19 Quantum Physics

H2 Physics 9478

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Learning Outcomes

Candidates should be able to:

(a) show an understanding that the existence of a threshold frequency in the photoelectric effect provides evidence that supports the particulate nature of electromagnetic radiation while phenomena such as interference and diffraction provide evidence that supports its wave nature

(b) state that a photon is a quantum of electromagnetic radiation, and recall and use the equation $E = hf$ for the energy of a photon to solve problems, where h is the Planck constant

(c) show an understanding that while a photon is massless, it has a momentum given by $p = E/c$ and $p = h/\lambda$, where c is the speed of light in free space

(d) show an understanding that electron diffraction and double-slit interference of single particles provide evidence that supports the wave nature of particles

(e) recall and use the equation $\lambda = h/p$ for the de Broglie wavelength to solve problems

(f) show an understanding that the state of a particle can be represented as a wavefunction ψ, e.g. for an electron cloud in an atom, and that the square of the wavefunction amplitude $|\psi|^2$ is the probability density function (including calculation of normalisation factors for square and sinusoidal wavefunctions)

(g) show an understanding that the principle of superposition applies to the wavefunctions describing a particle's position, leading to standing wave solutions for a particle in a box and phenomena such as single-particle interference in double-slit experiments

(h) show an understanding that the Heisenberg position-momentum uncertainty principle $\Delta x \Delta p \gtrsim h$ relates to the necessity of a spread of momenta for localised particles, and apply this to solve problems

(i) show an understanding of standing wave solutions ψ_n for the wavefunction of a particle in a one-dimensional infinite square well potential

(j) solve problems using $E_n = \frac{h^2}{8mL^2}n^2$ for the allowed energy levels of a particle of mass *m* in a one-dimensional infinite square well of width *L*

(k) show an understanding of the existence of discrete electronic energy levels for the electron's wavefunction in isolated atoms (e.g. atomic hydrogen) and deduce how this leads to the observation of spectral lines

(l) distinguish between emission and absorption line spectra

(m) solve problems involving photon absorption or emission during atomic energy level transitions.

Introduction

Wave theory of light has been highly successful in describing phenomena such as diffraction, interference and polarisation, leading to the creation of radio waves, radar and optical filters, just to name a few. However, wave theory of light is unable to explain phenomena such as blackbody radiation, **photoelectric effect** and **atomic line spectra**.

The search for an explanation for these experiments led to breakthrough at the beginning of the 20th century, resulting in the birth of modern physics – **quantum mechanics** and **relativity**. While quantum mechanics deals with the "lows" (low temperature, small sizes), Einstein's relativity deals with the "highs" (high velocities, large distances).

In this chapter, we will discuss important aspects of quantum theory – quantisation, duality and uncertainty. The concept of quantisation was first suggested by Max Planck during his study of blackbody radiation in 1900. Inspired by Planck's work, Einstein theorised that electromagnetic (EM) radiation itself is quantised – that EM radiation transports energy in quanta called photons – and successfully explained the photoelectric effect in 1905. James Franck and Gustav Hertz then showed conclusively that energy levels in atoms are quantised in 1914, which then provided an explanation for atomic line spectra.

The bizarre behaviour of EM radiation – that it has both wave and particle properties – led de Broglie to propose the **wave-particle duality** for EM radiation and matter in his doctoral dissertation in 1924. His idea was way ahead of its time and there was a real possibility that de Broglie failed his doctoral interview, if not for the intervention by Einstein. Experiments conducted by Clinton Davisson and Lester Germer in 1927 showed that electrons, indeed, have wavelike properties.

19.1 The Photoelectric Effect

❖ Theories of Light

Two apparently contradictory theories of the nature of light were competing in the 17th century. The corpuscular theory proposed by Sir Isaac Newton (English, 1643–1727) regarded light as a stream of tiny particles travelling at high speed in a straight line. The corpuscular theory did account for rectilinear propagation, reflection and refraction – the latter by assuming that on entering an optically denser medium the corpuscles are attracted, thereby causing bending towards the normal. On the other hand, the theory proposed by Christiaan Huygens (Dutch, 1629–1695) in 1678 considered light as a wave. His wave model can also account for reflection and refraction.

Opponents of the wave theory argued that waves require a medium for transmission and there did not appear to be one for light which was able to travel in vacuum. Subsequently a medium, called the ether, was invented but it defied all attempts at detection. An apparently crucial difference between the two theories was that whereas the corpuscular theory predicted light to have a greater speed in any medium denser than air while the wave theory predicted the opposite. Thomas Young (English, 1773–1829) demonstrated interference of light through his famous Young's double-slit experiment in 1801 which were readily explicable in terms of waves. The wave theory prediction was further confirmed in 1862 when Jean Bernard Léon Foucault (French, 1819–1868) found the speed of light in water was less than that in air. In 1865, Maxwell derived theoretically that electric and magnetic fields travel through space as waves moving at the speed of light. He proposed that visible light is a type of electromagnetic wave, and his equations can be used to derive the laws of reflection and refraction that were well established in geometrical optics. This firmly establishes that light is a wave phenomenon.

The photoelectric effect was first discovered in 1887 by Heinrich Hertz (German, 1857–1894). In his experiments to prove the existence of electromagnetic radiation, he discovered that electrodes illuminated with ultraviolet light create electric sparks more easily.

This phenomenon, known as the **photoelectric effect**, can be easily demonstrated with the gold-leaf electroscope shown in Fig. 19.1.

The electroscope is given a negative charge. When ultraviolet (UV) light of wavelength 254 nm is incident on the zinc plate, the gold leaf falls rapidly. No change in the position of the leaf is observed when UV light of wavelength 365 nm or a much brighter (higher intensity) white light is incident on a negatively charged electroscope.

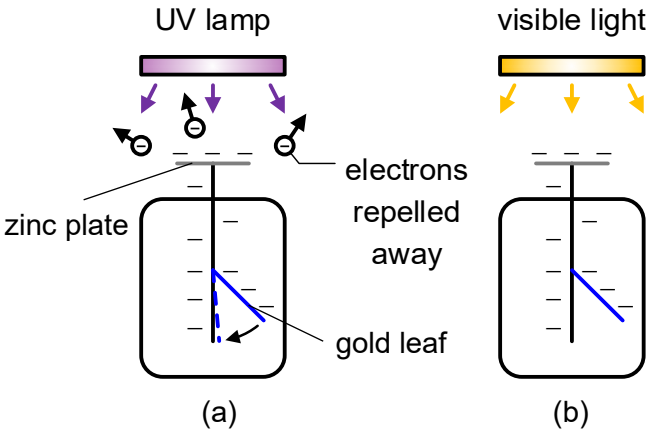


Fig. 19.1 (a) Leaf falls rapidly as electrons are repelled away. (b) No change in position of leaf since no electrons are emitted.

Based on these observations, we can conclude that negatively charged particles escaped from the surface of the zinc plate when light is incident on it but this effect is dependent on **frequency** or **wavelength** but not on intensity of light. Specific charge (q/m) of these ejected particles confirms that they are indeed electrons.

According to the wave theory, one plausible explanation of the photoelectric effect is that when EM radiation is incident on a surface of a material, the oscillating electric field causes the electrons to oscillate. Over time, these electrons may acquire sufficient energies to escape from the surface. Fig. 19.2 shows the electric and magnetic fields as functions of position for a linearly polarised sinusoidal plane electromagnetic wave.

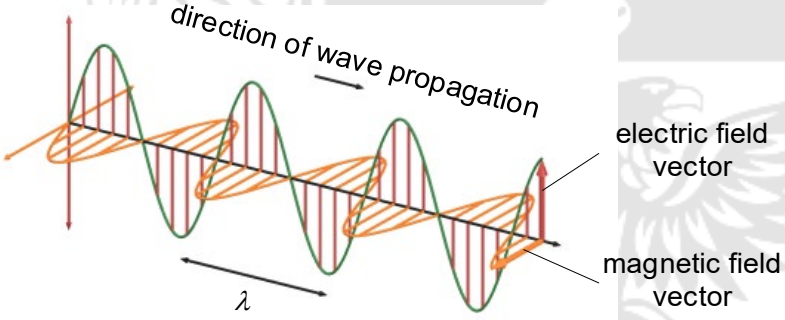


Fig. 19.2

However, this implies that photoelectric emission should always occur when a metal surface is illuminated by light of any frequency which contradicts the observation that there is a minimum (threshold) frequency of light necessary for photoelectric effect to take place.

❖ Quantum Theory of Light

Einstein solved the puzzle of the photoelectric effect by proposing that light behaves as if it consists of localised bundles, or quanta, of light

energy. Gilbert Lewis (American, 1875–1946), a chemist, coined the term photon in 1926 to refer to a quantum of energy of EM radiation

Photon

A **photon** is a quantum of energy of electromagnetic radiation.

The energy E of a photon is proportional to its frequency f:

$$E = hf$$

where $h = 6.63 \times 10^{-34}$ J s is the Planck constant.

A photon has zero mass. Its energy E and momentum p are related by the equation:

$$p = \frac{E}{c}$$

where $c = 3.00 \times 10^{8}$ m s^{-1} is the speed of light in free space.

The equation $p = E/c$ can be obtained from the relativistic energy-momentum relation $E^2 = (pc)^2 + (mc^2)^2$ by setting $m = 0$ as photons are massless.

