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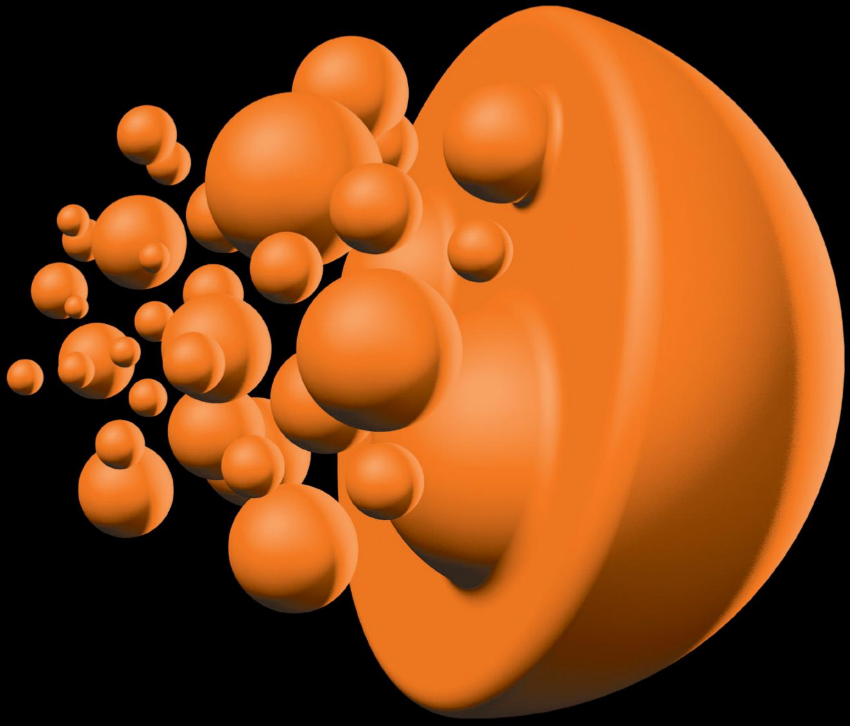
# Atkins'
# PHYSICAL CHEMISTRY

## Quantum Chemistry, Spectroscopy, and Statistical Thermodynamics

11th Edition



Peter Atkins | Julio de Paula | James Keeler

# FUNDAMENTAL CONSTANTS

| Constant | Symbol | Value | | |
|---|---|---|---|---|
| | | | Power of 10 | Units |
| Speed of light | $c$ | 2.997 924 58* | $10^{8}$ | m s$^{-1}$ |
| Elementary charge | $e$ | 1.602 176 565 | $10^{-19}$ | C |
| Planck's constant | $h$ | 6.626 069 57 | $10^{-34}$ | J s |
| | $\hbar = h/2\pi$ | 1.054 571 726 | $10^{-34}$ | J s |
| Boltzmann's constant | $k$ | 1.380 6488 | $10^{-23}$ | J K$^{-1}$ |
| Avogadro's constant | $N_A$ | 6.022 141 29 | $10^{23}$ | mol$^{-1}$ |
| Gas constant | $R = N_Ak$ | 8.314 4621 | | J K$^{-1}$ mol$^{-1}$ |
| Faraday's constant | $F = N_Ae$ | 9.648 533 65 | $10^{4}$ | C mol$^{-1}$ |
| Mass | | | | |
| Electron | $m_e$ | 9.109 382 91 | $10^{-31}$ | kg |
| Proton | $m_p$ | 1.672 621 777 | $10^{-27}$ | kg |
| Neutron | $m_n$ | 1.674 927 351 | $10^{-27}$ | kg |
| Atomic mass constant | $m_u$ | 1.660 538 921 | $10^{-27}$ | kg |
| Vacuum permeability | $\mu_0$ | $4\pi$* | $10^{-7}$ | J s$^{2}$ C$^{-2}$ m$^{-1}$ |
| Vacuum permittivity | $\varepsilon_0 = 1/\mu_0c^2$ | 8.854 187 817 | $10^{-12}$ | J$^{-1}$ C$^{2}$ m$^{-1}$ |
| | $4\pi\varepsilon_0$ | 1.112 650 056 | $10^{-10}$ | J$^{-1}$ C$^{2}$ m$^{-1}$ |
| Bohr magneton | $\mu_B = e\hbar/2m_e$ | 9.274 009 68 | $10^{-24}$ | J T$^{-1}$ |
| Nuclear magneton | $\mu_N = e\hbar/2m_p$ | 5.050 783 53 | $10^{-27}$ | J T$^{-1}$ |
| Proton magnetic moment | $\mu_p$ | 1.410 606 743 | $10^{-26}$ | J T$^{-1}$ |
| $g$-Value of electron | $g_e$ | 2.002 319 304 | | |
| Magnetogyric ratio | | | | |
| Electron | $\gamma_e = -g_ee/2m_e$ | −1.001 159 652 | $10^{10}$ | C kg$^{-1}$ |
| Proton | $\gamma_p = 2\mu_p/\hbar$ | 2.675 222 004 | $10^{8}$ | C kg$^{-1}$ |
| Bohr radius | $a_0 = 4\pi\varepsilon_0\hbar^2/e^2m_e$ | 5.291 772 109 | $10^{-11}$ | m |
| Rydberg constant | $\tilde{R}_\infty = m_ee^4/8h^3c\varepsilon_0^2$ | 1.097 373 157 | $10^{5}$ | cm$^{-1}$ |
| | $hc\tilde{R}_\infty/e$ | 13.605 692 53 | | eV |
| Fine-structure constant | $\alpha = \mu_0e^2c/2h$ | 7.297 352 5698 | $10^{-3}$ | |
| | $\alpha^{-1}$ | 1.370 359 990 74 | $10^{2}$ | |
| Stefan–Boltzmann constant | $\sigma = 2\pi^5k^4/15h^3c^2$ | 5.670 373 | $10^{-8}$ | W m$^{-2}$ K$^{-4}$ |
| Standard acceleration of free fall | $g$ | 9.806 65* | | m s$^{-2}$ |
| Gravitational constant | $G$ | 6.673 84 | $10^{-11}$ | N m$^{2}$ kg$^{-2}$ |

* Exact value. For current values of the constants, see the National Institute of Standards and Technology (NIST) website.

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## Quantum Chemistry, Spectroscopy, and Statistical Thermodynamics

Eleventh edition

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The cover image symbolizes the structure of the text, as a collection of Topics that merge into a unified whole. It also symbolizes the fact that physical chemistry provides a basis for understanding chemical and physical change.

# PREFACE

Our *Physical Chemistry* is continuously evolving in response to users' comments and our own imagination. The principal change in this edition is the addition of a new co-author to the team, and we are very pleased to welcome James Keeler of the University of Cambridge. He is already an experienced author and we are very happy to have him on board.

As always, we strive to make the text helpful to students and usable by instructors. We developed the popular 'Topic' arrangement in the preceding edition, but have taken the concept further in this edition and have replaced chapters by Focuses. Although that is principally no more than a change of name, it does signal that groups of Topics treat related groups of concepts which might demand more than a single chapter in a conventional arrangement. We know that many instructors welcome the flexibility that the Topic concept provides, because it makes the material easy to rearrange or trim.

We also know that students welcome the Topic arrangement as it makes processing of the material they cover less daunting and more focused. With them in mind we have developed additional help with the manipulation of equations in the form of annotations, and *The chemist's toolkits* provide further background at the point of use. As these Toolkits are often relevant to more than one Topic, they also appear in consolidated and enhanced form on the website. Some of the material previously carried in the 'Mathematical backgrounds' has been used in this enhancement. The web also provides a number of sections called *A deeper look*. As their name suggests, these sections take the material in the text further than we consider appropriate for the printed version but are there for students and instructors who wish to extend their knowledge and see the details of more advanced calculations.

Another major change is the replacement of the 'Justifications' that show how an equation is derived. Our intention has been to maintain the separation of the equation and its derivation so that review is made simple, but at the same time to acknowledge that mathematics is an integral feature of learning. Thus, the text now sets up a question and the *How is that done?* section that immediately follows develops the relevant equation, which then flows into the following text.

The worked *Examples* are a crucially important part of the learning experience. We have enhanced their presentation by replacing the 'Method' by the more encouraging *Collect your thoughts*, where with this small change we acknowledge that different approaches are possible but that students welcome guidance. The *Brief illustrations* remain: they are intended simply to show how an equation is implemented and give a sense of the order of magnitude of a property.

It is inevitable that in an evolving subject, and with evolving interests and approaches to teaching, some subjects wither and die and are replaced by new growth. We listen carefully to trends of this kind, and adjust our treatment accordingly. The topical approach enables us to be more accommodating of fading fashions because a Topic can so easily be omitted by an instructor, but we have had to remove some subjects simply to keep the bulk of the text manageable and have used the web to maintain the comprehensive character of the text without overburdening the presentation.

This book is a living, evolving text. As such, it depends very much on input from users throughout the world, and we welcome your advice and comments.

PWA
JdeP
JK

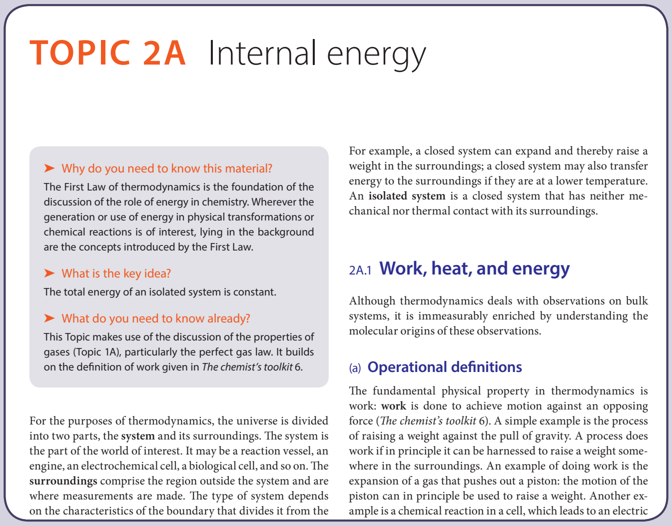
# USING THE BOOK

## TO THE STUDENT

For this eleventh edition we have developed the range of learning aids to suit your needs more closely than ever before. In addition to the variety of features already present, we now derive key equations in a helpful new way, through the *How is that done?* sections, to emphasize how mathematics is an interesting, essential, and integral feature of understanding physical chemistry.

### Innovative structure

Short Topics are grouped into Focus sections, making the subject more accessible. Each Topic opens with a comment on why it is important, a statement of its key idea, and a brief summary of the background that you need to know.



**TOPIC 2A** Internal energy

➤ Why do you need to know this material?

The First Law of thermodynamics is the foundation of the discussion of the role of energy in chemistry. Wherever the generation or use of energy in physical transformations or chemical reactions is of interest, lying in the background are the concepts introduced by the First Law.

➤ What is the key idea?

The total energy of an isolated system is constant.

➤ What do you need to know already?

This Topic makes use of the discussion of the properties of gases (Topic 1A), particularly the perfect gas law. It builds on the definition of work given in *The chemist's toolkit* 6.

For the purposes of thermodynamics, the universe is divided into two parts, the **system** and its surroundings. The system is the part of the world of interest. It may be a reaction vessel, an engine, an electrochemical cell, a biological cell, and so on. The **surroundings** comprise the region outside the system and are where measurements are made. The type of system depends on the characteristics of the boundary that divides it from the

For example, a closed system can expand and thereby raise a weight in the surroundings; a closed system may also transfer energy to the surroundings if they are at a lower temperature. An **isolated system** is a closed system that has neither mechanical nor thermal contact with its surroundings.

2A.1 **Work, heat, and energy**

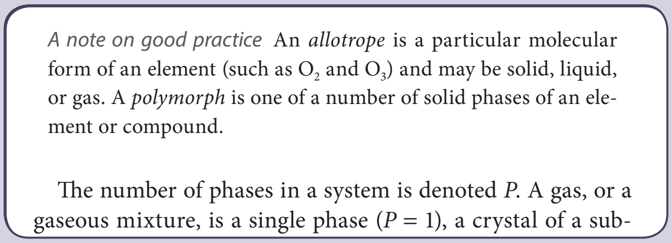
Although thermodynamics deals with observations on bulk systems, it is immeasurably enriched by understanding the molecular origins of these observations.

(a) **Operational definitions**

The fundamental physical property in thermodynamics is work: **work** is done to achieve motion against an opposing force (*The chemist's toolkit* 6). A simple example is the process of raising a weight against the pull of gravity. A process does work if in principle it can be harnessed to raise a weight somewhere in the surroundings. An example of doing work is the expansion of a gas that pushes out a piston: the motion of the piston can in principle be used to raise a weight. Another example is a chemical reaction in a cell, which leads to an electric

### Notes on good practice

Our 'Notes on good practice' will help you avoid making common mistakes. Among other things, they encourage conformity to the international language of science by setting out the conventions and procedures adopted by the International Union of Pure and Applied Chemistry (IUPAC).

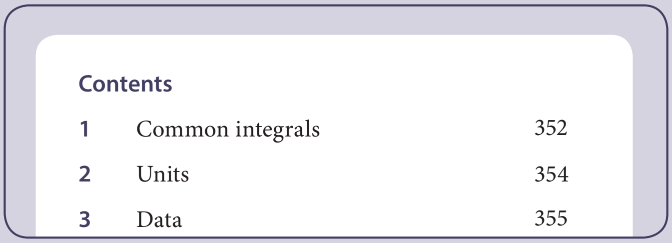


*A note on good practice* An *allotrope* is a particular molecular form of an element (such as $O_2$ and $O_3$) and may be solid, liquid, or gas. A *polymorph* is one of a number of solid phases of an element or compound.

The number of phases in a system is denoted *P*. A gas, or a gaseous mixture, is a single phase ($P = 1$), a crystal of a sub-

### Resource section

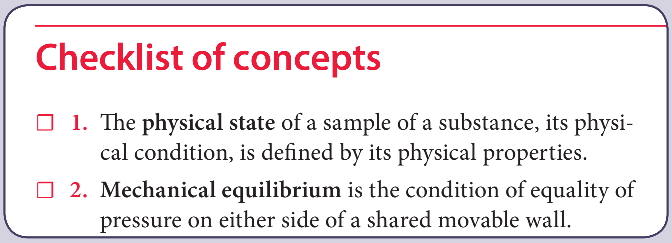
The *Resource section* at the end of the book includes a table of useful integrals, extensive tables of physical and chemical data, and character tables. Short extracts of most of these tables appear in the Topics themselves: they are there to give you an idea of the typical values of the physical quantities mentioned in the text.



**Contents**

### Checklist of concepts

A checklist of key concepts is provided at the end of each Topic, so that you can tick off the ones you have mastered.



**Checklist of concepts**

☐ 1. The **physical state** of a sample of a substance, its physical condition, is defined by its physical properties.

☐ 2. **Mechanical equilibrium** is the condition of equality of pressure on either side of a shared movable wall.

# PRESENTING THE MATHEMATICS

## How is that done?

You need to understand how an equation is derived from reasonable assumptions and the details of the mathematical steps involved. This is accomplished in the text through the new *'How is that done?'* sections, which replace the *Justifications* of earlier editions. Each one leads from an issue that arises in the text, develops the necessary mathematics, and arrives at the equation or conclusion that resolves the issue. These sections maintain the separation of the equation and its derivation so that you can find them easily for review, but at the same time emphasize that mathematics is an essential feature of physical chemistry.

**How is that done? 4A.1** Deducing the phase rule

The argument that leads to the phase rule is most easily appreciated by first thinking about the simpler case when only one component is present and then generalizing the result to an arbitrary number of components.

**Step 1** *Consider the case where only one component is present*

When only one phase is present ($P = 1$), both $p$ and $T$ can be varied independently, so $F = 2$. Now consider the case where two phases α and β are in equilibrium ($P = 2$). If the phases are in equilibrium at a given pressure and temperature, their chemical potentials must be equal:

## The chemist's toolkits

*The chemist's toolkits*, which are much more numerous in this edition, are reminders of the key mathematical, physical, and chemical concepts that you need to understand in order to follow the text. They appear where they are first needed. Many of these Toolkits are relevant to more than one Topic, and a compilation of them, with enhancements in the form of more information and brief illustrations, appears on the web site. **www.oup.com/uk/pchem11e/**

**The chemist's toolkit 2** Properties of bulk matter

The state of a bulk sample of matter is defined by specifying the values of various properties. Among them are:

The **mass**, $m$, a measure of the quantity of matter present (unit: kilogram, kg).

The **volume**, $V$, a measure of the quantity of space the sample occupies (unit: cubic metre, $\mathrm{m^3}$).

The **amount of substance**, $n$, a measure of the number of specified entities (atoms, molecules, or formula units) present (unit: mole, mol).

## Annotated equations and equation labels

We have annotated many equations to help you follow how they are developed. An annotation can take you across the equals sign: it is a reminder of the substitution used, an approximation made, the terms that have been assumed constant, an integral used, and so on. An annotation can also be a reminder of the significance of an individual term in an expression. We sometimes colour a collection of numbers or symbols to show how they carry from one line to the next. Many of the equations are labelled to highlight their significance.

$$C_{V,\mathrm{m}}^{\mathrm{V}} \overset{\boxed{U_\mathrm{m}(T)=U_\mathrm{m}(0)+N_\mathrm{A}\langle\varepsilon^\mathrm{V}\rangle}}{=} \frac{\mathrm{d}N_\mathrm{A}\langle\varepsilon^\mathrm{V}\rangle}{\mathrm{d}T} = R\theta^\mathrm{V}\frac{\mathrm{d}}{\mathrm{d}T}\frac{1}{\mathrm{e}^{\theta^\mathrm{V}/T}-1} \overset{\boxed{\mathrm{d}(1/f)/\mathrm{d}x=-(1/f^2)\mathrm{d}f/\mathrm{d}x \text{ used twice}}}{=} R\left(\frac{\theta^\mathrm{V}}{T}\right)^2\frac{\mathrm{e}^{\theta^\mathrm{V}/T}}{(\mathrm{e}^{\theta^\mathrm{V}/T}-1)^2}$$

By noting that $\mathrm{e}^{\theta^\mathrm{V}/T}=(\mathrm{e}^{\theta^\mathrm{V}/2T})^2$, this expression can be rearranged into

$$C_{V,\mathrm{m}}^{\mathrm{V}} = Rf(T) \quad f(T)=\left(\frac{\theta^\mathrm{V}}{T}\right)^2\left(\frac{\mathrm{e}^{-\theta^\mathrm{V}/2T}}{1-\mathrm{e}^{-\theta^\mathrm{V}/T}}\right)^2$$

Vibrational contribution to $C_{V,\mathrm{m}}$ (13E.3)

## Checklists of equations

A handy checklist at the end of each topic summarizes the most important equations and the conditions under which they apply. Don't think, however, that you have to memorize every equation in these checklists.

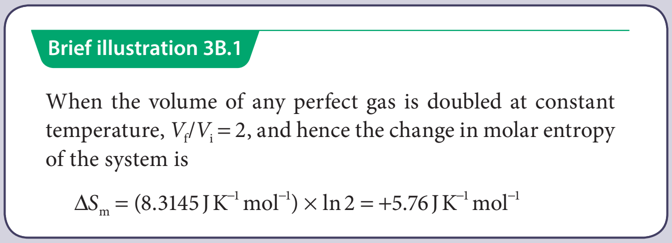
## Checklist of equations

| Property | Equation |
|---|---|
| Gibbs energy of mixing | $\Delta_\mathrm{mix}G = nRT(x_\mathrm{A}\ln x_\mathrm{A} + x_\mathrm{B}\ln x_\mathrm{B})$ |
| Entropy of mixing | $\Delta_\mathrm{mix}S = -nR(x_\mathrm{A}\ln x_\mathrm{A} + x_\mathrm{B}\ln x_\mathrm{B})$ |

# SETTING UP AND SOLVING PROBLEMS

## Brief illustrations

A *Brief illustration* shows you how to use an equation or concept that has just been introduced in the text. It shows you how to use data and manipulate units correctly. It also helps you to become familiar with the magnitudes of quantities.



**Brief illustration 3B.1**

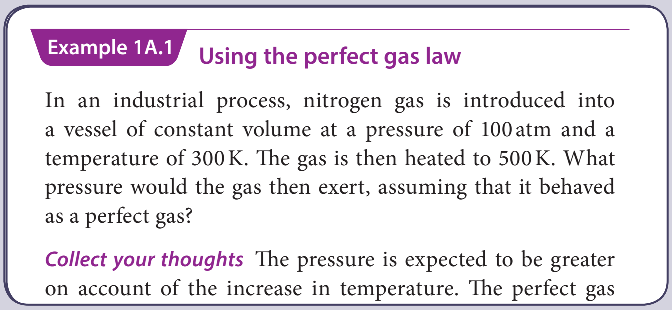
When the volume of any perfect gas is doubled at constant temperature, $V_f/V_i = 2$, and hence the change in molar entropy of the system is

$$\Delta S_m = (8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}}) \times \ln 2 = +5.76\,\mathrm{J\,K^{-1}\,mol^{-1}}$$

## Examples

Worked *Examples* are more detailed illustrations of the application of the material, and typically require you to assemble and deploy the relevant concepts and equations.

We suggest how you should collect your thoughts (that is a new feature) and then proceed to a solution. All the worked *Examples* are accompanied by Self-tests to enable you to test your grasp of the material after working through our solution as set out in the *Example*.



**Example 1A.1** **Using the perfect gas law**

In an industrial process, nitrogen gas is introduced into a vessel of constant volume at a pressure of 100 atm and a temperature of 300 K. The gas is then heated to 500 K. What pressure would the gas then exert, assuming that it behaved as a perfect gas?

