Unit 23

Quantization of Energy

This unit online, with its interactives:
science-playground.com/s/12f23

Fill a thin glass tube with hydrogen and pass a spark through it, and it glows pink. Look at that glow through a prism or a diffraction grating, and the pink comes apart into just four bright lines, red, blue-green, blue and violet, with darkness between. Not a rainbow, four colors. Why should hydrogen, the simplest atom of all, give out light of only a few exact wavelengths?

The answer turned physics over. Inside an atom, energy can't take any value it likes: it comes in steps, **quantized**. This unit follows that idea from Bohr's model of the hydrogen atom, its orbits, energy levels and spectral lines, to the surprising discovery that electrons behave as waves, the limit on what can ever be measured about them, and then to X-rays: how they are made, what they are used for, and how crystals reveal their wavelength.



Figure 23.1 *Niels Bohr in about 1922, the year he won the Nobel Prize in Physics.*

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A STORY FROM SCIENCE

Niels Bohr and the atom that shouldn't exist

Niels Bohr (1885–1962) was born in Copenhagen, Denmark, the son of a professor of physiology, and grew up among scientists and philosophers who came to dinner. As a young physicist he went to England in 1911, first to Cambridge and then to Manchester, where **Ernest Rutherford** had just found that an atom is a tiny, heavy, positive nucleus with electrons somewhere around it.

Rutherford's atom had a fatal flaw. An electron going round in a circle is accelerating, and an accelerating charge gives out light, losing energy. By the physics of the time, every electron should spiral into its nucleus in about a hundred-billionth of a second, and every atom should collapse. Yet atoms last for billions of years.

In 1913, aged 27, Bohr simply declared that some orbits are allowed and the electron does not radiate in them. It was a rule without a reason, but from it he calculated the exact wavelengths of hydrogen's spectral lines, which had been measured for thirty years and never explained. He won the **Nobel Prize in Physics in 1922** (the full story). His institute in Copenhagen became the place where quantum mechanics was worked out in the 1920s. During the Second World War he escaped from occupied Denmark to Sweden in a fishing boat, and afterwards argued for the open, peaceful use of atomic energy.

23.1 Bohr's atomic model

Why don't the electrons in an atom spiral into the nucleus?

The German physicist **Max Planck** had shown in 1900 that light is given out and absorbed in packets, **quanta**, each of energy $E = hf$, where f is the frequency and h **Planck's constant**, 6.63×10^{-34} J s (the full story). Bohr applied the same idea, that energy comes in steps, to the atom.

In 1911 Rutherford's **nuclear model** had shown that an atom is a tiny, dense, positive nucleus with electrons going round it. But the model met two problems it couldn't solve:

1. **The stability of atoms.** An electron going round the nucleus is always changing direction, so it is accelerating, and by classical electromagnetism an accelerating charge radiates energy. The electron should lose energy continuously and spiral into the nucleus, and the atom should collapse (Figure 23.2). Yet atoms are stable.
2. **The line spectrum of hydrogen.** A spiraling electron would go round faster and faster, giving out light of every frequency: a continuous spectrum. But hot hydrogen gives out light of only certain exact wavelengths, separate bright **lines**.

In 1913 **Niels Bohr** kept Rutherford's nucleus but added three rules, his **postulates**:

Postulates of Bohr's atomic model

i. **Stationary orbits.** An electron goes round the nucleus only in certain allowed circular orbits, each with a definite radius and a definite energy. In these orbits it does **not** radiate energy, however long it stays. They are called **stationary orbits** (or stationary states).

ii. **Quantization of angular momentum.** The allowed orbits are those in which the electron's **angular momentum** is a whole-number multiple of $\dfrac{h}{2\pi}$. If an electron of mass m moves with speed v in an orbit of radius r,

$$mvr = \frac{nh}{2\pi} \qquad (23.1)$$

where $n = 1, 2, 3, \ldots$ is the **principal quantum number**. Equation (23.1) is **Bohr's quantization condition**. ($h/2\pi$ is often written $\hbar$, "h-bar", the reduced Planck constant.)

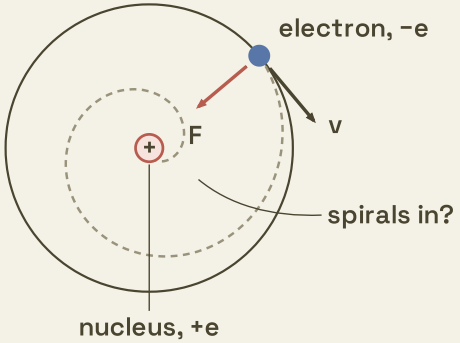


Figure 23.2 *Rutherford's atom: an electron (charge $-e$) goes round the nucleus ($+e$) with speed v, pulled towards it by the electric force F. By classical physics it should radiate, lose energy and spiral inwards (dashed) into the nucleus.*

iii. **Frequency condition.** An atom gives out energy only when an electron **jumps** from an orbit of higher energy to one of lower energy, and takes in energy only when it jumps from a lower to a higher one. The energy goes out or comes in as a single photon. If the electron jumps from the orbit of energy E_2 to the orbit of energy E_1, the frequency f of the light is given by

$$hf = E_2 - E_1 \qquad (23.2)$$

Equation (23.2) is **Bohr's frequency condition**.

CAREFUL

Two kinds of rule

Postulate (ii) says which orbits are allowed; postulate (iii) says what light comes out when the electron changes orbit. The frequency of the light is set by the **difference in energy** between two orbits, not by how fast the electron goes round in either of them, which was the surprise: in classical physics a charge going round f times a second radiates at frequency f.

Check 1

In Bohr's model, an electron in a stationary orbit:

a radiates energy continuously as it goes round
b does not radiate, however long it stays there
c slowly spirals towards the nucleus
d can have any angular momentum

23.2 Bohr's theory of the hydrogen atom

How big is a hydrogen atom, and how much energy does its electron have?

A hydrogen atom is a nucleus (a proton) of charge $+e$ and one electron of charge $-e$ going round it in a circle of radius r_n. The electric force between them is

$$F = \frac{1}{4\pi\varepsilon_0}\frac{e^2}{r_n^2}$$

where ε_0 is the permittivity of free space; $k = \dfrac{1}{4\pi\varepsilon_0} = 9 \times 10^9$ N m² C^{-2}.

Radius of the nth orbit

For the electron to go round in a circle, it needs a **centripetal force** $\dfrac{mv_n^2}{r_n}$, and the electric attraction provides it:

$$\frac{1}{4\pi\varepsilon_0}\frac{e^2}{r_n^2} = \frac{mv_n^2}{r_n} \qquad (23.3)$$

From Bohr's quantization condition, $mv_n r_n = \dfrac{nh}{2\pi}$, so

$$v_n = \frac{nh}{2\pi m r_n} \qquad (23.4)$$

Putting this v_n into equation (23.3) and multiplying both sides by r_n:

$$\frac{e^2}{4\pi\varepsilon_0 r_n} = m\left(\frac{nh}{2\pi m r_n}\right)^2 = \frac{n^2h^2}{4\pi^2 m r_n^2}$$

Multiplying both sides by $4\pi\varepsilon_0 r_n^2$ and dividing by e^2:

$$r_n = \frac{n^2h^2\varepsilon_0}{\pi m e^2} \qquad (23.5)$$

With $h = 6.63 \times 10^{-34}$ J s, $\varepsilon_0 = 8.85 \times 10^{-12}$ C² N^{-1} m^{-2}, $e = 1.6 \times 10^{-19}$ C and $m = 9.1 \times 10^{-31}$ kg,

$$r_n = n^2 \times 0.53 \times 10^{-10}\ \text{m} = 0.53\, n^2\ \text{Å}$$

So $r_n \propto n^2$: the radii of the stationary orbits are in the ratio $1 : 4 : 9 : 16$ ... The smallest, $r_1 = 0.53$ Å, is the **Bohr radius**, the size of a hydrogen atom in its normal state. (1 ångström, Å, is 10^{-10} m.)

For a nucleus of charge $+Ze$ with one electron (He$^+$, Li^{2+} ...), the force is $Ze^2/4\pi\varepsilon_0 r^2$, and the same steps give

$$r_n = \frac{n^2h^2\varepsilon_0}{\pi m Z e^2}$$

Speed of the electron in the nth orbit

Putting r_n from (23.5) into (23.4):

$$v_n = \frac{nh}{2\pi m}\cdot\frac{\pi m e^2}{n^2h^2\varepsilon_0} = \frac{e^2}{2\varepsilon_0 nh} \qquad (23.6)$$

With the values of e, h and ε_0, this is $v_n = \dfrac{2.19 \times 10^6}{n}$ m/s, or $\dfrac{c}{137\,n}$: in the first orbit the electron goes at about 1/137 of the speed of light. So $v_n \propto \dfrac{1}{n}$: the farther out the orbit, the slower the electron.

Energy of the electron in the nth orbit

The electron's total energy is its kinetic energy (from its motion) plus its potential energy (from the attraction of the nucleus):

$$E_n = KE + PE$$

Kinetic energy. From equation (23.3), $mv_n^2 = \dfrac{e^2}{4\pi\varepsilon_0 r_n}$, so

$$KE = \frac{1}{2}mv_n^2 = \frac{e^2}{8\pi\varepsilon_0 r_n}$$

Potential energy. The potential of the nucleus at distance r_n is $V = \dfrac{e}{4\pi\varepsilon_0 r_n}$, and the electron's charge is $-e$, so

$$PE = (-e)V = -\frac{e^2}{4\pi\varepsilon_0 r_n}$$

Total energy.

$$E_n = \frac{e^2}{8\pi\varepsilon_0 r_n} - \frac{e^2}{4\pi\varepsilon_0 r_n} = -\frac{e^2}{8\pi\varepsilon_0 r_n}$$

Putting in r_n from (23.5):

$$E_n = -\frac{e^2}{8\pi\varepsilon_0} \cdot \frac{\pi m e^2}{n^2 h^2 \varepsilon_0} = -\frac{me^4}{8\varepsilon_0^2 n^2 h^2} \qquad (23.7)$$

With the values of the constants, $\frac{me^4}{8\varepsilon_0^2 h^2} \approx 2.17 \times 10^{-18}$ J, and since 1 eV $= 1.6 \times 10^{-19}$ J,

$$E_n = -\frac{13.6}{n^2} \text{ eV}$$

DID YOU KNOW?

Half and minus one

Look at the three energies: $KE = \frac{e^2}{8\pi\varepsilon_0 r}$, $PE = -\frac{e^2}{4\pi\varepsilon_0 r}$, $E = -\frac{e^2}{8\pi\varepsilon_0 r}$. So $PE = -2\,KE$ and $E = -KE$. In the ground state the electron's kinetic energy is +13.6 eV, its potential energy −27.2 eV, and its total −13.6 eV. The same relation holds for a satellite round the Earth: any orbit held by an inverse-square force has it.