Since $E = hf$,

$$p = \frac{E}{c} = \frac{hf}{c} = \frac{h}{\lambda}$$

where λ is the wavelength of the photon.

Thus, the energy and momentum of a photon are both proportional to the frequency and inversely proportional to the wavelength of the corresponding electromagnetic radiation.

❖ Existence of Threshold Frequency

Observations in photoelectric experiments show that there exists a minimum value of frequency of the incident light beam known as the **threshold frequency f_0**, below which there will be no photoelectric emission, regardless of the intensity of the light beam. Einstein provided a simple explanation for these observations. For a given material, a minimum energy (known as work function ϕ) is required to free an electron from the surface. According to Einstein, light consists of photons, and a **single** electron absorbs all the energy of a **single** photon arriving at the surface. The electron can escape from the surface only if the energy it acquires is at least equal to work function ϕ. Thus, electrons will be ejected only if:

This minimum energy is called the work function ϕ.

$$hf \geq \phi$$

$$f \geq \frac{\phi}{h}$$

The threshold frequency for photoemission is $f_0 = \frac{\phi}{h}$.

19.2 Wave-Particle Duality

Light acts like a wave even though it consists of particles called photons. Some phenomena such as interference and diffraction demonstrate the wave nature of light. Others such as the photoelectric effect point to the particle nature of light. This wave-particle duality means that light has two aspects that seem to be in conflict. That is not the case as both the

wave descriptions and the particle descriptions are complementary. Both are needed to complete the model of nature, but they are not used at the same time to describe a single part of an occurrence.

In 1925, Louis de Broglie suggested that particles might also exhibit this duality and have wave properties. If a particle acts like a wave, it should have a wavelength and a frequency. De Broglie postulated that a free particle with rest mass m, moving with speed v, should have a wavelength λ related to its momentum p in exactly the same way as a photon. The **de Broglie wavelength** of a particle is then:

$$\lambda = \frac{h}{p}$$

De Broglie Wavelength

The de Broglie wavelength is the wavelength associated with a particle that is moving.

❖ Electron Diffraction

Diffraction of electrons was discovered by Davisson and Germer when it was shown that a beam of electrons directed at a single crystal produced a diffraction pattern.

At around the same time, Sir George Paget Thomson (son of Sir Joseph John Thomson) tested de Broglie's theory by directing electrons at a thin metal foil. Thin metal foils contain lots of tiny crystals called grains. Thomson showed that the electrons were diffracted to form a pattern of rings. The same pattern is obtained when X-rays are directed at the foil. Such a result shows that particles do have a wavelike nature. In other words, matter has a dual nature which is wavelike or particle-like.

Fig. 19.3 shows the pattern captured on a coated fluorescent screen when a beam of electron falls on a thin layer of graphite atom and is dispersed. The pattern is identical to that obtained due to interference of electromagnetic radiation. This is known as **electron diffraction** phenomenon.

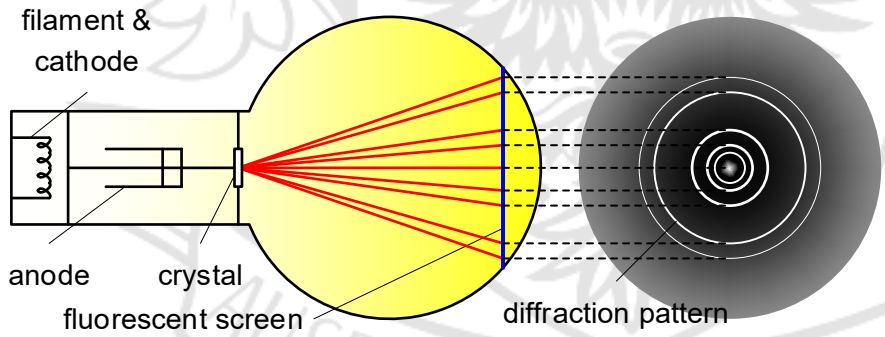


Fig. 19.3

❖ Double-slit Interference of Single Particles

Only since the early 1960s has there existed sufficiently precise technology to conduct double-slit experiments with electrons. The basic setup of the experiment is shown in Fig. 19.4(a).

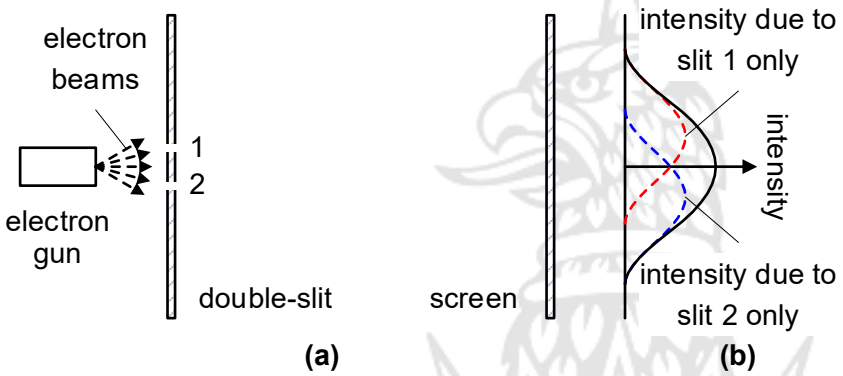


Fig. 19.4

If one slit is closed, the interference pattern on the screen disappears, and only the image of that slit (dotted line in Fig. 19.4(b)) is produced.

An electron is emitted from a plate that is heated in an electron gun and then accelerated across a potential difference *V*. It then passes through a double slit on its way to the screen. If electrons behave like particles, they will travel in straight lines from the electron gun through one of the slits and on to the screen. As the electrons might get slightly deflected as they pass through the slit, the distribution of the electrons passing through each slit will be somewhat smeared out (dashed lines in Fig. 19.4(b)). Due to the very small slit separation, the distributions of the electrons passing through the two slits overlap on the screen and the total intensity is high along the principal axis (solid line in Fig. 19.4(b)). This is the expected intensity distribution when electrons exhibit particle-like behaviour when passing through the double-slit.

In 1976, P. G. Merli and his colleagues fired individual electrons through a double slit towards a screen. The distribution of the electrons on the screen was observed over time (Fig. 19.5).

Electron Interference

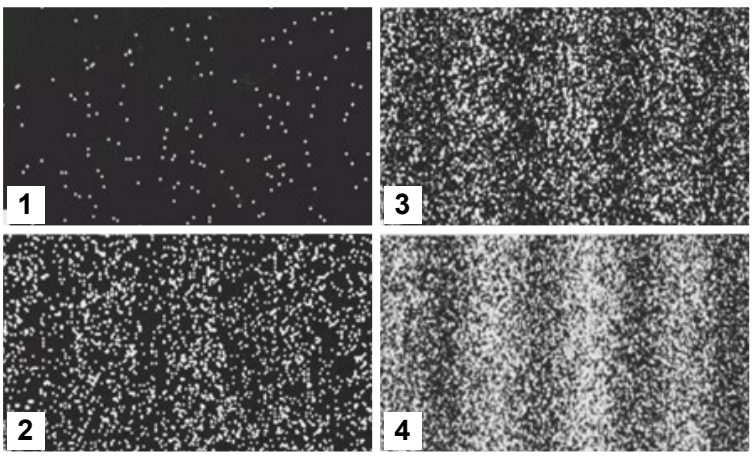


Fig. 19.5

Single Photon Interference

The interference fringes were clearly visible and the experiment clearly demonstrated the wave-like behaviour of electrons. Since photons have particle-like properties, it might be expected that photons striking the double slits would exhibit similar behaviour. Indeed, when the double-slit experiment was performed using one photon at a time, a distribution pattern of photons similar to Fig. 19.5 was observed. This will be further discussed in a later section.

Example 1

Calculate the de Broglie wavelength of

(a) a bullet of mass 30 g moving at a velocity of 250 m s^{-1},

(b) electrons in an electron beam which has been accelerated through a potential difference of 4000 V.

[Solution]

(a)

(b) By principle of conservation of energy,

loss in electric potential energy = gain in kinetic energy

For a particle to have an observable wave nature, the de Broglie wavelength should not be too small. As the value of *h* is very small, this implies that the mass *m* of the particle must also be very small for the wavelength to be noticeable. That is the reason why only electrons and subatomic particles exhibit observable wavelike properties.

19.3 Wavefunction of a Particle

We have now seen compelling evidence that on an atomic or subatomic scale, an object such as an electron cannot be described simply as a classical point particle. Instead, its wave-like characteristics must be considered. We will explore how to describe the state of a particle by using only the language of waves. This new description, called **quantum mechanics**, replaces the classical scheme of describing the state of a particle by its coordinates and velocity.

In quantum mechanics, the state of a particle is described by its wavefunction ψ. It encapsulates information about the particle such as momentum, position and energy.