***Collect your thoughts*** The pressure is expected to be greater on account of the increase in temperature. The perfect gas

## Discussion questions

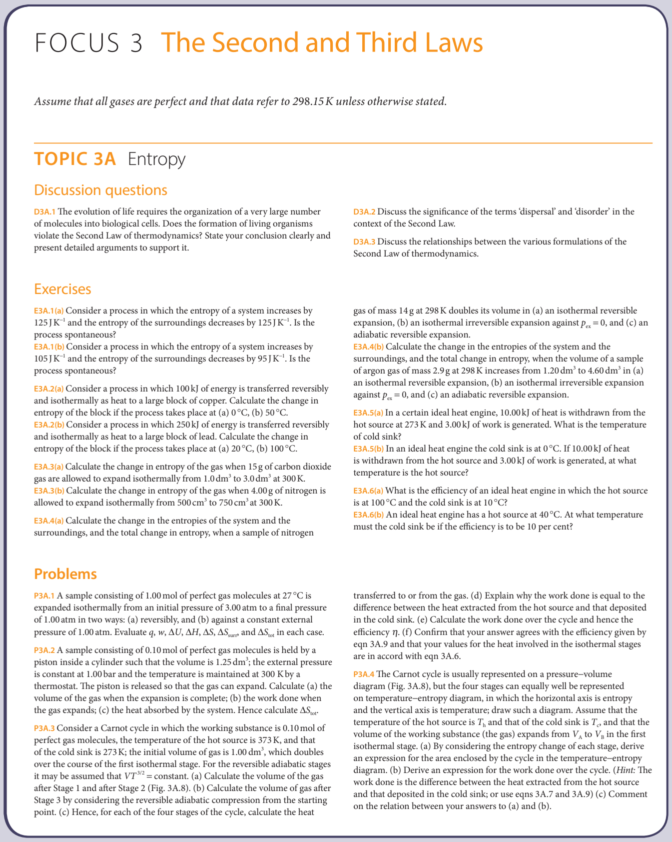
Discussion questions appear at the end of every Focus, and are organised by Topic. These questions are designed to encourage you to reflect on the material you have just read, to review the key concepts, and sometimes to think about its implications and limitations.

## Exercises and problems

Exercises and Problems are also provided at the end of every Focus and organised by Topic. Exercises are designed as relatively straightforward numerical tests; the Problems are more challenging and typically involve constructing a more detailed answer. The Exercises come in related pairs, with final numerical answers available online for the 'a' questions. Final numerical answers to the odd-numbered Problems are also available online.

## Integrated activities

At the end of every Focus you will find questions that span several Topics. They are designed to help you use your knowledge creatively in a variety of ways.



FOCUS 3 **The Second and Third Laws**

*Assume that all gases are perfect and that data refer to 298.15 K unless otherwise stated.*

**TOPIC 3A** Entropy

**Discussion questions**

**D3A.1** The evolution of life requires the organization of a very large number of molecules into biological cells. Does the formation of living organisms violate the Second Law of thermodynamics? State your conclusion clearly and present detailed arguments to support it.

**D3A.2** Discuss the significance of the terms 'dispersal' and 'disorder' in the context of the Second Law.

**D3A.3** Discuss the relationships between the various formulations of the Second Law of thermodynamics.

**Exercises**

**E3A.1(a)** Consider a process in which the entropy of a system increases by 125 J K$^{-1}$ and the entropy of the surroundings decreases by 125 J K$^{-1}$. Is the process spontaneous?
**E3A.1(b)** Consider a process in which the entropy of a system increases by 105 J K$^{-1}$ and the entropy of the surroundings decreases by 95 J K$^{-1}$. Is the process spontaneous?

**E3A.2(a)** Consider a process in which 100 kJ of energy is transferred reversibly and isothermally as heat to a large block of copper. Calculate the change in entropy of the block if the process takes place at (a) 0 °C, (b) 50 °C.
**E3A.2(b)** Consider a process in which 250 kJ of energy is transferred reversibly and isothermally as heat to a large block of lead. Calculate the change in entropy of the block if the process takes place at (a) 20 °C, (b) 100 °C.

**E3A.3(a)** Calculate the change in entropy of the gas when 15 g of carbon dioxide gas are allowed to expand isothermally from 1.0 dm$^3$ to 3.0 dm$^3$ at 300 K.
**E3A.3(b)** Calculate the change in entropy of the gas when 4.00 g of nitrogen is allowed to expand isothermally from 500 cm$^3$ to 750 cm$^3$ at 300 K.

**E3A.4(a)** Calculate the change in the entropies of the system and the surroundings, and the total change in entropy, when a sample of nitrogen gas of mass 14 g at 298 K doubles its volume in (a) an isothermal reversible expansion, (b) an isothermal irreversible expansion against $p_{ex} = 0$, and (c) an adiabatic reversible expansion.
**E3A.4(b)** Calculate the change in the entropies of the system and the surroundings, and the total change in entropy, when the volume of a sample of argon gas of mass 2.9 g at 298 K increases from 1.20 dm$^3$ to 4.60 dm$^3$ in (a) an isothermal reversible expansion, (b) an isothermal irreversible expansion against $p_{ex} = 0$, and (c) an adiabatic reversible expansion.

**E3A.5(a)** In a certain ideal heat engine, 10.00 kJ of heat is withdrawn from the hot source at 273 K and 3.00 kJ of work is generated. What is the temperature of cold sink?
**E3A.5(b)** In an ideal heat engine the cold sink is at 0 °C. If 10.00 kJ of heat is withdrawn from the hot source and 3.00 kJ of work is generated, at what temperature is the hot source?

**E3A.6(a)** What is the efficiency of an ideal heat engine in which the hot source is at 100 °C and the cold sink is at 10 °C?
**E3A.6(b)** An ideal heat engine has a hot source at 40 °C. At what temperature must the cold sink be if the efficiency is to be 10 per cent?

**Problems**

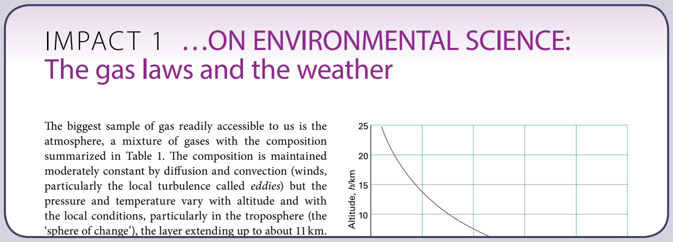
**P3A.1** A sample consisting of 1.00 mol of perfect gas molecules at 27 °C is expanded isothermally from an initial pressure of 3.00 atm to a final pressure of 1.00 atm in two ways: (a) reversibly, and (b) against a constant external pressure of 1.00 atm. Evaluate $q$, $w$, $\Delta U$, $\Delta H$, $\Delta S$, $\Delta S_{surr}$, and $\Delta S_{tot}$ in each case.

**P3A.2** A sample consisting of 0.10 mol of perfect gas molecules is held by a piston inside a cylinder such that the volume is 1.25 dm$^3$; the external pressure is constant at 1.00 bar and the temperature is maintained at 300 K by a thermostat. The piston is released so that the gas can expand. Calculate (a) the volume of the gas when the expansion is complete; (b) the work done when the gas expands; (c) the heat absorbed by the system. Hence calculate $\Delta S_{tot}$.

**P3A.3** Consider a Carnot cycle in which the working substance is 0.10 mol of perfect gas molecules, the temperature of the hot source is 373 K, and that of the cold sink is 273 K; the initial volume of gas is 1.00 dm$^3$, which doubles over the course of the first isothermal stage. For the reversible adiabatic stages it may be assumed that $VT^{3/2}$ = constant. (a) Calculate the volume of the gas after Stage 1 and after Stage 2 (Fig. 3A.8). (b) Calculate the volume of gas after Stage 3 by considering the reversible adiabatic compression from the starting point. (c) Hence, for each of the four stages of the cycle, calculate the heat transferred to or from the gas. (d) Explain why the work done is equal to the difference between the heat extracted from the hot source and that deposited in the cold sink. (e) Calculate the work done over the cycle and hence the efficiency $\eta$. (f) Confirm that your answer agrees with the efficiency given by eqn 3A.9 and that your values for the heat involved in the isothermal stages are in accord with eqn 3A.6.

**P3A.4** The Carnot cycle is usually represented on a pressure–volume diagram (Fig. 3A.8), but the four stages can equally well be represented on temperature–entropy diagram, in which the horizontal axis is entropy and the vertical axis is temperature; draw such a diagram. Assume that the temperature of the hot source is $T_h$ and that of the cold sink is $T_c$, and that the volume of the working substance (the gas) expands from $V_A$ to $V_B$ in the first isothermal stage. (a) By considering the entropy change of each stage, derive an expression for the area enclosed by the cycle in the temperature–entropy diagram. (b) Derive an expression for the work done over the cycle. (*Hint*: The work done is the difference between the heat extracted from the hot source and that deposited in the cold sink; or use eqns 3A.7 and 3A.9) (c) Comment on the relation between your answers to (a) and (b).

# THERE IS A LOT OF ADDITIONAL MATERIAL ON THE WEB



IMPACT 1 …ON ENVIRONMENTAL SCIENCE: The gas laws and the weather

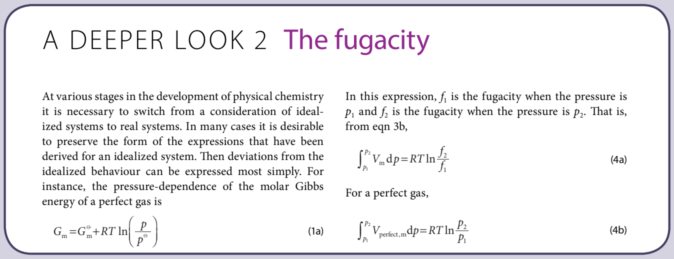
The biggest sample of gas readily accessible to us is the atmosphere, a mixture of gases with the composition summarized in Table 1. The composition is maintained moderately constant by diffusion and convection (winds, particularly the local turbulence called *eddies*) but the pressure and temperature vary with altitude and with the local conditions, particularly in the troposphere (the 'sphere of change'), the layer extending up to about 11 km.

## 'Impact' sections

*'Impact'* sections show how physical chemistry is applied in a variety of modern contexts. They showcase physical chemistry as an evolving subject. **www.oup.com/uk/pchem11e/**

## A deeper look

These online sections take some of the material in the text further and are there if you want to extend your knowledge and see the details of some of the more advanced derivations **www.oup.com/uk/pchem11e/**



A DEEPER LOOK 2 The fugacity

At various stages in the development of physical chemistry it is necessary to switch from a consideration of idealized systems to real systems. In many cases it is desirable to preserve the form of the expressions that have been derived for an idealized system. Then deviations from the idealized behaviour can be expressed most simply. For instance, the pressure-dependence of the molar Gibbs energy of a perfect gas is

$$G_m = G_m^{\ominus} + RT \ln\left(\frac{p}{p^{\ominus}}\right) \qquad (1a)$$

In this expression, $f_1$ is the fugacity when the pressure is $p_1$ and $f_2$ is the fugacity when the pressure is $p_2$. That is, from eqn 3b,

$$\int_{p_1}^{p_2} V_m \mathrm{d}p = RT \ln\frac{f_2}{f_1} \qquad (4a)$$

For a perfect gas,

$$\int_{p_1}^{p_2} V_{\text{perfect,m}} \mathrm{d}p = RT \ln\frac{p_2}{p_1} \qquad (4b)$$

## Group theory tables

Comprehensive group theory tables are available to download.

## Molecular modelling problems

Files containing molecular modelling problems can be downloaded, designed for use with the Spartan Student™ software. However they can also be completed using any modelling software that allows Hartree–Fock, density functional, and MP2 calculations. The site can be accessed at **www.oup.com/uk/pchem11e/**.

# TO THE INSTRUCTOR

We have designed the text to give you maximum flexibility in the selection and sequence of Topics, while the grouping of Topics into Focuses helps to maintain the unity of the subject. Additional resources are:

## Figures and tables from the book

Lecturers can find the artwork and tables from the book in ready-to-download format. These may be used for lectures without charge (but not for commercial purposes without specific permission).

## Key equations

Supplied in Word format so you can download and edit them.

Lecturer resources are available only to registered adopters of the textbook. To register, simply visit **www.oup.com/uk/pchem11e/** and follow the appropriate links.

# SOLUTIONS MANUALS

Two solutions manuals have been written by Peter Bolgar, Haydn Lloyd, Aimee North, Vladimiras Oleinikovas, Stephanie Smith, and James Keeler.

The *Student's Solutions Manual* (ISBN 9780198830085) provides full solutions to the 'a' Exercises and to the odd-numbered Problems.

The *Instructor's Solutions Manual* provides full solutions to the 'b' Exercises and to the even-numbered Problems (available to download online for registered adopters of the book only).

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Photograph by Natasha Ellis-Knight.

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Photograph by Nathan Pitt, ©University of Cambridge.

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# BRIEF CONTENTS

**Resource section**

# FULL CONTENTS

# CONVENTIONS

To avoid intermediate rounding errors, but to keep track of values in order to be aware of values and to spot numerical errors, we display intermediate results as *n.nnn*… and round the calculation only at the final step.

Blue terms are used when we want to identify a term in an equation. An entire quotient, numerator/denominator, is coloured blue if the annotation refers to the entire term, not just to the numerator or denominator separately.

# LIST OF TABLES

# LIST OF *THE CHEMIST’S TOOLKITS*

# LIST OF MATERIAL PROVIDED AS *A DEEPER LOOK*

| **Number** | **Title** |
|---|---|
| 1 | The Debye–Hückel theory |
| 2 | The fugacity |
| 3 | Separation of variables |
| 4 | The energy of the bonding molecular orbital of $H_2^+$ |
| 5 | Rotational selection rules |
| 6 | Vibrational selection rules |
| 7 | The van der Waals equation of state |
| 8 | The electric dipole–dipole interaction |
| 9 | The virial and the virial equation of state |
| 10 | Establishing the relation between bulk and molecular properties |
| 11 | The random walk |
| 12 | The RRK model |
| 13 | The BET isotherm |

# LIST OF *IMPACTS*

# PROLOGUE Energy, temperature, and chemistry

Energy is a concept used throughout chemistry to discuss molecular structures, reactions, and many other processes. What follows is an informal first look at the important features of energy. Its precise definition and role will emerge throughout the course of this text.

The transformation of energy from one form to another is described by the laws of **thermodynamics**. They are applicable to bulk matter, which consists of very large numbers of atoms and molecules. The 'First Law' of thermodynamics is a statement about the quantity of energy involved in a transformation; the 'Second Law' is a statement about the dispersal of that energy (in a sense that will be explained).

To discuss the energy of individual atoms and molecules that make up samples of bulk matter it is necessary to use **quantum mechanics**. According to this theory, the energy associated with the motion of a particle is 'quantized', meaning that the energy is restricted to certain values, rather than being able to take on any value. Three different kinds of motion can occur: *translation* (motion through space), *rotation* (change of orientation), and *vibration* (the periodic stretching and bending of bonds). Figure 1 depicts the relative sizes and spacing of the energy states associated with these different kinds of motion of typical molecules and compares them with the typical energies of electrons in atoms and molecules. The allowed energies associated with translation are so close together in normal-sized containers that they form a continuum. In contrast, the separation between the allowed electronic energy states of atoms and molecules is very large.

The link between the energies of individual molecules and the energy of bulk matter is provided by one of the most important concepts in chemistry, the **Boltzmann distribution**. Bulk matter consists of large numbers of molecules, each of which is in one of its available energy states. The total number of molecules with a particular energy due to translation, rotation, vibration, and its electronic state is called the 'population' of that state. Most molecules are found in the lowest energy state, and higher energy states are occupied by progressively fewer molecules. The Boltzmann distribution gives the population, $N_i$, of any energy state in terms of the energy of the state, $\varepsilon_i$, and the absolute temperature, $T$:

$$N_i \propto \mathrm{e}^{-\varepsilon_i/kT}$$

In this expression, $k$ is *Boltzmann's constant* (its value is listed inside the front cover), a universal constant (in the sense of having the same value for all forms of matter). Figure 2 shows the Boltzmann distribution for two temperatures: as the temperature increases higher energy states are populated at the expense of states lower in energy. According to the Boltzmann distribution, the temperature is the single parameter that governs the spread of populations over the available energy states, whatever their nature.

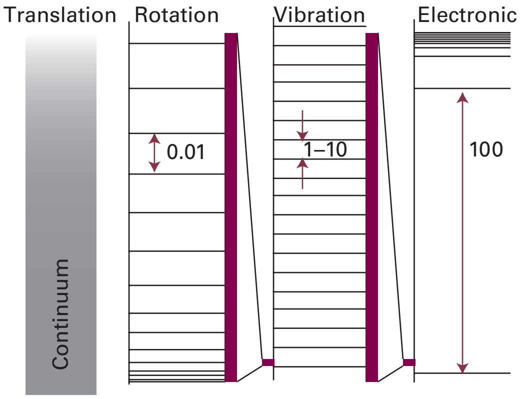
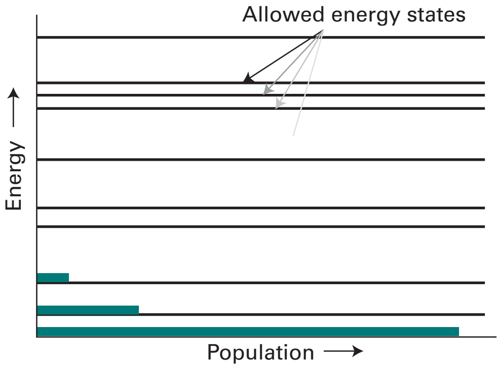
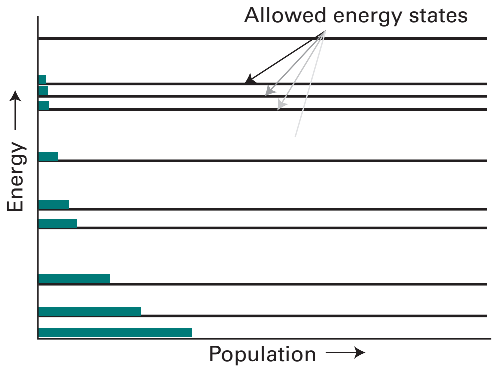


**Figure 1** The relative energies of the allowed states of various kinds of atomic and molecular motion.



(a) Low temperature



(b) High temperature

**Figure 2** The relative populations of states at (a) low, (b) high temperature according to the Boltzmann distribution.

The Boltzmann distribution, as well as providing insight into the significance of temperature, is central to understanding much of chemistry. That most molecules occupy states of low energy when the temperature is low accounts for the existence of compounds and the persistence of liquids and solids. That highly excited energy levels become accessible at high temperatures accounts for the possibility of reaction as one substance acquires the ability to change into another. Both features are explored in detail throughout the text.

You should keep in mind the Boltzmann distribution (which is treated in greater depth later in the text) whenever considering the interpretation of the properties of bulk matter and the role of temperature. An understanding of the flow of energy and how it is distributed according to the Boltzmann distribution is the key to understanding thermodynamics, structure, and change throughout chemistry.

# FOCUS 7

# Quantum theory

It was once thought that the motion of atoms and subatomic particles could be expressed using 'classical mechanics', the laws of motion introduced in the seventeenth century by Isaac Newton, for these laws were very successful at explaining the motion of everyday objects and planets. However, a proper description of electrons, atoms, and molecules requires a different kind of mechanics, 'quantum mechanics', which is introduced in this Focus and applied widely throughout the text.

## 7A The origins of quantum mechanics

Experimental evidence accumulated towards the end of the nineteenth century showed that classical mechanics failed when it was applied to particles as small as electrons. More specifically, careful measurements led to the conclusion that particles may not have an arbitrary energy and that the classical concepts of a particle and wave blend together. This Topic shows how these observations set the stage for the development of the concepts and equations of quantum mechanics in the early twentieth century.

7A.1 **Energy quantization;** 7A.2 **Wave–particle duality**

## 7B Wavefunctions

In quantum mechanics, all the properties of a system are expressed in terms of a wavefunction which is obtained by solving the equation proposed by Erwin Schrödinger. This Topic focuses on the interpretation of the wavefunction, and specifically what it reveals about the location of a particle.

7B.1 **The Schrödinger equation;** 7B.2 **The Born interpretation**

## 7C Operators and observables

A central feature of quantum theory is its representation of observables by 'operators', which act on the wavefunction and extract the information it contains. This Topic shows how operators are constructed and used. One consequence of their use is the 'uncertainty principle', one of the most profound departures of quantum mechanics from classical mechanics.

7C.1 **Operators;** 7C.2 **Superpositions and expectation values;** 7C.3 **The uncertainty principle;** 7C.4 **The postulates of quantum mechanics**

## 7D Translational motion

Translational motion, motion through space, is one of the fundamental types of motion treated by quantum mechanics. According to quantum theory, a particle constrained to move in a finite region of space is described by only certain wavefunctions and can possess only certain energies. That is, quantization emerges as a natural consequence of solving the Schrödinger equation and the conditions imposed on it. The solutions also expose a number of non-classical features of particles, especially their ability to tunnel into and through regions where classical physics would forbid them to be found.

7D.1 **Free motion in one dimension;** 7D.2 **Confined motion in one dimension;** 7D.3 **Confined motion in two and more dimensions;** 7D.4 **Tunnelling**

## 7E Vibrational motion

This Topic introduces the 'harmonic oscillator', a simple but very important model for the description of vibrations. It shows that the energies of an oscillator are quantized and that an oscillator may be found at displacements that are forbidden by classical physics.

7E.1 **The harmonic oscillator;** 7E.2 **Properties of the harmonic oscillator**

## 7F Rotational motion

The constraints on the wavefunctions of a body rotating in two and three dimensions result in the quantization of its energy.

In addition, because the energy is related to the angular momentum, it follows that angular momentum is also restricted to certain values. The quantization of angular momentum is a very important aspect of the quantum theory of electrons in atoms and of rotating molecules.

7F.1 **Rotation in two dimensions;** 7F.2 **Rotation in three dimensions**

## **Web resources** What is an application of this material?

*Impact* 11 highlights an application of quantum mechanics which still requires much research before it becomes a useful technology. It is based on the expectation that a 'quantum computer' can carry out calculations on many states of a system simultaneously, leading to a new generation of very fast computers. 'Nanoscience' is the study of atomic and molecular assemblies with dimensions ranging from 1 nm to about 100 nm, and 'nanotechnology' is concerned with the incorporation of such assemblies into devices. *Impact* 12 explores quantum mechanical effects that show how the properties of a nanometre-sized assembly depend on its size.

