CHAPTER 1

Introduction and History of the Molecular Orbital Theory

INTRODUCTION

Chemistry is the science that studies the composition, structure and transformations of matter. As soon as it was established that virtually all the matter that surrounds us and builds us up is the result of combinations of atoms forming molecules, it became necessary to understand how the bonds between these atoms are formed and broken. To do this, it became essential to understand the models that describe the arrangement of electrons in atoms and molecules (chemical bonding theories).

A fundamental breakthrough was made in the early twentieth century by G.N. Lewis, who observed the special stability of inert gases. He proposed that the constituent atoms of molecules tend to present the same electronic configuration of such inert gases, which is eight electrons in their valence shell (Figure 1.1). Indeed, Lewis' bonding theory was the only general description of bond formation in chemical compounds until the mid-1920s. Lewis' bonding theory made it possible to interpret and predict important properties of molecules in a simple manner. In fact, this model still provides a good qualitative description of the nature of bonds in organic compounds and is therefore still in use.

However, Lewis' bonding theory has serious limitations and, for example, cannot accurately describe or predict the geometry and reactivity of certain types of compounds. Some of these limitations were alleviated by extending Lewis' theory to include resonance theory. However, this model was still an intuitive and imprecise approximation. Quantum mechanics, a new branch of physics that revolutionised science by allowing a better understanding of various physical, chemical and biological processes, was developed in the 1920s and 1930s. The application of quantum mechanics to distinct issues in chemistry has been in the form of valence bond theory and molecular orbital (MO) theory. The basic idea of valence bond theory is that covalent bonds can be formed by the

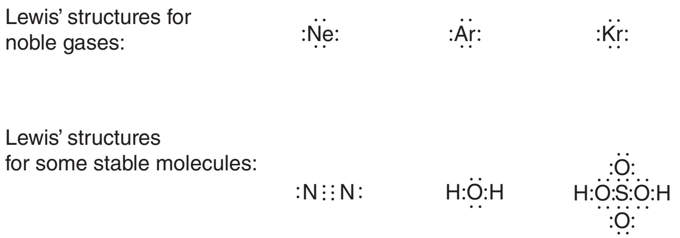


FIGURE 1.1 Some examples of Lewis' molecular structures.

overlapping of localised half-occupied atomic orbitals. This model provides a simple rationalisation of some molecular aspects, such as the geometries of molecules. However, valence bond theory cannot explain other important aspects of bonding and reactivity, such as those originating from the excited states of molecules. In other words, not all chemical bonding phenomena and not all molecular properties can be satisfactorily explained by localised bonding models.

Some properties of chemical bonds are best explained by a more complex quantum model, MO theory. The MO theory allows description of the electronic arrangement of molecules in terms of MOs, whose role is analogous to that of atomic orbitals in atoms. The fundamental characteristic of MOs is that they are distributed over all the atoms in a molecule; that is, the MOs comprise the whole molecule, rather than being associated with just one atom or being localised in a particular region between a pair of atoms.

In order to explain MO theory (and valence bond theory, discussed later in Chapters 3 and 4), it is necessary to understand the basic concepts of quantum mechanics. These concepts and their historical development are discussed in this chapter. In particular, the study of light absorbed or emitted by chemical species, such as atoms and molecules, has provided much of the basic knowledge of quantum mechanics. Therefore, we will begin by studying the properties of light. We will then go on to analyse concepts such as quantised energy, wave-particle duality, the uncertainty principle and others.

NATURE OF ELECTROMAGNETIC RADIATION

As mentioned earlier, different approaches to understanding the nature of electromagnetic radiation and its interaction with matter led to the development of quantum mechanics. To understand current atomic theory, it is necessary to comprehend the properties of electromagnetic radiation. Visible light, X-rays, radio waves and microwaves are some of the types of electromagnetic radiation. They all consist of energy propagated by electric and magnetic fields that increase and decrease in intensity as they move through space. The nature of light was debated as early as the seventeenth century. For the Dutch astronomer and physicist Christiaan Huygens (1678), light had to be a wave, such as the waves in water. By contrast, Englishman Isaac Newton (1704) suggested that light had to consist of small luminous 'corpuscles' (particles) travelling in a straight line at a finite speed and with an associated momentum. Scientific debate on this subject continued for many years later and culminated in the realisation of the dual behaviour of electromagnetic radiation. Before entering a more detailed discussion, let us first describe the properties of electromagnetic radiation in its wave-like behaviour.

THE WAVE NATURE OF LIGHT

Light is a form of electromagnetic radiation, consisting of electric and magnetic fields oscillating as a wave and travelling through empty space at about 3×10^8 m s^{-1} (Figure 1.2). The wave properties of electromagnetic radiation are described by three variables and a constant.

Frequency (ν, Greek nu). The frequency of electromagnetic radiation, expressed in the unit 1/second (s^{-1}; also called Hertz [Hz]), is the number of complete waves or cycles passing through a given point per second. For example, a 960 kHz AM radio station transmits waves with a frequency of 960 000 cycles per second.

Wavelength (λ, Greek lambda). The wavelength is the distance between any one point of a wave and the corresponding point of the next oscillation (Figure 1.3). For example, the distance from one peak to another, or valley-to-valley. In other words, it is the distance the wave travels in one cycle.

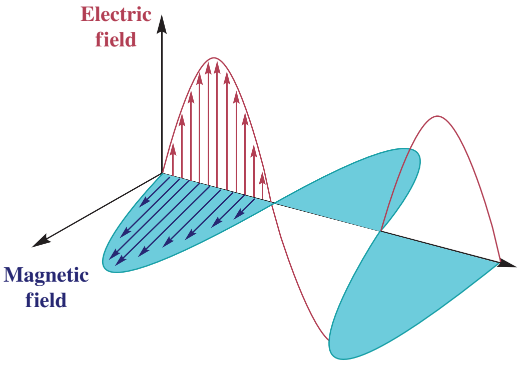


FIGURE 1.2 Light as both electric and magnetic fields.

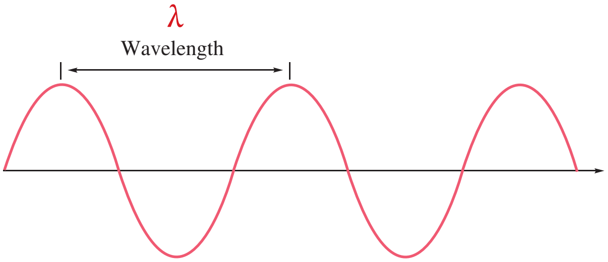


FIGURE 1.3 Wavelength concept.

The wavelength can have units of length as large as metres or, for very short wavelengths, nanometres (nm, 10^{-9} m) or picometres (pm, 10^{-12} m). An alternative unit is angstroms (Å, 10^{-10} m).

Velocity (u). The speed of a wave is the distance travelled per unit of time, which is the product of its frequency in cycles second^{-1} and its wavelength in meters cycle^{-1}:

$$u = \frac{\cancel{\text{cycles}}}{\text{s}} \times \frac{m}{\cancel{\text{cycles}}} = \frac{m}{\text{s}} \tag{1.1}$$

In vacuum, the speed of electromagnetic radiation is 2.99792458×10^8 m s^{-1}, which can be rounded to 3.0×10^8 m s^{-1} with three significant figures (i.e. 300 000 km s^{-1}). This is a physical constant called the speed of light (c) expressed in the formula

$$c = \nu \times \lambda \tag{1.2}$$

Since the product of ν and λ is a constant, ν and λ have an inverse relationship. Take the waves shown in Figure 1.4, which travel at the speed of light (c). If the wavelength of the light is very short, a large number of complete oscillations will pass through a given point in one second. If, on the other hand, the wavelength is long, a smaller number of complete oscillations will pass through the point in one second. Therefore, a short wavelength corresponds to high-frequency (high energy) radiation and a long wavelength corresponds to low-frequency (low energy) radiation.

The amplitude is the wave height above the centreline (Figure 1.5). For an electromagnetic wave, amplitude is related to radiation intensity, or brightness in the case of visible light. Light of a given colour presents a specific frequency (and therefore wavelength), but its amplitude can vary. The light can be softer (lower amplitude, less intense) or brighter (higher amplitude, more intense).

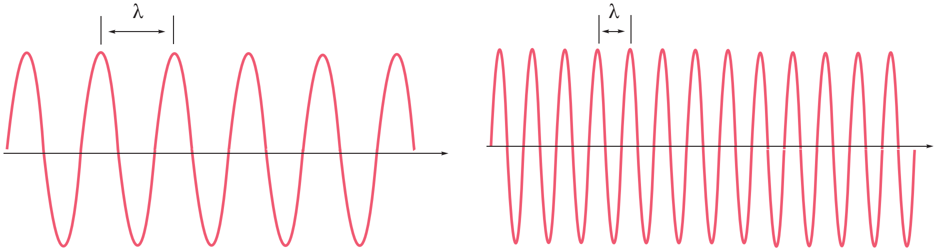


FIGURE 1.4 The relationship between frequency (ν) and wavelength (λ): Longer λ corresponds to a reduced frequency (lower energy, left side) and smaller λ corresponds to an increased frequency (higher energy, right side).

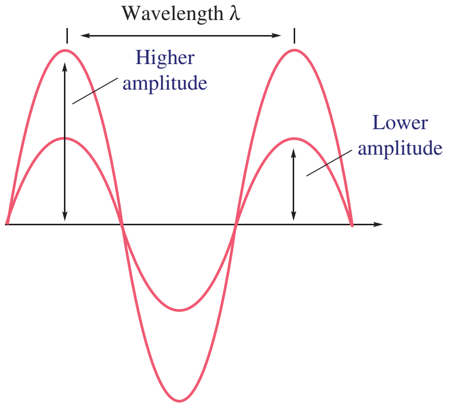


FIGURE 1.5 The concept of amplitude of a wave.

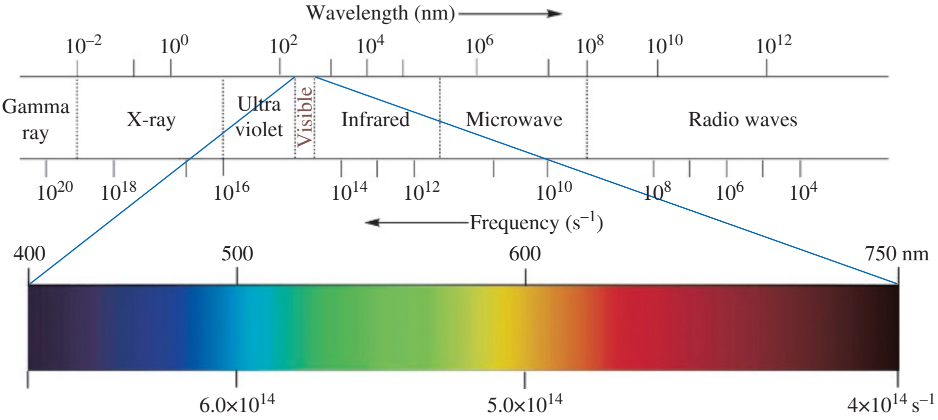


FIGURE 1.6 The electromagnetic spectrum.

