1 Wave–Particle Duality

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1.1 OVERVIEW OF QUANTUM MECHANICS

Matter is composed of atoms that are bound together to form molecules, which can then assemble into larger structures. What are the basic principles that govern the formation of chemical bonds? An understanding of this fascinating phenomenon requires that we abandon familiar ways of thinking. We must learn to think in terms of quantum mechanics, which constitutes the fundamental principles upon which our understanding of chemical bonding is based.

The development of quantum mechanics in the first half of the twentieth century is one of the great paradigm upheavals in human history. It required that our basic concepts for describing the material world, as manifest in the postulates of classical mechanics, be replaced by the postulates of quantum mechanics. Although it would be logical to see what follows from these postulates and compare the results with reality, this task is quite complex for even the most simple cases. How then to develop our understanding of chemistry? In this chapter we sketch some of the key historical features of quantum mechanics development and illustrate its fundamental idea, wave–particle duality. In Chapter 2 we jump directly into quantum mechanics, focusing on simple cases.

1.1.1 Historical Highlights

An important root for growing quantum mechanics was the electromagnetic theory developed by James Clark Maxwell (1831–1879). In 1865 Maxwell predicted the formation of electromagnetic waves, and his theory unified optics with electricity and magnetism. In 1888 Heinrich Hertz (1857–1894) was able to generate and detect electromagnetic waves. Thus, the wave nature of light was established and the basis of modern communication techniques was set. Physics based on Newton’s mechanics and Maxwell’s electrodynamics is now called classical physics.

An important observation that remained unexplained for a long time was the radiation emitted when heating a black body such as the burner of an electric stove. A heated body first becomes dull red, then white, and finally blue. The maximum intensity shifts to a higher frequency when increasing the temperature. In complete disagreement with this observation, Maxwell’s theory predicted that the radiation intensity should continuously increase with frequency (ultraviolet catastrophe). What is the reason for this discrepancy? Max Planck (1858–1947) modeled the molecules of the black body by oscillators, as had
earlier investigators. In classical physics, oscillators can be excited to assume any energy. Max Planck, however, had the revolutionary idea that an oscillator can have only discrete energies $E = n\hbar\nu$, where $n$ is an integer, $\hbar$ is a proportionality constant, and $\nu$ is the oscillator’s frequency. Using this assumption, he obtained agreement with experiment by setting $\hbar = 6.626 \times 10^{-34}$ J s (Planck radiation law, 1900).

Albert Einstein (1879–1955) extended Planck’s hypothesis by proposing that the radiation itself existed in packages of energy $E = h\nu$ (photons). On that basis he explained the photoelectric effect discovered by Heinrich Hertz: a metal, illuminated by light, emits electrons with a speed that can be measured (see Section 1.2.1). Maxwell’s theory predicted that the speed increases proportionally with the intensity of the incident light. In contrast, experiment showed that the number of emitted electrons increases with intensity, but the speed depends on the frequency of the incident light and is independent of intensity. Einstein explained this strong discrepancy in 1905 by his description of light as a beam of photons. Altogether these observations suggest that light has the properties both of waves and particles (wave particle duality).

Niels Bohr (1885–1962) saw a correspondence between the actual behavior of electrons and what follows from classical physics. On that basis he proposed a model of the hydrogen atom that explained the emission spectrum of hydrogen (1913).

Louis de Broglie (1892–1987) speculated that matter, like light, may show wave particle duality. He postulated that the wavelength of an electron moving with speed $v$ is $\lambda = \hbar/(m_e v)$, where $m_e$ is the electronic mass (1924). This revolutionary view confirmed the idea behind Bohr’s model. de Broglie waves were first observed experimentally in 1926 by N. Davisson, L. H. Germer, G. P. Thomson, and A. Reid.

In 1926, Erwin Schrödinger (1887–1961) generalized this way of thinking by postulating an equation, now called the Schrödinger equation, that allowed one to calculate the distribution of electrons over a molecule. Werner Heisenberg (1901–1976) proposed his uncertainty principle in 1927. Together with the view that the Schrödinger equation gives the probability of finding an electron in a given volume element (Max Born, 1882–1970) and the fact that only distinct solutions of the Schrödinger equation are meaningful (exclusion principle by Wolfgang Pauli, 1900–1958, formulated in 1925), the Schrödinger equation is the basis of quantum chemistry.

This situation was expressed in 1929 by Paul Dirac (1902–1984) in his famous sentence: “The underlying physical laws necessary for the mathematical theory of a large part of physics and the whole of chemistry are thus completely known, and the difficulty is only that the exact application of these laws leads to equations much too complicated to be soluble.” This is where quantum chemistry—the search for approximation methods—begins.

### 1.1.2 An Approach to Quantum Mechanics

Now we proceed smoothly and straightforwardly to an increasingly deeper quantum mechanical understanding of atoms and molecules.