❖ Probability and Normalisation

The square of the absolute value of the wavefunction $|\psi|^2$ of a particle at each point is known as the **probability density function**. For a particle that can move only along the *x*-direction, the quantity $|\psi|^2 dx$ is the probability that the particle will be found at a coordinate in the range from

$|\psi|^2$ itself is not a probability. It is the probability density function also known as

x to $x + dx$. The particle is most likely to be found in regions where $|\psi|^2$ is large. This interpretation, first made by Max Born (German, 1882–1970), requires that the wavefunction ψ be **normalised**. Mathematically, this means that the integral of $|\psi|^2 dx$ over all possible values of x must equal exactly 1. Physically, this condition implies that the probability of finding the particle somewhere in space is 1 (or 100%).

the probability distribution function.

$$\int_{-\infty}^{\infty} |\psi|^2 dx = 1$$

This integral over all space of the probability density is also known as the **normalisation integral**.

Wavefunctions of which the normalisation integral is finite is said to be **normalisable**. Only normalisable wavefunctions can represent a quantum state and such functions are physically admissible. On the other hand, any wavefunction of which its normalisation integral is infinite cannot properly represent a quantum state and therefore is not physically admissible.

Besides the normalisation condition, a wavefunction must be **single-valued**, **continuous** and **smoothly varying** in regions that the particle can be found.

❖ Particle in an Infinite Potential Well

Consider a particle confined to the region $0 \le x \le L$ and the potential energy U distribution in space is that of an **infinite potential well** (Fig. 19.6) such that the potential energy of the particle is as follows:

The trapped particle bounces back and forth between the walls of the well. We assume that the walls are infinitely hard so that the particle instantly reverses its velocity each time it strikes the wall without any energy loss.

$$U(x) = \begin{cases} \infty & x < 0 \\ 0 & 0 \le x \le L \\ \infty & x > L \end{cases}$$

This function is often called the **square well potential**.

Fig. 19.6

The motion of the particle is akin to a travelling wave reflecting off a fixed end giving rise to a standing wave.

The wavefunction ψ of a quantum particle is zero outside the region $0 \le x \le L$ as the particle cannot be found outside the well.

The wavefunction within the region $0 \le x \le L$ is very much like a standing wave in a string stretched between the walls of the well, in which the ends of the string must be nodes (at the walls):

The particle is free ($U = 0$) within the region.

$$\psi(x) = A\cos(\kappa x) + B\sin(\kappa x)$$

where $\kappa = \dfrac{2\pi}{\lambda}$ is the wave number.

Since ψ must be continuous at the boundaries, ψ must also be zero at $x = 0$ and $x = L$. These are known as the **boundary conditions** for the particle.

At $x = 0$,

$$\psi(0) = 0$$

$$A\cos(\kappa \cdot 0) + B\sin(\kappa \cdot 0) = 0$$

$$A = 0$$

That is, $\psi(x) = B\sin(\kappa x)$ in the interval between 0 and L.

At $x = L$,

$$\psi(L) = 0$$

$$B\sin(\kappa L) = 0$$

$$\kappa L = n\pi$$

$$\kappa = \frac{n\pi}{L}$$

$$\frac{2\pi}{\lambda_n} = \frac{n\pi}{L}$$

$$\lambda_n = \frac{2L}{n} \qquad (n \in \mathbb{Z}^+)$$

Although $n = 0$ is also a solution, it is physically inadmissible as the wavelength would be infinite for any finite value of L.

These are the possible wavelengths of the particle trapped in this potential well.

Normalising the wavefunction,

$$\int_{-\infty}^{\infty} |\psi(x)|^2 \, dx = 1$$

$$B^2 \int_0^L \sin^2\left(\frac{n\pi x}{L}\right) dx = 1$$

$$\tfrac{1}{2} B^2 \int_0^L 1 - \cos\left(\frac{2n\pi x}{L}\right) dx = 1$$

$$\tfrac{1}{2} B^2 \left[x - \frac{L}{2n\pi} \sin\left(\frac{2n\pi x}{L}\right) \right]_0^L = 1$$

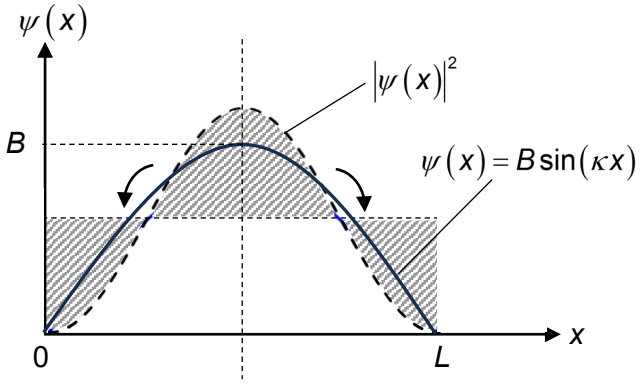
$$B = \sqrt{\frac{2}{L}}$$

$\psi(x) = 0$ for $x < 0$ and $x > L$.

$\sin(2n\pi) = 0$ as $n \in \mathbb{Z}^+$

For simplicity, the positive root is chosen.

Graphically, normalising the wavefunction means to equate the area under $|\psi(x)|^2 - x$ graph to 1.



area under $|\psi(x)|^2 - x$ graph $= 1$

$$\left(\frac{B^2}{2}\right)L = 1$$

$$B = \sqrt{\frac{2}{L}}$$

Therefore, the normalised wavefunction is $\psi_n(x) = \sqrt{\frac{2}{L}}\sin\left(\frac{n\pi x}{L}\right)$.

The solutions for a particle in an infinite potential well are:

$$\psi_n(x) = \begin{cases} 0 & x < 0 \\ \sqrt{\frac{2}{L}}\sin\left(\frac{n\pi x}{L}\right) & 0 \le x \le L \\ 0 & x > L \end{cases}$$

where n is now known as the **quantum number**.

Fig. 19.7 shows the wavefunctions ψ and probability density function $|\psi|^2$ for the four lowest quantum numbers. Each plot shows the relative likelihood of finding the particle at particular positions in the well when performing a position measurement.

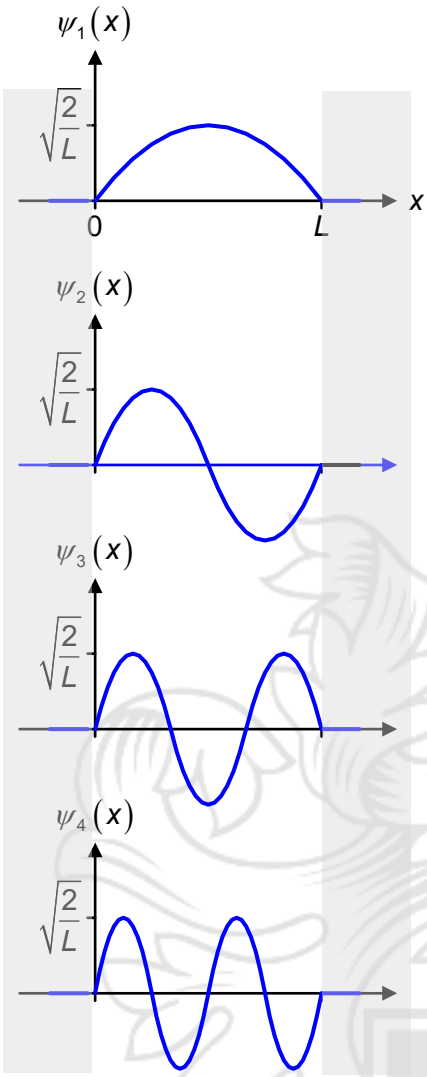


Fig. 19.7(a)

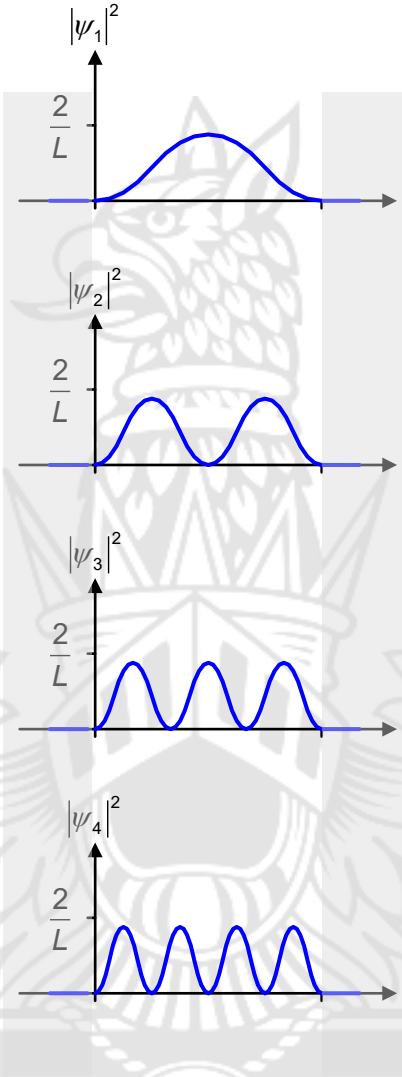


Fig. 19.7(b)

We see from Fig. 19.7(b) that $|\psi|^2 = 0$ at some points, so there is zero probability of finding the particle at exactly these points.

Shaded regions are regions where the particle cannot exist.

Example 2

A particle is trapped in an infinite potential well in the region $0 \le x \le L$ and is equally likely to be found at any position between $x = 0$ and $x = L$. Determine the wavefunction ψ in terms of L.

