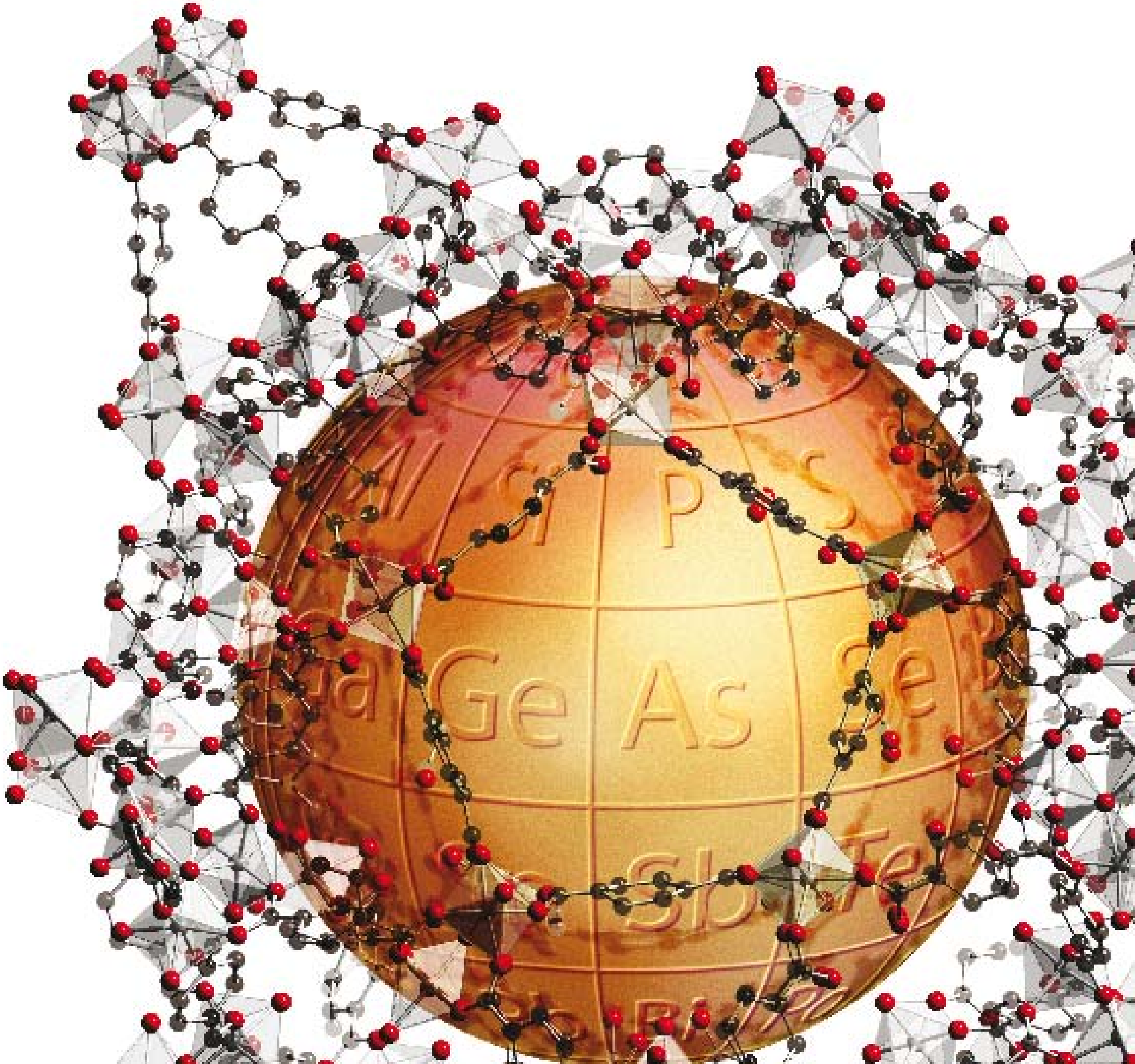
Fifth Edition

Shriver & Atkins

Inorganic Chemistry

Atkins • Overton • Rourke • Weller • Armstrong



The elements

Name	Symbol	Atomic number	Molar mass (g mol^{-1})
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	264
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
Copernicum	?	112	?
Copper	Cu	29	63.55
Curium	Cm	96	247
Darmstadtium	Ds	110	271
Dubnium	Db	105	262
Dysprosium	Dy	66	162.50
Einsteinium	Es	99	252
Erbium	Er	68	167.27
Europium	Eu	63	151.96
Fermium	Fm	100	257
Fluorine	F	9	19.00
Francium	Fr	87	223
Gadolinium	Gd	64	157.25
Gallium	Ga	31	69.72
Germanium	Ge	32	72.64
Gold	Au	79	196.97
Hafnium	Hf	72	178.49
Hassium	Hs	108	269
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	55.84
Krypton	Kr	36	83.80
Lanthanum	La	57	138.91
Lawrencium	Lr	103	262
Lead	Pb	82	207.2
Lithium	Li	3	6.94
Lutetium	Lu	71	174.97
Magnesium	Mg	12	24.31
Manganese	Mn	25	54.94
Meitnerium	Mt	109	268
Mendelevium	Md	101	258
Mercury	Hg	80	200.59
Molybdenun	Mo	42	95.94
Neodymium	Nd	60	144.24
Neon	Ne	10	20.18
Neptunium	Np	93	237
Nickel	Ni	28	58.69
Niobium	Nb	41	92.91
Nitrogen	N	7	14.01
Nobelium	No	102	259
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	272
Rubidium	Rb	37	85.47
Ruthenium	Ru	44	101.07
Rutherfordium	Rf	104	261
Samarium	Sm	62	150.36
Scandium	Sc	21	44.96
Seaborgium	Sg	106	266
Selenium	Se	34	78.96
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
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	173.04
Yttrium	Y	39	88.91
Zinc	Zn	30	65.41
Zirconium	Zr	40	91.22

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Shriver & Atkins'

Inorganic Chemistry

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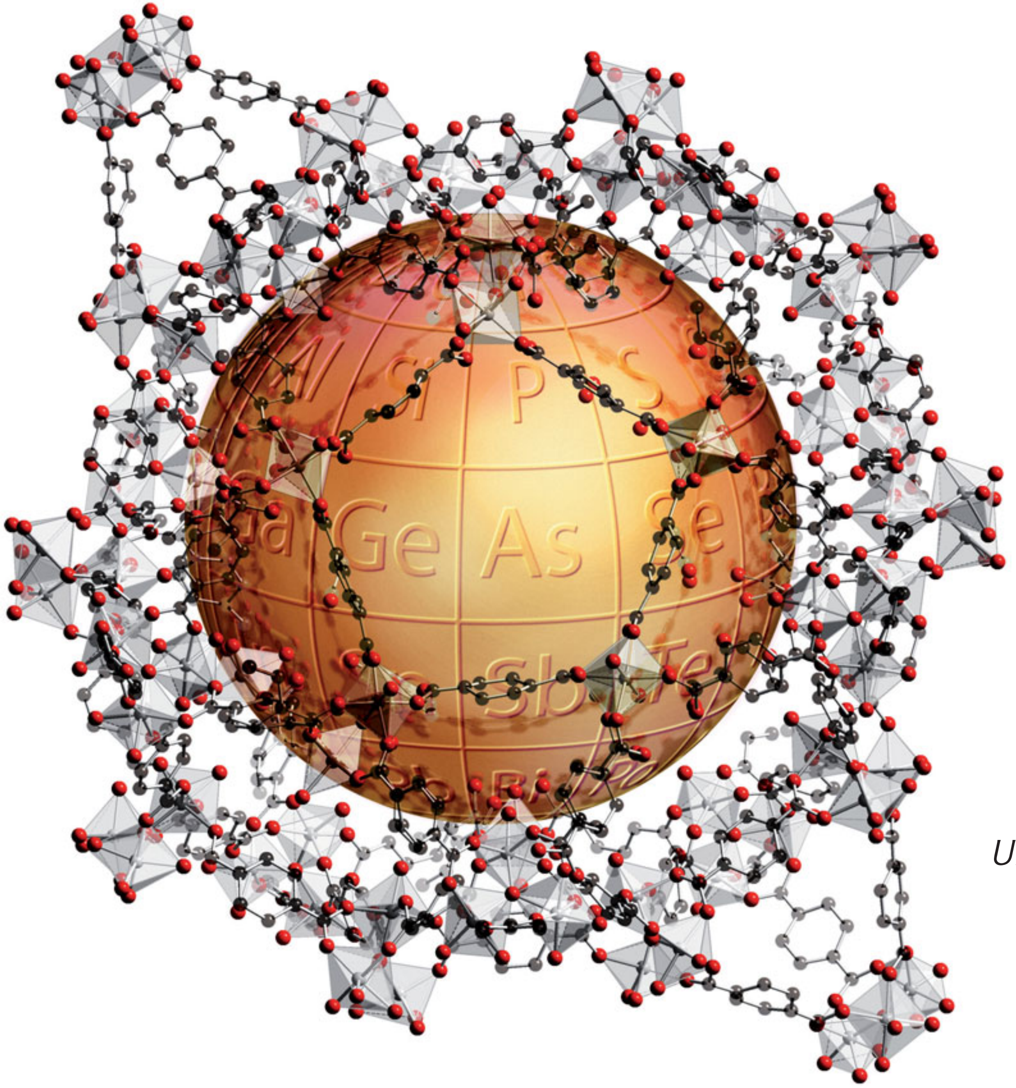

Fifth Edition

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Preface

Our aim in the fifth edition of *Shriver and Atkins' Inorganic Chemistry* is to provide a comprehensive 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. These elements range from highly reactive metals, such as sodium, to noble metals, such as gold. The nonmetals include solids, liquids, and gases, and range from the aggressive oxidizing agent fluorine to 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 discipline. 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 a foundation on which to build understanding.

Inorganic compounds vary from ionic solids, which can be described by simple applications of classical electrostatics, to covalent compounds and metals, which are best described by models that have their origin in quantum mechanics. We can rationalize and interpret the properties of most inorganic compounds by using qualitative models that are based on quantum mechanics, such as atomic orbitals and their use to form molecular orbitals. The text builds on similar qualitative bonding models that should already be familiar from introductory chemistry courses. Although qualitative models of bonding and reactivity clarify and systematize the subject, inorganic chemistry is essentially an experimental subject. New areas of inorganic chemistry are constantly being explored and new and often unusual inorganic compounds are constantly being synthesized and identified. These new inorganic syntheses continue to enrich the field with compounds that give us new perspectives on structure, bonding, and reactivity.

Inorganic chemistry has considerable impact on our everyday lives and on other scientific disciplines. The chemical industry is strongly dependent on it. Inorganic chemistry is essential to the formulation and improvement of modern materials such as catalysts, semiconductors, optical devices, superconductors, and advanced ceramic materials. The environmental and biological impact of inorganic chemistry is also huge. Current topics in industrial, biological, and environmental chemistry are mentioned throughout the book and are developed more thoroughly in later chapters.

In this new edition we have refined the presentation, organization, and visual representation. All of the book has been revised, much has been rewritten and there is some completely new material. We have written with the student in mind, and we have added new pedagogical features and have enhanced others.

The topics in Part 1, *Foundations*, have been revised to make them more accessible to the reader with more qualitative explanation accompanying the more mathematical treatments.

Part 2, *The elements and their compounds*, has been reorganized. The section starts with a new chapter which draws together periodic trends and cross references forward to the descriptive chapters. The remaining chapters start with hydrogen and proceed across the periodic table from the s-block metals, across the p block, and finishing with the d- and f-block elements. Most of these chapters have been reorganized into two sections: *Essentials* describes the essential chemistry of the elements and the *Detail* provides a more thorough account. The chemical properties of each group of elements and their compounds are enriched with descriptions of current applications. The patterns and trends that emerge are rationalized by drawing on the principles introduced in Part 1.

Part 3, *Frontiers*, takes the reader to the edge of knowledge in several areas of current research. These chapters explore specialized subjects that are of importance to industry, materials, and biology, and include catalysis, nanomaterials, and bioinorganic chemistry.

All the illustrations and the marginal structures—nearly 1500 in all—have been redrawn and are presented in full colour. We have used colour systematically rather than just for decoration, and have ensured that it serves a pedagogical purpose.

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 inorganic chemistry. It should help to rationalize the sometimes bewildering diversity of descriptive 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.

Peter Atkins
Tina Overton
Jonathan Rourke
Mark Weller
Fraser Armstrong
Mike Hagerman

March 2009

Acknowledgements

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 would particularly like to thank Jennifer Armstrong, University of Southampton; Sandra Dann, University of Loughborough; Rob Deeth, University of Warwick; Martin Jones, Jennifer Creen, and Russ Egdell, University of Oxford, for their guidance and advice.

Many of the figures in Chapter 27 were produced using PyMOL software; for more information see DeLano, W.L. The PyMOL Molecular Graphics System (2002), De Lano Scientific, San Carlos, CA, USA.