In a first approach our basic postulate is wave particle duality. It constitutes a form of the general postulates of quantum mechanics valid only in the special case of free electrons. In order to appreciate better this postulate we compare its predictions with experiments on waves and particles. Our next postulate is the variational principle. In Chapter 2 we use this postulate to gain a basic understanding of the stability, size, and shape of the hydrogen
atom, and of the $\text{H}_2^+$ molecular ion. In this way we illustrate the importance of quantum mechanics in understanding the occurrence of chemical bonds.

How best to achieve these goals? First it is necessary to become familiar with a basic process in science: to consider distinct experiments and to identify the logical underlying pattern, in other words to draw conclusions just from these experiments. Keeping this in mind we select key experiments that lead to the postulate of wave particle duality as directly as possible. In this way it is possible to obtain, right at the beginning, a first idea of the fascinating revolutionary change in thinking that is necessary to understand the fundamental principles of chemistry.

In a second approach we replace the postulates of wave particle duality by a more general postulate, the time-independent Schrödinger equation (Chapter 3), which holds for a wide range of chemical systems. The variational principle, considered as a postulate in Chapter 2, is now a theorem, following from the time-independent Schrödinger equation (Chapter 5).

In a third step of generalization we replace the time-independent Schrödinger equation (so far considered as a postulate) by postulating operators that lead to an equation called the time-dependent Schrödinger equation (Chapter 3, Section 3.5). This equation includes the time-independent Schrödinger equation discussed in Chapter 3 (Section 3.1–3.4) as a special case. In a fourth step the antisymmetry condition (Pauli exclusion principle) is introduced as a last additional postulate (Chapter 5, Section 5.4.3).

1.2 LIGHT

In classical physics light is described as a wave phenomenon. However, light can also be described as a stream of particles. Some phenomena, such as the photoelectric effect or photochemical reactions, reflect the particle nature of light (see Section 1.2.1). Other phenomena, such as interference in soap films or the diffraction of light from a slit, demonstrate the wave nature of light (see Section 1.2.2). Section 1.2.3 presents a discussion of the theory that combines these two properties into a whole.
1.2.1 Particle Nature of Light: Photoelectric Effect

Electrons can be ejected from the surface of a metal by light (Fig. 1.1). This phenomenon is called the photoelectric effect. The speed $v$ of the electrons leaving the surface depends on the color of the light; it is higher for violet light and lower for red light. Increasing the intensity of the light causes more electrons to leave the surface, but does not increase their speed.

The sketch in Fig. 1.2a shows an experimental setup for studying this phenomenon. Two metal electrodes are placed inside a vacuum chamber (e.g., an evacuated glass flask), and the electrodes are connected to an external electrical circuit that controls the voltage between them and measures the current flowing in the circuit. Let us choose one of the electrode materials to be composed of Cs, a metal that emits electrons easily, and choose the other electrode to be composed of an inert metal, such as Au or Pt. Now we place a voltage $V$ across the electrodes, with the polarity such that electrons are decelerated in traveling from the Cs electrode (the cathode) to the opposite electrode (the anode). When we shine monochromatic light on the Cs cathode, we observe current flowing in the circuit as long as $V$ is low enough. If we keep the light intensity constant and increase the size of $V$, the current remains constant until a certain value, $V_0$, is reached where the current drops abruptly to zero (Fig. 1.2b). $V_0$ is called the stopping voltage. If the experiment is performed with different colors of light the behavior is similar, but the value of $V_0$ changes.

If we perform this experiment at different light intensities, we find that the value of the current increases as the light intensity increases, but the stopping voltage $V_0$ remains the
same. To summarize, the current depends on the intensity of the light, and the stopping voltage \( V_0 \) depends on the color of the light.

To analyze the observations we use energy conservation and recall that an electron traveling through a voltage \( V \) changes its energy by the amount \( eV \), where \( -e \) is the electron’s charge. When an electron (mass \( m_e \)) leaves the cathode with speed \( v \), it has kinetic energy \( \frac{1}{2}m_ev^2 \), and as it moves through the retarding potential \( V \) it converts its kinetic energy into potential energy. The electron will reach the anode if its initial kinetic energy \( \frac{1}{2}m_ev^2 \) is greater than or equal to its final potential energy at the anode, \( eV \), where \( e \) is the elementary charge. At the stopping voltage \( V_0 \), the potential energy is equal to the initial kinetic energy so that

\[
E_{\text{kin}} = \frac{1}{2}m_ev^2 = eV_0. \tag{1.1}
\]

For a source of violet light (such as that produced by a tunable laser) and Cs metal the observed stopping voltage is 1.801 V. Given the elementary charge of \( e = 1.602 \times 10^{-19} \) C, we obtain

\[
E_{\text{kin}} = 1.602 \times 10^{-19} \text{ C} \times 1.801 \text{ V} = 2.885 \times 10^{-19} \text{ J}.
\]

