

TOPIC 14

The atom and quantum mechanics

14.1 Overview

14.1.1 Module 8: From the universe to the atom

Quantum mechanical nature of the atom

Inquiry question: How is it known that classical physics cannot explain the properties of the atom?

Students:

- assess the limitations of the Rutherford and Bohr atomic models
- investigate the line emission spectra to examine the Balmer series in hydrogen (ACSPH138)
- relate qualitatively and quantitatively the quantised energy levels of the hydrogen atom and the law of conservation of energy to the line emission spectrum of hydrogen using:
 - $E = hf$
 - $E = \frac{hc}{\lambda}$
 - $\frac{1}{\lambda} = R \left[\frac{1}{n_f^2} - \frac{1}{n_i^2} \right]$ (ACSPH136)
- investigate de Broglie's matter waves, and the experimental evidence that developed the following formula:
 - $\lambda = \frac{h}{mv}$ (ACSPH140)
- analyse the contribution of Schrödinger to the current model of the atom.

FIGURE 14.1 Photograph of 'aurora australis', the southern lights. In an aurora, atoms of the gases in the upper atmosphere emit radiation after being excited by interactions with charged particles from the Sun.



14.2 Limitations of the Rutherford atomic model

14.2.1 Rutherford unhinged

With all the success of Thomson and Rutherford in developing a picture and working model of the atom, several problems remained. In a planetary model of the atom, orbiting electrons that are accelerating should emit electromagnetic radiation continuously; however, this was never observed. Electrons should spiral into the nucleus as they emit this radiation. Following this model to its conclusion implied that all atoms are inherently unstable; again, this was not observed. Further, there was a second difficulty: excited atoms do emit electromagnetic radiation, but the spectrum is discrete, consisting of specific colours and unique for each element (much like the unique harmonic structure and timbre of a musical instrument), which are properties associated with waves. This puzzle concerning the stability of atoms was yet to be solved, but the emergence of quantum mechanics would unify all these confusing and often contradictory observations.

14.2.2 Bohr's model of the atom

Niels Bohr (1885–1962), a Danish physicist, was one of eleven Nobel prize winners who were trained by Rutherford. Before moving to Manchester to work with Rutherford, Bohr had worked for a short time at the Cavendish Laboratory under J. J. Thomson. Bohr and Thomson did not get along. At their first meeting, Bohr informed Thomson that one of Thomson's equations was wrong. There were several similar incidents and Bohr later recalled his disappointment that Thomson was not interested to learn that his work was incorrect. Bohr did acknowledge that his own lack of knowledge of the English language contributed to the failure of the two men to hit it off. One of Bohr's first contributions was to predict that a hydrogen atom would contain only one electron outside the positively charged nucleus. (At the same time, others predicted that one-electron atoms could not exist.)

Bohr attempted to apply the new quantum ideas of Planck and Einstein to the model of the hydrogen atom. Planck had managed to find an equation that solved the problem of the 'ultraviolet catastrophe' that troubled the theory of black-body radiation. Planck held a traditionalist's view of physics and was opposed to the statistical processes of Boltzmann. After attempting to explain his black-body equation, Planck reluctantly tried to derive it using the methods of Boltzmann. This involved dividing the energies up into small amounts and eventually should have finished with an integration in which all the energies would have been added together and would have experienced the problem of an infinite energy. However, before that final step, Planck realised that he had reached his equation for black-body radiation and therefore did not 'complete' the process. Einstein later showed that the problem of infinities will occur in any process where 'classical' theories and quantum theories are linked.

Planck interpreted his result as meaning that the 'atomic oscillators' that produced the radiation could vibrate only with certain discrete amounts of energy. These discrete amounts of energy were called **quanta**.

Einstein later extended this idea to the radiation itself being quantised. Einstein's 'quanta of light' were later named '**photons**' by Gilbert Lewis (1875–1946).

Bohr uses quantum theory to explain the spectrum of hydrogen

Bohr knew that, somehow, atoms must produce radiation that formed a characteristic spectrum for each element (see Physics in focus on 'The spectra of gases'). Bohr realised that the 'atomic oscillators' of Planck were

FIGURE 14.2 Niels Bohr



probably electrons in the atom. The Rutherford model failed to provide any information about the radius of the atom or the orbital frequencies of the electrons. Bohr attempted to introduce the quantum ideas of Planck to the atom, but at first failed.

Early in 1913, Bohr was introduced to Balmer's equation (see below) for the wavelengths of the spectral lines of hydrogen and it 'made everything clear to him'. After seeing this equation, Bohr realised how electrons were arranged in the hydrogen atom and also how quantum ideas could be introduced to the atom.

14.2.3 Balmer's equation for the hydrogen atom

Johann Jakob Balmer (1825–1898) completed a PhD in mathematics in 1849. He became a teacher at a girls' school in Basel, Switzerland, and had a desire to 'grasp the harmonic relationships of nature and art numerically'. Anders Angström (1814–1874) had measured the wavelengths of four of the spectral lines of hydrogen (now known as the Balmer series). Balmer found an equation that enabled him to calculate the wavelengths of these and, he believed, the infinite number of spectral lines emitted by hydrogen.

Balmer's equation was $\lambda = b \left(\frac{n^2}{n^2 - 2^2} \right)$ and the constant b was found empirically to be 364.56 nm.

Janne Rydberg (1854–1919) modified Balmer's equation for wavelength to produce the familiar equation:

$$\frac{1}{\lambda} = R_H \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right)$$

where

λ = wavelength of the emitted radiation

R_H = Rydberg's constant ($R_H = 1.097 \times 10^7 \text{ m}^{-1}$)

n_f and n_i are integers.

The wavelengths of the visible lines of hydrogen correspond to $n_f = 2$ and $n_i = 3, 4, 5$ or 6 . Of course, this is an **empirical equation** (Balmer played around with numbers until he arrived at something that worked).

Sometimes the equation $\frac{1}{\lambda} = R_H \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right)$ is known as the

Rydberg equation. Sometimes it is called Balmer's equation. Rydberg had attempted to find his own equation for the spectral lines of hydrogen. He was unsuccessful and, as his contribution was to modify Balmer's equation, we will continue to refer to it as the Balmer equation.

FIGURE 14.3 Johann Jakob Balmer

Permission clearance pending

14.2 SAMPLE PROBLEM 1

CALCULATING THE WAVELENGTHS OF HYDROGEN SPECTRAL LINES

Calculate the wavelength of the visible spectral line of hydrogen with the longest wavelength.

SOLUTION:

From Balmer's equation $\frac{1}{\lambda} = R_H \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right)$, we can see that the longest wavelength will occur when

the term $\left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right)$ is smallest.

As the visible spectral lines correspond to $n_f = 2$, the smallest value will be when $n_i = 3$.

$$\begin{aligned}\frac{1}{\lambda} &= R_H \left(\frac{1}{2^2} - \frac{1}{3^2} \right) \\ &= 1.097 \times 10^7 \left(\frac{1}{2^2} - \frac{1}{3^2} \right) \\ &= 1.524 \times 10^6 \\ \lambda &= 6.562 \times 10^{-7} \text{ m}\end{aligned}$$

The wavelength is 6.562×10^{-7} m. This is the wavelength of the red line in the hydrogen spectrum in figure 14.4.

14.2 Exercise 1

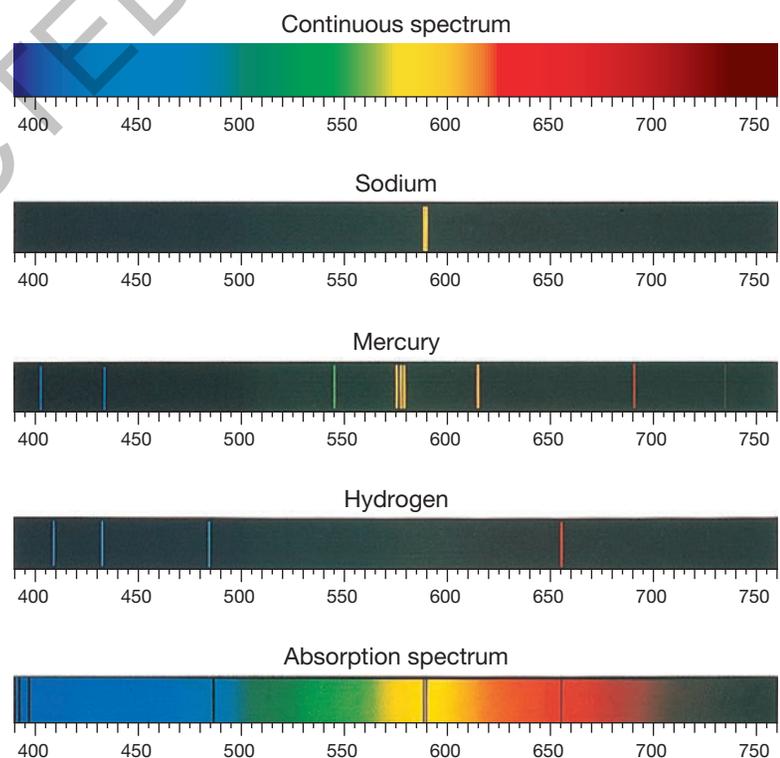
- 1 A hydrogen atom makes a transition from the third excited state ($n = 4$) to the ground state. Use Balmer's equation to determine the wavelength and, hence, the energy of the photon emitted.
- 2 Is this photon in the visible part of the electromagnetic spectrum? If not, classify the photon.

14.2.4 The spectra of gases

There are three types of emission spectra: continuous spectra, bright-line spectra and band spectra. Continuous spectra are produced by incandescent objects, bright-line spectra are produced by excited gases and band spectra are produced by excited molecules. We will consider the bright-line emission spectra of excited gases and also the absorption spectra of cool gases (as shown in figure 14.4).

Spectral lines are produced as images of the slit that is an essential component of any spectroscope. After passing through the slit, the different wavelengths of light are diffracted by different amounts by a grating or dispersed by a prism by different amounts. Hence, the images of the slit corresponding to the different wavelengths are separated. When the slit is very narrow, closely spaced lines can be resolved (distinguished from one another). If the slit is wider, more light is admitted, but at the expense of the resolution.

FIGURE 14.4 A continuous white light spectrum, the emission spectra of excited atoms of the elements sodium, mercury and hydrogen, and an absorption spectrum. The red line in the hydrogen spectrum is known as the H_α line, and the other lines as H_β , H_γ and H_δ respectively.



An **emission spectrum** (see figure 14.5) is produced when a gas is excited. A gas can be excited by heating it or by passing an electrical discharge through it. The emission spectrum is a series of narrow coloured lines on a dark background. Each element has its own characteristic spectrum and this can be used to identify the gas.

An **absorption spectrum** (see figure 14.6) is produced when white light is passed through a cool gas. The atoms in the gas absorb energy from the white light. The atoms will then re-emit the energy that was absorbed. The energy will be emitted as light and it will be emitted in random directions. Therefore, the transmitted beam of light will be deficient in light at those energies or wavelengths. When this light is analysed, it will show a continuous spectrum of the white light with a series of narrow dark lines across it.