# TOPIC 7A The origins of quantum mechanics

### ➤ Why do you need to know this material?

Quantum theory is central to almost every explanation in chemistry. It is used to understand atomic and molecular structure, chemical bonds, and most of the properties of matter.

### ➤ What is the key idea?

Experimental evidence led to the conclusion that energy can be transferred only in discrete amounts, and that the classical concepts of a 'particle' and a 'wave' blend together.

### ➤ What do you need to know already?

You should be familiar with the basic principles of classical mechanics, especially momentum, force, and energy set out in *The chemist's toolkits* 3 (in Topic 1B) and 6 (in Topic 2A). The discussion of heat capacities of solids makes light use of material in Topic 2A.

The classical mechanics developed by Newton in the seventeenth century is an extraordinarily successful theory for describing the motion of everyday objects and planets. However, late in the nineteenth century scientists started to make observations that could not be explained by classical mechanics. They were forced to revise their entire conception of the nature of matter and replace classical mechanics by a theory that became known as **quantum mechanics**.

## 7A.1 Energy quantization

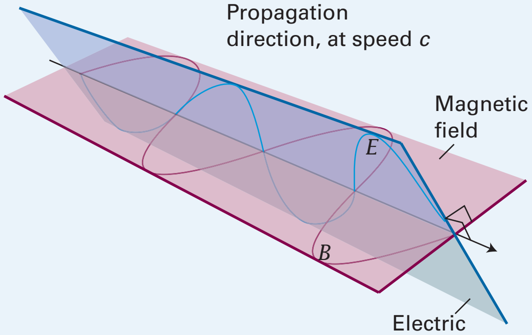
Three experiments carried out near the end of the nineteenth century drove scientists to the view that energy can be transferred only in discrete amounts.

### (a) Black-body radiation

The key features of electromagnetic radiation according to classical physics are described in *The chemist's toolkit* 13. It is observed that all objects emit electromagnetic radiation over a range of frequencies with an intensity that depends on the temperature of the object. A familiar example is a heated metal bar that first glows red and then becomes 'white hot' upon further heating. As the temperature is raised, the colour shifts from red towards blue and results in the white glow.

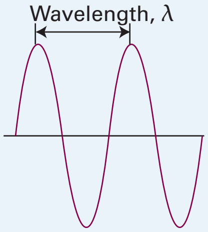
**The chemist's toolkit 13** Electromagnetic radiation

**Electromagnetic radiation** consists of oscillating electric and magnetic disturbances that propagate as waves. The two components of an electromagnetic wave are mutually perpendicular and are also perpendicular to the direction of propagation (Sketch 1). Electromagnetic waves travel through a vacuum at a constant speed called the **speed of light**, $c$, which has the defined value of exactly $2.997\,924\,58 \times 10^8\,\mathrm{m\,s^{-1}}$.

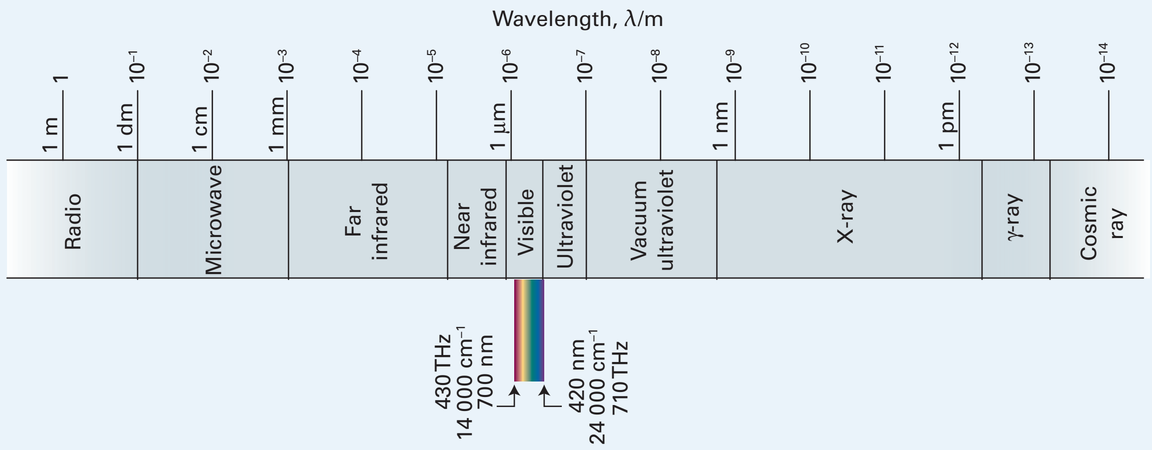


Sketch 1

A wave is characterized by its **wavelength**, $\lambda$ (lambda), the distance between consecutive peaks of the wave (Sketch 2). The classification of electromagnetic radiation according to its wavelength is shown in Sketch 3. Light, which is electromagnetic radiation that is visible to the human eye, has a wavelength in the range 420 nm (violet light) to 700 nm (red light). The properties of a wave may also be expressed in terms of its **frequency**, $\nu$ (nu), the number of oscillations in a time interval divided by the duration of the interval. Frequency is reported in hertz, Hz, with $1\,\mathrm{Hz} = 1\,\mathrm{s^{-1}}$ (i.e. 1 cycle per second). Light spans the frequency range from 710 THz (violet light) to 430 THz (red light).



Sketch 2



**Sketch 3**

The wavelength and frequency of an electromagnetic wave are related by:

$$c = \lambda\nu$$

The relation between wavelength and frequency in a vacuum

It is also common to describe a wave in terms of its **wavenumber**, $\tilde{\nu}$ (nu tilde), which is defined as

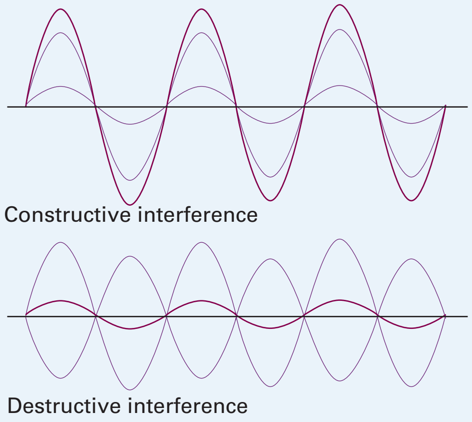
$$\tilde{\nu} = \frac{1}{\lambda} \text{ or equivalently } \tilde{\nu} = \frac{\nu}{c}$$

Wavenumber [definition]

Thus, wavenumber is the reciprocal of the wavelength and can be interpreted as the number of wavelengths in a given distance. In spectroscopy, for historical reasons, wavenumber is usually reported in units of reciprocal centimetres (cm$^{-1}$). Visible light therefore corresponds to electromagnetic radiation with a wavenumber of 14 000 cm$^{-1}$ (red light) to 24 000 cm$^{-1}$ (violet light).

Electromagnetic radiation that consists of a single frequency (and therefore single wavelength) is **monochromatic**, because it corresponds to a single colour. *White light* consists of electromagnetic waves with a continuous, but not uniform, spread of frequencies throughout the visible region of the spectrum.

A characteristic property of waves is that they interfere with one another, which means that they result in a greater amplitude where their displacements add and a smaller amplitude where their displacements subtract (Sketch 4). The former is called 'constructive interference' and the latter 'destructive interference'. The regions of constructive and destructive interference show up as regions of enhanced and diminished intensity. The phenomenon of **diffraction** is the interference caused by an object in the path of waves and occurs when the dimensions of the object are comparable to the wavelength of the radiation. Light waves, with wavelengths of the order of 500 nm, are diffracted by narrow slits.



**Sketch 4**

The radiation emitted by hot objects is discussed in terms of a **black body**, a body that emits and absorbs electromagnetic radiation without favouring any wavelengths. A good approximation to a black body is a small hole in an empty container (Fig. 7A.1). Figure 7A.2 shows how the intensity of the radiation from a black body varies with wavelength at several temperatures. At each temperature $T$ there is a wavelength, $\lambda_{\text{max}}$, at which the intensity of the radiation is a maximum, with $T$ and $\lambda_{\text{max}}$ related by the empirical **Wien's law**:

$$\lambda_{\text{max}} T = 2.9 \times 10^{-3}\ \text{m K} \qquad \text{Wien's law} \qquad (7\text{A}.1)$$

The intensity of the emitted radiation at any temperature declines sharply at short wavelengths (high frequencies). The intensity is effectively a window on to the energy present inside the container, in the sense that the greater the intensity at a given wavelength, the greater is the energy inside the container due to radiation at that wavelength.

The **energy density**, $\mathcal{E}(T)$, is the total energy inside the container divided by its volume. The **energy spectral density**, $\rho(\lambda,T)$, is defined so that $\rho(\lambda,T)\mathrm{d}\lambda$ is the energy density at temperature $T$ due to the presence of electromagnetic radiation with wavelengths between $\lambda$ and $\lambda + \mathrm{d}\lambda$. A high energy

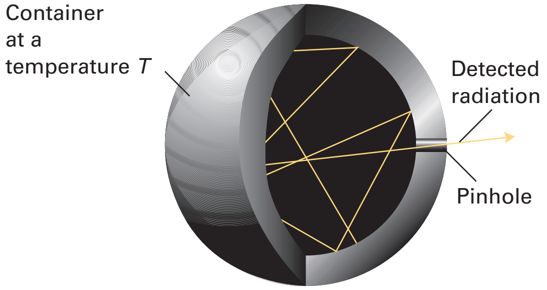


**Figure 7A.1** Black-body radiation can be detected by allowing it to leave an otherwise closed container through a pinhole. The radiation is reflected many times within the container and comes to thermal equilibrium with the wall. Radiation leaking out through the pinhole is characteristic of the radiation inside the container.

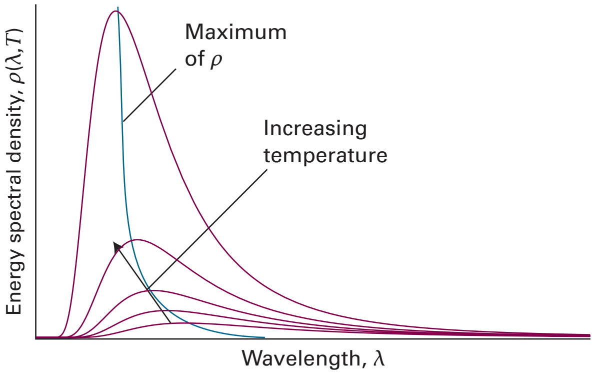


**Figure 7A.2** The energy spectral density of radiation from a black body at several temperatures. Note that as the temperature increases, the maximum in the energy spectral density moves to shorter wavelengths and increases in intensity overall.

spectral density at the wavelength $\lambda$ and temperature $T$ simply means that there is a lot of energy associated with wavelengths lying between $\lambda$ and $\lambda + d\lambda$ at that temperature. The energy density is obtained by summing (integrating) the energy spectral density over all wavelengths:

$$\mathcal{E}(T)=\int_0^\infty \rho(\lambda,T)\mathrm{d}\lambda \qquad (7A.2)$$

The units of $\mathcal{E}(T)$ are joules per metre cubed ($\mathrm{J\,m^{-3}}$), so the units of $\rho(\lambda,T)$ are $\mathrm{J\,m^{-4}}$. Empirically, the energy density is found to vary as $T^4$, an observation expressed by the **Stefan–Boltzmann law**:

$$\mathcal{E}(T) = \text{constant} \times T^4 \qquad \text{Stefan–Boltzmann law} \qquad (7A.3)$$

with the constant equal to $7.567 \times 10^{-16}\,\mathrm{J\,m^{-3}\,K^{-4}}$.

The container in Fig. 7A.1 emits radiation that can be thought of as oscillations of the electromagnetic field stimulated by the oscillations of electrical charges in the material of the wall. According to classical physics, every oscillator is excited to some extent, and according to the equipartition principle (*The chemist's toolkit* 7 in Topic 2A) every oscillator, regardless of its frequency, has an average energy of $kT$. On this basis, the physicist Lord Rayleigh, with minor help from James Jeans, deduced what is now known as the **Rayleigh–Jeans law**:

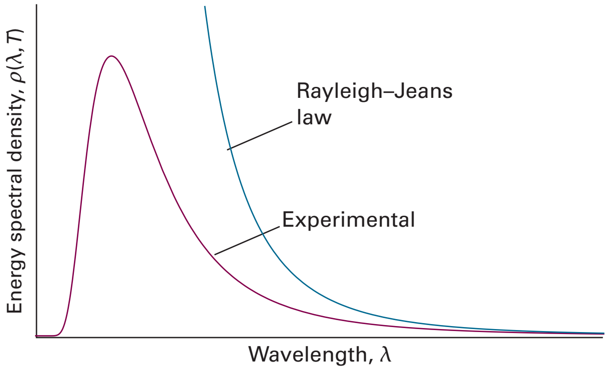


**Figure 7A.3** Comparison of the experimental energy spectral density with the prediction of the Rayleigh–Jeans law (eqn 7A.4). The latter predicts an infinite energy spectral density at short wavelengths and infinite overall energy density.

$$\rho(\lambda,T)=\frac{8\pi kT}{\lambda^4} \qquad \text{Rayleigh–Jeans law} \qquad (7A.4)$$

where $k$ is Boltzmann's constant ($k = 1.381 \times 10^{-23}\,\mathrm{J\,K^{-1}}$).

The Rayleigh–Jeans law is not supported by the experimental measurements. As is shown in Fig. 7A.3, although there is agreement at long wavelengths, it predicts that the energy spectral density (and hence the intensity of the radiation emitted) increases without going through a maximum as the wavelength decreases. That is, the Rayleigh–Jeans law is inconsistent with Wien's law. Equation 7A.4 also implies that the radiation is intense at very short wavelengths and becomes infinitely intense as the wavelength tends to zero. The concentration of radiation at short wavelengths is called the **ultraviolet catastrophe**, and is an unavoidable consequence of classical physics.

In 1900, Max Planck found that the experimentally observed intensity distribution of black-body radiation could be explained by proposing that the energy of each oscillator is limited to discrete values. In particular, Planck assumed that for an electromagnetic oscillator of frequency $\nu$, the permitted energies are integer multiples of $h\nu$:

$$E = nh\nu \qquad n = 0, 1, 2, \ldots \qquad (7A.5)$$

In this expression $h$ is a fundamental constant now known as **Planck's constant**. The limitation of energies to discrete values is called **energy quantization**. On this basis Planck was able to derive an expression for the energy spectral density which is now called the **Planck distribution**:

$$\rho(\lambda,T)=\frac{8\pi hc}{\lambda^5(\mathrm{e}^{hc/\lambda kT}-1)} \qquad \text{Planck distribution} \qquad (7A.6a)$$

This expression is plotted in Fig. 7A.4 and fits the experimental data very well at all wavelengths. The value of $h$, which is an

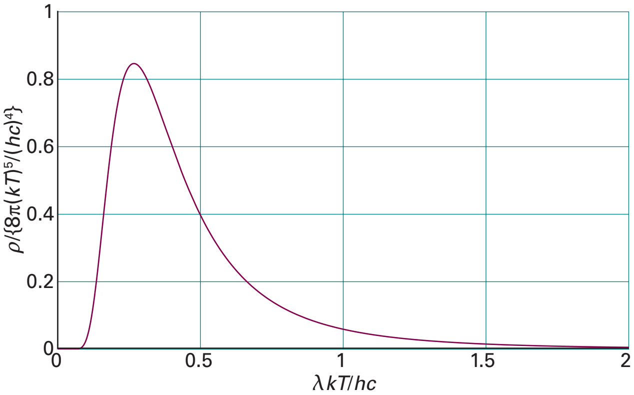


**Figure 7A.4** The Planck distribution (eqn 7A.6a) accounts for the experimentally determined energy distribution of black-body radiation. It coincides with the Rayleigh–Jeans distribution at long wavelengths.

undetermined parameter in the theory, can be found by varying its value until the best fit is obtained between the eqn 7A.6a and experimental measurements. The currently accepted value is $h = 6.626 \times 10^{-34}\,\text{J s}$.

For short wavelengths, $hc/\lambda kT >> 1$, and because $e^{hc/\lambda kT} \to \infty$ faster than $\lambda^5 \to 0$ it follows that $\rho \to 0$ as $\lambda \to 0$. Hence, the energy spectral density approaches zero at short wavelengths, and so the Planck distribution avoids the ultraviolet catastrophe. For long wavelengths in the sense $hc/\lambda kT << 1$, the denominator in the Planck distribution can be replaced by (see *The chemist's toolkit* 12 in Topic 5B)

$$e^{hc/\lambda kT} - 1 = \left(1 + \frac{hc}{\lambda kT} + \cdots\right) - 1 \approx \frac{hc}{\lambda kT}$$

When this approximation is substituted into eqn 7A.6a, the Planck distribution reduces to the Rayleigh–Jeans law, eqn 7A.4. The wavelength at the maximum can be found by differentiation, and is given by $\lambda_{\text{max}}T = \text{constant}$, in accord with Wien's law; the value of the constant found in this way, $hc/5k$, agrees with the experimentally determined value. Finally, the total energy density is

$$\mathcal{E}(T) = \int_0^\infty \frac{8\pi hc}{\lambda^5(e^{hc/\lambda kT} - 1)}\,d\lambda = aT^4 \quad \text{with} \quad a = \frac{8\pi^5 k^4}{15(hc)^3} \qquad (7\text{A}.7)$$

which is finite and agrees with the Stefan–Boltzmann law (eqn 7A.3), including predicting the value of its constant correctly.

**Brief illustration 7A.1**

Consider eqn 7A.6a with $\lambda_1 = 450\,\text{nm}$ (blue light) and $\lambda_2 = 700\,\text{nm}$ (red light), and $T = 298\,\text{K}$. It follows that

$$\frac{hc}{\lambda_1 kT} = \frac{(6.626\times10^{-34}\,\text{J s})\times(2.998\times10^8\,\text{m s}^{-1})}{(450\times10^{-9}\,\text{m})\times(1.381\times10^{-23}\,\text{J K}^{-1})\times(298\,\text{K})} = 107.2\ldots$$

$$\frac{hc}{\lambda_2 kT} = \frac{(6.626\times10^{-34}\,\text{J s})\times(2.998\times10^8\,\text{m s}^{-1})}{(700\times10^{-9}\,\text{m})\times(1.381\times10^{-23}\,\text{J K}^{-1})\times(298\,\text{K})} = 68.9\ldots$$

and

$$\frac{\rho(450\,\text{nm}, 298\,\text{K})}{\rho(700\,\text{nm}, 298\,\text{K})} = \left(\frac{700\times10^{-9}\,\text{m}}{450\times10^{-9}\,\text{m}}\right)^5 \times \frac{e^{68.9\ldots} - 1}{e^{107.2\ldots} - 1}$$

$$= 9.11 \times (2.30\times10^{-17}) = 2.10\times10^{-16}$$

At room temperature, the proportion of shorter wavelength radiation is insignificant.

There is a single reason why Planck's approach is successful but Rayleigh's is not. Instead of allowing each oscillator to have the same average energy, regardless of its frequency, Planck used the Boltzmann distribution (see the *Prologue* to this text) to argue that higher frequency oscillators, which generate shorter wavelength radiation, are less likely to be excited than lower frequency oscillators. Indeed, for very high frequencies the minimum excitation energy of $h\nu$ is too large for the oscillator to be excited at all. This elimination of the contribution from very high frequency oscillators avoids the ultraviolet catastrophe.

It is sometimes convenient to express the Planck distribution in terms of the frequency. Then $\rho(\nu,T)d\nu$ is the energy density at temperature $T$ due to the presence of electromagnetic radiation with frequencies between $\nu$ and $\nu + d\nu$, and

$$\rho(\nu,T) = \frac{8\pi h\nu^3}{c^3(e^{h\nu/kT} - 1)} \qquad (7\text{A}.6\text{b})$$

Planck distribution in terms of frequency

## (b) Heat capacity

When energy is supplied as heat to a substance its temperature rises; the heat capacity (Topic 2A) is the constant of proportionality between the energy supplied and the temperature rise ($C = dq/dT$ and, at constant volume, $C_{V,\text{m}} = (\partial U_\text{m}/\partial T)_V$). Experimental measurements made during the nineteenth century had shown that at room temperature the molar heat capacities of many monatomic solids are about $3R$, where $R$ is the gas constant.[1] However, when measurements were made at much lower temperatures it was found that the heat capacity decreased, tending to zero as the temperature approached zero.

Classical physics was unable to explain this temperature dependence. The classical picture of a solid is of atoms oscillating about fixed positions, with the expectation that each oscillating atom will have the same average energy $kT$. This model predicts that a solid consisting of $N$ atoms, each free to oscillate in three dimensions, will have energy $U = 3NkT$ and hence heat capacity $C_V = (\partial U/\partial T)_V = 3Nk$. The molar heat capacity is therefore predicted to be $3N_\text{A}k$ which, recognizing that $N_\text{A}k = R$, is equal to $3R$ at all temperatures. In 1905, Einstein suggested applying Planck's hypothesis and supposing that each oscillating atom

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[1] The gas constant occurs in the context of solids because it is actually the more fundamental Boltzmann's constant in disguise: $R = N_\text{A}k$.

could have an energy $nh\nu$, where $n$ is an integer and $\nu$ is the frequency of the oscillation. Einstein went on to show by using the Boltzmann distribution that each oscillator is unlikely to be excited to high energies and at low temperatures few oscillators can be excited at all. As a consequence, because the oscillators cannot be excited, the heat capacity falls to zero. The quantitative result that Einstein obtained (as shown in Topic 13E) is

$$C_{V,\mathrm{m}}(T)=3Rf_{\mathrm{E}}(T), \quad f_{\mathrm{E}}(T)=\left(\frac{\theta_{\mathrm{E}}}{T}\right)^2\left(\frac{\mathrm{e}^{\theta_{\mathrm{E}}/2T}}{\mathrm{e}^{\theta_{\mathrm{E}}/T}-1}\right)^2$$

Einstein formula (7A.8a)

In this expression $\theta_{\mathrm{E}}$ is the **Einstein temperature**, $\theta_{\mathrm{E}}=h\nu/k$.