It will be shown at the end of Section 1.2.2 that it takes \( 2.080 \times 10^{-19} \text{ J} \) to pull an electron out of the metallic bonding of the Cs metal (work function \( E_{\text{work}} \)). So the violet light supplies each ejected electron with

\[
E = E_{\text{kin}} + E_{\text{work}} = (2.885 + 2.080) \times 10^{-19} \text{ J} = 4.965 \times 10^{-19} \text{ J}
\]

of energy. By repeating the photoelectric effect experiment with light of other colors, we find that yellow light transfers \( 3.310 \times 10^{-19} \) J of energy to each electron, and red light transfers \( 2.837 \times 10^{-19} \) J of energy to each electron.

We conclude from these experiments that light interacts with electrons in discrete amounts, or energy packets (energy packets of \( 4.965 \times 10^{-19} \) J for violet light and those of \( 2.837 \times 10^{-19} \) J for red light). These energy packets are called light quanta or photons.

The energy of each photon depends on the color of the light.

### 1.2.2 Wave Nature of Light: Diffraction

#### 1.2.2.1 Water Surface Waves

The diffraction and interference properties of waves are easily seen in water surface waves. Figure 1.3a illustrates how a wave passing through a small hole in a barrier acts like a source, sending new waves into the region beyond the barrier. The hole is considered small if it is about one-tenth of the wave’s characteristic wavelength. This phenomenon is called diffraction.

If two holes are opened in the barrier, then waves originate from each hole by diffraction (Fig. 1.3b). These waves can overlap to reinforce each other or to cancel each other. This phenomenon is called interference. Figure 1.3b shows how the waves interfere both constructively (reinforcing each other) and destructively (cancelling each other). A wave has an amplitude \( \psi \). For water waves \( \psi \) is the distance between the average height of the water’s surface and its highest height (peak), or alternatively the distance between the average height and the lowest point (trough). More generally, the amplitude of a wave is the maximum displacement, which for water waves is the distance of the water surface below the average level.
above or below the average height. To describe the interference of the waves we sum the waves’ amplitudes at each point in space and time to obtain the net wave displacement. This process is called superposition.

1.2.2.2 Light Waves

If light travels through a single slit or a double slit, a pattern of light (a change in brightness as a function of position) can be observed on the screen behind the slits, as illustrated in Fig. 1.4. We can interpret this experimental fact as evidence that light has the properties of a wave. The brightness at a given point P on the screen measures the intensity $I$ of the light at point P:

$$I = \frac{\text{power of light on area } A \text{ of the screen at point } P}{\text{area } A}$$ (1.2)

(power = energy per time). Furthermore, we can determine the wavelength $\lambda$ of the light by measuring the distance between successive minima (positions where the intensity is

1. We assume that the area $A$ about point P is sufficiently small to be uniform in brightness. The area equals $A$ if the screen is perpendicular to the direction of the light beam, otherwise it is $A \cdot \cos \alpha$, where $\alpha$ is the angle between the direction of the light beam and the direction of the normal on the screen.

---

**Fig. 1.3** (a) Formation of secondary waves from a small hole (for water waves, the surface of the water is forced to a wave motion by periodically dipping a stick into the water). Thick lines represent maxima of the waves. Thin lines represent minima of the waves. Reflection of the primary waves and disturbance of the secondary waves by the barrier are neglected. The distance between two subsequent thick lines corresponds to the wavelength $\lambda$. (b) Interference of two water waves. Amplitude maxima are shown as thick lines crossing; amplitude minima are shown by thin lines crossing; amplitude zero occurs at thin and thick lines crossing.

**Fig. 1.4** (a) Diffraction of light by a single slit. (b) Interference of light from a double slit.
Fig. 1.5  Diffraction of light from an edge. (a) Experimental arrangement and interference bands on the screen. (b) (dots) Measured intensity pattern on the screen as a function of distance $x$ from the geometrically constructed shadow boundary. The intensity was measured by replacing the screen with a photographic plate and measuring the density of the photographic image at each point on the screen. Calculated dependences of $\psi$, $\psi^2$, and $\psi^4$ on the distance $x$ are shown as solid lines. In each case, the experimental points are adjusted to the first maximum. Only the curve for $\psi^2$ is in accordance with the experimental intensity pattern.

zero) or maxima (positions where the light intensity is highest) on the screen in Fig. 1.4b. Figure 1.5a shows the intensity pattern of light on a screen when it diffracts from a sharp edge. The light’s brightness as a function of position can be quantified by using a digital camera or some other spatially sensitive photodetector (Fig. 1.5b). Comparison of the light wave’s calculated amplitude $\psi$ and the measured intensity shows that the intensity is proportional to $\psi^2$. Figure 1.5b shows three theoretical curves, for $|\psi|$, $\psi^2$, and $\psi^4$, and it is evident that the experimental curve of intensity versus distance is proportional to the calculated curve of $\psi^2$ versus distance $x$.