The probability distribution for finding a particle at any particular

[Solution]

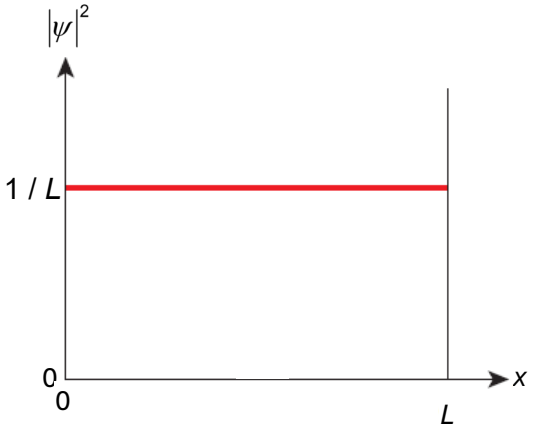
The wavefunction takes the form:

$$\psi = C$$

where C is a constant.

Imposing the normalisation condition,

position trapped in an infinite potential well.



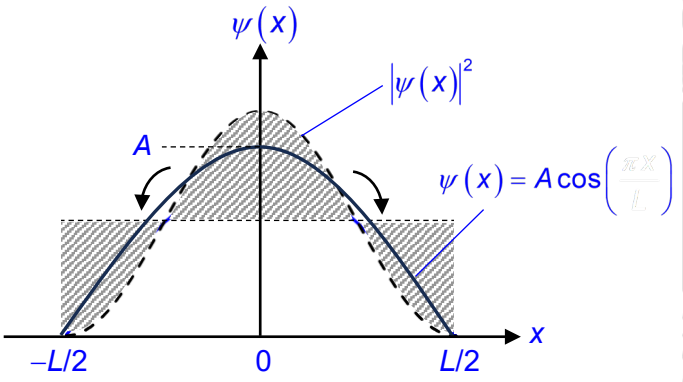
Hence, the normalised wavefunction is

Example 3

A particle is trapped in an infinite potential well in the region $-L/2 \le x \le L/2$. Determine the normalised wavefunction ψ of the longest possible wavelength in this potential well in terms of x and L.

[Solution]

$\psi(x) = A\cos(\kappa x) = A\cos(\quad)$ $(\because$ longest wavelength $\lambda =$ $)$



❖ **Energy of Particle in a Well**

For a particle of mass m in an infinite potential well of width L, the total energy E_n corresponding to the quantum number n is given by the equation:

$$E_n = K_n + U = \frac{p_n^{\,2}}{2m}$$

where K_n is the kinetic energy and U is the potential energy ($U = 0$).

Since $p_n = \dfrac{h}{\lambda_n}$ and $\lambda_n = \dfrac{2L}{n}$,

$$E_n = \frac{p_n^{\,2}}{2m} = \frac{h^2}{2m\lambda_n^{\,2}} = n^2 \cdot \frac{h^2}{8mL^2} = n^2 E_1 \qquad (n \in \mathbb{Z}^+)$$

where $E_1 = \dfrac{h^2}{8mL^2}$ is the **ground-state energy**.

The lowest energy of a particle in a well is non-zero.

This is a consequence of the Heisenberg uncertainty principle (§19.5). A particle in a zero-energy state would have a definite value of momentum (precisely zero), so the uncertainty in its position would be infinite, and the particle could be found anywhere along the x-axis. But this is impossible, since a particle in a well must be confined between $x = 0$ and $x = L$. Hence $E = 0$ is not allowed.

The total energy is proportional to n^2, and inversely proportional to m and L^2. Fig. 19.8 shows the **energy-level diagram** for the five lowest quantum numbers.

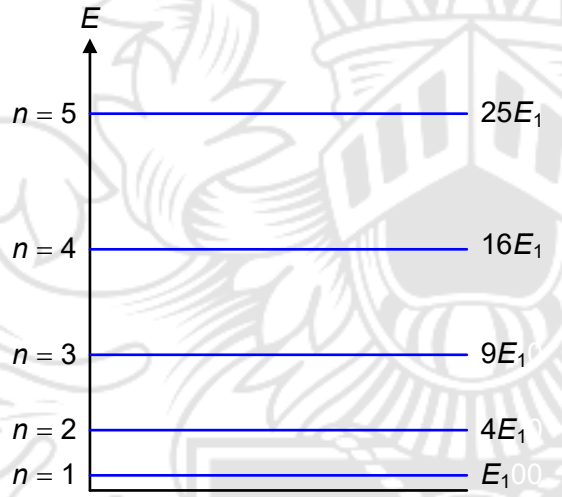


Fig. 19.8

Because the energies of these states are lower than the (infinite) height of the potential well, the states are referred to as **bound states.** The infinite potential well has an infinite number of bound states.

Example 4

Determine, in eV, the ground-state energy of an electron confined within a box of width 2.00×10^{-10} m.

$1\ \text{eV} = 1.60 \times 10^{-19}$ J

Typical diameters of atoms are in the order of 10^{-10} m, so this result allows us to estimate the energies (order of 10 eV) of orbital electrons in atoms, even though the potential energy of real atoms are not the same as an infinite potential well.

Example 5

Calculate the energy difference between the first two energy levels for an electron confined to a one-dimensional box of width 5.00×10^{-10} m.

[Solution]

Difference in energy

ΔE between the two lowest energy levels is 4.52 eV. An electron confined to a box is different from an electron bound in an atom, but it is reassuring that this result is of the same order of magnitude as the difference between actual atomic energy levels.

Example 6

Show that for a proton confined to a box of width 1.1×10^{-14} m (diameter of an intermediate-sized nucleus), the energies of the first two levels are about a million times larger than that of the electron in example 5.

[Solution]

Difference in energy

ΔE between the two lowest energy levels of a proton in the nucleus is in the order of MeV. This suggests why gamma ray emitted from radioactive decay has much higher energy than a photon from the line spectrum of atoms.

❖ **Double-Slit Experiment Revisited and Wavefunction**

Young performed the original double-slit experiment with sunlight in 1801. Soon after de Broglie's hypothesis in 1923 that matter can be described as a wave, diffraction experiments were performed with other particles. Young's double-slit interference experiment has been performed with electrons (1961), neutrons (1988), helium atoms (1991), and even with C60 buckyballs (1999).

The double-slit experiment is entirely consistent with the wave picture of light or matter and so would not appear to include any particle-like behavior. However, if we can control the source well enough to reduce the incident intensity so low that only one particle leaves the source every second, then we can observe particle behavior with our own eyes. In the case of light beam, the particles of light are photons. For the electron beam in Fig. 19.4(a), the particles are electrons. Given that the relevant detection screen used is sensitive enough, the low intensity source produces individual blips on the screen corresponding to the arrivals of the individual particles.

At first, these blips appear at random places on the screen (particle nature). However, as more blips are recorded, we begin to see that the density of blips coincides with the interference pattern from the wave model (wavelike nature). These observations are in line with wave-particle duality.

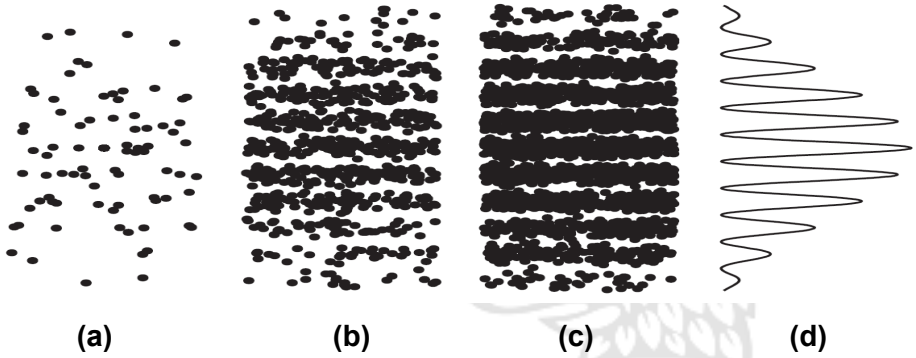


Fig. 19.9 The arrival of particles (photons or electrons) at the detection screen in a double-slit experiment, showing (a) random early arrivals, (b) and (c) the buildup of an interference pattern and (d) a plot of the interference intensity distribution

Fig. 19.10 The intensity distribution from the single-particle double-slit experiment is plotted based on the histogram that shows the counts, i.e. number of particles (e.g. electrons) hitting the screen in a coordinate interval.

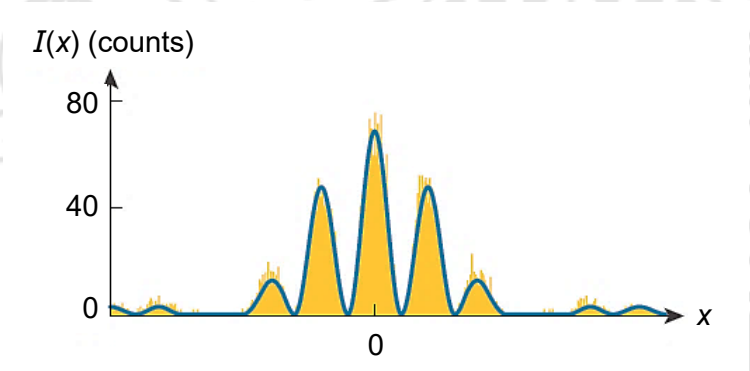


Fig. 19.10

Note that the interference pattern in Fig. 19.10 is not a result of multiple particles passing through the slits simultaneously and interacting with one another. Even when the incident intensity is reduced so that only one particle encounters the double slits at a time, the pattern still builds up. Because this interference pattern obeys the principle of superposition, we are forced to conclude that the particle wavefunction must pass through both slits simultaneously and interfere with itself. Only by describing the particle as a wavefunction can we account for its wave-like interference and its detection as a localised event.