ELECTROMAGNETIC SPECTRUM

In a vacuum, all electromagnetic waves travel at the same speed and differ in frequency and therefore wavelength. The electromagnetic spectrum (Figure 1.6) is the classification of electromagnetic waves by frequency or wavelength. The types of radiation vary in the order of increasing wavelength (decrease in frequency). Visible light represents only a tiny region of the spectrum, between about 750 and 400 nm, corresponding to red and violet light, respectively. This represents less than one-millionth of one percent of the measured electromagnetic spectrum. At frequencies lower than red, we have infrared radiation, microwaves and radio waves (in the kilohertz and megahertz range). At frequencies above violet, we have ultraviolet radiation (these higher frequency waves cause sunburn), X-rays and finally gamma rays. These present frequencies above 10 exahertz (10^{19} Hz).

THE DISTINCTION BETWEEN ENERGY AND MATTER

Understanding the difference between the properties of energy waves and particles (matter) is essential to grasping the dual behaviour of light. In a world where we are used to observing objects moving, it is more complex to understand the nature of radiant energy, which does not contain matter and travels in diffuse waves. The differences between the behaviour of particles and that of energy waves will be the subject of discussion in the following.

Light travels at different speeds in different transparent media. We know that it travels at 300 000 km s^{-1} in a vacuum, slightly slower in air (299 708 km s^{-1}) and about three-quarters of that speed in water. When a light wave changes direction and speed as it passes obliquely from one medium to another, it undergoes a phenomenon known as refraction. A schematic representation of refraction is shown in Figure 1.7. The angle of refraction depends on the two media and the wavelength of the light. Light of different frequencies (such as white light) travels at different speeds in transparent materials and is refracted to different degrees. The separation of white into frequency-ordered colours is called dispersion and is a phenomenon observed in rainbows and diamonds (refracting objects). On the other hand, none of these phenomena is observed in the case of particles. If, for example, a stone is thrown through the air and falls into a body of water, its speed will simply decrease gradually as it follows a curved path.

Another difference between energy waves and particles is that the former are subject to the process of diffraction. If two slits are opened in a solid plate and a screen is placed behind them, and we throw particles against the plate (for example, a jet of sand), some particles will pass through one of the slits and others will pass through the other, thus forming two piles, one in front of each slit. In the case of energetic waves, the situation is completely different.

When a wave (of any kind) hits the edge of an object, it bends in a phenomenon called diffraction (Figure 1.8). If the wave passes through a slit that is wide compared to its wavelength, the waves continue through the slit, bending only at the corners. If the wave passes through a slit that is similar in

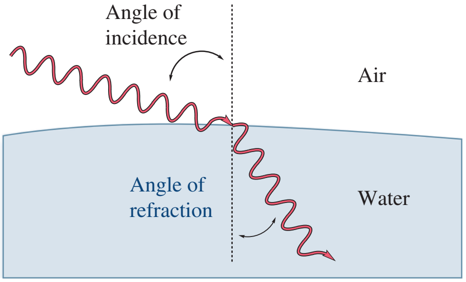


FIGURE 1.7 Representation of the refraction phenomenon.

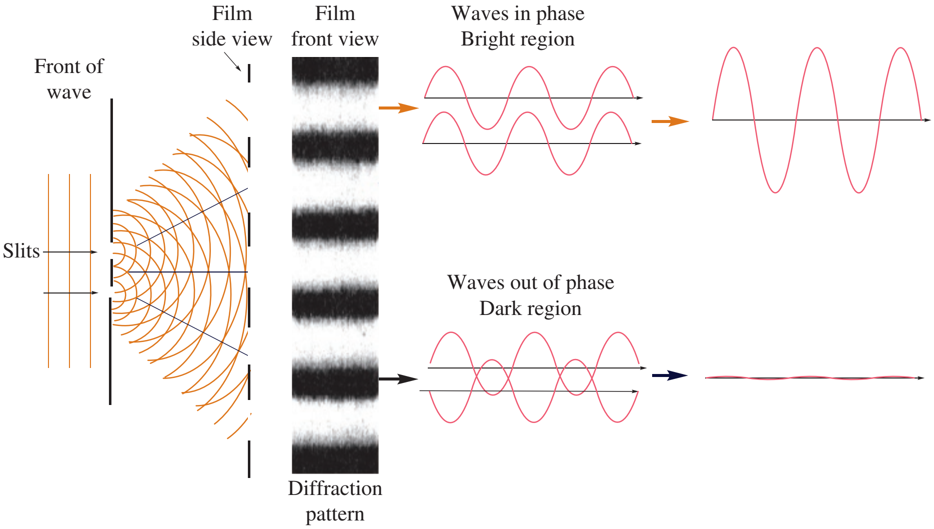


FIGURE 1.8 Constructive and destructive interference of waves.

width to its wavelength, it will bend completely around both edges of the slit, forming a semi-circular wave on the other side of the slit. Now suppose a wave hits the plate with two slits. As it arrives, the wave splits into two, each wave exiting through one of the slits. Nearby circular waves interact by the process of interference.

Figure 1.8 shows constructive and destructive interference. We can see that the superposition in phase of a pair of identical waves produces a wave of the same frequency but twice the amplitude, the bright spots in the diffraction pattern. When the waves are exactly out of phase, that is, when a peak coincides with a trough, their superposition cancels out completely. This cancellation produces the dark areas of the pattern. If they are out of phase by other amounts, partial cancellation occurs.

THE PARTICLE NATURE OF LIGHT

Towards the end of the nineteenth century, scientists were puzzled as they gathered more and more data on electromagnetic radiation that could not be explained by classical mechanics. The observation of diverse phenomena such as blackbody radiation and the photoelectric effect led to a radically new view of energy.

Every object emits electromagnetic radiation, and the hotter it is, the more intense and higher the frequency of the radiation. For example, at high temperatures, an iron bar begins to glow, emitting red light, and as it heats up further, the emitted light becomes brighter and whiter (this phenomenon is called incandescence). These changes in the intensity and wavelength of the light emitted as an object heats up are characteristic of the radiation emitted by a hot black body. A black body is an idealised object that absorbs all incident radiation, and its light emission depends only on the temperature of the object. The black body does not favour the absorption or emission of radiation of any particular wavelength. We could imagine a tightly closed oven that absorbs all the light that reaches it and emits nothing to the outside. Inside the oven, the walls are at a uniform temperature and are constantly emitting and absorbing light, which bounces off each other. In practice, it is possible to make a small hole that allows some of the light to escape from the inside; it is no longer a perfect black body, but if the hole is small enough, the disturbance is minimal. The light emitted by a black body can then be studied by passing it through filters of different frequencies, and the intensity of the filtered light can be measured. Figure 1.9 shows a plot of the intensity of the radiation emitted (spectral radiance) by a heated black body as a function of wavelength and at various temperatures. Experimentally (solid lines in Figure 1.9), as the temperature increases (for example, from 3000 to 5000 K), the peak of the emitted radiation appears at shorter wavelengths. This observation could not be explained by classical physics since the emitted radiation was predicted to increase indefinitely at higher frequencies into the ultraviolet range (dashed line in Figure 1.9). This hypothetical phenomenon is known as 'ultraviolet catastrophe'.

In 1900, the German physicist Max Planck developed a formula that fitted the results obtained from the black body emission. He proposed that the exchange of energy between matter and radiation occurs in quanta, or packets,

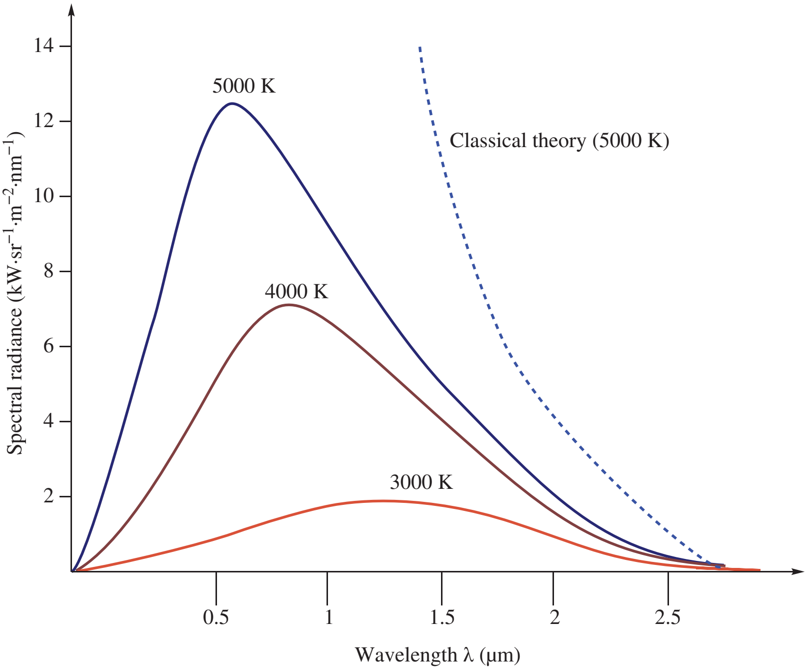


FIGURE 1.9 Spectral radiance emitted by a heated black body.

of energy. The central idea was that within matter there are microscopic oscillators (atoms, molecules) vibrating at certain frequencies that absorb and emit energy in the form of electromagnetic waves. Each oscillator can only absorb or emit energy that is an integer multiple of its fundamental energy, which is directly proportional to its frequency of vibration:

$$E = h\nu \tag{1.3}$$

where h is Planck's constant and has a value of $6.626 \times 10^{34}\ \mathrm{J \cdot s}$. If the oscillating atom releases an energy packet of magnitude E into the surroundings, then radiation of frequency $\nu = E/h$ will be detected. From Eq. (1.2) $c = \nu \times \lambda$ therefore,

$$\frac{c}{\lambda} = \nu \tag{1.4}$$

and substituting c/λ for frequency, ν, in Eq. (1.3), we find the relationships which indicate that energy is directly proportional to frequency and inversely proportional to wavelength.

$$E = h\nu = \frac{hc}{\lambda} \tag{1.5}$$

The Planck hypothesis states that radiation of a given frequency is produced only when an oscillator has acquired the minimum energy necessary to start oscillating at that frequency and then emits it as a packet of electromagnetic radiation of energy $h\nu$. At low temperatures, there is not enough energy to drive oscillations at very high frequencies as ultraviolet radiation. In contrast, classical physics assumed that an oscillator could oscillate at any energy, and therefore even at low temperatures, high-frequency oscillators could contribute to the emitted radiation causing the 'ultraviolet catastrophe'.

However, Planck was convinced that his premise of 'energy packets' was just a mathematical trick to arrive at the corrected result. A trick that worked for a while but had to be replaced by a more rigorous postulate. The postulate that consolidated Planck's theory came from the explanation of the photoelectric effect. The photoelectric effect is the phenomenon that occurs when monochromatic light of sufficient frequency strikes a metal plate and promotes the flow of an electric current, i.e. electrons are released and set in motion in the metal.

The experimental observations of the photoelectric effect were as follows: the current is generated only if the incident light has a frequency above a certain threshold, which depends on the metal; otherwise, the effect does not take place, no matter how intense the light. Another observation was that electrons were ejected immediately, regardless of how low the intensity of the radiation was. However, wave theory predicted that with low-intensity light there would be a time lag before the current flowed because the electrons had to absorb enough energy prior to their release (Figure 1.10).

