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

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[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).
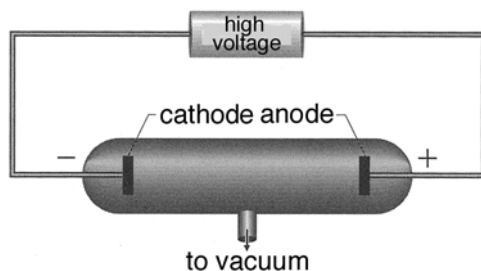

Fig. 2.1 Discovery of the cathode ray
The cathode ray generated in a vacuum tube when a high vacuum
was applied provided very significant information on the structure of the atom.

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/(1.76×10^8 C g^{-1}) = 1.6×10^{-19} C/(1.76×10^8 C g^{-1}) = 9.1×10^{-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 x 10^{23} = 1.67 x 10^{-24}g.   Hence, $m_e : m_H$ = 9.1 x 10^{-28}g : 1.67 x10^{-24}g = 1 : 1.83 x 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 x 10^{23} = 3 x 10^{-23} cm^3 = 30 x 10^{-24} cm. The length of an edge is $\sqrt[3]{30}$ x 10^{-8} cm = 3.1 x 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.
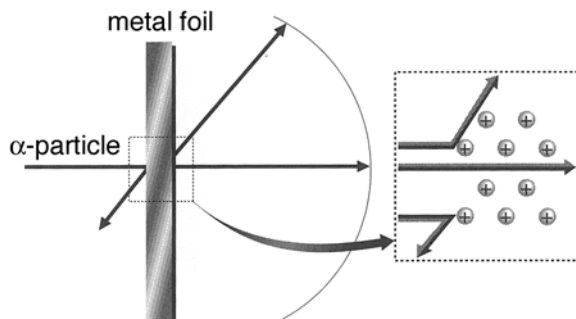

Fig. 2.2 Scattering experiment of α particles by Rutherford

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).

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

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

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[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.

$$\varepsilon = nh\nu \ (n = 1, 2, 3, ...) \tag{2.2}$$

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.,

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

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,

$$e^2/4\pi\varepsilon_0 r^2 = mv^2/r \tag{2.4}$$

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.

$$e^2/4\pi\varepsilon_0 r^2 = mn^2h^2/4\pi^2m^2r^3$$
$$\therefore\ r = n^2\varepsilon_0h^2/(2\pi)^2me^2,\ n = 1, 2, 3,... \tag{2.5}$$

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.

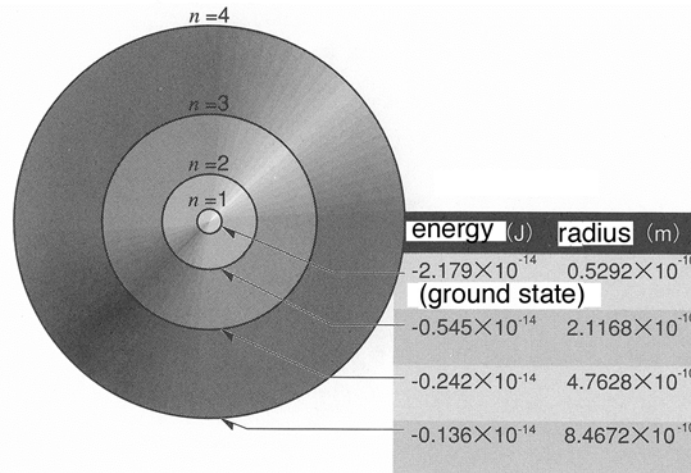$$r = n^2a_B,\quad n = 1, 2, 3,... \tag{2.6}$$

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, 5.2918×10^{-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,

$$E = mv^2/2 - e^2/4\pi\varepsilon_0 r \tag{2.7}$$

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.

$$E = -me^4/8\varepsilon_0^2n^2h^2,\quad n = 1, 2, 3... \tag{2.8}$$

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,

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

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.
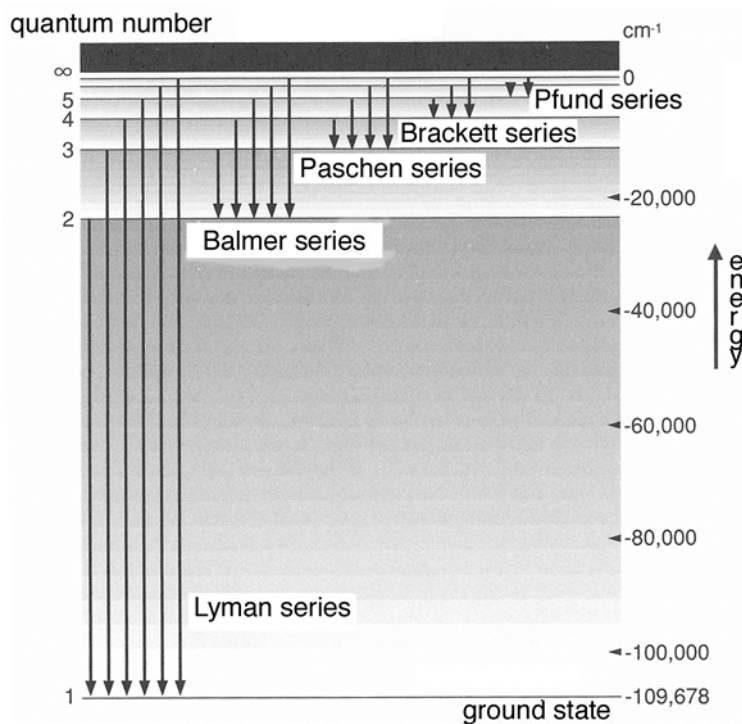