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David Weatherburn, University of Victoria, Wellington
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Jingdong Zhang, Denmark Technical University

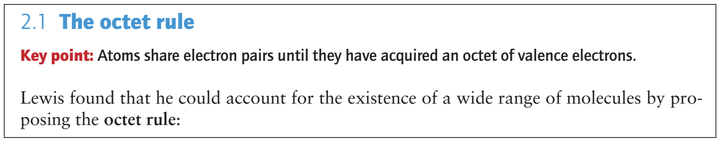
About the book

Inorganic chemistry is an extensive subject that at first sight can seem daunting. We have made every effort to help by organizing the information in this textbook systematically, and by including numerous features that are designed to make learning inorganic chemistry more effective and more enjoyable. Whether you work through the book chronologically or dip in at an appropriate point in your studies, this text will engage you and help you to develop a deeper understanding of the subject. We have also provided further electronic resources in the accompanying Book Companion Site. The following paragraphs explain the features of the text and website in more detail.

Organizing the information

Key points

The key points act as a summary of the main take-home message(s) of the section that follows. They will alert you to the principal ideas being introduced.



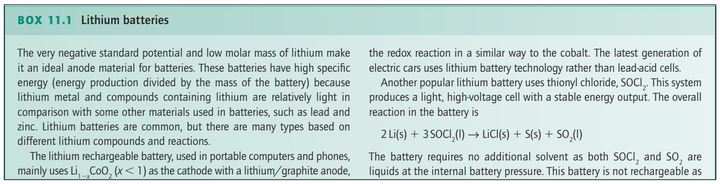
2.1 The octet rule

Key point: Atoms share electron pairs until they have acquired an octet of valence electrons.

Lewis found that he could account for the existence of a wide range of molecules by proposing the **octet rule**:

Context boxes

The numerous context boxes illustrate the diversity of inorganic chemistry and its applications to advanced materials, industrial processes, environmental chemistry, and everyday life, and are set out distinctly from the text itself.



BOX 11.1 Lithium batteries

The very negative standard potential and low molar mass of lithium make it an ideal anode material for batteries. These batteries have high specific energy (energy production divided by the mass of the battery) because lithium metal and compounds containing lithium are relatively light in comparison with some other materials used in batteries, such as lead and zinc. Lithium batteries are common, but there are many types based on different lithium compounds and reactions.

The lithium rechargeable battery, used in portable computers and phones, mainly uses $Li_{1-x}CoO_2$ ($x < 1$) as the cathode with a lithium/graphite anode, the redox reaction in a similar way to the cobalt. The latest generation of electric cars uses lithium battery technology rather than lead-acid cells.

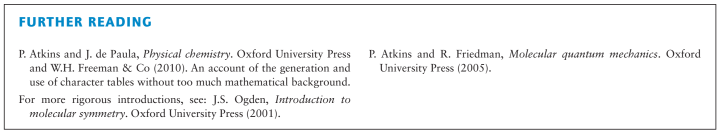
Another popular lithium battery uses thionyl chloride, $SOCl_2$. This system produces a light, high-voltage cell with a stable energy output. The overall reaction in the battery is

$$2\,Li(s) + 3\,SOCl_2(l) \rightarrow LiCl(s) + S(s) + SO_2(l)$$

The battery requires no additional solvent as both $SOCl_2$ and SO_2 are liquids at the internal battery pressure. This battery is not rechargeable as

Further reading

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



FURTHER READING

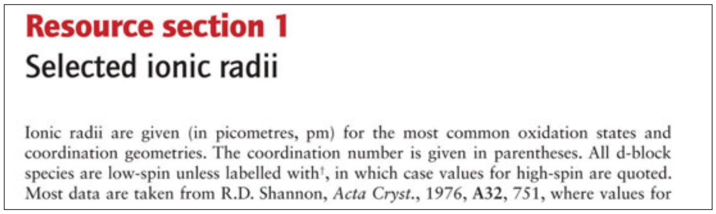
P. Atkins and J. de Paula, *Physical chemistry*. Oxford University Press and W.H. Freeman & Co (2010). An account of the generation and use of character tables without too much mathematical background.

For more rigorous introductions, see: J.S. Ogden, *Introduction to molecular symmetry*. Oxford University Press (2001).

P. Atkins and R. Friedman, *Molecular quantum mechanics*. Oxford University Press (2005).

Resource section

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

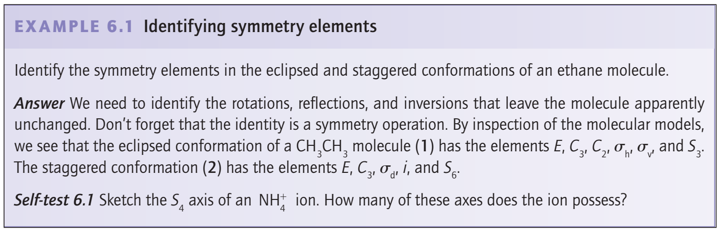


Resource section 1

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. All d-block species are low-spin unless labelled with†, in which case values for high-spin are quoted. Most data are taken from R.D. Shannon, *Acta Cryst.*, 1976, **A32**, 751, where values for

Problem solving



EXAMPLE 6.1 Identifying symmetry elements

Identify the symmetry elements in the eclipsed and staggered conformations of an ethane molecule.

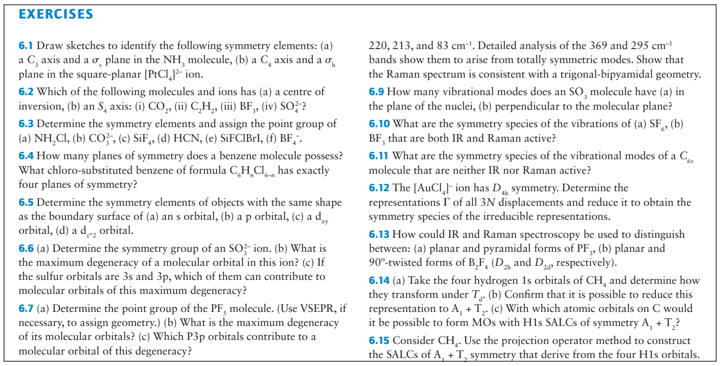
Answer We need to identify the rotations, reflections, and inversions that leave the molecule apparently unchanged. Don't forget that the identity is a symmetry operation. By inspection of the molecular models, we see that the eclipsed conformation of a CH_3CH_3 molecule (**1**) has the elements E, C_3, C_2, σ_h, σ_v, and S_3. The staggered conformation (**2**) has the elements E, C_3, σ_d, i, and S_6.

Self-test 6.1 Sketch the S_4 axis of an NH_4^+ ion. How many of these axes does the ion possess?

Examples and Self-tests

We have provided numerous *Worked examples* throughout the text. Each one illustrates an important aspect of the topic under discussion or provides practice with calculations and problems.

Each *Example* is followed by a *Self-test*, where the answer is provided as a check that the method has been mastered. Think of *Self-tests* as in-chapter exercises designed to help you monitor your progress.



EXERCISES

6.1 Draw sketches to identify the following symmetry elements: (a) a C_3 axis and a σ_v plane in the NH_3 molecule, (b) a C_4 axis and a σ_h plane in the square-planar $[PtCl_4]^{2-}$ ion.

6.2 Which of the following molecules and ions has (a) a centre of inversion, (b) an S_4 axis: (i) CO_2, (ii) C_2H_2, (iii) BF_3, (iv) SO_4^{2-}?

6.3 Determine the symmetry elements and assign the point group of (a) NH_2Cl, (b) CO_3^{2-}, (c) SiF_4, (d) HCN, (e) SiFClBrI, (f) BF_4^-.

6.4 How many planes of symmetry does a benzene molecule possess? What chloro-substituted benzene of formula $C_6H_nCl_{6-n}$ has exactly four planes of symmetry?

6.5 Determine the symmetry elements of objects with the same shape as the boundary surface of (a) an s orbital, (b) a p orbital, (c) a d_{xy} orbital, (d) a $d_{z\wedge2}$ orbital.

6.6 (a) Determine the symmetry group of an SO_3^{2-} ion. (b) What is the maximum degeneracy of a molecular orbital in this ion? (c) If the sulfur orbitals are 3s and 3p, which of them can contribute to molecular orbitals of this maximum degeneracy?

6.7 (a) Determine the point group of the PF_5 molecule. (Use VSEPR, if necessary, to assign geometry.) (b) What is the maximum degeneracy of its molecular orbitals? (c) Which P3p orbitals contribute to a molecular orbital of this degeneracy?

220, 213, and 83 cm^{-1}. Detailed analysis of the 369 and 295 cm^{-1} bands show them to arise from totally symmetric modes. Show that the Raman spectrum is consistent with a trigonal-bipyamidal geometry.

6.9 How many vibrational modes does an SO_3 molecule have (a) in the plane of the nuclei, (b) perpendicular to the molecular plane?

6.10 What are the symmetry species of the vibrations of (a) SF_6, (b) BF_3 that are both IR and Raman active?

6.11 What are the symmetry species of the vibrational modes of a C_{6v} molecule that are neither IR nor Raman active?

6.12 The $[AuCl_4]^-$ ion has D_{4h} symmetry. Determine the representations Γ of all $3N$ displacements and reduce it to obtain the symmetry species of the irreducible representations.

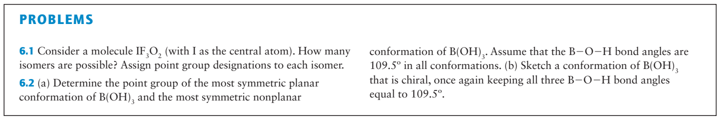
6.13 How could IR and Raman spectroscopy be used to distinguish between: (a) planar and pyramidal forms of PF_3, (b) planar and 90°-twisted forms of B_2F_4 (D_{2h} and D_{2d}, respectively).

6.14 (a) Take the four hydrogen 1s orbitals of CH_4 and determine how they transform under T_d. (b) Confirm that it is possible to reduce this representation to $A_1 + T_2$. (c) With which atomic orbitals on C would it be possible to form MOs with H1s SALCs of symmetry $A_1 + T_2$?

6.15 Consider CH_4. Use the projection operator method to construct the SALCs of $A_1 + T_2$ symmetry that derive from the four H1s orbitals.

Exercises

There are many brief *Exercises* at the end of each chapter. Answers are found in the *Answers* section and fully worked answers are available in the separate *Solutions manual*. 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.



PROBLEMS

6.1 Consider a molecule IF_3O_2 (with I as the central atom). How many isomers are possible? Assign point group designations to each isomer.

6.2 (a) Determine the point group of the most symmetric planar conformation of $B(OH)_3$ and the most symmetric nonplanar conformation of $B(OH)_3$. Assume that the B−O−H bond angles are 109.5° in all conformations. (b) Sketch a conformation of $B(OH)_3$ that is chiral, once again keeping all three B−O−H bond angles equal to 109.5°.

Problems

The *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. 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.

New Molecular Modelling Problems

Over the past two decades computational chemistry has evolved from a highly specialized tool, available to relatively few researchers, into a powerful and practical alternative to experimentation, accessible to all chemists. The driving force behind this evolution is the remarkable progress in computer technology. Calculations that previously required hours or days on giant mainframe computers may now be completed in a fraction of time on a personal computer. It is natural and necessary that computational chemistry finds its way into the undergraduate chemistry curriculum. This requires a hands-on approach, just as teaching experimental chemistry requires a laboratory.

With this edition we have the addition of new molecular modelling problems for almost every chapter, which can be found on the text's companion web site. The problems were written to be performed using the popular *Spartan Student*™ software. With purchase of this text, students can purchase Wavefunction's *Spartan Student*™ at a significant discount from www.wavefun.com/cart/spartaned.html using the code WHFICHEM. While the problems are written to be performed using *Spartan Student*™ they can be completed using any electronic structure program that allows Hartree-Fock, density functional, and MP2 calculations.

About the Book Companion Site

The Book Companion Site which accompanies this book provides teaching and learning resources to augment the printed book. It is free of charge, and provides additional material for download, much of which can be incorporated into a virtual learning environment.

You can access the Book Companion Site by visiting
www.whfreeman.com/ichem5e

Please note that instructor resources are available only to registered adopters of the textbook. To register, simply visit www.whfreeman.com/ichem5e and follow the appropriate links. You will be given the opportunity to select your own username and password, which will be activated once your adoption has been verified.

Student resources are openly available to all, without registration.

Instructor resources

Artwork

An instructor may wish to use the figures from this text in a lecture. Almost all the figures are available in PowerPoint® format and can be used for lectures without charge (but not for commercial purposes without specific permission).

Tables of data

All the tables of data that appear in the chapter text are available and may be used under the same conditions as the figures.

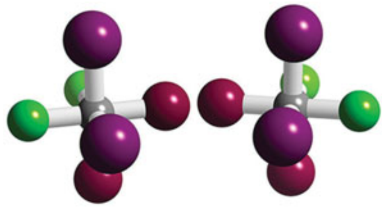
New Molecular Modelling Problems

With this edition we have the addition of new molecular modelling problems for almost every chapter, which can be found on the text's companion web site. The problems were written to be performed using the popular *Spartan Student*™ software. With purchase of this text, students can purchase Wavefunction's *Spartan Student*™ at a significant discount from www.wavefun.com/cart/spartaned.html using the code WHFICHEM. While the problems are written to be performed using *Spartan Student*™ they can be completed using any electronic structure program that allows Hartree-Fock, density functional, and MP2 calculations.