Albert Einstein (1905) found an explanation for these observations that profoundly changed our understanding of the electromagnetic field. He proposed that electromagnetic radiation is made up of particles, later called photons. In this theory, light is also quantised, and each photon is a packet of energy related to the frequency of the radiation by the equation $E = h\nu$ (Eq. 1.3). For example, a beam of red light can be thought of as a group of photons of equal energy, while a beam of blue light can be thought of as a group of photons of equal energy but higher than that of red light. It is important to note that the intensity of the radiation is an indication of the number of photons present, whereas $E = h\nu$ is a measure of the energy of each individual photon.

Observations of the photoelectric effect have been explained as follows. If the incident radiation is of frequency ν, it consists of photons of energy $h\nu$. When the photons collide with the electrons of the metal, they absorb part of their energy. The energy required to extract an electron from a metal is called the work function of the metal and is denoted ϕ (phi, Figure 1.10). If the energy of an incident photon is less than the energy required to extract an electron from the metal, then no electron will be ejected no matter how many energy packets the metal receives (Figure 1.10a). On the other hand, if the photon energy is greater than ϕ, the electrons are immediately released from the metal (Figure 1.10b). An electron cannot be released by accumulating energy from several photons of lower energy than required and then expelled with a time delay. A photon of sufficient energy will rapidly eject an electron. Nevertheless, the electric current can be weak under radiation with light of sufficient energy but low intensity. This is because fewer photons

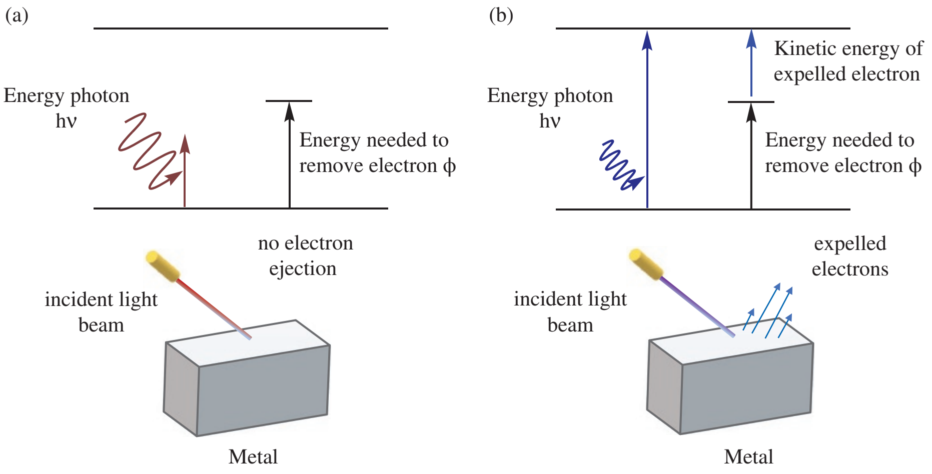


FIGURE 1.10 The photoelectric effect.

release fewer electrons per unit of time, although the current (electron flow) is still generated.

Planck's hypothesis of the quantisation of electromagnetic radiation and Einstein's proposal that light waves also exhibit particle-like behaviour led to the development of quantum mechanics.

MASS AND MOMENTUM ASSOCIATED WITH A LIGHT QUANTUM

Until 1900, the principles of classical mechanics dictated the analysis of the motion of bodies and its consequences. Everything from the interaction of two grains of sand to the orbits of the planets was studied according to the rules derived from classical mechanics. In contrast, electrical and magnetic phenomena, such as light, belonged to a separate field governed by ideas derived from electromagnetic theory. This separation between mechanical and electromagnetic phenomena came to an end when, in 1905, A. Einstein developed his equation,

$$E = mc^2 \tag{1.6}$$

Equation (1.6) implies, of course, that mass and energy are just different manifestations of the same thing. That is, every transfer of energy is accompanied by matter, and every mass (at rest or in motion) represents energy. As discussed earlier, the energy of these 'packets' is related to frequency (ν) or wavelength (λ) by Eqs. (1.3) and (1.5), $E = h\nu$ and $E = hc/\lambda$, respectively. Both equations indicate that Planck's constant h limits the size of light quanta in the same way that Avogadro's number limits the size of atoms. For instance, it can be verified that one mole of water can be heated from 0° to 100 °C with 2/3 moles of quanta of infrared light with $\nu = 3 \times 10^3$ cycles s^{-1}. That is, the quanta are small.

In this context, the photon possesses what is known in physics as a quantity of motion or momentum. In classical physics, the momentum of a body is a very important concept and is defined as the product of its mass times its velocity

$$p = mu \tag{1.7}$$

If it is true that, according to Einstein's equation, light has the properties typically ascribed to matter, then, from the combination of Eqs. (1.6) and (1.5), we obtain that

$$m = \frac{h\nu}{c^2} \tag{1.8}$$

and as the momentum is $p = mc$ (Eq. 1.7, considering velocity u as the velocity of light c), then

$$p = \frac{h\nu}{c} = \frac{h}{\lambda} \tag{1.9}$$

An experimental verification of this reasoning was achieved by observing that X-ray (light) radiation behaves physically as expected for particles with mass. Let us first consider the behaviour of two billiard balls colliding with each other. As shown in Figure 1.11, the moving red ball

$$p_1 = m_1 u_1 \tag{1.10}$$

hits the stationary black ball and sets it in motion

$$p_2 = m_2 u_2 \tag{1.11}$$

When the ball m_1 collides with m_2 through a point that is not its centre, the direction they take in their subsequent displacement is expressed by angles θ and ϕ, relative to the collinear axis of approach (Figure 1.11). These trajectories possess, of course, projections on the y-axis, perpendicular to the axis of contact; vectorially, the motions in these projections on the y-axis are

$$p_1^y = m_1 u_1' sin\phi \tag{1.12}$$

$$p_2^y = m_2 u_2 sin\theta \tag{1.13}$$

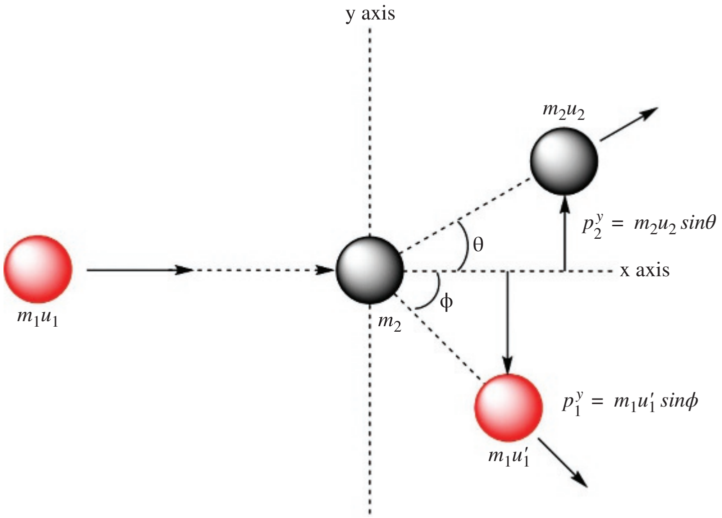


FIGURE 1.11 Collision of two billiard balls or two particles.

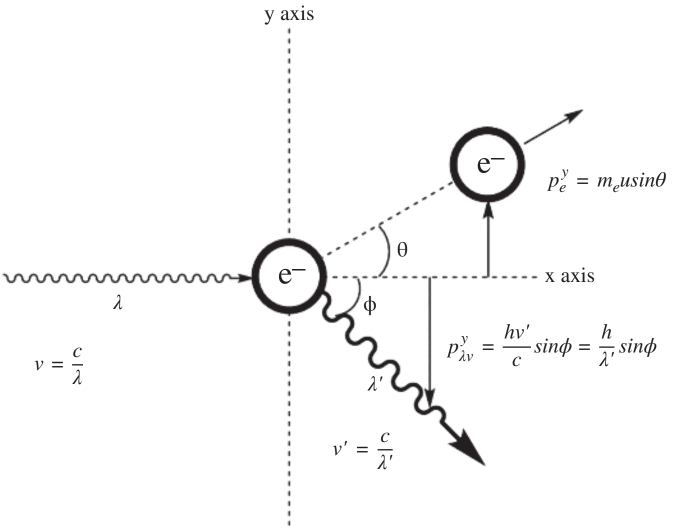


FIGURE 1.12 The Compton effect.

$$p_{h\nu}^{y} = \frac{h\nu'}{c}\sin\phi \tag{1.14}$$

$$p_e^{y} = m_e u \sin\theta \tag{1.15}$$

A similar behaviour of electromagnetic light waves was demonstrated by A. H. Compton in 1922, who observed that when X-ray radiation $\left(\nu = \frac{c}{\lambda}(\text{Eq. } 1.4)\right)$ collides with an electron, it continues its path at an angle ϕ that varies from the original one, with a lower momentum than the initial, and with a projection on the y-axis that is exactly as predicted by Einstein's equation $p_{h\nu}^{y} = \frac{h\nu'}{c}\sin\phi$ (Eq. 1.14). The resulting effect is an increase in the wavelength of the photon after the collision, an indication that it has lost energy. Compton found that the energy loss of the photon is equal to the energy gain by the electron. Similarly, following collision, the electron acquires a momentum whose projection on the y-axis is equal to $p_e^{y} = m_e u \sin\theta$ (Eq. 1.15 and Figure 1.12). Just as billiard balls transfer momentum when colliding, photons transfer momentum to electrons. In this experiment, photons behaved like particles.

WAVE-PARTICLE DUALITY

In 1924, Louis de Broglie reasoned that if radiation could exhibit the properties of both particles and waves, then electrons could as well (indeed, any moving particle, whether a planet, a baseball, or an electron). This phenomenon is known as wave-particle duality. The de Broglie relation $\lambda = h/mu$ or $\lambda = h/p$ is derived from the combination of the mass–energy equivalence relation ($E = mc^2$, Eq. 1.6) and the energy of a photon ($E = hc/\lambda$, Eq. 1.5). It dictates that a particle of momentum (mu) has an associated wave of wavelength λ (or that a particular wavelength λ can be associated with a particle). In other words, the wavelength associated with matter is inversely proportional to the mass of the particle, m and its velocity, u. It is known that the phenomenon of light diffraction in crystalline lattices is possible when the spacings in the crystal are comparable to the wavelength of the light radiation. This observation led Davisson and Germer in 1927 to search for the appropriate crystal spacing for a particle to give rise to the phenomenon of scattering.

Specifically, an electron of mass $m_\mathrm{e} = 9.1 \times 10^{-28}$ g, moving at 0.01 times the speed of light $u = 0.01c = 3 \times 10^8$ cm s^{-1} (an electron acquires this speed when a potential of $E = 26$ V is applied to it), has a momentum $p_e = m_e u_e = 27.3 \times 10^{-20}$ g cm s^{-1}. Consequently,

$$\lambda_e = \frac{h}{p_e} = \frac{6.6 \times 10^{-27}\,\text{erg s}}{27.3 \times 10^{-20}\,\text{g cm s}^{-1}} \tag{1.16}$$

$$\lambda_e = 0.24 \times 10^{-7}\,\text{cm} = 2.4\ \text{Å}$$

Indeed, Davisson and Germer found that a crystal with a lattice spacing = 2.4 Å caused diffraction patterns of the studied electrons, just as electromagnetic waves do!

