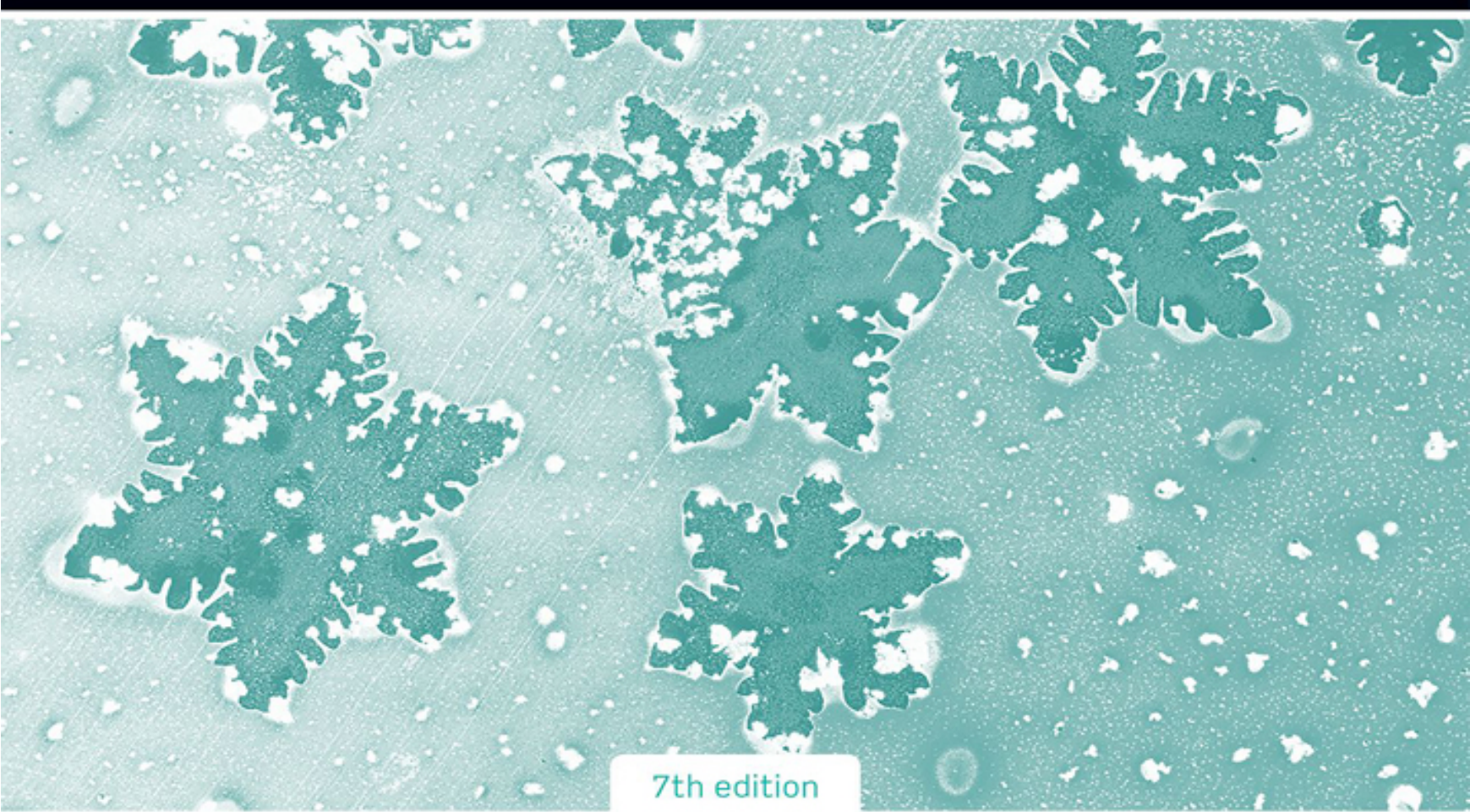


OXFORD

# INORGANIC CHEMISTRY



7th edition

WELLER | OVERTON | ROURKE | ARMSTRONG

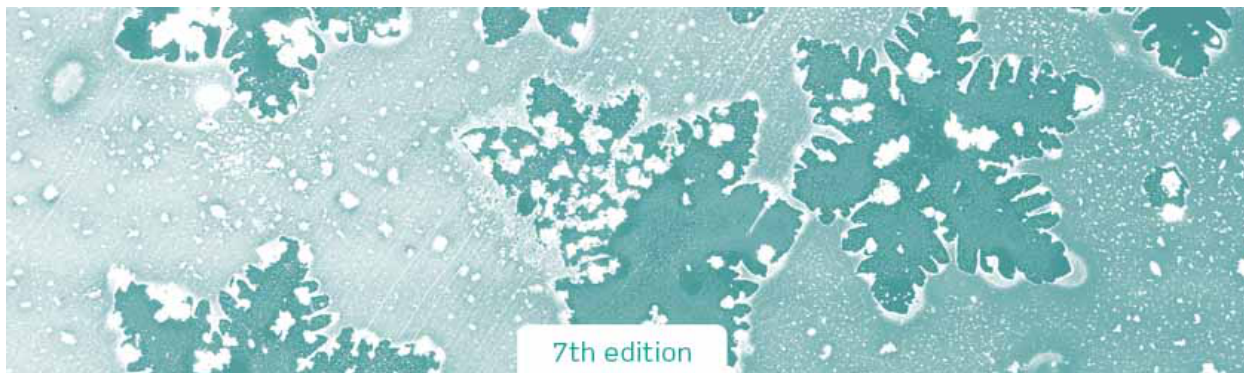
# The elements

Name	Symbol	Atomic number	Molar mass (g mol <sup>-1</sup> )
Actinium	Ac	89	227
Aluminium (aluminum)	Al	13	26.98
Americium	Am	95	243
Antimony	Sb	51	121.76
Argon	Ar	18	39.95
Arsenic	As	33	74.92
Astatine	At	85	210
Barium	Ba	56	137.33
Berkelium	Bk	97	247
Beryllium	Be	4	9.01
Bismuth	Bi	83	208.98
Bohrium	Bh	107	270
Boron	B	5	10.81
Bromine	Br	35	79.90
Cadmium	Cd	48	112.41
Caesium (cesium)	Cs	55	132.91
Calcium	Ca	20	40.08
Californium	Cf	98	251
Carbon	C	6	12.01
Cerium	Ce	58	140.12
Chlorine	Cl	17	35.45
Chromium	Cr	24	52.00
Cobalt	Co	27	58.93
Copernicium	Cn	112	285
Copper	Cu	29	63.55
Curium	Cm	96	247
Darmstadtium	Ds	110	281
Dubnium	Db	105	270
Dysprosium	Dy	66	162.50
Einsteinium	Es	99	252
Erbium	Er	68	167.27
Europium	Eu	63	151.96
Fermium	Fm	100	257
Flerovium	Fl	114	289
Fluorine	F	9	19.00
Francium	Fr	87	223
Gadolinium	Gd	64	157.25
Gallium	Ga	31	69.72
Germanium	Ge	32	72.63
Gold	Au	79	196.97
Hafnium	Hf	72	178.49
Hassium	Hs	108	270
Helium	He	2	4.00
Holmium	Ho	67	164.93

Hydrogen	H	1	1.008
Indium	In	49	114.82
Iodine	I	53	126.90
Iridium	Ir	77	192.22
Iron	Fe	26	55.85
Krypton	Kr	36	83.80
Lanthanum	La	57	138.91
Lawrencium	Lr	103	262
Lead	Pb	82	207.2
Lithium	Li	3	6.94
Livermorium	Lv	116	293
Lutetium	Lu	71	174.97
Magnesium	Mg	12	24.31
Manganese	Mn	25	54.94
Meitnerium	Mt	109	278
Mendelevium	Md	101	258
Mercury	Hg	80	200.59
Molybdenum	Mo	42	95.95
Moscovium	Mc	115	289
Neodymium	Nd	60	144.24
Neon	Ne	10	20.18
Neptunium	Np	93	237
Nickel	Ni	28	58.69
Nihonium	Nh	113	286
Niobium	Nb	41	92.91
Nitrogen	N	7	14.01
Nobelium	No	102	259
Oganesson	Og	118	294
Osmium	Os	76	190.23
Oxygen	O	8	16.00
Palladium	Pd	46	106.42
Phosphorus	P	15	30.97
Platinum	Pt	78	195.08
Plutonium	Pu	94	244
Polonium	Po	84	209
Potassium	K	19	39.10
Praseodymium	Pr	59	140.91
Promethium	Pm	61	145
Protactinium	Pa	91	231.04
Radium	Ra	88	226
Radon	Rn	86	222
Rhenium	Re	75	186.21
Rhodium	Rh	45	102.91
Roentgenium	Rg	111	281
Rubidium	Rb	37	85.47
Ruthenium	Ru	44	101.07
Rutherfordium	Rf	104	267
Samarium	Sm	62	150.36
Scandium	Sc	21	44.96
Seaborgium	Sg	106	269
Selenium	Se	34	78.97
Silicon	Si	14	28.09

Silver	Ag	47	107.87
Sodium	Na	11	22.99
Strontium	Sr	38	87.62
Sulfur	S	16	32.06
Tantalum	Ta	73	180.95
Technetium	Tc	43	98
Tellurium	Te	52	127.60
Tennessine	Ts	117	293
Terbium	Tb	65	158.93
Thallium	Tl	81	204.38
Thorium	Th	90	232.04
Thulium	Tm	69	168.93
Tin	Sn	50	118.71
Titanium	Ti	22	47.87
Tungsten	W	74	183.84
Uranium	U	92	238.03
Vanadium	V	23	50.94
Xenon	Xe	54	131.29
Ytterbium	Yb	70	173.05
Yttrium	Y	39	88.91
Zinc	Zn	30	65.41
Zirconium	Zr	40	91.22

# INORGANIC CHEMISTRY



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Impression: 1

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# Preface

## Introducing *Inorganic Chemistry*

Our aim in the seventh edition of *Inorganic Chemistry* is to provide a comprehensive, fully updated, and contemporary introduction to the diverse and fascinating discipline of inorganic chemistry. Inorganic chemistry deals with the properties of all of the elements in the periodic table. Those classified as metallic range from the highly reactive sodium and barium to the noble metals, such as gold and platinum. The nonmetals include solids, liquids, and gases, and their properties encompass those of the aggressive, highly-oxidizing fluorine and the unreactive gases such as helium. Although this variety and diversity are features of any study of inorganic chemistry, there are underlying patterns and trends which enrich and enhance our understanding of the subject. These trends in reactivity, structure, and properties of the elements and their compounds provide an insight into the landscape of the periodic table and provide the foundation on which to build a deeper understanding of the chemistry of the elements and their compounds.

Inorganic compounds vary from ionic solids, which can be described by simple extensions of classical electrostatics, to covalent compounds and metals, which are best described by models that have their origins in quantum mechanics. We can rationalize and interpret the properties of many inorganic compounds by using qualitative models that are based on quantum mechanics, including the interaction of atomic orbitals to form molecular orbitals and the band structures of solids. The text builds on similar qualitative bonding models that should already be familiar from introductory chemistry courses.