1.2.2.3 Wavelength of Light from Interference Pattern
Because superposition and interference of waves is such an important feature of quantum mechanics, it is worthwhile to show how the interference pattern can be used to determine the wavelength of the light source. Consider two slits with a separation $d$ and a screen at distance $a$ from the slits (Fig. 1.6). At point $P_1$, which is midway between the slit positions, the distances between each of the slits and the screen are the same. In this case the light

Fig. 1.6  Diffraction for a double slit (slits separated by $d$). The intensity of the light arriving on a screen at distance $a$ from the slits is measured at points $P_1$ and $P_2$. Usually, the distance $x$ between points $P_1$ and $P_2$ is much larger than the distance $d$ between the slits. In this case the triangle ABC can be approximated as a right triangle, leading to the relation $\alpha' = \alpha$. 

waves stay in phase and add constructively when they arrive at the point P1, and an intensity maximum is therefore observed at P1. The next intensity maximum occurs at the point P2. At this position the distances are \( r_1 \) (from the upper slit) and \( r_1 + \lambda \) (from the lower slit), so that the phase shift is exactly one wavelength, and the two waves add constructively again. In Justification 1.1 we calculate the wavelength \( \lambda \) from the distance \( x \) between the points P1 and P2 in Fig. 1.6.

If we perform the double-slit experiment on the same monochromatic light sources used in the photoelectric effect measurements, we find \( \lambda = 400 \text{ nm} \) for violet light, \( \lambda = 600 \text{ nm} \) for yellow light, and \( \lambda = 700 \text{ nm} \) for red light.

1.2.2.4 Relation Between Photon Energy \( E \) and Wavelength \( \lambda \)

For a given color of light, the energy \( E \) per photon can be measured by a photoelectric effect experiment, and the wavelength \( \lambda \) of the light can be measured by a diffraction experiment. Table 1.1 lists the corresponding energies (per photon) and wavelengths for several colors of light.

The fourth column of Table 1.1 gives the product of \( E \) and \( \lambda \) for each case. It can be seen that this product is the same for each entry. We can hypothesize that a law of nature makes the product of \( E \) and \( \lambda \) the same for each color of light. When the experiments are repeated carefully for different colors of light, the same relationship is always found:

\[
E\lambda = 19.86 \times 10^{-26} \text{ J m.} \tag{1.3}
\]

From this relationship we can assign a wavelength \( \lambda \) to a photon whose energy is determined in a photoelectric effect experiment, or alternatively we can determine the wavelength of the light and assign an energy to the photons in the light wave.

We can write Equation 1.3 in a different form by relating the light’s wavelength \( \lambda \) to its frequency \( \nu \). The product of a wave’s frequency \( \nu \) and its wavelength \( \lambda \) is its speed \( \nu \lambda \),

\[
\nu\lambda = v \tag{1.4}
\]

(see Fig. 1.7). Equation 1.4 is called a dispersion relation. In the photoelectric effect experiment the light is moving through a vacuum, so its speed is \( v = c_0 = 2.998 \times 10^8 \text{ m s}^{-1} \). For 400-nm violet light, we can compute a frequency

\[
\nu = \frac{c_0}{\lambda} = \frac{2.998 \times 10^8 \text{ m s}^{-1}}{400 \times 10^{-9} \text{ m}} = 0.749 \times 10^{15} \text{ s}^{-1}.
\]

<table>
<thead>
<tr>
<th>Color</th>
<th>( E \times 10^{-19} \text{ J} )</th>
<th>( \lambda ) nm</th>
<th>( E\lambda \times 10^{-26} \text{ J m} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Violet</td>
<td>4.965</td>
<td>400</td>
<td>19.86</td>
</tr>
<tr>
<td>Yellow</td>
<td>3.310</td>
<td>600</td>
<td>19.86</td>
</tr>
<tr>
<td>Red</td>
<td>2.837</td>
<td>700</td>
<td>19.86</td>
</tr>
</tbody>
</table>
1.2 LIGHT

Fig. 1.7 A traveling wave: (a) at time $t = T$, (b) at time $t = 2T$. A string is shaken periodically with a frequency $v$. The disturbance propagates to the right. After time $T$ ($T$ is the period) the wavefront has traveled the distance $\lambda = vT$. As $T = 1/v$ ($v = \text{frequency}$), we obtain $\lambda = v/v$ or $\lambda v = v$

From Equations 1.3 and 1.4 it follows with $v = c_0$ that

$$E = \frac{19.86 \times 10^{-26} \text{ J m}}{\lambda} = \frac{19.86 \times 10^{-26} \text{ J m}}{c_0} \times v = (6.62 \times 10^{-34} \text{ J s}) \times v = h v.$$

The constant $h$ is Planck's constant. Very precise and exact measurements have established the value $6.62606896 \times 10^{-34}$ J s for $h$. Thus our law of nature is written most simply as

$$E = h v \quad (1.5)$$

This fundamental relationship between frequency and the energy of a light quantum is well established. It is important to note that the value of $h$ obtained by Einstein from the photoelectric effect agrees with the value independently obtained by Planck from black body radiation (see Section 1.1.1).

