_2 molecule, in which A denotes an atom of a period 3 element, expected to be linear? If so, which

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4. dπ - pπ BONDS.

There are several structural phenomena that have traditionally been attributed to the formation of dπ - pπ Bonds. Recent work has raised some doubts. The phenomena in questions are exemplified by:

1. The fact that for amines such as $(R_3Si)_2$ NCH_3, $(R_3Si)_3$ N and $(H_3Ge)_3$ N, the central NSi_2C, NSi_3 and NGe_3 skeletons are planar.

2. Many tetrahedral species such as SiO_4^{-4}, PO_4^{-3}, SO_4^{-2} and ClO^-_4 have bond lengths shorter than those predicted from conventional tables of single bond radii. In silicates the Si-O-Si units also show what were considered to be Si-O distance that are "too short" for single bonds.

Recent re-examinations of these phenomena by both theoretical and experimental methods together with earlier arguments now suggest that the dπ - pπ contributions to these effects are at best small. Thus, in reading literature written prior to 1985, where such interactions are often accorded great importance, one should now be sceptical of all but the facts themselves.

This is not to say that dπ - pπ bonding in main group compounds is never important. Probably in the case of - S - N = S units, and in $F_3F \equiv N$, where the S - N distances are very short indeed. However, it is always dangerous to attribute all structural effects to simple orbital overlaps, even if the explanation seems to fit, and the rise and fall of the dπ - pπ overlap hypothesis is a case in point.

In a multiple bonded molecule having bond pairs + lone pairs = 4, 5 or 6, the π bonds will be pπ - dπ bond. In this case the central atom uses all its p-orbitals for hybridisations and has only d-orbitals available to overlap with p-orbitals of the adjacent atom to give dπ- pπ bond.

The formation of dπ - pπ bond is common for all the second period elements and is not important for the elements of third and higher periods. The pπ-dπ bonding is more favourable than the dπ - pπ bonding for higher atoms of third and higher periods.

4.1. dπ - pπ Bonding in Phosphorous Group Elements

Phosphine Oxide, $R_3P = 0$, presents an important example of the participation of d-atomic orbitals of nonmetallic elements in π bonding. Presence of π bonding is defected with the help of the evidences, such as reduction in the bond length, increase in the bond strength and the stabilisation of charge distribution. On these grounds, compared to

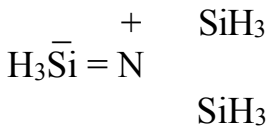
ammine oxide, phosphine oxide presents a strong evidence of the presence of dπ - pπ bond, in a very high stability of P = O.

Similarly the fact that almost all t-phosphines are readily oxidised into $R_3P = 0$, also indicates that dπ- pπ bond is present in the P = O bonding. This is supported by the lower dipole moment of triethyl phosphine oxide (1.4×10^{-3} Cm. cf 16.7×10^{-3} Cm. of trimethyl amine oxide), higher dissociation energy of P = O bond (500-600 KJ, cf 200-300 KJ of N"O bond) and the smaller P-O bond lengths in phosphoryl compounds.

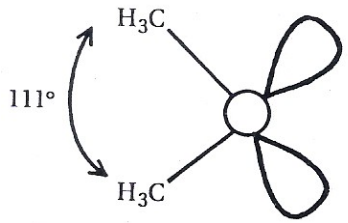
4.2. dπ-pπ Bonding in Nitrogen, Oxygen and Sulphur Compounds

There are number of examples, which show dπ- pπ bonding in nitrogen, oxygen and sulphur compounds:

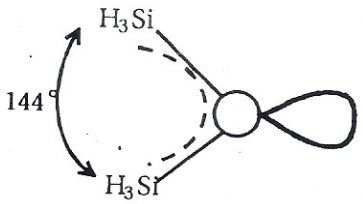
(i) Mobile π bonding in trisilyl amine results in the resonance in the molecule :



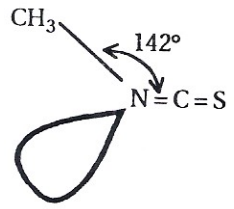
(ii) The bond angles in disiloxane, $H_3SiOSiH_3$, and silyl isothiocyanate, H_3Si-N=C=S indicates pπ - dπ back-bonding (in comparison to ether and methyl isothiocyanate) :



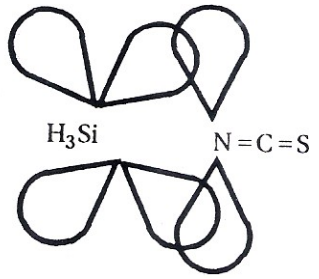
Dimethyl ether
(Sp^3-hybridised. 0 + 2 lp)
Addition compound with BF_3



Disiloxane
(Sp^3-hybridised. 0 + 1 lp)
No addition compound withBF_3



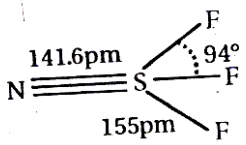
Methyl isothicyanate
(one lp on N; Angular)



Silyl isothiocynate
lp used in π bonding, Linear

The argument given against the use of d atomic orbitals in bonding by non-metallic elements is that a very high excitation energy is required for the same. Hence it may be concluded that the use of d-atomic orbitals in bonding by non-metallic elements will be possible only in their higher oxidation states and when they are linked with strong electronegative elements, eg. PF_5,SF_6,OPX_3 etc.:

(i) The N - S bond length in $N \equiv SF_3$ indicates. The bond order = 2.7 indicating dπ - pπ bonding:

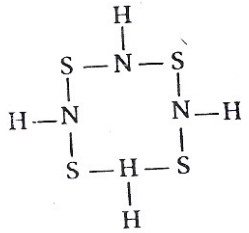


Thiazytrifluoride

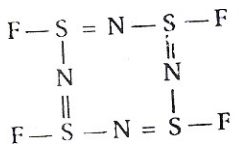
N - S bond length = 141.6 pm; Bond order = 2.7

(cf N - S = 174 pm, b.0 = 1, N = S = 154 pm; b.0 = 2)

(ii) In S4N4F4 also there is indication of dπ - pπ bonding (compare with S4H4N4):

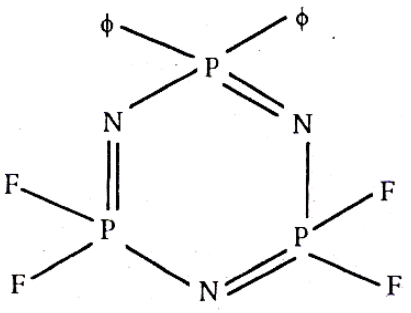


Tetra Sulphur tetramide
(Isoelectronic and
Isomorphous with S_8



Tetra sulphur tetramide fluoride
(Alternate S = N bond)

(ii) In diphenyl phosphonitrilic fluoride, there is evidence of π bonding in the ring:



Check Your Progress-3

Notes: 1. Write your answers in the space given below.

2. Compare your answers with those given at the end of this unit.

(a). In which of the following molecule there is a possibility of dπ-pπ bonding?

$S_4N_4F_4$, $S_4H_4N_4$, N ≅ SF_3, $H_3SiOSiH_3$, $CH_3N = C=S$ and Et_3NO.

Ans: (i) _____ (ii)_____

(iii) _____

(b) Which are the evidences in favour of dπ-pπ bonding in R_3PO molecule?

Ans: (i) _____

(ii) _____

(iii) _____