## Making inorganic chemistry relevant

Although qualitative models of bonding and reactivity clarify and systematize the subject, inorganic chemistry is essentially an experimental subject. Inorganic chemistry lies at the heart of many of the most important recent advances in chemistry. New, often unusual, inorganic compounds and materials are constantly being synthesized and identified. Modern inorganic syntheses continue to enrich the field with compounds that give us fresh perspectives on structure, bonding, and reactivity.

Inorganic chemistry has considerable impact on our everyday lives and on other scientific disciplines. The chemical industry depends strongly on inorganic chemistry as it is essential to the formulation and improvement of the modern materials and compounds used as catalysts, energy storage materials, semiconductors, optoelectronics, superconductors, and advanced ceramics. The environmental, biological and medical impacts of inorganic chemistry on our lives are enormous. Current topics in industrial, materials, biological, and environmental chemistry are highlighted throughout the early sections of the book to illustrate their importance and encourage the reader to explore further. These aspects of inorganic chemistry are then developed more thoroughly later in the text including, in this edition, a brand-new chapter devoted to green chemistry.

## What is new to this edition?

In this new edition we have refined the presentation, organization, and visual representation. The book has been extensively revised, much has been rewritten and there is some completely new material, including additional content on characterization techniques in chapter 8. The text now includes twelve new boxes that showcase recent developments and exciting discoveries; these include boxes 11.3 on sodium ion batteries, 13.7 on touchscreens, 23.2 on d-orbital participation in lanthanoid chemistry, 25.1 on renewable energy, and 26.1 on cellulose degradation.

We have written our book with the student in mind, and have added new pedagogical features and enhanced others. Additional context boxes on recent innovations link theory to practice, and encourage understanding of the real-world significance of inorganic chemistry. Extended examples, self-test questions, and new exercises and tutorial problems stimulate thinking, and encourage the development of data analysis skills, and a closer engagement with research. We have also improved the clarity of the text with a new two-column format throughout. Many of the 2000 illustrations and the marginal structures have been redrawn, many have been enlarged for improved clarity, and all are presented in full colour. We have used colour systematically rather than just for decoration, and have ensured that it serves a pedagogical purpose, encouraging students to recognize patterns and trends in bonding and reactivity.

## How is this textbook organized?

The topics in Part 1, *Foundations*, have been revised to make them more accessible to the reader, with additional qualitative explanation accompanying the more mathematical treatments. The material has been reorganized to allow a more coherent progression through the topics of symmetry and bonding and to present the important topic of catalysis early on in the text.

Part 2, *The elements and their compounds*, has been thoroughly updated, building on the improvements made in earlier editions, and

includes additional contemporary contexts such as solar cells, new battery materials, and touchscreen technology. The opening chapter draws together periodic trends and cross references ahead of their more detailed treatment in the subsequent descriptive chapters. These chapters start with hydrogen and proceed across the periodic table, taking in the s-block metals and the diverse elements of the p block, before ending with extensive coverage of the d- and f-block elements.

Each of these chapters is organized into two sections: *Essentials* describes the fundamental chemistry of the elements and the *Detail* provides a more extensive account. The chemical properties of each group of elements and their compounds are further enriched with descriptions of current applications and recent advances made in inorganic chemistry. The patterns and trends that emerge are rationalized by drawing on the principles introduced in Part 1. Chapter 22 has been expanded considerably to include homogeneous catalytic processes that rely on the organometallic chemistry described there, with much of this new material setting the scene for the new chapter on green chemistry in Part 3.

Part 3, *Expanding our horizons*, takes the reader to the forefront of knowledge in several areas of current research. These chapters explore specialized, vibrant topics that are of importance to industry and biology, and include the new Chapter 25 on green chemistry. A comprehensive chapter on materials chemistry, Chapter 24, covers the latest discoveries in energy materials, heterogeneous catalysis, and nanomaterials. Chapter 26 discusses the natural roles of different elements in biological systems and the various and extraordinarily subtle ways in which each one is exploited; for instance, at the active sites of enzymes where they are responsible for catalytic activities that are essential for living organisms. Chapter 27 describes how medical science is exploiting the 'stranger' elements, such as platinum, gold, lithium, arsenic and synthetic technetium, to treat and diagnose illness.

We are confident that this text will serve the undergraduate chemist well. It provides the theoretical building blocks with which to build knowledge and understanding of the distinctions between chemical elements and should help to rationalize the sometimes bewildering diversity of descriptive inorganic chemistry. It also takes the student to the forefront of the discipline and should therefore complement many courses taken in the later stages of a programme of study.

Mark Weller  
Tina Overton  
Jonathan Rourke  
Fraser Armstrong

## About the authors

**Mark Weller** is Professor of Chemistry at the University of Bath and President of the Materials Chemistry Division of the Royal Society of Chemistry. His research interests cover a wide range of synthetic and structural inorganic chemistry including photovoltaic compounds, zeolites, battery materials, and specialist pigments; he is the author of over 300 primary literature publications in these fields. Mark has taught both inorganic chemistry and physical chemistry methods at undergraduate and postgraduate levels for over 35 years, with his lectures covering topics across materials chemistry, the inorganic chemistry of the s- and f- block elements, and analytical methods applied to inorganic compounds. He is a co-author of OUP's *Characterisation Methods in Inorganic Chemistry* and an OUP Primer (23) on *Inorganic Materials Chemistry*.

**Tina Overton** is Professor of Chemistry Education at Monash University in Australia and Honorary Professor at the University of Nottingham, UK. Tina has published on the topics of critical thinking, context and problem-based learning, the development of problem solving skills, work-based learning and employability, and has co-authored several textbooks in inorganic chemistry and skills development. She has been awarded the Royal Society of Chemistry's HE Teaching Award, Tertiary Education Award and Nyholm Prize, the Royal Australian Chemical Institute's Fensham Medal, and is a National Teaching Fellow and Senior Fellow of the Higher Education Academy.

**Jonathan Rourke** is Associate Professor of Chemistry at the University of Warwick. He received his PhD at the University of Sheffield on organometallic polymers and liquid crystals, followed by postdoctoral work in Canada with Professor Richard Puddephatt and back in Britain with Duncan Bruce. His initial independent research career began at Bristol University and then at Warwick, where he's been ever since. Over the years Dr Rourke has taught most aspects of inorganic chemistry, all the way from basic bonding, through symmetry analysis to advanced transition metal chemistry.

**Fraser Armstrong** is a Professor of Chemistry at the University of Oxford and a Fellow of St John's College, Oxford. In 2008, he was elected as a Fellow of the Royal Society of London. His interests span the fields of electrochemistry, renewable energy, hydrogen, enzymology, and biological inorganic chemistry, and he heads a research group investigating electrocatalysis by enzymes. He was an Associate Professor at the University of California, Irvine, before joining the Department of Chemistry at Oxford in 1993.



# Acknowledgements

We would particularly like to acknowledge the inspirational role and major contributions of Peter Atkins, whose early editions of *Inorganic Chemistry* formed the foundations of this text.

We have taken care to ensure that the text is free of errors. This is difficult in a rapidly changing field, where today's knowledge is soon replaced by tomorrow's. We thank all those colleagues who so willingly gave their time and expertise to a careful reading of a variety of draft chapters.

Many of the figures in Chapter 26 were produced using PyMOL software; for more information see W.L. DeLano, *The PyMOL Molecular Graphics System* (2002), De Lano Scientific, San Carlos, CA, USA.

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# About the book

*Inorganic Chemistry* provides numerous learning features to help you master this wide-ranging subject. In addition, the text has been designed so that you can either work through the chapters chronologically, or dip in at an appropriate point in your studies. The book's online resources provide support to you in your learning.

The material in this book has been logically and systematically laid out in three distinct sections. Part 1, *Foundations*, outlines the underlying principles of inorganic chemistry, which are built on in the subsequent two sections. Part 2, *The elements and their compounds*, divides the descriptive chemistry into 'essentials' and 'details', enabling you to easily draw out the key principles behind the reactions, before exploring them in greater depth. Part 3, *Expanding our horizons*, introduces you to exciting interdisciplinary research at the forefront of inorganic chemistry.

The paragraphs below describe the learning features of the text and online resources in further detail.

---

## Organizing the information

### Key points

The key points outline the main take-home message(s) of the section that follows. These will help you to focus on the principal ideas being introduced in the text.

**KEY POINTS** The blocks of the periodic table reflect the identity of the orbitals that are occupied last in the building-up process. The period number is the principal quantum number of the valence shell. The group number is related to the number of valence electrons.

The layout of the periodic table reflects the electronic structure of the atoms of the elements (Fig. 1.22). We can

### Context boxes

Context boxes demonstrate the diversity of inorganic chemistry and its wide-ranging applications to, for example, advanced materials, industrial processes, environmental chemistry, and everyday life.

**BOX 26.1** How does a copper enzyme degrade cellulose?

Most of the organic material that is produced by photosynthesis is unavailable for use by industry or as fuels. Biomass largely consists of polymeric carbohydrates—polysaccharides such as cellulose and lignin, that are very difficult to break down to simpler sugars as they are resistant to hydrolysis. However, a breakthrough has occurred with the discovery that certain

### Notes on good practice

In some areas of inorganic chemistry, the nomenclature commonly in use can be confusing or archaic. To address this we have included brief 'notes on good practice' to help you avoid making common mistakes.

**A NOTE ON GOOD PRACTICE**

In expressions for equilibrium constants and rate equations, we omit the brackets that are part of the chemical formula of the complex; the surviving square brackets denote molar concentration of a species (with the units mol dm<sup>-3</sup> removed).

## Further reading

Each chapter lists sources where further information can be found. We have tried to ensure that these sources are easily available and have indicated the type of information each one provides.

### FURTHER READING

P.T. Anastas and J.C. Warner, *Green chemistry: theory and practice*. Oxford University Press (1998). The definitive guide to green chemistry.

M. Lancaster, *Green chemistry: an introductory text*. Royal Society of Chemistry (2002). A readable text with industrial examples.

## Resource section

At the back of the book is a comprehensive collection of resources, including an extensive data section and information relating to group theory and spectroscopy.

### Resource section 1

#### Selected ionic radii

Ionic radii are given (in picometres, pm) for the most common oxidation states and coordination geometries. The coordination number is given in parentheses. (4) refers to tetrahedral and (6S) refers to square planar. All d-block species are low-spin unless labelled with 'h', in which case values for high-spin are quoted. Most data are taken from R.D. Shannon, *Acta Crystallogr.*, 1976, A32, 751. Values for other coordination geometries can be Where Shannon values are not available, Pauling ions are quoted and are indicated by \*.

---

## Problem solving

### Brief illustrations

A *Brief illustration* shows you how to use equations or concepts that have just been introduced in the main text, and will help you to understand how to manipulate data correctly.

#### A BRIEF ILLUSTRATION

The cyclic silicate anion  $[\text{Si}_6\text{O}_6]^{4-}$  is a six-membered ring with alternating Si and O atoms and six terminal O atoms, two on each Si atom. Because each terminal O atom contributes  $-1$  to the charge, the overall charge is  $-6$ . From another perspective, the conventional oxidation numbers of silicon and oxygen,  $+4$

## Worked examples and Self-tests

Numerous worked *Examples* provide a more detailed illustration of the application of the material being discussed. Each one demonstrates an important aspect of the topic under discussion or provides practice with calculations and problems. Each *Example* is followed by a *Self-test* designed to help you monitor your progress.