1.2.2.5 Evaluation of work function $E_{\text{work}}$

For a more detailed evaluation the measured values of the kinetic energy $E_{\text{kin}}$ of the emitted photoelectrons are plotted versus the wavenumber $1/\lambda$ of the incident light in Fig. 1.8.

Fig. 1.8 Photoelectric effect: evaluation of work function. The kinetic energy $E_{\text{kin}}$ measured for the emitted photoelectrons in the experiment depicted in Fig. 1.2 is shown versus the wavenumber $1/\lambda$ of the incident light (filled circles). At $1/\lambda_0 = 10.470 \text{ cm}^{-1}$ the kinetic energy of the photoelectron yield approaches zero (open circle).
A linear relationship is observed with slope \( a = 1.986 \times 10^{-25} \text{ J m} \) and intercept with the abscissa at wavenumber \( 1/\lambda_0 = 10, 473 \text{ cm}^{-1} \):

\[
E_{\text{kin}} = a \left( \frac{1}{\lambda} - \frac{1}{\lambda_0} \right) = \frac{1}{\lambda} - \frac{1}{\lambda_0} = E - E_{\text{work}}.
\]

Then for the energy \( E \) of the incident photons and for the work function \( E_{\text{work}} \) we obtain

\[
E = a \frac{1}{\lambda} \quad \text{and} \quad E_{\text{work}} = a \frac{1}{\lambda_0} = 2.080 \times 10^{-19} \text{ J}.
\]

### 1.2.3 Interpretation of the Experiments

We can describe the observed phenomena on the basis of the following postulates:

- **Postulate:** Light behaves as a wave with wavelength \( \lambda \) traveling from a light source.
- **Postulate:** The probability that a light quantum is detected in a small area at a position \( x, y, z \) is proportional to this area and proportional to \( \psi^2 \), where \( \psi \) is the amplitude of the light wave at the position \( x, y, z \). Quanta of light of wavelength \( \lambda \) are packages of energy \( E = h\nu \), where \( \nu = c_0/\lambda \).

The first postulate does not say that light is a wave phenomenon (which would be in contradiction to the results of the photoelectric effect experiments). It only makes the weaker assertion that light does exactly what we expect a wave to do in certain experiments. The assumption of a wavelength \( \lambda \) also does not imply that a wave really exists, only that the diffraction experiments can be quantitatively analyzed in terms of this quantity.

The second postulate connects the wave and particle descriptions of light. We saw in Section 1.2.1 that the number of photons interacting with matter is proportional to the intensity of light falling on the object. In Section 1.2.2, we found that the intensity \( I \) of light is proportional to the square of its amplitude \( \psi \) in the wave picture.\(^2\) Thus the number of photons in a given small area on the screen is proportional to \( \psi^2 \) and to the area; hence, the probability of detecting one photon by its interaction with matter is proportional to \( \psi^2 \) and this area. To summarize, the probability that a light quantum is detected in a small area is proportional to this area and to \( \psi^2 \).

It is therefore clear that the properties of light cannot be described by the wave picture alone or by the particle picture alone. We require both features together to describe the observed phenomena, known as *wave–particle duality*.

### 1.3 ELECTRONS

Wave–particle duality is also required to describe the behavior of electrons, not just light. It is common to think of atoms, electrons, and the like as particles that follow Newton’s laws; however, the wave characteristics of electrons can also be important. Because of their small mass, the wave properties of electrons are easy to observe and are essential for describing the structure of atoms and molecules. The particle nature of electrons is discussed

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\(^2\) This experimental finding is not surprising, as \( I \sim \psi^2 \) follows from Maxwell’s electrodynamic theory.
in Section 1.3.1, the wave nature of electrons in Section 1.3.2, and a unified perspective for electrons is provided in Section 1.3.3.

1.3.1 Particle Nature of Electrons

The particle nature of electrons is evident in many situations, such as the Wilson cloud chamber, Geiger counters, and scintillation on a fluorescent screen. Important particle properties of the electron include its discrete mass $m_e = 9.10938215 \times 10^{-31}$ kg and charge $-e = -1.602176487 \times 10^{-19}$ C ($e$ = elementary charge). Below we describe the original measurements by Millikan, which demonstrated that electrical charge occurs in discrete amounts.