Figure 2.4 The atomic spectra of hydrogen.
The Bohr theory can explain the origin of all transitions.

(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**).

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

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 0.14299×10^{-9} m. The wavelength of the same series of the characteristic X-ray of a known element Ir ($Z = 77$) is 0.13485×10^{-9} m. Assuming s $= 7.4$, estimate the atomic number of the unknown element.
Solution
First, estimate $\sqrt{c}$ from Eq. (2.1).

$$\sqrt{\frac{1}{0.13485 \times 10^{-9}(m)}} = \sqrt{c}(77 - 7.4) = 69.6\sqrt{c}$$

$$\therefore \ \sqrt{c} = 1237.27$$

Then,

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

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:

$$E = h\nu$$
$$\nu = c/\lambda ; \ hc/\lambda = E$$
$$\therefore \ h/\lambda = p \tag{2.12}$$

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

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.

$$\Delta x \Delta p = h \tag{2.13}$$

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).
$$\Delta p \fallingdotseq h/\Delta x = 6.626 \times 10^{-34}\,(\text{J s})/5 \times 10^{-12}\,(\text{m}) = 1.33 \times 10^{-22}\,(\text{J s m}^{-1})$$
Since the mass of an electron is 9.1065×10^{-31} kg, the uncertainty of the velocity Δv can be

estimated as follows.[a]

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

The estimated uncertainty of velocity amounts to nearly half of the velocity of light (2.998×10^8 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:

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

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:

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

$$\Psi = 0 \text{ at } x = 0 \text{ and } x = a \tag{2.16}$$

The following equation is obtained by solving the above equations.

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

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.*,

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

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[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

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

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	$m(m_l)$	$0, \pm 1, \pm 2,... \pm l$
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**.
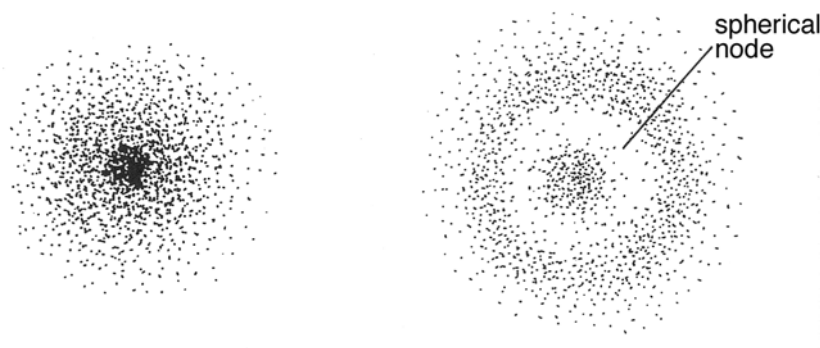

Figure 2.5 Electron cloud.
The probability of finding an electron will become smaller as the distance
from the nucleus is larger. (a) 1s orbital of hydrogen. (b) 2s orbital of hydrogen.

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

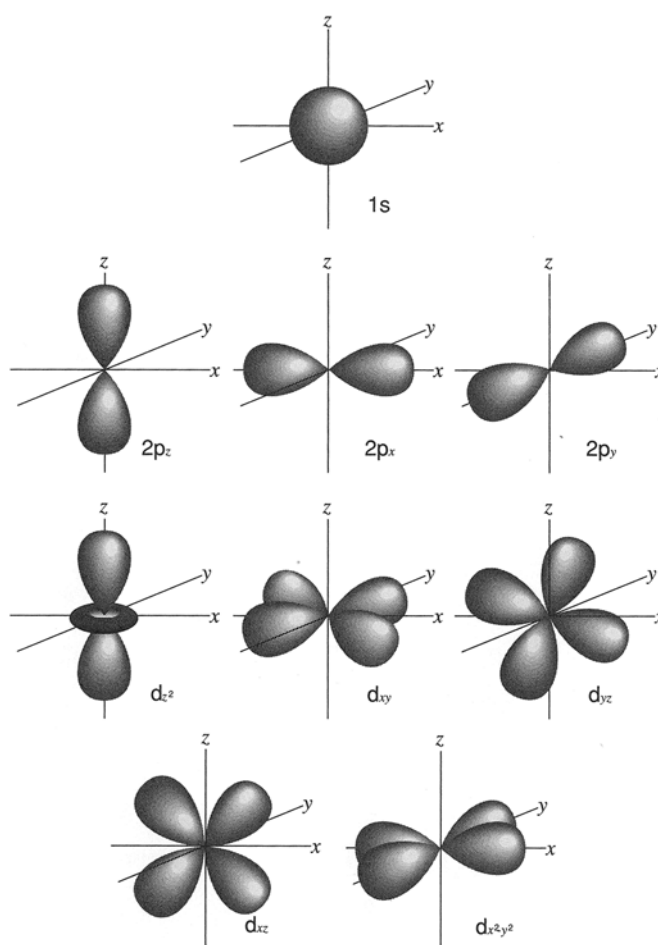the boundary is, say, 95% confidence level, we can approximately visualize orbitals as shown in Figure 2.6.