#### EXAMPLE 17.3 Analysing the recovery of $\text{Br}_2$ from brine

Show that from a thermodynamic standpoint bromide ions can be oxidized to  $\text{Br}_2$  by  $\text{Cl}_2$  and by  $\text{O}_2$  and suggest a reason why  $\text{O}_2$  is not used for this purpose.

**Answer** We need to consider the relevant standard potentials

## Exercises

There are many brief *Exercises* at the end of each chapter. You can find the answers online and fully worked answers are available in the separate *Solutions manual* (see below). The *Exercises* can be used to check your understanding and gain experience and practice in tasks such as balancing equations, predicting and drawing structures, and manipulating data.

## Tutorial Problems

The *Tutorial Problems* are more demanding in content and style than the *Exercises* and are often based on a research paper or other additional source of information. *Tutorial problems* generally require a discursive response and there may not be a single correct answer. They may be used as essay type questions or for classroom discussion.

## TUTORIAL PROBLEMS

3.1 Consider a molecule  $\text{IF}_3\text{O}_2$  (with I as the central atom). How many isomers are possible? Assign point group designations to each isomer.

3.2 How many isomers are there for 'octahedral' molecules with the formula  $\text{MA}_3\text{B}_3$ , where A and B are monoatomic ligands?

## Solutions Manual

A Solutions Manual (ISBN: 9780198814689) by Alen Hadzovic is available to accompany the text and provides complete solutions to the self-tests and end-of-chapter exercises.

# Online resources

The online resources that accompany this book provide a number of useful teaching and learning resources to augment the printed book, and are free of charge.

The site can be accessed at: [www.oup.com/uk/ichem7e/](http://www.oup.com/uk/ichem7e/)

Please note that lecturer resources are available only to registered adopters of the textbook. To register, simply visit [www.oup.com/uk/ichem7e/](http://www.oup.com/uk/ichem7e/) and follow the appropriate links.

Student resources are openly available to all, without registration.



---

## For registered adopters of the text:

### Figures and tables from the book

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

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## For students:

### 3D rotatable molecular structures

**Numbered structures** can be found online as interactive 3D structures. Type the following URL into your browser, adding the relevant structure number:

[www.chemtube3d.com/weller7/\[chapter number\]S\[structure number\]](http://www.chemtube3d.com/weller7/[chapter number]S[structure number]).

For example, for structure 10 in Chapter 1, type [www.chemtube3d.com/weller7/1S10](http://www.chemtube3d.com/weller7/1S10).

Those **figures** with  in the caption can also be found online as interactive 3D structures. Type the following URL into your browser, adding the relevant figure number:

[www.chemtube3d.com/weller7/\[chapter number\]F\[figure number\]](http://www.chemtube3d.com/weller7/[chapter number]F[figure number]).

For example, for Figure 4 in chapter 7, type [www.chemtube3d.com/weller7/7F04](http://www.chemtube3d.com/weller7/7F04).

Visit [www.chemtube3d.com/weller7/\[chapter number\]](http://www.chemtube3d.com/weller7/[chapter number]) for all interactive structures organised by chapter.

### Group theory tables

Comprehensive group theory tables are available to download.

The screenshot shows the ChemTube3D website. At the top left is the University of Liverpool logo. The main header features the 'ChemTube3D' logo. Below this is a navigation menu with options like 'Home', 'About', 'Features', 'Support', and 'Contact'. The central part of the page displays a large 3D ball-and-stick model of a complex organic molecule. To the right of the model, there is an 'Information' section describing the software's capabilities for creating 3D animations and structures. Below the information is a 'Quick links' section with various resources. At the bottom left, there is a section for 'New! Download ChemTube3D' which lists various educational materials available for download.

## Answers to Self-tests and Exercises

A PDF document containing final answers to the end-of-chapter exercises in this book can be downloaded online.



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# Glossary of chemical abbreviations

Ac	acetyl, CH <sub>3</sub> CO
acac	acetylacetonato
aq	aqueous solution species
bpy	2,2'-bipyridine
cod	1,5-cyclooctadiene
cot	cyclooctatetraene
Cp	cyclopentadienyl
Cp*	pentamethylcyclopentadienyl
Cy	cyclohexyl
cyclam	tetraazacyclotetradecane
dien	diethylenetriamine
DMF	dimethylformamide
DMSO	dimethyl sulfoxide
η	hapticity
edta	ethylenediaminetetraacetato
en	ethylenediamine (1,2-diaminoethane)
Et	ethyl
gly	glycinato
Hal	halide
iPr	isopropyl
L	a ligand
μ	signifies a bridging ligand
M	a metal
Me	methyl
mes	mesityl, 2,4,6-trimethylphenyl
Ox	an oxidized species
ox	oxalato
Ph	phenyl
phen	phenanthroline
py	pyridine
Red	a reduced species
Sol	solvent, or a solvent molecule
soln	nonaqueous solution species
tBu	tertiary butyl
THF	tetrahydrofuran
TMEDA	<i>N,N,N',N'</i> -tetramethylethylenediamine
trien	2,2',2''-triaminotriethylene
X	generally halogen, also a leaving group or an anion
Y	an entering group

# Foundations

The eight chapters in this part of the book lay the foundations of inorganic chemistry.

The first four chapters develop an understanding of the structures of atoms, the bonding in molecules and solids, and the role symmetry plays in chemistry. Chapter 1 introduces the structure of atoms in terms of quantum theory and describes important periodic trends in their properties. Chapter 2 develops molecular structure in terms of increasingly sophisticated models of covalent bonding and explores how the energetics of reactions form the basis of understanding catalysis.

Chapter 3 shows how a systematic consideration of the symmetry of molecules can be used to discuss the bonding and structure of molecules and help interpret data from some of the techniques described in Chapter 8. Chapter 4 describes ionic bonding, the structures and properties of a range of typical solids, the role of defects in materials, and the electronic properties of solids.

The next two chapters focus on two major types of reactions. Chapter 5 explains how acid–base properties are defined, measured, and applied across a wide area of chemistry. Chapter 6 describes oxidation and reduction, and demonstrates how electrochemical data can be used to predict and explain the outcomes of reactions in which electrons are transferred between molecules. Chapter 7 describes the coordination compounds of the elements where we discuss bonding, structure, and reactions of complexes, and see how symmetry considerations can provide insight into this important class of compounds. Chapter 8 provides a toolbox for inorganic chemistry: it describes a wide range of the instrumental techniques that are used to identify and determine the structures and compositions of inorganic compounds.

# Atomic structure

# 1

## The structures of hydrogenic atoms

- 1.1 Spectroscopic information
- 1.2 Some principles of quantum mechanics
- 1.3 Atomic orbitals

## Many-electron atoms

- 1.4 Penetration and shielding
- 1.5 The building-up principle
- 1.6 The classification of the elements
- 1.7 Atomic properties

## Further reading

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This chapter lays the foundations for the explanation of the trends in the physical and chemical properties of all inorganic compounds. To understand the behaviour of molecules and solids we need to understand atoms: our study of inorganic chemistry must therefore begin with a review of their structures and properties. We start with a discussion of the origin of matter in the solar system and then consider the development of our understanding of atomic structure and the behaviour of electrons in atoms. We introduce quantum theory qualitatively and use the results to rationalize properties such as atomic radii, ionization energy, electron affinity, and electronegativity. A knowledge of these properties allows us to begin to understand the diverse chemical properties of nearly 120 elements known today.

The observation that the universe is expanding has led to the current view that about 14 billion years ago the currently visible universe was concentrated into a point-like region that exploded in an event called the **Big Bang**. With initial temperatures immediately after the Big Bang of about  $10^9$  K, the fundamental particles produced in the explosion had too much kinetic energy to bind together in the forms we know today. However, the universe cooled as it expanded, the particles moved more slowly, and they soon began to adhere together under the influence of a variety of forces. In particular, the **strong force**, a short-range but powerful attractive force between nucleons (protons and neutrons), bound these particles together into nuclei. As the temperature fell still further, the **electromagnetic force**, a relatively weak but long-range force between electric charges, bound electrons to nuclei to form atoms, and the universe acquired the potential for complex chemistry and the existence of life (Box 1.1).

About two hours after the start of the universe, the temperature had fallen so much that most of the matter was in the form of H atoms (89%) and He atoms (11%). In one sense, not much has happened since then for, as Fig. 1.1 shows, hydrogen and helium remain overwhelmingly the most abundant elements in the universe. However, nuclear reactions have formed dozens of other elements and have immeasurably enriched the variety of matter in the universe, and thus given rise to the whole area of chemistry (Boxes 1.2 and 1.3).

Table 1.1 summarizes the properties of the subatomic particles that we need to consider in chemistry. All the known elements—by 2018 all up to 118 had been confirmed—that are formed from these subatomic particles are distinguished by their **atomic number**,  $Z$ , the number of protons in the nucleus of an atom of the element. Many elements have a number of **isotopes**, which are atoms with the same atomic number but different atomic masses. These isotopes are distinguished by the **mass number**,  $A$ , which is the total number of protons and neutrons in the nucleus. The mass number is also sometimes termed the *nucleon number*. Hydrogen, for instance, has three isotopes. In each

case  $Z = 1$ , indicating that the nucleus contains one proton. The most abundant isotope has  $A = 1$ , denoted  $^1\text{H}$ , its nucleus consisting of a single proton. Far less abundant (only 1 atom in 6000) is deuterium, with  $A = 2$ . This mass number indicates that, in addition to a proton, the nucleus contains one neutron. The formal designation of deuterium is  $^2\text{H}$ , but it is commonly denoted D. The third, short-lived, radioactive isotope of hydrogen is tritium,  $^3\text{H}$  or T. Its nucleus consists of one proton and two neutrons. In certain cases it is helpful to display the atomic number of the element as a left suffix; so the three isotopes of hydrogen would then be denoted  $^1_1\text{H}$ ,  $^2_1\text{H}$ , and  $^3_1\text{H}$ . Hydrogen is the only element for which there are such significant chemical distinctions between the isotopes that the isotopes warrant individual names.

Those **figures** with an  in the caption can be found online as interactive 3D structures. Type the following URL into your browser, adding the relevant figure number: [www.chemtube3d.com/weller7/\[chapter number\]F\[figure number\]](http://www.chemtube3d.com/weller7/[chapter number]F[figure number]). For example, for Figure 3 in Chapter 7, type [www.chemtube3d.com/weller7/7F03](http://www.chemtube3d.com/weller7/7F03).

Many of the **numbered structures** can also be found online as interactive 3D structures: visit [www.chemtube3d.com/weller7/\[chapter number\]](http://www.chemtube3d.com/weller7/[chapter number]) for all 3D resources organized by chapter.

## Box 1.

### How are elements created?

The earliest stars resulted from the gravitational condensation of clouds of H and He atoms. This gave rise to high temperatures and densities within the clouds, and fusion reactions began as nuclei merged together.

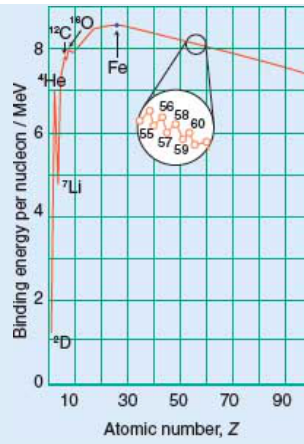
Energy is released when light nuclei fuse together to give elements of higher atomic number. Nuclear reactions are very much more energetic than normal chemical reactions because the **strong force** which binds protons and neutrons together is much stronger than the electromagnetic force that binds electrons to nuclei. Whereas a typical chemical reaction might release about  $10^3 \text{ kJ mol}^{-1}$ , a nuclear reaction typically releases a million times more energy, about  $10^9 \text{ kJ mol}^{-1}$ .