Millikan’s oil drop experiment is straightforward in its physical design (see Fig. 1.9), and it demonstrates the discrete nature of electrical charge. Liquid droplets, generated by an aerosol nozzle, are injected into a chamber between two metal plates. By irradiation with X-rays the air in the chamber is ionized, and thus a negative electric charge $Q$ is transferred to the droplets. By applying an electric field $F = V/d$ between the two metal plates at distance $d$ the charged droplets can be trapped and levitated. Any uncharged droplets fall down and are not trapped. With the particles trapped, Millikan was able to determine the charge on a droplet by comparing the gravitational force (which depends on the mass of the droplet $m_{\text{drop}}$ and the gravitational constant $g$) acting on it to the electrostatic force ($QF$). He found that the total charge on the droplets occurred in clumps. By performing experiments on a large number of droplets and over a wide range of conditions, he found that all of his total charge measurements could be described by an integer multiple of a single value of the charge, that is, $Q = -ne$, where $n$ is the number of elementary charges). He determined the fundamental charge $e$ to be $1.591 \times 10^{-19}$ C, which is quite close to the more precise modern value of $e = 1.602176487 \times 10^{-19}$ C.

1.3.2 Wave Nature of Electrons

1.3.2.1 Diffraction Experiments

The wave nature of electrons can be demonstrated by diffraction experiments analogous to those for light. Instead of monochromatic light, electron diffraction experiments use a beam of electrons of a definite speed $v$. Such beams can be produced from a heated filament...
Photographic plate
Gold foil
Vacuum
Light
Electron

Fig. 1.10 Diffraction of electrons. (a) Production of an electron beam ($V_f$, voltage for heating filament; $V_a$, accelerating voltage) and diffraction from a gold foil (Davisson-Germer experiment). (b) Diffraction rings on a photographic plate (schematic). (c) Interference bands from diffraction by an edge in the case of monochromatic light ($\lambda = 633$ nm, left, see also Figure 1.5a) compared to the case of electrons of distinct speed ($v = 1 \times 10^6$ m s$^{-1}$, right). The enlargement of the photographs is chosen so that the distance between the first and second maximum is the same in each case. This distance is related to the wavelength $\lambda$ and the distance between edge and screen (see Fig. 1.5).

in an evacuated tube with an accelerating voltage (Fig. 1.10). Electrons leaving the heated filament acquire kinetic energy $eV_a$ in traveling through the accelerating voltage $V_a$. Such a device is called an electron gun. Because the accelerating voltage determines the kinetic energy, we can write the kinetic energy as

$$E_{\text{kin}} = \frac{1}{2} m_e v^2 = eV_a$$

and calculate the average speed as

$$v = \sqrt{\frac{2eV_a}{m_e}}. \quad (1.6)$$

If $V_a = 100$ V, for example, then

$$v = \sqrt{\frac{2 \times 1.602 \times 10^{-19} \text{C} \times 100 \text{V}}{9.109 \times 10^{-31} \text{kg}}} = 5.93 \times 10^6 \text{ m s}^{-1}.$$  

If an electron beam passes through a double slit, then a diffraction pattern, an image of bright and dark bands (as in Fig. 1.4b), can be observed on a fluorescent screen. The wavelength of the electrons can be calculated from the distance between bright bands, as in the case for light. We call the electron wavelength $\Lambda$ to distinguish it from the wavelength $\lambda$ of light.

The double-slit method for electrons requires special techniques, because the wavelength of electrons in practical experiments is very small. The slits must be placed extremely close together to produce an interference pattern. Experimentally, it is easier to use a thin piece of gold foil in which the crystal lattice of the gold foil acts as a diffraction grating for the
1.3 ELECTRONS

Table 1.2 lists the wavelengths $\Lambda$ found for electrons at different accelerating voltages $V_a$. The last column gives the product of the electron’s wavelength $\Lambda$ and its speed $v$. We see that essentially the same value $v\Lambda = 7.2 \times 10^{-4}$ m$^2$ s$^{-1}$ is obtained for both cases. If we try the experiment with still more speeds, we find the same relationship every time. This finding is reminiscent of that for light, where the product of the energy and the wavelength were a constant, suggesting that we might try to express the constant $7.2 \times 10^{-4}$ m$^2$ s$^{-1}$ in terms of the constant $h$. For the case of light the product had units of J s, or kg m$^2$ s$^{-1}$. The units suggest that we include a mass term, so we could try to divide $h$ by the mass of the electron. We find that

$$v\Lambda = \frac{h}{m_e} = \frac{6.63 \times 10^{-34} \text{ J s}}{9.109 \times 10^{-31} \text{ kg}} = 7.27 \times 10^{-4} \text{ m}^2 \text{ s}^{-1}.$$  

So, within the bounds of experimental error, the new constant $v\Lambda$ really can be written as a combination of the fundamental constants $h$ and $m_e$. We can hypothesize a new fundamental relationship for electrons as

$$\Lambda = \frac{h}{m_e v}$$  

This is called the de Broglie relationship, which is the fundamental expression relating wave and particle properties of the electron. As the speed $v$ of the electron increases, its wavelength $\Lambda$ decreases; in other words, $v$ and $\Lambda$ are inversely proportional.