At high temperatures (in the sense $T >> \theta_{\mathrm{E}}$) the exponentials in $f_{\mathrm{E}}$ can be expanded as $\mathrm{e}^x=1+x+\cdots$ and higher terms ignored (*The chemist's toolkit* 12 in Topic 5B). The result is

$$f_{\mathrm{E}}(T)=\left(\frac{\theta_{\mathrm{E}}}{T}\right)^2\left\{\frac{1+\theta_{\mathrm{E}}/2T+\cdots}{(1+\theta_{\mathrm{E}}/T+\cdots)-1}\right\}^2\approx\left(\frac{\theta_{\mathrm{E}}}{T}\right)^2\left\{\frac{1}{\theta_{\mathrm{E}}/T}\right\}^2\approx 1$$

(7A.8b)

and the classical result ($C_{V,\mathrm{m}}=3R$) is obtained. At low temperatures (in the sense $T << \theta_{\mathrm{E}}$), $\mathrm{e}^{\theta_{\mathrm{E}}/T}>>1$ and

$$f_{\mathrm{E}}(T)\approx\left(\frac{\theta_{\mathrm{E}}}{T}\right)^2\left(\frac{\mathrm{e}^{\theta_{\mathrm{E}}/2T}}{\mathrm{e}^{\theta_{\mathrm{E}}/T}}\right)^2=\left(\frac{\theta_{\mathrm{E}}}{T}\right)^2\mathrm{e}^{-\theta_{\mathrm{E}}/T} \quad (7A.8c)$$

The strongly decaying exponential function goes to zero more rapidly than $1/T^2$ goes to infinity; so $f_{\mathrm{E}}\to 0$ as $T\to 0$, and the heat capacity approaches zero, as found experimentally. The physical reason for this success is that as the temperature is lowered, less energy is available to excite the atomic oscillations. At high temperatures many oscillators are excited into high energy states leading to classical behaviour.

Figure 7A.5 shows the temperature dependence of the heat capacity predicted by the Einstein formula and some experimental data; the value of the Einstein temperature is adjusted to obtain the best fit to the data. The general shape of the curve is satisfactory, but the numerical agreement is in fact quite poor. This discrepancy arises from Einstein's assumption that all the atoms oscillate with the same frequency. A more sophisticated treatment, due to Peter Debye, allows the oscillators to have a range of frequencies from zero up to a maximum. This approach results in much better agreement with the experimental data and there can be little doubt that mechanical motion as well as electromagnetic radiation is quantized.

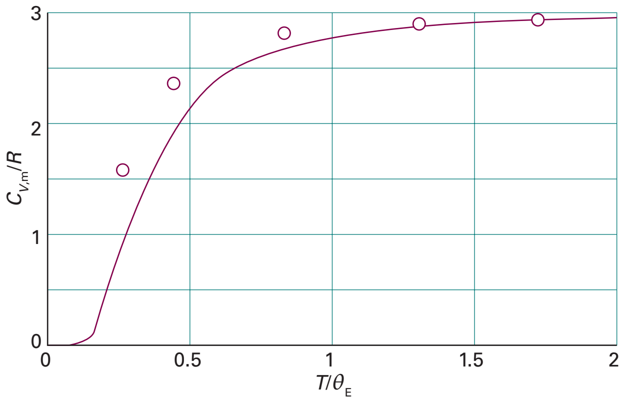


**Figure 7A.5** Experimental low-temperature molar heat capacities (open circles) and the temperature dependence predicted on the basis of Einstein's theory (solid line). His equation (eqn 7A.8) accounts for the dependence fairly well, but is everywhere too low.

## (c) Atomic and molecular spectra

The most compelling and direct evidence for the quantization of energy comes from **spectroscopy**, the detection and analysis of the electromagnetic radiation absorbed, emitted, or scattered by a substance. The record of the variation of the intensity of this radiation with frequency ($\nu$), wavelength ($\lambda$), or wavenumber ($\tilde{\nu}=\nu/c$, see *The chemist's toolkit* 13) is called its **spectrum** (from the Latin word for appearance).

An atomic emission spectrum is shown in Fig. 7A.6, and a molecular absorption spectrum is shown in Fig. 7A.7. The obvious feature of both is that radiation is emitted or absorbed at a series of discrete frequencies. This observation can be understood if the energy of the atoms or molecules is also confined to discrete values, because then the energies that a molecule can discard or acquire are also confined to discrete values (Fig. 7A.8). If the energy of an atom or molecule decreases by $\Delta E$, and this energy is carried away as radiation, the frequency of the radiation $\nu$ and the change in energy are related by the **Bohr frequency condition**:

$$\Delta E=h\nu$$

Bohr frequency condition (7A.9)

A molecule is said to undergo a **spectroscopic transition**, a change of state, and as a result an emission 'line', a sharply defined peak, appears in the spectrum at frequency $\nu$.

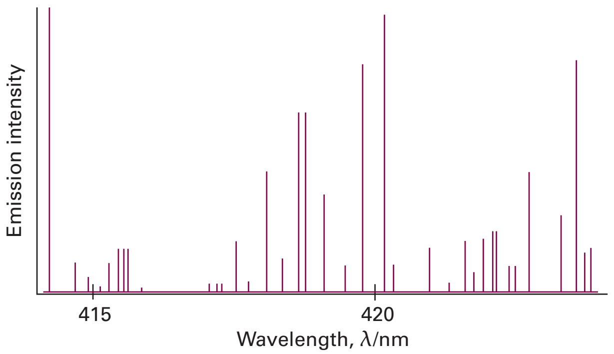


**Figure 7A.6** A region of the spectrum of radiation emitted by excited iron atoms consists of radiation at a series of discrete wavelengths (or frequencies).

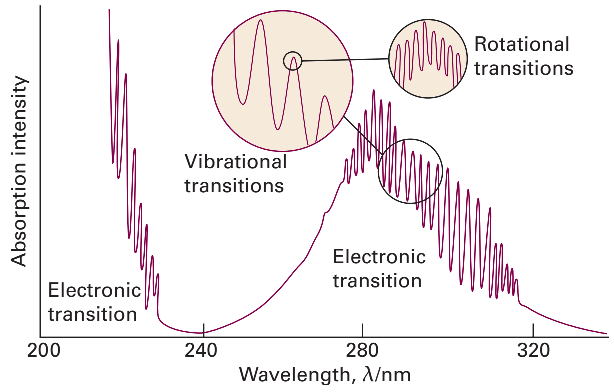


**Figure 7A.7** A molecule can change its state by absorbing radiation at definite frequencies. This spectrum is due to the electronic, vibrational, and rotational excitation of sulfur dioxide ($SO_2$) molecules. The observation of discrete spectral lines suggests that molecules can possess only discrete energies, not an arbitrary energy.

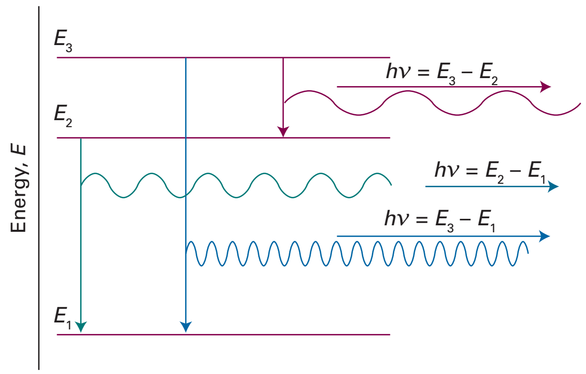


**Figure 7A.8** Spectroscopic transitions, such as those shown in Fig. 7A.6, can be accounted for by supposing that an atom (or molecule) emits electromagnetic radiation as it changes from a discrete level of high energy to a discrete level of lower energy. High-frequency radiation is emitted when the energy change is large. Transitions like those shown in Fig. 7A.7 can be explained by supposing that a molecule (or atom) absorbs radiation as it changes from a low-energy level to a higher-energy level.

**Brief illustration 7A.2**

Atomic sodium produces a yellow glow (as in some street lamps) resulting from the emission of radiation of 590 nm. The spectroscopic transition responsible for the emission involves electronic energy levels that have a separation given by eqn 7A.9:

$$\Delta E = h\nu = \frac{hc}{\lambda} = \frac{(6.626\times10^{-34}\,\mathrm{J\,s})\times(2.998\times10^{8}\,\mathrm{m\,s^{-1}})}{590\times10^{-9}\,\mathrm{m}}$$

$$=3.37\times10^{-19}\,\mathrm{J}$$

This energy difference can be expressed in a variety of ways. For instance, multiplication by Avogadro's constant results in an energy separation per mole of atoms, of 203 kJ mol$^{-1}$, comparable to the energy of a weak chemical bond.

## 7A.2 Wave–particle duality

The experiments about to be described show that electromagnetic radiation—which classical physics treats as wave-like—actually also displays the characteristics of particles. Another experiment shows that electrons—which classical physics treats as particles—also display the characteristics of waves. This **wave–particle duality**, the blending together of the characteristics of waves and particles, lies at the heart of quantum mechanics.

### (a) The particle character of electromagnetic radiation

The Planck treatment of black-body radiation introduced the idea that an oscillator of frequency $\nu$ can have only the energies 0, $h\nu$, $2h\nu$, …. This quantization leads to the suggestion (and at this stage it is only a suggestion) that the resulting electromagnetic radiation of that frequency can be thought of as consisting of 0, 1, 2, … particles, each particle having an energy $h\nu$. These particles of electromagnetic radiation are now called **photons**. Thus, if an oscillator of frequency $\nu$ is excited to its first excited state, then one photon of that frequency is present, if it is excited to its second excited state, then two photons are present, and so on. The observation of discrete spectra from atoms and molecules can be pictured as the atom or molecule generating a photon of energy $h\nu$ when it discards an energy of magnitude $\Delta E$, with $\Delta E = h\nu$.

**Example 7A.1** Calculating the number of photons

Calculate the number of photons emitted by a 100 W yellow lamp in 1.0 s. Take the wavelength of yellow light as 560 nm, and assume 100 per cent efficiency.

***Collect your thoughts*** Each photon has an energy $h\nu$, so the total number $N$ of photons needed to produce an energy $E$ is $N = E/h\nu$. To use this equation, you need to know the frequency of the radiation (from $\nu = c/\lambda$) and the total energy emitted by the lamp. The latter is given by the product of the power ($P$, in watts) and the time interval, $\Delta t$, for which the lamp is turned on: $E = P\Delta t$ (see *The chemist's toolkit* 8 in Topic 2A).

***The solution*** The number of photons is

$$N = \frac{E}{h\nu} = \frac{P\Delta t}{h(c/\lambda)} = \frac{\lambda P \Delta t}{hc}$$

Substitution of the data gives

$$N = \frac{(5.60\times10^{-7}\,\mathrm{m})\times(100\,\mathrm{J\,s^{-1}})\times(1.0\,\mathrm{s})}{(6.626\times10^{-34}\,\mathrm{J\,s})\times(2.998\times10^{8}\,\mathrm{m\,s^{-1}})} = 2.8\times10^{20}$$

*A note on good practice* To avoid rounding and other numerical errors, it is best to carry out algebraic calculations first, and to substitute numerical values into a single, final formula. Moreover, an analytical result may be used for other data without having to repeat the entire calculation.

***Self-test 7A.1*** How many photons does a monochromatic (single frequency) infrared rangefinder of power 1 mW and wavelength 1000 nm emit in 0.1 s?

*Answer:* $5 \times 10^{14}$

So far, the existence of photons is only a suggestion. Experimental evidence for their existence comes from the measurement of the energies of electrons produced in the **photoelectric effect**, the ejection of electrons from metals when they are exposed to ultraviolet radiation. The experimental characteristics of the photoelectric effect are as follows:

- No electrons are ejected, regardless of the intensity of the radiation, unless its frequency exceeds a threshold value characteristic of the metal.
- The kinetic energy of the ejected electrons increases linearly with the frequency of the incident radiation but is independent of the intensity of the radiation.
- Even at low radiation intensities, electrons are ejected immediately if the frequency is above the threshold value.

Figure 7A.9 illustrates the first and second characteristics.

These observations strongly suggest that in the photoelectric effect a particle-like projectile collides with the metal and, if the kinetic energy of the projectile is high enough, an electron is ejected. If the projectile is a photon of energy $h\nu$ ($\nu$ is the frequency of the radiation), the kinetic energy of the electron is $E_\mathrm{k}$, and the energy needed to remove an electron from the metal, which is called its **work function**, is $\Phi$ (uppercase phi), then as illustrated in Fig. 7A.10, the conservation of energy implies that

$$h\nu = E_\mathrm{k} + \Phi \quad \text{or } E_\mathrm{k} = h\nu - \Phi \qquad \text{Photoelectric effect} \qquad (7A.10)$$

This model explains the three experimental observations:

- Photoejection cannot occur if $h\nu < \Phi$ because the photon brings insufficient energy.
- The kinetic energy of an ejected electron increases linearly with the frequency of the photon.
- When a photon collides with an electron, it gives up all its energy, so electrons should appear as soon as the collisions begin, provided the photons have sufficient energy.

A practical application of eqn 7A.10 is that it provides a technique for the determination of Planck's constant, because the slopes of the lines in Fig. 7A.9 are all equal to $h$.

The energies of photoelectrons, the work function, and other quantities are often expressed in the alternative energy unit the **electronvolt** (eV): 1 eV is defined as the kinetic energy acquired when an electron (of charge $-e$) is accelerated from rest through a potential difference $\Delta\phi = 1\,\mathrm{V}$. That kinetic energy is $e\Delta\phi$, so

$$E_\mathrm{k} = e\Delta\phi = (1.602\times10^{-19}\,\mathrm{C})\times 1\,\mathrm{V} = 1.602\times10^{-19}\,\mathrm{C\,V} = 1\,\mathrm{eV}$$

Because $1\,\mathrm{C\,V} = 1\,\mathrm{J}$, it follows that the relation between electronvolts and joules is

$$1\,\mathrm{eV} = 1.602\times10^{-19}\,\mathrm{J}$$

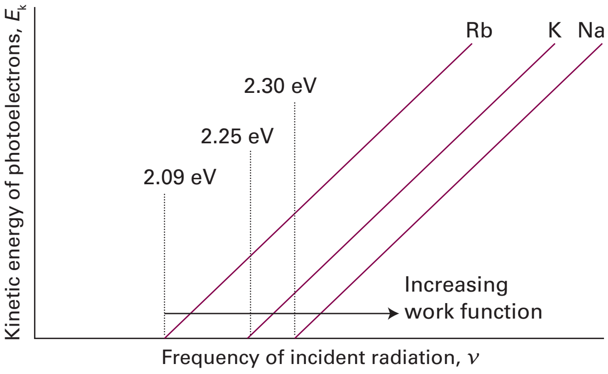


**Figure 7A.9** In the photoelectric effect, it is found that no electrons are ejected when the incident radiation has a frequency below a certain value that is characteristic of the metal. Above that value, the kinetic energy of the photoelectrons varies linearly with the frequency of the incident radiation.

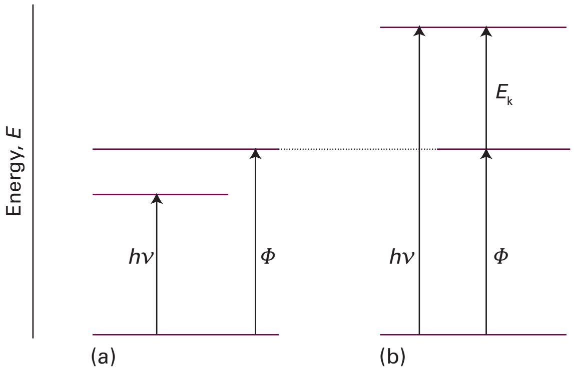


**Figure 7A.10** The photoelectric effect can be explained if it is supposed that the incident radiation is composed of photons that have energy proportional to the frequency of the radiation. (a) The energy of the photon is insufficient to drive an electron out of the metal. (b) The energy of the photon is more than enough to eject an electron, and the excess energy is carried away as the kinetic energy of the photoelectron (the ejected electron).

### Example 7A.2 Calculating the longest wavelength capable of photoejection

A photon of radiation of wavelength 305 nm ejects an electron with a kinetic energy of 1.77 eV from a metal. Calculate the longest wavelength of radiation capable of ejecting an electron from the metal.

***Collect your thoughts*** You can use eqn 7A.10, rearranged into $\Phi = h\nu - E_k$, to compute the work function because you know the frequency of the photon from $\nu = c/\lambda$. The threshold for photoejection is the lowest frequency at which electron ejection occurs without there being any excess energy; that is, the kinetic energy of the ejected electron is zero. Setting $E_k = 0$ in $E_k = h\nu - \Phi$ gives the minimum photon frequency as $\nu_{\min} = \Phi/h$. Use this value of the frequency to calculate the corresponding wavelength, $\lambda_{\max}$.

***The solution*** The minimum frequency for photoejection is

$$\nu_{\min} = \frac{\Phi}{h} = \frac{h\nu - E_k}{h} \overset{\boxed{\nu=c/\lambda}}{=} \frac{c}{\lambda} - \frac{E_k}{h}$$

The longest wavelength that can cause photoejection is therefore

$$\lambda_{\max} = \frac{c}{\nu_{\min}} = \frac{c}{c/\lambda - E_k/h} = \frac{1}{1/\lambda - E_k/hc}$$

Now substitute the data. The kinetic energy of the electron is

$$E_k = 1.77\,\text{eV} \times (1.602\times10^{-19}\,\text{J eV}^{-1}) = 2.83\ldots\times10^{-19}\,\text{J}$$

so

$$\frac{E_k}{hc} = \frac{2.83\ldots\times10^{-19}\,\text{J}}{(6.626\times10^{-34}\,\text{J s})\times(2.998\times10^{8}\,\text{m s}^{-1})} = 1.42\ldots\times10^{6}\,\text{m}^{-1}$$

Therefore, with $1/\lambda = 1/305\,\text{nm} = 3.27\ldots\times10^{6}\,\text{m}^{-1}$,

$$\lambda_{\max} = \frac{1}{(3.27\ldots\times10^{6}\,\text{m}^{-1}) - (1.42\ldots\times10^{6}\,\text{m}^{-1})} = 5.40\times10^{-7}\,\text{m}$$

or 540 nm.

***Self-test 7A.2*** When ultraviolet radiation of wavelength 165 nm strikes a certain metal surface, electrons are ejected with a speed of 1.24 Mm s$^{-1}$. Calculate the speed of electrons ejected by radiation of wavelength 265 nm.

*Answer*: 735 km s$^{-1}$

## (b) The wave character of particles

Although contrary to the long-established wave theory of radiation, the view that radiation consists of particles had been held before, but discarded. No significant scientist, however, had taken the view that matter is wave-like. Nevertheless, experiments carried out in 1925 forced people to consider that possibility. The crucial experiment was performed by Clinton Davisson and Lester Germer, who observed the diffraction of electrons by a crystal (Fig. 7A.11). As remarked in *The chemist's toolkit* 13, diffraction is the interference caused by an object in the path of waves. Davisson and Germer's success was a lucky accident, because a chance rise of temperature caused their polycrystalline sample to anneal, and the ordered planes of atoms then acted as a diffraction grating. The Davisson–Germer experiment, which has since been repeated with other particles (including α particles, molecular hydrogen, and neutrons), shows clearly that particles have wave-like properties. At almost the same time, G.P. Thomson showed that a beam of electrons was diffracted when passed through a thin gold foil.

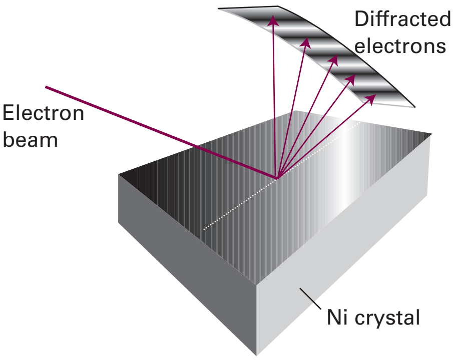


**Figure 7A.11** The Davisson–Germer experiment. The scattering of an electron beam from a nickel crystal shows a variation in intensity characteristic of a diffraction experiment in which waves interfere constructively and destructively in different directions.

Some progress towards accounting for wave–particle duality had already been made by Louis de Broglie who, in 1924, suggested that any particle, not only photons, travelling with a linear momentum $p = mv$ (with $m$ the mass and $v$ the speed of the particle) should have in some sense a wavelength given by what is now called the **de Broglie relation**:

$$\lambda = \frac{h}{p} \qquad \text{de Broglie relation} \qquad (7A.11)$$

That is, a particle with a high linear momentum has a short wavelength. Macroscopic bodies have such high momenta even when they are moving slowly (because their mass is so great), that their wavelengths are undetectably small, and the wave-like properties cannot be observed. This undetectability is why classical mechanics can be used to explain the behaviour of macroscopic bodies. It is necessary to invoke quantum mechanics only for microscopic bodies, such as atoms and molecules, in which masses are small.

### Example 7A.3 Estimating the de Broglie wavelength

Estimate the wavelength of electrons that have been accelerated from rest through a potential difference of 40 kV.

***Collect your thoughts*** To use the de Broglie relation, you need to know the linear momentum, $p$, of the electrons. To calculate the linear momentum, note that the energy acquired by an electron accelerated through a potential difference $\Delta\phi$ is $e\Delta\phi$, where $e$ is the magnitude of its charge. At the end of the period of acceleration, all the acquired energy is in the form of kinetic energy, $E_k = \frac{1}{2}m_e v^2 = p^2/2m_e$. You can therefore calculate $p$ by setting $p^2/2m_e$ equal to $e\Delta\phi$. For the manipulation of units use 1 V C = 1 J and 1 J = 1 kg m$^2$ s$^{-2}$.

***The solution*** The expression $p^2/2m_e = e\Delta\phi$ implies that $p = (2m_e e\Delta\phi)^{1/2}$ then, from the de Broglie relation $\lambda = h/p$,

$$\lambda = \frac{h}{(2m_e e\Delta\phi)^{1/2}}$$

Substitution of the data and the fundamental constants gives

$$\begin{aligned}\lambda &= \frac{6.626\times10^{-34}\,\mathrm{J\,s}}{\{2\times(9.109\times10^{-31}\,\mathrm{kg})\times(1.602\times10^{-19}\,\mathrm{C})\times(4.0\times10^{4}\,\mathrm{V})\}^{1/2}}\\ &= 6.1\times10^{-12}\,\mathrm{m}\end{aligned}$$

or 6.1 pm.