Elements up to  $Z = 26$  (iron) were formed inside stars. These elements are the products of the nuclear fusion reactions referred to as 'nuclear burning'. The burning reactions, which should not be confused with chemical combustion, involved H and He nuclei and a complicated fusion cycle catalysed by C nuclei. The stars that formed in the earliest stages of the evolution of the cosmos lacked C nuclei and used noncatalysed H-burning. Nucleosynthesis reactions are rapid at temperatures of  $5\text{--}10 \times 10^6 \text{ K}$ . Here we have another contrast between chemical and nuclear reactions, because chemical reactions take place at temperatures a hundred thousand times lower. Moderately energetic collisions between atoms or molecules can result in chemical change, but only highly vigorous collisions can provide the energy required to bring about most nuclear transformations.

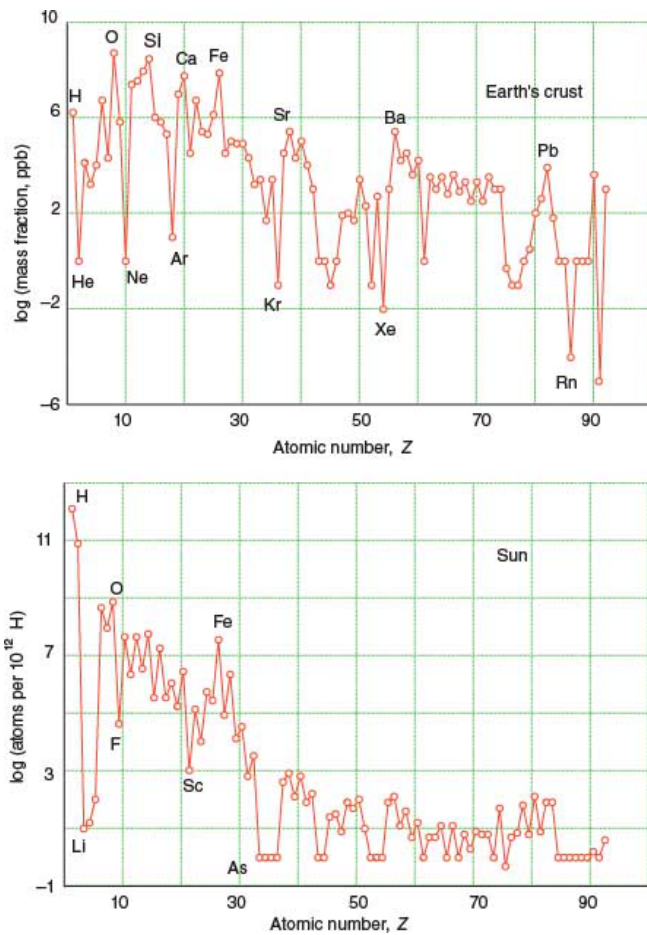
The elements beyond iron ( $Z > 26$ ) are produced in significant quantities when hydrogen burning is complete and the collapse of the star's core raises its density to  $10^8 \text{ kg m}^{-3}$  (about  $10^5$  times the density of water) and the temperature to  $10^8 \text{ K}$ . Under these extreme conditions, a star will become a red giant and helium burning can occur.

The high abundance of iron and nickel in the universe is consistent with these elements having the most stable of all nuclei. This stability is expressed in terms of the **binding energy**, which is the difference in energy between the nucleus itself and the same numbers of individual protons and neutrons. This binding energy is often presented in terms of the difference in mass between the nucleus and its individual protons and neutrons because, according to Einstein's theory of relativity, mass and energy are related by  $E=mc^2$ , where  $c$  is the speed of light. Therefore, if the mass of a nucleus differs from the total mass of its components by  $\Delta m = m_{\text{nucleons}} - m_{\text{nucleus}}$ , then its binding energy is  $E_{\text{bind}} = (\Delta m)c^2$ . The binding energy of  $^{56}\text{Fe}$ , for example, is the difference in energy between the  $^{56}\text{Fe}$  nucleus and 26 protons and 30 neutrons. A positive binding energy corresponds to a nucleus that has a lower, more favourable, energy (and lower mass) than its constituent nucleons.

Figure B1.1 shows the binding energy per nucleon,  $E_{\text{bind}}/A$  (obtained by dividing the total binding energy by the number of nucleons), for all the isotopes. Iron and nickel occur at the maximum of the curve, showing that their nucleons are bound together more strongly than in any other nuclide. Harder to see from the graph is an alternation of binding energies as the atomic number varies from even to odd, with even- $Z$  nuclides slightly more stable than their odd- $Z$  neighbours. There is a corresponding alternation in cosmic abundances, with nuclides of even atomic number being marginally more abundant than those of odd atomic number. This stability of even- $Z$  nuclides is attributed to the lowering of energy by pairing nucleons in the nucleus.



**FIGURE B1.1** Nuclear binding energies. The greater the binding energy, the more stable is the nucleus. Note the alternation in stability shown in the inset.



**FIGURE 1.1** The abundances of the elements in the Earth's crust and the Sun. Elements with odd  $Z$  are less stable than their neighbours with even  $Z$ .

## Box 1.2

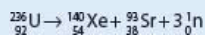
### What are nuclear fusion and nuclear fission?

If two nuclei with mass numbers lower than 56 merge to produce a new nucleus with a larger nuclear binding energy, the excess energy is released. This process is called **fusion**. For example, two neon-20 nuclei may fuse to give a calcium-40 nucleus:



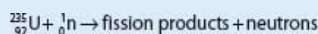
The value of the binding energy per nucleon,  $E_{\text{bind}}/A$ , for  $^{20}\text{Ne}$  is approximately 8.0 MeV. Therefore, the total binding energy of the species on the left-hand side of the equation is  $2 \times 20 \times 8.0 \text{ MeV} = 320 \text{ MeV}$ . The value of  $E_{\text{bind}}/A$  for  $^{40}\text{Ca}$  is close to 8.6 MeV and so the total energy of the species on the right-hand side is  $40 \times 8.6 \text{ MeV} = 344 \text{ MeV}$ . The difference in the binding energies of the products and reactants is therefore 24 MeV.

For nuclei with  $A > 56$ , binding energy can be released when they split into lighter products with higher values of  $E_{\text{bind}}/A$ . This process is called **fission**. For example, uranium-236 can undergo fission into (among many other modes) xenon-140 and strontium-93 nuclei:



The values of  $E_{\text{bind}}/A$  for  $^{236}\text{U}$ ,  $^{140}\text{Xe}$ , and  $^{93}\text{Sr}$  nuclei are 7.6, 8.4, and 8.7 MeV, respectively. Therefore, the energy released in this reaction is  $(140 \times 8.4) + (93 \times 8.7) - (236 \times 7.6) \text{ MeV} = 191.5 \text{ MeV}$  for the fission of each  $^{236}\text{U}$  nucleus.

Fission can also be induced by bombarding heavy elements with neutrons:



The kinetic energy of fission products from  $^{235}\text{U}$  is about 165 MeV, that of the neutrons is about 5 MeV, and the  $\gamma$ -rays produced have an energy of about 7 MeV. The fission products are themselves radioactive and decay by  $\beta$ -,  $\gamma$ -, and X-radiation, releasing about 23 MeV. In a nuclear fission reactor the neutrons that are not consumed by fission are captured with the release of about 10 MeV. The energy produced is reduced by about 10 MeV, which escapes from the reactor as radiation, and about 1 MeV which remains as undecayed fission products in the spent fuel. Therefore, the total energy produced for one fission event is about 200 MeV, or 32 pJ. It follows that about 1 W of reactor heat (where  $1 \text{ W} = 1 \text{ J s}^{-1}$ ) corresponds to about  $3.1 \times 10^{10}$  fission events per second. A nuclear reactor producing 3 GW has an electrical output of approximately 1 GW and corresponds to the fission of 3 kg of  $^{235}\text{U}$  per day.

The use of nuclear power is controversial in large part on account of the risks associated with the highly radioactive, long-lived spent fuel. The declining stocks of fossil fuels, however, make nuclear power very attractive as it is estimated that stocks of uranium could last for hundreds of years. The cost of uranium ores is currently very low and 100 g of uranium oxide generates as much energy as sixty barrels of oil or 20 tonnes of coal. The increased use of nuclear power would also drastically reduce the rate of emission of greenhouse gases into the atmosphere. The environmental drawback with nuclear power is the storage and disposal of radioactive waste and the public are nervous about possible nuclear accidents, such as that in Fukushima in 2011, and the misuse of nuclear capabilities in pursuit of political ambitions.

## Box 1.3

### Technetium—what is a synthetic element?

A synthetic element is one that does not occur naturally on Earth but that can be artificially generated by nuclear reactions. The first synthetic element was technetium (Tc,  $Z = 43$ ), named from the Greek word for ‘artificial’. Its discovery—or more precisely, its preparation—filled a gap in the periodic table and its properties matched those predicted by Mendeleev. The longest-lived isotope of technetium ( $^{98}\text{Tc}$ ) has a half-life of 4.2 million years so any produced when the Earth was formed has long since decayed. Technetium is produced in red-giant stars.

The most widely used isotope of technetium is  $^{99\text{m}}\text{Tc}$ , where the ‘m’ indicates a metastable isotope. Technetium-99m emits high-energy  $\gamma$ -rays but has a relatively short half-life of 6.01 hours. These properties make the isotope particularly attractive for use *in vivo* as the  $\gamma$ -ray energy is sufficient for it to be detected outside the body and its half-life means that most of it will have decayed within 24 hours. Consequently,  $^{99\text{m}}\text{Tc}$  is widely used in nuclear medicine, for example in radiopharmaceuticals for imaging and in functional studies of the brain, bones, blood, lungs, liver, heart, thyroid gland, and kidneys (Section 27.9). Technetium-99m is generated through nuclear fission in nuclear power plants but a more useful laboratory source of the isotope is a technetium generator, which uses the decay of  $^{99}\text{Mo}$  to  $^{99\text{m}}\text{Tc}$ .

The half-life of  $^{99}\text{Mo}$  is 66 hours, which makes it more convenient for transport and storage than  $^{99\text{m}}\text{Tc}$  itself. Most commercial generators are based on  $^{99}\text{Mo}$  in the form of the molybdate ion,  $\text{MoO}_4^{2-}$ , adsorbed on  $\text{Al}_2\text{O}_3$ . The  $^{99}\text{MoO}_4^{2-}$  ion decays by beta emission to the pertechnetate ion,  $^{99\text{m}}\text{TcO}_4^{2-}$ , which is less tightly bound to the alumina (Section 27.8).



Sterile saline solution is washed through a column of the immobilized  $^{99}\text{Mo}$  and the  $^{99\text{m}}\text{Tc}$  solution is collected.