The discovery of the wave-particle duality not only changed our understanding of electromagnetic radiation and matter, but also revolutionised physics. In classical physics, a particle in motion has a definite position at any given moment. In contrast, we cannot simultaneously determine the position and linear momentum of a wavelike object. This phenomenon is known as the uncertainty principle, formulated around 1927 by the German physicist Werner Heisenberg. It states that the product of the uncertainty in each quantity is less than $h/2\pi$, and that the position and momentum of a particle cannot be known simultaneously with such precision.

Under this premise, we must think of the electron from a different perspective and consider the *probability* of finding the electron in a given volume of space rather than attempting to define its exact position and momentum.

APPLICATION OF QUANTUM MECHANICS TO ATOMIC STRUCTURE

The simplest atom we can study is the hydrogen atom, which has only one proton and one electron. A proper atomic theory should explain, for instance, the reason for the characteristic reactivity of each element. In the case of hydrogen, one might ask, for example, why the reaction $2\ \mathrm{H}\cdot \rightarrow \mathrm{H_2}$ is exothermic $(\Delta H^\circ = -104.2\,\text{kcal mol}^{-1})$, but why $3\mathrm{H}\cdot \nrightarrow \mathrm{H_3}$.

The determination of the visible spectrum of the hydrogen atom required quantum theory. As shown in Figure 1.13, photolysis of the hydrogen molecule gives rise to hydrogen atoms in excited states, H·*; a deexcitation (relaxation) process then occurs in which the emission of energy brings the hydrogen atoms back to their basal state.

The recording of the emitted light (the spectrum of the hydrogen atom) showed a surprising peculiarity: the emissions corresponded only to certain energy values (spectral lines); that is, they were quantised. This result is not consistent with Rutherford's incipient planetary model (1911) for atoms, in which the Coulombic attraction of the nucleus/electron is compensated by the centrifugal force of the electron in its orbitals because in this model any amount of energy would be absorbed and emitted, varying only the distance between the nucleus and the electron. Niels Bohr proposed a model for the hydrogen atom that predicted the existence of line spectra. Bohr used Planck's and Einstein's ideas about quantised energy and proposed the following postulates: (1) The H atom has only certain energy levels, called stationary states, which are associated with a fixed circular orbit of the electron around the nucleus (Figure 1.14). The higher the energy level, the further away from the nucleus the electron orbit is. The atom does not change its energy while the electron is orbiting. In other words, it does not release energy while it is in one of its stationary states. The atom only changes to another stationary state (the electron moves to another orbit) by absorbing or emitting a photon. When an electron 'jumps' from an orbit of higher energy to one of lower energy, it emits a quantum of light with exactly the energy difference between the two orbits (Figure 1.14a). This quantum has an associated frequency and wavelength λ, given by Planck's formula $E = h\nu$. Similarly, if a quantum of light with just the right energy comes along, it will be absorbed by an electron by 'hopping' to a higher-energy orbital (Figure 1.14b). In the first case, emission lines are produced; in the second, absorption lines are observed. This is how the origin of spectral lines was explained by Bohr's atomic model.

Thus, the spectrum of the hydrogen atom gave rise to the quantum model shown in Figure 1.15 (the y-axis represents the energy of the stationary states [orbitals]). By means of this model, it is understood how the recorded emissions result from energetic jumps between different stationary states (E_1, E_2, E_3, etc.), which are related by a simple formula involving the quantum number, $n = 1, 2, 3$, etc. Thus, certain emissions between nearby energy levels are of low energy (visible region) whereas decay to the basal state E_1 are of higher energy (235–313 kcal mol^{-1}) and occur in the ultraviolet region.

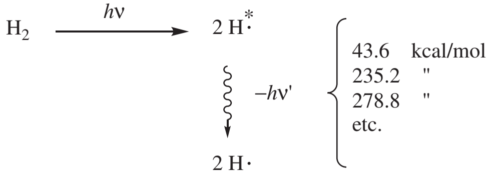


FIGURE 1.13 Photolysis of a hydrogen molecule.

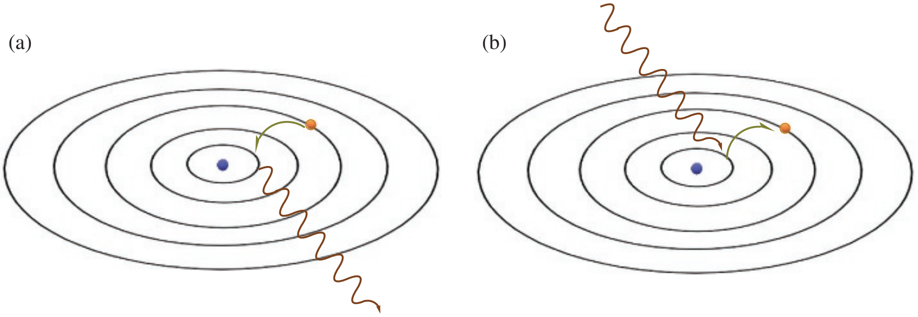


FIGURE 1.14 (a) Quantum of light emission when an electron 'jumps' from an orbit of higher energy to another of lower energy. (b) A quantum of light is absorbed by an electron when it goes to a higher-energy orbital.

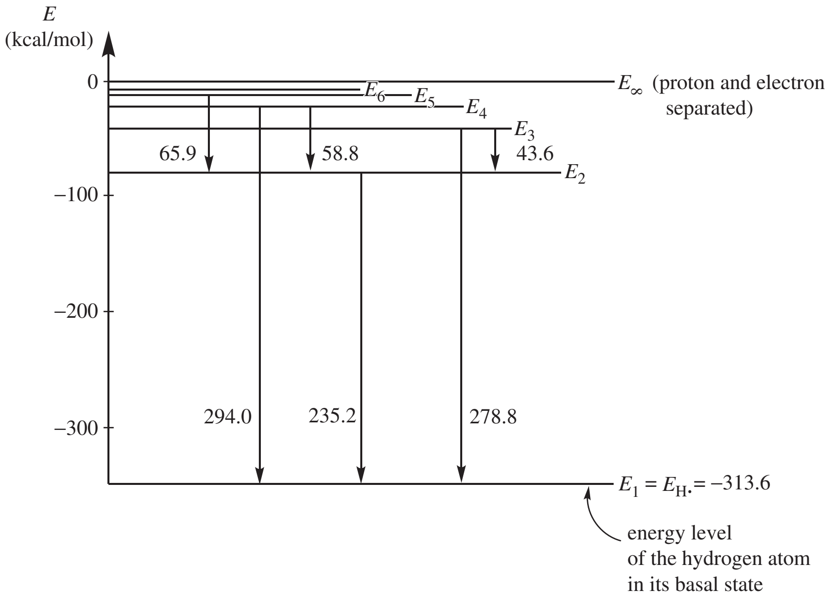


FIGURE 1.15 Quantum model of the hydrogen spectrum.

Despite its success in predicting the spectral lines of the hydrogen atom, Bohr's model could not predict the spectrum of any other atom with more than one electron. This is because it did not consider electron–electron repulsions and nucleus-electron attractions that give rise to rather complex electrostatic interactions. Furthermore, since any spinning electric charge emits electromagnetic radiation, an electron spinning around the nucleus should lose energy. Since all energy in the atom is conserved, any radiation must take place at the expense of the motional energy of the charged particle. The result would be that, following rotations, the electron would eventually ‘fall’ back into the nucleus. The most fundamental deficiency of Bohr’s model is that electrons do not move in fixed and defined orbits (as we will see later). Moreover, this model does not explain why the energy levels of atoms should be quantised. Nevertheless, this model gave rise to the concept of quantum number, which is so important in more recent theories, and we retain the central idea that the energy of an atom is produced at discrete levels and that it changes when the atom absorbs or emits a photon of a particular energy. Indeed, the term orbital is still used in wave mechanics.

The definitive step was then taken by Erwin Schrödinger in 1926, who understood the connection between the existence of the stationary states of hydrogen and the wave properties of the electron. For this, some systems that absorb or release energy in special quantities have been known since then. For example, the guitar string and the drum produce sounds (vibrations) of characteristic energy, which contrasts with other systems that can accept or release energy in any magnitude: a baseball, the weights of a balance, etc. Unlike these systems that can be perfectly studied by classical mechanics, a guitar string of a certain length is only allowed certain vibrations; hence its characteristic tones (Figure 1.16).

As can be seen in Figure 1.16, the length of the string determines the vibrations that can be produced; that is, the vibrations are quantised. The displacement of the string at its peaks and troughs corresponds to the amplitude of the vibration, which also has a characteristic number of nodes: the points where the peaks become troughs and vice versa, i.e. where the phase of the vibration changes sign. It is clear from Figure 1.16 that the higher the number of nodes, the higher the vibrational energy. It can also be seen that the wavelength of the vibration (and therefore its energy E) is determined by the length of the string

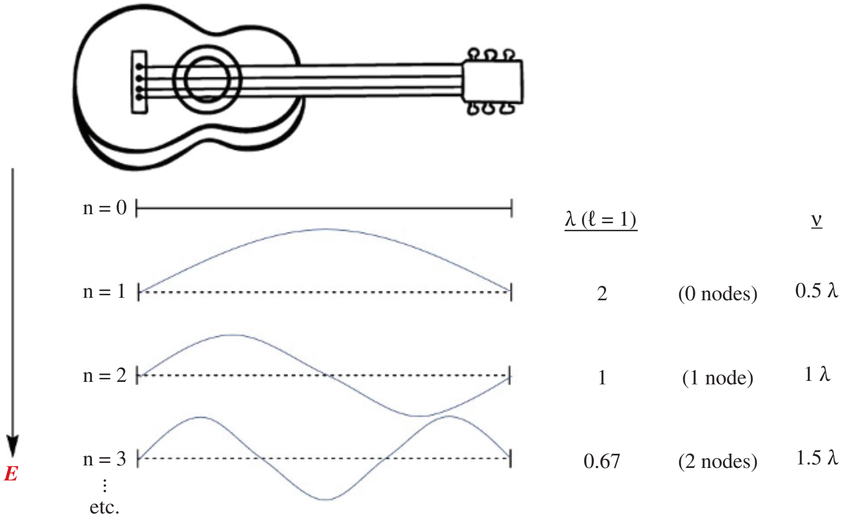


FIGURE 1.16 Vibrations allowed by the string of a guitar.

and the quantum number n (Eq. 1.17). The variable n is an integer number that indicates whether it is the fundamental ($n = 1$) or an overtone or harmonic ($n = 2, 3, 4, \ldots$). This number is strictly analogous to atomic quantum numbers.

$$\lambda = \left(\frac{2}{n}\right)\ell \tag{1.17}$$

It should be noted that the points at which the string is attached to the guitar, which determine its length, also limit the number of possible vibrations by preventing certain unsymmetrical or illogical vibrations from being allowed. Figure 1.17 shows two examples of prohibited vibrations.