FIGURE 14.5 When the light emitted from an excited gas is passed through a prism, a series of coloured lines is observed. The lines correspond to the colours (wavelengths) of light emitted by the gas.

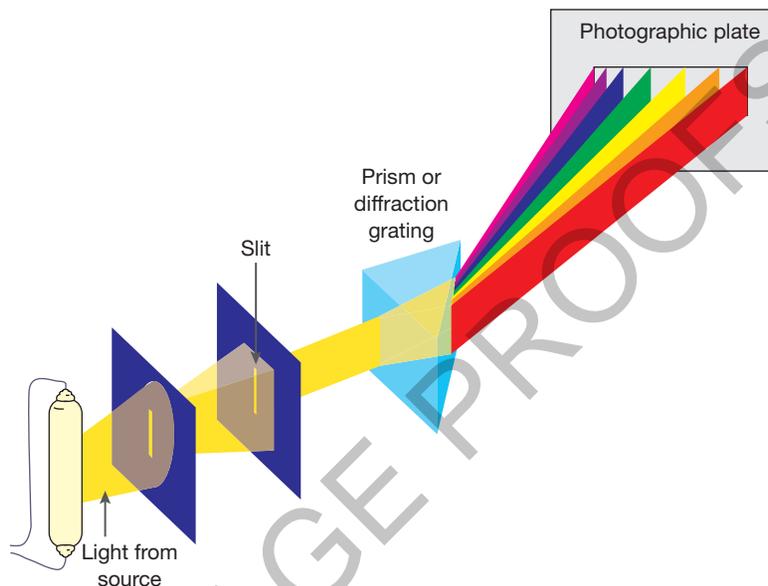
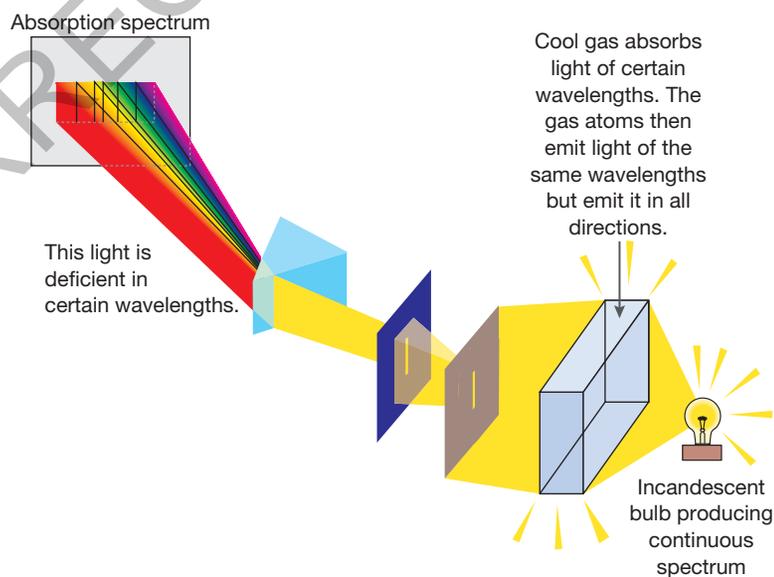


FIGURE 14.6 When white light is passed through a cool gas, the gas absorbs radiation from the light. After the light has been passed through a prism, the colours corresponding to the wavelengths of light absorbed by the gas are absent from the spectrum. An absorption spectrum of dark lines on a bright coloured background is observed.



14.2.5 Bohr's postulates

While Bohr believed that he knew the arrangement of electrons, he could not explain why the electrons were arranged in this way. Bohr published three papers between April and August 1913. In these papers, known as the great trilogy, he started with the problem of electrons in the Rutherford model and pointed out that the accelerating electrons must lose energy by radiation and collapse into the nucleus. He then applied quantum theory to the atom. He generally assumed that the orbits of the electron were circular.

Bohr was awarded the Nobel Prize for Physics in 1922 and in his Nobel lecture stated in reference to Rutherford's discovery of the nucleus:

'This discovery made it quite clear that by classical conceptions alone it was quite impossible to understand the most essential properties of atoms. One was therefore led to seek for a formulation of the principles of the quantum theory that could immediately account for the stability in atomic structure and the radiation sent out from atoms, of which the observed properties bear witness. Such a formulation I proposed [1913] in the form of two postulates.'

Bohr continued with rather lengthy statements of his postulates. Simpler statements are:

1. Electrons in an atom exist in '**stationary states**' in which they possess an unexplainable stability. Any permanent change in their motion must consist of a complete transition from one stationary state to another. When an electron is in a stationary state, it will orbit the nucleus without emitting any electromagnetic radiation.
2. In contradiction to the classical electromagnetic theory, no radiation is emitted from an atom in a stationary state. A transition between two stationary states will be accompanied by emission or absorption of electromagnetic radiation (a photon). The frequency, f , of this photon is given by the relation:

$$hf = E_1 - E_2$$

where

h = Planck's constant

E_1 and E_2 = values of the energy of two stationary states that form the initial and final states of the atom.

Bohr then introduced what is generally known as his quantisation condition and is sometimes called his third postulate.

An electron in a stationary state has an **angular momentum** that is an integral multiple of $\frac{h}{2\pi}$ (Planck's constant divided by 2π).

Bohr actually proposed that the kinetic energy of an electron was $\frac{n}{2hf}$ but this reduces to the quantisation condition given if the orbits are circular.

In his first postulate, Bohr put forward one of the most audacious hypotheses ever proposed in physics by predicting that electrons exist in states in which they do not radiate energy. The second postulate involves the quantum of energy being emitted or absorbed when an electron jumps from one stationary state to another and hence explains the origin of spectral lines. The quantisation condition is really an intuitive guess.

Using these postulates together with the energy of electrons calculated from 'classical' physics applied to the Rutherford model, it is possible to derive a theoretical equation for the wavelengths of the spectral lines of hydrogen. It is a great success of the Bohr model that this theoretical equation is the same as the empirical equation of Balmer. Many famous physicists had addressed the problem of electrons being in non-uniform motion without radiating energy. This had become important after Thomson had discovered the electron and was not just associated with the Rutherford model.

14.2.6 Mathematics of the Rutherford and Bohr models

In the following sections we will derive an expression for the classical energy of the Rutherford hydrogen atom and then impose Bohr's postulates on that atom. This will enable us to calculate the energies of the stationary states of the hydrogen atom and then calculate the change in energy of an electron involved in a transition between two stationary states. Finally, this change in energy will enable us to calculate the frequency (or wavelength) of the spectral lines of hydrogen.

The 'classical' energy of the Rutherford hydrogen atom

When you studied the escape velocity of an object fired from the Earth, you found the total energy of the object was the sum of its kinetic energy and its gravitational potential energy. When this total energy was zero, the object had just enough energy to escape from the Earth. If the total energy was negative, the object was unable to escape the Earth.

In a similar way we can calculate the total energy of a proton and electron. This time it is the sum of the kinetic energy and the electrical potential energy. The zero point will be when the electron has just enough energy to escape from the proton.

Kinetic energy of electron:

$$E_k = \frac{1}{2}m_e v^2.$$

The electron is held in orbit around the proton by the electrical force of magnitude:

$$F = \frac{kq_e^2}{r^2}$$

where

q_e = magnitude of the charge on the proton and electron (1.602×10^{-19} C).

We know that this electrical force provides the centripetal force of magnitude:

$$F_e = \frac{m_e v^2}{r}$$

$$F_e = F_E$$

$$\frac{m_e v^2}{r} = \frac{kq_e^2}{r^2}$$

$$\frac{1}{2} \frac{m_e v^2}{r} = \frac{1}{2} \frac{kq_e^2}{r^2}$$

$$\frac{1}{2} m_e v^2 = \frac{1}{2} \frac{kq_e^2}{r}$$

$$E_k = \frac{1}{2} \frac{kq_e^2}{r}.$$

The potential energy of the electron is given by:

$$E_p = -\frac{kq_e^2}{r}.$$

The total energy is the sum of the kinetic and potential energies.

$$\begin{aligned} \text{Total energy} &= E_k + E_p \\ &= \frac{1}{2} \frac{kq_e^2}{r} - \frac{kq_e^2}{r} \\ &= -\frac{1}{2} \frac{kq_e^2}{r} \end{aligned}$$

This is the total 'classical' energy of Rutherford's hydrogen atom.

Radii of the 'stationary states' of the Bohr hydrogen atom

When Bohr's quantisation condition is applied to the 'classical' hydrogen atom, the electron is restricted to stationary states in which the angular momentum of the electron is an integer multiple of Planck's constant, divided by 2π .

$$\begin{aligned} \text{Angular momentum} &= \frac{nh}{2\pi} \\ m_e v r &= \frac{nh}{2\pi} \end{aligned}$$

In this equation, n is an integer, known as the **principal quantum number**. We can obtain an expression for the radius of the stationary states corresponding to each value of the integer, n :

$$\begin{aligned} m_e v r &= \frac{nh}{2\pi} \\ r &= \frac{nh}{2\pi m_e v} \\ r^2 &= \frac{n^2 h^2}{4\pi^2 m_e^2 v^2} \end{aligned}$$

From the earlier equation, $\frac{m_e v^2}{r} = \frac{kq_e^2}{r^2}$, we can obtain an expression for v^2 :

$$v^2 = \frac{kq_e^2}{m_e r}$$

Substituting this gives:

$$\begin{aligned} r^2 &= \frac{n^2 h^2}{4\pi^2 m_e^2 \frac{kq_e^2}{m_e r}} \\ r_n &= \frac{n^2 h^2}{4\pi^2 m_e kq_e^2} \end{aligned}$$

where

r_n = the radius of the stationary state corresponding to the integer n .

The radius of the stationary state corresponding to $n = 1$ will be:

$$\begin{aligned} r_1 &= \frac{1^2 h^2}{4\pi^2 m_e kq_e^2} \\ &= \frac{h^2}{4\pi^2 m_e kq_e^2} \end{aligned}$$

We can combine the expressions for r_n and r_1 to give $r_n = n^2 r_1$.