**TABLE 1.1** Subatomic particles of relevance to chemistry

Particle	Symbol	Mass/ $m_{\text{u}}^*$	Mass number	Charge/ $e^{\dagger}$	Spin
Electron	$e^{-}$	$5.486 \times 10^{-4}$	0	-1	$\frac{1}{2}$
Proton	$p$	1.0073	1	+1	$\frac{1}{2}$
Neutron	$n$	1.0087	1	0	$\frac{1}{2}$
Photon	$\gamma$	0	0	0	1
Neutrino	$\nu$	c. 0	0	0	$\frac{1}{2}$
Positron	$e^{+}$	$5.486 \times 10^{-4}$	0	+1	$\frac{1}{2}$
$\alpha$ particle	$\alpha$	[ ${}^4_2\text{He}^{2+}$ nucleus]	4	+2	0
$\beta$ particle	$\beta$	[ $e^{-}$ ejected from nucleus]	0	-1	$\frac{1}{2}$
$\gamma$ photon	$\gamma$	[electromagnetic radiation from nucleus]	0	0	1

\* Masses are expressed relative to the atomic mass constant,  $m_{\text{u}} = 1.6605 \times 10^{-27}$  kg.

† The elementary charge is  $e = 1.602 \times 10^{-19}$  C.

## The structures of hydrogenic atoms

So far we have discussed the nuclear properties of the elements. As chemists we are much more interested in the electronic structure of atoms and the organization of the periodic table is a direct consequence of periodic variations in the electronic structure of atoms. Initially, we consider hydrogen-like or **hydrogenic atoms**, which have only one electron and so are free of the complicating effects of electron–electron repulsions. Hydrogenic atoms include ions such as  $\text{He}^{+}$  and  $\text{C}^{5+}$  (found in the interiors of stars) as well as the hydrogen atom itself. Then we use the concepts that these atoms introduce to build up an approximate description of the structures of **many-electron atoms** (or *polyelectron atoms*).

### 1.1 Spectroscopic information

**KEY POINTS** Spectroscopic observations on hydrogen atoms suggest that an electron can occupy only certain energy levels and that the emission of discrete frequencies of electromagnetic radiation occurs when an electron makes a transition between these levels.

Electromagnetic radiation is emitted when an electric discharge is applied to hydrogen gas. When passed through a prism or diffraction grating, this radiation is found to consist of a series of components: one in the ultraviolet region, one in the visible region, and several in the infrared region of the electromagnetic spectrum (Fig. 1.2; Box 1.4). The nineteenth-century spectroscopist Johann Rydberg found that all the wavelengths ( $\lambda$ , lambda) can be described by the expression

$$\frac{1}{\lambda} = R \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \quad (1.1)$$

where  $R$  is the **Rydberg constant**, an empirical constant with the value  $1.097 \times 10^7 \text{ m}^{-1}$ . The  $n$  are integers, with  $n_1 = 1, 2, \dots$  and  $n_2 = n_1 + n_1 + 2, \dots$ . The series with  $n_1 = 1$  is called the *Lyman series* and lies in the ultraviolet region. The series with  $n_1 = 2$  lies in the visible region and is called the *Balmer series*. The infrared series include the *Paschen series* ( $n_1 = 3$ ) and the *Brackett series* ( $n_1 = 4$ ).

The energy of a photon is given by the equation  $E = h\nu$ , where  $h$  is Planck's constant,  $6.626 \times 10^{-34}$  J s, and  $\nu$  is frequency, the number of times per second that a wave travels through a complete cycle, expressed in units of hertz, where  $1 \text{ Hz} = 1 \text{ s}^{-1}$ . We can use this expression and the equation  $\nu = c/\lambda$ , where  $c$  is the speed of light ( $2.998 \times 10^8 \text{ m s}^{-1}$ ) and  $\lambda$  is wavelength in metres, to derive the expression  $E = hc/\lambda$ . The quantity  $1/\lambda$  is referred to as the wavenumber  $\bar{\nu}$ , and gives the number of wavelengths in a given distance: it is directly proportional to the energy of the photon.

The structure of the spectrum is explained if it is supposed that the emission of radiation takes place when an electron makes a transition

from a state of energy  $-hcR/n_1^2$  to a state of energy  $-hcR/n_2^2$  and that the energy difference, which is equal to  $hcR(1/n_1^2 - 1/n_2^2)$ , is carried away as a photon of energy,  $E=hc/\lambda$ . By equating  $E=hcR(1/n_1^2 - 1/n_2^2)$  and  $E=hc/\lambda$ , and cancelling  $hc$ , we obtain eqn. 1.1.

### A NOTE ON GOOD PRACTICE

Although wavelength is usually expressed in nano- or picometres, wavenumbers are usually expressed in  $\text{cm}^{-1}$ , or reciprocal centimetres. A wavenumber of  $1 \text{ cm}^{-1}$  denotes one complete wavelength in a distance of 1 cm.  $1 \text{ cm}^{-1}$  is equivalent to  $11.96 \text{ J mol}^{-1}$ .

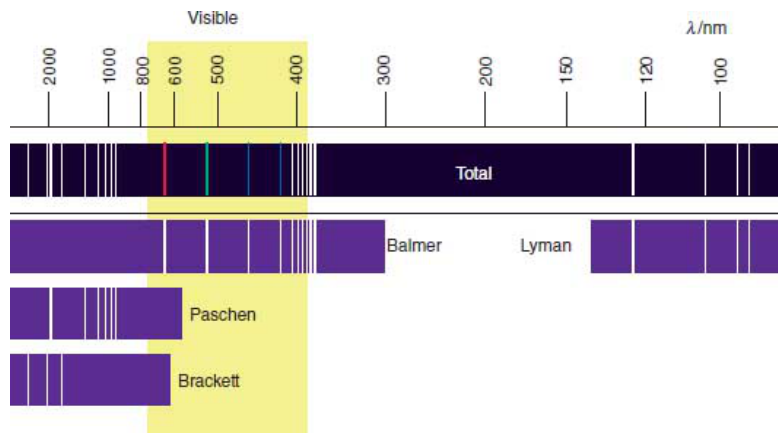


FIGURE 1.2 The spectrum of atomic hydrogen and its analysis into series.

### Box 1.4

#### How do sodium atoms light our streets?

The emission of light when atoms are excited is put to good use in lighting streets in many parts of the world. The widely used yellow street lamps are based on the emission of light from excited sodium atoms.

Low pressure sodium (LPS) lamps consist of a glass tube coated with indium tin oxide (ITO). The indium tin oxide reflects infrared light and transmits visible light. Two inner glass tubes hold solid sodium and a small amount of neon and argon, the same mixture as found in neon lights. When the lamp is turned on the neon and argon emit a red glow which heats the sodium metal. Within a few minutes, the sodium starts to vaporize, the electrical discharge excites electrons in the atoms to a high energy level, and they re-emit the energy as yellow light.

One advantage of these lamps over other types of street lighting is that they do not lose light output as they age. They do, however, use more energy towards the end of their life which may make them less attractive from environmental and economic perspectives.

The question these observations raise is why the energy of the electron in the atom is limited to the values  $-hcR/n^2$  and why  $R$  has the value observed. An initial attempt to explain these features was made by Niels Bohr in 1913 using an early form of quantum theory in which he supposed that the electron could exist in only certain circular orbits. Although he obtained the correct value of  $R$ , his model was later shown to be untenable as it conflicted with the version of quantum theory developed by Erwin Schrödinger and Werner Heisenberg in 1926.

### Predicting the wavelength of lines in the atomic spectrum of hydrogen

Predict the wavelengths of the first three lines in the Balmer series.

**Answer** For the Balmer series,  $n_1 = 2$  and  $n_2 = 3, 4, 5, 6$ . So if we substitute into eqn. 1.1 we obtain  $\frac{1}{\lambda} = R \left( \frac{1}{2^2} - \frac{1}{n_2^2} \right)$  for the first line which gives  $1\,513\,888 \text{ m}^{-1}$  or 661 nm. Using values of  $n_2 = 4$  and 5 for the next two lines give values of  $\lambda$  of 486 and 434 nm, respectively.



**Self-test 1.1** (a) Predict the wavenumber and wavelength of the second line in the Paschen series. (b) Calculate the values of  $n_1$  and  $n_2$  for the line in the Lyman series with a wavelength of 103 nm.

## 1.2 Some principles of quantum mechanics

**KEY POINTS** Electrons can behave as particles or as waves; solution of the Schrödinger equation gives wavefunctions, which describe the location and properties of electrons in atoms. The probability of finding an electron at a given location is proportional to the square of the wavefunction. Wavefunctions generally have regions of positive and negative amplitude, and may undergo constructive or destructive interference with one another.

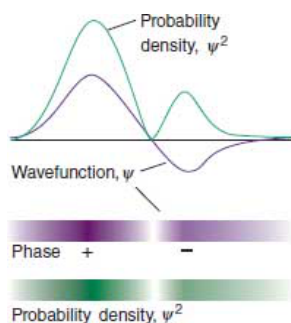
In 1924, Louis de Broglie suggested that because electromagnetic radiation could be considered to consist of particles called photons yet at the same time exhibit wave-like properties, such as interference and diffraction, then the same might be true of electrons. This dual nature is called **wave–particle duality**. An immediate consequence of duality is that it is impossible to know the linear momentum (the product of mass and velocity) and the location of an electron (and any particle) simultaneously. This restriction is called the **Heisenberg uncertainty principle** that states that the product of the uncertainty in momentum and the uncertainty in position cannot be less than a quantity of the order of Planck’s constant (specifically,  $\frac{1}{2}\hbar$ , where  $\hbar = h/2\pi$ ).<sup>1</sup>

Schrödinger formulated an equation that took account of wave–particle duality and accounted for the motion of electrons in atoms. To do so, he introduced the **wavefunction**,  $\psi$  (psi), a mathematical function of the position coordinates  $x$ ,  $y$ , and  $z$ , which describes the behaviour of an electron. The **Schrödinger equation**, of which the wavefunction is a solution, for an electron free to move in one dimension is

$$\underbrace{-\frac{\hbar^2}{2m_e} \frac{d^2\psi}{dx^2}}_{\text{Kinetic energy contribution}} + \underbrace{V(x)\psi(x)}_{\text{Potential energy contribution}} = \underbrace{E\psi(x)}_{\text{Total energy}} \quad (1.2)$$

where  $m_e$  is the mass of an electron,  $V$  is the potential energy of the electron, and  $E$  is its total energy. The Schrödinger equation is a second-order differential equation that can be solved exactly for a number of simple systems (such as a hydrogen atom) and can be solved numerically for many more complex systems (such as many-electron atoms and molecules). However, we shall use only qualitative aspects of its solutions. The generalization of eqn. 1.2 to three dimensions is straightforward, but we do not need its explicit form.

One crucial feature of eqn. 1.2 and its analogues in three dimensions and the imposition of certain requirements (called ‘boundary conditions’) is that physically acceptable solutions exist only for certain values of  $E$ . Therefore, the **quantization** of energy, the fact that an electron can possess only certain discrete energies in an atom, follows naturally from the Schrödinger equation.

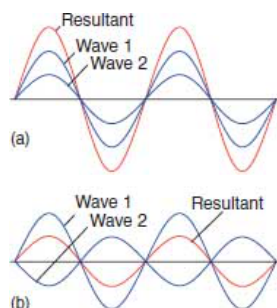


**FIGURE 1.3** The Born interpretation of the wavefunction is that its square is a probability density. There is zero probability density at a node. The shaded bar represents the probability density.