Student resources

3D rotatable molecular structures

Nearly all the numbered molecular structures featured in the book are available in a three-dimensional, viewable, rotatable form along with many of the crystal structures and bioinorganic molecules. These have been produced in collaboration with Dr Karl Harrison, University of Oxford.



Group theory tables

Comprehensive group theory tables are available for downloading.

Videos of chemical reactions

Video clips showing demonstrations of inorganic chemistry reactions are available for viewing.

Solutions manual

As with the previous edition, Michael Hagerman, Christopher Schnabel, and Kandalam Ramanujachary have produced the solutions manual to accompany this book. A *Solution Manual* (978-142-925255-3) provides completed solutions to most end of chapter Exercises and Self-tests.

Spartan Student discount

With purchase of this text, students can purchase Wavefunction's *Spartan Student*™ at a significant discount at www.wavefun.com/cart/spartaned.html using the code WHFICHEM.

Answers to Self-tests and Exercises

Please visit the Book Companion Site at www.whfreeman.com/ichem5e/ to download a PDF document containing answers to the end-of-chapter exercises in this book.

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Glossary of chemical abbreviations

Ac	acetyl, CH_3CO
acac	acetylacetonato
aq	aqueous solution species
bpy	2,2'-bipyridine
cod	1,5-cyclooctadiene
cot	cyclooctatetraene
Cy	cyclohexyl
Cp	cyclopentadienyl
Cp*	pentamethylcyclopentadienyl
cyclam	tetraazacyclotetradecane
dien	diethylenetriamine
DMSO	dimethylsulfoxide
DMF	dimethylformamide
η	hapticity
edta	ethylenediaminetetraacetato
en	ethylenediamine (1,2-diaminoethane)
Et	ethyl
gly	glycinato
Hal	halide
^{i}Pr	isopropyl
KCP	$K_2Pt(CN)_4Br_{0.3}\cdot 3H_2O$
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
Sol	solvent, or a solvent molecule
soln	nonaqueous solution species
^{t}Bu	tertiary butyl
THF	tetrahydrofuran
TMEDA	*N*, *N*,*N*′,*N*′-tetramethylethylenediamine
trien	2,2′,2″-triaminotriethylene
X	generally halogen, also a leaving group or an anion
Y	an entering group

PART 1

Foundations

The eight chapters in this part of the book lay the foundations of inorganic chemistry. The first three chapters develop an understanding of the structures of atoms, molecules, and solids. 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. Chapter 3 describes ionic bonding and the structures and properties of a range of typical ionic solids. The next two chapters focus on two major types of reactions. Chapter 4 introduces the definitions of acids and bases, and uses their properties to systematize many inorganic reactions. Chapter 5 describes oxidation and reduction, and demonstrates how electrochemical data can be used to predict and explain the outcomes of redox reactions. Chapter 6 shows how a systematic consideration of the symmetry of molecules can be used to discuss the bonding and structure of molecules and help interpret the techniques described in Chapter 8. Chapter 7 describes the coordination compounds of the elements. We discuss bonding, structure, and reactions of complexes, and see how symmetry considerations can provide useful 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 of compounds.

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Atomic structure

1

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 begin with 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. An understanding of these properties allows us to begin to rationalize the diverse chemical properties of the more than 110 elements known today.

The observation that the universe is expanding has led to the current view that about 15 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.

Table 1.1 summarizes the properties of the only subatomic particles that we need to consider in chemistry. All the known elements—by 2008, 112 had been confirmed and several more are candidates for confirmation—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**

Table 1.1 Subatomic particles of relevance to chemistry

Practice	Symbol	Mass/m_u*	Mass number	Charge/e†	Spin
Electron	e^-	5.486×10^{-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	γ	0	0	0	1
Neutrino	v	c. 0	0	0	$\frac{1}{2}$
Positron	e^+	5.486×10^{-4}	0	$+1$	$\frac{1}{2}$
α particle	α	[$^4_2He^{2+}$ nucleus]	4	$+2$	0
β particle	β	[e^- ejected from nucleus]	0	-1	$\frac{1}{2}$
γ photon	γ	[electromagnetic radiation from nucleus]	0	0	1

* Masses are expressed relative to the atomic mass constant, $m_u = 1.6605 \times 10^{-27}$ kg.
† The elementary charge is $e = 1.602 \times 10^{-19}$ C.

number, A, which is the total number of protons and neutrons in the nucleus. The mass number is also sometimes termed more appropriately 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 ${}^1H$, 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 ${}^2H$, but it is commonly denoted D. The third, short-lived, radioactive isotope of hydrogen is tritium, ${}^3H$ 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 ${}^1_1H$, ${}^2_1H$, and ${}^3_1H$.

The origin of the elements

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 per cent) and He atoms (11 per cent). In one sense, not much has happened since then for, as Fig. 1.1 shows, hydrogen and helium

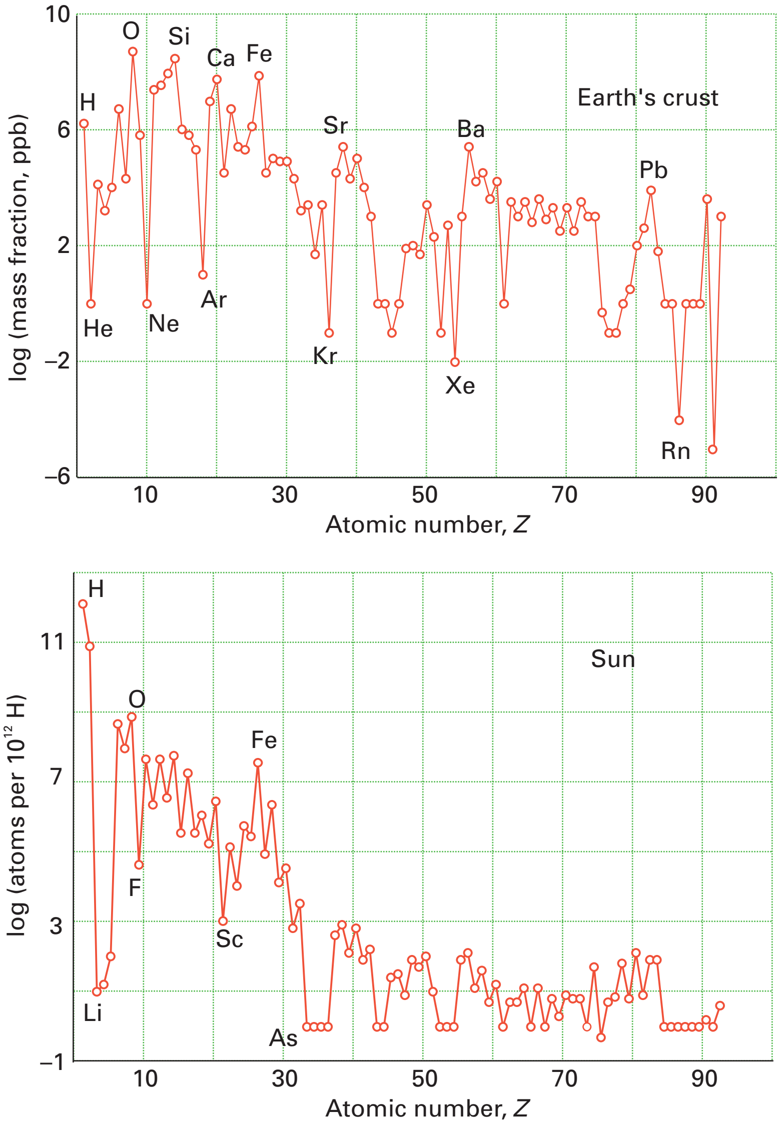

Figure 1.1 The abundances of the elements in the Earth's crust and the Sun. Elements with odd Z are less stable than their neighbours with even Z.

remain overwhelmingly the most abundant elements in the universe. However, nuclear reactions have formed a wide assortment of other elements and have immeasurably enriched the variety of matter in the universe, and thus given rise to the whole area of chemistry.

1.1 The nucleosynthesis of light elements

Key points: The light elements were formed by nuclear reactions in stars formed from primeval hydrogen and helium; total mass number and overall charge are conserved in nuclear reactions; a large binding energy signifies a stable nucleus.

The earliest stars resulted from the gravitational condensation of clouds of H and He atoms. The compression of these clouds under the influence of gravity gave rise to high temperatures and densities within them, and fusion reactions began as nuclei merged together. The earliest nuclear reactions are closely related to those now being studied in connection with the development of controlled nuclear fusion.

Energy is released when light nuclei fuse together to give elements of higher atomic number. For example, the nuclear reaction in which an α particle (a ^{4}He nucleus with two protons and two neutrons) fuses with a carbon-12 nucleus to give an oxygen-16 nucleus and a γ-ray photon (γ) is

$${}^{12}_{6}\mathrm{C} + {}^{4}_{2}\alpha \rightarrow {}^{16}_{8}\mathrm{O} + \gamma$$

This reaction releases 7.2 MeV of energy.[1] Nuclear reactions are very much more energetic than normal chemical reactions because the strong force is much stronger than the electromagnetic force that binds electrons to nuclei. Whereas a typical chemical reaction might release about 10^3 kJ mol^{-1}, a nuclear reaction typically releases a million times more energy, about 10^9 kJ mol^{-1}. In this nuclear equation, the **nuclide**, a nucleus of specific atomic number Z and mass number A, is designated ${}^{A}_{Z}\mathrm{E}$, where E is the chemical symbol of the element. Note that, in a balanced nuclear equation, the sum of the mass numbers of the reactants is equal to the sum of the mass numbers of the products (12 + 4 = 16). The atomic numbers sum similarly (6 + 2 = 8) provided an electron, e^-, when it appears as a β particle, is denoted ${}^{0}_{-1}\mathrm{e}$ and a positron, e^+, is denoted ${}^{0}_{1}\mathrm{e}$. A positron is a positively charged version of an electron: it has zero mass number (but not zero mass) and a single positive charge. When it is emitted, the mass number of the nuclide is unchanged but the atomic number decreases by 1 because the nucleus has lost one positive charge. Its emission is equivalent to the conversion of a proton in the nucleus into a neutron: ${}^{1}_{1}\mathrm{p} \rightarrow {}^{1}_{0}\mathrm{n} + \mathrm{e}^+ + \nu$. A neutrino, ν (nu), is electrically neutral and has a very small (possibly zero) mass.

Elements up to $Z = 26$ were formed inside stars. Such 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 reactions.) Some of the most important nuclear reactions in the cycle are

Proton (p) capture by carbon-12: ${}^{12}_{6}\mathrm{C} + {}^{1}_{1}\mathrm{p} \rightarrow {}^{13}_{7}\mathrm{N} + \gamma$

Positron decay accompanied by neutrino (ν) emission: ${}^{13}_{7}\mathrm{N} \rightarrow {}^{13}_{6}\mathrm{C} + \mathrm{e}^+ + \nu$

Proton capture by carbon-13: ${}^{13}_{6}\mathrm{C} + {}^{1}_{1}\mathrm{p} \rightarrow {}^{14}_{7}\mathrm{N} + \gamma$

Proton capture by nitrogen-14: ${}^{14}_{7}\mathrm{N} + {}^{1}_{1}\mathrm{p} \rightarrow {}^{15}_{8}\mathrm{O} + \gamma$

Positron decay, accompanied by neutrino emission: ${}^{15}_{8}\mathrm{O} \rightarrow {}^{15}_{7}\mathrm{N} + \mathrm{e}^+ + \nu$

Proton capture by nitrogen-15: ${}^{15}_{7}\mathrm{N} + {}^{1}_{1}\mathrm{p} \rightarrow {}^{12}_{6}\mathrm{C} + {}^{4}_{2}\alpha$

The net result of this sequence of nuclear reactions is the conversion of four protons (four ^{1}H nuclei) into an α particle (a ^{4}He nucleus):

$$4\,{}^{1}_{1}\mathrm{p} \rightarrow {}^{4}_{2}\alpha + 2\mathrm{e}^+ + 2\nu + 3\gamma$$

---

[1] An electronvolt (1 eV) is the energy required to move an electron through a potential difference of 1 V. It follows that 1 eV = 1.602×10^{-19} J, which is equivalent to 96.48 kJ mol^{-1}; 1 MeV = 10^6 eV.

The reactions in the sequence are rapid at temperatures between 5 and 10 MK (where 1 MK = 10^6 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 species can result in chemical change, but only highly vigorous collisions can provide the energy required to bring about most nuclear processes.

Heavier elements are produced in significant quantities when hydrogen burning is complete and the collapse of the star's core raises the density there to 10^8 kg m^{-3} (about 10^5 times the density of water) and the temperature to 100 MK. Under these extreme conditions, helium burning becomes viable. The low abundance of beryllium in the present-day universe is consistent with the observation that ${}^{8}_{4}\mathrm{Be}$ formed by collisions between α particles goes on to react with more α particles to produce the more stable carbon nuclide ${}^{12}_{6}\mathrm{C}$:

$${}^{8}_{4}\mathrm{Be} + {}^{4}_{2}\alpha \rightarrow {}^{12}_{6}\mathrm{C} + \gamma$$

Thus, the helium-burning stage of stellar evolution does not result in the formation of Be as a stable end product; for similar reasons, low concentrations of Li and B are also formed. The nuclear reactions leading to these three elements are still uncertain, but they may result from the fragmentation of C, N, and O nuclei by collisions with high-energy particles.