**Comment.** Electrons accelerated in this way are used in the technique of electron diffraction for imaging biological systems and for the determination of the structures of solid surfaces (Topic 19A).

***Self-test 7A.3*** Calculate the wavelength of (a) a neutron with a translational kinetic energy equal to $kT$ at 300 K, (b) a tennis ball of mass 57 g travelling at 80 km h$^{-1}$.

*Answer*: (a) 178 pm, (b) $5.2\times10^{-34}$ m

## Checklist of concepts

☐ **1.** A **black body** is an object capable of emitting and absorbing all wavelengths of radiation without favouring any wavelength.

☐ **2.** An electromagnetic field of a given frequency can take up energy only in discrete amounts.

☐ **3.** Atomic and molecular spectra show that atoms and molecules can take up energy only in discrete amounts.

☐ **4.** The **photoelectric effect** establishes the view that electromagnetic radiation, regarded in classical physics as wave-like, consists of particles (photons).

☐ **5.** The diffraction of electrons establishes the view that electrons, regarded in classical physics as particles, are wave-like with a wavelength given by the **de Broglie relation**.

☐ **6.** **Wave–particle duality** is the recognition that the concepts of particle and wave blend together.

## Checklist of equations

| Property | Equation | Comment | Equation number |
|---|---|---|---|
| Wien's law | $\lambda_{\max}T = 2.9\times10^{-3}\,\mathrm{m\,K}$ | | 7A.1 |
| Stefan–Boltzmann law | $\mathcal{E}(T) = \text{constant}\times T^4$ | | 7A.3 |
| Planck distribution | $\rho(\lambda,T) = 8\pi hc/\{\lambda^5(e^{hc/\lambda kT}-1)\}$ | Black-body radiation | 7A.6 |
| | $\rho(\nu,T) = 8\pi h\nu^3/\{c^3(e^{h\nu/kT}-1)\}$ | | |
| Einstein formula for heat capacity of a solid | $C_{V,m}(T) = 3Rf_E(T)$ | Einstein temperature: $\theta_E = h\nu/k$ | 7A.8 |
| | $f_E(T) = (\theta_E/T)^2\{e^{\theta_E/2T}/(e^{\theta_E/T}-1)\}^2$ | | |
| Bohr frequency condition | $\Delta E = h\nu$ | | 7A.9 |
| Photoelectric effect | $E_k = h\nu - \Phi$ | $\Phi$ is the work function | 7A.10 |
| de Broglie relation | $\lambda = h/p$ | $\lambda$ is the wavelength of a particle of linear momentum $p$ | 7A.11 |

# TOPIC 7B Wavefunctions

### ➤ Why do you need to know this material?

Wavefunctions provide the essential foundation for understanding the properties of electrons in atoms and molecules, and are central to explanations in chemistry.

### ➤ What is the key idea?

All the dynamical properties of a system are contained in its wavefunction, which is obtained by solving the Schrödinger equation.

### ➤ What do you need to know already?

You need to be aware of the shortcomings of classical physics that drove the development of quantum theory (Topic 7A).

In classical mechanics an object travels along a definite path or trajectory. In quantum mechanics a particle in a particular state is described by a **wavefunction**, $\psi$ (psi), which is spread out in space, rather than being localized. The wavefunction contains all the dynamical information about the object in that state, such as its position and momentum.

## 7B.1 The Schrödinger equation

In 1926 Erwin Schrödinger proposed an equation for finding the wavefunctions of any system. The **time-independent Schrödinger equation** for a particle of mass $m$ moving in one dimension with energy $E$ in a system that does not change with time (for instance, its volume remains constant) is

$$-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2}+V(x)\psi=E\psi \qquad (7B.1)$$

Time-independent Schrödinger equation

The constant $\hbar = h/2\pi$ (which is read $h$-cross or $h$-bar) is a convenient modification of Planck's constant used widely in quantum mechanics; $V(x)$ is the potential energy of the particle at $x$. Because the total energy $E$ is the sum of potential and kinetic energies, the first term on the left must be related (in a manner explored later) to the kinetic energy of the particle. The Schrödinger equation can be regarded as a fundamental postulate of quantum mechanics, but its plausibility can be demonstrated by showing that, for the case of a free particle, it is consistent with the de Broglie relation (Topic 7A).

**How is that done? 7B.1** Showing that the Schrödinger equation is consistent with the de Broglie relation

The potential energy of a freely moving particle is zero everywhere, $V(x) = 0$, so the Schrödinger equation (eqn 7B.1) becomes

$$\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2}=-\frac{2mE}{\hbar^2}\psi$$

**Step 1** *Find a solution of the Schrödinger equation for a free particle*

A solution of this equation is $\psi = \cos kx$, as you can confirm by noting that

$$\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2}=\frac{\mathrm{d}^2\cos kx}{\mathrm{d}x^2}=-k^2\cos kx=-k^2\psi$$

It follows that $-k^2 = -2mE/\hbar^2$ and hence

$$k=\left(\frac{2mE}{\hbar^2}\right)^{1/2}$$

The energy, which is only kinetic in this instance, is related to the linear momentum of the particle by $E = p^2/2m$ (*The chemist's toolkit* 6 in Topic 2A), so it follows that

$$k=\left(\frac{2m(p^2/2m)}{\hbar^2}\right)^{1/2}=\frac{p}{\hbar}$$

The linear momentum is therefore related to $k$ by $p = k\hbar$.

**Step 2** *Interpret the wavefunction in terms of a wavelength*

Now recognize that a wave (more specifically, a 'harmonic wave') can be described mathematically by a sine or cosine function. It follows that $\cos kx$ can be regarded as a wave that goes through a complete cycle as $kx$ increases by $2\pi$. The wavelength is therefore given by $k\lambda=2\pi$, so $k=2\pi/\lambda$. Therefore, the linear momentum is related to the wavelength of the wavefunction by

$$p=k\hbar=\frac{2\pi}{\lambda}\times\frac{h}{2\pi}=\frac{h}{\lambda}$$

which is the de Broglie relation. The Schrödinger equation therefore has solutions consistent with the de Broglie relation.

## 7B.2 The Born interpretation

One piece of dynamical information contained in the wavefunction is the location of the particle. Max Born used an analogy with the wave theory of radiation, in which the square of the amplitude of an electromagnetic wave in a region is interpreted as its intensity and therefore (in quantum terms) as a measure of the probability of finding a photon present in the region. The **Born interpretation** of the wavefunction is:

> If the wavefunction of a particle has the value $\psi$ at $x$, then the probability of finding the particle between $x$ and $x + \mathrm{d}x$ is proportional to $|\psi|^2\mathrm{d}x$ (Fig. 7B.1).

Born interpretation

The quantity $|\psi|^2 = \psi^*\psi$ allows for the possibility that $\psi$ is complex (see *The chemist's toolkit* 14). If the wavefunction is real (such as $\cos kx$), then $|\psi|^2 = \psi^2$.

Because $|\psi|^2\mathrm{d}x$ is a (dimensionless) probability, $|\psi|^2$ is the **probability density**, with the dimensions of 1/length (for a one-dimensional system). The wavefunction $\psi$ itself is called the **probability amplitude**. For a particle free to move in three dimensions (for example, an electron near a nucleus in an atom), the wavefunction depends on the coordinates $x$, $y$, and $z$ and is denoted $\psi(\boldsymbol{r})$. In this case the Born interpretation is (Fig. 7B.2):

> If the wavefunction of a particle has the value $\psi$ at $\boldsymbol{r}$, then the probability of finding the particle in an infinitesimal volume $\mathrm{d}\tau = \mathrm{d}x\mathrm{d}y\mathrm{d}z$ at that position is proportional to $|\psi|^2\mathrm{d}\tau$.

**The chemist's toolkit 14** Complex numbers

Complex numbers have the general form

$$z = x + \mathrm{i}y$$

where $\mathrm{i}=\sqrt{-1}$. The real number $x$ is the 'real part of $z$', denoted $\mathrm{Re}(z)$; likewise, the real number $y$ is 'the imaginary part of $z$', $\mathrm{Im}(z)$. The **complex conjugate** of $z$, denoted $z^*$, is formed by replacing i by −i:

$$z^* = x - \mathrm{i}y$$

The product of $z^*$ and $z$ is denoted $|z|^2$ and is called the **square modulus** of $z$. From the definition of $z$ and $z^*$ and $\mathrm{i}^2 = -1$ it follows that

$$|z|^2 = z^*z = (x + \mathrm{i}y)(x - \mathrm{i}y) = x^2 + y^2$$

The square modulus is a real, non-negative number. The **absolute value** or **modulus** is denoted $|z|$ and is given by:

$$|z| = (z^*z)^{1/2} = (x^2 + y^2)^{1/2}$$

For further information about complex numbers, see *The chemist's toolkit* 16 in Topic 7C.

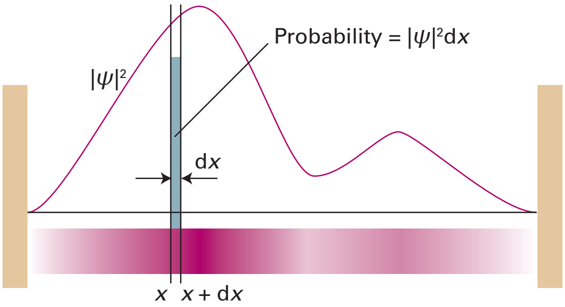


**Figure 7B.1** The wavefunction $\psi$ is a probability amplitude in the sense that its square modulus ($\psi^*\psi$ or $|\psi|^2$) is a probability density. The probability of finding a particle in the region between $x$ and $x$ + d$x$ is proportional to $|\psi|^2$d$x$. Here, the probability density is represented by the density of shading in the superimposed band.

In this case, $|\psi|^2$ has the dimensions of 1/length$^3$ and the wavefunction itself has dimensions of 1/length$^{3/2}$ (and units such as $\mathrm{m}^{-3/2}$).

The Born interpretation does away with any worry about the significance of a negative (and, in general, complex) value of $\psi$ because $|\psi|^2$ is always real and nowhere negative. There is no *direct* significance in the negative (or complex) value of a wavefunction: only the square modulus is directly physically significant, and both negative and positive regions of a wavefunction may correspond to a high probability of finding a particle in a region (Fig. 7B.3). However, the presence of positive and negative regions of a wavefunction is of great *indirect* significance, because it gives rise to the possibility of constructive and destructive interference between different wavefunctions.

A wavefunction may be zero at one or more points, and at these locations the probability density is also zero. It is important to distinguish a point at which the wavefunction is zero (for instance, far from the nucleus of a hydrogen atom) from the point at which it passes *through* zero. The latter is called a **node**. A location where the wavefunction approaches zero without actually passing through zero is not a node. Thus, the

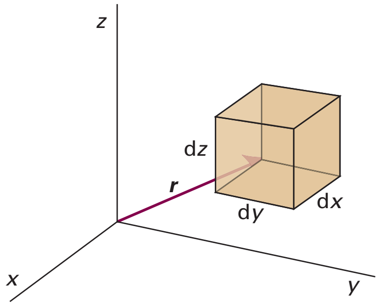


**Figure 7B.2** The Born interpretation of the wavefunction in three-dimensional space implies that the probability of finding the particle in the volume element $\mathrm{d}\tau = \mathrm{d}x\mathrm{d}y\mathrm{d}z$ at some position $\boldsymbol{r}$ is proportional to the product of d$\tau$ and the value of $|\psi|^2$ at that position.

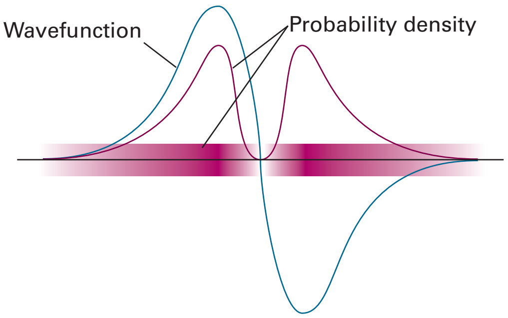


Figure 7B.3 The sign of a wavefunction has no direct physical significance: the positive and negative regions of this wavefunction both correspond to the same probability distribution (as given by the square modulus of $\psi$ and depicted by the density of the shading).

wavefunction $\cos kx$ has nodes wherever $kx$ is an odd integral multiple of $\frac{1}{2}\pi$ (where the wave passes through zero), but the wavefunction $e^{-kx}$ has no nodes, despite becoming zero as $x \to \infty$.

### Example 7B.1 Interpreting a wavefunction

The wavefunction of an electron in the lowest energy state of a hydrogen atom is proportional to $e^{-r/a_0}$, where $a_0$ is a constant and $r$ the distance from the nucleus. Calculate the relative probabilities of finding the electron inside a region of volume $\delta V = 1.0\,\text{pm}^3$, which is small even on the scale of the atom, located at (a) the nucleus, (b) a distance $a_0$ from the nucleus.

***Collect your thoughts*** The region of interest is so small on the scale of the atom that you can ignore the variation of $\psi$ within it and write the probability, $P$, as proportional to the probability density ($\psi^2$; note that $\psi$ is real) evaluated at the point of interest multiplied by the volume of interest, $\delta V$. That is, $P \propto \psi^2\delta V$, with $\psi^2 \propto e^{-2r/a_0}$.

***The solution*** In each case $\delta V = 1.0\,\text{pm}^3$. (a) At the nucleus, $r = 0$, so

$$P \propto e^0 \times (1.0\,\text{pm}^3) = 1 \times (1.0\,\text{pm}^3) = 1.0\,\text{pm}^3$$

(b) At a distance $r = a_0$ in an arbitrary direction,

$$P \propto e^{-2} \times (1.0\,\text{pm}^3) = 0.14\ldots \times (1.0\,\text{pm}^3) = 0.14\,\text{pm}^3$$

Therefore, the ratio of probabilities is 1.0/0.14 = 7.1.

**Comment.** Note that it is more probable (by a factor of 7) that the electron will be found at the nucleus than in a volume element of the same size located at a distance $a_0$ from the nucleus. The negatively charged electron is attracted to the positively charged nucleus, and is likely to be found close to it.

***Self-test 7B.1*** The wavefunction for the electron in its lowest energy state in the ion $He^+$ is proportional to $e^{-2r/a_0}$. Repeat the calculation for this ion and comment on the result.

*Answer*: 55; the wavefunction is more compact

## (a) Normalization

A mathematical feature of the Schrödinger equation is that if $\psi$ is a solution, then so is $N\psi$, where $N$ is any constant. This feature is confirmed by noting that because $\psi$ occurs in every term in eqn 7B.1, it can be replaced by $N\psi$ and the constant factor $N$ cancelled to recover the original equation. This freedom to multiply the wavefunction by a constant factor means that it is always possible to find a **normalization constant**, $N$, such that rather than the probability density being *proportional* to $|\psi|^2$ it becomes *equal* to $|\psi|^2$.

A normalization constant is found by noting that, for a normalized wavefunction $N\psi$, the probability that a particle is in the region $dx$ is equal to $(N\psi^*)(N\psi)dx$ ($N$ is taken to be real). Furthermore, the sum over all space of these individual probabilities must be 1 (the probability of the particle being somewhere is 1). Expressed mathematically, the latter requirement is

$$N^2\int_{-\infty}^{\infty}\psi^*\psi\,dx = 1 \qquad (7B.2)$$

and therefore

$$N = \frac{1}{\left(\int_{-\infty}^{\infty}\psi^*\psi\,dx\right)^{1/2}} \qquad (7B.3)$$

Provided this integral has a finite value (that is, the wavefunction is 'square integrable'), the normalization factor can be found and the wavefunction 'normalized' (and specifically 'normalized to 1'). From now on, unless stated otherwise, all wavefunctions are assumed to have been normalized to 1, in which case in one dimension

$$\int_{-\infty}^{\infty}\psi^*\psi\,dx = 1 \qquad (7B.4a)$$

and in three dimensions

$$\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\psi^*\psi\,dx\,dy\,dz = 1 \qquad (7B.4b)$$

In quantum mechanics it is common to write all such integrals in a short-hand form as

$$\int\psi^*\psi\,d\tau = 1 \qquad (7B.4c)$$

where $d\tau$ is the appropriate volume element and the integration is understood as being over all space.

### Example 7B.2 Normalizing a wavefunction

Carbon nanotubes are thin hollow cylinders of carbon with diameters between 1 nm and 2 nm, and lengths of several micrometres. According to one simple model, the lowest-energy electrons of the nanotube are described by the wavefunction $\sin(\pi x/L)$, where $L$ is the length of the nanotube. Find the normalized wavefunction.

***Collect your thoughts*** Because the wavefunction is one-dimensional, you need to find the factor $N$ that guarantees that the integral in eqn 7B.4a is equal to 1. The wavefunction is real, so $\psi^* = \psi$. Relevant integrals are found in the *Resource section*.

***The solution*** Write the wavefunction as $\psi = N\sin(\pi x/L)$, where $N$ is the normalization factor. The limits of integration are $x = 0$ to $x = L$ because the wavefunction spans the length of the tube. It follows that

$$\int\psi^*\psi\,\mathrm{d}\tau = N^2\overbrace{\int_0^L \sin^2\frac{\pi x}{L}\,\mathrm{d}x}^{\text{Integral T.2}} = \tfrac{1}{2}N^2L$$

For the wavefunction to be normalized, this integral must be equal to 1; that is, $\tfrac{1}{2}N^2L = 1$, and hence

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

The normalized wavefunction is therefore

$$\psi = \left(\frac{2}{L}\right)^{1/2}\sin\frac{\pi x}{L}$$

**Comment.** Because $L$ is a length, the dimensions of $\psi$ are $1/\text{length}^{1/2}$, and therefore those of $\psi^2$ are 1/length, as is appropriate for a probability density in one dimension.

***Self-test 7B.2*** The wavefunction for the next higher energy level for the electrons in the same tube is $\sin(2\pi x/L)$. Normalize this wavefunction.

*Answer:* $N = (2/L)^{1/2}$

To calculate the probability of finding the system in a finite region of space the probability density is summed (integrated) over the region of interest. Thus, for a one-dimensional system, the probability $P$ of finding the particle between $x_1$ and $x_2$ is given by

$$P = \int_{x_1}^{x_2}|\psi(x)|^2\,\mathrm{d}x \qquad (7B.5)$$

Probability [one-dimensional region]

### Example 7B.3 Determining a probability

As seen in *Example* 7B.2, the lowest-energy electrons of a carbon nanotube of length $L$ can be described by the normalized wavefunction $(2/L)^{1/2}\sin(\pi x/L)$. What is the probability of finding the electron between $x = L/4$ and $x = L/2$?

***Collect your thoughts*** Use eqn 7B.5 and the normalized wavefunction to write an expression for the probability of finding the electron in the region of interest. Relevant integrals are given in the *Resource section*.

***The solution*** From eqn 7B.5 the probability is

$$P = \frac{2}{L}\overbrace{\int_{L/4}^{L/2}\sin^2(\pi x/L)\,\mathrm{d}x}^{\text{Integral T.2}}$$

It follows that

$$P = \frac{2}{L}\left(\frac{x}{2} - \frac{\sin(2\pi x/L)}{4\pi/L}\right)\Bigg|_{L/4}^{L/2} = \frac{2}{L}\left(\frac{L}{4} - \frac{L}{8} - 0 + \frac{L}{4\pi}\right) = 0.409$$

**Comment.** There is a chance of about 41 per cent that the electron will be found in the region.

***Self-test 7B.3*** As remarked in *Self-test* 7B.2, the normalized wavefunction of the next higher energy level of the electron in this model of the nanotube is $(2/L)^{1/2}\sin(2\pi x/L)$. What is the probability of finding the electron between $x = L/4$ and $x = L/2$?

*Answer:* 0.25

## (b) Constraints on the wavefunction

The Born interpretation puts severe restrictions on the acceptability of wavefunctions. The first constraint is that $\psi$ must not be infinite over a finite region, because if it were, the Born interpretation would fail. This requirement rules out many possible solutions of the Schrödinger equation, because many mathematically acceptable solutions rise to infinity and are therefore physically unacceptable. The Born interpretation also rules out solutions of the Schrödinger equation that give rise to more than one value of $|\psi|^2$ at a single point because it would be absurd to have more than one value of the probability density for the particle at a point. This restriction is expressed by saying that the wavefunction must be *single-valued*; that is, it must have only one value at each point of space.

The Schrödinger equation itself also implies some mathematical restrictions on the type of functions that can occur. Because it is a second-order differential equation (in the sense that it depends on the second derivative of the wavefunction), $\mathrm{d}^2\psi/\mathrm{d}x^2$ must be well-defined if the equation is to be applicable everywhere. The second derivative is defined only if the first derivative is continuous: this means that (except as specified below) there can be no kinks in the function. In turn, the first derivative is defined only if the function is continuous: no sharp steps are permitted.

Overall, therefore, the constraints on the wavefunction, which are summarized in Fig. 7B.4, are that it

- must not be infinite over a finite region;
- must be single-valued;
- must be continuous;
- must have a continuous first derivative (slope).

Constraints on the wavefunction

The last of these constraints does not apply if the potential energy has abrupt, infinitely high steps (as in the particle-in-a-box model treated in Topic 7D).

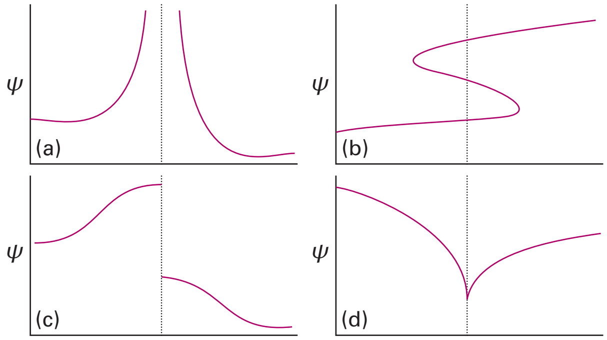


**Figure 7B.4** The wavefunction must satisfy stringent conditions for it to be acceptable: (a) unacceptable because it is infinite over a finite region; (b) unacceptable because it is not single-valued; (c) unacceptable because it is not continuous; (d) unacceptable because its slope is discontinuous.