Electron Interference

For discussion purposes, consider a single electron fired at two closely spaced slits. Its wavefunction is ψ.

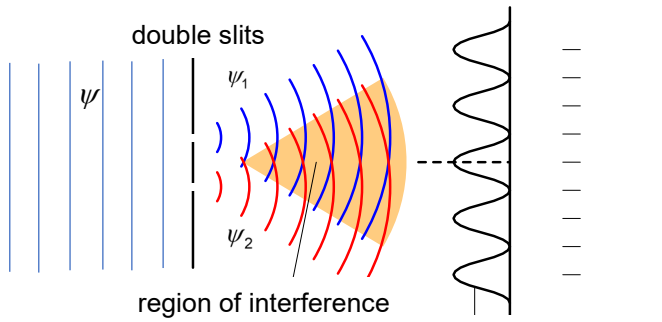


Fig. 19.11(a)

The electron's wavefunction ψ undergoes diffraction at each slit, two coherent wavefunctions ψ_1 and ψ_2 emerge from the slits and interfere with one another, as shown in Fig. 19.11(a). The resultant wavefunction of the electron is the **superposition** of the wavefunctions from each slit, expressed as $\psi_{total} = \psi_1 + \psi_2$, where

ψ_1 is the wavefunction of the electron if only slit 1 is open,
ψ_1 is the wavefunction of the electron if only slit 2 is open.

Fig. 19.11(b) shows the electron's resultant wavefunction ψ_{total} as a function of *x*, the position coordinate on the detection screen.

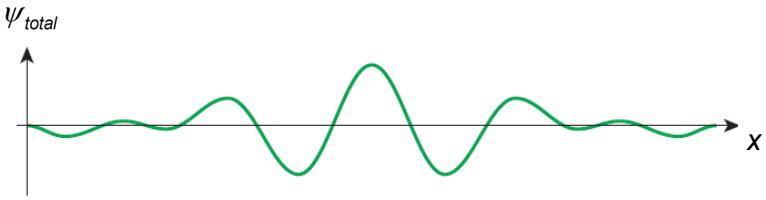


Fig. 19.11(b)

Fig. 19.11(c) shows the intensity distribution of electrons hitting the screen in the double-slit experiment.

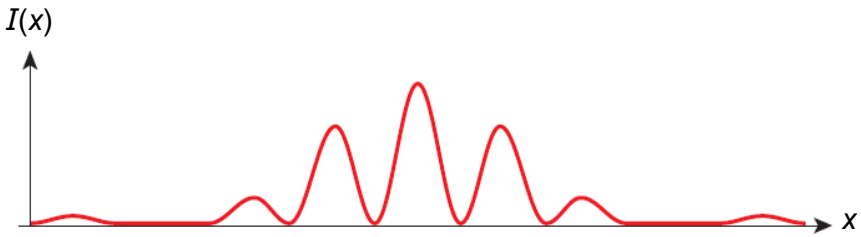


Fig. 19.11(c)

$|\psi_{total}|^2$ gives the probability density function of where the electron will land. The intensity when both slits are open is proportional to $|\psi_1 + \psi_2|^2$. The interference pattern reflects the probabilistic nature of the wavefunction.

While ψ_{total} behaves like a wave (obeying principle of superposition), the electron is always detected as a single discrete point when it hits the screen—a process known as *wavefunction collapse*.

The double-slit experiment acts as a fundamental demonstration of quantum mechanics, validating that a single particle's wavefunction interferes with itself to create a probabilistic interference pattern while

The intensity is proportional to the square of the absolute value of the wavefunction, i.e. $|\psi|^2$

$|\psi_{total}|^2 \neq |\psi_1|^2 + |\psi_2|^2$ due to interference effect.

If the electron beam is directed at the double-slit with one slit blocked half of the time, and then the other slit is blocked during the remaining time, the intensity distribution will be proportional to $|\psi_1|^2 + |\psi_2|^2$, i.e. there is no interference.

being detected as a localised particle on a screen, thus illustrating wave-particle duality.

19.4 Energy Levels of Atoms and Line Spectra

In the early 1900s, scientists were fascinated with the spectra obtained from gaseous elements and were carrying out investigations on the properties of these spectra. However, during that time, one could neither explain why the spectral lines form such distinctive patterns nor how they came about.

❖ Energy Levels in Atoms

In 1913, Niels Bohr proposed an explanation for the line spectra by considering the spectral lines of the hydrogen gas and applying Planck's quantum theory to the atom. Bohr's model of the atom is like a miniature solar system. He imagined the electron of the hydrogen atom whirling round the nucleus (proton), like a planet revolving around the Sun shown in Fig. 19.12.

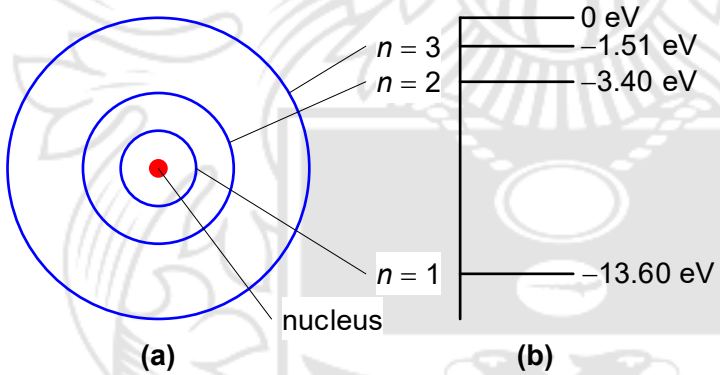


Fig. 19.12

Fig. 19.12(a) Allowed orbits**. (b)** Corresponding energy levels of hydrogen atom. The uppermost level corresponds to $n = \infty$ and energy $E = 0$.

Bohr postulated that for the hydrogen atom or any other **isolated** atoms:

1. There are only certain allowed orbits in the atom, and each corresponds to a fixed energy value. Electrons are only allowed to revolve about the nucleus in these orbits. This means that the electrons can only take on a discrete set of energy values when they are bound to the atom.
2. An atom in its lowest energy state is said to be in the **ground state** ($n = 1$). Usually, the atoms are in the ground state unless they are at a very high temperature.

"States" and "levels" are used interchangeably.

3. An atom can absorb energy (Fig. 19.13) ΔE, e.g. by absorbing a photon, to cause an electron to transit from a lower energy state E_l to a higher energy state E_h where $\Delta E = E_h - E_l$. The atom is then said to be excited and the higher energy state is known as an excited

state. Since E_h and E_l both belong to a discrete set of values, ΔE and hence λ also take on a discrete set of values. This is why the absorption spectrum is discrete.

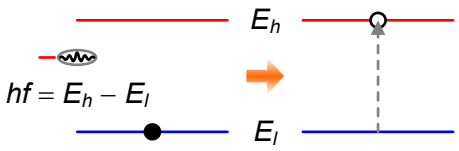


Fig. 19.13 shows only one possible way for an electron to be excited to higher energy level.

Fig. 19.13 Absorption of photon to cause excitation.

4. An atom in an excited state will typically quickly de-excites to a lower energy state, usually the ground state. During the process, a photon of energy $hf = E_h - E_l$ is emitted, giving rise to the emission spectrum. Evidently, the possible wavelengths of the emission spectrum are the same as that of the absorption spectrum.

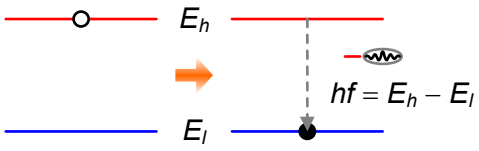


Fig. 19.14 Emission of photon during de-excitation.

❖ Excitation of Electrons in Atoms

There are two main ways in which an electron can be ionised or excited to a higher energy state.

1. **Particle collision** (with atoms, ions or electrons)

   A high-speed particle may collide with an atom and impart energy to cause an electron to be excited to a higher energy level. The incident particle may transfer part or whole of its energy to the electron.

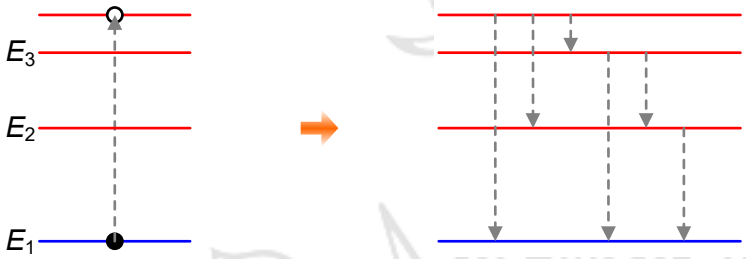
   The amount of energy transferred must be sufficient for the orbital electron to excite to a higher energy level. The energy of the incident electron **need not exactly match** the difference in energy levels of the atom.