A wavefunction contains all the dynamical information possible about the electron, including where it is and how fast it is travelling. As Heisenberg’s uncertainty principle means it is impossible to know all this information simultaneously, this leads naturally to the concept of the probability of finding an electron at a given location. Specifically, the probability of finding an electron at a given location is proportional to the square of the wavefunction at that point,  $\psi^2$ . According to this interpretation, there is a high probability of finding the electron where  $\psi^2$  is large, and the electron will not be found where  $\psi^2$  is zero (Fig. 1.3). The quantity  $\psi^2$  is called the **probability density** of the electron. It is a ‘density’ in the sense that the product of  $\psi^2$  and the infinitesimal volume element  $d\tau = dx dy dz$  (where  $\tau$  is tau) is proportional to the probability of finding the electron in that volume. The probability is *equal* to  $\psi^2 d\tau$  if the wavefunction is ‘normalized’. A normalized wavefunction is one that is scaled so that the total probability of finding the electron somewhere is 1. The wavefunction of an electron in an atom is called an **atomic orbital**.

Like other waves, wavefunctions in general have regions of positive and negative amplitude, or sign. To help keep track of the relative signs of different regions of a wavefunction, or atomic orbital, in illustrations we label regions of opposite sign with dark and light shading

corresponding to + and – signs, respectively. The sign of the wavefunction is of crucial importance when two wavefunctions spread into the same region of space and interact. Then a positive region of one wavefunction may add to a positive region of the other wavefunction to give a region of enhanced amplitude. This enhancement is called **constructive interference** (Fig. 1.4a). It means that, where the two wavefunctions spread into the same region of space, such as occurs when two atoms are close together, there may be a significantly enhanced probability of finding the electrons in that region. Conversely, a positive region of one wavefunction may be cancelled by a negative region of the second wavefunction (Fig. 1.4b). This **destructive interference** between wavefunctions reduces the probability that an electron will be found in that region. As we shall see, the interference of wavefunctions is of great importance in the explanation of chemical bonding.



**FIGURE 1.4** Wavefunctions interfere where they spread into the same region of space. (a) If they have the same sign in a region, they interfere constructively and the total wavefunction has an enhanced amplitude in the region. (b) If the wavefunctions have opposite signs, then they interfere destructively, and the resulting superposition has a reduced amplitude.

## 1.3 Atomic orbitals

Chemists use hydrogenic atomic orbitals to develop models that are central to the interpretation of inorganic chemistry, and we shall spend some time describing their shapes and significance.

### (a) Hydrogenic energy levels

**KEY POINTS** The energy of the bound electron is determined by  $n$ , the principal quantum number; in addition,  $l$  specifies the magnitude of the orbital angular momentum and  $m_l$  specifies the orientation of that angular momentum.

Each of the wavefunctions obtained by solving the Schrödinger equation for a hydrogenic atom is uniquely labelled by a set of three integers called **quantum numbers**. These quantum numbers are designated  $n$ ,  $l$ , and  $m_l$ ;  $n$  is called the **principal quantum number**,  $l$  is the **orbital angular momentum quantum number** (formerly the ‘azimuthal quantum number’), and  $m_l$  is called the **magnetic quantum number**. Each quantum number specifies a physical property of the electron:  $n$  specifies the energy,  $l$  labels the magnitude of the orbital angular momentum, and  $m_l$  labels the orientation of that angular momentum. The value of  $n$  also indicates the size of the orbital, with larger  $n$ , high-energy orbitals, more diffuse than low  $n$ , compact, tightly bound, low-energy orbitals. The value of  $l$  also indicates the angular shape of the orbital, with the number of lobes increasing as  $l$  increases. The value of  $m_l$  also indicates the orientation of these lobes.

The allowed energies are specified by the principal quantum number,  $n$ . For a hydrogenic atom of atomic number  $Z$ , they are given by

$$E_n = -\frac{hcRZ^2}{n^2} \quad (1.3)$$

with  $n = 1, 2, 3, \dots$  and

$$R = \frac{m_e e^4}{8h^3 c \epsilon_0^2} \quad (1.4)$$

(The fundamental constants in this expression are given inside the back cover.) The calculated numerical value of  $R$  is  $1.097 \times 10^7 \text{ m}^{-1}$ , in excellent agreement with the empirical value determined spectroscopically by Rydberg. For future reference, the value of  $hcR$  corresponds to 13.6 eV or 1312.196 kJ mol<sup>-1</sup>.

#### A NOTE ON GOOD PRACTICE

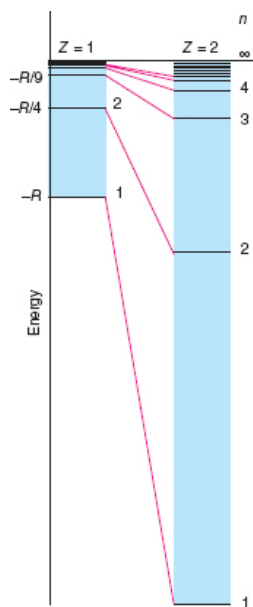
An electronvolt is the amount of kinetic energy gained by an electron as it accelerates through a potential of one volt. It is a useful, but non-SI, unit. In chemistry, kinetic energy gained by a mole of electrons passing through a potential of one volt is 96.485 kJ mol<sup>-1</sup>. The approximation 1 eV  $\approx$  100 kJ mol<sup>-1</sup> is worth remembering. The Faraday constant,  $F$ , the electric charge of a mole of electrons is 96 485

The energies given by eqn. 1.3 are all negative, signifying that the energy of the electron in a bound state is lower than a widely separated stationary electron and nucleus. The zero of energy (at  $n = \infty$ ) corresponds to the electron and nucleus being widely separated and stationary. Positive values of the energy correspond to unbound states of the electron in which it may travel with any velocity and hence possess any energy. Finally, because the energy is proportional to  $1/n^2$ , the energy levels in the bound state converge as the energy increases (becomes less negative, Fig. 1.5).

The value of  $l$  specifies the magnitude of the orbital angular momentum through  $\{l(l+1)\}^{1/2}\hbar$ , with  $l = 0, 1, 2, \dots$ . We can think of  $l$  as indicating the momentum with which the electron circulates around the nucleus via the lobes of the orbital. As we shall see shortly, the third quantum number  $m_l$  specifies the orientation of this momentum, for instance whether the circulation is clockwise or anticlockwise.

### (b) Shells, subshells, and orbitals

**KEY POINTS** All orbitals with a given value of  $n$  belong to the same shell, all orbitals of a given shell with the same value of  $l$  belong to the same subshell, and individual orbitals are distinguished by the value of  $m_l$ .



**FIGURE 1.5** The quantized energy levels of an H atom ( $Z=1$ ) and an  $\text{He}^+$  ion ( $Z=2$ ). The energy levels of a hydrogenic atom are proportional to  $Z^2$ .

In a hydrogenic atom, all orbitals with the same value of  $n$  have the same energy and are said to be **degenerate**. The principal quantum number therefore defines a series of **shells** of the atom, or sets of orbitals with the same value of  $n$  and hence with the same energy and approximately the same radial extent. Shells with  $n = 1, 2, 3, \dots$  are sometimes referred to as K, L, M,  $\dots$  shells, for example when electronic transitions between these shells are referred to in X-ray spectroscopy.

The orbitals belonging to each shell are classified into **subshells** distinguished by a quantum number  $l$ . For a given value of  $n$ , the quantum number  $l$  can have the values  $l = 0, 1, \dots, n-1$ , giving  $n$  different values in all. For example, the shell with  $n = 1$  consists of just one subshell with  $l = 0$ , the shell with  $n = 2$  consists of two subshells, one with  $l = 0$  and the other with  $l = 1$ , the shell with  $n = 3$  consists of three subshells, with values of  $l$  of 0, 1, and 2. It is common practice to refer to each subshell by a letter:

Value of $l$	0	1	2	3	4	$\dots$
Subshell designation	s	p	d	f	g	$\dots$

For most purposes in chemistry we need consider only s, p, d, and f subshells.<sup>2</sup>

A subshell with quantum number  $l$  consists of  $2l + 1$  individual orbitals. These orbitals are distinguished by the **magnetic quantum number**,  $m_l$ , which can have the  $2l + 1$  integer values from  $+l$  down to  $-l$ . This quantum number specifies the component of orbital angular momentum around an arbitrary axis (commonly designated  $z$ ) passing through the nucleus. So, for example, a d subshell of an atom ( $l = 2$ )

consists of five individual atomic orbitals that are distinguished by the values  $m_l = +2, +1, 0, -1, -2$ . An f subshell ( $l = 3$ ) consists of seven individual atomic orbitals with the values  $m_l = +3, +2, +1, 0, -1, -2, -3$ .

### A NOTE ON GOOD PRACTICE

Write the sign of  $m_l$  even when it is positive. Thus, we write  $m_l = +2$ , not  $m_l = 2$ .

The practical conclusion for chemistry from these rules is that there is only one orbital in an s subshell ( $l = 0$ ), the one with  $m_l = 0$ : this orbital is called an **s orbital**. There are three orbitals in a p subshell ( $l = 1$ ), with quantum numbers  $m_l = +1, 0, -1$ ; they are called **p orbitals**. The five orbitals of a d subshell ( $l = 2$ ) are called **d orbitals**, with quantum numbers  $m_l = +2, +1, 0, -1, -2$  and so on (Fig. 1.6).

### Identifying orbitals from quantum numbers

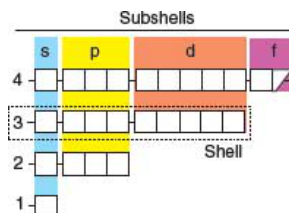
Which set of orbitals is defined by  $n = 4$  and  $l = 1$ ? How many orbitals are there in this set?

**Answer** We need to remember that the principal quantum number  $n$  identifies the shell and that the orbital quantum number  $l$  identifies the subshell. The subshell with  $l = 1$  consists of p orbitals. The allowed values of  $m_l = +l, \dots, -l$  give the number of orbitals of that type. In this case,  $m_l = +1, 0, \text{ and } -1$ . There are therefore three 4p orbitals.

**Self-test 1.2** (a) Which set of orbitals is defined by the quantum numbers  $n = 3$  and  $l = 2$ ? How many orbitals are there in this set? (b) What are the quantum numbers  $n$  and  $l$  that define a 5f orbital? How many orbitals are there in this set?

### (c) Electron spin

**KEY POINTS** The intrinsic spin angular momentum of an electron is defined by the two quantum numbers  $s$  and  $m_s$ . Four quantum numbers are needed to define the state of an electron in a hydrogenic atom.



**FIGURE 1.6** The classification of orbitals into subshells (same value of  $l$ ) and shells (same value of  $n$ ).

In addition to the three quantum numbers required to specify the spatial distribution of an electron in a hydrogenic atom, two more quantum numbers are needed to define the state of an electron. These additional quantum numbers relate to the intrinsic angular momentum of an electron, its **spin**. This evocative name suggests that an electron can be regarded as having an angular momentum arising from a spinning motion, rather like the daily rotation of the earth as it travels in its annual orbit around the sun. However, spin is a quantum mechanical property and this analogy must be viewed with great caution.