The wavelengths of the lines: Rydberg's formula

Let the electron jump from an orbit with quantum number n_2 to a lower one with n_1 ($n_2 > n_1$). From (23.7) their energies are

$$E_{n_1} = -\frac{me^4}{8\varepsilon_0^2 n_1^2 h^2}, \qquad E_{n_2} = -\frac{me^4}{8\varepsilon_0^2 n_2^2 h^2}$$

By Bohr's frequency condition, the photon given out has

$$hf = E_{n_2} - E_{n_1} = \frac{me^4}{8\varepsilon_0^2 h^2}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

so

$$f = \frac{me^4}{8\varepsilon_0^2 h^3}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

For light, $c = f\lambda$, so $f = c/\lambda$, and

$$\frac{1}{\lambda} = \frac{me^4}{8\varepsilon_0^2 ch^3}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

$1/\lambda$, the number of waves in one meter, is called the **wave number**. The constant in front, $\frac{me^4}{8\varepsilon_0^2 ch^3}$, is written R and called **Rydberg's constant**; its measured value is $R = 1.097 \times 10^7$ m^{-1}. So

$$\frac{1}{\lambda} = R\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \qquad (23.8)$$

This is the **Rydberg formula**. The Swedish physicist Johannes Rydberg had found it in 1888 by fitting the measured wavelengths, with no idea why it worked. Bohr's theory gave its reason, and the value of R worked out from m, e, h and ε_0 agrees with the measured one: that was the triumph of the theory.

Check 2

In Bohr's model of hydrogen, the radius of the electron's orbit for n = 3 is:

a 3 times that for n = 1
b 9 times that for n = 1
c one-third of that for n = 1
d the same as for n = 1

Check 3

As the electron moves to orbits farther out (larger n), its speed and its total energy:

a both increase

b its speed decreases and its total energy increases (becomes less negative)

c its speed increases and its total energy decreases

d both stay the same

23.3 Limitations of Bohr's atomic model

Bohr's model was a great step, but it has limits:

1. It works only for hydrogen and for ions with a single electron (He^+, Li^{2+}); it can't describe atoms with more than one electron accurately.
2. It can't explain the **fine structure** of spectral lines (a line seen with a better spectrometer is really two or more close lines), or the splitting of lines in a magnetic field (the **Zeeman effect**).
3. It doesn't take into account the **wave nature** of electrons, or quantum mechanics as it was later worked out.
4. It can't explain the chemical behavior of atoms or how they bond into molecules.
5. It gives the electron an exact orbit, an exact position and an exact momentum at once, which the **uncertainty principle** (Section 23.11) says is impossible.

In modern quantum mechanics, the electron has no orbit at all, only a cloud of where it is likely to be found. But Bohr's energies, $-13.6/n^2$ eV, come out exactly the same.

WORKED EXAMPLE

Example 23.1: the minus sign

What does the negative sign in the energy levels of the hydrogen atom signify?

Answer

Energy is measured from a zero at which the electron is **free**: at rest, far away from the nucleus. The negative sign says that the electron in the atom has **less** energy than that: it is **bound** to the nucleus. To set it free (to ionize the atom), energy must be supplied, 13.6 eV from the ground state. The more negative the energy, the more tightly the electron is held.

WORKED EXAMPLE

Example 23.2: closer means more negative

Why does the energy of an electron become more negative as it moves closer to the nucleus in Bohr's model?

Answer

The energy is $E_n = -\dfrac{e^2}{8\pi\varepsilon_0 r_n}$: the smaller r_n, the larger its size, and it is negative, so it is more negative.

In terms of what happens: as the electron moves in, the attraction of the nucleus does work on it, so the potential energy, $-e^2/4\pi\varepsilon_0 r$, falls (becomes more negative) by a certain amount. Half of that goes into the electron's kinetic energy (it moves faster in a smaller orbit); the other half must be given out, as a photon. So the total energy falls: the electron is bound more tightly, and the atom is more stable.

WORKED EXAMPLE

Example 23.3: a stationary orbit

What is a stationary orbit in Bohr's atomic model?

Answer

A **stationary orbit** is one of the allowed circular orbits round the nucleus, those for which the electron's angular momentum is $nh/2\pi$. In such an orbit the electron goes round **without radiating energy**: its energy stays constant for as long as it stays there.

WORKED EXAMPLE

Example 23.4: where the lines come from

Which postulate of Bohr's model explains the discrete spectral lines of hydrogen?

Answer

The **third postulate** (the frequency condition): an atom gives out or takes in energy only when an electron jumps between two stationary orbits, as one photon whose energy hf equals the difference between their energies. Since the orbits have only certain energies, only certain photon energies, and so certain wavelengths, are possible: separate lines.

WORKED EXAMPLE

Example 23.5: the size of a hydrogen atom

Calculate the radius of the hydrogen atom in its ground state, and the speed of the electron in this orbit. Take $m = 9.1 \times 10^{-31}$ kg, $e = 1.6 \times 10^{-19}$ C, $h = 6.62 \times 10^{-34}$ J s and $\varepsilon_0 = 8.85 \times 10^{-12}$ C^2 N^{-1} m^{-2}.

Answer

For the ground state, $n = 1$:

$$r_1 = \frac{h^2 \varepsilon_0}{\pi m e^2} = \frac{(6.62 \times 10^{-34})^2 \times 8.85 \times 10^{-12}}{\pi \times 9.1 \times 10^{-31} \times (1.6 \times 10^{-19})^2} = \mathbf{0.53 \times 10^{-10}}\ \text{m} = 0.53\ \text{Å}$$

$$v_1 = \frac{e^2}{2\varepsilon_0 h} = \frac{(1.6 \times 10^{-19})^2}{2 \times 8.85 \times 10^{-12} \times 6.62 \times 10^{-34}} = \mathbf{2.19 \times 10^{6}}\ \text{m/s}$$

That is about 1/137 of the speed of light.

WORKED EXAMPLE

Example 23.6: from the third orbit to the second

Find the wavelength of the radiation emitted by a hydrogen atom when its electron jumps from the third orbit to the second. ($\varepsilon_0 = 8.85 \times 10^{-12}$ C^2 N^{-1} m^{-2}, $h = 6.63 \times 10^{-34}$ J s, $m = 9.1 \times 10^{-31}$ kg, $e = 1.6 \times 10^{-19}$ C)

Answer

The energies of the two orbits are

$$E_3 = -\frac{me^4}{8\varepsilon_0^2 h^2 \times 9}, \qquad E_2 = -\frac{me^4}{8\varepsilon_0^2 h^2 \times 4}$$

So the photon's frequency is

$$f = \frac{E_3 - E_2}{h} = \frac{me^4}{8\varepsilon_0^2 h^3}\left(\frac{1}{4} - \frac{1}{9}\right) = \frac{me^4}{8\varepsilon_0^2 h^3} \cdot \frac{5}{36}$$

and $\lambda = \dfrac{c}{f} = \dfrac{8\varepsilon_0^2 c h^3}{me^4} \cdot \dfrac{36}{5}$:

$$\lambda = \frac{8 \times (8.85 \times 10^{-12})^2 \times 3 \times 10^8 \times (6.63 \times 10^{-34})^3 \times 36}{9.1 \times 10^{-31} \times (1.6 \times 10^{-19})^4 \times 5} = \mathbf{6.6 \times 10^{-7}}\ \text{m}$$

This is the red line of hydrogen, H-alpha, measured at 656 nm.

WORKED EXAMPLE

Example 23.7: how close an alpha particle gets

An alpha particle with kinetic energy 7.68 MeV is fired straight at a copper nucleus (Z = 29). Calculate its distance of closest approach.

Answer

$KE = 7.68$ MeV $= 7.68 \times 10^6 \times 1.6 \times 10^{-19} = 1.23 \times 10^{-12}$ J.

At the closest point the alpha particle stops for an instant: all its kinetic energy has become electric potential energy. The alpha particle's charge is $2e$, the nucleus's Ze:

$$KE = \frac{1}{4\pi\varepsilon_0}\frac{(Ze)(2e)}{r_0} \quad \Rightarrow \quad r_0 = \frac{9 \times 10^9 \times 29 \times 2 \times (1.6 \times 10^{-19})^2}{1.23 \times 10^{-12}} = \mathbf{1.09 \times 10^{-14}}\ \text{m}$$

The alpha particle gets within about 10^{-14} m of the center: the nucleus must be smaller than that, ten thousand times smaller than the atom.

23.4 Spectral series of the hydrogen atom

Why do hydrogen's lines come in families?

When an electron in a hydrogen atom drops from a higher level to a lower one, the energy difference goes out as light of one particular wavelength: a **spectral line**. Different pairs of levels give different lines. All the lines given by jumps that **end on the same lower level** n_1 form a **spectral series** (Figure 23.3). Each comes from the Rydberg formula, $\dfrac{1}{\lambda} = R\left(\dfrac{1}{n_1^2} - \dfrac{1}{n_2^2}\right)$, with a different n_1.

1. Lyman series. Jumps from $n_2 = 2, 3, 4, \ldots$ to $n_1 = 1$:

$$\frac{1}{\lambda} = R\left(\frac{1}{1^2} - \frac{1}{n_2^2}\right), \quad n_2 = 2, 3, 4, \ldots$$

These are big jumps, so the photons have large energies: the lines lie in the **ultraviolet** (121.6 nm down to 91.2 nm).

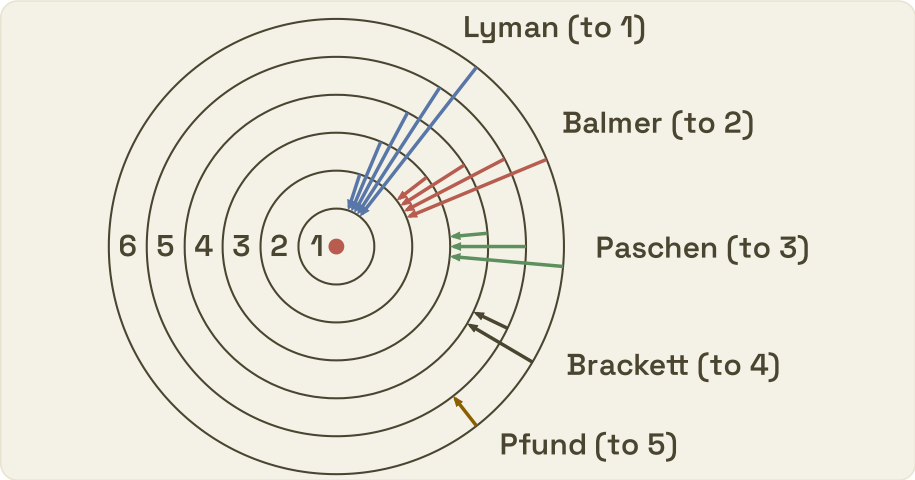


Figure 23.3 *The first six orbits of hydrogen (radii not to scale) and the jumps that give its spectral series. Jumps to $n = 1$ give the Lyman series, to $n = 2$ the Balmer series, to $n = 3$ the Paschen series, to $n = 4$ Brackett and to $n = 5$ Pfund.*

2. Balmer series. Jumps from $n_2 = 3, 4, 5, \ldots$ to $n_1 = 2$:

$$\frac{1}{\lambda} = R\left(\frac{1}{2^2} - \frac{1}{n_2^2}\right), \quad n_2 = 3, 4, 5, \ldots$$

Its first lines are in the **visible** region: 656 nm (red), 486 nm (blue-green), 434 nm (blue) and 410 nm (violet), the four lines of the opening. The rest crowd together towards 365 nm, in the ultraviolet.

3. Paschen series. Jumps from $n_2 = 4, 5, 6, \ldots$ to $n_1 = 3$:

$$\frac{1}{\lambda} = R\left(\frac{1}{3^2} - \frac{1}{n_2^2}\right), \quad n_2 = 4, 5, 6, \ldots$$

in the **infrared** (1875 nm down to 820 nm).