Energies of the ‘stationary states’ of the Bohr atom

If we now return to the classical energy of the Rutherford hydrogen atom (energy = $-\frac{1}{2} \frac{kq_e^2}{r}$) and impose the restriction that the only possible energies correspond to values of radius given by $r_n = \frac{n^2 h^2}{4\pi^2 m_e k q_e^2}$, we can calculate the value of these energy states:

$$\begin{aligned} E_n &= -\frac{1}{2} \frac{kq_e^2}{\frac{n^2 h^2}{4\pi^2 m_e k q_e^2}} \\ &= -\frac{1}{2} \frac{4\pi^2 k^2 m_e q_e^4}{n^2 h^2} \\ &= -\frac{1}{n^2} \left(\frac{2\pi^2 k^2 m_e q_e^4}{h^2} \right). \end{aligned}$$

Again we can see that:

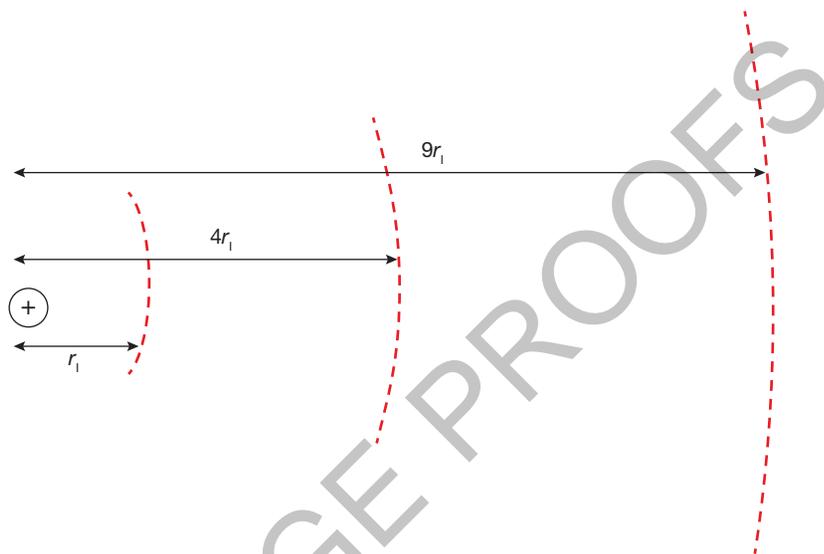
$$E_4 = - \left(\frac{2\pi^2 k^2 m_e q_e^4}{h^2} \right)$$

and hence

$$E_n = \frac{1}{n^2} E_4$$

remembering that E_4 has a negative value.

FIGURE 14.7 The relative radii of the orbits of an electron in different stationary states in a hydrogen atom



14.2 SAMPLE PROBLEM 2

CALCULATING THE ENERGIES OF ELECTRONS IN THE HYDROGEN ATOM

Given that the energy of an electron in the first stationary state of hydrogen is $E_4 = -2.179 \times 10^{-18}$ J, determine the energy in electron volts (eV) of an electron in the following stationary states of the hydrogen atom:

- the first stationary state ($n = 1$)
- the second stationary state ($n = 2$)
- the tenth stationary state ($n = 10$).

SOLUTION:

- We have been given this energy in joules so it is only a matter of converting to electron volts:

$$\begin{aligned} 1 \text{ eV} &= 1.602 \times 10^{-19} \text{ J} \\ 2.179 \times 10^{-18} \text{ J} &= \frac{2.179 \times 10^{-18}}{1.602 \times 10^{-19}} \text{ eV} \\ &= 13.60 \text{ eV}. \end{aligned}$$

The energy of the first stationary state is -13.6 eV.

ii. The energy of an electron in the second stationary state, for which $n = 2$ is given by:

$$\begin{aligned}E_n &= \frac{1}{n^2}E_1 \\E_2 &= \frac{1}{2^2}E_1 \\&= \frac{-13.6}{4} \\&= -3.4 \text{ eV}.\end{aligned}$$

iii. The energy of an electron in the tenth stationary state, for which $n = 10$ is given by:

$$\begin{aligned}E_n &= \frac{1}{n^2}E_1 \\E_{10} &= \frac{1}{10^2}E_1 \\&= \frac{-13.6}{100} \\&= -1.36 \times 10^{-1} \text{ eV}.\end{aligned}$$

When an electron gains energy accelerated across a potential difference of V volts, its gain in energy is given by $W = q_e V$.

When the electron is accelerated across a potential difference of 1.0 V , it will gain energy equal to $1.602 \times 10^{-19} \times 1.0 = 1.602 \times 10^{-19} \text{ J}$.

The gain in energy of an electron accelerated across a potential difference of 1.0 V is also called 1.0 electron volts (eV). $1.0 \text{ eV} = 1.602 \times 10^{-19} \text{ J}$.

Theoretical expression for wavelengths of the spectral lines of hydrogen

We are able to combine the expression for the energies of the stationary states with Bohr's second postulate to derive an expression for the energy differences between stationary states and, hence, the energies of the photons that may be emitted or absorbed by hydrogen.

We will consider the emission of a photon as an electron jumps from a higher energy initial state, E_i , to a lower energy final state, E_f .

The change in energy of the electron is:

$$\begin{aligned}\Delta E &= E_i - E_f \\&= \frac{1}{n_i^2}E_1 - \frac{1}{n_f^2}E_1 \\&= E_1 \left(\frac{1}{n_i^2} - \frac{1}{n_f^2} \right).\end{aligned}$$

This is the energy of the emitted photon, hf .

We can now derive an expression for the frequency and wavelength of the photon.

$$hf = E_i \left(\frac{1}{n_i^2} - \frac{1}{n_f^2} \right)$$

$$f = \frac{-E_i}{h} \left(\frac{1}{n_i^2} - \frac{1}{n_f^2} \right)$$

$$\frac{c}{\lambda} = \frac{-E_i}{h} \left(\frac{1}{n_i^2} - \frac{1}{n_f^2} \right)$$

$$\frac{1}{\lambda} = \frac{-E_i}{hc} \left(\frac{1}{n_i^2} - \frac{1}{n_f^2} \right)$$

This equation is of the same form as Balmer's equation. If the value of $\frac{-E_1}{hc}$ is calculated, it agrees with the value of the Rydberg constant in Balmer's equation. (Remember that E_1 is a negative quantity and, hence, $-E_1$ is positive.)

Balmer's equation is an empirical equation. A theoretical equation derived from Bohr's model of the atom now agrees with the empirical equation. This is a major achievement and offers very strong support for the Bohr model.

14.2 SAMPLE PROBLEM 3

EMISSION OF PHOTONS FROM A HYDROGEN ATOM

- Given that the energy of the first stationary state of hydrogen is -13.60 eV, calculate the energy of the fourth stationary state of the hydrogen atom.
- Use this information to calculate the frequency of the photon emitted when an electron undergoes a transition from the state $n = 4$ to the state $n = 1$.
- Calculate the wavelength of the radiation emitted.

SOLUTION:

- The energy of the fourth stationary state is:

$$E_n = \frac{1}{n^2} E_1$$

$$E_4 = \frac{1}{4^2} E_1$$

$$= \frac{-13.6}{16}$$

$$= -0.85 \text{ eV.}$$

- The energy emitted by the photon will be:

$$13.60 \text{ eV} - 0.85 \text{ eV} = 12.75 \text{ eV.}$$

$$\text{Energy of photon} = 12.75 \times 1.602 \times 10^{-19} \text{ J}$$

$$f = \frac{E}{h}$$

$$= \frac{12.75 \times 1.602 \times 10^{-19}}{6.626 \times 10^{-34}}$$

$$= 3.083 \times 10^{15} \text{ Hz}$$

(c) The wavelength will be calculated from:

$$\begin{aligned}\lambda &= \frac{c}{f} \\ &= \frac{3.00 \times 10^8}{3.083 \times 10^{15}} \\ &= 9.73 \times 10^{-8} \text{ m.}\end{aligned}$$

(Of course the wavelength could have been calculated directly from Balmer's equation.)

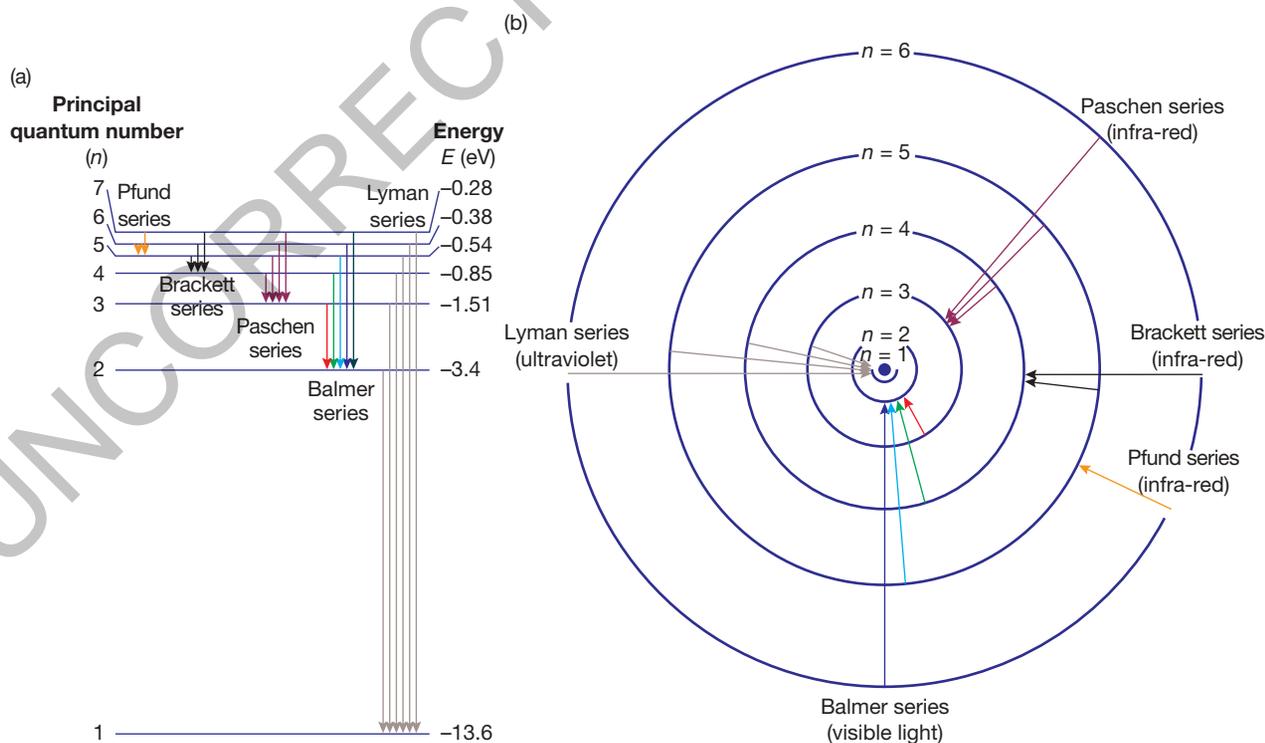
14.2.7 The hydrogen atom explained but with limitations

We are now able to calculate the wavelengths of the many spectral lines of the hydrogen atom. The original series of spectral lines was known as the Balmer series and contained the four spectral lines in the visible region of the spectrum. These lines correspond to electron jumps to the second lowest energy state, or first excited state, ($n = 2$) of the hydrogen atom.