Spin is described by two quantum numbers,  $s$  and  $m_s$ . The former is the analogue of  $l$  for orbital motion but it is restricted to the single, unchangeable value  $s = \frac{1}{2}$ . The magnitude of the spin angular momentum is given by the expression  $\{s(s + 1)\}^{1/2}\hbar$ , so when we substitute for  $s = \frac{1}{2}$  we find that this magnitude is fixed at  $\frac{1}{2}\sqrt{3}\hbar$  for any electron. The second quantum number, the **spin magnetic quantum number**,  $m_s$ , may take only two values,  $+\frac{1}{2}$  (anticlockwise spin, imagined from above) and  $-\frac{1}{2}$  (clockwise spin). The two states are often represented by the two arrows  $\uparrow$  ('spin-up',  $m_s = +\frac{1}{2}$ ) and  $\downarrow$  ('spin-down',  $m_s = -\frac{1}{2}$ ) or by the Greek letters  $\alpha$  and  $\beta$ , respectively.

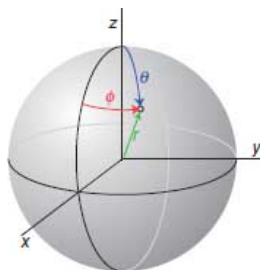
Because the spin state of an electron must be specified if the state of the atom is to be specified fully, it is common to say that the state of an electron in a hydrogenic atom is characterized by four quantum numbers, namely  $n$ ,  $l$ ,  $m_l$ , and  $m_s$ .

### (d) Nodes

**KEY POINT** Regions where wavefunctions pass through zero are called nodes. Inorganic chemists generally find it adequate to use visual representations of atomic orbitals rather than mathematical expressions. However, we need to be aware of the mathematical expressions that underlie these representations.

Because the potential energy of an electron in the field of a nucleus is spherically symmetric (it is proportional to  $Z/r$  and independent of orientation relative to the nucleus), the orbitals are best expressed in terms of the spherical polar coordinates defined in Fig. 1.7, rather than the Cartesian coordinates,  $x$ ,  $y$ , and  $z$ . In these coordinates, the orbitals all have the form

$$\psi_{nlm} = \overbrace{R_{nl}(r)}^{\text{Variation with radius}} \times \overbrace{Y_{lm}(\theta, \phi)}^{\text{Variation with angle}} \quad (1.5)$$



**FIGURE 1.7** Spherical polar coordinates:  $r$  is the radius,  $\theta$  (theta) the colatitude, and  $\phi$  (phi) the azimuth.

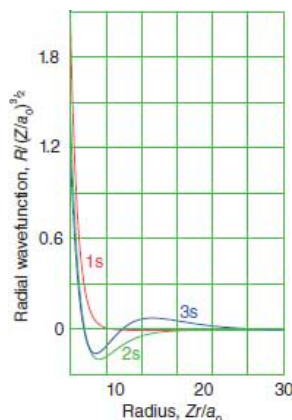
This expression reflects the simple idea that a hydrogenic orbital can be written as the product of a function  $R(r)$  of the radius (the distance the electron is from the nucleus) and a function  $Y(\theta, \phi)$  of the angular coordinates. The positions where either component of the wavefunction passes through zero are called **nodes**. Consequently, there are two types of nodes. **Radial nodes** occur where the radial component of the wavefunction passes through zero and **angular nodes** occur where the angular component of the wavefunction passes through zero. The numbers of both types of node increase with increasing energy and are related to the quantum numbers  $n$  and  $l$ . The total number of radial and angular nodes for any orbital is equal to  $n - 1$ .

### (e) The radial variation of atomic orbitals

**KEY POINT** An s orbital has nonzero amplitude at the nucleus; all other orbitals (those with  $l > 0$ ) vanish at the nucleus.

Figures 1.8 and 1.9 show the radial variations of some atomic orbitals. A 1s orbital, the wavefunction with  $n = 1$ ,  $l = 0$ , and  $m_l = 0$ , decays exponentially with distance from the nucleus and never passes through zero (it has no nodes). All orbitals decay exponentially at sufficiently great distances from the nucleus and this distance increases as  $n$  increases. Some orbitals oscillate through zero close to the nucleus and thus have one or more radial nodes before beginning their final exponential decay. As the principal quantum number of an electron increases, it is likely to be found further away from the nucleus and its energy increases.

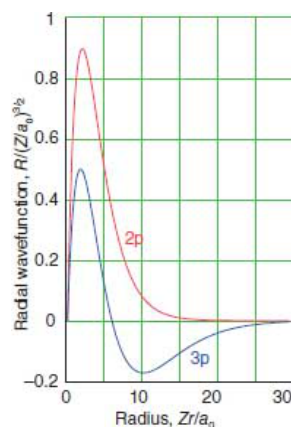
An orbital with quantum numbers  $n$  and  $l$  has  $n - l - 1$  radial nodes. This oscillation is evident in the 2s orbital, the orbital with  $n = 2$ ,  $l = 0$ , and  $m_l = 0$ , which passes through zero once and hence has one radial node. A 3s orbital passes through zero twice and so has two radial nodes (Fig. 1.8). A 2p orbital (one of the three orbitals with  $n = 2$  and  $l = 1$ ) has no radial node because its radial wavefunction does not pass through zero anywhere. For any series of the same type of orbital, the first occurrence has no radial node, the second has one radial node, and so on.



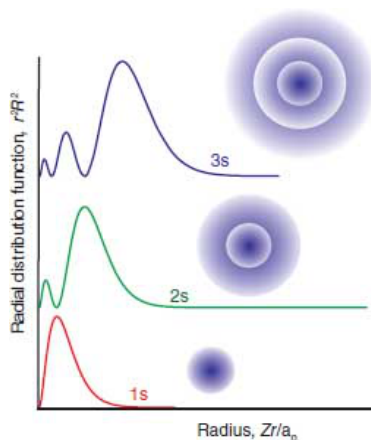
**FIGURE 1.8** The radial wavefunctions of the 1s, 2s, and 3s hydrogenic orbitals. Note that the number of radial nodes is 0, 1, and 2, respectively. Each orbital has a nonzero amplitude at the nucleus (at  $r = 0$ ).

Although an electron in an s orbital may be found at the nucleus, an electron in any other type of orbital will not be found there. We shall

soon see that this apparently minor detail, which is a consequence of the absence of orbital angular momentum when  $l = 0$ , is one of the key concepts for understanding the layout of the periodic table and the chemistry of the elements.



**FIGURE 1.9** The radial wavefunctions of the 2p and 3p hydrogenic orbitals. Note that the number of radial nodes is 0 and 1, respectively. Each orbital has zero amplitude at the nucleus (at  $r = 0$ ).



**FIGURE 1.10** The 1s, 2s, and 3s orbitals showing the radial nodes.

### Predicting numbers of radial nodes

How many radial nodes do 3p, 3d, and 4f orbitals each have?

**Answer** We need to make use of the fact that the number of radial nodes is given by the expression  $n - l - 1$  and use it to find the number of radial nodes using values of  $n$  and  $l$ . The 3p orbitals have  $n = 3$  and  $l = 1$  and so the number of radial nodes is  $n - l - 1 = 1$ . The 3d orbitals have  $n = 3$  and  $l = 2$ . Therefore, the number of radial nodes is  $n - l - 1 = 0$ . The 4f orbitals have  $n = 4$  and  $l = 3$  and the number of radial nodes is  $n - l - 1 = 0$ . The 3d and 4f orbitals are the first occurrence of the d and f orbitals so this also indicates that they will have no radial node. The 3p orbitals are the second occurrence of the p orbitals and so we would expect them to have one radial node.

**Self-test 1.3** (a) How many radial nodes does a 5s orbital have? (b) Which p orbital has two radial nodes?

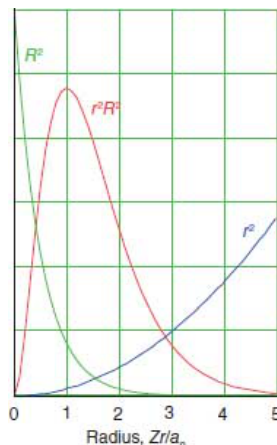
### (f) The radial distribution function

**KEY POINT** A radial distribution function gives the probability that an electron will be found at a given distance from the nucleus, regardless of the direction.

The Coulombic (electrostatic) force that binds the electron is centred on the nucleus, so it is often of interest to know the probability of

finding an electron at a given distance from the nucleus, regardless of its direction. This information enables us to judge how tightly the electron is bound. The total probability of finding the electron in a spherical shell of radius  $r$  and thickness  $dr$  is the integral of  $\psi^2 d\tau$  over all angles. This result is written  $P(r)dr$ , where  $P(r)$  is called the **radial distribution function**. In general,

$$P(r) = r^2 R(r)^2 \quad (1.6)$$



**FIGURE 1.11** The radial distribution function,  $r^2 R^2$ , of a hydrogenic 1s orbital.  $r^2 R^2$  is the product of  $r^2$  (which increases as  $r$  increases) and the square of the radial component of the wavefunction  $\Psi$  (labelled  $R^2$  in the figure and which decreases exponentially). The radial distribution function passes through a maximum at  $r = a_0/Z$ .

(For s orbitals, this expression is the same as  $P = 4\pi r^2 \psi^2$ .) If we know the value of  $P$  at some radius  $r$ , then we can state the probability of finding the electron somewhere in a shell of thickness  $dr$  at that radius simply by multiplying  $P$  by  $dr$ .

Because the wavefunction of a 1s orbital decreases exponentially with distance from the nucleus and the factor  $r^2$  in eqn. 1.6 increases, the radial distribution function of a 1s orbital goes through a maximum (Fig. 1.11). Therefore, there is a distance at which the electron is most likely to be found. In general, this most probable distance decreases as the nuclear charge increases (because the electron is attracted more strongly to the nucleus), and specifically

$$r_{\max} = \frac{a_0}{Z} \quad (1.7)$$

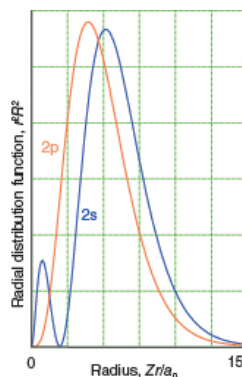
where  $a_0$  is the **Bohr radius**,  $a_0 = \epsilon_0 \hbar^2 / \pi m_e e^2$ , a quantity that appeared in Bohr's formulation of his model of the atom; its numerical value is 52.9 pm. The most probable distance increases as  $n$  increases because the higher the energy, the more likely it is that the electron will be found far from the nucleus.

### Interpreting radial distribution functions

Figure 1.12 shows the radial distribution functions for 2s and 2p hydrogenic orbitals. Which orbital gives the electron a greater probability of close approach to the nucleus?

**Answer** By examining Fig. 1.12 we can see that the radial distribution function of a 2p orbital approaches zero near the nucleus faster than a 2s electron does. This difference is a consequence of the fact that a 2p orbital has zero amplitude at the nucleus on account of its orbital angular momentum. The 2s electron has a greater probability of close approach to the nucleus indicated by the inner maximum. Note that the 2s orbital extends further into space.