4. Brackett series. Jumps from $n_2 = 5, 6, 7, \ldots$ to $n_1 = 4$:

$$\frac{1}{\lambda} = R\left(\frac{1}{4^2} - \frac{1}{n_2^2}\right), \quad n_2 = 5, 6, 7, \ldots$$

also in the **infrared**.

5. Pfund series. Jumps from $n_2 = 6, 7, 8, \ldots$ to $n_1 = 5$:

$$\frac{1}{\lambda} = R\left(\frac{1}{5^2} - \frac{1}{n_2^2}\right), \quad n_2 = 6, 7, 8, \ldots$$

in the **far infrared**.

In each series, the **first line** ($n_2 = n_1 + 1$) has the **longest** wavelength, and the lines get closer together towards the **series limit** ($n_2 \to \infty$), the shortest wavelength, $\lambda = n_1^2/R$.

DID YOU KNOW?

Hydrogen's red glow in the sky

Most of the visible universe is hydrogen, and wherever hot young stars light up a cloud of it, the gas glows in Balmer's red line, H-alpha at 656 nm. The pink and red clouds in photographs of the Orion Nebula, which you can find below Orion's belt on a winter night in Nepal, are that one line. Astronomers photograph the sky through filters that pass only 656 nm to map where new stars are being born.

WORKED EXAMPLE

Example 23.8: the visible series

Which spectral series of hydrogen lies in the visible region?

Answer

The **Balmer series** (jumps to $n_1 = 2$): its first four lines, 656, 486, 434 and 410 nm, are visible.

WORKED EXAMPLE

Example 23.9: where the Paschen series comes from

How does the Paschen series arise in the hydrogen spectrum?

Answer

It is given out when electrons jump from the higher orbits, $n_2 = 4, 5, 6, \ldots$, down to the **third** orbit, $n_1 = 3$. Its wavelengths are

$$\frac{1}{\lambda} = R\left(\frac{1}{3^2} - \frac{1}{n_2^2}\right)$$

and all of them are in the infrared.

WORKED EXAMPLE

Example 23.10: the first Balmer line

Rydberg's constant is $1.09678 \times 10^7\ \text{m}^{-1}$. Calculate the wavelength of the first line (first member) of the Balmer series.

Answer

For the Balmer series $n_1 = 2$, and for its first line $n_2 = 3$:

$$\frac{1}{\lambda} = R\left(\frac{1}{2^2} - \frac{1}{3^2}\right) = R \cdot \frac{5}{36} \quad \Rightarrow \quad \lambda = \frac{36}{5R} = \frac{36}{5 \times 1.09678 \times 10^7} = \mathbf{6.565 \times 10^{-7}}\ \text{m} = 6565\ \text{Å}$$

WORKED EXAMPLE

Example 23.11: the second Balmer line from the first

The first line of the Balmer series of hydrogen has a wavelength of 6563 Å. Find the wavelength of its second line.

Answer

First line, $n_2 = 3$: $\dfrac{1}{\lambda_1} = R\left(\dfrac{1}{4} - \dfrac{1}{9}\right) = \dfrac{5R}{36}$.

Second line, $n_2 = 4$: $\dfrac{1}{\lambda_2} = R\left(\dfrac{1}{4} - \dfrac{1}{16}\right) = \dfrac{3R}{16}$.

Dividing,

$$\frac{\lambda_2}{\lambda_1} = \frac{5/36}{3/16} = \frac{5}{36} \times \frac{16}{3} = \frac{20}{27} \quad \Rightarrow \quad \lambda_2 = \frac{20}{27} \times 6563 = \mathbf{4861}\ \text{Å}$$

The blue-green line, H-beta.

23.5 Energy level diagram of the hydrogen atom

How can all of hydrogen's lines be shown in one picture?

From equation (23.7), the energy of the electron in the nth orbit is

$$E_n = -\frac{me^4}{8\varepsilon_0^2 n^2 h^2} = -\frac{13.6}{n^2}\ \text{eV}$$

so

- $E_1 = -13.6$ eV ($n = 1$), the **ground state** of the hydrogen atom: its normal state, of lowest energy;
- $E_2 = -13.6/2^2 = -3.4$ eV, the **first excited state**;
- $E_3 = -13.6/3^2 = -1.51$ eV, the second excited state;
- $E_4 = -0.85$ eV, $E_5 = -0.54$ eV, $E_6 = -0.38$ eV, and so on;
- $E_\infty = 0$ for $n = \infty$.

As n increases, the energy becomes less negative and approaches **zero**. For large n the levels are so close together that they almost form a continuous band. At $n = \infty$ the electron is no longer bound to the nucleus: it is **free**, and above zero it can have any energy at all.

Drawing each energy as a horizontal line at its height, with the jumps as arrows, gives the **energy level diagram** of the hydrogen atom (Figure 23.4). Each arrow is one spectral line; its length is the photon's energy.

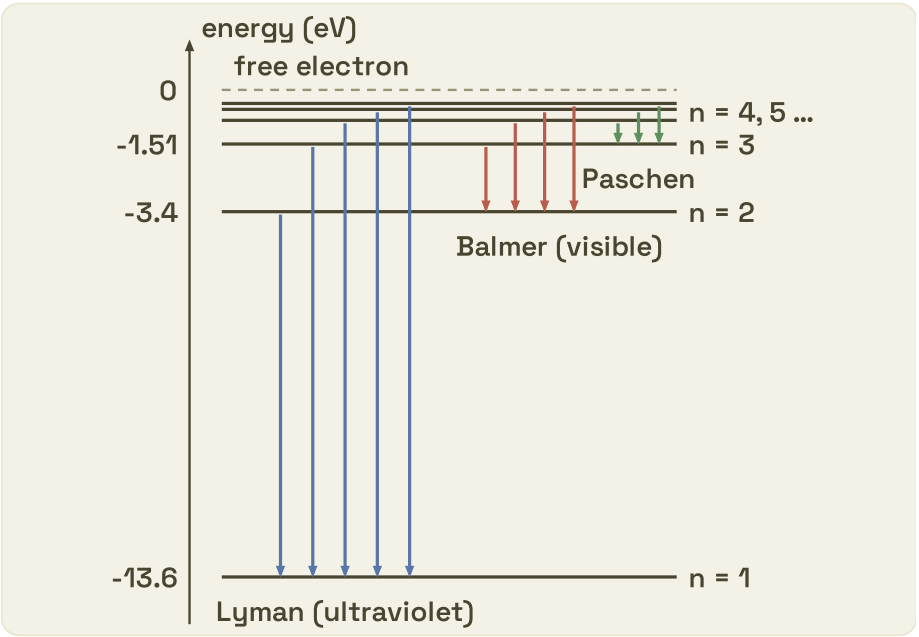


Figure 23.4 *The energy level diagram of hydrogen, energies in eV (drawn to scale). The arrows are jumps that give out light: to n = 1 the Lyman series (ultraviolet), to n = 2 Balmer (visible), to n = 3 Paschen (infrared). The Brackett and Pfund jumps, to n = 4 and 5, are too short to draw at this scale. At 0 eV and above the electron is free.*

23.6 Excitation and ionization potentials

How much energy does it take to lift the electron, or to take it out of the atom?

Excitation energy and potential

Excitation energy is the energy needed to raise an electron from the ground state to a higher level, an **excited state**. For hydrogen, the electron in the ground state has $E_1 = -13.6$ eV, and in the first excited state

$E_2 = -3.4$ eV, so the energy needed to raise it from the ground state to the first excited state is

$$E_2 - E_1 = -3.4 - (-13.6) = 10.2 \text{ eV}$$

This, 10.2 eV, is the **first excitation energy** of hydrogen.

An electron accelerated through a potential difference of 1 V gains 1 eV of energy. So an electron accelerated through **10.2 V** has just enough energy to raise a hydrogen atom it hits from the ground state to the first excited state. The accelerating voltage that gives an electron the excitation energy is the **excitation potential**: 10.2 V is the first excitation potential of hydrogen.

Similarly, from $n = 1$ to $n = 3$:

$$E_3 - E_1 = -1.51 - (-13.6) = 12.09 \text{ eV}$$

the **second excitation energy**; the second excitation potential is 12.09 V.

Ionization energy and potential

Ionization energy is the energy needed to remove the electron completely from the atom in its ground state, to an infinite distance from the nucleus, where it is free with no kinetic energy. For hydrogen, that is a jump from $n = 1$ to $n = \infty$:

$$\text{ionization energy} = E_\infty - E_1 = 0 - (-13.6) = 13.6 \text{ eV}$$

It equals the size of the ground state energy, as a positive number, because energy must be **supplied**. The accelerating potential that gives an electron this energy, **13.6 V**, is the **ionization potential** of hydrogen. What is left is a positive ion, for hydrogen a bare proton: hence the name.

> CAREFUL
> **Energy in eV, potential in V**
>
> Excitation and ionization **energies** are in electron volts (eV) or joules; the **potentials** are in volts (V). They have the same number, because an electron accelerated through V volts gains V eV: the ionization energy of hydrogen is 13.6 eV, its ionization potential 13.6 V.

23.7 Emission and absorption spectra

Why does a spectrum sometimes show bright lines, and sometimes dark ones?

Emission spectra

An **emission spectrum** is the spectrum of the light given out by a substance when its atoms or molecules lose energy, their electrons dropping from higher to lower levels. There are three kinds (Figure 23.5):

1. **Continuous spectrum.** All wavelengths, with no gaps, one color merging into the next. It is given out by hot **solids, liquids and dense gases**, where the atoms are so close together that their levels merge. Examples: the filament of an old light bulb, a red-hot iron rod, and (nearly) the Sun.
2. **Line spectrum.** Separate bright lines of particular wavelengths on a dark background. It is given out by **atoms of a gas** (spread far apart, so each behaves on its own), when they are excited by heat or an electric discharge. Each line is one jump between two levels. Example: the hydrogen spectrum, sodium's yellow street lamps. Every element has its own lines, like a fingerprint, so a line spectrum identifies the element.
3. **Band spectrum.** Bands, each made of many lines so close that they look like a smudge with one sharp edge. It is given out by **molecules** (such as N_2, O_2 or CO_2), whose energy changes when they vibrate and rotate as well as when their electrons jump, so each electron jump comes with many slightly different extra energies.

Absorption spectra

When white light, with all wavelengths, passes through a **cooler gas**, the atoms of the gas absorb exactly those wavelengths whose photons can lift their electrons to higher levels, and let the rest pass. The spectrum of the light that comes through is continuous, but crossed by **dark lines** at the absorbed wavelengths. This is an **absorption spectrum**. Its dark lines are at exactly the same wavelengths as the bright lines in the same gas's emission spectrum, since the same pairs of levels are involved.