Elements can also be produced by nuclear reactions such as neutron (n) capture accompanied by proton emission:

$${}^{14}_{7}\mathrm{N} + {}^{1}_{0}\mathrm{n} \rightarrow {}^{14}_{6}\mathrm{C} + {}^{1}_{1}\mathrm{p}$$

This reaction still continues in our atmosphere as a result of the impact of cosmic rays and contributes to the steady-state concentration of radioactive carbon-14 on Earth.

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 represents 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 a 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 $\Delta m = m_{\mathrm{nucleons}} - m_{\mathrm{nucleus}}$, then its binding energy is $E_{\mathrm{bind}} = (\Delta m)c^2$. The binding energy of ^{56}Fe, for example, is the difference in energy between the ^{56}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 (Box 1.1).

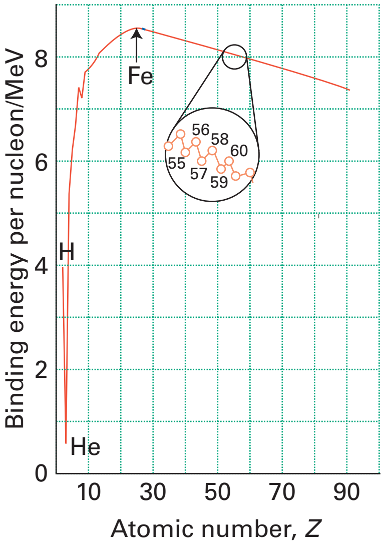

Figure 1.2 Nuclear binding energies. The greater the binding energy, the more stable is the nucleus. Note the alternation in stability shown in the inset.

Figure 1.2 shows the binding energy per nucleon, E_{bind}/A (obtained by dividing the total binding energy by the number of nucleons), for all the elements. Iron and nickel occur at the maximum of the curve, showing that their nucleons are bound 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.

1.2 The nucleosynthesis of heavy elements

Key point: Heavier nuclides are formed by processes that include neutron capture and subsequent β decay.

Nuclei close to iron are the most stable and heavier elements are produced by a variety of processes that require energy. These processes include the capture of free neutrons, which are not present in the earliest stages of stellar evolution but are produced later in reactions such as

$${}^{23}_{10}\mathrm{Na} + {}^{4}_{2}\alpha \rightarrow {}^{26}_{12}\mathrm{Mg} + {}^{1}_{0}\mathrm{n}$$

BOX 1.1 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:

$$2\,{}^{20}_{10}\text{Ne} \rightarrow {}^{40}_{20}\text{Ca}$$

The value of E_{bind}/A for Ne is approximately 8.0 MeV. Therefore, the total binding energy of the species on the left-hand side of the equation is $2 \times 20 \times 8.0$ MeV $= 320$ MeV. The value of E_{bind}/A for Ca is close to 8.6 MeV and so the total energy of the species on the right-hand side is 40×8.6 MeV $= 344$ 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_{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:

$${}^{236}_{92}\text{U} \rightarrow {}^{140}_{54}\text{Xe} + {}^{93}_{38}\text{Sr} + {}^{1}_{0}\text{n}$$

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

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

$${}^{235}_{92}\text{U} + {}^{1}_{0}\text{n} \rightarrow \text{fission products} + \text{neutrons}$$

The kinetic energy of fission products from ^{235}U is about 165 MeV, that of the neutrons is about 5 MeV, and the γ-rays produced have an energy of about 7 MeV. The fission products are themselves radioactive and decay by β-, γ-, 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 W = 1 J s^{-1}) corresponds to about 3.1×10^{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}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 about 100 years. The cost of uranium ores is currently very low and one small pellet of uranium oxide generates as much energy as three barrels of oil or 1 tonne of coal. The use of nuclear power would also drastically reduce the rate of emission of greenhouse gases. The environmental drawback with nuclear power is the storage and disposal of radioactive waste and the public's continued nervousness about possible nuclear accidents and misuse in pursuit of political ambitions.

Under conditions of intense neutron flux, as in a supernova (one type of stellar explosion), a given nucleus may capture a succession of neutrons and become a progressively heavier isotope. However, there comes a point at which the nucleus will eject an electron from the nucleus as a β particle (a high-velocity electron, e$^-$). Because β decay leaves the mass number of the nuclide unchanged but increases its atomic number by 1 (the nuclear charge increases by 1 unit when an electron is ejected), a new element is formed. An example is

Neutron capture: $${}^{98}_{42}\text{Mo} + {}^{1}_{0}\text{n} \rightarrow {}^{99}_{42}\text{Mo} + \gamma$$

Followed by β decay accompanied by neutrino emission: $${}^{99}_{42}\text{Mo} \rightarrow {}^{99}_{43}\text{Tc} + \text{e}^- + \nu$$

The **daughter nuclide**, the product of a nuclear reaction (${}^{99}_{33}$Tc , an isotope of technetium, in this example), can absorb another neutron, and the process can continue, gradually building up the heavier elements (Box 1.2).

BOX 1.2 Technetium—the first 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—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}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 $^{99\text{m}}$Tc, where the 'm' indicates a metastable isotope. Technetium-99m emits high-energy γ-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 γ-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, $^{99\text{m}}$Tc is widely used in nuclear medicine, for example in radiopharmaceuticals for imaging and functional studies of the brain, bones, blood, lungs, liver, heart, thyroid gland, and kidneys. 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}Mo to $^{99\text{m}}$Tc. The half-life of ^{99}Mo is 66 hours, which makes it more convenient for transport and storage than $^{99\text{m}}$Tc itself. Most commercial generators are based on ^{99}Mo in the form of the molybdate ion, MoO_4^{2-}, adsorbed on Al_2O_3. The $^{99}\text{MoO}_4^{2-}$ ion decays to the pertechnetate ion, $^{99\text{m}}\text{TcO}_4^-$, which is less tightly bound to the alumina. Sterile saline solution is washed through a column of the immobilized ^{99}Mo and the $^{99\text{m}}$Tc solution is collected.

EXAMPLE 1.1 Balancing equations for nuclear reactions

Synthesis of heavy elements occurs in the neutron-capture reactions believed to take place in the interior of cool 'red giant' stars. One such reaction is the conversion of ${}^{68}_{30}\mathrm{Zn}$ to ${}^{69}_{31}\mathrm{Ga}$ by neutron capture to form ${}^{69}_{30}\mathrm{Zn}$, which then undergoes β decay. Write balanced nuclear equations for this process.

Answer We use the fact that the sum of the mass numbers and the sum of the atomic numbers on each side of the equation must be the same. Neutron capture increases the mass number of a nuclide by 1 but leaves the atomic number (and hence the identity of the element) unchanged:

$${}^{68}_{30}\mathrm{Zn} + {}^{1}_{0}\mathrm{n} \rightarrow {}^{69}_{30}\mathrm{Zn} + \gamma$$

The excess energy is carried away as a photon. The loss of an electron from the nucleus by β decay leaves the mass number unchanged but increases the atomic number by 1. Because zinc has atomic number 30, the daughter nuclide has $Z = 31$, corresponding to gallium. Therefore, the nuclear reaction is

$${}^{69}_{30}\mathrm{Zn} \rightarrow {}^{69}_{31}\mathrm{Ga} + \mathrm{e}^-$$

In fact, a neutrino is also emitted, but this cannot be inferred from the data as a neutrino is effectively massless and electrically neutral.

Self-test 1.1 Write the balanced nuclear equation for neutron capture by ${}^{80}_{35}\mathrm{Br}$.

The structures of hydrogenic atoms

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 He^+ and C^{5+} (found in stellar interiors) as well as the hydrogen atom itself. Then we use the concepts these atoms introduce to build up an approximate description of the structures of **many-electron atoms** (or *polyelectron atoms*), which are atoms with more than one electron.

1.3 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 passed through 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. 1.3; Box 1.3).

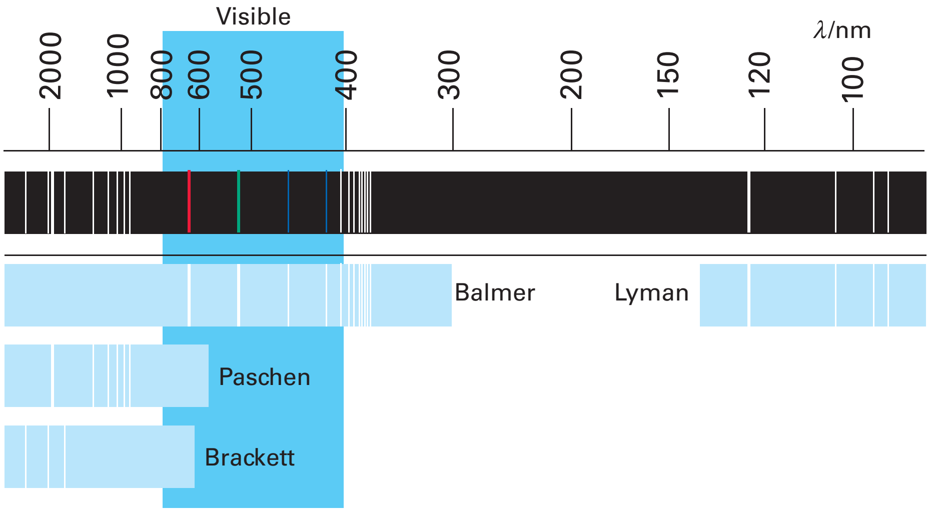

Figure 1.3 The spectrum of atomic hydrogen and its analysis into series.

BOX 1.3 Sodium street lamps

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), a solid solution of In_2O_3 with typically 10 per cent by mass SnO_2. The indium tin oxide reflects the infrared radiation and transmits the 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 and heat the sodium metal. The sodium rapidly starts to vaporize and the electrical discharge excites the atoms and they re-emit the energy as yellow light from the transition 3p → 3s. One advantage of sodium lamps over other types of street lighting is that their light output does not diminish with 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 nineteenth-century spectroscopist Johann Rydberg found that all the wavelengths (λ, lambda) can be described by the expression

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

where R is the **Rydberg constant**, an empirical constant with the value $1.097 \times 10^7\ \mathrm{m}^{-1}$. The n are integers, with $n_1 = 1, 2, \ldots$ and $n_2 = n_1 + 1, n_1 + 2, \ldots$. The series with $n_1 = 1$ is called the *Lyman series* and lies in the ultraviolet. 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 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 $-hcR/n_2^{\,2}$ to a state of energy $-hcR/n_1^{\,2}$ and that the difference, which is equal to $hcR(1/n_1^{\,2} - 1/n_2^{\,2})$, is carried away as a photon of energy hc/λ. By equating these two energies, and cancelling hc, we obtain eqn 1.1.

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.

1.4 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 the content of Heisenberg's **uncertainty principle**, 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, $\tfrac{1}{2}\hbar$, where $\hbar = h/2\pi$).

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**, ψ (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

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

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 need 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 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, in addition to the imposition of certain requirements ('boundary conditions') that restrict the number of acceptable solutions.

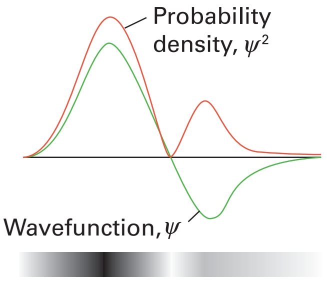

Figure 1.4 The Born interpretation of the wavefunction is that its square is a probability density. There is zero probability density at a node.

A wavefunction contains all the dynamical information possible about the electron, including where it is and what it is doing. Specifically, the probability of finding an electron at a given location is proportional to the square of the wavefunction at that point, ψ^2. According to this interpretation, there is a high probability of finding the electron where ψ^2 is large, and the electron will not be found where ψ^2 is zero (Fig. 1.4). The quantity ψ^2 is called the **probability density** of the electron. It is a 'density' in the sense that the product of ψ^2 and the infinitesimal volume element $d\tau = dxdydz$ (where τ 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.

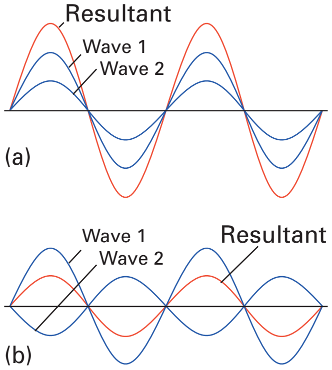

Figure 1.5 Wavefunctions interfere where they spread into the same region of space. (a) If they have the same sign in a region, they interfere constructively and the total wavefunction has an enhanced amplitude in the region. (b) If the wavefunctions have opposite signs, then they interfere destructively, and the resulting superposition has a reduced amplitude.

Like other waves, wavefunctions in general have regions of positive and negative amplitude, or sign. 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. 1.5a). 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. 1.5b). 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. To help keep track of the relative signs of different regions of a wavefunction in illustrations, we label regions of opposite sign with dark and light shading (sometimes white in the place of light shading).