The wavelengths of the spectral lines in other series can be calculated using Bohr's equation and are shown in figure 14.8. The Paschen series of infra-red lines had already been discovered but other series of lines were found later and their wavelengths were in agreement with Bohr's theory. The series of lines in the ultraviolet and infra-red, named after their discoverers, are:

- Lyman series, discovered in 1916. These were ultraviolet lines with transitions to the **ground state** ($n = 1$). An electron has the lowest possible amount of energy when it is in the ground state.
- Paschen series, discovered in 1908. These were infra-red lines with transitions to the second **excited state** ($n = 3$). If it exists in a stationary state in which it has more energy, it is said to be in an excited state.

FIGURE 14.8 (a) Atomic energy level view of the spectral series of hydrogen (b) Electron orbit view of the spectral series of hydrogen. Note that the radii of the orbits of the electrons are not to scale.



- Brackett series, discovered in 1922. These were infra-red lines with transitions to the third excited state ($n = 4$).
- Pfund series, discovered in 1924. These were infra-red lines with transitions to the fourth excited state ($n = 5$).

Limitations of the Bohr model of the atom

The Bohr model takes the first step to introduce quantum theory to the hydrogen atom but it is only a first step. The model has the following limitations:

- it is not possible to calculate the wavelengths of the spectral lines of all other atoms
- the Bohr model works reasonably well for atoms with one electron in their outer shell but does not work for any of the others
- examination of spectra shows that the spectral lines are not of equal intensity but the Bohr model does not explain why some electron transitions would be favoured over others
- careful observations with better instruments showed that there were other lines known as the hyperfine lines. There must be some splitting of the energy levels of the Bohr atom but the Bohr model cannot account for this.
- when a gas is excited while in a magnetic field, the emission spectrum produced shows a splitting of the spectral lines (called the Zeeman effect). Again, the Bohr model cannot account for this.
- finally, the Bohr model is a mixture of classical physics and quantum physics and this, in itself, is a problem.

14.2 Exercise 2

Use the equation $E_n = \frac{1}{n^2}E_1$ where $E_1 = -13.6$ eV to calculate the energy of a photon emitted when a hydrogen atom undergoes a transition from the $n = 5$ state (4th excited state) to the $n = 2$ state (1st excited state). State your answer in both eV and in joules.

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14.3 Matter waves

14.3.1 The wave behaviour of electrons

By the end of the nineteenth century, it was clear that light exhibited wave properties and could be very well modelled as consisting of waves. It was also firmly established, at that time, that matter could be modelled as consisting of particles. Early in the twentieth century, however, it was found that because of the photoelectric effect it was necessary for light to also be modelled as a particle. Was it possible that electrons, too, could exhibit wave phenomena as well as demonstrating particle behaviour?

Even though Bohr could calculate their energies, he could not explain why hydrogen electrons occupied only orbits whose energies were discrete. Why were they the only possible electron orbits? What was so special about them?

How did atoms make sure they emitted the right frequency to ensure they landed in another stationary state?

In fact Rutherford wrote to Bohr:

Your ideas are very ingenious and seem to work out well . . . There seems to me to be one grave difficulty in your hypothesis . . . namely, how does an electron decide what frequency it is going to vibrate at when it passes from one stationary state into another? It seems to me that you would have to assume that the electron knows beforehand where it is going to stop.

In 1923 French nobleman Louis de Broglie (1892–1987) suggested that matter also had a wavelength associated with it. He was intrigued by the fact that light exhibited both wavelike and particle-like properties, and on this basis proposed that matter may also exhibit wavelike properties. This work was done as his PhD thesis. De Broglie proposed that the wavelength of a particle, λ , is related to its momentum, p , according to the following equation:

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

The constant h , Planck's constant, is related to the particle-like behaviour of light and has a value of 6.63×10^{-34} J s, or 4.15×10^{-15} eVs. The momentum of matter is given by the product of its mass and velocity.

We can appreciate why the wave properties of matter are difficult to observe. Let's calculate the **de Broglie wavelength** of a 70 kg athlete running at a speed of 10 m s^{-1} . The de Broglie wavelength is the wavelength associated with a particle or discrete piece of matter. Using the formula $\lambda = \frac{h}{mv}$:

$$\begin{aligned}\lambda &= \frac{6.63 \times 10^{-34} \text{ J s}}{70 \text{ kg} \times 10 \text{ m s}^{-1}} \\ &= 9.5 \times 10^{-37} \text{ m}.\end{aligned}$$

This wavelength is much too small to allow for the ready observation of diffraction effects as an athlete runs through a narrow opening! However, for a particle with a small mass, such as an electron travelling at low speed, this is not the case. Electrons accelerated through a 100 V potential difference would have a speed of approximately $6.0 \times 10^6 \text{ m s}^{-1}$, and because the mass of an electron is $9.1 \times 10^{-31} \text{ kg}$ it would have a momentum of:

$$\begin{aligned}p &= mv \\ &= 9.1 \times 10^{-31} \text{ kg} \times 6.0 \times 10^6 \text{ m s}^{-1} \\ &= 5.5 \times 10^{-24} \text{ kg m s}^{-1}\end{aligned}$$

The de Broglie wavelength for these electrons is:

$$\begin{aligned}\lambda &= \frac{6.63 \times 10^{-34} \text{ J s}}{5.5 \times 10^{-24} \text{ m s}^{-1}} \\ &= 1.2 \times 10^{-10} \text{ m}.\end{aligned}$$

This wavelength has the same order of magnitude as the spacing between atoms in many crystals. When the ratio of wavelength λ to slit width w , $\frac{\lambda}{w}$, is sufficiently large, say greater than $\frac{1}{10}$ for example, then diffraction effects are readily observable.

The framework for testing to see if matter had an associated wavelength had now been constructed. Researchers could build an apparatus to fire a beam of electrons of specific energy and hence specific momentum and wavelength at a crystal and see if any diffraction effects appeared.

14.3 SAMPLE PROBLEM 1

- Calculate the de Broglie wavelength of a 10 g snail whose speed is 0.10 mm s^{-1} .
- How fast would an electron have to travel to have a de Broglie wavelength of $1 \mu\text{m}$?

SOLUTION:

(a) The de Broglie wavelength is given by the expression:

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

Thus

$$\begin{aligned}\lambda &= \frac{6.63 \times 10^{-34}}{10 \times 10^{-3} \times 0.10 \times 10^{-3}} \\ &= 6.63 \times 10^{-33} \text{ m,}\end{aligned}$$

keeping in mind that mass must be in kilograms and velocity in metres per second.

(b) The expression $\lambda = \frac{h}{mv}$ can be transposed to make v the subject. Thus $v = \frac{h}{m\lambda}$.

$$\begin{aligned}v &= \frac{6.63 \times 10^{-34}}{9.1 \times 10^{-31} \times 1 \times 10^{-6}} \\ &= 728.571\end{aligned}$$

$$= 7.3 \times 10^2 \text{ m s}^{-1} \text{ (to 2 significant figures)}$$

The speed of the electron is $7.3 \times 10^2 \text{ m s}^{-1}$.

14.3 Exercise 1

- Which has the greater de Broglie wavelength: a proton ($m = 1.67 \times 10^{-27} \text{ kg}$) travelling at $2.0 \times 10^4 \text{ m s}^{-1}$ or an electron ($m = 9.1 \times 10^{-31} \text{ kg}$) travelling at $2.0 \times 10^5 \text{ m s}^{-1}$?
- If an electron is made to travel at a higher speed, what effect does this have on its de Broglie wavelength?
- A research scientist is trying to produce a beam of electrons with a de Broglie wavelength of $1.0 \times 10^{-11} \text{ m}$ ($m = 9.1 \times 10^{-31} \text{ kg}$) using an electron gun to study a new molecule that is being proposed in a novel medical application. She would like to know the speed of an electron in this beam. Calculate the speed of an electron in this proposed beam.

Note: Diffraction patterns produced from this type of experiment are able to be used to determine the shape of such molecules. This is how we know the shape of the DNA molecule — by diffraction pattern analysis.

Finally, it is worth noting that the de Broglie wavelength associated with a piece of matter is inversely proportional to both the speed and mass. Hence, to create matter with large wavelengths, necessary for wave properties to manifest themselves, matter has to travel slowly and have little mass. Since electrons have a mass that is approximately $\frac{1}{1800}$ that of a proton or neutron, it is easier to detect the wave properties of electrons over those of other fundamental particles such as protons and neutrons.

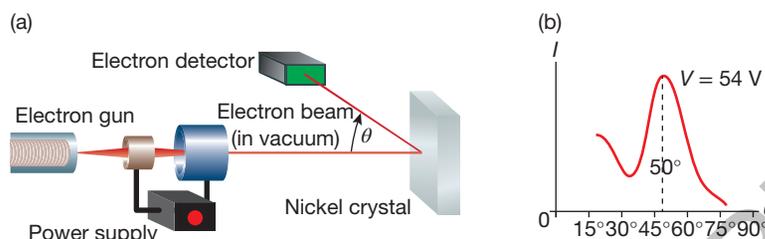
14.3.2 Matter waves show themselves

De Broglie suggested conducting an experiment to confirm whether or not a beam of electrons could be diffracted from the surface of a crystal. The openings between atoms could be used as a diffraction grating in much the same way that X-rays were diffracted by thin crystals as suggested by Max von Laue in 1912. Clinton Davisson (1881–1958) and Lester Germer (1896–1971) directed a beam of electrons at a metal crystal in 1927, and the scattered electrons came off in regular peaks as shown in the figure on top of next page.

This pattern is indicative of diffraction taking place with individual electrons as they scattered off the crystal surface. In fact, the wavelength determined from the diffraction experiments was exactly as predicted by the de Broglie wavelength formula. In this way, electrons were shown to have wavelike properties. Since then,

protons, neutrons and, more recently, atoms have been shown to exhibit wavelike properties, but it begs the question: if matter can exhibit wave characteristics, what is it that is ‘waving’? More technically, the question is what physical variable is it that has an amplitude and phase?

FIGURE 14.9 The Davisson and Germer experiment. (a) Electrons emitted from a heated filament are accelerated towards the crystal surface. The intensity of reflected electrons is recorded as the angle of the detector is changed. (b) Electron intensity as a function of angle



14.3 SAMPLE PROBLEM 2

What would be the dimensions of the array of slits required to observe diffraction of 60 g tennis balls travelling at 30 m s^{-1} ? What about electrons travelling at $3.0 \times 10^6 \text{ m s}^{-1}$?

SOLUTION:

To observe diffraction effects, the size of the opening needs to be of the same order of magnitude or smaller than the wavelength of the waves. We can see below that the de Broglie wavelength of the tennis ball is of the order of 10^{-34} m and the electron of the order of 10^{-10} m .

The de Broglie wavelength of:

the tennis ball	the electron
$\lambda = \frac{6.6262 \times 10^{-34} \text{ J s}}{0.060 \text{ kg} \times 30 \text{ m s}^{-1}}$	$\lambda = \frac{6.6262 \times 10^{-34} \text{ J s}}{9.109 \times 10^{-31} \text{ kg} \times 3.0 \times 10^6 \text{ m s}^{-1}}$
$= 3.7 \times 10^{-34} \text{ m}$	$= 2.4 \times 10^{-10} \text{ m}$

The distances between atoms in a crystal are of the order of 10^{-10} m , so we could observe diffraction and interference when these electrons are scattered from a crystal. It is not surprising that we never observe diffraction and interference effects with tennis balls, due to the extremely small wavelength, 10^{-34} m , that they have.