Thus, the vibrations of a guitar string are quantised and defined by an integer number n, a node pattern (vibration frequency), and the frequency of the vibration. In the same way that the vibrations of a guitar string and the motion of an electron in a hydrogen atom produce characteristic spectra, both can be described mathematically using a *wave equation*.

The wave equation for a standing wave in two dimensions is more complex than the wave equation for a vibrating string because the vibration takes place in more dimensions. The best analogy for a standing wave in two dimensions is probably a vibrating drumhead. Like a guitar string, the vibrations of the leather on a drum have characteristic and defined tones. The circumference of the drum is fixed and represents the boundary condition that limits how the leather can vibrate; that is, it limits the number of specific frequencies that are possible. As shown in Figure 1.18, instead of nodal points (guitar string), we now have nodal lines associated with the different two-dimensional vibrations. In the Figure, the positive wave-like phases and negative wave-like phases are moving in opposite directions with respect to the viewer.

Like the guitar string, the drum produces line spectra corresponding to quantised vibrations of specific energy. These musical phenomena can be described mathematically by a wave equation. Therefore, when the Austrian physicist Erwin Schrödinger learnt that the hydrogen atom also has a characteristic line spectrum and that electrons are diffracted like electromagnetic waves, he concluded that the electron's motion must be governed by a wave equation.

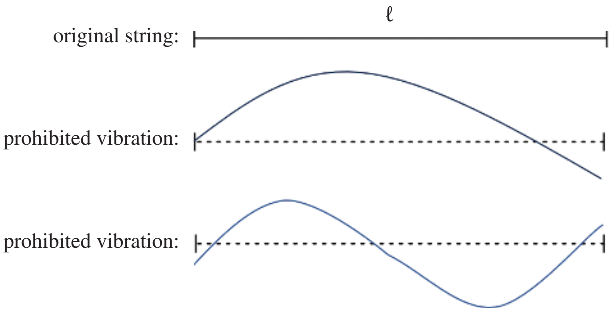


FIGURE 1.17 Examples of forbidden vibrations.

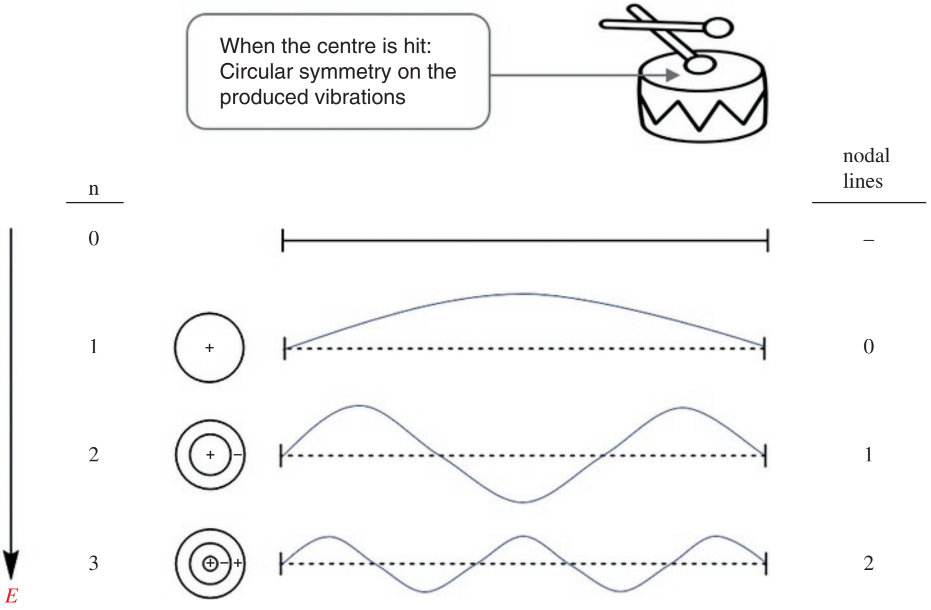


FIGURE 1.18 Two-dimensional vibrations allowed by a drum.

Central to quantum mechanics is the premise that electrons in an atom or molecule can be reasonably treated as standing waves in three dimensions. In three dimensions, the picture becomes much more complex, although the same rules apply. The nodes now become surfaces rather than points or lines of the guitar string and the drum, respectively. In a 3D standing wave, there are two types of nodal surfaces: spherical surface nodes and flat surface nodes. The Schrödinger equation for the energy of an electron in an atom is a second-order differential equation for a standing wave in three dimensions and is the mathematical cornerstone of the quantum mechanical model. Being a standing wave equation means that only certain solutions can exist. This is the first explanation of the origin of the quantisation of atomic energy levels. The Schrödinger equation, in its basic form, is described in the following.

SCHRÖDINGER'S EQUATION

The determination of the spectrum of the hydrogen atom with its line pattern, which is similar to that of a guitar string, and the demonstration of the wave properties of the electron led Schrödinger to develop a wave equation suitable for describing the motion of the electron in the hydrogen atom. In its condensed form, the Schrödinger equation can be reduced to the following:

$$H\psi = E\psi \tag{1.18}$$

where ψ is the wave function, a function describing the wave nature of the electron. E is the energy of the system (i.e. the electron) and H is the Hamiltonian operator. In general, an operator is a set of mathematical instructions to transform one function into another. In this case, the operator H acts on a function (ψ) and returns the same function (ψ) multiplied by a scalar quantity (E). In quantum mechanics, each observable (e.g. position, momentum and kinetic energy) is represented by an independent operator. This operator is used to obtain physical information in quantum mechanical formalism. For example, in classical mechanics, the energy of the system can be expressed as the sum of the kinetic and potential energy. For quantum mechanics, the kinetic and potential energies are transformed into their corresponding quantum mechanical operators, which in turn correspond to the Hamiltonian (H) operator. For a particle of mass m moving in one dimension in a region where the potential energy is $V(x)$, the term H is:

$$\underset{\substack{\text{Hamiltonian}\\ \textit{operator}}}{H} = -\underbrace{\frac{h^2}{8\pi^2 m}\frac{\partial^2\psi(x)}{\partial x^2}}_{\substack{\text{Operator}\\ \text{associated with}\\ \text{kinetic energy}}} + \underbrace{V(x)\psi}_{\substack{\text{Term associated}\\ \text{with potential}\\ \text{energy}}} \tag{1.19}$$

The Hamiltonian (H) of a system is an operator corresponding to the total energy of a given system; including both kinetic and potential energy (H for hydrogen will be different from that for helium because of the extra electron involved in the latter atom and different for the other atoms). The kinetic energy is related to the momentum (expressed as its corresponding operator) and mass (m) of the particle, whereas the potential energy is the energy associated with electrostatic interactions. Therefore, the potential energy depends only on the charge and position of the particles as dictated by Coulomb's law (that is, the nucleus-electron attraction, nucleus-nucleus repulsion, and electron-electron repulsive interactions). Replacing H from Eq. (1.19) in Eq. (1.18) gives Schrödinger equation in the form:

$$-\frac{h^2}{8\pi^2 m}\frac{\partial^2\psi(x)}{\partial x^2} + V(x)\psi = E\psi(x) \tag{1.20}$$

The wave function (ψ) and its associated energies are solutions of the Schrödinger equation. The German physicist Max Born proposed a physical interpretation of ψ. He stated that the probability density (probability per unit volume) of finding an electron in a given region is given by the square of the wave function (ψ^2). Technically, since the wave function can contain imaginary numbers, squaring ψ cancels out any imaginary numbers and makes the probability density positive. A plot of the wave function squared (ψ^2) represents an orbital, a probability distribution map of the electron's position. This result can be extended to give information about MOs.

The Schrödinger equation cannot be solved exactly in most cases. To get a better understanding of what the equation involves, consider a simple model system for which an exact solution is possible: the particle in a box quantum model. In classical mechanics, a particle trapped in a large box can move at any speed inside the box and is no more likely to be in one position than another (Figure 1.19a). In quantum mechanics, however, the particle can only occupy certain energy levels and is more likely to be in certain positions than others, depending on its energy level (Figure 1.19b).

In terms of quantum mechanics, a particle of mass m moves inside a one-dimensional box along a line of length L between two potential energy barriers, which are the ends of the box. Therefore, the potential energy V inside the box is zero because the particle is free to move. Inside the box, where the potential energy term $V(x) = 0$, the Schrödinger equation simplifies to

$$-\frac{h^2}{8\pi^2 m}\frac{\partial^2 \psi(x)}{\partial x^2} = E\psi \tag{1.21}$$

From Eq. (1.21) it is appreciated that the energy is:

$$E = \frac{n^2 h^2}{8mL^2} \quad n = 1, 2, 3, 4, \ldots \tag{1.22}$$

One way of deriving the above formula is as follows: The kinetic energy of a particle of mass m is related to its velocity u by the equation $E_\text{k} = 1/2\ mu^2$. Thus, noting that the linear momentum is $p = mu$, and using the de Broglie relation, one can relate this energy to the wavelength of the particle:

$$E_k = \frac{1}{2} m u^2 = \frac{1}{2}\frac{(\overbrace{mu}^{P})^2}{m} = \frac{(\overbrace{p}^{h/\lambda \,\leftarrow\, \text{de Broglie relationship}})^2}{2m} = \frac{h/\lambda}{2m} = \frac{h^2}{2m\lambda^2} \tag{1.23}$$

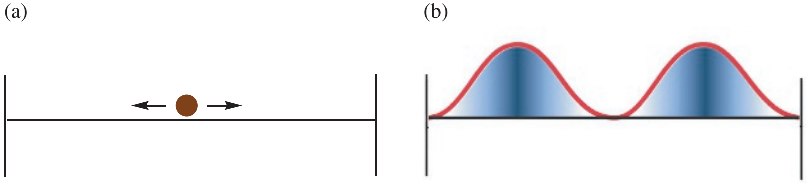


FIGURE 1.19 (a) A classical mechanics view of a particle in a box its position and its momentum are known. (b) In quantum mechanics, the particle occupies certain energy levels and is more likely to be in certain positions than others.

Assuming that the potential energy of the particle is zero throughout the interior of the box, the total energy is equal to the kinetic energy. Here we see that, like the guitar string (see as mentioned earlier), only integer multiples of half a wavelength can enter the box (see Figure 1.20; the waves have one, two, three valleys or crests, etc., where each valley or crest is half a wavelength). This means that the wavelengths that are possible for a particle to enter a box of length L must satisfy the condition that:

$$L = \frac{1}{2}\lambda, \frac{2}{2}\lambda,\ \frac{3}{2}\lambda \ldots = n \times \frac{1}{2}\lambda \text{ with } n = 1, 2, 3, \ldots \tag{1.24}$$

Therefore, the allowed wavelengths (λ) are:

$$\lambda = \frac{2L}{n} \text{ with } n = 1, 2, 3, \ldots \tag{1.25}$$

Substituting λ into Eq. (1.23), we obtain the formula 1.22:

$$E = \frac{h^2}{2m\,({}^{2L}\!/_{n})^2} = \frac{n^2 h^2}{8mL^2} \tag{1.26}$$

Note that the energy of the particle is quantised because n presents only integer values. The values of n are called quantum numbers (see the following). Equation (1.26) shows that the distance between neighbouring energy levels decreases as L (the length of the box) or m (the mass of the particle) increases. Put another way, the difference between consecutive energy levels is extremely small and essentially continuous. Therefore, until very small systems were studied, no one realised that energy was quantised!