1.5 Atomic orbitals

The wavefunction of an electron in an atom is called an **atomic orbital**. 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 high 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

$$E_n = -\frac{hcRZ^2}{n^2} \tag{1.3}$$

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

$$R = \frac{m_e e^4}{8h^3 c\varepsilon_0^2} \tag{1.4}$$

(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. For future reference, the value of hcR corresponds to 13.6 eV. 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. 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. Finally, because the energy is proportional to $1/n^2$, the energy levels converge as the energy increases (becomes less negative, Fig. 1.6).

The value of l specifies the magnitude of the orbital angular momentum through $\{l(l + 1)\}^{1/2}\hbar$, with $l = 0, 1, 2, \ldots$. We can think of l as indicating the rate at which the electron circulates around the nucleus. 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.

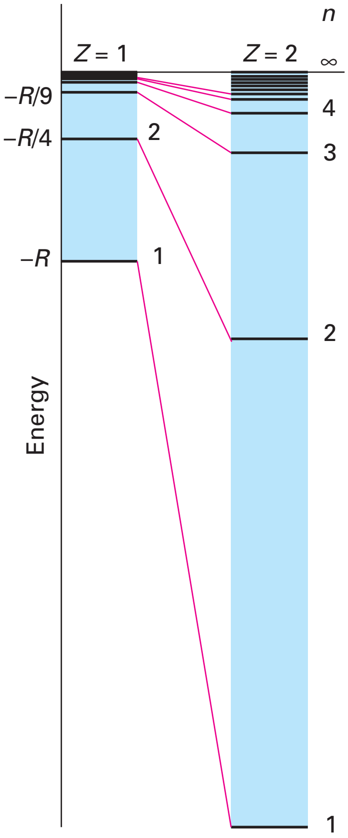

Figure 1.6 The quantized energy levels of an H atom ($Z = 1$) and an He^+ ion ($Z = 2$). The energy levels of a hydrogenic atom are proportional to Z^2.

(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.

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 $n = 1, 2, 3 \ldots$ are commonly referred to as K, L, M, ... shells.

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 $l = 0, 1, \ldots, n - 1$, 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	...
Subshell designation	s	p	d	f	g	...

For most purposes in chemistry we need consider only s, p, d, and f subshells.

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 $m_l = +2, +1, 0, -1, -2$.

> ***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 remarks 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**, and so on (Fig. 1.7).

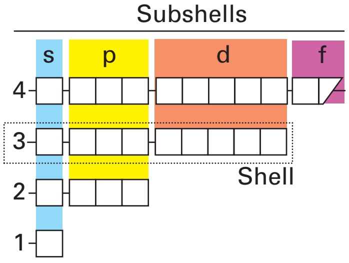

Figure 1.7 The classification of orbitals into subshells (same value of l) and shells (same value of n).

EXAMPLE 1.2 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 $m_l = l, l - 1, \ldots, -l$ give the number of orbitals of that type. In this case, $m_l = +1$, 0, and -1. There are therefore three 4p orbitals.

Self-test 1.2 Which set of orbitals is defined by the quantum numbers $n = 3$ and $l = 2$? 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.

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 a planet 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 for an electron 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 ↑ ('spin-up', $m_s = +\frac{1}{2}$) and ↓ ('spin-down', $m_s = -\frac{1}{2}$) or by the Greek letters α and β, 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 (the fifth quantum number, s, is fixed at $\frac{1}{2}$).

(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. 1.8. In these coordinates, the orbitals all have the form

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

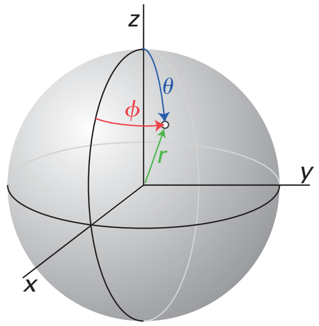

Figure 1.8 Spherical polar coordinates: r is the radius, θ (theta) the colatitude, and ϕ (phi) the azimuth.

This expression expresses the simple idea that a hydrogenic orbital can be written as the product of a function $R(r)$ of the radius 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.

(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 1.9 and 1.10 show the radial variation 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. 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 found further away from the nucleus and its energy increases.

An orbital with quantum numbers n and l in general 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. A 2p orbital (one of the three orbitals with $n = 2$ and $l = 1$) has no radial nodes because its radial wavefunction does not pass through zero anywhere. However, a 2p orbital, like *all* orbitals other than s orbitals, is zero at the nucleus. For any series of the same type of orbital, the first occurrence has no radial nodes, the second has one radial node, and so on.

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 chemistry.

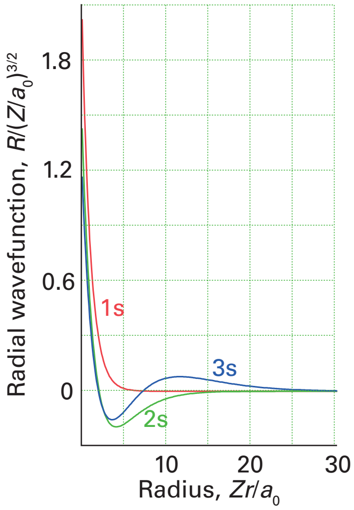

Figure 1.9 The radial wavefunctions of the 1s, 2s, and 3s hydrogenic orbitals. Note that the number of radial nodes is 0, 1, and 2, respectively. Each orbital has a nonzero amplitude at the nucleus (at $r = 0$).

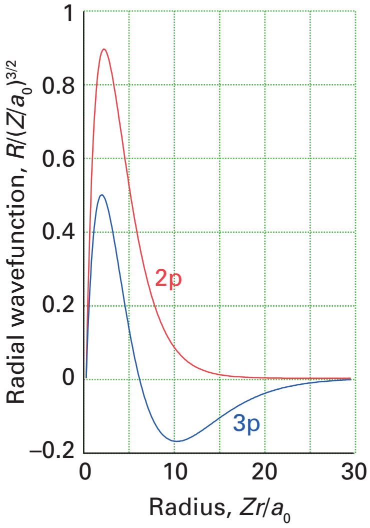

Figure 1.10 The radial wavefunctions of the 2p and 3p hydrogenic orbitals. Note that the number of radial nodes is 0 and 1, respectively. Each orbital has zero amplitude at the nucleus (at $r = 0$).

EXAMPLE 1.3 Predicting numbers of radial nodes

How many radial nodes do 3p, 3d, and 4f orbitals 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 values of n and l. The 3p orbitals have $n = 3$ and $l = 1$ and the number of radial nodes will be $n - l - 1 = 1$. The 3d orbitals have $n = 3$ and $l = 2$. Therefore, the number of radial nodes will $n - l - 1 = 0$. The 4f orbitals have $n = 4$ and $l = 3$ and the number of radial nodes will be $n - l - 1 = 0$. 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 nodes.

Self-test 1.3 How many radial nodes does a 5s orbital have?

(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 ψ^2dτ over all angles. This result is written $P(r)$ dr, where $P(r)$ is called the **radial distribution function**. In general,

$$P(r) = r^2 R(r)^2 \tag{1.6}$$

(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. In general, a radial distribution function for an orbital in a shell of principal quantum number n has $n - 1$ peaks, the outermost peak being the highest.

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

$$r_{\max} = \frac{a_0}{Z} \tag{1.7}$$

where a_0 is the **Bohr radius**, $a_0 = \varepsilon_0\hbar^2/\pi m_e e^2$, 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.

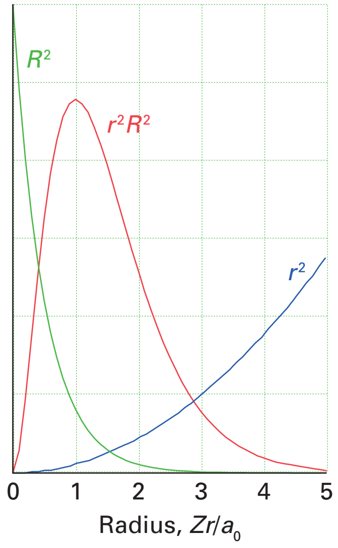

Figure 1.11 The radial distribution function of a hydrogenic 1s orbital. The product of $4\pi r^2$ (which increases as r increases) and ψ^2 (which decreases exponentially) passes through a maximum at $r = a_0/Z$.

EXAMPLE 1.4 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. Thus, the 2s electron has a greater probability of close approach to the nucleus.

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

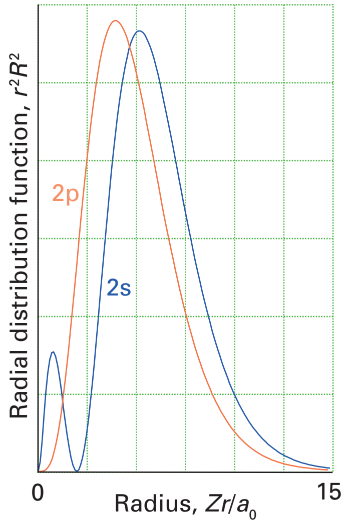

Figure 1.12 The radial distribution functions of hydrogenic orbitals. Although the 2p orbital is *on average* closer to the nucleus (note where its maximum lies), the 2s orbital has a high probability of being close to the nucleus on account of the inner maximum.

(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 per cent) probability of finding the electron. 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.

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

All orbitals with $l > 0$ have amplitudes that vary with angle. 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). This representation is the origin of the labels p_x, p_y, and p_z, which are

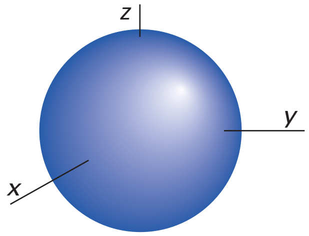

Figure 1.13 The spherical boundary surface of an s orbital.

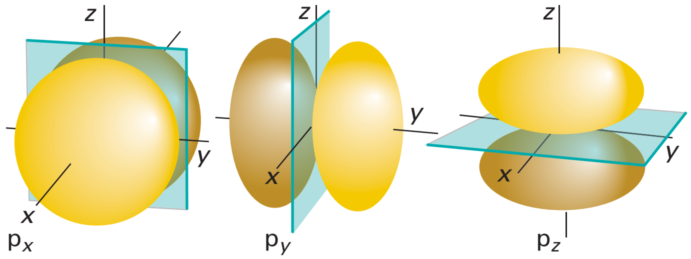

Figure 1.14 The boundary surfaces of p orbitals. Each orbital has one nodal plane running through the nucleus. For example, the nodal plane of the p orbital is the *xy*-plane. The lightly shaded lobe has a positive amplitude, the more darkly shaded one is negative.

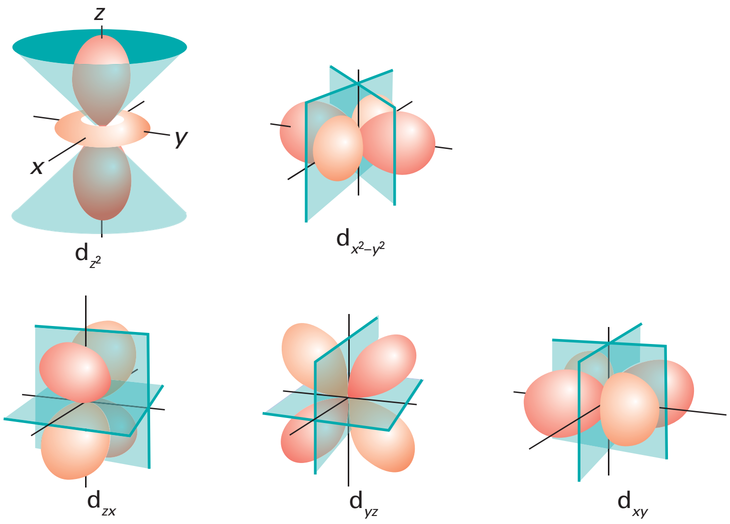

Figure 1.15 One representation of the boundary surfaces of the d orbitals. Four of the orbitals have two perpendicular nodal planes that intersect in a line passing through the nucleus. In the d_{z^2} orbital, the nodal surface forms two cones that meet at the nucleus.

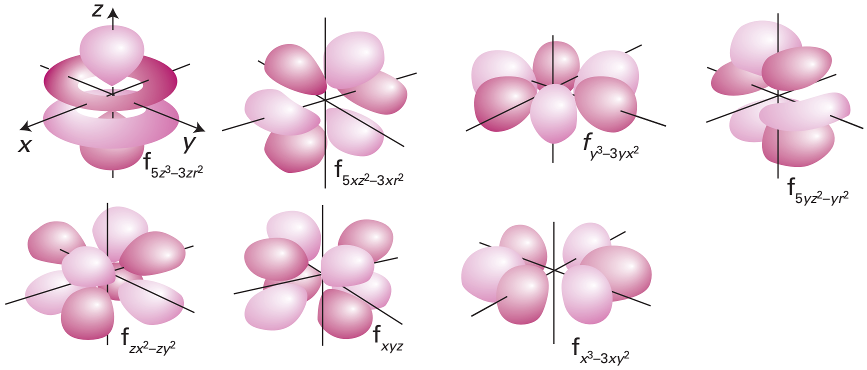

Figure 1.16 One representation of the boundary surfaces of the f orbitals. Other representations (with different shapes) are also sometimes encountered.

alternatives to the use of m_l to label the individual orbitals. 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. One of these orbitals is $d_{x^2-y^2}$. The d_{z^2} orbital can be thought of as the superposition of two contributions, one with lobes along the *z*- and *x*-axes and the other with lobes along the *z*- and *y*-axes. 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.