14.3 SAMPLE PROBLEM 3

What voltage is required to accelerate electrons to a speed of $3.0 \times 10^6 \text{ m s}^{-1}$?

SOLUTION:

To accelerate electrons to a speed of $3.0 \times 10^6 \text{ m s}^{-1}$, we need to calculate the work done by a voltage V .

$$\Delta E_{k \text{ electron}} = \frac{1}{2} m_e v^2$$

$$\Delta E_{k \text{ electron}} = -\Delta E_{p \text{ electron}}$$

$$= q_e V$$

where

q_e is the *magnitude* of the charge of the electron.

$$\begin{aligned}\Rightarrow V &= \frac{m_e v^2}{2q_e} \\ &= \frac{9.109 \times 10^{-31} \text{ kg} \times (3.0 \times 10^6 \text{ m s}^{-1})^2}{2 \times 1.6 \times 10^{-19} \text{ C}} \\ &= +26 \text{ V}\end{aligned}$$

So, only 26 V is required to accelerate an electron to $3 \times 10^6 \text{ m s}^{-1}$.

14.3.3 Electrons through foils

Intense, creative interest in fundamental physics ran in the Thomson family. Remember, it was J. J. Thomson whose ingenious experiment yielded the measurement of the charge-to-mass ratio of the electron. At that time there was no doubt that electrons were extremely well modelled as particles. However, G. P. Thomson, son of J. J., continued the exploration of the wave properties of electrons. He fired electrons through a thin polycrystalline metallic foil. The electrons had a much greater momentum than those used by Davisson and Germer. They were able to penetrate the foil and produce a pattern demonstrating diffraction of the electrons by the atoms of the foil — further evidence for wavelike behaviour of electrons. The polycrystalline nature of the foil results in a series of rings of high intensity. A single crystal would produce a pattern of spots. Thomson used identical analysis techniques to those used for diffraction of X-rays through foils, to confirm the de Broglie relationship.

Both Thomsons were awarded Nobel prizes — J. J. in 1897 for measuring a particle-like characteristic of electrons, and G. P. in 1937, together with C. J. Davisson, for demonstrating their wave properties.

Just as light requires a wave model and a particle model to interpret and explain how it behaves, so too does matter: it behaves like a particle in the sense that work can be done on it to increase its kinetic energy under the action of forces, but matter can also be made to diffract through sufficiently narrow openings and around obstacles. This requires a wave model and the de Broglie wavelength is used to determine the extent of matter's wave behaviour. It appears we need both a particle and a wave model for both light and matter. Electrons passed through a voltage V acquire a kinetic energy E_k equal to qV . Since they have kinetic energy, they also possess momentum and, according to de Broglie, a wavelength. We can determine a useful relationship between the de Broglie wavelength of an electron (λ) and the accelerating voltage (V) used.

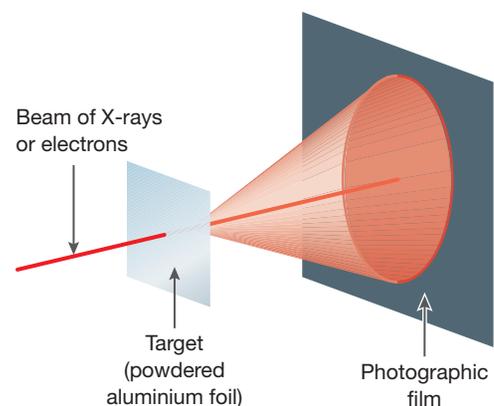
By equating the kinetic energy of the electron (E_k) to the work done by an accelerating voltage acting on an electron ($q_e V$), we get:

$$E_k = \frac{1}{2} m_e v^2 = q_e V$$

$$m_e v^2 = 2q_e V$$

$$m_e^2 v^2 = 2m_e q_e V.$$

FIGURE 14.10 Diffraction of X-rays and electrons by polycrystalline foils



The left-hand side is just the square of the momentum of the electron, and hence by taking the square root of both sides:

$$p = \sqrt{2m_e q_e V} \quad \text{or} \quad p = \sqrt{2m_e E_k},$$

remembering that E_k is equal to $q_e V$.

Since the de Broglie wavelength λ is given by $\frac{h}{p}$, it follows that:

$$\lambda = \frac{h}{\sqrt{2m_e q_e V}}$$

for a given accelerating voltage V , or

$$\lambda = \frac{h}{\sqrt{2m_e E_k}}$$

when the kinetic energy E_k of the electron in joules is known.

14.3 SAMPLE PROBLEM 4

Some of the X-rays used in G. P. Thomson's experiment had a wavelength of 7.1×10^{-11} m. Confirm that the 600 eV electrons have a similar wavelength.

SOLUTION:

Electrons of energy 600 eV have passed through a voltage equal to 600 V; thus, their energy is $1.6 \times 10^{-19} \times 600$ J. From this their de Broglie wavelength can be determined. Use the relationship:

$$\lambda = \frac{h}{\sqrt{2m_e E_k}}$$

Thus:

$$\begin{aligned} \lambda &= \frac{6.63 \times 10^{-34}}{\sqrt{2 \times 9.1 \times 10^{-31} \times 1.6 \times 10^{-19} \times 600}} \\ &= 5.0 \times 10^{-11} \text{ m.} \end{aligned}$$

This is a similar value to the 7.1×10^{-11} m wavelength of the X-rays.

14.3 SAMPLE PROBLEM 5

Consider a photon and an electron that both have a wavelength of 2.0×10^{-10} m.

- Calculate the momentum of the photon and the electron. What do you notice?
- Calculate the energy of the photon and the electron. What do you notice?
- Summarise what you have found concerning the momentum and energy of a photon and an electron with the same wavelength.

SOLUTION:

- The momentum of the photon and the electron are governed by the same equation, namely $p = \frac{h}{\lambda}$. Hence, both the photon and the electron will have the same momentum because they have the same associated wavelength. Thus:

$$p = \frac{6.63 \times 10^{-34}}{2.0 \times 10^{-10}}$$

$$= 3.3 \times 10^{-24} \text{ N}\cdot\text{s}.$$

We notice here that both the photon and the electron have the same momentum.

- (b) To determine the energy of an object from its momentum, we now have to ask if it is a photon or an object with mass. The relations are different. For the photon, $E = pc$. Thus:

$$E = 3.3 \times 10^{-24} \times 3.0 \times 10^8$$

$$= 9.9 \times 10^{-16} \text{ J or } 6.2 \text{ keV}.$$

For the electron, however, $E = \frac{p^2}{2m}$. Thus:

$$E = \frac{(3.3 \times 10^{-24})^2}{2 \times 9.1 \times 10^{-31}}$$

$$= 6.0 \times 10^{-18} \text{ J or } 37 \text{ eV}.$$

The electron has substantially less kinetic energy than the photon, even though they have the same momentum.

- (c) Light and matter with the same wavelength will have the same momentum, and vice versa. However, when photons and electrons have the same momentum, they will not necessarily have the same energy. In the problem above, the photon has substantially more energy than the electron.

14.3 Exercise 2

- 1 Consider a photon and an electron that both have a wavelength $1.0 \times 10^{-10} \text{ m}$.
 - (a) Calculate the momentum of the photon and the electron. What do you notice?
 - (b) Calculate the energy of the photon and the electron. What do you notice?
- 2 A photon and an electron both have energy $2.0 \times 10^{-16} \text{ J}$.
 - (a) Calculate the momentum of the photon and the electron. What do you notice?
 - (b) Use your results in (a) to find the wavelength of the photon and the electron. What do you notice?
- 3 An electron gun with an accelerating voltage of 28 V is applied to electrons emitted from a tungsten filament to make a beam of electrons all having the same energy.
 - (a) What is the energy in both eV and joules that these electrons acquire? Assume the kinetic energy of the electrons emitted from the tungsten filament is zero.
 - (b) Use your result to part (a) to determine the momentum of an electron in this beam.
 - (c) Calculate the de Broglie wavelength of an electron in this beam.
 - (d) If the accelerating voltage is increased, what effect would this have on the de Broglie wavelength of an electron in this beam?

14.3.4 Atoms and standing waves

Individual electrons act like waves when they are diffracted by atoms in crystals. Do electrons *in* the atoms also exhibit wavelike properties? They certainly do! Thinking of electrons behaving like waves solved the puzzle of stationary states. This wave model for electrons that are bound within atoms also neatly explained why atoms absorb and emit photons of only particular frequencies, and provided the answers to Rutherford's questioning of the Bohr model of the atom. In essence, only waves whose de Broglie wavelength multiplied by an integer $n\lambda$ set equal to the circumference of a traditional electron orbit are allowed to exist due to these waves being the only ones able to constructively interfere to produce a standing wave. De Broglie speculated about the electron in a hydrogen atom displaying wavelike behaviour in 1924. A complete description of

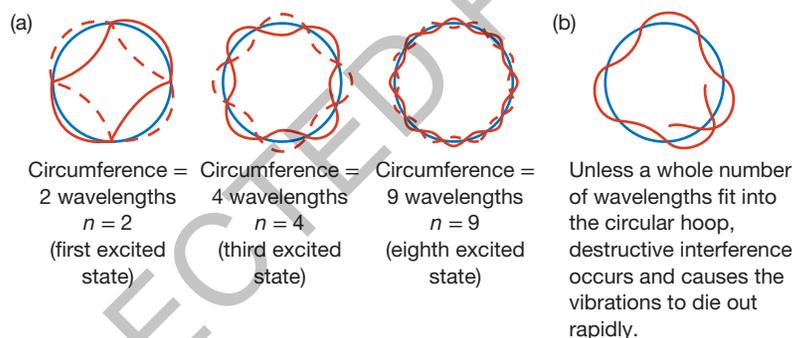
the hydrogen atom awaited a more sophisticated mathematical treatment called quantum mechanics. The fundamentals of this model were developed by Erwin Schrödinger and Werner Heisenberg later in the 1920s.

Louis de Broglie's picture

Louis de Broglie pictured the electron in a hydrogen atom travelling along one of the allowed orbits around the nucleus, together with its associated wave. In de Broglie's mind the circumference of each allowed orbit contained a *whole number* of wavelengths of the electron-wave so that it formed a standing wave around the orbit. Thus, $n\lambda = 2\pi r$ or $\lambda = \frac{2\pi r}{n}$ fixes the allowed wavelength. An electron-wave whose wavelength was slightly longer, or shorter, would not join onto itself smoothly. It would quickly collapse due to destructive interference. Only orbits corresponding to standing waves would survive. This is shown below. The concept is identical to the formation of standing waves on stringed instruments.