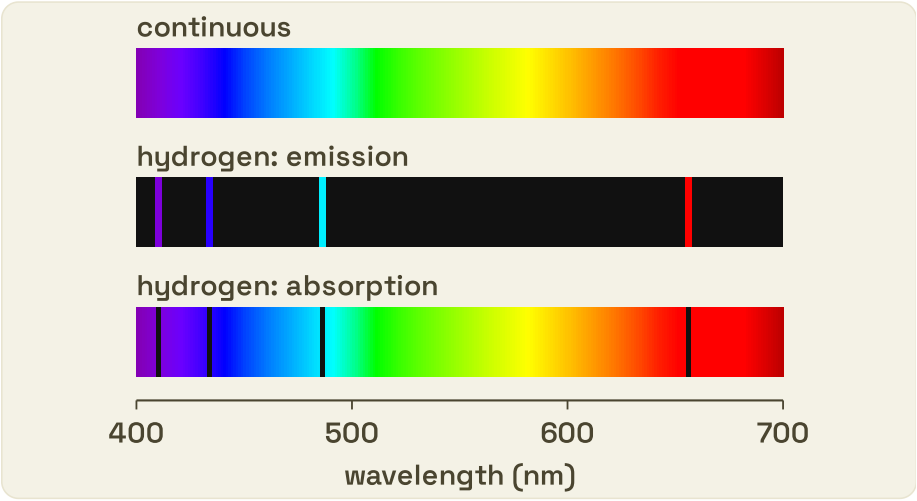


Figure 23.5 *Three spectra from 400 to 700 nm. Top: a continuous spectrum, every color. Middle: hydrogen's emission spectrum, four bright lines (410, 434, 486 and 656 nm) on black. Bottom: hydrogen's absorption spectrum, white light with dark lines at the same four wavelengths.*

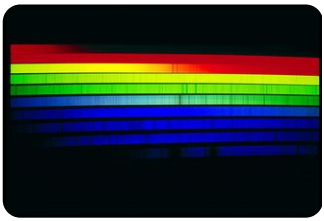


Figure 23.6 *The Sun's spectrum, from red (top left) to violet (bottom right), cut into strips so that it fits on a page. Each dark line is an absorption line: the gases of the Sun's cooler outer layers take their own wavelengths out of the light from the hotter layers below.*

Photo: N.A. Sharp, NOAO/NSO/Kitt Peak FTS/AURA/NSF, CC BY 4.0

DID YOU KNOW?

The element found in the Sun first

In 1868, during a solar eclipse seen from India, astronomers found a bright yellow line in the light of the Sun's edge at 587.6 nm, close to sodium's but not the same. No element on Earth gave it. They named the unknown element after the Greek for the Sun, *helios*: **helium**. It wasn't found on Earth until 1895, in a uranium mineral.

WORKED EXAMPLE

Example 23.12: excitation and ionization

Distinguish between excitation energy and ionization energy.

Answer

Excitation energy is the energy needed to raise an electron from the ground state to a higher level, while it still stays in the atom. For hydrogen, the first excitation energy (from n = 1 to n = 2) is $-3.4 - (-13.6) = 10.2$ eV.

Ionization energy is the energy needed to remove the electron from the ground state completely, to $n = \infty$. For hydrogen it is $0 - (-13.6) = 13.6$ eV. After ionization the atom has become a positive ion.

WORKED EXAMPLE

Example 23.13: how a line spectrum forms

How is a line spectrum formed?

Answer

Atoms of an element in a gas (far apart, so they don't affect each other) are excited, by heating or by an electric discharge, to higher energy levels. Their electrons then fall back to lower levels, each jump giving out one photon whose energy is the difference between the two levels. Since an atom has only certain levels, only certain photon energies and wavelengths are given out: separate bright lines, each line one particular jump.

WORKED EXAMPLE

Example 23.14: lines after absorbing a photon

A hydrogen atom in its ground state is excited by light of wavelength 975 Å. How many different lines are possible in the resulting spectrum? Calculate the longest wavelength among them. (Ionization energy of hydrogen = 13.6 eV, $h = 6.62 \times 10^{-34}$ J s)

Answer

The energy levels are $E_n = -13.6/n^2$ eV: $E_1 = -13.6$, $E_2 = -3.4$, $E_3 = -1.51$, $E_4 = -0.85$ eV.
The energy of the photon absorbed:

$$E = \frac{hc}{\lambda} = \frac{6.62 \times 10^{-34} \times 3 \times 10^{8}}{975 \times 10^{-10} \times 1.6 \times 10^{-19}} = 12.73 \text{ eV}$$

After absorbing it, the atom has $-13.6 + 12.73 = -0.87$ eV, which (within the rounding) is the level $n = 4$, -0.85 eV. So the photon lifts the electron to **n = 4**.
From n = 4 the electron can come down by any route: 4→3, 4→2, 4→1, 3→2, 3→1, 2→1. That is **6 lines** (Figure 23.7). In general, from level n the number of possible lines is

$$\frac{n(n-1)}{2} = \frac{4 \times 3}{2} = 6$$

The **longest** wavelength comes from the **smallest** energy jump, 4→3:

$$E_4 - E_3 = -0.85 - (-1.51) = 0.66 \text{ eV}$$

$$\lambda_{\max} = \frac{hc}{E_4 - E_3} = \frac{6.62 \times 10^{-34} \times 3 \times 10^{8}}{0.66 \times 1.6 \times 10^{-19}} = \mathbf{1.88 \times 10^{-6}} \text{ m} \approx 18\,800 \text{ Å}$$

in the infrared (the first Paschen line).

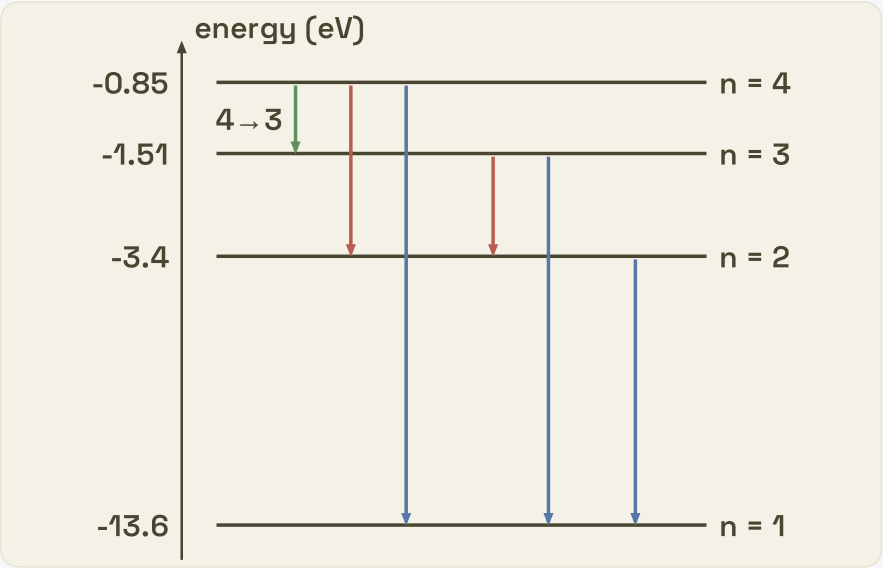


Figure 23.7 *The six possible jumps down from n = 4 (not to scale). The smallest jump, 4→3, gives the longest wavelength.*

23.8 Dual nature of radiation

Is light a wave or a stream of particles?

Both, depending on what we do with it. **Interference**, **diffraction** and **polarization** of light can be explained only if light is an electromagnetic **wave**. But the **photoelectric effect** and the **Compton effect** (X-rays bouncing off electrons as if they were billiard balls) can be explained only if light comes as **particles**, photons, each of energy hf and momentum h/λ. Radiation has a **dual nature**: it shows wave properties in some experiments and particle properties in others.

23.9 de Broglie's dual hypothesis

If light can behave like particles, can particles behave like waves?

In 1924 the French physicist **Louis de Broglie** (pronounced "duh BROY") argued from the symmetry of nature: the universe is made of radiation and matter, and if radiation has a dual nature, matter should too. A moving particle, an electron for example, should behave as a particle when it is given out or absorbed, but as a **wave** while it travels.

It was soon confirmed. Electrons passed through a thin crystal (or a pair of slits) make **interference and diffraction patterns**, exactly as light and X-rays do. The **electron microscope**, which magnifies up to millions of times, works because electrons are waves of very short wavelength. Protons, neutrons, atoms and even large molecules have since been seen to diffract.

de Broglie hypothesis

A moving material particle behaves sometimes as a wave and sometimes as a particle. The wave linked with a moving particle is called a **matter wave** (or de Broglie wave), and its wavelength, the **de Broglie wavelength**, is

$$\lambda = \frac{h}{mv} \qquad (23.9)$$

where m and v are the particle's mass and speed, and h is Planck's constant.

Where the formula comes from

By Planck's quantum theory, a photon of light of frequency f and wavelength λ has energy

$$E = hf$$

By the theory of relativity, anything that travels at the speed of light with energy E carries momentum

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

So a photon has momentum

$$p = \frac{hf}{c} = \frac{h}{c/f} = \frac{h}{\lambda} \quad \text{or} \quad \lambda = \frac{h}{p} \qquad (23.10)$$

de Broglie assumed that equation (23.10) holds for material particles as well as for photons. A particle of mass m moving with speed v has momentum $p = mv$, so the wavelength of its wave is

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

This is the **de Broglie wave equation** for a material particle.

> CAREFUL
> **A photon has no mass**
>
> Some books get $p = h/\lambda$ by giving the photon a "mass" $m = E/c^2 = hf/c^2$, so that $p = mc$. The result is right, but a photon has no rest mass: it is never at rest. It is better to say that a photon has energy $E = hf$ and momentum $p = E/c$.

23.10 de Broglie wavelength of an electron

What is the wavelength of an electron fired by a voltage?

An electron of mass m and charge e, starting from rest, is accelerated through a potential difference V. It gains kinetic energy equal to the work done on it:

$$\frac{1}{2}mv^2 = eV \quad \Rightarrow \quad v = \sqrt{\frac{2eV}{m}}$$

Its de Broglie wavelength is then

$$\lambda = \frac{h}{mv} = \frac{h}{m\sqrt{2eV/m}} = \frac{h}{\sqrt{2meV}} \qquad (23.11)$$

Putting in $h = 6.63 \times 10^{-34}$ J s, $m = 9.1 \times 10^{-31}$ kg and $e = 1.6 \times 10^{-19}$ C:

$$\lambda = \frac{6.63 \times 10^{-34}}{\sqrt{2 \times 9.1 \times 10^{-31} \times 1.6 \times 10^{-19} \times V}} = \frac{12.27}{\sqrt{V}} \times 10^{-10}\ \text{m} = \frac{12.27}{\sqrt{V}}\ \text{Å}$$

An electron accelerated through 100 V has a wavelength of 1.23 Å, about the spacing of atoms in a crystal, which is why crystals diffract electrons. At the 100 000 V or so of an electron microscope, the wavelength is a few hundredths of an ångström, a hundred thousand times shorter than light's: that is why it can show such small things.

Check 4

A proton and an electron are moving at the same speed. Which has the longer de Broglie wavelength?

a the electron
b the proton
c both the same
d neither has a wavelength

23.11 Uncertainty principle

Can we know exactly where an electron is and how fast it moves?

In classical physics, a moving particle has at every moment an exact position, an exact momentum and an exact energy, and all of them can, in principle, be measured at once as accurately as we like. Pairs of quantities such as position and momentum, or energy and time, are called **complementary** (or conjugate) **variables**.