2. **Absorption of photons**

   For an orbital electron to gain energy from an incident photon, the energy of the photon must be **exactly equal** to the energy difference between the two energy levels of the transition, i.e., $hf = E_h - E_l$. In this case, the photon will be absorbed by the electron and ceases to exist. If the energy of the photon is not exactly equal to the energy difference between two energy levels in the atom, then there will be no transition and the photon will **not** be absorbed but is merely scattered away.

❖ De-Excitation of Electrons in Atoms

An electron at a higher energy state will de-excite to a lower energy state by emitting photons. For electrons at E_3 state or higher, there are multiple possible "paths" for the electron to de-excite to the ground state. Therefore, one or more photons of different energies may be emitted.



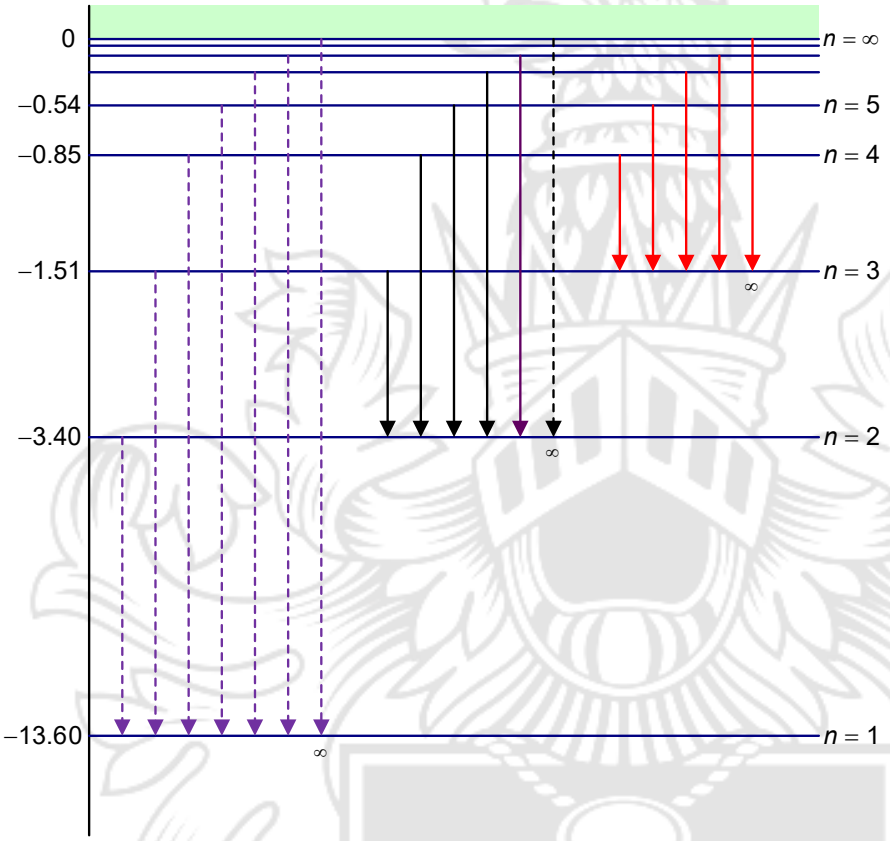
heating or electric discharge

possible transitions when electrons de-excite to ground state

Fig. 19.15 An electron in the 2nd-excited state E_3 may de-excite to either E_1 or E_2, which then further de-excites down to E_1.

❖ Energy Levels of Hydrogen Atom

By using these postulates, Bohr was able to work out the energy states of the hydrogen atom and account for the wavelengths observed in the hydrogen spectrum. Fig. 19.16 shows the energy-level diagram for the hydrogen atom and the possible transitions from higher energy states to lower energy states.



If the ground state is assigned an energy value of 0 eV (i.e., the reference level), then the higher levels will have energy of positive values.

Fig. 19.16 Energy level diagram for hydrogen atom.

Key features of the energy-level diagram

1. n is the principal quantum number and can only take integer values from 1 to ∞.
2. The **ground state** refers to the lowest energy state ($n = 1$) in which the atom is the most stable. An atom is said to be in an **excited state** ($n \geq 2$) when its electrons are found in the higher energy states.
3. The highest energy state $n = \infty$ corresponds to an energy state whereby the electron is no longer bound to the atom, i.e., the electron has escaped from the atom. Conventionally, it is assigned an energy value of 0 eV.
4. The **ionisation energy** of an atom is the minimum energy required to remove an electron completely from the atom. This corresponds to a transition from the ground state to highest energy state $n = \infty$. The ionisation energy for hydrogen atom is 13.60 eV.
5. The energy difference between any two adjacent states gets smaller as n increases.

Ionisation is the process of creating charged particles. A positive ion is produced when electrons are removed from a neutral atom.

❖ Emission Line Spectrum

When gas like hydrogen or neon fills a discharge tube at low pressure with a high voltage applied between the ends of the tube, the gas starts to glow, and light is emitted from the electric discharge tube. If this light is examined through a diffraction grating with a spectrometer, a spectrum consisting of well defined, distinct lines is observed as shown in Fig.19.17. This type of spectrum is known as an **emission line spectrum**.

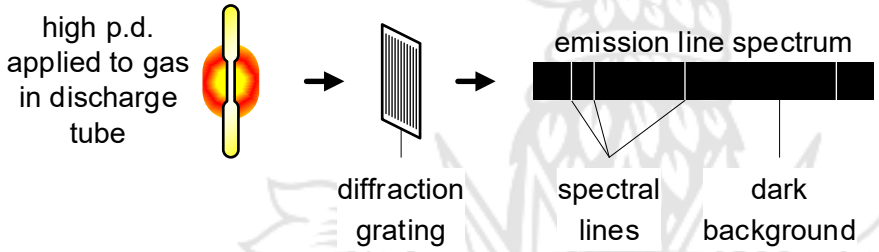


Fig. 19.17

When a gas is heated or bombarded by electrons (in discharge tube), the electrons in the gas atoms (typically in ground state) are excited to higher energy states. The excited electrons quickly de-exciting to lower energy states by emitting photons with energy corresponding to the energy difference between the two energy states.

As the energy levels are discrete, the energy differences between the energy levels are also discrete. Hence, the wavelengths of the emitted photons are discrete. These wavelengths correspond to the series of lines on the emission line spectrum.

Gaseous atoms of different elements emit characteristic electromagnetic radiations. For example, neon tubes glow orange-red while sodium lamps emit yellow.

Features of the emission line spectrum:

- The emission line spectrum consists of **discrete bright lines** of definite wavelengths (different colours) on a **dark background**.
- A series of lines is observed which form a definite pattern that is unique to the element.

Fig. 19.18 shows the spectral lines of hydrogen.

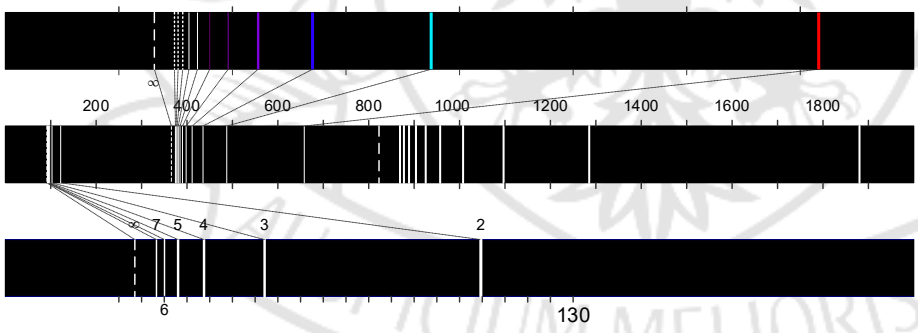


Fig. 19.18

Fig. 19.18 Line spectra of hydrogen – consisting of Lyman, Balmer and Paschen series.

The **Lyman** (ultraviolet) series of lines corresponds to electron transitions (de-excitation) to the level $n = 1$, the Balmer (visible) series are produced by transitions to $n = 2$ and the Paschen (infrared) series

are produced by transitions to $n = 3$; each series being named after its discoverer.

❖ Absorption Line Spectrum

If **white light** (containing all visible wavelengths) passes through a cool gas, the atoms of the cool gas absorb photons of certain frequencies to jump from a lower energy level to a higher one. The frequency of the photon absorbed must be exactly equal to the energy difference between the two energy levels.

By cool gas, we mean most of the gas atoms are at the ground state.

After the absorption, the excited atom will quickly return to the lower energy state by emitting a photon. However, these emissions occur in all directions and therefore have lower intensities. Hence, when the light emerging from the discharge tube is passed through a diffraction grating, light of these frequencies appears to be **missing** from the continuous spectrum.

This continuous bright spectrum crossed by dark lines is called the **absorption line spectrum**.

Fig. 19.19 shows the setup to obtain an absorption line spectrum.