It is worth noting that the standing waves produced on a stringed instrument of length l have a series of possible wavelengths $\lambda_n = \frac{2l}{n}$ where n is a positive integer (1, 2, 3 and so on). This series of wavelengths is called a harmonic series. At this level of physics, which is only an introduction to the conceptual nature of quantum mechanics, the harmonic series provides for a series of associated momenta that are discrete in value. This in turn provides for a series of energy states that are also discrete. This connection is in complete agreement with the observation of emission and absorption spectra. When you pluck a guitar string, only certain frequencies are produced. Likewise, when you energise an atom, only certain energy levels are able to be sustained, resulting in the emission of well-defined frequencies of light in the form of individual photons.

FIGURE 14.11 A model of the atom showing the electron as a standing wave



In de Broglie's model of the atom, electrons are viewed as standing waves. It is this interpretation that provides a reasonable explanation for the emission spectra of atoms. It answers Rutherford's remark to Bohr (see page 13). When a guitar string is plucked, how does it know what frequencies to vibrate at? The answer is: the frequencies that equate to the standing waves with wavelengths compatible with the length of the string.

Electrons viewed as standing waves can exist only in stable orbits with precise or discrete wavelengths. This implies that the electrons can have only discrete quantities of momentum. This in turn implies that the electrons can have only discrete amounts of energy. Energy transitions that are made by electrons occur in jumps from one high-energy standing wave to another standing wave of lower energy. In this way the emission spectra and, hence, absorption spectra can be understood as arising from transitions between quantised energy levels due to electrons having a wave-like character.

It's a consistent story — light displays both wave and particle behaviour and so do electrons and all other forms of matter. The two models are complementary. You observe behaviour consistent with wave properties or particle properties, but not the two simultaneously. Remember how William Bragg expressed it: 'On Mondays, Wednesdays and Fridays light behaves like waves, on Tuesdays, Thursdays and Saturdays like particles, and like nothing at all on Sundays'? This delicate juggling of the two models by both light and matter is known as **wave-particle duality**. Wave-particle duality describes light as having characteristics of

both waves and particles. This duality means that neither the wave model nor the particle model adequately explains the properties of light on its own.

There have been many conceptual hurdles for physicists in arriving at this amazingly consistent view of the interaction between light and matter. Their guiding questions always kept them probing for the evidence. Observations and careful analysis gave them the answers. Imagination, creativity and ingenuity were vital in their search for a more complete picture of light and matter.

We now know that both light and matter can exhibit both wave-like and particle-like behaviour, depending on the types of experiments performed. For example, when light strikes a material object, it transfers energy as if it is a particle (the photoelectric effect), but when light passes through a narrow opening or a pair of slits, it acts as if it is a wave. Likewise, matter can have work done on it via well-understood forces accelerating it, but matter can also be diffracted when it passes through a crystal, producing diffraction patterns similar to those of X-rays. Also, the behaviour of electrons within atoms can only be understood by treating them as a type of wave phenomena.

A more detailed model for the seemingly paradoxical result of both wavelike and particle-like behaviour for both light and matter was developed in the 1910s and 1920s. The model is called quantum mechanics, and in it wave and particle behaviour for both light and matter are unified successfully.

14.3.5 Schrödinger and the development of quantum mechanics

So far we have encountered quantum theory as applied to the Bohr model of the atom. That model, however, suffers from not being a complete quantum theory. It is basically a classical model with some quantum ideas superimposed on it. This ‘old quantum theory’ reached a peak in 1922 but was eventually replaced by a complete quantum theory now known as quantum mechanics.

The first three ‘quantum numbers’ are the principal quantum number, n from the Bohr model, the angular momentum quantum number, l , and the magnetic quantum number, m .

Heisenberg’s uncertainty principle

Pauli used Bohr’s idea of shells of electrons and in 1925 realised that if he introduced a fourth quantum number, he could explain the maximum number of electrons in each shell. The fourth quantum number was associated with ‘spin’. The maximum number of electrons in each shell corresponded to the number of different sets of quantum numbers available for each shell. Pauli’s exclusion principle states that no two electrons can have the same set of quantum numbers.

Pauli’s exclusion principle provided the reason for electrons in atoms being arranged in shells with the maximum number of electrons being 2, 8, 18, 32, 18, 8 from the first to sixth shell.

De Broglie’s work on the wave nature of particles might not have received wide publicity if it had not been brought to the attention of Einstein. In 1925, Erwin Schrödinger read a comment by Einstein on de Broglie’s work that referred to it as more than a mere analogy. Schrödinger then set about trying to restore some of the familiar concepts of waves to quantum theory. He eventually derived equations that looked like the equations used to describe real waves and it seemed that he had managed to bring quantum ideas back toward a much more comfortable formulation associated in some way with classical physics.

Heisenberg did not like Schrödinger’s approach. Heisenberg did not see how continuous waves could be used to describe the discontinuous behaviour of an electron jumping from one state to another. Many papers started appearing on Schrödinger’s wave mechanics and very few on Heisenberg’s matrix mechanics. Schrödinger did not like Heisenberg’s non-visual interpretation or the use of matrices. Most physicists of the time preferred Schrödinger’s approach to Heisenberg’s approach.

However, it was not long before Schrödinger demonstrated that the two different approaches were simply different versions of the same thing. He showed that Heisenberg’s matrices could be generated in Schrödinger’s theory and Schrödinger’s waves could be produced from Heisenberg’s matrices.

Schrödinger later spent time with Bohr and was most disappointed to find that his ‘waves’ were not real waves at all. Max Born showed that they were associated with the probability of finding an electron at a particular location.

Schrödinger tried unsuccessfully to restore ‘common sense’ to quantum theory, but his name has become associated with ‘Schrödinger’s cat’, which brings a quantum nature to a large-scale system. The idea of Schrödinger’s cat is that a cat is locked in a box with a deadly cyanide pellet. The release of the cyanide pellet will be triggered by a radioactive decay that might occur at some time. If the box is opened and the cat is observed; it will be alive if the pellet has not been released and dead if it has been released. However, the quantum mechanical view is that if the box is still closed and the cat is not observed, it will be a quantum state that is the superposition of its two possible

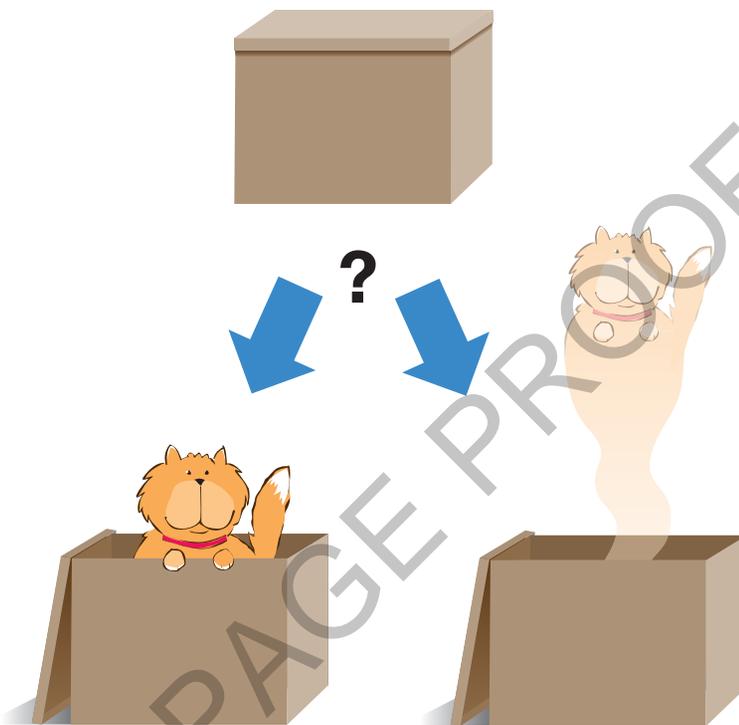
states; it will be in a state in which it is both dead and alive. Opening the box to observe the cat is said to ‘collapse the wave function’ into either the dead state or the alive state.

In late 1926, Heisenberg showed that uncertainty is an inherent property of quantum mechanics and that there are pairs of quantities that cannot be determined simultaneously. If we know the accurate position of a particle, say an electron, then you cannot know its momentum accurately. This is because any method that you use to observe the position of the particle will transfer energy to the particle and, hence, change its momentum. Also, the methods that allow the measurement of the momentum of a particle will change its position. This is represented by Heisenberg’s uncertainty principle:

$$\Delta x \times \Delta p \geq \frac{h}{4\pi}$$

where Δx and Δp are the inherent uncertainties in position and momentum and h is Planck’s constant.

FIGURE 14.12 Schrödinger’s cat could be considered to be both alive and dead at the same time until the box is actually opened and the observation made.



TRY THIS!

Material: A blindfold, a ruler and a ping-pong ball.

This may help you to get a better grip on the uncertainty principle! Blindfold a volunteer and give them a ruler. Now, place the ping-pong ball at a random location on the bench and get the volunteer to attempt to locate the exact position of the ping-pong ball using only the end of the ruler *without moving the ball!*

(*Note:* Be kind to your volunteer while they are blindfolded!)

The Dirac equation

Paul Dirac extended quantum mechanics and derived the Dirac equation, which added relativity to quantum theory. It predicted correctly the spin of electrons (which is a relativistic effect). It also predicted the existence

of a particle similar to an electron but with a positive charge. The anti-electron or positron was observed by Carl Anderson in 1932.

Dirac discovered that the equations of quantum mechanics have the same structure as the equations of classical physics and that the equations of classical physics can be obtained from quantum mechanics by using very large quantum numbers or setting Planck's constant to zero.

14.3.6 What does it all mean?

The complete quantum theory came about after the breakthrough of Heisenberg and Schrödinger, who independently in 1925 and 1926 discovered different forms of the same theory. Heisenberg introduced the uncertainty principle and Bohr completed the theory with his principle of complementarity.

By the Solvay Conference of October 1927, the old quantum theory had been replaced. At this conference, Schrödinger presented a paper on his wave function theory but he declined to discuss the interpretation of the wave functions (which Born interpreted as being related to the probability of finding an electron in a certain location). The theory is now called quantum mechanics, and Bohr's ideas along with Heisenberg's uncertainty principle and Born's probability interpretation became known as the Copenhagen interpretation.

At the Solvay Conference, Einstein raised his first public objections to quantum mechanics, and he was to continue to debate with Bohr this interpretation of quantum mechanics. Einstein never accepted that quantum mechanics was a 'complete' theory, and the Copenhagen interpretation is still considered obscure by some physicists today. It is no wonder that Bohr made his famous statement, 'Anyone who is not shocked by quantum theory has not understood it'.

We have not even scratched the surface of quantum mechanics. We have seen that there were major problems with the ideas of the original quantum theory and that in the process of overcoming those problems, a new theory was developed that required a modification of our ideas about the physical world.

In this strange new theory there is no such thing as a particle or a wave but rather there is a wave-particle duality and making an accurate observation of one property means that another property cannot be measured accurately. We have not studied the mathematics of either the matrix mechanics of Heisenberg or the wave mechanics of Schrödinger and we have not studied the probability interpretation of Born. We are therefore not in a position to see why quantum theory and in particular the Copenhagen interpretation is as shocking as Bohr suggests.