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	$(2 = 2 \times 1^2)$
2	L	0	2s	2	$(8 = 2 \times 2^2)$
		1	2p	6	
3	M	0	3s	2	
		1	3p	6	$(18 = 2 \times 3^2)$
		2	3d	10	
4	N	0	4s	2	
		1	4p	6	$(32 = 2 \times 4^2)$
		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 $(1s^2 2s^2 2p^2)$.
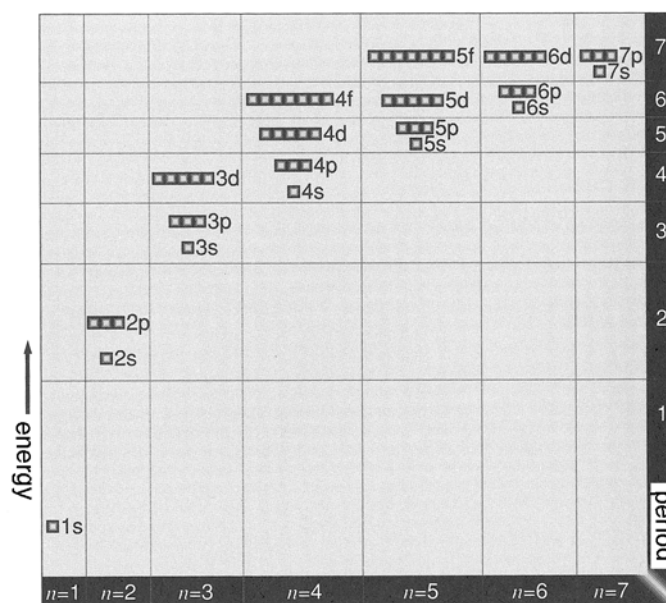
Figure 2.7 Energy level of electrons

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 $-2.718 \times 10^{-18}/n^2$ (J)

2.1 Answer

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

$$\Lambda E = -2.178 \times 10^{-18} \left[\frac{1}{3^2} - \frac{1}{1^2} \right] = +1.94 \times 10^{-18} \text{ (J)}$$

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.

$$\lambda = \frac{6.626 \times 10^{-34} (\text{Js}) \times 2.9979 \times 10^8 (\text{ms}^{-1})}{1.94 \times 10^{-18} (\text{J})} = 1.02 \times 10^{-7} (\text{m}) = 102 (\text{nm})$$

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

$$\Delta E = E_\infty - E_2 = |E_2| = \left| \frac{1}{4} E_1 \right| = 5.45 \times 10^{-19} \text{ (J)}$$

2.3 De Broglie's equation

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

2.3 Answer

$$\lambda = \frac{h}{mv} = \frac{6.626 \times 10^{-34} (\text{Js})}{9.11 \times 10^{-34} (\text{kg}) \times 5.31 \times 10^6 \text{m s}^{-1}} = \frac{6.626 \times 10^{-34} (\text{kg m}^2 \text{ s}^{-2} \text{ s})}{9.11 \times 10^{-34} (\text{kg}) \times 5.31 \times 10^6 \text{m s}^{-1}}$$
$$= 1.37 \times 10^{-10} (\text{m}) = 0.137 (\text{nm})$$

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

$$E = \frac{n^2 h^2}{8 m_e a^2} = n^2 \frac{(6.626 \times 10^{34})^2 (\text{Js})^2}{8(9.110 \times 10^{-31} (\text{kg})(0.3 \times 10^{-9})^2 (\text{m}^2)} = n^2 (6.69 \times 10^{-19})(\text{J})$$

The frequency and the wavelength of electron is:

$$\nu = \frac{\Delta E}{h} = \frac{(4-1)(6.69 \times 10^{-19})(\text{J})}{6.626 \times 10^{-34} (\text{Js})} = 3.03 \times 10^{15} \text{s}^{-1}$$

$$\lambda = \frac{c}{\nu} = \frac{3.00 \times 10^8 \text{ m s}^{-1}}{3.03 \times 10^{-15} \text{ s}^{-1}} = 99 \times 10^{-9} \text{m} = 99 \text{nm}$$

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