### 1.3.3 Interpretation of the Experiments

The postulates that we developed for light can be recast for electrons:

- **Postulate:** An electron traveling from an electron source with speed $v$ behaves as a wave with wavelength $\Lambda = h/(m_e v)$. 

Postulate: The probability that an electron is detected in a small area at a position \(x, y, z\) is proportional to this area and proportional to \(\psi^2\), where \(\psi\) is the amplitude of the electron wave at the position \(x, y, z\) (wavefunction).

The second postulate is called Born’s probability postulate. Note the essence of our procedure: considering distinct experiments and drawing distinct conclusions (the two postulates).

1.3.4 Formal Similarity Between Electron and Photon

The formal similarity between an electron and a photon can be carried somewhat further by using Einstein’s relation \(E = mc^2\) from relativity theory, which relates the mass of a particle directly to its energy. As we have a way for determining the energy \(E\) of a photon, we can assign a mass to it, so that

\[
m_{\text{photon}} = E/c_0^2.
\]  

Combining Equations 1.5 and 1.8, we obtain

\[
E = m_{\text{photon}}c_0^2 = h\nu = \frac{hc_0}{\lambda},
\]

or

\[
\lambda = \frac{h}{m_{\text{photon}}c_0},
\]  

which looks very similar to the de Broglie relationship.

Nevertheless, photons and electrons differ in fundamental ways. For a photon, the speed \(c_0\) is a constant of nature. We can only speak of a mass for the photon in the sense of its motion at the speed of light; its rest mass is zero. When a photon interacts with matter, its entire quantum of energy can be transferred to the particle, in which case the photon ceases to exist. For electrons, the mass \(m_e\) is a constant of nature, and the wavelength \(\lambda\) depends on the speed \(v\).

1.4 QUESTIONS ARISING ABOUT WAVE–PARTICLE DUALITY

1.4.1 Single Event—Probability Statement; Collective Behavior—Definite Statement

Wave–particle duality is a basic tenet of our modern theoretical descriptions of the world and its behavior. We have seen that light and electrons behave on the one hand like particles,

\[E_{\text{kin}} = \frac{1}{2} m v^2 \frac{1}{\sqrt{1 - (v/c_0)^2}}.
\]

The effect is not significant, however, until the electron’s speed \(v\) approaches the speed of light \(c_0\). We neglect relativistic effects here.
1.4 QUESTIONS ARISING ABOUT WAVE–PARTICLE DUALITY

Fig. 1.11 Diffraction occurs for both light and electrons: (a) violet light or fast electrons, (b) red light or slow electrons.

and on the other hand like waves of wavelength

$$\lambda = \frac{h}{m_{\text{photon}} c_0} \quad \text{(light)} \quad \text{or} \quad \Lambda = \frac{h}{m_e v} \quad \text{(electrons)}.$$

The probability that a photon or an electron appears in a given small range at the position \(x, y, z\) is proportional to \(\psi^2(x, y, z)\) where \(\psi\) is the wavefunction. Experiments with very many photons or electrons lead to interference patterns like those in Fig. 1.11. If we carry out the corresponding experiment with only a few particles, however, then the patterns can look very different. Figure 1.12 shows the results of computer simulations with 26, 182, and 1900 particles. In the first case (Fig. 1.12a) no pattern is seen, in the second case (Fig. 1.12b) the pattern starts to become apparent, and in the third case (Fig. 1.12c) it is clearly evident. With increasing particle number it becomes less and less likely that the observed interference pattern deviates from the pattern that would be produced by an infinite number of particles.

For simplicity, let us assume that a particle appears in the area of each of the three interference bands of Fig. 1.12c with probability

$$P = \frac{1}{3}.$$

Then, for \(N\) particles, the probability that all of them appear in the top band, for example, is

$$P = \left(\frac{1}{3}\right)^N.$$

Fig. 1.12 Interference pictures: computer simulation with (a) 26, (b) 182, and (c) 1900 particles.
That is, \( \frac{1}{6} \) for \( N = 2 \), \( \frac{1}{35} \) for \( N = 4 \), and \( 2 \times 10^{-48} \) for \( N = 100 \). A detailed statistical analysis shows that the most likely distribution of particles is \( 1/3 \) in each band and that this occurs very rapidly as \( N \) increases.

Only probabilistic statements can be made about single events (“where will the next particle appear on the screen?”). Definite statements can be given for collective behavior: the interference pattern is reproducible with very large numbers of particles. In other words, a causal relationship is possible only for the collective behavior of large numbers of particles but not for single events.