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. There is no hope of finding 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.

1.6 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. 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 '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 ↑ and the other ↓; the pair is denoted ↑↓. 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.

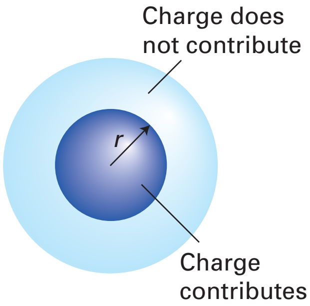

Figure 1.17 The electron at the *r* radius experiences a repulsion from the total charge within the sphere of radius *r*; charge outside that radius has no net effect.

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 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, Ze, to $Z_{\mathrm{eff}}e$, where Z_{eff} (more precisely, $Z_{\mathrm{eff}}e$) is called the **effective nuclear charge.** 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**, σ, by writing $Z_{\mathrm{eff}} = Z - \sigma$. The shielding constant can be determined by fitting hydrogenic orbitals to those computed numerically.

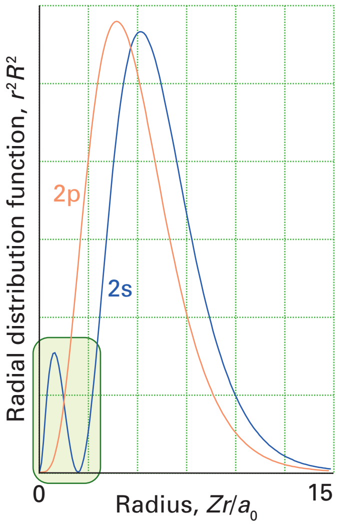

Figure 1.18 The penetration of a 2s electron through the inner core is greater than that of a 2p electron because the latter vanishes at the nucleus. Therefore, the 2s electrons are less shielded than the 2p electrons.

The closer to the nucleus that an electron can approach, the closer is the value of Z_{eff} to Z itself because the electron is repelled less by the other electrons present in the atom. With this point in mind, consider a 2s electron in the Li atom. There is a nonzero probability that the 2s electron can be found inside the 1s shell and experience the full nuclear charge (Fig. 1.18). The presence of an electron inside shells of other electrons is called **penetration.** A 2p electron does not penetrate so effectively through the **core,** the filled inner shells of electrons, because its wavefunction goes to zero at the nucleus. As a consequence, it is more fully shielded from the nucleus by the core electrons. We can conclude that a 2s electron has a lower energy (is bound more tightly) than a 2p electron, and therefore that the 2s orbital will be occupied before the 2p orbitals, giving a ground-state electron configuration for Li of $1s^22s^1$. This configuration is commonly denoted $[He]2s^1$, where [He] denotes the atom's helium-like $1s^2$ core.

Table 1.2 Effective nuclear charge, Z_{eff}

	H							He
Z	1							2
1s	1.00							1.69
	Li	Be	B	C	N	O	F	Ne
Z	3	4	5	6	7	8	9	10
1s	2.69	3.68	4.68	5.67	6.66	7.66	8.65	9.64
2s	1.28	1.91	2.58	3.22	3.85	4.49	5.13	5.76
2p			2.42	3.14	3.83	4.45	5.10	5.76
	Na	Mg	Al	Si	P	S	Cl	Ar
Z	11	12	13	14	15	16	17	18
1s	10.63	11.61	12.59	13.57	14.56	15.54	16.52	17.51
2s	6.57	7.39	8.21	9.02	9.82	10.63	11.43	12.23
2p	6.80	7.83	8.96	9.94	10.96	11.98	12.99	14.01
3s	2.51	3.31	4.12	4.90	5.64	6.37	7.07	7.76
3p			4.07	4.29	4.89	5.48	6.12	6.76

The pattern of energies in lithium, with 2s lower than 2p, and in general *n*s lower than *n*p, is a general feature of many-electron atoms. This pattern can be seen from Table 1.2, which gives the values of Z_{eff} for a number of valence-shell atomic orbitals in the ground-state electron configuration of atoms. The typical trend in effective nuclear charge is an increase across a period, for in most cases the increase in nuclear charge in successive groups is not cancelled by the additional electron. The values in the table also confirm that an s electron in the outermost shell of the atom is generally less shielded than a p electron of that shell. So, for example, $Z_{\text{eff}} = 5.13$ for a 2s electron in an F atom, whereas for a 2p electron $Z_{\text{eff}} = 5.10$, a lower value. Similarly, the effective nuclear charge is larger for an electron in an *n*p orbital than for one in an *n*d orbital.

As a result of penetration and shielding, the order of energies in many-electron atoms is typically $ns < np < nd < nf$ because, in a given shell, s orbitals are the most penetrating and f orbitals are the least penetrating. The overall effect of penetration and shielding is depicted in the energy-level diagram for a neutral atom shown in Fig. 1.19.

Figure 1.20 summarizes the energies of the orbitals through the periodic table. The effects are quite subtle, and the order of the orbitals depends strongly on the numbers of

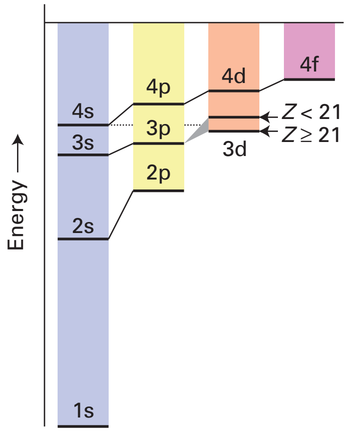

Figure 1.19 A schematic diagram of the energy levels of a many-electron atom with $Z < 21$ (as far as calcium). There is a change in order for $Z \geq 21$ (from scandium onwards). This is the diagram that justifies the building-up principle, with up to two electrons being allowed to occupy each orbital.

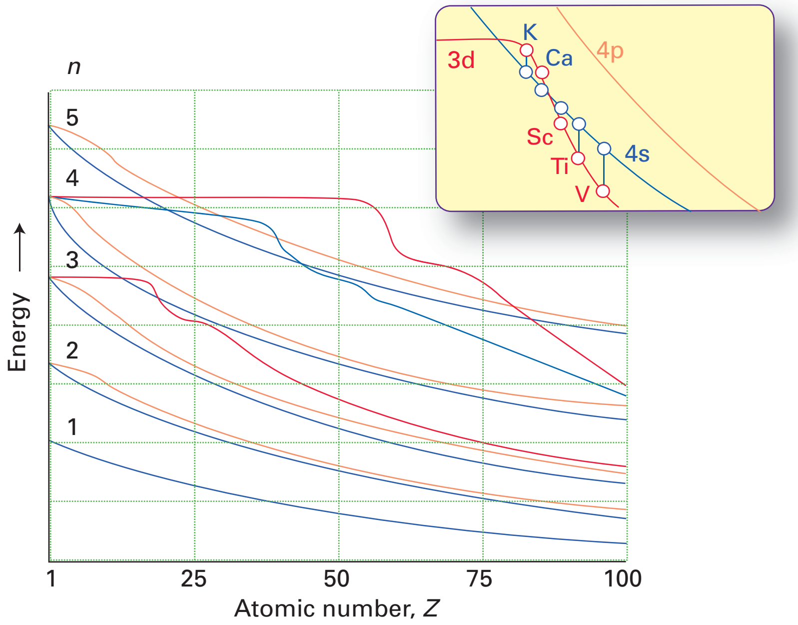

Figure 1.20 A more detailed portrayal of the energy levels of many-electron atoms in the periodic table. The inset shows a magnified view of the order near $Z = 20$, where the 3d series of elements begins.

electrons present in the atom and may change on ionization. For example, the effects of penetration are very pronounced for 4s electrons in K and Ca, and in these atoms the 4s orbitals lie lower in energy than the 3d orbitals. However, from Sc through Zn, the 3d orbitals in the neutral atoms lie close to but lower than the 4s orbitals. In atoms from Ga ($Z = 31$) onwards, the 3d orbitals lie well below the 4s orbital in energy, and the outermost electrons are unambiguously those of the 4s and 4p subshells.

1.7 The building-up principle

The ground-state electron configurations of many-electron atoms are determined experimentally by spectroscopy and are summarized in *Resource section 2*. To account for them, we need to consider both the effects of penetration and shielding on the energies of the orbitals and the role of the Pauli exclusion principle. The **building-up principle** (which is also known as the *Aufbau principle* and is described below) is a procedure that leads to plausible ground-state configurations. It is not infallible, but it is an excellent starting point for the discussion. Moreover, as we shall see, it provides a theoretical framework for understanding the structure and implications of the periodic table.

(a) Ground-state electron configurations

Key points: The order of occupation of atomic orbitals follows the order 1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, ... Degenerate orbitals are occupied singly before being doubly occupied; certain modifications of the order of occupation occur for d and f orbitals.

According to the building-up principle, orbitals of neutral atoms are treated as being occupied in the order determined in part by the principal quantum number and in part by penetration and shielding:

Order of occupation: 1s 2s 3s 3p 4s 3d 4p…

Each orbital can accommodate up to two electrons. Thus, the three orbitals in a p subshell can accommodate a total of six electrons and the five orbitals in a d subshell can accommodate up to ten electrons. The ground-state configurations of the first five elements are therefore expected to be

H	He	Li	Be	B
$1s^1$	$1s^2$	$1s^22s^1$	$1s^22s^2$	$1s^22s^22p^1$

This order agrees with experiment. When more than one orbital of the same energy is available for occupation, such as when the 2p orbitals begin to be filled in B and C, we adopt **Hund's rule**:

> *When more than one orbital has the same energy, electrons occupy separate orbitals and do so with parallel spins* (↑↑).

The occupation of separate orbitals of the same value of l (such as a p_x orbital and a p_y orbital) can be understood in terms of the weaker repulsive interactions that exist between electrons occupying different regions of space (electrons in different orbitals) than between those occupying the same region of space (electrons in the same orbital). The requirement of parallel spins for electrons that do occupy different orbitals is a consequence of a quantum mechanical effect called **spin correlation**, the tendency for two electrons with parallel spins to stay apart from one another and hence to repel each other less. One consequence of this effect is that half-filled shells of electrons with parallel spins are particularly stable. For example, the ground state of the chromium atom is $4s^13d^5$ rather than $4s^23d^4$. Further examples of the effect of spin correlation will be seen later in this chapter.

It is arbitrary which of the p orbitals of a subshell is occupied first because they are degenerate, but it is common to adopt the alphabetical order p_x, p_y, p_z. It then follows from the building-up principle that the ground-state configuration of C is $1s^22s^22p_x^12p_y^1$ or, more simply, $1s^22s^22p^2$. If we recognize the helium-like core ($1s^2$), an even briefer notation is $[He]2s^22p^2$, and we can think of the electronic valence structure of the atom as consisting of two paired 2s electrons and two parallel 2p electrons surrounding a closed helium-like core. The electron configurations of the remaining elements in the period are similarly

C	N	O	F	Ne
[He]$2s^22p^2$	[He]$2s^22p^3$	[He]$2s^22p^4$	[He]$2s^22p^5$	[He]$2s^22p^6$

The $2s^22p^6$ configuration of neon is another example of a **closed shell**, a shell with its full complement of electrons. The configuration $1s^22s^22p^6$ is denoted [Ne] when it occurs as a core.

EXAMPLE 1.5 Accounting for trends in effective nuclear charge

The increase in Z_{eff} between C and N is 0.69 whereas the increase between N and O is only 0.62. Suggest a reason why the increase in Z_{eff} for a 2p electron is smaller between N and O than between C and N given the configurations of the atoms listed above.

Answer We need to identify the general trend and then think about an additional effect that might modify it. In this case, we expect to see an increase in effective nuclear charge across a period. However, on going from C to N, the additional electron occupies an empty 2p orbital whereas on going from N to O, the additional electron must occupy a 2p orbital that is already occupied by one electron. It therefore experiences stronger electron–electron repulsion, and the increase in Z_{eff} is not as great.

Self-test 1.5 Account for the larger increase in effective nuclear charge for a 2p electron on going from B to C compared with a 2s electron on going from Li to Be.

The ground-state configuration of Na is obtained by adding one more electron to a neon-like core, and is [Ne]$3s^1$, showing that it consists of a single electron outside a completely filled $1s^22s^22p^6$ core. Now a similar sequence of filling subshells begins again, with the 3s and 3p orbitals complete at argon, with configuration [Ne]$3s^23p^6$, which can be denoted [Ar]. Because the 3d orbitals are so much higher in energy, this configuration is effectively closed. Moreover, the 4s orbital is next in line for occupation, so the configuration of K is analogous to that of Na, with a single electron outside a noble-gas core: specifically, it is [Ar]$4s^1$. The next electron, for Ca, also enters the 4s orbital, giving [Ar]$4s^2$, which is the analogue of Mg. However, in the next element, Sc, the added electron occupies a 3d orbital, and filling of the d orbitals begins.