Quantum theory says no. It is **impossible** to know both the exact position and the exact momentum of a particle at the same time. The more precisely its position is pinned down (the smaller the uncertainty Δx), the less precisely its momentum can be known (the larger Δp), and the other way round. In the same way, the more precisely an energy is known, the longer the time over which it must be measured. This isn't a fault of our instruments: it is how nature is, because a particle is also a wave, and a wave squeezed into a small space has no single wavelength, so no single momentum.

Heisenberg's uncertainty principle

In any simultaneous measurement of a pair of complementary variables of a particle, the product of their uncertainties is at least about $\frac{h}{2\pi}$. For position and momentum,

$$\Delta x \cdot \Delta p \geq \frac{h}{2\pi}$$

and for energy and time,

$$\Delta E \cdot \Delta t \geq \frac{h}{2\pi}$$

where Δx, Δp, ΔE, Δt are the uncertainties in position, momentum, energy and time. The German physicist **Werner Heisenberg** stated it in 1927 (the full story).

CAREFUL

h/2π or h/4π?

The uncertainty principle is a rule about the **order of size** of the smallest uncertainties, and books write its right-hand side in different ways: $h/2\pi$ (as here), $h/4\pi$ (the exact limit, when the uncertainties are measured as standard deviations), or simply h. They differ by a factor of 2 or so, which doesn't change any conclusion. Use the form your teacher and your course use, and say which one you used.

Applications of the uncertainty principle

1. Electrons can't be inside the nucleus. If an electron were inside a nucleus, its position would be known to within the nucleus's size, about $\Delta x = 2 \times 10^{-14}$ m. Then its momentum would be uncertain by at least

$$\Delta p = \frac{h}{2\pi \Delta x} = \frac{6.62 \times 10^{-34}}{2\pi \times 2 \times 10^{-14}} = 5.3 \times 10^{-21} \text{ kg m/s}$$

so its momentum would be at least this large. Dividing by the electron's mass, as Newton's mechanics would, gives a speed of $5.3 \times 10^{-21} / 9.1 \times 10^{-31} \approx 5.8 \times 10^{9}$ m/s, nineteen times the speed of light: impossible. Worked out properly with relativity, an electron with this momentum would have an energy of at least $E \approx pc = 5.3 \times 10^{-21} \times 3 \times 10^{8} = 1.6 \times 10^{-12}$ J, about **10 MeV**. That is far more than the energies of the electrons that nuclei give out in beta decay, mostly under 1 MeV. So electrons **can't exist inside the nucleus**. (The electrons of beta decay are created at the moment they are emitted.)

2. The stability of atoms. An electron that fell into the nucleus would have its position known almost exactly, so its momentum, and with it its kinetic energy, would be enormous. The size of an atom is the balance: squeezing the electron closer lowers its potential energy but raises its kinetic energy. The smallest total energy comes at about 0.5 Å, the size of the hydrogen atom. So the uncertainty principle explains why atoms don't collapse.

3. Energy levels in atoms. An electron held in the small space of an atom behaves as a wave confined to that space, and only certain waves fit, just as only certain notes fit on a guitar string. That is why its energy can have only certain values.

4. The width of spectral lines. An atom stays in an excited state only for a short time, about 10^{-8} s, so the energy of that state is uncertain by $\Delta E \approx h/2\pi\Delta t$. The photons given out then have slightly different energies, and every spectral line has a small natural **width** instead of being perfectly sharp.

WORKED EXAMPLE

Example 23.15: why we don't see matter waves

If matter has a wave nature, why don't we notice it in daily life?

Answer

The de Broglie wavelength is $\lambda = h/mv$, and h is tiny. For a cricket ball of 0.16 kg at 30 m/s,

$$\lambda = \frac{6.63 \times 10^{-34}}{0.16 \times 30} = 1.4 \times 10^{-34} \text{ m}$$

far smaller than an atomic nucleus. No slit or obstacle could ever be that small, so the ball never diffracts. Only particles of very small mass, such as electrons, have wavelengths large enough (about the size of atoms) for their wave nature to show.

WORKED EXAMPLE

Example 23.16: a photon and an electron with the same wavelength

A photon and an electron have the same de Broglie wavelength. Which has the greater total energy? Explain.

Answer

The same wavelength means the same momentum, $p = h/\lambda$.
The photon's energy is $E_{\text{photon}} = pc$.
By relativity, the electron's total energy (including its rest-mass energy) is $E_{\text{electron}} = \sqrt{p^2c^2 + m_0^2c^4}$, which is always more than pc.
So the **electron** has the greater total energy. (In the same way: the electron's total energy is $mc^2 = pc^2/v$, and since $v < c$, it is larger than pc: $E_{\text{electron}}/E_{\text{photon}} = c/v > 1$.)

WORKED EXAMPLE

Example 23.17: matter waves and Bohr's orbits

Show that de Broglie's hypothesis supports Bohr's idea of stationary orbits.

Answer

An electron going round in an orbit is a wave running round a circle. The wave can last only if it joins up with itself after one turn, with a crest meeting a crest: the circumference must hold a **whole number of wavelengths** (Figure 23.9). Otherwise it would cancel itself out. So

$$2\pi r = n\lambda, \quad n = 1, 2, 3, \ldots$$

With $\lambda = \dfrac{h}{mv}$:

$$2\pi r = \frac{nh}{mv} \quad \Rightarrow \quad mvr = \frac{nh}{2\pi}$$

which is exactly Bohr's quantization condition. The allowed orbits are those in which the electron's wave fits round the orbit.

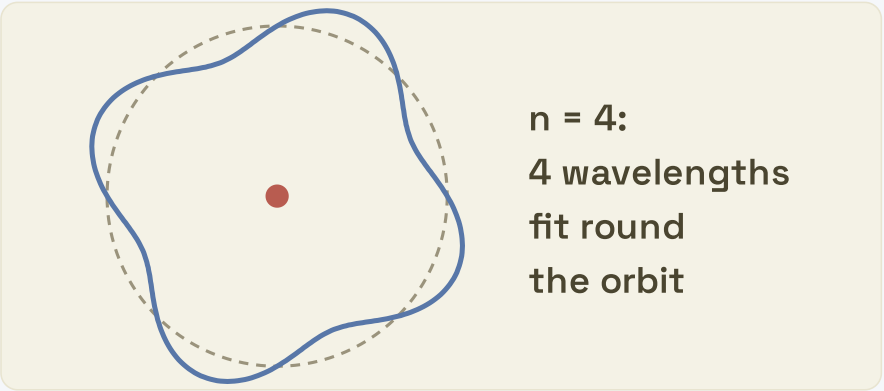


Figure 23.9 *The electron's wave fits round the fourth orbit with exactly 4 wavelengths ($n = 4$), so it joins up with itself.*

WORKED EXAMPLE

Example 23.18: how sharp an energy level is

The lifetime of an excited state of an atom is about 10^{-8} s. Calculate the minimum uncertainty in the energy of the excited state.

Answer

$\Delta t = 10^{-8}$ s. From $\Delta E \cdot \Delta t \geq \dfrac{h}{2\pi}$:

$$\Delta E = \frac{h}{2\pi \Delta t} = \frac{6.6 \times 10^{-34}}{2\pi \times 10^{-8}} = 1.05 \times 10^{-26}\ \text{J} = \frac{1.05 \times 10^{-26}}{1.6 \times 10^{-19}}\ \text{eV} = \mathbf{6.6 \times 10^{-8}}\ \text{eV}$$

Tiny compared with the few eV between levels, which is why spectral lines are so sharp. (With $h/4\pi$, half of this.)

WORKED EXAMPLE

Example 23.19: a neutron's wavelength

Find the de Broglie wavelength of a neutron of kinetic energy 150 eV. (Mass of a neutron $= 1.675 \times 10^{-27}$ kg)

Answer

$KE = 150\ \text{eV} = 150 \times 1.6 \times 10^{-19} = 2.4 \times 10^{-17}$ J.

From $KE = \dfrac{1}{2}mv^2$, the momentum is $mv = \sqrt{2m \cdot KE}$, so

$$\lambda = \frac{h}{\sqrt{2m \cdot KE}} = \frac{6.62 \times 10^{-34}}{\sqrt{2 \times 1.675 \times 10^{-27} \times 2.4 \times 10^{-17}}} = \mathbf{2.34 \times 10^{-12}}\ \text{m}$$

23.12 Discovery of X-rays

How did a covered photographic plate get fogged?

X-rays were discovered by accident in 1895 by the German physicist **Wilhelm Conrad Röntgen**. He was studying the discharge of electricity through a gas at very low pressure in a glass tube (a cathode ray tube). He noticed that a screen coated with a fluorescent chemical, lying near the tube, glowed, even though the tube was completely covered in thick black paper. Photographic plates kept near the tube, wrapped in black paper, were found fogged. When he put objects between the tube and the screen, their shadows appeared on it, and the shadow of his own hand showed the bones inside.

He concluded that some unknown radiation was coming from the tube, one that could pass through things opaque to ordinary light. Since nothing was known about it, he called it **X-rays**, X for the unknown. They are also called **Röntgen rays**. He won the first **Nobel Prize in Physics, in 1901** (the full story).



Figure 23.10 *One of the first X-ray photographs: the hand of Röntgen's wife, Anna Bertha, taken on 22 December 1895. The bones and her ring stop the X-rays; the flesh lets them through.*
Photo: Wilhelm Röntgen, Public domain

23.13 Production of X-rays

How can X-rays be made?

X-rays are produced when **fast electrons** strike a **target made of a heavy element** and are suddenly stopped. A device that does this is an **X-ray tube**. It needs three things:

i. a source of electrons;
ii. a way to accelerate them to high speed (a high voltage);
iii. a metal target of high atomic number for them to strike.

Röntgen's early tubes were gas-filled tubes, which got their electrons from the gas; they were hard to control and are now obsolete. The tube used today in hospitals and industry was designed by the American physicist **William Coolidge**.

23.14 Coolidge X-ray tube

How does a modern X-ray tube work?

The modern X-ray tube was invented by **W. D. Coolidge** in 1913. It works in a high **vacuum**, and is called the **Coolidge tube**.

Construction

The **Coolidge tube** (Figure 23.11) is a highly evacuated glass bulb, containing:

- a **filament** of tungsten, the **cathode** C, heated by a low-voltage supply (a few volts) so that it gives out electrons (thermionic emission);
- a **focusing cup** M, a metal shield round the filament at the cathode's negative potential, which pushes the electrons into a narrow beam;
- a **target** T, the anode (also called the anticathode), a block of tungsten set in a thick copper rod, its face sloped at about 45° to the beam so the X-rays come out sideways;
- a **high voltage** (from about 10 000 V to over 100 000 V) between the cathode and the target, which accelerates the electrons;

- **cooling**: the copper rod carries away the heat through fins in air, or with circulating water or oil.

The tube sits in a box lined with lead about 5 mm thick, with a small window for the X-rays to come out.