### (c) Quantization

The constraints just noted are so severe that acceptable solutions of the Schrödinger equation do not in general exist for arbitrary values of the energy $E$. In other words, a particle may possess only certain energies, for otherwise its wavefunction would be physically unacceptable. That is,

> As a consequence of the restrictions on its wavefunction, the energy of a particle is quantized.

These acceptable energies are found by solving the Schrödinger equation for motion of various kinds, and selecting the solutions that conform to the restrictions listed above.

## Checklist of concepts

☐ 1. A **wavefunction** is a mathematical function that contains all the dynamical information about a system.

☐ 2. The **Schrödinger equation** is a second-order differential equation used to calculate the wavefunction of a system.

☐ 3. According to the **Born interpretation**, the probability density at a point is proportional to the square of the wavefunction at that point.

☐ 4. A **node** is a point where a wavefunction passes through zero.

☐ 5. A wavefunction is **normalized** if the integral over all space of its square modulus is equal to 1.

☐ 6. A wavefunction must be single-valued, continuous, not infinite over a finite region of space, and (except in special cases) have a continuous slope.

☐ 7. The quantization of energy stems from the constraints that an acceptable wavefunction must satisfy.

## Checklist of equations

| Property | Equation | Comment | Equation number |
|---|---|---|---|
| The time-independent Schrödinger equation | $-(\hbar^2/2m)(\mathrm{d}^2\psi/\mathrm{d}x^2) + V(x)\psi = E\psi$ | One-dimensional system* | 7B.1 |
| Normalization | $\int \psi^*\psi \, \mathrm{d}\tau = 1$ | Integration over all space | 7B.4c |
| Probability of a particle being between $x_1$ and $x_2$ | $P = \int_{x_1}^{x_2} \lvert\psi(x)\rvert^2 \mathrm{d}x$ | One-dimensional region | 7B.5 |

* Higher dimensions are treated in Topics 7D, 7F, and 8A.

# TOPIC 7C Operators and observables

### ➤ Why do you need to know this material?

To interpret the wavefunction fully it is necessary to be able to extract dynamical information from it. The predictions of quantum mechanics are often very different from those of classical mechanics, and those differences are essential for understanding the structures and properties of atoms and molecules.

### ➤ What is the key idea?

The dynamical information in the wavefunction is extracted by calculating the expectation values of hermitian operators.

### ➤ What do you need to know already?

You need to know that the state of a system is fully described by a wavefunction (Topic 7B), and that the probability density is proportional to the square modulus of the wavefunction.

A wavefunction contains all the information it is possible to obtain about the dynamical properties of a particle (for example, its location and momentum). The Born interpretation (Topic 7B) provides information about location, but the wavefunction contains other information, which is extracted by using the methods described in this Topic.

## 7C.1 Operators

The Schrödinger equation can be written in the succinct form

$$\hat{H}\psi = E\psi \qquad (7C.1a)$$

Operator form of Schrödinger equation

Comparison of this expression with the one-dimensional Schrödinger equation

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

shows that in one dimension

$$\hat{H}=-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2}{\mathrm{d}x^2}+V(x) \qquad (7C.1b)$$

Hamiltonian operator

The quantity $\hat{H}$ (commonly read h-hat) is an **operator**, an expression that carries out a mathematical operation on a function. In this case, the operation is to take the second derivative of $\psi$, and (after multiplication by $-\hbar^2/2m$) to add the result to the outcome of multiplying $\psi$ by $V(x)$.

The operator $\hat{H}$ plays a special role in quantum mechanics, and is called the **hamiltonian operator** after the nineteenth century mathematician William Hamilton, who developed a form of classical mechanics which, it subsequently turned out, is well suited to the formulation of quantum mechanics. The hamiltonian operator (and commonly simply 'the hamiltonian') is the operator corresponding to the total energy of the system, the sum of the kinetic and potential energies. In eqn 7C.1b the second term on the right is the potential energy, so the first term (the one involving the second derivative) must be the operator for kinetic energy.

In general, an operator acts on a function to produce a new function, as in

(operator)(function) = (new function)

In some cases the new function is the same as the original function, perhaps multiplied by a constant. Combinations of operators and functions that have this property are of great importance in quantum mechanics.

**Brief illustration 7C.1**

For example, when the operator $\mathrm{d}/\mathrm{d}x$, which means 'take the derivative of the following function with respect to $x$', acts on the function $\sin ax$, it generates the new function $a\cos ax$. However, when $\mathrm{d}/\mathrm{d}x$ operates on $\mathrm{e}^{-ax}$ it generates $-a\mathrm{e}^{-ax}$, which is the original function multiplied by the constant $-a$.

### (a) Eigenvalue equations

The Schrödinger equation written as in eqn 7C.1a is an **eigenvalue equation**, an equation of the form

(operator)(function) = (constant factor) × (same function) (7C.2a)

In an eigenvalue equation, the action of the operator on the function generates the *same* function, multiplied by a constant. If a general operator is denoted $\hat{\Omega}$ (where $\Omega$ is uppercase omega) and the constant factor by $\omega$ (lowercase omega), then an eigenvalue equation has the form

$$\hat{\Omega}\psi=\omega\psi \qquad (7C.2b)$$

Eigenvalue equation

If this relation holds, the function $\psi$ is said to be an **eigenfunction** of the operator $\hat{\Omega}$, and $\omega$ is the **eigenvalue** associated with that eigenfunction. With this terminology, eqn 7C.2a can be written

$$\text{(operator)(eigenfunction)} = \text{(eigenvalue)} \times \text{(eigenfunction)} \tag{7C.2c}$$

Equation 7C.1a is therefore an eigenvalue equation in which $\psi$ is an eigenfunction of the hamiltonian and $E$ is the associated eigenvalue. It follows that 'solving the Schrödinger equation' can be expressed as 'finding the eigenfunctions and eigenvalues of the hamiltonian operator for the system'.

Just as the hamiltonian is the operator corresponding to the total energy, there are operators that represent other **observables**, the measurable properties of the system, such as linear momentum or electric dipole moment. For each such operator $\hat{\Omega}$ there is an eigenvalue equation of the form $\hat{\Omega}\psi = \omega\psi$, with the following significance:

> If the wavefunction is an eigenfunction of the operator $\hat{\Omega}$ corresponding to the observable $\Omega$, then the outcome of a measurement of the property $\Omega$ will be the eigenvalue corresponding to that eigenfunction.

Quantum mechanics is formulated by constructing the operator corresponding to the observable of interest and then predicting the outcome of a measurement by examining the eigenvalues of the operator.

## (b) The construction of operators

A basic postulate of quantum mechanics specifies how to set up the operator corresponding to a given observable.

Observables are represented by operators built from the following position and linear momentum operators:

$$\hat{x} = x\times \qquad \hat{p}_x = \frac{\hbar}{\mathrm{i}}\frac{\mathrm{d}}{\mathrm{d}x} \qquad \text{Specification of operators} \tag{7C.3}$$

That is, the operator for location along the $x$-axis is multiplication (of the wavefunction) by $x$, and the operator for linear momentum parallel to the $x$-axis is $\hbar/\mathrm{i}$ times the derivative (of the wavefunction) with respect to $x$.

The definitions in eqn 7C.3 are used to construct operators for other spatial observables. For example, suppose the potential energy has the form $V(x) = \frac{1}{2}k_\mathrm{f}x^2$, where $k_\mathrm{f}$ is a constant (this potential energy describes the vibrations of atoms in molecules). Because the operator for $x$ is multiplication by $x$, by extension the operator for $x^2$ is multiplication by $x$ and then by $x$ again, or multiplication by $x^2$. The operator corresponding to $\frac{1}{2}k_\mathrm{f}x^2$ is therefore

$$\hat{V}(x) = \tfrac{1}{2}k_\mathrm{f}x^2\times \tag{7C.4}$$

In practice, the multiplication sign is omitted and multiplication is understood. To construct the operator for kinetic energy, the classical relation between kinetic energy and linear momentum, $E_\mathrm{k} = p_x^2/2m$ is used. Then, by using the operator for $p_x$ from eqn 7C.3:

$$\hat{E}_\mathrm{k} = \frac{1}{2m}\overbrace{\left(\frac{\hbar}{\mathrm{i}}\frac{\mathrm{d}}{\mathrm{d}x}\right)}^{\hat{p}_x}\overbrace{\left(\frac{\hbar}{\mathrm{i}}\frac{\mathrm{d}}{\mathrm{d}x}\right)}^{\hat{p}_x} = -\frac{\hbar^2}{2m}\frac{\mathrm{d}^2}{\mathrm{d}x^2} \tag{7C.5}$$

It follows that the operator for the total energy, the hamiltonian operator, is

$$\hat{H} = \hat{E}_\mathrm{k} + \hat{V} = -\frac{\hbar^2}{2m}\frac{\mathrm{d}^2}{\mathrm{d}x^2} + \hat{V}(x) \qquad \text{Hamiltonian operator} \tag{7C.6}$$

where $\hat{V}(x)$ is the operator corresponding to whatever form the potential energy takes, exactly as in eqn 7C.1b.

**Example 7C.1** Determining the value of an observable

What is the linear momentum of a free particle described by the wavefunctions (a) $\psi(x) = \mathrm{e}^{\mathrm{i}kx}$ and (b) $\psi(x) = \mathrm{e}^{-\mathrm{i}kx}$?

***Collect your thoughts*** You need to operate on $\psi$ with the operator corresponding to linear momentum (eqn 7C.3), and inspect the result. If the outcome is the original wavefunction multiplied by a constant (that is, if the application of the operator results in an eigenvalue equation), then you can identify the constant with the value of the observable.

***The solution*** (a) For $\psi(x) = \mathrm{e}^{\mathrm{i}kx}$,

$$\hat{p}_x\psi = \frac{\hbar}{\mathrm{i}}\frac{\mathrm{d}\psi}{\mathrm{d}x} = \frac{\hbar}{\mathrm{i}}\frac{\mathrm{d}\mathrm{e}^{\mathrm{i}kx}}{\mathrm{d}x} = \frac{\hbar}{\mathrm{i}}\times\mathrm{i}k\mathrm{e}^{\mathrm{i}kx} = \overbrace{+k\hbar}^{\text{Eigenvalue}}\psi$$

This is an eigenvalue equation, with eigenvalue $+k\hbar$. It follows that a measurement of the momentum will give the value $p_x = +k\hbar$.

(b) For $\psi(x) = \mathrm{e}^{-\mathrm{i}kx}$,

$$\hat{p}_x\psi = \frac{\hbar}{\mathrm{i}}\frac{\mathrm{d}\psi}{\mathrm{d}x} = \frac{\hbar}{\mathrm{i}}\frac{\mathrm{d}\mathrm{e}^{-\mathrm{i}kx}}{\mathrm{d}x} = \frac{\hbar}{\mathrm{i}}\times(-\mathrm{i}k)\mathrm{e}^{-\mathrm{i}kx} = \overbrace{-k\hbar}^{\text{Eigenvalue}}\psi$$

Now the eigenvalue is $-k\hbar$, so $p_x = -k\hbar$. In case (a) the momentum is positive, meaning that the particle is travelling in the positive $x$-direction, whereas in (b) the particle is moving in the opposite direction.

**Comment.** A general feature of quantum mechanics is that taking the complex conjugate of a wavefunction reverses the direction of travel. An implication is that if the wavefunction is real (such as $\cos kx$), then taking the complex conjugate leaves the wavefunction unchanged: there is no net direction of travel.

***Self-test 7C.1*** What is the kinetic energy of a particle described by the wavefunction $\cos kx$?

*Answer:* $E_\mathrm{k} = \hbar^2k^2/2m$

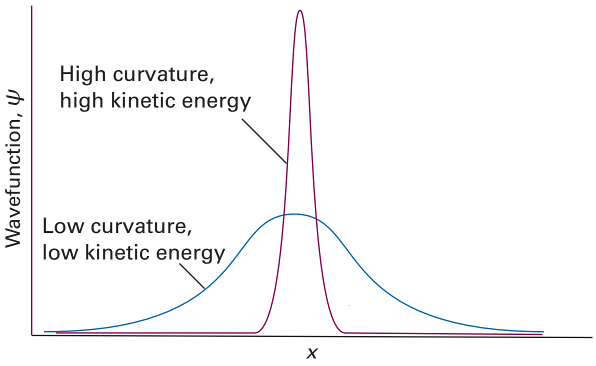


**Figure 7C.1** The average kinetic energy of a particle can be inferred from the average curvature of the wavefunction. This figure shows two wavefunctions: the sharply curved function corresponds to a higher kinetic energy than the less sharply curved function.

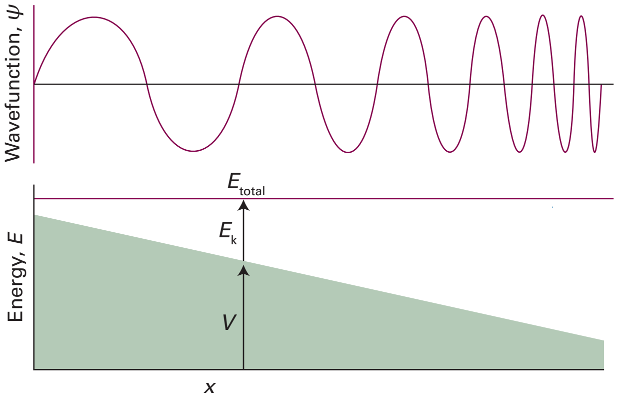


**Figure 7C.3** The wavefunction of a particle with a potential energy $V$ that decreases towards the right. As the total energy is constant, the kinetic energy $E_k$ increases to the right, which results in a faster oscillation and hence greater curvature of the wavefunction.

The expression for the kinetic energy operator (eqn 7C.5) reveals an important point about the Schrödinger equation. In mathematics, the second derivative of a function is a measure of its curvature: a large second derivative indicates a sharply curved function (Fig. 7C.1). It follows that a sharply curved wavefunction is associated with a high kinetic energy, and one with a low curvature is associated with a low kinetic energy.

The curvature of a wavefunction in general varies from place to place (Fig. 7C.2): wherever a wavefunction is sharply curved, its contribution to the total kinetic energy is large; wherever the wavefunction is not sharply curved, its contribution to the overall kinetic energy is low. The observed kinetic energy of the particle is an average of all the contributions of the kinetic energy from each region. Hence, a particle can be expected to have a high kinetic energy if the average curvature of its wavefunction is high. Locally there can be both positive and negative contributions to the kinetic energy (because the curvature can be either positive, ∪, or negative, ∩) locally, but the average is always positive.

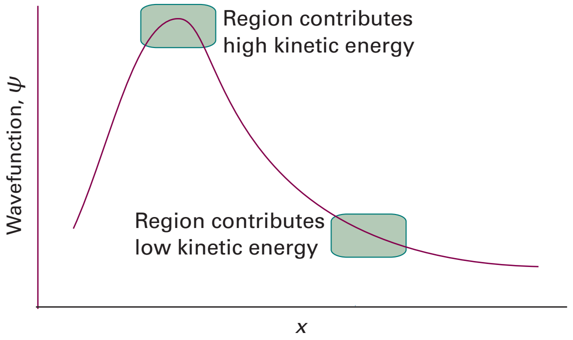


**Figure 7C.2** The observed kinetic energy of a particle is an average of contributions from the entire space covered by the wavefunction. Sharply curved regions contribute a high kinetic energy to the average; less sharply curved regions contribute only a small kinetic energy.

The association of high curvature with high kinetic energy is a valuable guide to the interpretation of wavefunctions and the prediction of their shapes. For example, suppose the wavefunction of a particle with a given total energy and a potential energy that decreases with increasing $x$ is required. Because the difference $E - V = E_k$ increases from left to right, the wavefunction must become more sharply curved by oscillating more rapidly as $x$ increases (Fig. 7C.3). It is therefore likely that the wavefunction will look like the function sketched in the illustration, and more detailed calculation confirms this to be so.

## (c) Hermitian operators

All the quantum mechanical operators that correspond to observables have a very special mathematical property: they are 'hermitian'. A **hermitian operator** is one for which the following relation is true:

$$\int \psi_i^* \hat{\Omega} \psi_j \, d\tau = \left\{ \int \psi_j^* \hat{\Omega} \psi_i \, d\tau \right\}^* \qquad \text{Hermiticity [definition]} \qquad (7C.7)$$

As stated in Topic 7B, in quantum mechanics $\int \ldots d\tau$ implies integration over the full range of all relevant spatial variables.

It is easy to confirm that the position operator ($x \times$) is hermitian because in this case the order of the factors in the integrand can be changed:

$$\int \psi_i^* x \psi_j \, d\tau = \int \psi_j x \psi_i^* d\tau = \left\{ \int \psi_j^* x \psi_i \, d\tau \right\}^*$$

The final step uses $(\psi^*)^* = \psi$. The demonstration that the linear momentum operator is hermitian is more involved because the order of functions being differentiated cannot be changed.

### How is that done? 7C.1 Showing that the linear momentum operator is hermitian

The task is to show that

$$\int \psi_i^* \hat{p}_x \psi_j \mathrm{d}\tau = \left\{ \int \psi_j^* \hat{p}_x \psi_i \mathrm{d}\tau \right\}^*$$

with $\hat{p}_x$ given in eqn 7C.3. To do so, use 'integration by parts' (see *The chemist's toolkit* 15) which, when applied to the present case, gives

$$\int \psi_i^* \hat{p}_x \psi_j \mathrm{d}\tau = \frac{\hbar}{\mathrm{i}} \int_{-\infty}^{\infty} \overbrace{\psi_i^*}^{f} \overbrace{\frac{\mathrm{d}\psi_j}{\mathrm{d}x}}^{\mathrm{d}g/\mathrm{d}x} \mathrm{d}x$$

$$= \overbrace{\frac{\hbar}{\mathrm{i}} \overbrace{\psi_i^* \psi_j}^{fg} \Big|_{-\infty}^{\infty}}^{0} - \frac{\hbar}{\mathrm{i}} \int_{-\infty}^{\infty} \overbrace{\psi_j}^{g} \overbrace{\frac{\mathrm{d}\psi_i^*}{\mathrm{d}x}}^{\mathrm{d}f/\mathrm{d}x} \mathrm{d}x$$

The blue term is zero because all wavefunctions are either zero at $x = \pm\infty$ (see Topic 7B) or the product $\psi_i^* \psi_j$ converges to the same value at $x = +\infty$ and $x = -\infty$. As a result

$$\int \psi_i^* \hat{p}_x \psi_j \mathrm{d}\tau = -\frac{\hbar}{\mathrm{i}} \int_{-\infty}^{\infty} \psi_j \frac{\mathrm{d}\psi_i^*}{\mathrm{d}x} \mathrm{d}x = \left\{ \frac{\hbar}{\mathrm{i}} \int_{-\infty}^{\infty} \psi_j^* \frac{\mathrm{d}\psi_i}{\mathrm{d}x} \mathrm{d}x \right\}^*$$

$$= \left\{ \int \psi_j^* \hat{p}_x \psi_i \mathrm{d}\tau \right\}^*$$

as was to be proved. The final line uses $(\psi^*)^* = \psi$ and $\mathrm{i}^* = -\mathrm{i}$.

Hermitian operators are enormously important in quantum mechanics because their eigenvalues are *real*: that is, $\omega^* = \omega$. Any measurement must yield a real value because a position, momentum, or an energy cannot be complex or imaginary. Because the outcome of a measurement of an observable is one of the eigenvalues of the corresponding operator, those eigenvalues must be real. It therefore follows that an operator that represents an observable must be hermitian. The proof that their eigenfunctions are real makes use of the definition of hermiticity in eqn 7C.7.

### How is that done? 7C.2 Showing that the eigenvalues of hermitian operators are real

Begin by setting $\psi_i$ and $\psi_j$ to be the same, writing them both as $\psi$. Then eqn 7C.7 becomes

$$\int \psi^* \hat{\Omega} \psi \mathrm{d}\tau = \left\{ \int \psi^* \hat{\Omega} \psi \mathrm{d}\tau \right\}^*$$

Next suppose that $\psi$ is an eigenfunction of $\hat{\Omega}$ with eigenvalue $\omega$. That is, $\hat{\Omega}\psi = \omega\psi$. Now use this relation in both integrals on the left- and right-hand sides:

$$\int \psi^* \omega \psi \mathrm{d}\tau = \left\{ \int \psi^* \omega \psi \mathrm{d}\tau \right\}^*$$

The eigenvalue is a constant that can be taken outside the integrals:

$$\omega \int \psi^* \psi \mathrm{d}\tau = \left\{ \omega \int \psi^* \psi \mathrm{d}\tau \right\}^* = \omega^* \int \psi \psi^* \mathrm{d}\tau$$

Finally, the (blue) integrals cancel, leaving $\omega = \omega^*$. It follows that $\omega$ is real.

## (d) Orthogonality

To say that two different functions $\psi_i$ and $\psi_j$ are **orthogonal** means that the integral (over all space) of $\psi_i^* \psi_j$ is zero:

$$\int \psi_i^* \psi_j \mathrm{d}\tau = 0 \quad \text{for } i \neq j \qquad (7\text{C}.8)$$

Orthogonality [definition]

Functions that are both normalized and mutually orthogonal are called **orthonormal**. Hermitian operators have the important property that

> Eigenfunctions that correspond to different eigenvalues of a hermitian operator are orthogonal.

The proof of this property also follows from the definition of hermiticity (eqn 7C.7).