(b) Exceptions

The energy levels in Figs 1.19 and 1.20 are for individual atomic orbitals and do not fully take into account repulsion between electrons. For elements with an incompletely filled d subshell, the determination of actual ground states by spectroscopy and calculation shows that it is advantageous to occupy orbitals predicted to be *higher* in energy (the 4s orbitals). The explanation for this order is that the occupation of orbitals of higher energy can result in a reduction in the repulsions between electrons that would occur if the lower-energy 3d orbitals were occupied. It is essential when assessing the total energy of the electrons to consider all contributions to the energy of a configuration, not merely the one-electron orbital energies. Spectroscopic data show that the ground-state configurations of these atoms are mostly of the form $3d^n4s^2$, with the 4s orbitals fully occupied despite individual 3d orbitals being lower in energy.

An additional feature, another consequence of spin correlation, is that in some cases a lower total energy may be obtained by forming a half-filled or filled d subshell, even though that may mean moving an s electron into the d subshell. Therefore, as a half-filled d shell is approached the ground-state configuration is likely to be d^5s^1 and not d^4s^2 (as for Cr). As a full d subshell is approached the configuration is likely to be $d^{10}s^1$ rather than d^9s^2 (as for Cu) or $d^{10}s^0$ rather than d^8s^2 (as for Pd). A similar effect occurs where f orbitals are being occupied, and a d electron may be moved into the f subshell so as to achieve an f^7 or an f^{14} configuration, with a net lowering of energy. For instance, the ground-state electron configuration of Gd is [Xe]$4f^75d^16s^2$ and not [Xe]$4f^86s^2$.

For cations and complexes of the d-block elements the removal of electrons reduces the complicating effects of electron–electron repulsions and the 3d orbital energies fall well below that of the 4s orbitals. Consequently, all d-block cations and complexes have d^n configurations and no electrons in the outermost s orbitals. For example, the configuration of Fe is [Ar]$3d^64s^2$ whereas that of $[Fe(CO)_5]$ is [Ar]$3d^8$ and Fe^{2+} is [Ar]$3d^6$. For the purposes of chemistry, the electron configurations of the d-block ions are more important than those of the neutral atoms. In later chapters (starting in Chapter 19), we shall see the great significance of the configurations of the d-metal ions, for the subtle modulations of their energies provide the basis for the explanations of important properties of their compounds.

EXAMPLE 1.6 Deriving an electron configuration

Predict the ground-state electron configurations of (a) Ti and (b) Ti^{3+}.

Answer We need to use the building-up principle and Hund's rule to populate atomic orbitals with electrons. (a) For the neutral atom, for which $Z = 22$, we must add 22 electrons in the order specified above, with no more than two electrons in any one orbital. This procedure results in the configuration $[Ar]4s^2 3d^2$, with the two 3d electrons in different orbitals with parallel spins. However, because the 3d orbitals lie below the 4s orbitals for elements beyond Ca, it is appropriate to reverse the order in which they are written. The configuration is therefore reported as $[Ar]3d^2 4s^2$. (b) The cation has 19 electrons. We should fill the orbitals in the order specified above remembering, however, that the cation will have a d^n configuration and no electrons in the s orbital. The configuration of Ti^{3+} is therefore $[Ar]3d^1$.

Self-test 1.6 Predict the ground-state electron configurations of Ni and Ni^{2+}.

1.8 The classification of the elements

Key points: The elements are broadly divided into metals, nonmetals, and metalloids according to their physical and chemical properties; the organization of elements into the form resembling the modern periodic table is accredited to Mendeleev.

A useful broad division of elements is into **metals** and **nonmetals**. Metallic elements (such as iron and copper) are typically lustrous, malleable, ductile, electrically conducting solids at about room temperature. Nonmetals are often gases (oxygen), liquids (bromine), or solids that do not conduct electricity appreciably (sulfur). The chemical implications of this classification should already be clear from introductory chemistry:

1. Metallic elements combine with nonmetallic elements to give compounds that are typically hard, nonvolatile solids (for example sodium chloride).
2. When combined with each other, the nonmetals often form volatile molecular compounds (for example phosphorus trichloride).
3. When metals combine (or simply mix together) they produce alloys that have most of the physical characteristics of metals (for example brass from copper and zinc).

Some elements have properties that make it difficult to classify them as metals or nonmetals. These elements are called **metalloids**. Examples of metalloids are silicon, germanium, arsenic, and tellurium.

A note on good practice You will sometimes see metalloids referred to as 'semi-metals'. This name is best avoided because a semi-metal has a well defined and quite distinct meaning in physics (see Section 3.19).

(a) The periodic table

A more detailed classification of the elements is the one devised by Dmitri Mendeleev in 1869; this scheme is familiar to every chemist as the **periodic table**. Mendeleev arranged the known elements in order of increasing atomic weight (molar mass). This arrangement resulted in families of elements with similar chemical properties, which he arranged into the groups of the periodic table. For example, the fact that C, Si, Ge, and Sn all form hydrides of the general formula EH_4 suggests that they belong to the same group. That N, P, As, and Sb all form hydrides with the general formula EH_3 suggests that they belong to a different group. Other compounds of these elements show family similarities, as in the formulas CF_4 and SiF_4 in the first group, and NF_3 and PF_3 in the second.

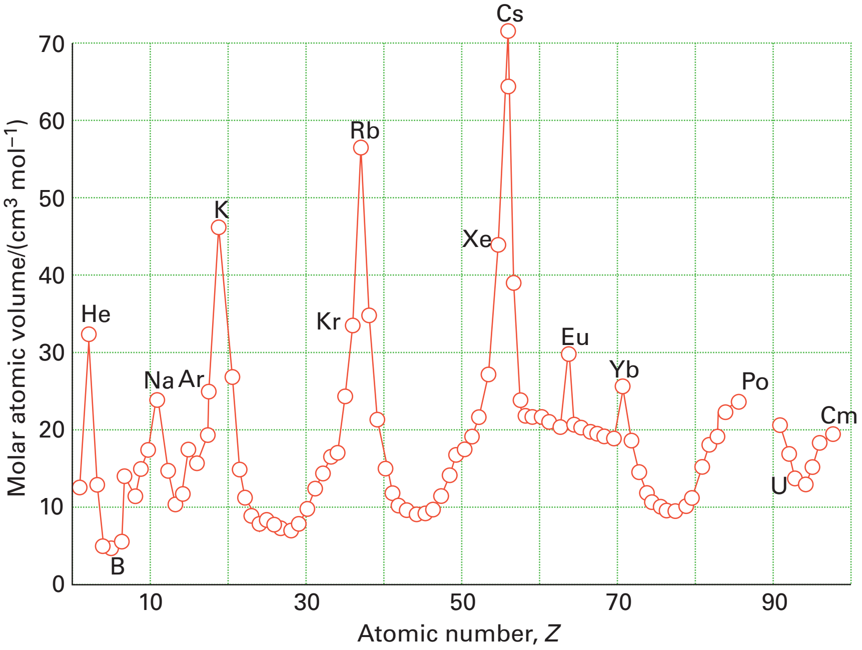

Figure 1.21 The periodic variation of molar volume with atomic number.

Mendeleev concentrated on the chemical properties of the elements. At about the same time Lothar Meyer in Germany was investigating their physical properties, and found that similar values repeated periodically with increasing molar mass. Figure 1.21 shows a classic example, where the molar volume of the element (its volume per mole of atoms) at 1 bar and 298 K is plotted against atomic number.

Mendeleev provided a spectacular demonstration of the usefulness of the periodic table by predicting the general chemical properties, such as the numbers of bonds they form, of unknown elements corresponding to gaps in his original periodic table. (He also predicted elements that we now know cannot exist and denied the presence of elements that we now know do exist, but that is overshadowed by his positive achievement and has been quietly forgotten.) The same process of inference from periodic trends is still used by inorganic chemists to rationalize trends in the physical and chemical properties of compounds and to suggest the synthesis of previously unknown compounds. For instance, by recognizing that carbon and silicon are in the same family, the existence of alkenes $R_2C{=}CR_2$ suggests that $R_2Si{=}SiR_2$ ought to exist too. Compounds with silicon–silicon double bonds (disilaethenes) do indeed exist, but it was not until 1981 that chemists succeeded in isolating one. The periodic trends in the properties of the elements are explored further in Chapter 9.

(b) The format of the periodic table

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 now see, for instance, that a **block** of the table indicates the type of subshell currently being occupied according to the building-up principle. Each **period**, or row, of the table corresponds to the completion of the s and p subshells of a given shell. The period number is the value of the principal quantum number n of the shell which according to the building-up principle is currently being occupied in the main groups of the table. For example, Period 2 corresponds to the $n = 2$ shell and the filling of the 2s and 2p subshells.

The group numbers, G, are closely related to the number of electrons in the **valence shell**, the outermost shell of the atom. In the '1–18' numbering system recommended by IUPAC:

Block:	s	p	d
Number of electrons in valence shell:	G	$G - 10$	G

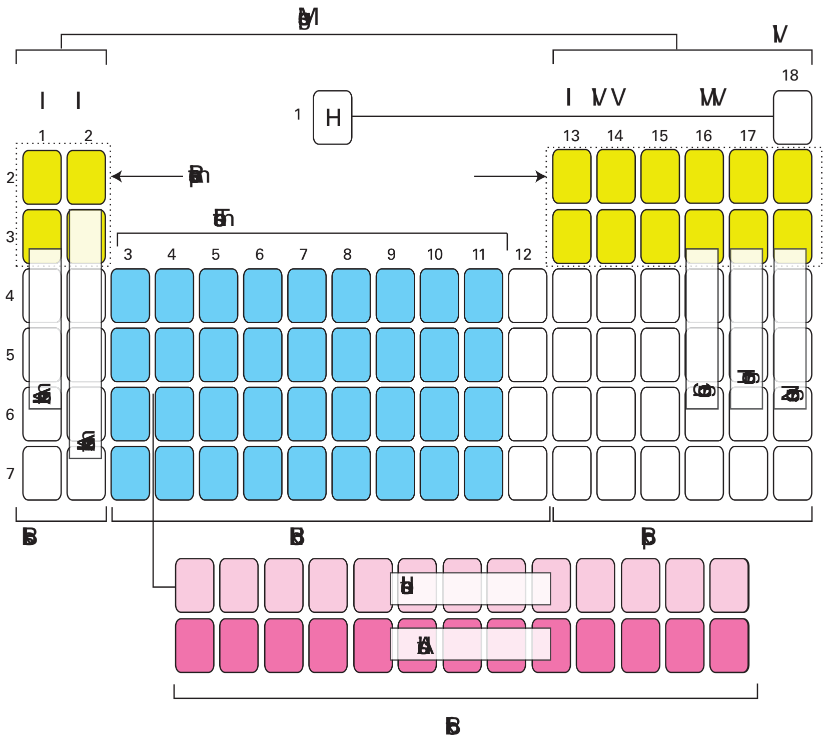

Figure 1.22 The general structure of the periodic table. Compare this template with the complete table inside the front cover for the identities of the elements that belong to each block.

For the purpose of this expression, the 'valence shell' of a d-block element consists of the *n*s and ($n - 1$)d orbitals, so a Sc atom has three valence electrons (two 4s and one 3d electron). The number of valence electrons for the p-block element Se (Group 16) is $16 - 10 = 6$, which corresponds to the configuration s^2p^4.

EXAMPLE 1.7 Placing elements within the periodic table.

State to which period, group, and block of the periodic table the element with the electron configuration $1s^22s^22p^63s^23p^4$ belongs. Identify the element.

Answer We need to remember that the period number is given by the principal quantum number, *n*, that the group number can be found from the number of valence electrons, and that the identity of the block is given by the type of orbital last occupied according to the building-up principle. The valence electrons have $n = 3$, therefore the element is in Period 3 of the periodic table. The six valence electrons identify the element as a member of Group 16. The electron added last is a p electron, so the element is in the p block. The element is sulfur.

Self-test 1.7 State to which period, group, and block of the periodic table the element with the electron configuration $1s^22s^22p^63s^23p^64s^2$ belongs. Identify the element.

1.9 Atomic properties

Certain characteristic properties of atoms, particularly their radii and the energies associated with the removal and addition of electrons, show regular periodic variations with atomic number. These atomic properties are of considerable importance for understanding the chemical properties of the elements and are discussed further in Chapter 9. A knowledge of these trends enables chemists to rationalize observations and predict likely chemical and structural behaviour without having to refer to tabulated data for each element.

(a) Atomic and ionic radii

Key points: Atomic radii increase down a group and, within the s and p blocks, decrease from left to right across a period. The lanthanide contraction results in a decrease in atomic radius for elements following the f block. All monatomic anions are larger than their parent atoms and all monatomic cations are smaller.

One of the most useful atomic characteristics of an element is the size of its atoms and ions. As we shall see in later chapters, geometrical considerations are central to explaining the structures of many solids and individual molecules. In addition, the average distance of electrons from the nucleus of an atom correlates with the energy needed to remove it in the process of forming a cation.