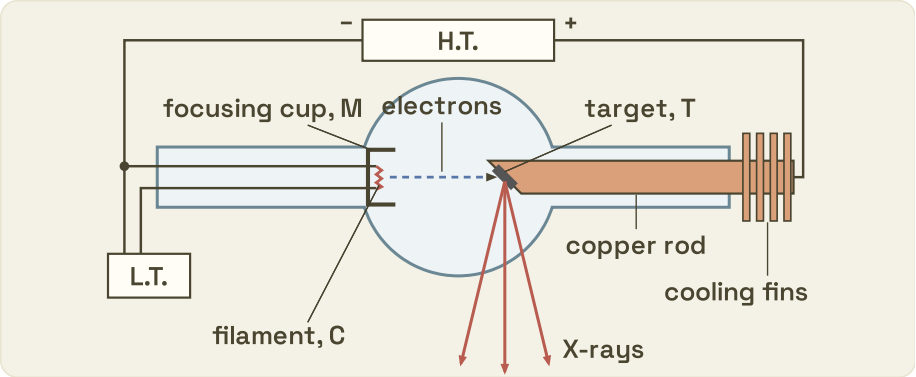


Figure 23.11 *A Coolidge X-ray tube. A low-voltage supply heats the tungsten filament (C), which gives out electrons; the focusing cup (M) narrows them into a beam. A high voltage accelerates them onto the tungsten target (T) set in a copper rod with cooling fins. X-rays come out of the sloping target face, through the glass, downwards.*

The target must have:

i. a **high atomic number** (heavy atoms), since the X-rays produced increase with it;
ii. a **high melting point**, to stand the heat;
iii. a **high thermal conductivity**, to carry the heat away;
iv. inner energy levels far enough apart that the jumps between them give out X-rays.

Platinum, tungsten and tantalum all have these properties, but **tungsten** (atomic number 74, melting point 3422 °C) is the most suitable.

Working

When a current is passed through the filament, it gives out electrons, which leave it with almost no speed. The high potential difference V between the filament and the target accelerates them. Each electron reaches the target with kinetic energy

$$\frac{1}{2}mv^2 = eV$$

In the target, the electron is slowed down and stopped by collisions with the atoms. In most collisions it just gives energy to the atoms, which heats the target. But sometimes, as it swerves past a nucleus and is sharply slowed down, it gives out an X-ray photon carrying part or all of its kinetic energy (this X-ray light, of every wavelength above a smallest one, is called **braking radiation**, *Bremsstrahlung* in German). And sometimes it knocks an electron out of an **inner** shell of a target atom; an outer electron then drops into the gap, giving out an X-ray photon of a particular energy, characteristic of the metal. So the X-rays have a **continuous spectrum** with a few sharp **characteristic lines** on top. For a tungsten target the innermost (K) electrons are held so tightly that the tube needs more than 69.5 kV to knock them out; below that, tungsten's strongest characteristic lines are missing.

Only about 1 % of the electrons' energy (often less) becomes X-rays; the rest becomes heat in the target.

Control of the quality and the intensity

In a Coolidge tube, the quality and the intensity of the X-rays can be controlled separately:

i. Quality (penetrating power). The energy of each electron is eV. A higher voltage gives faster electrons and so more energetic X-ray photons, of shorter wavelength, which go through materials more easily. X-rays of high energy (from high voltages) are called **hard X-rays**, those of low energy **soft X-rays**. Hard X-rays penetrate more. So the **voltage** controls the quality.

ii. Intensity. The intensity of the X-rays (how many photons come out each second) depends on how many electrons strike the target each second, that is, on the tube current, which depends on the filament's temperature. So the **filament current** controls the intensity.

iii. The highest frequency and shortest wavelength. The most energetic X-ray photon is made when an electron gives up **all** its kinetic energy in one go:

$$hf_{\max} = eV \quad \Rightarrow \quad f_{\max} = \frac{eV}{h}$$

and since $\lambda = c/f$, the **shortest wavelength** is

$$\lambda_{\min} = \frac{c}{f_{\max}} = \frac{hc}{eV}$$

So $\lambda_{\min} \propto \dfrac{1}{V}$: the higher the voltage, the shorter the shortest wavelength. This is the **Duane–Hunt law**. With $hc/e = 1.24 \times 10^{-6}$ V m, $\lambda_{\min} = \dfrac{12\,400}{V}$ Å when V is in volts.

WORKED EXAMPLE

Example 23.20: why tungsten

The target of a Coolidge tube is made of tungsten, not aluminium or steel. Why?

Answer

The target must:

a. have a **high melting point**, since almost all the electrons' energy becomes heat (tungsten melts at 3422 °C, aluminium at 660 °C, steel at about 1400 °C);

b. have a **high atomic number**, since heavier atoms give more X-rays (tungsten 74, aluminium 13, iron 26);

c. have inner energy levels whose differences are in the X-ray range.

Tungsten meets all three; aluminium and steel don't.

WORKED EXAMPLE

Example 23.21: a hot target

The target of a Coolidge tube gets hot when X-rays are produced. Why?

Answer

When the fast electrons are stopped by the target, their kinetic energy is given to it. Only a small part, about 0.5 to 1 %, becomes X-rays; the rest goes into the target's atoms as heat. So the target gets very hot, and must be cooled.

WORKED EXAMPLE

Example 23.22: X-rays from electrons, electrons from X-rays

X-rays can be produced by electrons, and electrons can be produced by X-rays. Explain.

Answer

When fast electrons are suddenly stopped by a heavy metal target, X-rays are produced (an X-ray tube). The other way round, when X-rays fall on a metal, they knock electrons out of it by the **photoelectric effect**. So the production of X-rays is the reverse of the photoelectric effect: in one, an electron's kinetic energy becomes a photon; in the other, a photon's energy becomes an electron's kinetic energy.

WORKED EXAMPLE

Example 23.23: the most energetic X-ray

What is the wavelength of the most energetic X-ray photon emitted when a metal target is struck by electrons of energy 100 keV?

Answer

The most energetic photon takes all the electron's energy:

$$E = 100 \times 10^3 \times 1.6 \times 10^{-19} = 1.6 \times 10^{-14}\ \text{J} = \frac{hc}{\lambda}$$

$$\lambda = \frac{6.625 \times 10^{-34} \times 3 \times 10^8}{1.6 \times 10^{-14}} = \mathbf{1.24 \times 10^{-11}}\ \text{m} = 0.124\ \text{Å}$$

WORKED EXAMPLE

Example 23.24: the energy of an X-ray photon

Calculate the energy in electron volts of a photon of X-rays of wavelength 0.15 nm. ($h = 6.62 \times 10^{-34}$ J s, $e = 1.6 \times 10^{-19}$ C)

Answer

$$E = \frac{hc}{\lambda} = \frac{6.62 \times 10^{-34} \times 3 \times 10^8}{0.15 \times 10^{-9}} = 1.324 \times 10^{-15}\ \text{J} = \frac{1.324 \times 10^{-15}}{1.6 \times 10^{-19}} = \mathbf{8275}\ \text{eV}$$

about 8.3 keV, some three thousand times the energy of a photon of visible light.

WORKED EXAMPLE

Example 23.25: the highest frequency

Calculate the maximum frequency of the X-rays from a tube operated at 50 000 V. ($h = 6.62 \times 10^{-34}$ J s, $e = 1.6 \times 10^{-19}$ C)

Answer

$$f_{\max} = \frac{eV}{h} = \frac{1.6 \times 10^{-19} \times 50\,000}{6.62 \times 10^{-34}} = \mathbf{1.21 \times 10^{19}}\ \text{Hz}$$

WORKED EXAMPLE

Example 23.26: energy and shortest wavelength

The potential difference between the anode and cathode of an X-ray tube is 20 000 V. Calculate (i) the energy of the electrons, and (ii) the shortest wavelength of the X-rays. ($h = 6.62 \times 10^{-34}$ J s, $e = 1.6 \times 10^{-19}$ C)

Answer

i. $E = eV = 1.6 \times 10^{-19} \times 20\,000 = \mathbf{3.2 \times 10^{-15}}$ J (20 keV).

ii. $\lambda_{\min} = \dfrac{hc}{eV} = \dfrac{6.62 \times 10^{-34} \times 3 \times 10^{8}}{3.2 \times 10^{-15}} = \mathbf{6.21 \times 10^{-11}}$ m (0.621 Å).

WORKED EXAMPLE

Example 23.27: electrons and heat in a tube

An X-ray tube works at an anode potential of 15 kV with a current of 20 mA. How many electrons hit the target each second, and how much heat is produced at the anode each second? ($e = 1.6 \times 10^{-19}$ C)

Answer

The current is the charge arriving each second, $I = ne$:

$$n = \frac{I}{e} = \frac{20 \times 10^{-3}}{1.6 \times 10^{-19}} = \mathbf{1.25 \times 10^{17}} \text{ electrons a second}$$

The power delivered by the electrons is $P = IV = 20 \times 10^{-3} \times 15\,000 = 300$ W. Since only about 1 % becomes X-rays, practically all of it, **about 300 J each second** (300 W), becomes heat at the anode.

23.15 Properties of X-rays

X-rays have the following properties:

i. They are **electromagnetic waves** of very short wavelength, from about 0.06 Å to 100 Å.

ii. They travel through a vacuum at the speed of light, 3×10^{8} m/s.

iii. They carry no charge, so they are **not deflected** by electric or magnetic fields.

iv. They affect **photographic plates** strongly.

v. They **ionize** the gas they pass through.

vi. They make some substances **fluoresce** (glow), such as zinc sulphide, barium platinocyanide and calcium tungstate.

vii. Like light, they cause the **photoelectric effect**.

viii. They travel in **straight lines**, and cast shadows of objects in their path.

ix. They **penetrate** materials opaque to visible and ultraviolet light: paper, wood, thin metal sheets and flesh, but not dense materials such as bone and heavy metals.

x. They are **harmful** to living things: they ionize atoms in cells and can damage them and their DNA.

xi. When they fall on a metal, they knock electrons out and make **secondary X-rays** characteristic of that metal.

CAREFUL

X-rays and safety

Because X-rays ionize, every dose carries a small risk, so they are used only when the picture is worth it. A chest X-ray gives about the same dose as ten days of natural background radiation; a CT scan, a few years' worth. Staff stand behind lead screens, and a pregnant woman should always tell the radiographer. Never stay near an X-ray machine at work if you don't need to.

23.16 Applications of X-rays

X-rays are used in many fields:

i. **Medical diagnosis:** to find fractures, kidney and gall stones, swallowed objects and bullets, and diseases of the lungs (tuberculosis, pneumonia), and to follow how a broken bone heals. A **CT scanner** takes X-ray pictures from all round the body and a computer builds them into slices.
ii. **Radiotherapy:** carefully aimed doses kill cancer cells. Softer X-rays are used for growths near the surface, harder ones for deep tumors.
iii. **Engineering:** to find cracks, flaws and gas bubbles in metal castings and welds, in bridges and pipelines, and in the engines of cars and airplanes.
iv. **Security and customs:** to scan luggage at airports, find explosives and smuggled goods (including gold hidden in the body), and tell real gems from fakes.
v. **Industry:** to test the uniformity of insulating materials and timber, find defects in tyres and balls, and find pearls inside oysters.
vi. **Scientific research:** to find the structure of crystals and molecules (Section 23.17); the double helix of DNA was found from an X-ray photograph.
vii. **Art:** to see the earlier paintings under an old painting, and changes the painter made.

DID YOU KNOW?

The X-rays at Tribhuvan Airport

Every bag at Tribhuvan International Airport passes through an X-ray scanner. It uses two X-ray energies. Light, organic matter (food, clothes, explosives) stops much of the soft X-rays but lets most of the hard ones through; metals stop both. Comparing how much of each gets through, the computer colors each object by what it is probably made of: orange for organic material, blue for metals, green for in between.

23.17 X-ray diffraction

How do we know X-rays are waves?