### The chemist's toolkit 15 Integration by parts

Many integrals in quantum mechanics have the form $\int f(x)h(x)\mathrm{d}x$ where $f(x)$ and $h(x)$ are two different functions. Such integrals can often be evaluated by regarding $h(x)$ as the derivative of another function, $g(x)$, such that $h(x) = \mathrm{d}g(x)/\mathrm{d}x$. For instance, if $h(x) = x$, then $g(x) = \frac{1}{2}x^2$. The integral is then found using **integration by parts**:

$$\int f \frac{\mathrm{d}g}{\mathrm{d}x} \mathrm{d}x = fg - \int g \frac{\mathrm{d}f}{\mathrm{d}x} \mathrm{d}x$$

The procedure is successful only if the integral on the right turns out to be one that can be evaluated more easily than the one on the left. The procedure is often summarized by expressing this relation as

$$\int f \mathrm{d}g = fg - \int g \mathrm{d}f$$

As an example, consider integration of $x\mathrm{e}^{-ax}$. In this case, $f(x) = x$, so $\mathrm{d}f(x)/\mathrm{d}x = 1$ and $\mathrm{d}g(x)/\mathrm{d}x = \mathrm{e}^{-ax}$, so $g(x) = -(1/a)\mathrm{e}^{-ax}$. Then

$$\int \overbrace{x}^{f} \overbrace{\mathrm{e}^{-ax}}^{\mathrm{d}g/\mathrm{d}x} \mathrm{d}x = \overbrace{x}^{f} \overbrace{\frac{-\mathrm{e}^{-ax}}{a}}^{g} - \int \overbrace{\frac{-\mathrm{e}^{-ax}}{a}}^{g} \overbrace{1}^{\mathrm{d}f/\mathrm{d}x} \mathrm{d}x$$

$$= -\frac{x\mathrm{e}^{-ax}}{a} + \frac{1}{a} \int \mathrm{e}^{-ax} \mathrm{d}x = -\frac{x\mathrm{e}^{-ax}}{a} - \frac{\mathrm{e}^{-ax}}{a^2} + \text{constant}$$

### How is that done? 7C.3 Showing that the eigenfunctions of hermitian operators are orthogonal

Start by supposing that $\psi_j$ is an eigenfunction of $\hat{\Omega}$ with eigenvalue $\omega_j$ (i.e. $\hat{\Omega}\psi_j = \omega_j\psi_j$) and that $\psi_i$ is an eigenfunction with a different eigenvalue $\omega_i$ (i.e. $\hat{\Omega}\psi_i = \omega_i\psi_i$, with $\omega_i \neq \omega_j$). Then eqn 7C.7 becomes

$$\int \psi_i^{\star}\omega_j\psi_j\,\mathrm{d}\tau = \left\{\int \psi_j^{\star}\,\omega_i\psi_i\,\mathrm{d}\tau\right\}^{\star}$$

The eigenvalues are constants and can be taken outside the integrals; moreover, they are real (being the eigenvalues of hermitian operators), so $\omega_i^{\star} = \omega_i$. Then

$$\omega_j\int \psi_i^{\star}\,\psi_j\,\mathrm{d}\tau = \omega_i\left\{\int \psi_j^{\star}\,\psi_i\,\mathrm{d}\tau\right\}^{\star}$$

Next, note that $\left\{\int \psi_j^{\star}\,\psi_i\,\mathrm{d}\tau\right\}^{\star} = \int \psi_j\psi_i^{\star}\,\mathrm{d}\tau$, so

$$\omega_j\int \psi_i^{\star}\psi_j\,\mathrm{d}\tau = \omega_i\int \psi_j\psi_i^{\star}\,\mathrm{d}\tau, \quad \text{hence} \quad (\omega_j-\omega_i)\int \psi_i^{\star}\,\psi_j\,\mathrm{d}\tau = 0$$

The two eigenvalues are different, so $\omega_j - \omega_i \neq 0$; therefore it must be the case that $\int \psi_i^{\star}\,\psi_j\,\mathrm{d}\tau = 0$. That is, the two eigenfunctions are orthogonal, as was to be proved.

The hamiltonian operator is hermitian (it corresponds to an observable, the energy, but its hermiticity can be proved specifically). Therefore, if two of its eigenfunctions correspond to different energies, the two functions must be orthogonal. The property of orthogonality is of great importance in quantum mechanics because it eliminates a large number of integrals from calculations. Orthogonality plays a central role in the theory of chemical bonding (Focus 9) and spectroscopy (Focus 11).

### Example 7C.2 Verifying orthogonality

Two possible wavefunctions for a particle constrained to move along the $x$ axis between $x = 0$ and $x = L$ are $\psi_1 = \sin(\pi x/L)$ and $\psi_2 = \sin(2\pi x/L)$. Outside this region the wavefunctions are zero. The wavefunctions correspond to different energies. Verify that the two wavefunctions are mutually orthogonal.

***Collect your thoughts*** To verify the orthogonality of two functions, you need to integrate $\psi_2^{\star}\,\psi_1 = \sin(2\pi x/L)\sin(\pi x/L)$ over all space, and show that the result is zero. In principle the integral is taken from $x = -\infty$ to $x = +\infty$, but the wavefunctions are zero outside the range $x = 0$ to $L$ so you need integrate only over this range. Relevant integrals are given in the *Resource section.*

***The solution*** To evaluate the integral, use Integral T.5 from the *Resource section* with $a = 2\pi/L$ and $b = \pi/L$:

$$\int_0^L \sin\,(2\pi x/L)\,\sin\,(\pi x/L)\,\mathrm{d}x = \left.\frac{\sin\,(\pi x/L)}{2(\pi/L)}\right|_0^L - \left.\frac{\sin\,(3\pi x/L)}{2(3\pi/L)}\right|_0^L = 0$$

The sine functions have been evaluated by using $\sin n\pi = 0$ for $n = 0, \pm1, \pm2, \ldots$. The two functions are therefore mutually orthogonal.

***Self-test 7C.2*** The next higher energy level has $\psi_3 = \sin(3\pi x/L)$. Confirm that the functions $\psi_1 = \sin(\pi x/L)$ and $\psi_3 = \sin(3\pi x/L)$ are mutually orthogonal.

*Answer:* $\int_0^L \sin(3\pi x/L)\sin(\pi x/L)\mathrm{d}x = 0$

## 7C.2 Superpositions and expectation values

The hamiltonian for a free particle moving in one dimension is

$$\hat{H} = -\frac{\hbar^2}{2m}\frac{\mathrm{d}^2}{\mathrm{d}x^2}$$

The particle is 'free' in the sense that there is no potential to constrain it, hence $V(x) = 0$. It is easily confirmed that $\psi(x) = \cos kx$ is an eigenfunction of this operator

$$\hat{H}\psi(x) = -\frac{\hbar^2}{2m}\frac{\mathrm{d}^2}{\mathrm{d}x^2}\cos kx = \frac{k^2\hbar^2}{2m}\cos kx$$

The energy associated with this wavefunction, $k^2\hbar^2/2m$, is therefore well defined, as it is the eigenvalue of an eigenvalue equation. However, the same is not necessarily true of other observables. For instance, $\cos kx$ is not an eigenfunction of the linear momentum operator:

$$\hat{p}_x\psi(x) = \frac{\hbar}{\mathrm{i}}\frac{\mathrm{d}\psi}{\mathrm{d}x} = \frac{\hbar}{\mathrm{i}}\frac{\mathrm{d}\cos kx}{\mathrm{d}x} = -\frac{k\hbar}{\mathrm{i}}\sin kx \qquad \text{(7C.9)}$$

This expression is not an eigenvalue equation, because the function on the right ($\sin kx$) is different from that on the left ($\cos kx$).

When the wavefunction of a particle is not an eigenfunction of an operator, the corresponding observable does not have a definite value. However, in the current example the momentum is not completely indefinite because the cosine wavefunction can be written as a **linear combination**, or sum,[1] of $\mathrm{e}^{\mathrm{i}kx}$ and $\mathrm{e}^{-\mathrm{i}kx}$: $\cos kx = \frac{1}{2}(\mathrm{e}^{\mathrm{i}kx} + \mathrm{e}^{-\mathrm{i}kx})$ (see *The chemist's toolkit* 16). As shown in *Example* 7C.1, these two exponential functions are eigenfunctions of $\hat{p}_x$ with eigenvalues $+k\hbar$ and $-k\hbar$, respectively. They therefore each correspond to a state of definite but different momentum. The wavefunction $\cos kx$ is said to be a **superposition** of the two individual wavefunctions $\mathrm{e}^{\mathrm{i}kx}$ and $\mathrm{e}^{-\mathrm{i}kx}$, and is written

$$\psi = \underbrace{\mathrm{e}^{+\mathrm{i}kx}}_{\substack{\text{Particle with linear}\\ \text{momentum } +k\hbar}} + \underbrace{\mathrm{e}^{-\mathrm{i}kx}}_{\substack{\text{Particle with linear}\\ \text{momentum } -k\hbar}}$$

The interpretation of this superposition is that if many repeated measurements of the momentum are made, then half the measurements would give the value $p_x = +k\hbar$, and half would give the value $p_x = -k\hbar$. The two values $\pm k\hbar$ occur equally often since $\mathrm{e}^{\mathrm{i}kx}$ and $\mathrm{e}^{-\mathrm{i}kx}$ contribute equally to the superposition. All that can be inferred from the wavefunction $\cos kx$ about the linear momentum is that the particle it describes is equally

---

[1] A linear combination is more general than a sum, for it includes weighted sums of the form $ax + by + \cdots$ where $a, b, \ldots$ are constants. A sum is a linear combination with $a = b = \cdots = 1$.

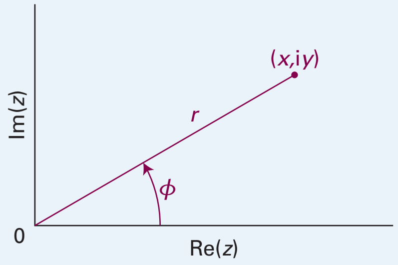
## The chemist's toolkit 16 Euler's formula

A complex number $z = x + iy$ can be represented as a point in a plane, the **complex plane**, with $\mathrm{Re}(z)$ along the $x$-axis and $\mathrm{Im}(z)$ along the $y$-axis (Sketch 1). The position of the point can also be specified in terms of a distance $r$ and an angle $\phi$ (the polar coordinates). Then $x = r\cos\phi$ and $y = r\sin\phi$, so it follows that

$$z = r(\cos\phi + \mathrm{i}\sin\phi)$$

The angle $\phi$, called the **argument** of $z$, is the angle that $r$ makes with the $x$-axis. Because $y/x = \tan\phi$, it follows that

$$r=(x^2+y^2)^{1/2}=|z| \qquad \phi=\arctan\frac{y}{x}$$



Sketch 1

One of the most useful relations involving complex numbers is **Euler's formula**:

$$\mathrm{e}^{\mathrm{i}\phi} = \cos\phi + \mathrm{i}\sin\phi$$

from which it follows that $z = r(\cos\phi + \mathrm{i}\sin\phi)$ can be written

$$z = r\mathrm{e}^{\mathrm{i}\phi}$$

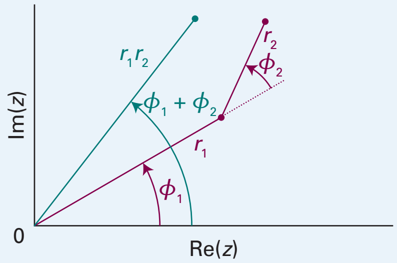
Two more useful relations arise by noting that $\mathrm{e}^{-\mathrm{i}\phi} = \cos(-\phi) + \mathrm{i}\sin(-\phi) = \cos\phi - \mathrm{i}\sin\phi$; it then follows that

$$\cos\phi = \tfrac{1}{2}(\mathrm{e}^{\mathrm{i}\phi} + \mathrm{e}^{-\mathrm{i}\phi}) \qquad \sin\phi = -\tfrac{1}{2}\mathrm{i}(\mathrm{e}^{\mathrm{i}\phi} - \mathrm{e}^{-\mathrm{i}\phi})$$

The polar form of a complex number is commonly used to perform arithmetical operations. For instance, the product of two complex numbers in polar form is

$$z_1z_2=(r_1\mathrm{e}^{\mathrm{i}\phi_1})(r_2\mathrm{e}^{\mathrm{i}\phi_2})=r_1r_2\mathrm{e}^{\mathrm{i}(\phi_1+\phi_2)}$$

This construction is illustrated in Sketch 2.



Sketch 2

likely to be found travelling in the positive and negative $x$ directions, with the same magnitude, $k\hbar$, of the momentum.

A similar interpretation applies to any wavefunction written as a linear combination of eigenfunctions of an operator. In general, a wavefunction can be written as the following linear combination

$$\psi=c_1\psi_1+c_2\psi_2+\cdots=\sum_k c_k\psi_k \qquad \text{(7C.10)}$$

Linear combination of eigenfunctions

where the $c_k$ are numerical (possibly complex) coefficients and the $\psi_k$ are different eigenfunctions of the operator $\hat{\Omega}$ corresponding to the observable of interest. The functions $\psi_k$ are said to form a **complete set** in the sense that any arbitrary function can be expressed as a linear combination of them. Then, according to quantum mechanics:

- A single measurement of the observable corresponding to the operator $\hat{\Omega}$ will give one of the eigenvalues corresponding to the $\psi_k$ that contribute to the superposition.
- The probability of measuring a specific eigenvalue in a series of measurements is proportional to the square modulus ($|c_k|^2$) of the corresponding coefficient in the linear combination.

Physical interpretation

The average value of a large number of measurements of an observable $\Omega$ is called the **expectation value** of the operator $\hat{\Omega}$, and is written $\langle\Omega\rangle$. For a normalized wavefunction $\psi$, the expectation value of $\hat{\Omega}$ is calculated by evaluating the integral

$$\langle\Omega\rangle=\int\psi^*\hat{\Omega}\psi\,\mathrm{d}\tau \qquad \text{(7C.11)}$$

Expectation value [normalized wavefunction, definition]

This definition can be justified by considering two cases, one where the wavefunction is an eigenfunction of the operator $\hat{\Omega}$ and another where the wavefunction is a superposition of that operator's eigenfunctions.

### How is that done? 7C.4 Justifying the expression for the expectation value of an operator

If the wavefunction $\psi$ is an eigenfunction of $\hat{\Omega}$ with eigenvalue $\omega$ (so $\hat{\Omega}\psi=\omega\psi$),

$$\langle\Omega\rangle=\int\psi^*\overbrace{\hat{\Omega}\psi}^{\omega\psi}\,\mathrm{d}\tau=\int\psi^*\omega\psi\,\mathrm{d}\tau\overset{\omega\text{ a constant}}{=}\omega\int\psi^*\psi\,\mathrm{d}\tau\overset{\psi\text{ normalized}}{=}\omega$$

The interpretation of this expression is that, because the wavefunction is an eigenfunction of $\hat{\Omega}$, each observation of the property $\Omega$ results in the same value $\omega$; the average value of all the observations is therefore $\omega$.

Now suppose the (normalized) wavefunction is the linear combination of two eigenfunctions of the operator $\hat{\Omega}$, each of which is individually normalized to 1. Then

$$\langle\Omega\rangle = \int(c_1\psi_1+c_2\psi_2)^*\hat{\Omega}(c_1\psi_1+c_2\psi_2)\mathrm{d}\tau$$

$$=\int(c_1\psi_1+c_2\psi_2)^*\left(c_1\overbrace{\hat{\Omega}\psi_1}^{\omega_1\psi_1}+c_2\overbrace{\hat{\Omega}\psi_2}^{\omega_2\psi_2}\right)\mathrm{d}\tau$$

$$=\int(c_1\psi_1+c_2\psi_2)^*(c_1\omega_1\psi_1+c_2\omega_2\psi_2)\,\mathrm{d}\tau$$

$$=c_1^*c_1\omega_1\overbrace{\int\psi_1^*\psi_1\mathrm{d}\tau}^{1}+c_2^*c_2\omega_2\overbrace{\int\psi_2^*\psi_2\mathrm{d}\tau}^{1}$$

$$+c_1^*c_2\omega_2\overbrace{\int\psi_1^*\psi_2\mathrm{d}\tau}^{0}+c_2^*c_1\omega_1\overbrace{\int\psi_2^*\psi_1\mathrm{d}\tau}^{0}$$

The first two integrals on the right are both equal to 1 because the wavefunctions $\psi_1$ and $\psi_2$ are individually normalized. Because $\psi_1$ and $\psi_2$ correspond to different eigenvalues of a hermitian operator, they are orthogonal, so the third and fourth integrals on the right are zero. Therefore

$$\langle\Omega\rangle = |c_1|^2\omega_1 + |c_2|^2\omega_2$$

The interpretation of this expression is that in a series of measurements each individual measurement yields either $\omega_1$ or $\omega_2$, but that the probability of $\omega_1$ occurring is $|c_1|^2$, and likewise the probability of $\omega_2$ occurring is $|c_2|^2$. The average is the sum of the two eigenvalues, but with each weighted according to the probability that it will occur in a measurement:

average = (probability of $\omega_1$ occurring) × $\omega_1$
+ (probability of $\omega_2$ occurring) × $\omega_2$

The expectation value therefore predicts the result of taking a series of measurements, each of which gives an eigenvalue, and then taking the weighted average of these values. This justifies the form of eqn 7C.11.

### Example 7C.3 Calculating an expectation value

Calculate the average value of the position of an electron in the lowest energy state of a one-dimensional box of length $L$, with the (normalized) wavefunction $\psi=(2/L)^{1/2}\sin(\pi x/L)$ inside the box and zero outside it.

***Collect your thoughts*** The average value of the position is the expectation value of the operator corresponding to position, which is multiplication by $x$. To evaluate $\langle x\rangle$, you need to evaluate the integral in eqn 7C.11 with $\hat{\Omega}=\hat{x}=x\times$

***The solution*** The expectation value of position is

$$\langle x\rangle=\int_0^L\psi^*\hat{x}\psi\,\mathrm{d}x \qquad \text{with } \psi=\left(\frac{2}{L}\right)^{1/2}\sin\frac{\pi x}{L} \quad \text{and } \hat{x}=x\times$$

The integral is restricted to the region $x = 0$ to $x = L$ because outside this region the wavefunction is zero. Use Integral T.11 from the *Resources section* to obtain

$$\langle x\rangle=\frac{2}{L}\overbrace{\int_0^L x\sin^2\frac{\pi x}{L}\mathrm{d}x}^{\text{Integral T.11}}=\frac{2}{L}\frac{L^2}{4}=\tfrac{1}{2}L$$

**Comment.** This result means that if a very large number of measurements of the position of the electron are made, then the mean value will be at the centre of the box. However, each different observation will give a different and unpredictable individual result somewhere in the range $0 \le x \le L$ because the wavefunction is not an eigenfunction of the operator corresponding to $x$.

***Self-test 7C.3*** Evaluate the mean square position, $\langle x^2\rangle$, of the electron; you will need Integral T.12 from the *Resource section.*

*Answer:* $L^2\{\frac{1}{3}-\frac{1}{2\pi^2}\}=0.217L^2$

The mean kinetic energy of a particle in one dimension is the expectation value of the operator given in eqn 7C.5. Therefore,

$$\langle E_\mathrm{k}\rangle=\int_{-\infty}^{\infty}\psi^*\hat{E}_\mathrm{k}\psi\,\mathrm{d}x=-\frac{\hbar^2}{2m}\int_{-\infty}^{\infty}\psi^*\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2}\mathrm{d}x \qquad (7C.12)$$

This conclusion confirms the previous assertion that the kinetic energy is a kind of average over the curvature of the wavefunction: a large contribution to the observed value comes from regions where the wavefunction is sharply curved (so $\mathrm{d}^2\psi/\mathrm{d}x^2$ is large) and the wavefunction itself is large (so that $\psi^*$ is large there too).

## 7C.3 The uncertainty principle

The wavefunction $\psi=\mathrm{e}^{ikx}$ is an eigenfunction of $\hat{p}_x$ with eigenvalue $+k\hbar$: in this case the wavefunction describes a particle with a definite state of linear momentum. Where, though, is the particle? The probability density is proportional to $\psi^*\psi$, so if the particle is described by the wavefunction $\mathrm{e}^{ikx}$ the probability density is proportional to $(\mathrm{e}^{ikx})^*\mathrm{e}^{ikx}=\mathrm{e}^{-ikx}\mathrm{e}^{ikx}=\mathrm{e}^{-ikx+ikx}=\mathrm{e}^0=1$. In other words, the probability density is the same for all values of $x$: the location of the particle is completely unpredictable. In summary, if the momentum of the particle is known precisely, it is not possible to predict its location.

This conclusion is an example of the consequences of the **Heisenberg uncertainty principle**, one of the most celebrated results of quantum mechanics:

> It is impossible to specify simultaneously, with arbitrary precision, both the linear momentum and the position of a particle.

Heisenberg uncertainty principle

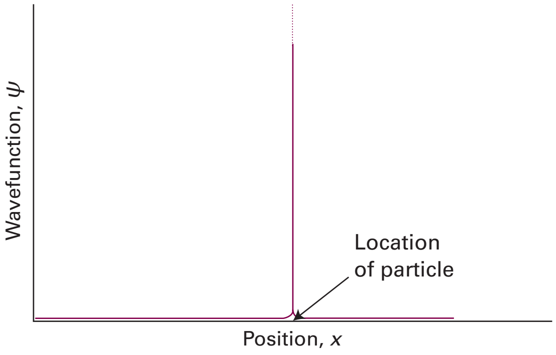


**Figure 7C.4** The wavefunction of a particle at a well-defined location is a sharply spiked function that has zero amplitude everywhere except at the position of the particle.

Note that the uncertainty principle also implies that if the position is known precisely, then the momentum cannot be predicted. The argument runs as follows.

Suppose the particle is known to be at a definite location, then its wavefunction must be large there and zero everywhere else (Fig. 7C.4). Such a wavefunction can be created by superimposing a large number of harmonic (sine and cosine) functions, or, equivalently, a number of $e^{ikx}$ functions (because $e^{ikx} = \cos kx + i\sin kx$). In other words, a sharply localized wavefunction, called a **wavepacket**, can be created by forming a linear combination of wavefunctions that correspond to many different linear momenta.