The wave functions ψ obtained from the Schrödinger equation for the particle in the box are given by Eq. (1.27):

$$\psi_n(x) = \left(\frac{2}{L}\right)^{1/2} \sin\left(\frac{n\pi x}{L}\right) \ n = 1,\ 2,\ 3 \ldots \tag{1.27}$$

Figure 1.20a shows the wave functions of the first five energy levels, while the probability density for these levels (proportional to the square of the wave function) is shown on the right (Figure 1.20b).

The shapes of the density distributions generated from the square of the wave functions of a particle in a box reveal valuable information. For example, at energy level 2, one can notice a node in the middle where the probability of finding the particle is zero. At this level, the particle has an energy of $h^2/2mL^2$ and is most likely to be found at the centres of the two hills. The probability densities are also highlighted by the shading of the bands underneath each wave function (Figure 1.19b).

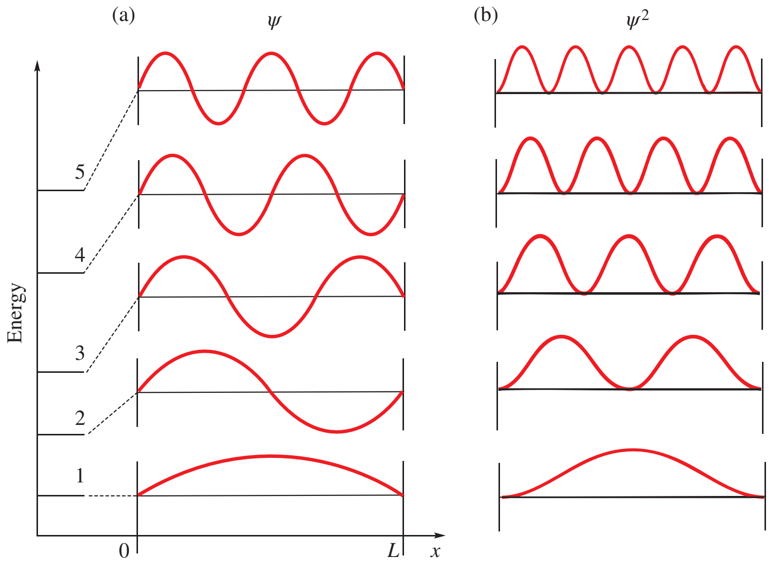


FIGURE 1.20 (a) Wave functions are obtained from the Schrödinger equation for a particle in a box for the first five energy levels. (b) The probability density for these levels (square of the wave function).

Some important mathematical properties for the wave function ψ are:

(a) ψ has boundary conditions that, like the boundary conditions on the guitar string, lead to a line spectrum. Some of the boundary conditions (or limits) of ψ are (i) at infinite distances $\psi = 0$ (the nucleus and the electron are separated). (ii) ψ is continuous and single-valued (i.e. presents a unique value for each region around the nucleus). Finally, (iii) the integration of ψ^2 over the whole space is equal to 1 (i.e. ψ is normalised) and (iv) the electron cannot move at infinite speed. (b) ψ is characterised by one or several nodes, that is surfaces where $\psi = 0$, implying a change of sign at its boundaries. (c) ψ presents amplitudes and phases. In addition, most importantly, (d) given their mathematical nature two or more wave functions ψ interact constructively or destructively.

The solution of the Schrödinger equation reproduces the hydrogen spectrum and explains the energy levels of the atom. It also allows the quantitative calculation of bond energies and bond lengths, molecular vibrational frequencies, etc. In short, the chemistry of the atom can be explained on the basis of quantum mechanics.

HYDROGENIC ORBITALS

Because the hydrogen atom has only one electron and therefore does not present electron–electron interactions, which would require explicit treatment, the Schrödinger equation can be solved exactly. The hydrogen electron can be thought of as a particle in a box, being confined to a small volume as a consequence of its attraction to the nucleus. Nevertheless, because of such attraction, the electron has potential energy, unlike the particle in the box. Furthermore, the electron can move in three dimensions, x, y and z, not just one.

Hydrogen has a positively charged nucleus Z, where $Z = 1$, and a negatively charged electron e at a distance r from the nucleus that is assumed to be static. Thus, by incorporating the kinetic energy of the electron and the potential energy of attraction of the nucleus/electron for the hydrogen atom, Eq. (1.18) is rewritten:

$$\left(-\frac{1}{2} \times \frac{h^2}{4\pi^2 m} \nabla^2 - \frac{Ze^2}{r}\right)\psi = E\psi \tag{1.28}$$

The Laplacian (∇^2) is a differential operator. In very general terms, the Laplacian of the wave function provides the kinetic energy, and it can be used to describe how a property is distributed and varies in a particular region; it can be expressed in Cartesian or spherical coordinates.

The solution of the Schrödinger equation gives rise to three quantum numbers that are necessary for the characterisation of each wave function. The fourth quantum number, spin angular momentum, was discovered experimentally by Stern and Gerlach in 1922. Table 1.1 lists the quantum numbers and includes a practical description of their meaning.

The orbital energy level or 'shell' is defined by the quantum number n and can be any positive integer between 1 and ∞. For a given energy level, there may be sub-shells, the number of which is defined by the quantum number ℓ. The term 'shell' reflects the fact that as n increases, the region of the highest probability density is like an almost concave shell of increasing radius. The average distance of an electron from the nucleus increases with the value of n.

TABLE 1.1 The Quantum Numbers and Their Meaning

Quantum number	Possible values	Characteristics
Principal quantum number, n	$1, 2, 3\ldots\infty$	$n - 1$ nodal surfaces. It is related to orbital size and energy
Orbital angular momentum, ℓ	$0, 1, 2, n - 1$	ℓ non-spherical nodal surfaces, related to the orbital shape
Magnetic, m_ℓ	$-\ell\ldots+\ell$	Orientation of non-spherical nodes, related to its orientation in space
Spin angular momentum, m_s	$\pm\frac{1}{2}$	Spin direction

TABLE 1.2 The Relationship and Meaning of Quantum Numbers $\boldsymbol{n}$ and $\boldsymbol{\ell}$

Value of n	Possible values of ℓ	Orbital name
1	0	1s
2	0, 1	2s, 2p
3	0, 1, 2	3s, 3p, 3d
4	0, 1, 2, 3	4s, 4p, 4d, 4f

TABLE 1.3 The Meaning of $\boldsymbol{m_\ell}$ in the Orbital's Orientation

Values of n	2	2
Values of ℓ	0	1
Name	2s	2p
Possible values of $\mathbf{m}_\ell$	0	+1, 0, −1
Name	2s	2 p_x, 2 p_y, 2 p_z *orientation of the orbitals*

As shown in Table 1.2, the values that ℓ can take depend on the value of $\boldsymbol{n}$: it can take any value from 0 to $n - 1 := 0, 1, 2, \ldots n - 1$. The different possible values of ℓ are labelled with letters instead of numbers, called *s*, *p*, *d* and *f* ('*s*' for sharp, '*p*' for principal, '*d*' for diffuse, and '*f*' for fundamental). The value of ℓ provides information about the region of space in which an electron can be located; that is, it describes the shape of the orbital. As its name suggests, ℓ describes the orbital angular momentum of the electron within the orbital, which is the mass times the angular velocity at which the electron 'orbits' (in classical terms) around the nucleus. For example, electrons in an *s* orbital where ℓ is 0 present zero orbital angular momentum, which means that one must refrain from thinking of them as orbiting the nucleus, but simply as being distributed around it. An electron in a *p* orbital ($\ell = 1$) has non-zero orbital angular momentum, so one can think of it as located in two lobes around the nucleus. An electron in a *d* orbital ($\ell = 2$) or an $f(\ell = 3)$ orbital has an increasing orbital angular momentum.

The third quantum number, $\boldsymbol{m_\ell}$, the magnetic quantum number, refers to the orientation of an orbital, which distinguishes the individual orbitals within a subshell. The possible values of $\boldsymbol{m_\ell}$ are given suffixes to the letters defining the quantum number ℓ. These letters refer to the orientation of the orbitals along the x, y or z axes (Table 1.3). Remember that momentum is a vector property, so the orbital angular momentum ℓ has an orientation and $\boldsymbol{m_\ell}$ describes that orbital orientation. There are $(2\ell + 1)$ possible orientations for the orbital angular momentum vector, corresponding to the possible values of $\boldsymbol{m_\ell}$ for a given value of ℓ. Thus, for an electron in a *p* orbital ($\ell = 1$), there are three possible orientations for the orbital angular momentum vector $(2(1) + 1 = 3)$. These values are assigned as −1, 0, +1.

An electron can be thought of as rotating about an axis passing through it and therefore has spin angular momentum in addition to the orbital angular momentum discussed earlier. According to quantum mechanics, an electron adopts two spin states, represented by the arrows ↑ (up) and ↓ (down) or the Greek letters α and β. One can imagine an electron rotating anti-clockwise around its axis at a given velocity or clockwise at exactly the same velocity. These two spin states are distinguished by a fourth quantum number, the magnetic spin quantum number, m_s, which can take two values: +½ indicates an ↑ electron and −½ indicates an ↓ electron.

Quantum numbers provide a comprehensive description of the behaviour of electrons in terms of their energy, spatial distribution, orientation, and intrinsic spin, and define the unique set of quantum states that electrons can occupy within an atom. Figure 1.21 presents a diagram showing how the quantum numbers divide and subdivide.

The mathematical expressions of ψ are complex, see Table 1.4 (the equations are presented for the purpose of illustration, consult specialist texts if you are interested in more in-depth information).

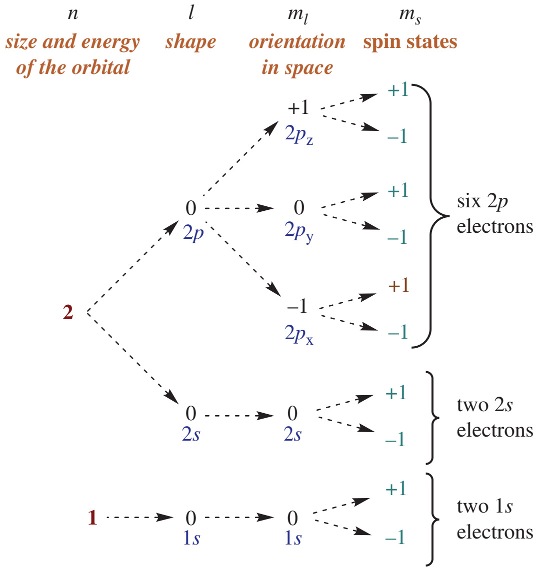


FIGURE 1.21 Diagram of the division and subdivision of the quantum numbers.