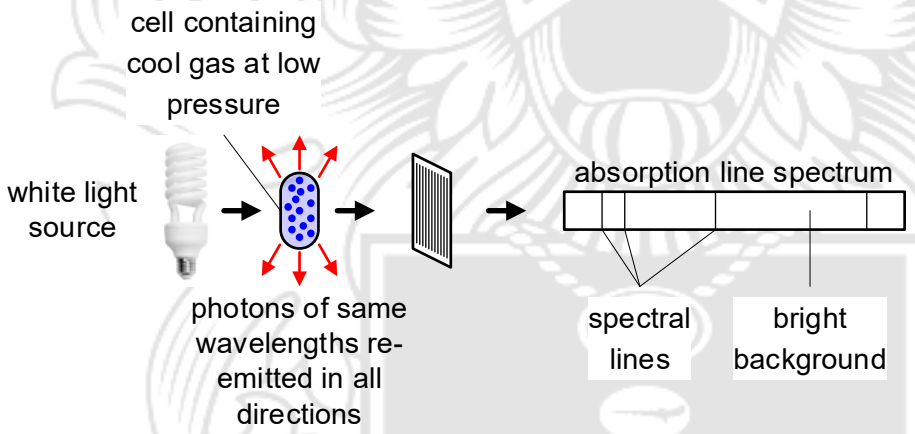


Fig. 19.19

Features of the absorption line spectrum:

- The absorption line spectrum consists of **dark lines on a bright background**.
- A series of lines is observed which form a definite pattern.
- Different gases will result in different patterns (unique to the atom).

Spectral lines are often used to identify atoms and molecules based on their electromagnetic radiation. These spectral lines are unique to each type of atoms and can serve as unique "fingerprints" for its identification via comparison to previously collected "fingerprints" of atoms and molecules. This method enables one to identify the atomic and molecular components of stars and planets, which otherwise would be impossible.

Fig. 19.20 shows the spectrometer (top view) set up to observe spectral lines.

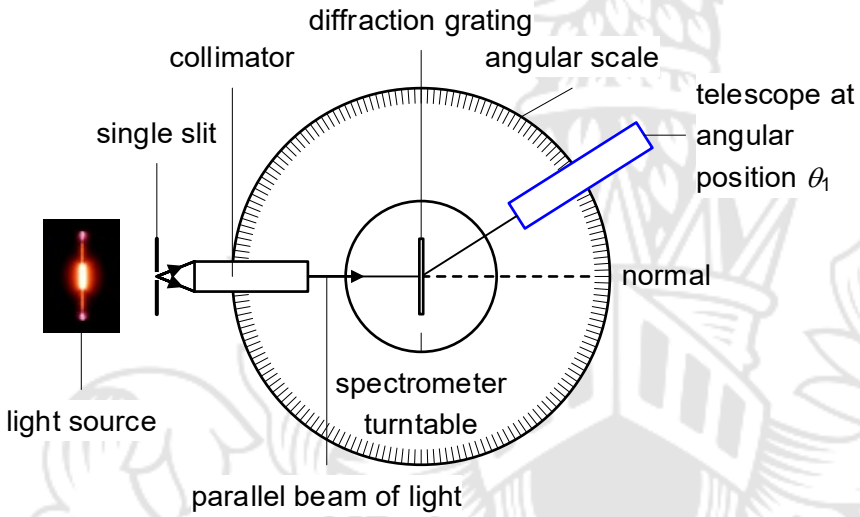


Fig. 19.20

Fig. 19.21 shows the different types of spectra that may be observed.

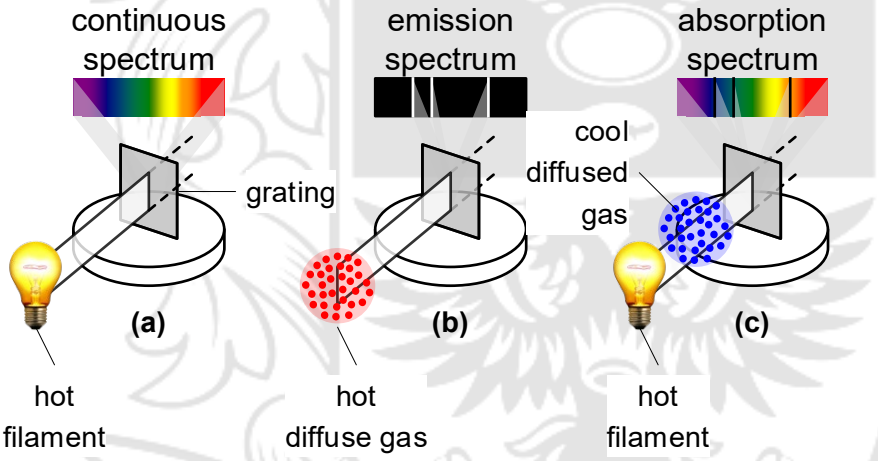


Fig. 19.21

(a) A hot solid emits a **continuous spectrum of light**.

(b) A hot diffuse gas emits specific wavelengths of light, resulting in an **emission line spectrum** that consists of **bright lines on a dark background**.

(c) White light after passing though cool diffuse gas, results in an **absorption spectrum** that consists of **dark lines on a bright background**.

Example 7

Explain how emission line spectra provided evidence that the energy levels of an atom are quantised.

[Solution]

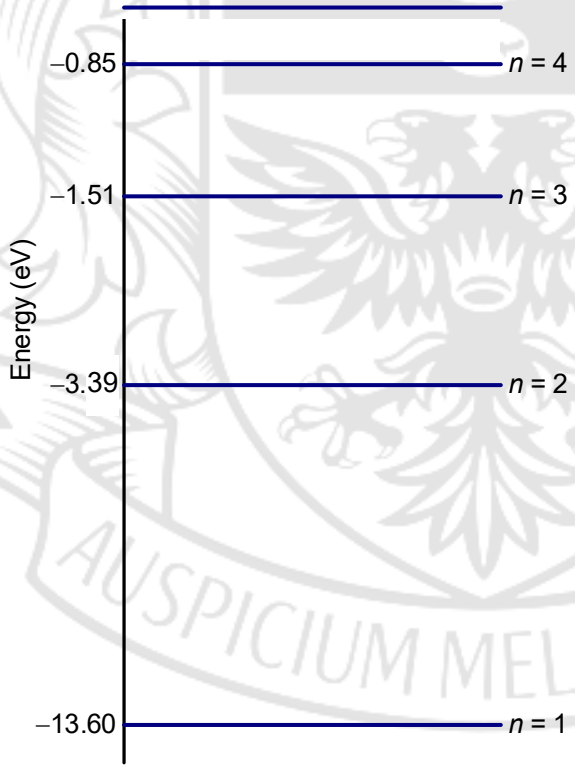
The line spectra of atoms consist of _____ of light emitted, rather than a _____ range. This shows that only certain photon energies are produced, since the energy of a photon is given by $E = \frac{hc}{\lambda}$.

Each _____ corresponds to an atom transitioning from a _____ to a _____ energy level, with the photon energy equal to the _____ between these two levels. The fact that only specific photon energies are observed means that only specific energy differences — and hence only _____ — exist within the atom.

Therefore, the line spectra provide evidence that the energy levels of atoms are _____, or _____.

Example 8

Figure below represents the energy levels of the four lowest states of a hydrogen atom.



(a) State the ionisation energy.

(b) Calculate the longest wavelength of the photon emitted by a spectral transition between any pair of the four energy levels.

(c) Mark on the figure a transition which will result in the emission of radiation of wavelength 489 nm. Show your calculation.

(d) Determine what happens to a beam of photons of energy

(i) 12.09 eV

(ii) 5.25 eV

when passed through a cool vapour of atomic hydrogen.

(e) Determine the total number of spectral lines, which will be detected in the emission spectrum of atomic hydrogen, due to transitions between the four energy levels.

[Solution]

(a)

(b) The longest wavelength corresponds to the _____ energy of photon.

(c) Energy of photon

Since photon is emitted, an orbital electron must transit between two energy levels which has an energy difference of 2.54 eV. Hence, the electron transits from _____ to _____ (a downward arrow from the energy level of energy _____ to _____).

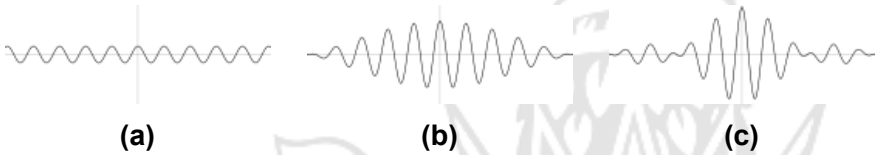
(d) **(i)** 12.09 eV exactly matches the energy difference between _____ state and the _____ excited state. Hence, some photons will be absorbed by electrons to excite the electrons to _____ energy level.

(ii) An orbital electron in the ground state would be excited to _____ energy level if it absorbs a 5.25 eV photon. This energy level _____ and hence the photons will _____.

(e) Total number of spectra lines is

19.5 Heisenberg Uncertainty Principle

Uncertainty is inherent in the nature of things, even with the use of perfect instruments and experimental techniques. To understand the uncertainty principle, first imagine that a particle has a single wavelength that is known exactly. According to the de Broglie relation $\lambda = h/p$, we will thus know the momentum of the particle to be precisely $p = h/\lambda$. In reality, a single-wavelength wave would exist throughout space; any region along this wave is hence the same as any other region, as illustrated in Fig. 19.22(a).



(a) **(b)** **(c)**

Fig. 19.22(a) Single wavelength **(b)** & **(c)** Multiple wavelengths.

If we were to ask, "Where is the particle that this wave represents?", there would be no special location in space along the wave that could be identified with the particle – all points along the wave are the same. Therefore, we have infinite uncertainty in the position of the particle and we know nothing about its location. Perfect knowledge of the particle's momentum has cost us all information about its location.