The superposition of a few harmonic functions gives a wavefunction that spreads over a range of locations (Fig. 7C.5). However, as the number of wavefunctions in the superposition increases, the wavepacket becomes sharper on account of the more complete interference between the positive and negative regions of the individual waves. When an infinite number of components are used, the wavepacket is a sharp, infinitely narrow spike, which corresponds to perfect localization of the particle. Now the particle is perfectly localized but all information about its momentum has been lost. A measurement of the momentum will give a result corresponding to any one of the infinite number of waves in the superposition, and which one it will give is unpredictable. Hence, if the location of the particle is known precisely (implying that its wavefunction is a superposition of an infinite number of momentum eigenfunctions), then its momentum is completely unpredictable.

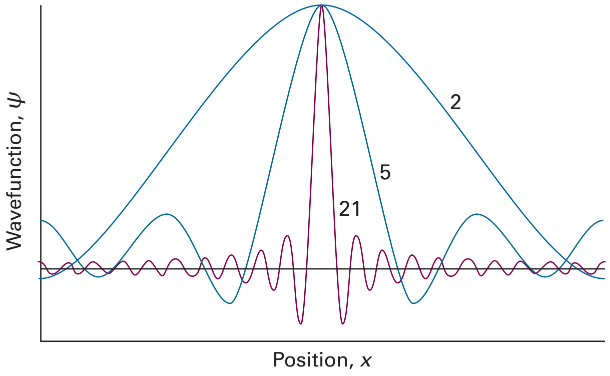


**Figure 7C.5** The wavefunction of a particle with an ill-defined location can be regarded as a superposition of several wavefunctions of definite wavelength that interfere constructively in one place but destructively elsewhere. As more waves are used in the superposition (as given by the numbers attached to the curves), the location becomes more precise at the expense of uncertainty in the momentum of the particle. An infinite number of waves are needed in the superposition to construct the wavefunction of the perfectly localized particle.

The quantitative version of the uncertainty principle is

$$\Delta p_q \Delta q \geq \tfrac{1}{2}\hbar \qquad \text{Heisenberg uncertainty principle} \qquad (7C.13a)$$

In this expression $\Delta p_q$ is the 'uncertainty' in the linear momentum parallel to the axis $q$, and $\Delta q$ is the uncertainty in position along that axis. These 'uncertainties' are given by the root-mean-square deviations of the observables from their mean values:

$$\Delta p_q = \{\langle p_q^2\rangle - \langle p_q\rangle^2\}^{1/2} \qquad \Delta q = \{\langle q^2\rangle - \langle q\rangle^2\}^{1/2} \qquad (7C.13b)$$

If there is complete certainty about the position of the particle ($\Delta q = 0$), then the only way that eqn 7C.13a can be satisfied is for $\Delta p_q = \infty$, which implies complete uncertainty about the momentum. Conversely, if the momentum parallel to an axis is known exactly ($\Delta p_q = 0$), then the position along that axis must be completely uncertain ($\Delta q = \infty$).

The $p$ and $q$ that appear in eqn 7C.13a refer to the same direction in space. Therefore, whereas simultaneous specification of the position on the $x$-axis and momentum parallel to the $x$-axis are restricted by the uncertainty relation, simultaneous location of position on $x$ and motion parallel to $y$ or $z$ are not restricted.

### Example 7C.4 Using the uncertainty principle

Suppose the speed of a projectile of mass 1.0 g is known to within 1 μm s$^{-1}$. What is the minimum uncertainty in its position?

***Collect your thoughts*** You can estimate $\Delta p$ from $m\Delta v$, where $\Delta v$ is the uncertainty in the speed; then use eqn 7C.13a to estimate the *minimum* uncertainty in position, $\Delta q$, by using it in the form $\Delta p\Delta q = \tfrac{1}{2}\hbar$ rearranged into $\Delta q = \tfrac{1}{2}\hbar/\Delta p$. You will need to use $1\,\text{J} = 1\,\text{kg}\,\text{m}^2\,\text{s}^{-2}$.

***The solution*** The minimum uncertainty in position is

$$\Delta q = \frac{\hbar}{2m\Delta v}$$

$$= \frac{1.055\times10^{-34}\,\text{J s}}{2\times(1.0\times10^{-3}\,\text{kg})\times(1\times10^{-6}\,\text{m s}^{-1})} = 5\times10^{-26}\,\text{m}$$

**Comment.** This uncertainty is completely negligible for all practical purposes. However, if the mass is that of an electron, then the same uncertainty in speed implies an uncertainty in position far larger than the diameter of an atom (the analogous calculation gives $\Delta q = 60\,\text{m}$).

***Self-test 7C.4*** Estimate the minimum uncertainty in the speed of an electron in a one-dimensional region of length $2a_0$, the approximate diameter of a hydrogen atom, where $a_0$ is the Bohr radius, 52.9 pm.

*Answer:* 500 km s$^{-1}$

The Heisenberg uncertainty principle is more general than even eqn 7C.13a suggests. It applies to any pair of observables, called **complementary observables**, for which the corresponding operators $\hat{\Omega}_1$ and $\hat{\Omega}_2$ have the property

$$\hat{\Omega}_1\hat{\Omega}_2\psi \neq \hat{\Omega}_2\hat{\Omega}_1\psi \qquad (7\text{C}.14)$$

Complementarity of observables

The term on the left implies that $\hat{\Omega}_2$ acts first, then $\hat{\Omega}_1$ acts on the result, and the term on the right implies that the operations are performed in the opposite order. When the effect of two operators applied in succession depends on their order (as this equation implies), they do not **commute**. The different outcomes of the effect of applying $\hat{\Omega}_1$ and $\hat{\Omega}_2$ in a different order are expressed by introducing the **commutator** of the two operators, which is defined as

$$[\hat{\Omega}_1,\hat{\Omega}_2] = \hat{\Omega}_1\hat{\Omega}_2 - \hat{\Omega}_2\hat{\Omega}_1 \qquad (7\text{C}.15)$$

Commutator [definition]

By using the definitions of the operators for position and momentum, an explicit value of this commutator can be found.

### How is that done? 7C.5 Evaluating the commutator of position and momentum

You need to consider the effect of $\hat{x}\hat{p}_x$ (i.e. the effect of $\hat{p}_x$ followed by the effect on the outcome of multiplication by $x$) on an arbitrary wavefunction $\psi$, which need not be an eigenfunction of either operator.

$$\hat{x}\hat{p}_x\psi = x \times \frac{\hbar}{\mathrm{i}}\frac{\mathrm{d}\psi}{\mathrm{d}x}$$

Then you need to consider the effect of $\hat{p}_x\hat{x}$ on the same function (that is, the effect of multiplication by $x$ followed by the effect of $\hat{p}_x$ on the outcome):

$$\hat{p}_x\hat{x}\psi = \frac{\hbar}{\mathrm{i}}\frac{\mathrm{d}(x\psi)}{\mathrm{d}x} \overset{\mathrm{d}(fg)/\mathrm{d}x = (\mathrm{d}f/\mathrm{d}x)g + f(\mathrm{d}g/\mathrm{d}x)}{=} \frac{\hbar}{\mathrm{i}}\left(\psi + x\frac{\mathrm{d}\psi}{\mathrm{d}x}\right)$$

The second expression is different from the first, so $\hat{p}_x\hat{x}\psi \neq \hat{x}\hat{p}_x\psi$ and therefore the two operators do not commute. You can infer the value of the commutator from the difference of the two expressions:

$$[\hat{x},\hat{p}_x]\psi = \hat{x}\hat{p}_x\psi - \hat{p}_x\hat{x}\psi = -\frac{\hbar}{\mathrm{i}}\psi = \mathrm{i}\hbar\psi, \quad \text{so } [\hat{x},\hat{p}_x]\psi = \mathrm{i}\hbar\psi$$

This relation is true for any wavefunction $\psi$, so the commutator is

$$[\hat{x},\hat{p}_x] = \mathrm{i}\hbar \qquad (7\text{C}.16)$$

Commutator of position and momentum operators

The commutator in eqn 7C.16 is of such central significance in quantum mechanics that it is taken as a fundamental distinction between classical mechanics and quantum mechanics. In fact, this commutator may be taken as a postulate of quantum mechanics and used to justify the choice of the operators for position and linear momentum in eqn 7C.3.

Classical mechanics supposed, falsely as is now known, that the position and momentum of a particle could be specified simultaneously with arbitrary precision. However, quantum mechanics shows that position and momentum are complementary, and that a choice must be made: position can be specified, but at the expense of momentum, or momentum can be specified, but at the expense of position.

## 7C.4 The postulates of quantum mechanics

The principles of quantum theory can be summarized as a series of postulates, which will form the basis for chemical applications of quantum mechanics throughout the text.

*The wavefunction:* All dynamical information is contained in the wavefunction $\psi$ for the system, which is a mathematical function found by solving the appropriate Schrödinger equation for the system.

*The Born interpretation:* If the wavefunction of a particle has the value $\psi$ at some position $\boldsymbol{r}$, then the probability of finding the particle in an infinitesimal volume $\mathrm{d}\tau = \mathrm{d}x\mathrm{d}y\mathrm{d}z$ at that position is proportional to $|\psi|^2\mathrm{d}\tau$.

*Acceptable wavefunctions:* An acceptable wavefunction must be single-valued, continuous, not infinite over a finite region of space, and (except in special cases) have a continuous slope.

*Observables:* Observables, $\Omega$, are represented by hermitian operators, $\hat{\Omega}$, built from the position and momentum operators specified in eqn 7C.3.

*Observations and expectation values:* A single measurement of the observable represented by the operator $\hat{\Omega}$ gives one of the eigenvalues of $\hat{\Omega}$. If the wavefunction is not an eigenfunction of $\hat{\Omega}$, the average of many measurements is given by the expectation value, $\langle\Omega\rangle$, defined in eqn 7C.11.

*The Heisenberg uncertainty principle:* It is impossible to specify simultaneously, with arbitrary precision, both the linear momentum and the position of a particle and, more generally, any pair of observables represented by operators that do not commute.

## Checklist of concepts

☐ 1. The Schrödinger equation is an **eigenvalue equation.**

☐ 2. An **operator** carries out a mathematical operation on a function.

☐ 3. The **hamiltonian operator** is the operator corresponding to the total energy of the system, the sum of the kinetic and potential energies.

☐ 4. The wavefunction corresponding to a specific energy is an **eigenfunction** of the hamiltonian operator.

☐ 5. Two different functions are **orthogonal** if the integral (over all space) of their product is zero.

☐ 6. **Hermitian operators** have real eigenvalues and orthogonal eigenfunctions.

☐ 7. **Observables** are represented by hermitian operators.

☐ 8. Sets of functions that are normalized and mutually orthogonal are called **orthonormal**.

☐ 9. When the system is not described by a single eigenfunction of an operator, it may be expressed as a **superposition** of such eigenfunctions.

☐ 10. The mean value of a series of observations is given by the **expectation value** of the corresponding operator.

☐ 11. The **uncertainty principle** restricts the precision with which complementary observables may be specified and measured simultaneously.

☐ 12. **Complementary observables** are observables for which the corresponding operators do not commute.

## Checklist of equations

| Property | Equation | Comment | Equation number |
|---|---|---|---|
| Eigenvalue equation | $\hat{\Omega}\psi=\omega\psi$ | $\psi$ eigenfunction; $\omega$ eigenvalue | 7C.2b |
| Hermiticity | $\int\psi_i^*\hat{\Omega}\psi_j\,\mathrm{d}\tau=\left\{\int\psi_j^*\hat{\Omega}\psi_i\,\mathrm{d}\tau\right\}^*$ | Hermitian operators have real eigenvalues and orthogonal eigenfunctions | 7C.7 |
| Orthogonality | $\int\psi_i^*\psi_j\,\mathrm{d}\tau=0$ for $i\neq j$ | Integration over all space | 7C.8 |
| Expectation value | $\langle\Omega\rangle=\int\psi^*\hat{\Omega}\psi\,\mathrm{d}\tau$ | Definition; assumes $\psi$ normalized | 7C.11 |
| Heisenberg uncertainty principle | $\Delta p_q\Delta q\geq\frac{1}{2}\hbar$ | For position and momentum | 7C.13a |
| Commutator of two operators | $[\hat{\Omega}_1,\hat{\Omega}_2]=\hat{\Omega}_1\hat{\Omega}_2-\hat{\Omega}_2\hat{\Omega}_1$ | The observables are complementary if $[\hat{\Omega}_1,\hat{\Omega}_2]\neq0$ | 7C.15 |
|  | Special case: $[\hat{x},\hat{p}_x]=\mathrm{i}\hbar$ |  | 7C.16 |

# TOPIC 7D Translational motion

### ➤ Why do you need to know this material?

The application of quantum theory to translational motion reveals the origin of quantization and non-classical features, such as tunnelling and zero-point energy. This material is important for the discussion of atoms and molecules that are free to move within a restricted volume, such as a gas in a container.

### ➤ What is the key idea?

The translational energy levels of a particle confined to a finite region of space are quantized, and under certain conditions particles can pass into and through classically forbidden regions.

### ➤ What do you need to know already?

You should know that the wavefunction is the solution of the Schrödinger equation (Topic 7B), and be familiar, in one instance, with the techniques of deriving dynamical properties from the wavefunction by using the operators corresponding to the observables (Topic 7C).

**Translation**, motion through space, is one of the basic types of motion. Quantum mechanics, however, shows that translation can have a number of non-classical features, such as its confinement to discrete energies and passage into and through classically forbidden regions.

## 7D.1 Free motion in one dimension

A free particle is unconstrained by any potential, which may be taken to be zero everywhere. In one dimension $V(x) = 0$ everywhere, so the Schrödinger equation becomes (Topic 7B)

$$-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2\psi(x)}{\mathrm{d}x^2} = E\psi(x) \tag{7D.1}$$

Free motion in one dimension

The most straightforward way to solve this simple second-order differential equation is to take the known general form of solutions of equations of this kind, and then show that it does indeed satisfy eqn 7D.1.

### How is that done? 7D.1 Finding the solutions to the Schrödinger equation for a free particle in one dimension

The general solution of a second-order differential equation of the kind shown in eqn 7D.1 is

$$\psi_k(x) = A\mathrm{e}^{\mathrm{i}kx} + B\mathrm{e}^{-\mathrm{i}kx}$$

where $k$, $A$, and $B$ are constants. You can verify that $\psi_k(x)$ is a solution of eqn 7D.1 by substituting it into the left-hand side of the equation, evaluating the derivatives, and then confirming that you have generated the right-hand side. Because $\mathrm{de}^{\pm ax}/\mathrm{d}x = \pm a\mathrm{e}^{\pm ax}$, the left-hand side becomes

$$-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2}{\mathrm{d}x^2}\overbrace{(A\mathrm{e}^{\mathrm{i}kx} + B\mathrm{e}^{-\mathrm{i}kx})}^{\psi_k(x)} = -\frac{\hbar^2}{2m}\{A(\mathrm{i}k)^2\mathrm{e}^{\mathrm{i}kx} + B(-\mathrm{i}k)^2\mathrm{e}^{-\mathrm{i}kx}\}$$

$$= \overbrace{\frac{k^2\hbar^2}{2m}}^{E_k}\overbrace{(A\mathrm{e}^{\mathrm{i}kx} + B\mathrm{e}^{-\mathrm{i}kx})}^{\psi_k(x)}$$

The left-hand side is therefore equal to a constant × $\psi_k(x)$, which is the same as the term on the right-hand side of eqn 7D.1 provided the constant, the term in blue, is identified with $E$. The value of the energy depends on the value of $k$, so henceforth it will be written $E_k$. The wavefunctions and energies of a free particle are therefore

$$\psi_k(x) = A\mathrm{e}^{\mathrm{i}kx} + B\mathrm{e}^{-\mathrm{i}kx} \qquad E_k = \frac{k^2\hbar^2}{2m} \tag{7D.2}$$

Wavefunctions and energies [one dimension]

The wavefunctions in eqn 7D.2 are continuous, have continuous slope everywhere, are single-valued, and do not go to infinity: they are therefore acceptable wavefunctions for all values of $k$. Because $k$ can take any value, the energy can take any non-negative value, including zero. As a result, *the translational energy of a free particle is not quantized*.

In Topic 7C it is explained that in general a wavefunction can be written as a superposition (a linear combination) of the eigenfunctions of an operator. The wavefunctions of eqn 7D.2 can be recognized as superpositions of the two functions $\mathrm{e}^{\pm\mathrm{i}kx}$ which are eigenfunctions of the linear momentum operator with eigenvalues $\pm k\hbar$ (Topic 7C). These eigenfunctions correspond to states with definite linear momentum:

$$\psi_k(x) = \underbrace{A\,\mathrm{e}^{+\mathrm{i}kx}}_{\text{Particle with linear momentum } +k\hbar} + \underbrace{B\,\mathrm{e}^{-\mathrm{i}kx}}_{\text{Particle with linear momentum } -k\hbar}$$

According to the interpretation given in Topic 7C, if a system is described by the wavefunction $\psi_k(x)$, then repeated measurements of the momentum will give $+k\hbar$ (that is, the particle travelling in the positive $x$-direction) with a probability proportional to $A^2$, and $-k\hbar$ (that is, the particle travelling in the negative $x$-direction) with a probability proportional to $B^2$. Only if $A$ or $B$ is zero does the particle have a definite momentum of $-k\hbar$ or $+k\hbar$, respectively.

**Brief illustration 7D.1**

Suppose an electron emerges from an accelerator moving towards positive $x$ with kinetic energy 1.0 eV ($1\,\text{eV} = 1.602 \times 10^{-19}\,\text{J}$). The wavefunction for such a particle is given by eqn 7D.2 with $B = 0$ because the momentum is definitely in the positive $x$-direction. The value of $k$ is found by rearranging the expression for the energy in eqn 7D.2 into

$$k = \left(\frac{2m_\text{e}E_k}{\hbar^2}\right)^{1/2} = \left(\frac{2\times(9.109\times10^{-31}\,\text{kg})\times(1.6\times10^{-19}\,\text{J})}{(1.055\times10^{-34}\,\text{J s})^2}\right)^{1/2}$$

$$= 5.1\times10^{9}\,\text{m}^{-1}$$

or $5.1\,\text{nm}^{-1}$ (with $1\,\text{nm} = 10^{-9}\,\text{m}$). Therefore, the wavefunction is $\psi(x) = A\text{e}^{5.1\text{i}x/\text{nm}}$.

So far, the motion of the particle has been confined to the $x$-axis. In general, the linear momentum is a vector (see *The chemist's toolkit* 17) directed along the line of travel of the particle. Then $\boldsymbol{p} = \boldsymbol{k}\hbar$ and the magnitude of the vector is $p = k\hbar$ and its component on each axis is $p_q = k_q\hbar$, with the wavefunction for each component proportional to $\text{e}^{\text{i}k_q q}$ with $q = x, y$, or $z$ and overall equal to $\text{e}^{\text{i}(k_x x + k_y y + k_z z)}$.[1]

## 7D.2 Confined motion in one dimension

Consider a **particle in a box** in which a particle of mass $m$ is confined to a region of one-dimensional space between two impenetrable walls. The potential energy is zero inside the box but rises abruptly to infinity at the walls located at $x = 0$ and $x = L$ (Fig. 7D.1). When the particle is between the walls, the Schrödinger equation is the same as for a free particle (eqn 7D.1), so the general solutions given in eqn 7D.2 are also the same. However, it will prove convenient to rewrite the wavefunction in terms of sines and cosines by using $\text{e}^{\pm\text{i}kx} = \cos kx \pm \text{i}\sin kx$ (*The chemist's toolkit* 16 in Topic 7C)

$$\begin{aligned}\psi_k(x) &= A\text{e}^{\text{i}kx} + B\text{e}^{-\text{i}kx}\\ &= A(\cos kx + \text{i}\sin kx) + B(\cos kx - \text{i}\sin kx)\\ &= (A+B)\cos kx + \text{i}(A-B)\sin kx\end{aligned}$$

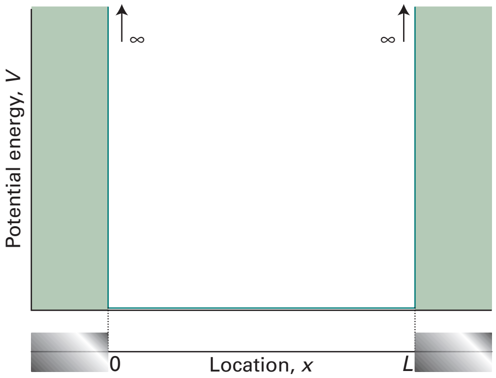


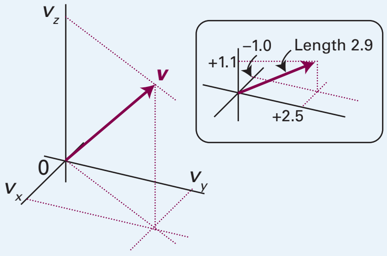
**Figure 7D.1** The potential energy for a particle in a one-dimensional box. The potential is zero between $x = 0$ and $x = L$, and then rises to infinity outside this region, resulting in impenetrable walls which confine the particle.

**The chemist's toolkit 17** Vectors

A vector is a quantity with both magnitude and direction. The vector $\boldsymbol{v}$ shown in Sketch 1 has components on the $x$, $y$, and $z$ axes with values $v_x$, $v_y$, and $v_z$, respectively, which may be positive or negative. For example, if $v_x = -1.0$, the $x$-component of the vector $\boldsymbol{v}$ has a magnitude of 1.0 and points in the $-x$ direction. The magnitude of a vector is denoted $v$ or $|\boldsymbol{v}|$ and is given by

$$v = (v_x^2 + v_y^2 + v_z^2)^{1/2}$$

Thus, a vector with components $v_x = -1.0$, $v_y = +2.5$, and $v_z = +1.1$ has magnitude 2.9 and would be represented by an arrow of length 2.9 units and the appropriate orientation (as in the inset in the Sketch). Velocity and momentum are vectors; the magnitude of a velocity vector is called the speed. Force, too, is a vector. Electric and magnetic fields are two more examples of vectors.



Sketch 1

The operations involving vectors (addition, multiplication, etc.) needed for this text are described in *The chemist's toolkit* 22 in Topic 8C.

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[1] In terms of scalar products, this overall wavefunction would be written $\text{e}^{\text{i}\boldsymbol{k}\cdot\boldsymbol{r}}$.