**Self-test 1.4** Which orbital, 3p or 3d, gives an electron a greater probability of being found close to the nucleus?

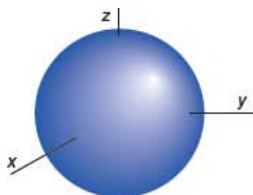


**FIGURE 1.12** The radial distribution functions of hydrogenic orbitals. Although the 2p orbital is *on average* closer to the nucleus (note where its maximum lies), an electron in a 2s orbital has a high probability of being close to the nucleus on account of the inner maximum.

### (g) The angular variation of atomic orbitals

**KEY POINTS** The boundary surface of an orbital indicates the region of space within which the electron is most likely to be found; orbitals with the quantum number  $l$  have  $l$  nodal planes.

The angular wavefunction expresses the variation of angle around the nucleus and this describes the orbital's angular shape. An s orbital has the same amplitude at a given distance from the nucleus whatever the angular coordinates of the point of interest: that is, an s orbital is spherically symmetrical. The orbital is normally represented by a spherical surface with the nucleus at its centre. The surface is called the **boundary surface** of the orbital, and defines the region of space within which there is a high (typically 90%) probability of finding the electron. This boundary surface is what chemists draw to represent the shape of an orbital. The planes on which the angular wavefunction passes through zero are called **angular nodes** or **nodal planes**. An electron will not be found anywhere on a nodal plane. A nodal plane cuts through the nucleus and separates the regions of positive and negative sign of the wavefunction.



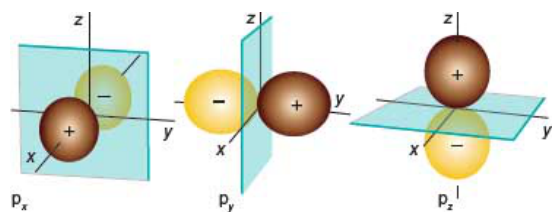
**FIGURE 1.13** The spherical boundary surface of an s orbital.

In general, an orbital with the quantum number  $l$  has  $l$  nodal planes. An s orbital, with  $l = 0$ , has no nodal plane and the boundary surface of the orbital is spherical (Fig. 1.13).

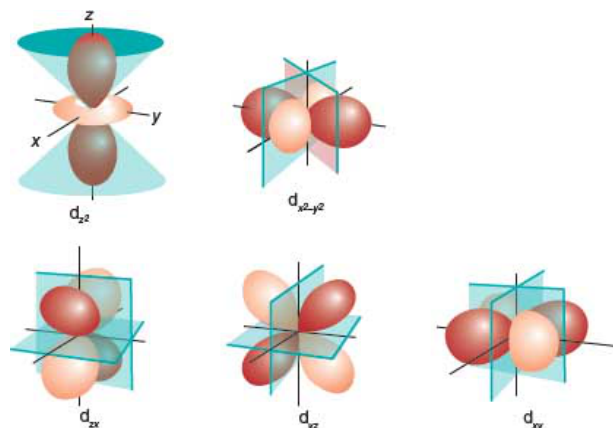
All orbitals with  $l > 0$  have amplitudes that vary with angle and, for p orbitals,  $m_l$  values of +1, 0, and -1. In the most common graphical representation, the boundary surfaces of the three p orbitals of a given shell are identical apart from the fact that their axes lie parallel to each of the three different Cartesian axes centred on the nucleus, and each one possesses a nodal plane passing through the nucleus (Fig. 1.14). In the diagrammatic representation of the orbitals the two lobes are shaded differently (dark and light respectively) or labelled '+' and '-' to indicate that one has a positive and one has a negative amplitude. This representation is the origin of the labels  $p_x$ ,  $p_y$ , and  $p_z$ . Each p orbital, with  $l = 1$ , has a single nodal plane.

The boundary surfaces and labels we use for the d and f orbitals are shown in Figs 1.15 and 1.16, respectively. The  $d_{z^2}$  orbital looks different from the remaining d orbitals. There are in fact six possible combinations of double dumb-bell shaped orbitals around three axes: three with lobes between the axes, as in  $d_{xy}$ ,  $d_{yz}$ , and  $d_{zx}$ , and three with lobes along the axis. However, only five d orbitals are allowed. One of these orbitals is assigned  $d_{x^2-y^2}$  and lies along the x and y axes. The remaining orbital is the  $d_{2z^2-x^2-y^2}$  from the algebra which is simplified to  $d_{z^2}$  and can be thought of as the superposition of the remaining two combinations, the  $d_{z^2}$  and the other the  $d_{z^2-x^2}$ . Note that a d orbital (with  $l = 2$ ) has two nodal planes that intersect at the nucleus; a typical f orbital ( $l = 3$ ) has three nodal planes.

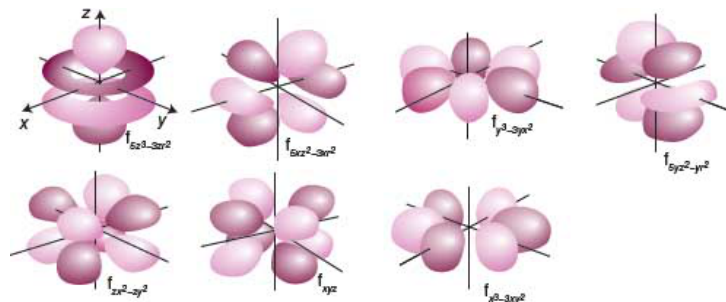




**FIGURE 1.14** The representation of the boundary surfaces of the p orbitals. Each orbital has one nodal plane running through the nucleus. For example, the nodal plane of the  $p_z$  orbital is the  $xy$ -plane. The darkly shaded lobe has a positive amplitude, the more lightly shaded one is negative.



**FIGURE 1.15** One representation of the boundary surfaces of the d orbitals. Four of the orbitals have two perpendicular nodal planes that intersect in a line passing through the nucleus. In the  $d_{z^2}$  orbital, the nodal surface forms two cones that meet at the nucleus.



**FIGURE 1.16** One representation of the boundary surfaces of the f orbitals. Other representations (with different shapes) are also sometimes encountered.

## Many-electron atoms

As we have remarked, a ‘many-electron atom’ is an atom with more than one electron, so even He, with two electrons, is technically a many-electron atom. The exact solution of the Schrödinger equation for an atom with  $N$  electrons would be a function of the  $3N$  coordinates of all the electrons. It would be extremely challenging to find exact formulas for such complicated functions; however, it is straightforward to perform numerical computations by using widely available software to obtain precise energies and probability densities. This software can also generate graphical representations of the resulting orbitals that can assist in the interpretation of the properties of the atom. For most of inorganic chemistry we rely on the **orbital approximation**, in which each electron occupies an atomic orbital that resembles those found in hydrogenic atoms. When we say that an electron ‘occupies’ an atomic orbital, we mean that it is described by the corresponding wavefunction and set of quantum numbers.

### 1.4 Penetration and shielding

**KEY POINTS** The ground-state electron configuration is a specification of the orbital occupation of an atom in its lowest energy state. The exclusion principle forbids more than two electrons to occupy a single orbital. The nuclear charge experienced by an electron is reduced by shielding by other electrons, including those in the same shell. Trends in effective nuclear charge can be used to rationalize the trends in many

**properties. As a result of the combined effects of penetration and shielding, the order of energy levels in a shell of a many-electron atom is  $s < p < d < f$ .**

It is quite easy to account for the electronic structure of the helium atom in its **ground state**, its state of lowest energy. According to the orbital approximation, we suppose that both electrons occupy an atomic orbital that has the same spherical shape as a hydrogenic 1s orbital. However, the orbital will be more compact because, as the nuclear charge of helium is greater than that of hydrogen, the electrons are drawn in towards the nucleus more closely than is the one electron of an H atom. The ground-state **configuration** of an atom is a statement of the orbitals its electrons occupy in the ground state. For helium, with two electrons in the 1s orbital, the ground-state configuration is denoted  $1s^2$  (read as ‘one s two’).

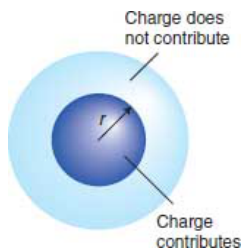
As soon as we come to the next atom in the periodic table, lithium ( $Z = 3$ ), we encounter several major new features. The configuration  $1s^3$  is forbidden by a fundamental feature of nature known as the **Pauli exclusion principle**:

*No more than two electrons may occupy a single orbital and, if two do occupy a single orbital, then their spins must be paired.*

By ‘paired’ we mean that one electron spin must be  $\uparrow$  ( $m_s = +\frac{1}{2}$ ) and the other  $\downarrow$  ( $m_s = -\frac{1}{2}$ ); the pair is denoted  $\uparrow\downarrow$ . Another way of expressing the principle is to note that, because an electron in an atom is described by four variable quantum numbers,  $n$ ,  $l$ ,  $m_l$ , and  $m_s$ , no two electrons can have the same four quantum numbers. The Pauli principle was introduced originally to account for the absence of certain transitions in the spectrum of atomic helium.

Because the configuration  $1s^3$  is forbidden by the Pauli exclusion principle, the third electron must occupy an orbital of the next higher shell, the shell with  $n = 2$ . The question that now arises is whether the third electron occupies a 2s orbital or one of the three 2p orbitals. To answer this question, we need to examine the energies of the two subshells and the effect of the other electrons in the atom. Although 2s and 2p orbitals have the same energy in a hydrogenic atom, spectroscopic data and calculations show that this is not the case in a many-electron atom.

In the orbital approximation, we treat the repulsion between electrons in an approximate manner by supposing that the electronic charge is distributed spherically around the nucleus. Then each electron moves in the attractive field of the nucleus and also experiences an average repulsive charge from the other electrons. According to classical electrostatics, the field that arises from a spherical distribution of charge is equivalent to the field generated by a single point charge at the centre of the distribution (Fig. 1.17). This negative charge reduces the actual charge of the nucleus,  $Z$ , to  $Z_{\text{eff}}$ , where  $Z_{\text{eff}}$  is called the **effective nuclear charge**.



**FIGURE 1.17** The electron at the  $r$  radius experiences a repulsion from the total charge within the sphere of radius  $r$ ; charge outside that radius has no net effect.

This effective nuclear charge depends on the values of  $n$  and  $l$  of the electron of interest because electrons in different shells and subshells approach the nucleus to different extents. The reduction of the true nuclear charge to the effective nuclear charge by the other electrons is called **shielding**. The effective nuclear charge is sometimes expressed in terms of the true nuclear charge and an empirical **shielding constant**,  $\sigma$ , by writing  $Z_{\text{eff}} = Z - \sigma$ . The shielding constant can be determined by fitting hydrogenic orbitals to those computed numerically.

It can also be approximated by using the empirical set of rules, Slater’s rules.

Slater’s rules attribute a numerical contribution to electrons in an atom in the following way:

Write out the electron configuration of the atom and group orbitals together in the form

$(1s)(2s2p)(3s3p)(3d)(4s4p)(4d)(4f)(5s5p)$  etc.

If the outermost electron is in an s or p orbital,

Each of the other electrons in the  $(ns np)$  grouping contributes 0.35 to  $\sigma$ ;

Each electron in the  $n - 1$  shell contributes 0.85 to  $\sigma$ ;

Each electron in lower shells contributes 1.0 to  $\sigma$ .

If the outermost electron is in a d or f orbital,

Each of the other electrons in the  $(nd)$  or  $(nf)$  grouping contributes 0.35 to  $\sigma$ ;