A deeper study of quantum mechanics leads to an atomic world that is fuzzy and nebulous and in which, according to Bohr and the Copenhagen interpretation, nothing actually exists until it is observed. The clock-work world of Newton becomes a world of quantum uncertainty where nothing is predictable. Even worse, events can occur without having a cause and quantum particles can suddenly pop into existence.

Yet, despite all the problems of interpretation, quantum mechanics is an incredibly successful theory. Quantum mechanics helps us explain and control the properties of metals, insulators, semiconductors and superconductors. The inventors of the transistor acknowledge the part quantum theory played in their discovery. That discovery led to the development of ever more powerful computers and microcomputers that have led to a revolution in communications and information. Lasers and masers are quantum devices. Quantum mechanics explains the structure of the atom and nucleus as well as mechanical and thermal properties of solids. Quantum mechanics gave chemistry a firm base and explained chemical bonding. The new areas of molecular biology and genetic engineering have arisen from quantum chemistry. In astrophysics, the processes that occur in stars can be explained by quantum mechanics and even our theories regarding such exotic objects as black holes are based on quantum mechanics. There has even been the suggestion that our universe began as a 'quantum fluctuation'. Perhaps in the not too distant future, quantum computing will become a reality and quantum computers will be vastly more powerful than today's computers.

Quantum mechanics is a theory that has changed the world and our view of it.

-  **Watch this eLesson:** De Broglie wavelength
Searchlight ID: med-0199
-  **Watch this eLesson:** The momentum of photons and matter
Searchlight ID: med-0423
-  **Explore more with this weblink:** The atomic lab: electron interference

14.4 Review

14.4.1 Summary

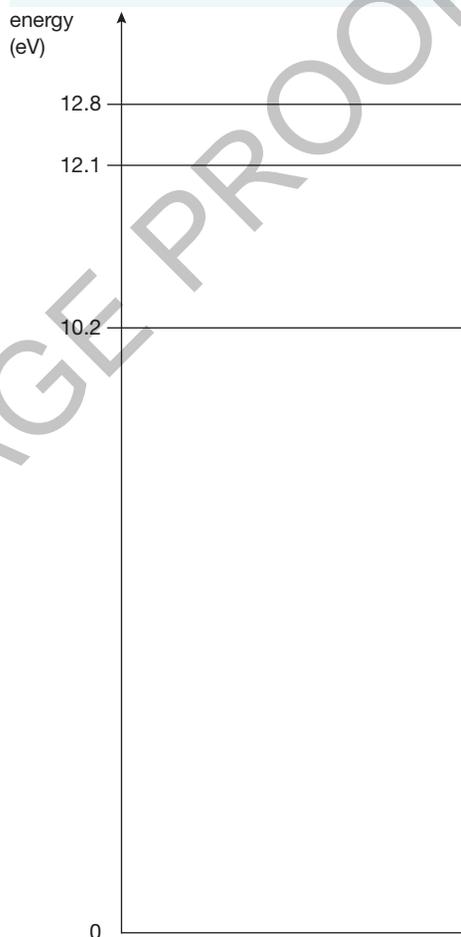
- The scattering of alpha particles through large angles by very thin gold foils led Rutherford to propose that an atom consisted of a very small, dense, positively charged nucleus. Electrons were in orbit about the nucleus at distances very large compared to the dimensions of the nucleus.
- A major problem with the Rutherford model was that it did not account for any properties of the electrons in the atom, in particular how the electrons could be accelerating without emitting electromagnetic radiation.
- Bohr extended the Rutherford model by formulating two postulates that enabled him to apply the quantum ideas of Planck and Einstein to the Rutherford atom.
- Bohr's postulates enabled him to describe an atom in which electrons existed in stable 'stationary states' where they did not emit electromagnetic radiation. The transition of an electron from one stationary state to another would be accompanied by the emission or absorption of a quantum of electromagnetic radiation or a photon.
- Using his model of the atom, Bohr was able to derive a theoretical expression for the wavelengths of the spectral lines of hydrogen which was in agreement with Balmer's empirical formula.
- To account for emission spectra, Neils Bohr proposed a radical model where electrons within atoms have stable orbits but only discrete energy levels are allowed.
- While successful in explaining the wavelengths of the spectral lines in the hydrogen spectrum, Bohr's model failed to account for the relative intensities of the lines, the existence of the hyperfine structure of the lines or for the splitting of spectral lines when the excited gas was in a magnetic field. Bohr's model was also a strange mixture of classical physics and quantum physics.
- When an atom jumps from a high energy level, E_{initial} , to a lower energy level, E_{final} , resulting in a difference, ΔE , a photon of light is emitted with frequency, f , according to the equation $hf = \Delta E$. Hence, the observation of emission spectra having precise frequencies is evidence for atoms having discrete energy levels.
- The best model for atoms having discrete energy levels is to interpret electrons in atoms as behaving as a standing wave. The allowable standing waves are known as orbitals.
- In 1924 Louis de Broglie suggested that electrons may exhibit wave properties under suitable conditions. He proposed a diffraction experiment using a beam of electrons and a crystal to act as a diffraction grating.
- The de Broglie wavelength, λ , can be determined from the momentum, p , according to the equation $\lambda = \frac{h}{p}$. Remember also that the momentum of a particle is given by $p = mv$, where m is the mass and v is the speed.
- In 1927 Clinton Davisson and Lester Germer established the wavelike behaviour of electrons when they performed a diffraction experiment. Not only did they observe diffraction effects, they also established that the wavelength of the electrons in the beam was consistent with Louis de Broglie's prediction.

- The theory now known as quantum mechanics was introduced by Heisenberg and developed by Bohr, Schrödinger and others.
- In particular, Schrödinger's wave equation describing the quantum behaviour of both light and matter became the cornerstone for modern quantum mechanics in the same way that Newton's laws of motion became the foundation of Classical Physics.

14.4.2 Questions

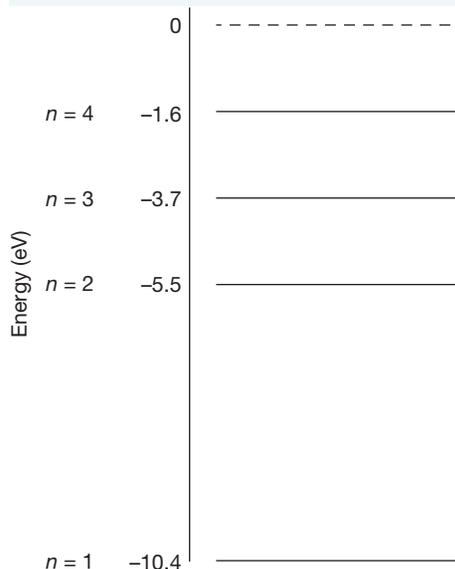
- List the strengths and weaknesses of the Rutherford model of the atom.
- There are two common ways of depicting the energy levels of an atom. In one method the ground state is taken to be zero energy, and in the other method the ionisation energy is taken to be zero. The first excited state of mercury atoms is known to be 4.9 eV above the ground state, the second excited state is 6.7 eV, the third excited state is 8.8 eV, and the ionisation energy is 10.4 eV above the ground state. Using the second method, where the ionisation energy is taken as 0 eV, give the energies of the ground state and the first 3 excited states. *Note:* Your values will be negative numbers, and a drawing of the energy level diagram will assist you.
- The ground state and the first three excited states of hydrogen are shown in the diagram on the right. An emission spectrum of hydrogen gas shows many different spectral lines.
 - Copy the diagram and label the ground state and first three excited states.
 - Draw arrows to represent all possible six transitions that may occur when hydrogen atoms in states lower than the fourth excited state emit a photon of light.
 - Calculate the energy of each of the possible six photons.
 - Determine the wavelength of the photon having the least and greatest energy in your answer to part (c).
- When sodium chloride (common salt) is placed in a flame, the flame glows bright gold. The following diagram shows some of the energy levels of a sodium atom.
- Use Balmer's equation to calculate the wavelength of the radiation emitted from an excited hydrogen atom when an electron undergoes a transition from the state $n = 5$ to:
 - the state $n = 1$
 - the state $n = 2$
 - the state $n = 3$.
- Calculate the wavelengths of the lines of the Balmer series corresponding to transitions from the states $n = 8$, $n = 10$, $n = 12$.
 - What trend do you notice in the wavelengths as the value of n increases?

FIGURE 14.13

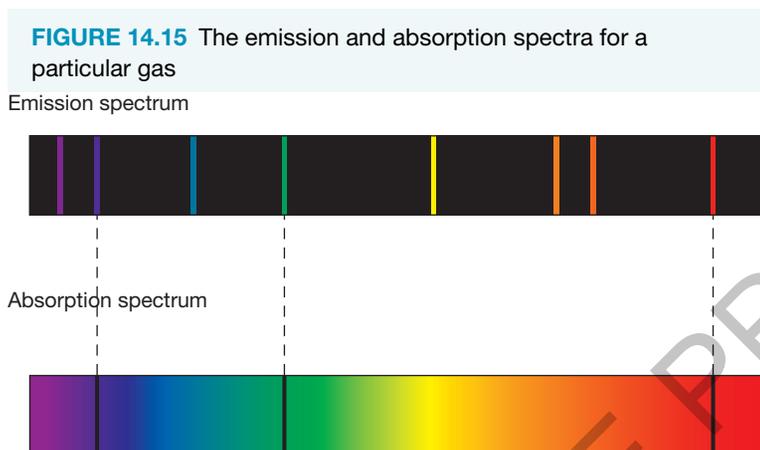


7. The radius of the orbit of an electron in the ground state of the hydrogen atom is 5.3×10^{-11} m. Calculate the radius of the orbit of an electron when it is in each of the following states:
- the state $n = 2$
 - the state $n = 3$
 - the state $n = 4$.
8. (a) State which photon, red or blue, has the higher frequency.
 (b) State which photon, red or blue, has the longer wavelength.
 (c) State which photon, red or blue, has the higher energy.
9. If the atoms in a sample of hydrogen were all in the state $n = 5$, how many different spectral lines could possibly be produced by the gas as the electrons returned to the ground state?
10. Given that $E_1 = -13.6$ eV, $E_2 = -3.40$ eV, $E_3 = -1.51$ eV, $E_4 = -0.85$ eV, $E_5 = -0.54$ eV, calculate the wavelengths of:
- the first two lines in the Lyman series
 - the first two lines in the Balmer Series
 - the first two lines in the Paschen series.
11. (a) What is the wavelength of the longest wavelength spectral line of the Pfund series?
 (b) What is the wavelength of the shortest wavelength line of the Pfund series?
12. The 'series limit' is the term applied to the shortest wavelength spectral line in each of the spectral series of hydrogen.
- What value of n_i would be used to calculate the wavelength of the series limit?
 - Calculate the series limit for the Lyman, Balmer and Paschen series of hydrogen.
 - How many electron volts of energy would be carried by a photon corresponding to the series limit of the Lyman series?
13. Figure 14.14 is an energy level diagram for energies of the stationary states in atoms of a gas, Q.
- Determine the energy of the photon emitted when an electron in the state $n = 3$ undergoes a transition to the state $n = 2$.
 - Determine the frequency and wavelength of this photon.
 - Determine the wavelength of the photon absorbed by this gas when an electron undergoes a transition from the state $n = 1$ to the state $n = 4$.