Conversely, we can construct a wave packet such as that shown in Fig. 19.22(b) by adding waves of different wavelengths together which will produce an interference pattern which will localise the wave. Since the wave packet has a finite spatial extent, we now have a better idea where the particle is located. However, we can no longer speak with certainty what the wavelength (and hence momentum) of the particle is, since the wave packet consists of waves of different wavelengths.

Another possible analogy would be to imagine you are holding one end of a rope and you generate a wave by shaking it up and down periodically. If someone asks, "Where precisely is that wave?", you would probably not be able to answer. The wave isn't precisely anywhere, but it is spread out over a length of say 10 m. On the other hand, if someone asks "What is the wavelength", you could give a reasonable answer, say 30 cm. By contrast, if you gave the rope a sudden jerk, you would get a relatively narrow bump travelling down the line. This time, the first question ("Where precisely is that wave?") is a sensible one, while the second question ("What is the wavelength?") is a nutty one as the motion isn't even periodic, so how can one assign a wavelength?

Fig. 19.23 shows a wave with a **larger uncertainty in wavelength** (and momentum) but a **smaller uncertainty in position**.

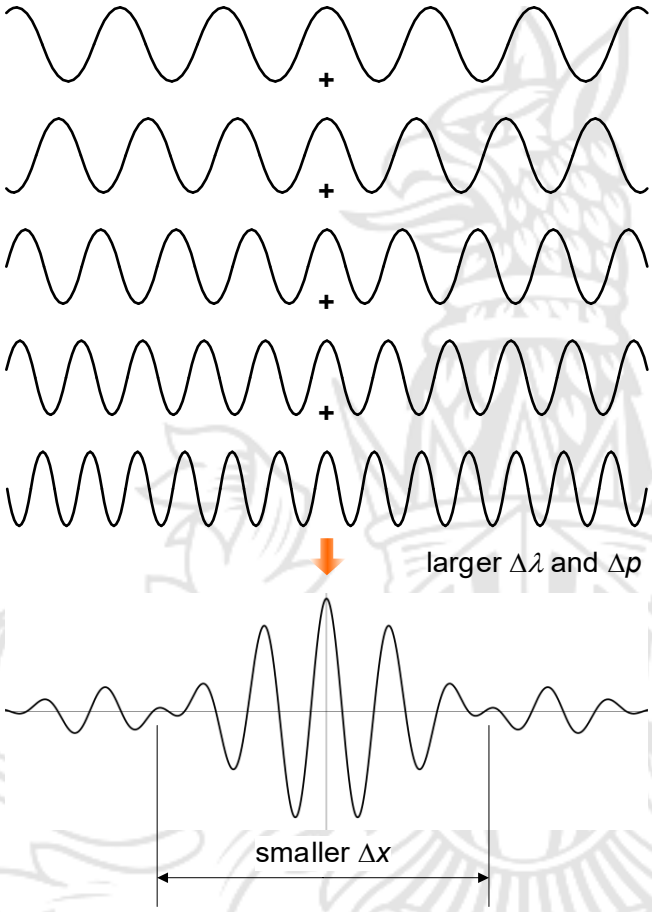


Fig. 19.23

Fig. 19.24 shows a wave with a **smaller uncertainty in wavelength** (and momentum), but a **larger uncertainty in position**.

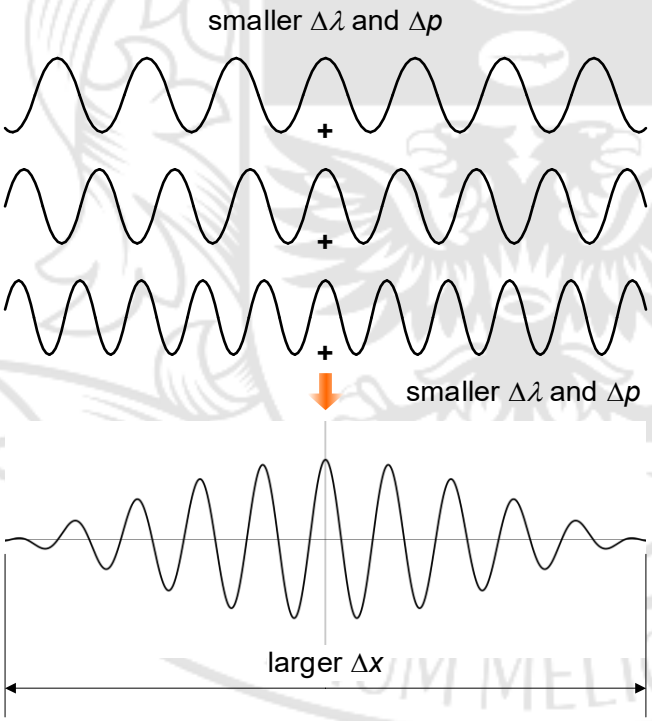


Fig. 19.24

This forms the crux of the Heisenberg uncertainty principle. In 1927, Werner Heisenberg (German, 1901–1976) suggested that nature

imposes a limit to the precision with which the position and momentum (in the same direction) of a particle can be measured simultaneously. However, Heisenberg was also careful to point out that these inevitable uncertainties arise from the quantum structure of matter instead of imperfections in practical measuring instruments. For intermediate cases, you can say that it has a fairly defined wavelength and a fairly defined position, but there is an inescapable trade-off between the position and momentum.

The Heisenberg uncertainty principle states that if a measurement of the position of a particle is made with uncertainty Δx and a simultaneous measurement of its x-component of momentum is made with uncertainty Δp, the product of the two uncertainties is approximately:

$$\Delta x \Delta p \gtrsim h$$

Example 9

The speed of an electron is measured to be 5.00×10^3 m s^{-1} to an accuracy of 0.0020%.

Calculate the uncertainty in determining the position of this electron.

[Solution]

Fractional uncertainty in momentum

From the Heisenberg uncertainty principle,

Example 10

Use the Heisenberg uncertainty principle to estimate the energy of the lowest bound state of a particle of mass m in a one-dimensional infinite square well of width L. Assume that uncertainty in position is the width of the well and the uncertainty in momentum is the same as that of the momentum itself.

[Solution]

The estimate is larger by a factor of 4 when compared to the exact result of $E = \frac{h^2}{8mL^2}$ which is not too bad.

Example 11

A bullet of mass 50 g and an electron are both moving at 300 m s^{-1}. The uncertainty in the speed measurement is 0.010%. If the position and speed are measured at the same time, determine the accuracy of the measurement of the position of each object.

[Solution]

Fractional uncertainty in momentum

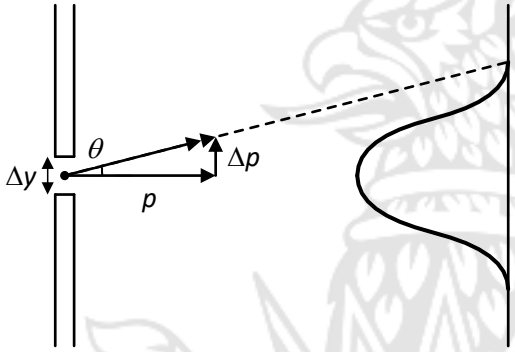
For bullet,

For electron,

We see that the _____ are only significant for _____ particles.

Example 12

A beam of electron of speed v ($\ll c$) is incident on a narrow slit of width b. Show that the width of the pattern detected on a screen far from the slit obeys the Heisenberg uncertainty principle.



[Solution]

When the beam of electron is made to pass through the narrow slit, the uncertainty in the y-position Δy:

From Heisenberg uncertainty principle,

The narrow beam is now spread over a small angular displacement θ.

Since θ is small,

which is the formula to determine the positions of the first minima for diffraction through a single slit of width b.

19.6 Appendix

The equation of motion that describes how a wavefunction depends on space and time is known as the Schrödinger equation. For one-dimensional problems, the time-independent Schrödinger equation is:

$$-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2}+U(x)\psi(x)=E\psi(x)$$

The first term in this equation is product of the kinetic energy and wavefunction. $U(x)$ represents the potential energy, which is a function of x, and E is the total mechanical energy of the wave. The time-independent Schrodinger equation is an expression of the principle of energy conservation:

$$\left[K(x)+U(x)\right]\psi(x)=E\psi(x)$$

For the case of the particle in the infinite potential well where $U = 0$, Schrödinger equation reduces to:

$$-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2}=E\psi(x)$$

$$\frac{d^2\psi(x)}{dx^2}=-\frac{2mE}{\hbar^2}\psi(x)$$

which is of the same form as the defining equation of simple harmonic motion where $\frac{d^2x}{dt^2}=-\omega^2x$.

Therefore, solutions to the Schrödinger equation are:

$$\psi(x)=\psi_0\sin(\kappa x)$$

where $\kappa^2=\frac{2mE}{\hbar^2}$.

Hence,

$$E_n=\frac{\hbar^2\kappa_n{}^2}{2m}=\frac{1}{2m}\left(\frac{h}{2\pi}\right)^2\left(\frac{2\pi}{\lambda_n}\right)^2=\frac{h^2}{2m}\left(\frac{n}{2L}\right)^2=\frac{h^2}{8mL^2}n^2$$