In 1912 the German physicist **Max von Laue** and his colleagues sent a narrow beam of X-rays through a crystal of zinc sulphide, with a photographic plate behind it (Figure 23.12). After several hours, the developed plate showed a bright central spot surrounded by many faint spots in a regular pattern, the **Laue pattern**. It was made by the **diffraction** of X-rays.

The experiment showed two things.

First, **X-rays are waves**, since they diffract. But why hadn't anyone diffracted them before? A slit or grating diffracts light noticeably only when its spacing is comparable to the wavelength. An ordinary diffraction grating has about 6000 lines a centimeter, so its lines are about 1.7×10^{-6} m apart, suited to visible light. X-ray

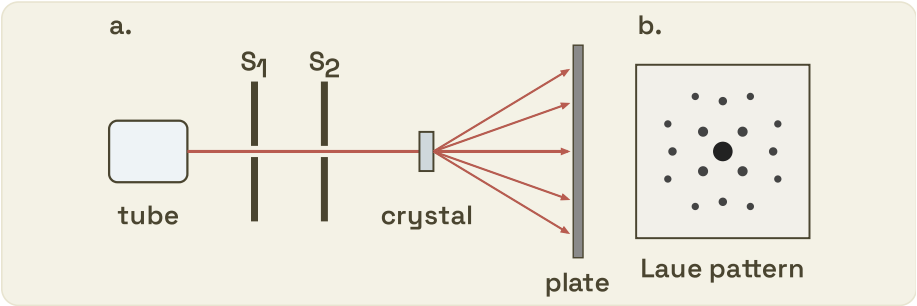


Figure 23.12 *a. Laue's experiment: X-rays from a tube pass through two slits S_1 and S_2, which make a narrow beam, then through a thin crystal of zinc sulphide onto a photographic plate. b. The Laue pattern on the plate: a central spot and fainter spots in a symmetrical pattern.*

wavelengths are about 10^{-10} m, thousands of times shorter: a grating for them would need lines thousands of times closer, which no one can rule.

Second, the regular pattern showed that the atoms in a crystal are arranged in a **regular three-dimensional pattern**, about 10^{-10} m apart. Laue realized that a crystal is a natural three-dimensional diffraction grating with just the right spacing for X-rays. **W. L. Bragg** soon explained the Laue spots in a much simpler way.

23.18 Determination of the wavelength of X-rays: Bragg's law

How can a crystal measure an X-ray's wavelength?

Visible light (400–700 nm) is diffracted by slits about its own size, but X-rays (about 0.1 nm) need "slits" the size of atoms, which no grating can have. A crystal, whose atoms are regularly spaced about 0.1 nm apart, does the job. In 1912–13 **W. L. Bragg** (then 22) and his father **W. H. Bragg** explained X-ray diffraction by thinking of the crystal as stacks of parallel layers of atoms, the **Bragg planes**, a distance d apart, and built the first X-ray spectrometer. They shared the 1915 Nobel Prize in Physics (the full story).

Bragg's law

A beam of X-rays of wavelength λ falls on a crystal at a **glancing angle** θ (the angle between the ray and the planes, not the normal). Each plane of atoms reflects a little of the beam, at an equal angle θ (Figure 23.13). The ray reflected from one plane interferes with the ray reflected from the plane below. The two rays travel almost the same path, but the lower one goes a little farther. They reinforce each other, giving a strong reflected beam, only when this **path difference** is a whole number of wavelengths:

$$\text{path difference} = n\lambda, \quad n = 1, 2, 3, \ldots$$

To find the path difference, drop perpendiculars PL and PM from the point P, where the upper ray is reflected, to the lower ray before and after its reflection at Q. Up to L, and from M on, the two rays have gone equal distances, so the extra path of the lower ray is $LQ + QM$. In the right-angled triangles PLQ and PMQ, the hypotenuse is $PQ = d$ and the angle at P is θ, so

$$LQ = QM = d \sin\theta$$

and the total path difference is $2d \sin\theta$. For a strong reflection,

$$2d \sin\theta = n\lambda \qquad (23.12)$$

This is **Bragg's law**. For X-rays of one wavelength, strong reflection happens only at certain glancing angles $\theta_1, \theta_2, \theta_3, \ldots$, for $n = 1, 2, 3, \ldots$, the first, second, third **orders** of reflection. At these angles the rays from all the planes add up and the crystal reflects strongly (obeying the law of reflection); at other angles the reflections from the many planes cancel, and almost nothing is reflected. For the first order,

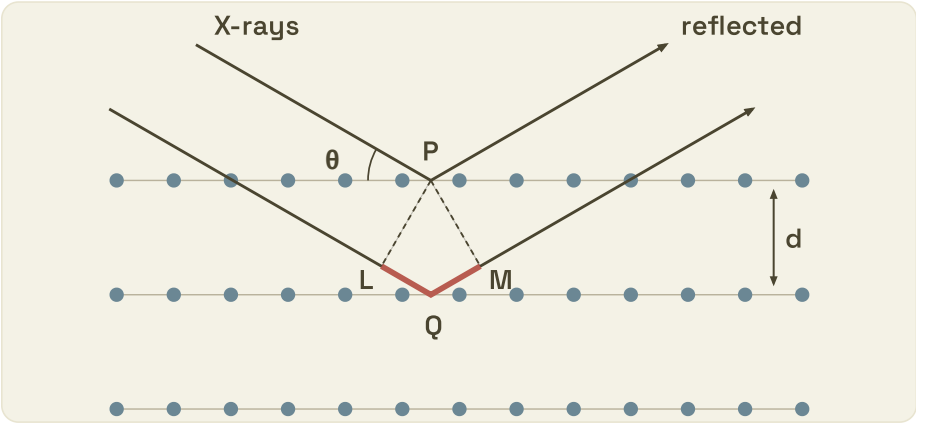


Figure 23.13 *X-rays reflected from two neighboring planes of atoms a distance d apart, at the glancing angle θ. The ray reflected at Q, on the lower plane, travels LQ + QM farther than the ray reflected at P, above it; each of these is d sin θ.*

So knowing the spacing d of the crystal's planes and measuring the glancing angle θ of the strong reflection gives the wavelength of the X-rays. The other way round, X-rays of known wavelength give the spacing of the atoms: that is how the structures of crystals, and of molecules such as DNA and proteins, are found.

Check 5

In Bragg's law, $2d\sin\theta = n\lambda$, θ is:

a the angle between the X-rays and the normal to the planes

b the glancing angle, between the X-rays and the planes of atoms

c the angle between the incident and the reflected rays

d the angle between two neighboring planes

WORKED EXAMPLE

Example 23.28: why a crystal

Why is a crystal needed to observe X-ray diffraction?

Answer

Diffraction is noticeable only when the spacing of the grating is about the same as the wavelength. X-rays have wavelengths of about 0.1 nm, far too small for any ruled grating. A crystal has regularly spaced planes of atoms about 0.1 nm apart, just right: it acts as a three-dimensional grating, reflecting strongly when $2d\sin\theta = n\lambda$.

WORKED EXAMPLE

Example 23.29: first and second order

What is meant by first-order and second-order diffraction in Bragg's law?

Answer

The **order** is the whole number n in $2d\sin\theta = n\lambda$.

In **first-order** diffraction, n = 1: the rays from neighboring planes differ in path by one wavelength.

In **second-order** diffraction, n = 2: they differ by two wavelengths, which happens at a larger glancing angle.

WORKED EXAMPLE

Example 23.30: the longest wavelength a crystal can study

The spacing of the planes of a crystal is 10^{-7} cm. What is the longest wavelength of X-rays that can be studied with this crystal?

Answer

$d = 10^{-7}$ cm $= 10^{-9}$ m. From $2d\sin\theta = n\lambda$, $\lambda = 2d\sin\theta/n$, which is largest when $\sin\theta = 1$ and $n = 1$:

$$\lambda_{\max} = 2d = 2 \times 10^{-9}\ \text{m} = \mathbf{20}\ \text{Å}$$

WORKED EXAMPLE

Example 23.31: first and second order

The planes of atoms in a crystal are 1.1×10^{-10} m apart. A beam of X-rays of one wavelength gives a first-order reflection at a glancing angle of 5°. Find the wavelength, and the glancing angle of the second-order reflection.

Answer

Wavelength, first order (n = 1):

$$\lambda = 2d\sin\theta_1 = 2 \times 1.1 \times 10^{-10} \times \sin 5^\circ = 2.2 \times 10^{-10} \times 0.0872 = \mathbf{1.92 \times 10^{-11}}\ \text{m}$$

Second order (n = 2):

$$\sin\theta_2 = \frac{2\lambda}{2d} = \frac{2 \times 1.92 \times 10^{-11}}{2 \times 1.1 \times 10^{-10}} = 0.174 \quad \Rightarrow \quad \theta_2 = \mathbf{10.0}^\circ$$

IN SHORT

Key ideas of Unit 23

- Bohr's postulates: electrons go round only in stationary orbits, without radiating; in them $mvr = nh/2\pi$; an atom gives out or takes in one photon, $hf = E_2 - E_1$, when an electron jumps between orbits.
- For hydrogen: $r_n = \dfrac{n^2h^2\varepsilon_0}{\pi me^2} = 0.53\,n^2$ Å, $v_n = \dfrac{e^2}{2\varepsilon_0 nh}$, $E_n = -\dfrac{me^4}{8\varepsilon_0^2 n^2 h^2} = -\dfrac{13.6}{n^2}$ eV.
- Rydberg formula: $\dfrac{1}{\lambda} = R\left(\dfrac{1}{n_1^2} - \dfrac{1}{n_2^2}\right)$, $R = 1.097 \times 10^7\ \text{m}^{-1}$. Series: Lyman (to n = 1, ultraviolet), Balmer (to 2, visible), Paschen (to 3), Brackett (to 4), Pfund (to 5, infrared).
- First excitation energy of hydrogen 10.2 eV (potential 10.2 V); ionization energy 13.6 eV (potential 13.6 V).
- Emission spectra: continuous (hot solids, liquids, dense gases), line (atoms), band (molecules). Absorption spectrum: dark lines where a cool gas absorbs its own wavelengths.
- Radiation and matter both have a dual nature. de Broglie: $\lambda = \dfrac{h}{mv} = \dfrac{h}{p}$; for an electron through V volts, $\lambda = \dfrac{h}{\sqrt{2meV}} = \dfrac{12.27}{\sqrt{V}}$ Å.
- Uncertainty principle: $\Delta x\,\Delta p \geq h/2\pi$, $\Delta E\,\Delta t \geq h/2\pi$ (about this size).
- X-rays: fast electrons stopped by a heavy target (Coolidge tube); voltage sets the quality, filament current the intensity; $\lambda_{\min} = hc/eV$, $f_{\max} = eV/h$.
- Bragg's law: $2d\sin\theta = n\lambda$, θ the glancing angle.