FIGURE 14.14 The energy level diagram for the gas, Q



14. The emission spectrum of a particular gas has eight bright lines in the visible region as shown in figure 14.15. The absorption spectrum of the same gas has only three lines in the visible region as shown.
- Explain why each of the absorption lines corresponds to one of the emission lines.
 - Explain why there is not a corresponding absorption line for five of the emission lines.



15. An absorption spectrum is produced when the atoms in a cool gas absorb energy from white light passing through the gas. These excited atoms then re-emit the energy and return to low energy states. How can this re-emission occur but there still be dark lines in the absorption spectrum?
16. Balmer predicted accurately the wavelengths of the visible spectral lines and invisible spectral lines of hydrogen that had not been detected. Bohr did the same about thirty years later. Explain why Bohr's prediction is considered more important than that of Balmer.
17. What evidence supports the idea that the electron energies in the hydrogen atom are discrete?
18. If electrons in hydrogen atoms obeyed the rules of classical mechanics instead of those of quantum mechanics, would the hydrogen atoms produce a line spectrum or a continuous spectrum? Explain your answer.
19. Explain why each element has its own characteristic spectrum.
20. Two spectral lines of hydrogen have frequencies of 2.7×10^{14} Hz (infra-red) and 4.6×10^{14} Hz (red).
- Explain how you could use this information to determine the frequency of a higher frequency spectral line of hydrogen.
 - Calculate the frequency of that line.
21. When de Broglie was examined for his PhD, his thesis was first thought by his examiners to bear little relationship to reality.
- What did de Broglie predict that made it seem to be unrelated to reality?
 - What did de Broglie suggest could be observed to support his prediction?
22. If a proton and an electron are travelling with equal velocities, which has the longer de Broglie wavelength?
23. If one electron travels twice as fast as another electron, which one has the greater wavelength?
24. (a) If an electron travelling at 1.0×10^4 m s⁻¹ was accelerated to 2.0×10^4 m s⁻¹, what would be the ratio of its new wavelength to its original wavelength?
- (b) If an electron travelling at 1.0×10^8 m s⁻¹ was accelerated to 2.0×10^8 m s⁻¹, would it change its wavelength by the same amount as the electron in part (a)? Explain your answer.
25. (a) Calculate the de Broglie wavelength of an electron in a TV set that hits the screen with a velocity of one tenth of the velocity of light.
- (b) With what velocity would you roll a ball of mass 0.1 kg if it is to have the same de Broglie wavelength as the electron in part (a)?

26. A neutron emitted when a uranium-235 nucleus undergoes fission may have an energy of about 1 MeV. A 'thermal' neutron that would be captured by a uranium-235 nucleus in a nuclear reactor would have an energy of about 0.02 MeV.
- Calculate the wavelength of a 1 MeV neutron.
 - Calculate the wavelength of a 0.02 MeV neutron.
27. Construct a time line to include the following physicists and indicate their contribution to the transition from classical mechanics to the development of quantum mechanics: J. J. Thomson, Rutherford, Bohr, Balmer, de Broglie, Heisenberg, Schrödinger.

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PRACTICAL INVESTIGATIONS

The Spectrum of Hydrogen

Aim

To observe the spectral lines of hydrogen, measure their wavelengths and compare these values with the theoretical values.

Apparatus

hydrogen spectral tube and power supply spectroscope

Theory

According to the Bohr model of the hydrogen atom, when an electron jumps from a higher energy state to a lower energy state, it will emit a photon. When an electron jumps to the state $n = 2$ from any of the states from $n = 3$ to $n = 6$, the emitted photon will be in the visible region of the spectrum.

A spectroscope can be used to measure the deviation of the spectral lines. The wavelengths of the spectral lines can then be calculated.

The wavelengths of the spectral lines will be given by:

$$\lambda = \frac{d \sin \theta}{n}$$

where

λ = wavelength

θ = angle of deviation

d = distance between lines on the grating

n = order of spectra.

The theoretical values of the wavelengths, based on Bohr's theory of the hydrogen atom, can be calculated after the energies of the states $n = 2$ to $n = 6$ have been calculated.

The energy of the ground state, $n = 1$ is -13.6 eV. The energies of the other states are given by $E_n = \frac{E_1}{n^2}$.

Method

In this experiment, the hydrogen spectral tube is switched on and the radiation viewed through a spectroscope.

Setting up the hydrogen spectral tube

Different types of spectral tube and power supply may be used but we will describe a special power supply that is designed for spectral tubes. The spectral tube can be clamped in place on a vertical metal rod mounted on top of the power supply. (The rod is maintained at Earth potential and is safe to touch when the power supply is switched on.)

Some hydrogen spectral tubes are very faint and this makes measurement of the spectral lines very difficult. Hydrogen spectral tubes should probably be replaced fairly regularly as they tend to become fainter over time.

The spectroscope

The spectroscope consists of two tubes, one of which can be rotated around a small central table. One tube, the fixed one, is a collimator and the moveable one is a telescope. A small prism or a diffraction grating can be mounted on the small table.

There is an adjustable narrow slit at the front of the collimator. The collimator is set up to shine parallel rays of light onto the diffraction grating or prism. (For the remainder of this practical activity, we will assume that a diffraction grating is being used. We will assume that the information about the number of lines per metre is provided. It is possible to calibrate a grating, and a procedure to do this is included in the last section of the method.)

The light that passes through the diffraction grating deviates through an angle that depends on the wavelength of the light and the number of lines per metre ruled on the diffraction grating.

The telescope is rotated around the table and the image of the narrow slit is observed at different angles for the different wavelengths of light. These angles can be measured, usually with the help of a vernier scale fixed to the telescope.

Setting up the spectroscope

Setting up the spectroscope involves two parts; adjusting the telescope for parallel light rays and then adjusting the collimator to produce parallel light rays.

There should be fine cross-wires visible in the eyepiece of the telescope. These cross-wires should be in sharp focus and an adjustment of the eyepiece in its holder may have to be made if they are not sharply focused.

The telescope should be pointed at a distant object and the focus adjusted using the objective lens of the telescope, lens L_3 , until the image of the distant object is sharply focused. (In fact any object outside should be far enough away.) The telescope is then aligned with the collimator and the lens on the collimator, is adjusted until the slit is seen sharply focused.

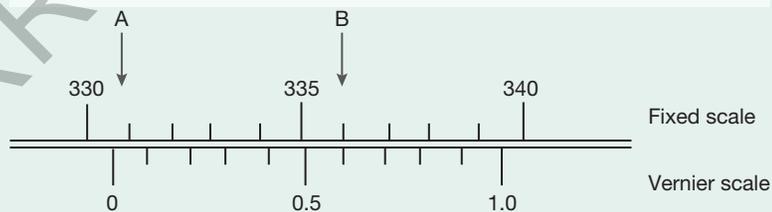
A light source, possibly a brighter spectral tube than the hydrogen tube, can now be set up in front of the slit and the slit width adjusted until narrow spectral lines can be viewed when the telescope is rotated to the appropriate position.

By clamping the telescope and then using the fine adjustment, it should be possible to align the cross-wires visible in the eyepiece with the spectral line. A measurement can then be made.

Reading a vernier scale

A vernier scale has ten lines on the moveable scale in the space of nine lines on the fixed scale. This enables an extra decimal place to be determined. This extra digit corresponds to the position of the line on the vernier, moveable scale that aligns with any one of the lines on the fixed scale.

FIGURE 14.16 Reading a vernier scale. The position of the zero mark on the vernier scale, indicated by arrow A, is just less than 331. The line on the vernier scale that matches a line on the fixed scale is 0.6, as indicated by arrow B. Therefore, the reading is 330.6° .



Measuring the wavelengths of the spectral lines of hydrogen

The lines will probably be quite faint and it will probably be necessary to have the apparatus in a darkened room to observe the lines clearly. The most difficult part is aligning the spectral lines with the cross-wires. If the room is completely dark, it will be impossible to see the cross-wires. A small amount of field illumination is necessary to be able to see the cross-wires.

There should be no problem with making the measurement for the straight through position. There should be sufficient light coming directly through the slit to make locating the image of the slit on the cross-wires quite easy.

Record this value and then record the reading of as many of the spectral lines as possible. (If it is possible to measure any of the spectral lines of the second order spectrum it is worth doing so.)

Calibration of diffraction grating

If necessary, the diffraction grating could be calibrated using a sodium vapour spectral tube. Set up this tube and observe the angle to the very bright orange line in the first order spectrum of sodium ($n = 1$). This line is really a double line, the wavelengths of the lines being 589.0 nm and 589.6 nm.

You can use the information in the equation $\lambda = \frac{d \sin \theta}{n}$ to calculate d .

Results

Record your results in a table similar to the table below and calculate the wavelengths of the spectral lines.

The number of lines per centimetre or perhaps even the number of lines per inch is probably supplied with the diffraction grating. It will be necessary to convert this to lines per metre and d is the inverse of this value.

Record the reading of the straight through position θ_0 .

SPECTRAL LINE COLOUR	POSITION θ	ANGLE $\theta - \theta_0$	ORDER OF SPECTRA (n)	WAVELENGTH
Faint violet			1	
Violet			1	
Blue-Green			1	
Red			1	
			2	
			2	
			2	
			2	

Analysis

1. The energy of the ground state of hydrogen is $E_1 = -13.6 \text{ eV}$.

The energies of the other states are given by

$$E_n = \frac{E_1}{n^2}$$

Determine the energy, in electron volts, of the energy states $n = 2, 3, 4, 5,$ and 6 .

2. Draw an energy level diagram and calculate the energies (in electron volts) of photons emitted when an electron jumps to the $n = 2$ state from each of the four higher energy states.
3. Convert these values from electron volts to joules and calculate the wavelengths of these photons.

Use:

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

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

where

$$1 \text{ eV} = 1.6 \times 10^{-19} \text{ J}$$

$$h = 6.602 \times 10^{-34} \text{ J s.}$$

4. Compare the values of the wavelengths calculated above with the values determined from the measurements of the angles.

Questions

1. How accurate do you consider your determination of the wavelengths of the spectral lines? Aside from any difficulty with aligning the spectral lines with the cross-wires, you are restricted to measuring the angle to the nearest 0.1° . Consider how a change in angle of 0.1° will alter your calculations.
2. Taking into account the expected accuracy of your observations, do you consider that your results are in agreement with the theoretical values of the wavelengths of these four spectral lines of hydrogen?