TABLE 1.4 Expressions of ψ for Orbitals 1*s*, 2*s* and 2*p*

$$\psi(1s) = \frac{1}{\sqrt{\pi}}\left(\frac{Z}{\sqrt{a_o}}\right)^{\frac{3}{2}} e^{\frac{-Zr}{2a_o}}$$

$$\psi(2s) = \frac{1}{4\sqrt{2\pi}}\left(\frac{Z}{a_o}\right)^{\frac{3}{2}}\left(2 - \frac{Zr}{a_o}\right) e^{\frac{-Zr}{2a_o}}$$

$$\psi(2\,p_x) = \frac{1}{4\sqrt{2\pi}}\left(\frac{Z}{a_o}\right)^{\frac{5}{2}}(x)\, e^{\frac{-Zr}{2a_o}}$$

$$\psi(2\,p_y) = \frac{1}{4\sqrt{2\pi}}\left(\frac{Z}{a_o}\right)^{\frac{5}{2}}(y)\, e^{\frac{-Zr}{2a_o}}$$

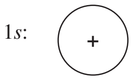
$$\psi(2\,p_z) = \frac{1}{4\sqrt{2\pi}}\left(\frac{Z}{a_o}\right)^{\frac{5}{2}}(z)\, e^{\frac{-Zr}{2a_o}}$$

where a_o is a collection of fundamental constants giving a conversion factor to atomic units of dimension; $\mathbf{a_o = 4\pi\,\varepsilon_o\,h^2/m_e\,e^2 = 0.529}$ Å (the Bohr radius), **Z** is the atomic number (**Z** = 1 for hydrogen) and **r** is the distance from the nucleus. Each ψ (atomic orbital) consists of three parts: (i) a normalisation constant so that the integration of the electron density over the whole space is equal to 1.0, (ii) a factor including the radical and angular nodes and (iii) an exponential term showing the decrease of ψ with the distance from the nucleus.

Therefore, it is convenient to use symbolic representations that correspond to three-dimensional images of the orbitals involved. For example, the 1*s* orbital contains no nodes but is always positive (or negative, depending on the label). One way of representing it is by means of a circle containing about 90% of the total electron density. Because a sphere adopts only one orientation, an *s* orbital presents only one value of m_ℓ: for any *s* orbital, $m_\ell = 0$. Figure 1.22 shows some of the plots used for the 1*s* orbit.

As can be seen, ψ is always positive for the 1*s* orbital. The probability density (ψ^2) decreases with increasing distance from the nucleus (r). It is worth noting that the electron density curve does not touch the axis, meaning that even though the probability of the electron being far from the nucleus is very small, it is never zero (Figure 1.22d). The values of ψ^2 are largest near the nucleus and then become smaller as one moves along a radius centred on the nucleus. This suggests that the electron does indeed spend some of its time in the region closest to the nucleus.

Nevertheless, integrating ψ^2 over the volume area shows that the maximum electron density is found at $r = a_0(0.529$ Å$)$. This is known as radial distribution. One does this by dividing the volume around the nucleus into thin, concentric, spherical layers. One then calculates the sum of the ψ^2 values in each layer to see which is most likely to contain the electron. In simple terms, we can say that we are plotting the number of points (probabilities) in each ring against the distance from the nucleus (Figure 1.23).



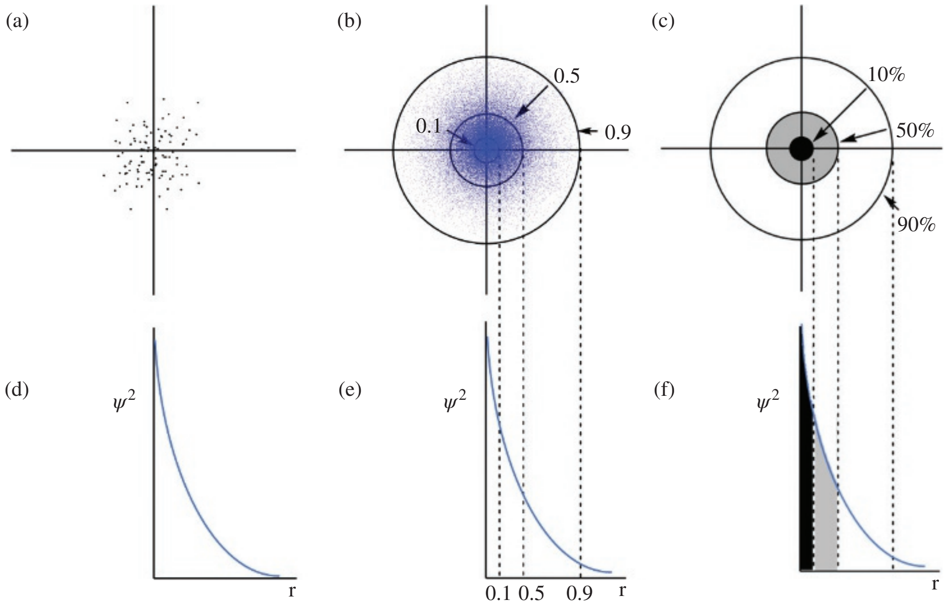


FIGURE 1.22 (a) Probability point diagram. It is an imaginary image of an electron changing position rapidly over time; this does not mean that an electron is a diffuse cloud of charge. (b) Density contours derived from representations in (a). (c) Representation of the volumes enclosing certain values of the probability of finding the electron. (d) Electron density plot from the nucleus. (e) Interpretation of electron density contours: they indicate where the electron spends most of the time. (f) Alternative representation of the volumes enclosing certain percentages of the electron density. *r* is given in Å.

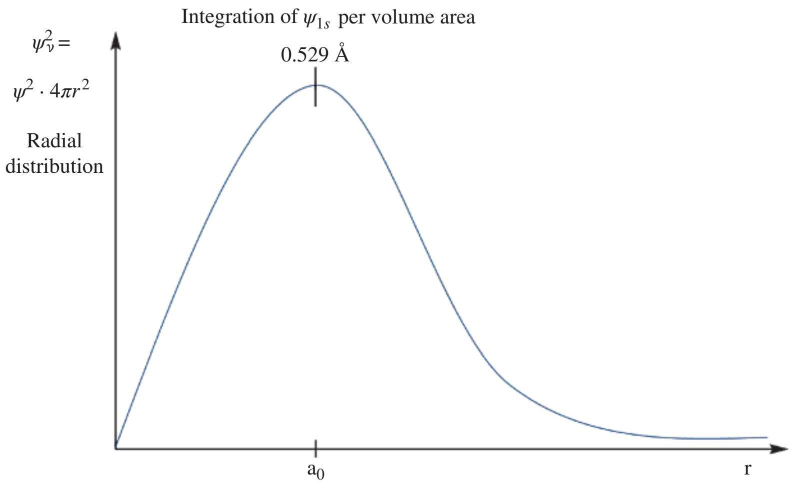


FIGURE 1.23 Probability of finding an electron in relation to the distance from the nucleus.

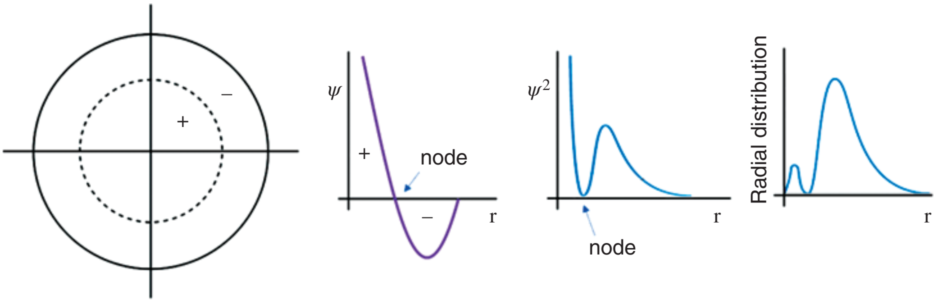


FIGURE 1.24 Representations of the 2*s* orbital.

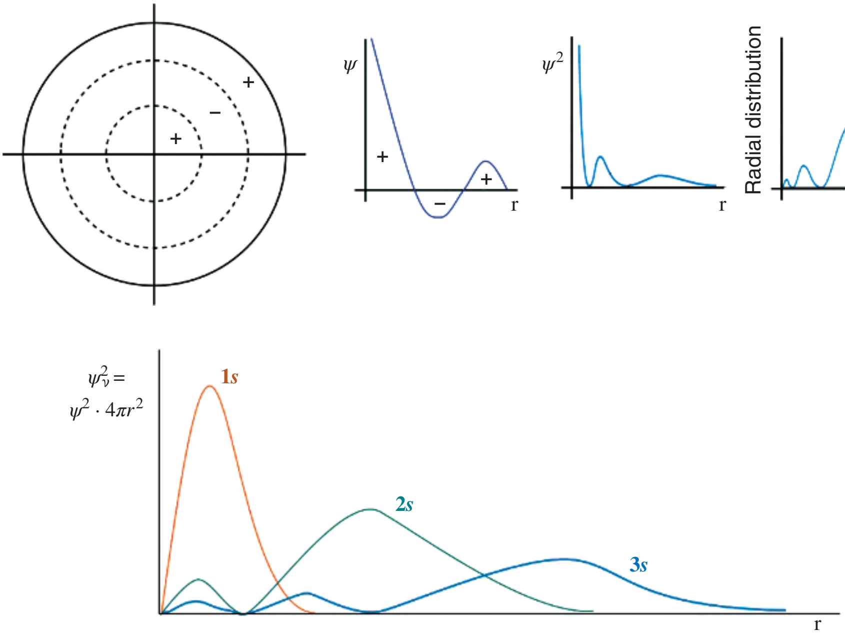
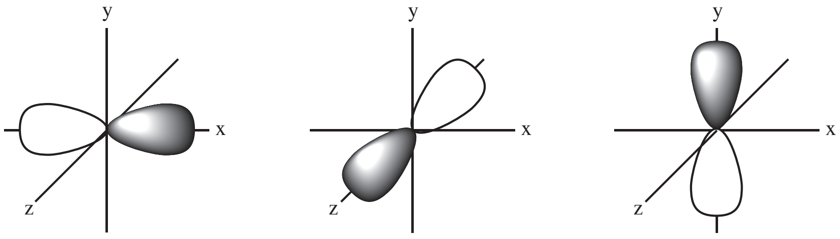


FIGURE 1.25 Top, representations of the 3*s* orbital. Down, radial distribution of orbitals 1*s*, 2*s* and 3*s*.

The 2*s* and 3*s* orbitals have both positive and negative ψ values on either side of a spherical nodal surface. Several representations of the 2*s* orbital are shown in Figure 1.24. The 2*s* orbital presents two regions of higher electron density. The radial probability distribution of the more distant region is larger than that of the closer one because the sum of ψ^2 is gathered over a much larger volume. There is a spherical node between the two regions, where the probability of finding the electron goes down to zero. This means that inside the 2*s* orbital, in contrast to the 1*s* orbital, there is a region in which there is no electron density at all. Since the 2*s* orbital is larger than the 1*s*, an electron in the 2*s* will spend more time away from the nucleus (in the larger of the two areas) than if occupying the 1*s* orbital.

There are three regions of high electron density and two nodes in the 3*s* orbital (Figure 1.25). Again, the highest radial probability appears in the region closest to the nucleus. This pattern of more nodes and a higher probability with increasing distance from the nucleus is continued with the 4*s* orbital, the 5*s* orbital and so on (Figure 1.25 down).