Exercise

Choose the correct option

Check 6

1. The reciprocal of wavelength is:

a frequency
b wave number
c amplitude
d wave velocity

Check 7

2. The angular momentum of the electron in the second orbit of a hydrogen atom is:

a $h/2\pi m$
b $h/2\pi$
c $2h/\pi$
d h/π

Check 8

3. How many electrons strike the target each second in an X-ray tube carrying a current of 0.02 A?

a 1.25×10^{17}
b 1.25×10^{18}
c 1.25×10^{19}
d 1.25×10^{20}

Check 9

4. Compared with the binding energy of a nucleus, the ionization energy of an atom is:

a more
b less
c equal
d sometimes more and sometimes less

Check 10

5. The ionization energy of a hydrogen atom is 13.6 eV. The energy needed to remove the electron from a singly ionized helium ion, He^+, in its ground state is:

a 13.6 eV
b 27.2 eV
c 6.8 eV
d 54.4 eV

Check 11

6. The energy of a hydrogen atom in its ground state is −13.6 eV. The energy of the level n = 5 is:

a −0.54 eV
b −5.40 eV
c −0.85 eV
d −2.72 eV

Check 12

7. The ionization energy of hydrogen is 13.6 eV. The energy needed to excite the electron of He^+ from its first orbit to its second is:

a 13.6 eV
b 2 × 13.6 eV
c 3 × 13.6 eV
d 4 × 13.6 eV

Answer these questions

18. a. State the postulates of Bohr's theory of the hydrogen atom, especially his idea of stationary orbits.
b. Derive expressions for the radius of the nth orbit, the speed of the electron in the nth orbit, and the total energy of the electron in the nth orbit of a hydrogen atom.

Check 13

8. An electron in the n = 1 orbit of hydrogen is bound by 13.6 eV. How much energy is needed to ionize a hydrogen atom in the n = 3 state?

a 13.6 eV
b 4.53 eV
c 3.4 eV
d 1.51 eV

Check 14

9. Which spectral series of hydrogen contains the line of wavelength 4860 Å?

a Lyman
b Balmer
c Paschen
d Brackett

Check 15

10. In a sodium ion with only one electron left (Z = 11), the electron's speed in the second orbit is v. Its speed in the fifth orbit would be:

a 2v/5
b 5v/2
c v/5
d 25v/4

Check 16

11. If the potential energy of a hydrogen atom in its ground state is taken as zero, its potential energy in the first excited state will be:

a 3.4 eV
b 6.8 eV
c 10.2 eV
d 20.4 eV

Check 17

12. The internal structure of a crystal can be studied with:

a X-rays
b γ-rays
c infrared rays
d ultraviolet rays

Check 18

13. The voltage across an X-ray tube is 20 kV. The shortest wavelength of its X-ray photons is:

a 6.2 Å
b 0.62 Å
c 0.062 Å
d 1 Å

Check 19

14. An X-ray tube works at 42 000 V. The maximum frequency of its X-rays is about:

a 10^{19} Hz
b 10^{18} Hz
c 10^{16} Hz
d 10^{29} Hz

Check 20

15. In radiotherapy, X-rays are used to:

a detect bone fractures
b treat cancer
c detect skin disease
d find faults in radio circuits

Check 21

16. Electrons of energy 10 keV strike a tungsten target in a vacuum. The radiation given out by the target is:

a visible light
b X-rays
c infrared radiation
d radio waves

Check 22

17. X-rays of wavelength 1 Å give a first-order reflection from the principal planes of a sodium chloride crystal at a glancing angle of 10°. The spacing of the planes is about:

a 2.8 Å
b 1.8 Å
c 0.8 Å
d 1.2 Å

22.

a. What are X-rays? How are they produced?

b. What is meant by the penetrating power and the intensity of X-rays? How are (i) the penetrating power and (ii) the intensity of the X-rays from a Coolidge tube controlled?

c. Can aluminium be used as the target in an X-ray tube?

23.

a. Explain Bragg's law of diffraction of X-rays.

b. X-rays fall on a zinc sulphide crystal whose planes are 3.08×10^{-8} cm apart. The first-order reflection is at a glancing angle of 12°. Calculate the wavelength of the X-rays.

24.

a. A proton and an electron have the same kinetic energy. Which has the longer de Broglie wavelength?

b. Using Bohr's theory of the hydrogen atom, calculate the circumference of the first orbit and the momentum of the electron in it. Find the de Broglie wavelength of this electron, and say how the two are related.

25.

a. When a Coolidge tube is used for a long time, it becomes hot. Where does the heat come from?

b. An X-ray tube operated at a d.c. potential difference of 10 kV produces heat at a rate of 720 W. If 0.5 % of the energy of the electrons is converted into X-rays, calculate the tube current and the speed of the electrons striking the target. ($e/m = 1.8 \times 10^{11}$ C/kg)

26. The diagram shows three of the energy levels of an isolated hydrogen atom. The lowest is the ground state.

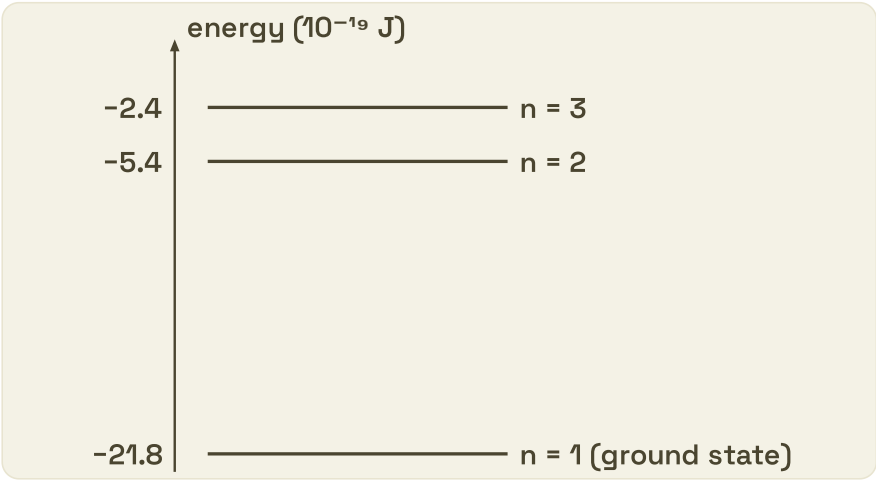


Figure 23.14 *Three energy levels of hydrogen, in units of 10^{-19} J: n = 1 (ground state) at −21.8, n = 2 at −5.4 and n = 3 at −2.4.*

a. Explain what happens to an electron in the ground state when it absorbs the energy of a photon of energy 21.8×10^{-19} J.

b. i. Explain why a photon is given out when an electron makes a transition from the level n = 3 to n = 2.

ii. Calculate the wavelength of the radiation given out in this transition.

27.

a. State what is meant by wave number.

b. The lowest energy levels of an isolated hydrogen atom are shown below.

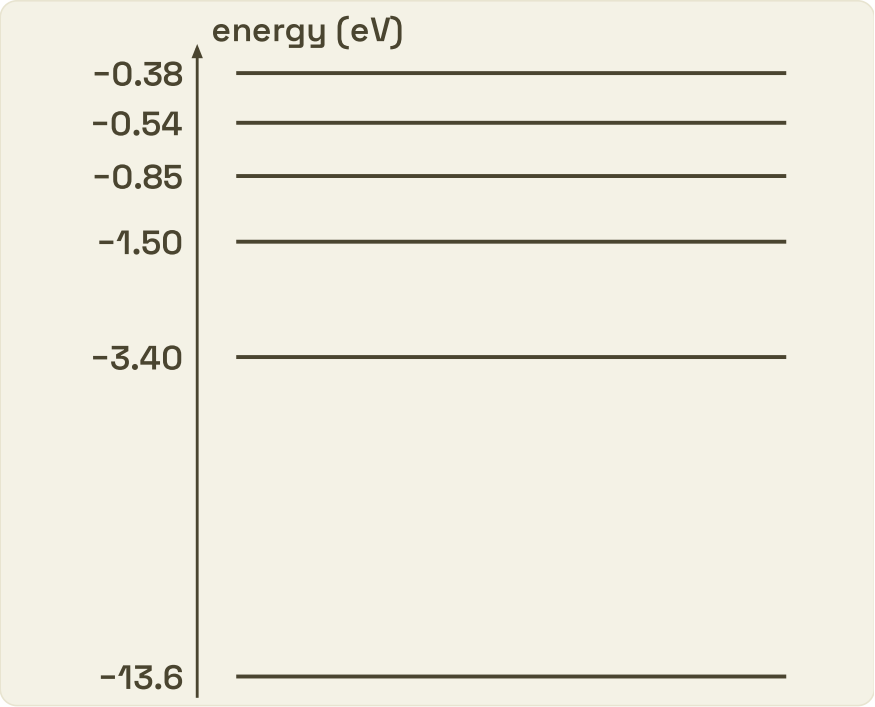


Figure 23.15 *The lowest energy levels of hydrogen, in eV: −13.6, −3.40, −1.50, −0.85, −0.54 and −0.38 (not to scale).*

i. An electron is at first in the level −0.85 eV. State how many different wavelengths may be given out as it loses energy.

ii. Photons from the electron's fall from the −0.85 eV level strike a sample of platinum, whose work function is 5.6 eV. Find: 1. the maximum kinetic energy, in eV, of a photoelectron from the platinum; 2. the wavelength of the photon that gives this photoelectron.

28.

a. State one effect that is evidence for (i) the wave nature of a particle, and (ii) the particle nature of electromagnetic radiation.

b. Four electron energy levels of an isolated atom are shown below. For the emission spectrum from these levels:

i. name the transition that gives the shortest wavelength (in the exam, mark it with an arrow on the diagram);

ii. show that the wavelength of this transition is 4.35×10^{-7} m.

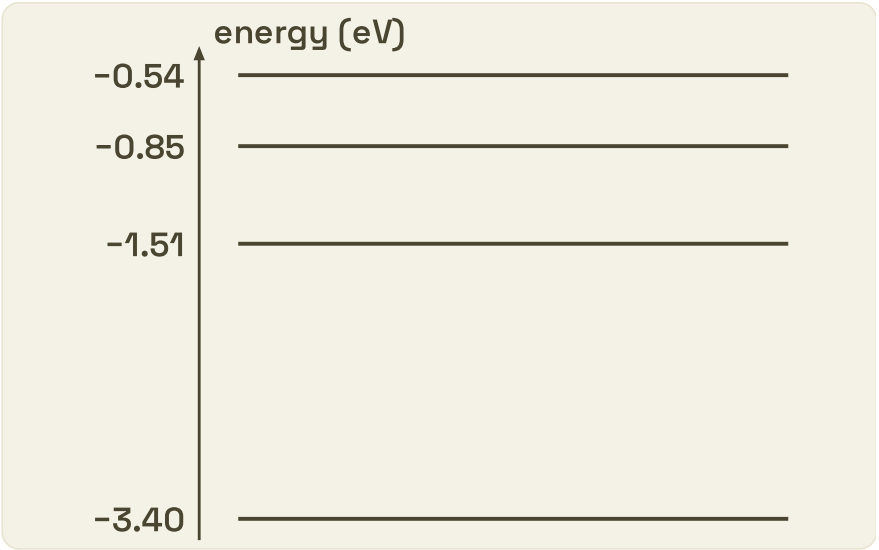


Figure 23.16 *Four energy levels of an atom: −0.54 eV, −0.85 eV, −1.51 eV and −3.40 eV (not to scale).*

c. i. State what is meant by the de Broglie wavelength.

ii. Calculate the speed of an electron whose de Broglie wavelength equals the wavelength in (b)(ii).

A companion to your textbook, not a replacement for it: study from the book your school uses, and where the two differ, follow your teacher. Found a mistake? Please tell us.