We now consider what happens as the wavelength of the wave–particle becomes small. As with the water waves of Fig. 1.3a, the diffraction becomes less and less noticeable. The diffraction patterns of both light waves and electron waves are transformed gradually into shadow patterns. For light, wave optics goes over to ray optics, and for electrons wave mechanics goes over to classical mechanics as the wavelength becomes small. For the case of very energetic photons or very fast electrons, we can predict with near certainty that the particle will appear on the screen within the geometrically constructed shadow boundary; in this limiting case definite statements about single events are possible.

1.4.2 Wave–Particle Duality and the Need to Abandon Familiar Ways of Thinking

The experiments considered here force us to abandon old ways of thinking. It is therefore of fundamental significance to reflect on the way in which we obtain new knowledge, how conclusions are drawn from experiments, and how this leads to proposing new experiments.

1.4.2.1 You Cannot Trace the Path of a Photon or an Electron

We can detect single photons or electrons as particles by their effect on a detector, such as a fluorescent screen, a photodiode, or a light-sensitive microchip in a digital camera. However, it is not possible to trace a path for the particle, to say that the particle has traveled through either one slit or the other. If one slit or the other is closed, something completely new is observed on the screen: photons or electrons appear at places where they were never observed before (at the positions where the waves added through interference in the double-slit case, but not in the single-slit case). Thus it is not useful to ask about a particular trajectory for the electron.

1.4.2.2 Intuitive Aids Assist You to Grasp the Mathematical Formalism

Describing Experiments with Photons or Electrons

Water surface waves were introduced in Section 1.2.2 as an intuitive aid, an instrument to express the mathematical formulas describing the phenomena (Figs. 1.4 and 1.11). Particles and waves are also mental pictures that we use to describe physical phenomena concretely. Once the underlying mathematical formulation is discovered, the aids used in our imagination to construct the mathematical expressions (waves in a given medium, particles as really existing entities) should then be thrown away, and the mathematical formalism alone should be used to describe the phenomena (Fig. 1.13).

1.4.2.3 Reflect on the Development of our Everyday View to Understand the Strangeness of the Behavior of Photons or Electrons

The goal of physical sciences is to reduce the multitude of data received by sensory perception to a simple order. Throughout the history of physical sciences this order has been developed and refined. Numerous designs are being utilized to classify our experience as
1.4 QUESTIONS ARISING ABOUT WAVE–PARTICLE DUALITY

simply and completely as possible, in an attempt to present a logical picture from the totality of data.

This process is not different from our own experience of growing up. Infants perceive a multitude of events and they start to make connections between them. An important step in an infant’s development is reached when sensory perceptions are received and correspond to objects in space, changing their location and form.

With this interpretation of visual impressions, the classical picture of the world is created in the human mind (Fig. 1.14). With time these pictures become a model of reality that increasingly broadens. More and more new models (or hypotheses) are established and predictions are made. According to the outcome of these predictions of facts the hypotheses are accepted, modified, or rejected. This classical picture of reality succeeds in describing everyday experiences and is therefore deeply rooted in human beings. However, this picture is falsified by the experiments that lead to the postulates of quantum mechanics. We are forced to change our hypothesis of reality to which we are all so accustomed.

The unusual model of reality that is taught to us by the experiments in this first chapter must be carefully considered to avoid future pitfalls. Reflect on how you arrive at the given postulates starting from experimental facts and reflect on how you can avoid including more in your picture of reality than the logical ordering scheme of sensory perception requires.

1.4.2.4 Evolutionary and Revolutionary Approach to Quantum Mechanics

We explained experiments by using the classical terms waves and particles, and our path forward is to develop the postulates of quantum mechanics by gradually generalizing (evolutionary approach). It would be more logical to delve right into the general postulates of quantum mechanics, attempting to understand the world of chemistry on that mathematically abstract basis without referring to classical concepts (revolutionary approach). However, we prefer using the evolutionary approach because humans are more used to thinking in a classical way. Thinking in terms like “as if an electron would be a wave” and “as if the electron would be a particle” is enlightening for a chemistry student’s intuitive understanding, whereas immediately being exposed to the general postulates of quantum mechanics might cause more difficulties.

Fig. 1.13 Intuitive aids, useful in the beginning, are thrown away.

Fig. 1.14 Recognition of facts. Perception, hypothesis, prediction, confirmation (this means it is not falsified).
1.5 CONCLUSION

Light falling on a detector (e.g., a charge-coupled device (CCD) camera or photographic plate) behaves like a beam of particles, each generating a latent image at the point where the particle hits the screen. The distribution of these bright points is as if the particle were carried by a wave. This effect is most astonishing if the beam of particles passes a double slit. The same behavior is observed in similar experiments with electrons. The wave–particle duality of electrons is the basis for understanding the existence of atoms and molecules and their properties.