The probability density plot for *p* orbitals is no longer spherically symmetric. There are three 2*p* orbitals with quantum number $\boldsymbol{n} = 2$, $\boldsymbol{\ell} = 1$ which are isoenergetic. As shown in Figure 1.26, the 2*p* orbitals exhibit a particular orientation in space as well as two lobes. In this case, the nodal point is a plane between the two lobes, which is known as the nodal plane. These orbitals are distinguished by their third quantum number $\boldsymbol{m_\ell}$, which takes the values +1, 0, −1, corresponding to the *p* orbitals aligned along the x, y and z axes. As shown in Figure 1.27, the 3*p* orbital presents two nodes: one plane and one spherical node; the result is orbitals oriented on the three Cartesian axes. The 4*p* orbital presents two radial nodes apart from its nodal plane (not shown). Similar to the pattern of *s* orbitals, a 3*p* orbital is larger than a 2*p*, a 4*p* is larger than a 3*p*, and so on.



$2p_x$

$n = 2$
$\ell = 1$
$m = +1$

$2p_z$

$n = 2$
$\ell = 1$
$m = 0$

$2p_y$

$n = 2$
$\ell = 1$
$m = -1$

FIGURE 1.26 Representation of the 2*p* orbitals. Note: It is not possible to assign a specific $\boldsymbol{m_\ell}$ quantum number to a specific type of *p* orbital, but for didactic purposes, they have been assigned to show that when electrons are located in the same atom they must have a unique combination of the four quantum numbers.

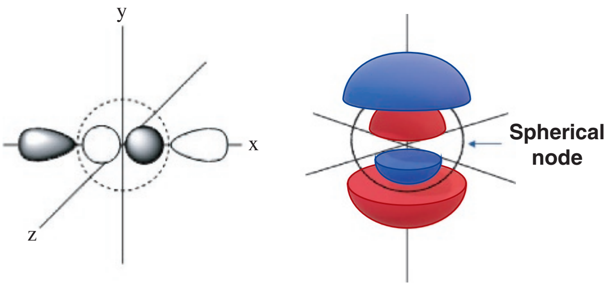


FIGURE 1.27 Representation of the $3p_x$ orbital: yz-plane nodes and a spherical node.

There are five 3*d* orbitals, which are isoenergetic and have two non-spherical nodes, either two orthogonal nodal planes or two nodal cones. The $3d_{xy}$, $3d_{xz}$ and $3d_{yz}$ orbitals present nodal planes along the xz and yz, xy and yz, and xy and xz planes, respectively. (Only $3d_{xy}$ is shown in Figure 1.28). The $3d_{x^2-y^2}$ orbital is obtained by rotating the $3d_{xy}$ orbit by 45°. The $3d_{z^2}$ orbit presents two nodal cones, which lie on the nucleus and are collinear with the z-axis (Figure 1.28).

The five 4*d* orbitals are constructed by superimposing a spherical node on the models described for the 3*d* orbitals (Figure 1.29).

The 4*f* orbitals constitute a set of seven orbitals with three nodes each. Six of these are orthogonal pairs whose shape can usually be obtained from the *d* orbitals by superimposing a nodal plane.

The energy of each hydrogen orbital is determined by the principal quantum number, n, according to Eq. (1.29).

$$E_n = -R \times \frac{Z^2 h}{n^2} \tag{1.29}$$

where R is the Rydberg constant, that is 313.6 kcal mol^{-1}, Z is the charge of the nucleus, $n = 1, 2, 3$ and the negative sign indicates that the energy of the orbital is lower than that of the separated proton and electron. In other words, as the

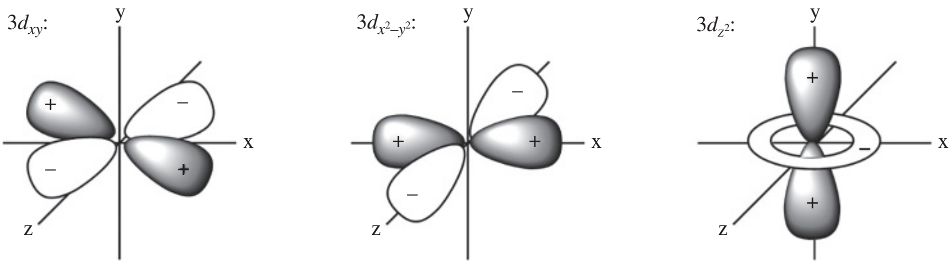


FIGURE 1.28 Symbolic representations of 3*d* orbitals.

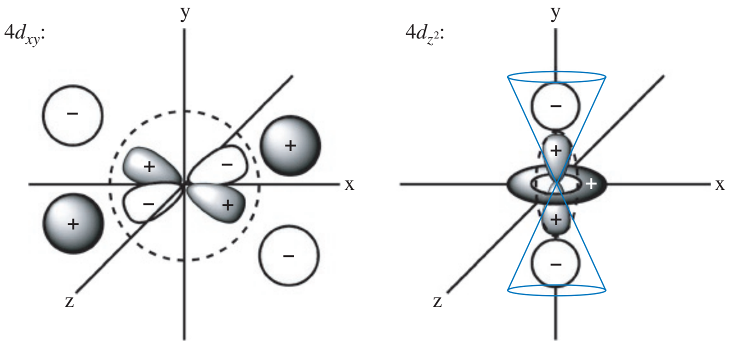


FIGURE 1.29 Symbolic representations of 4*d* orbitals.

electron approaches the nucleus, there is a favourable electrostatic interaction, so the energy decreases and becomes more negative.

According to Eq. (1.28), the order of the energy levels is $1s < 2s < 3s = 3p = 3d < 4s = 4p = 4d = 4f$. However, for atoms larger than hydrogen, electronic repulsion changes this energy order, so that experimentally it has been found that $1s < 2s < 2p < 3s < 3p < 4s < 3d < 4p < 5s < 4d < 5p < 6s < 4f < 5d < 6p < 7s$.

The quantum numbers $\boldsymbol{n}$ and $\boldsymbol{\ell}$ together determine the spatial size of the orbital, i.e. the average distance $\bar{r}$ of the electron from the nucleus (Eq. 1.30, where $a_0 = 0.529\ \mathring{A}$).

$$\bar{r} = a_0 \frac{n^2}{Z}\left[\frac{3}{2} - \frac{\ell(\ell+1)}{2n^2}\right] \tag{1.30}$$

In the quantum mechanical theory of the atom, the three quantum numbers n, ℓ and m determine the energy levels of the hydrogen atom and their shapes (nodal patterns). Determining the energy associated with each orbital allows the precise assignment of the spectrum of the hydrogen atom. Consider, for example, a hydrogen atom with its electron in the $2p$ orbital: this atom is 78.4 kcal mol^{-1} more stable than the separated nucleus and electron. However, when this atom emits energy and falls to a lower energy state, it must be into the $1s$ orbital, which is 313.6 kcal mol^{-1} lower in energy than the 0-reference level. This means that the $2p \rightarrow 1s$ transition is accompanied by the emission of 235.2 kcal mol^{-1}, which corresponds to one of the lines observed in the hydrogen spectrum (Figure 1.15). In fact, all the energy shifts observed in the hydrogen spectrum are explained by the differences in the estimated levels with respect to the quantum description of the hydrogen atom.

WHY DOESN'T THE ELECTRON FALL INTO THE NUCLEUS? BOHR'S LEGACY AND THE QUANTUM MECHANICAL MODEL

Given that the atomic electron and the atomic nucleus present opposite charges, the question arises, why doesn't the electron fall into the nucleus? As discussed in this chapter, the answer 'because the electron orbits the nucleus like a planet orbits the sun' is unacceptable because it would imply the emission (loss) of energy and a spiral trajectory of the electron until it collides with the nucleus. An electron cannot move in a circular orbit unless there is a force holding it in that orbit; if there is no force, it will escape from the orbit. According to classical theory, this is a shortcoming of the planetary model, since it implies that two forces balance each other to keep the electron in its atomic orbit: electrostatic attraction, which implies a tendency for the electron to fall into the nucleus, and the opposite tendency for the electron to move away from the nucleus as a consequence of its kinetic energy. If this is the case, the electron should be at rest or moving in a straight line at a constant speed. However, Bohr's model was successful in terms of its consistency with some atomic spectroscopic observations, indeed, we still use the terms 'ground state' and 'excited state' and retain the central idea that the energy of an atom exists in discrete levels and changes when the atom absorbs or emits a photon of a particular energy.

In the quantum mechanical model of the atom, the factor that causes the tendency of the electron and nucleus to separate arises from the wave-like properties of the electron as a particle. Consider again the iconic experiment of an 'electron in a box', which has a certain energy associated with it. Because of its wave nature, the electron presents a certain wavelength, which is determined by the dimensions of the box in which it is contained. The smaller the box, the smaller the wavelength must be, so its energy increases. This effect is called *confinement energy*.

Therefore, when the electron is confined to a certain volume, it also acquires confinement energy, which corresponds to its tendency to escape from confinement. In other words, the confinement energy is the factor that causes the electron in an atom to tend to move away from the nucleus.

When a nucleus is placed in a box containing an electron, the electrostatic attraction lowers the potential energy, and the total energy is a combination of the potential energy and the confinement energy (kinetic energy).

In short, since the nucleus and electron have opposite charges, they naturally tend to attract each other and bind. However, the electron is not just a particle; it also behaves like a wave. It is best to think of the electron as a diffuse cloud of matter and electric charge surrounding the nucleus. As the electron and the nucleus move closer together, the electron becomes more and more confined to a given volume and its wavelength becomes shorter and shorter in order to 'fit' into that space. Because its wavelength is shorter, the electron's energy increases, and eventually it will be large enough to dominate the electrostatic potential energy that attracts the nucleus and the electron. An equilibrium is reached in which the atom is stable and the electron neither falls into the nucleus nor separates from it.

In chemistry, quantum mechanics plays a crucial role in understanding and predicting the behaviour of molecules and their constituents. It explains phenomena such as atomic structure, chemical bonding, molecular spectroscopy, electronic structure and energy levels. Quantum mechanics is instrumental in understanding the properties of MOs and, as we will see in the following chapters.

FURTHER READING

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EXERCISES

1.1 The energy of a photon is 7.50×10^{-16}. Calculate the frequency and the wavelength of the light.

1.2 Calculate the wavelengths of the light with the following frequencies: 5.75×10^{14} Hz; 5.15×10^{14} Hz; 4.27×10^{14} Hz. To which colour of the visible spectrum does each frequency belong?

1.3 Show that to heat 1 mole of water from 0 to 100 °C requires 2/3 mole quanta of infrared light with $\nu = 3\times10^{13}$ cycles s^{-1}.

1.4 What is the energy of a single photon of blue light of frequency 6.4×10^{14} Hz and the energy per mole of photons of the same frequency?

1.5 Calculate the wavelength of a baseball that weighs 142 g travelling at 150 km h^{-1}.

1.6 Derive all possible sets of quantum numbers for $n = 2$ and describe the meaning of these sets of numbers.

1.7 Using Eqs. (1.28) and (1.29) determine the energy and average size of the 1*s*, 2*s*, 3*s*, 2*p*, 3*p* and 3*d* orbitals.