An atom does not have a precise radius because far from the nucleus the electron density falls off only exponentially (but sharply). However, we can expect atoms with numerous electrons to be larger, in some sense, than atoms that have only a few electrons. Such considerations have led chemists to propose a variety of definitions of atomic radius on the basis of empirical considerations.

The **metallic radius** of a metallic element is defined as half the experimentally determined distance between the centres of nearest-neighbour atoms in the solid (Fig. 1.23a, but see Section 3.7 for a refinement of this definition). The **covalent radius** of a nonmetallic element is similarly defined as half the internuclear distance between neighbouring atoms of the same element in a molecule (Fig. 1.23b). We shall refer to metallic and covalent radii jointly as **atomic radii** (Table 1.3). The periodic trends in metallic and covalent radii can be seen from the data in the table and are illustrated in Fig. 1.24. As will be familiar from introductory chemistry, atoms may be linked by single, double, and triple bonds, with multiple bonds shorter than single bonds between the same two elements. The **ionic radius** (Fig. 1.23c) of an element is related to the distance between the centres of neighbouring cations and anions in an ionic compound. An arbitrary decision has to be taken on how to apportion the cation–anion distance between the two ions. There have been many suggestions: in one common scheme, the radius of the O^{2-} ion is taken to be 140 pm (Table 1.4; see Section 3.7 for a refinement of this definition). For example, the ionic radius of Mg^{2+} is obtained by subtracting 140 pm from the internuclear distance between adjacent Mg^{2+} and O^{2-} ions in solid MgO.

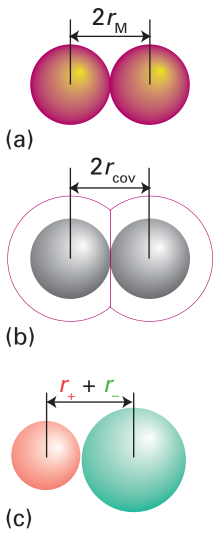

Figure 1.23 A representation of (a) metallic radius, (b) covalent radius, and (c) ionic radius.

The data in Table 1.3 show that *atomic radii increase down a group*, and that they *decrease from left to right across a period*. These trends are readily interpreted in terms of the electronic structure of the atoms. On descending a group, the valence electrons are found in orbitals of successively higher principal quantum number. The atoms within the group have a greater number of completed shells of electrons in successive periods and hence their radii increase down the group. Across a period, the valence electrons enter orbitals of the same shell; however, the increase in effective nuclear charge across the period draws in the electrons and results in progressively more compact atoms. The general increase in radius down a group and decrease across a period should be remembered as they correlate well with trends in many chemical properties.

Period 6 shows an interesting and important modification to these otherwise general trends. We see from Fig. 1.24 that the metallic radii in the third row of the d block are very similar to those in the second row, and not significantly larger as might be expected given their considerably greater numbers of electrons. For example, the atomic radii of Mo ($Z = 42$) and W ($Z = 74$) are 140 and 141 pm, respectively, despite the latter having many more electrons. The reduction of radius below that expected on the basis of a simple extrapolation down the group is called the **lanthanide contraction**. The name points to the

Table 1.3 Atomic radii, r/pm*

Li	Be											B	C	N	O	F
157	112											88	77	74	73	71
Na	Mg											Al	Si	P	S	Cl
191	160											143	118	110	104	99
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br
235	197	164	147	135	129	137	126	125	125	128	137	140	122	122	117	114
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I
250	215	182	160	147	140	135	134	134	137	144	152	150	140	141	135	133
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi		
272	224	188	159	147	141	137	135	136	139	144	155	155	154	152		

* The values refer to coordination number 12 for metallic radii (see Section 3.2).

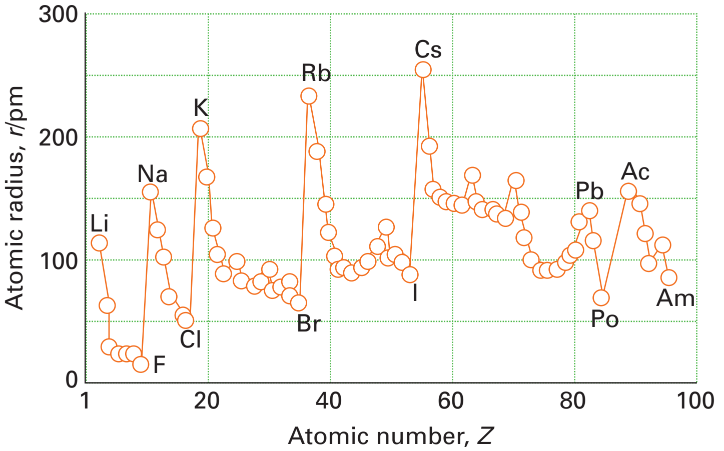

Figure 1.24 The variation of atomic radii through the periodic table. Note the contraction of radii following the lanthanoids in Period 6. Metallic radii have been used for the metallic elements and covalent radii have been used for the nonmetallic elements.

origin of the effect. The elements in the third row of the d block (Period 6) are preceded by the elements of the first row of the f block, the lanthanoids, in which the 4f orbitals are being occupied. These orbitals have poor shielding properties and so the valence electrons experience more attraction from the nuclear charge than might be expected. The repulsions between electrons being added on crossing the f block fail to compensate for the increasing nuclear charge, so Z_{eff} increases from left to right across a period. The dominating effect of the latter is to draw in all the electrons and hence to result in a more compact atom. A similar contraction is found in the elements that follow the d block for the same reasons. For example, although there is a substantial increase in atomic radius between C and Si (77 and 118 pm, respectively), the atomic radius of Ge (122 pm) is only slightly greater than that of Al.

Relativistic effects, especially the increase in mass as particles approach the speed of light, have an important role to play on the elements in and following Period 6 but are rather subtle. Electrons in s and p orbitals, which approach closely to the highly charged nucleus and experience strong accelerations, contract whereas electrons in the less penetrating d and f orbitals expand. One consequence of the latter expansion is that d and f electrons become less effective at shielding other electrons, and the outermost s electrons contract further. For light elements, relativistic effects can be neglected but for the heavier elements with high atomic numbers they become significant and can result in an approximately 20 per cent reduction in the size of the atom.

Another general feature apparent from Table 1.4 is that all monatomic anions are larger than their parent atoms and all monatomic cations are smaller than their parent atoms (in some cases markedly so). The increase in radius of an atom on anion formation is a result of the greater electron–electron repulsions that occur when an additional electron is added to form an anion. There is also an associated decrease in the value of Z_{eff}. The smaller radius of a cation compared with its parent atom is a consequence not only of the reduction in electron–electron repulsions that follow electron loss but also of the fact that cation formation typically results in the loss of the valence electrons and an increase in Z_{eff}. That loss often leaves behind only the much more compact closed shells of electrons. Once these gross differences are taken into account, the variation in ionic radii through the periodic table mirrors that of the atoms.

Although small variations in atomic radii may seem of little importance, in fact atomic radius plays a central role in the chemical properties of the elements. Small changes can have profound consequences, as we shall see in Chapter 9.

(b) Ionization energy

Key points: First ionization energies are lowest at the lower left of the periodic table (near caesium) and greatest near the upper right (near helium). Successive ionizations of a species require higher energies.

The ease with which an electron can be removed from an atom is measured by its **ionization energy**, I, the minimum energy needed to remove an electron from a gas-phase atom:

$$\mathrm{A(g)} \rightarrow \mathrm{A^+(g)} + \mathrm{e^-(g)} \quad I = E(\mathrm{A^+,g}) - E(\mathrm{A,g}) \tag{1.8}$$

Table 1.4 Ionic radii, r/pm*

Li^+	Be^{2+}	B^{3+}			N^{3-}	O^{2-}	F^-
59(4)	27(4)	11(4)			146	135(2)	128(2)
76(6)						138(4)	131(4)
						140(6)	133(6)
						142(8)	
Na^+	Mg^{2+}	Al^{3+}			P^{3-}	S^{2-}	Cl^-
99(4)	49(4)	39(4)			212	184(6)	181(6)
102(6)	72(6)	53(6)					
132(8)	103(8)						
K^+	Ca^{2+}	Ga^{3+}			As^{3-}	Se^{2-}	Br^-
138(6)	100(6)	62(6)			222	198(6)	196(6)
151(8)	112(8)						
159(10)	123(10)						
160(12)	134(12)						
Rb^+	Sr^{2+}	In^{3+}	Sn^{2+}	Sn^{4+}		Te^{2-}	I^-
148(6)	118(6)	80(6)	83(6)	69(6)		221(6)	220(6)
160(8)	125(8)	92(8)	93(8)				
173(12)	144(12)						
Cs^+	Ba^{2+}	Tl^{3+}					
167(6)	135(6)	89(6)					
174(8)	142(8)	Tl^+					
188(12)	175(12)	150(6)					

* Numbers in parentheses are the coordination number of the ion. For more values, see *Resource section 1*.

The **first ionization energy**, I_1, is the energy required to remove the least tightly bound electron from the neutral atom, the **second ionization energy**, I_2, is the energy required to remove the least tightly bound electron from the resulting cation, and so on. Ionization energies are conveniently expressed in electronvolts (eV), but are easily converted into kilojoules per mole by using 1 eV = 96.485 kJ mol^{-1}. The ionization energy of the H atom is 13.6 eV, so to remove an electron from an H atom is equivalent to dragging the electron through a potential difference of 13.6 V.

In thermodynamic calculations it is often more appropriate to use the **ionization enthalpy**, the standard enthalpy of the process in eqn 1.8, typically at 298 K. The molar ionization enthalpy is larger by $\frac{5}{2}RT$ than the ionization energy. This difference stems from the change from $T = 0$ (assumed implicitly for I) to the temperature T (typically 298 K) to which the enthalpy value refers, and the replacement of 1 mol of gas particles by 2 mol of gaseous ions plus electrons. However, because RT is only 2.5 kJ mol^{-1} (corresponding to 0.026 eV) at room temperature and ionization energies are of the order of 10^2–10^3 kJ mol^{-1} (1–10 eV), the difference between ionization energy and enthalpy can often be ignored.

To a large extent, the first ionization energy of an element is determined by the energy of the highest occupied orbital of its ground-state atom. First ionization energies vary systematically through the periodic table (Table 1.5), being smallest at the lower left (near Cs) and greatest near the upper right (near He). The variation follows the pattern of effective nuclear charge, and (as Z_{eff} itself shows) there are some subtle modulations arising from the effect of electron–electron repulsions within the same subshell. A useful approximation is that for an electron from a shell with principal quantum number n

$$I \propto \frac{Z_{\text{eff}}^2}{n^2}$$

Ionization energies also correlate strongly with atomic radii, and elements that have small atomic radii generally have high ionization energies. The explanation of the correlation is

Table 1.5 First, second, and third (and some fourth) ionization energies of the elements, $I/(\mathrm{kJ\ mol^{-1}})$

H							He
1312							2373
							5259
Li	Be	B	C	N	O	F	Ne
513	899	801	1086	1402	1314	1681	2080
7297	1757	2426	2352	2855	3386	3375	3952
11809	14844	3660	4619	4577	5300	6050	6122
		25018					
Na	Mg	Al	Si	P	S	Cl	Ar
495	737	577	786	1011	1000	1251	1520
4562	1476	1816	1577	1903	2251	2296	2665
6911	7732	2744	3231	2911	3361	3826	3928
		11574					
K	Ca	Ga	Ge	As	Se	Br	Kr
419	589	579	762	947	941	1139	1351
3051	1145	1979	1537	1798	2044	2103	3314
4410	4910	2963	3302	2734	2974	3500	3565
Rb	Sr	In	Sn	Sb	Te	I	Xe
403	549	558	708	834	869	1008	1170
2632	1064	1821	1412	1794	1795	1846	2045
3900	4210	2704	2943	2443	2698	3197	3097
Cs	Ba	Tl	Pb	Bi	Po	At	Rn
375	502	590	716	704	812	926	1036
2420	965	1971	1450	1610	1800	1600	
3400	3619	2878	3080	2466	2700	2900	

that in a small atom an electron is close to the nucleus and experiences a strong Coulombic attraction, making it difficult to remove. Therefore, as the atomic radius increases down a group, the ionization energy decreases and the decrease in radius across a period is accompanied by a gradual increase in ionization energy.

Some deviation from this general trend in ionization energy can be explained quite readily. An example is the observation that the first ionization energy of boron is smaller than that of beryllium, despite the former's higher nuclear charge. This anomaly is readily explained by noting that, on going to boron, the outermost electron occupies a 2p orbital and hence is less strongly bound than if it had occupied a 2s orbital. As a result, the value of I_1 decreases from Be to B. The decrease between N and O has a slightly different explanation. The configurations of the two atoms are

$$\mathrm{N}\ [\mathrm{He}]2\mathrm{s}^2 2\mathrm{p}_x^1 2\mathrm{p}_y^1 2\mathrm{p}_z^1 \qquad \mathrm{O}\ [\mathrm{He}]2\mathrm{s}^2 2\mathrm{p}_x^2 2\mathrm{p}_y^1 2\mathrm{p}_z^1$$

We see that, in an O atom, two electrons are present in a single 2p orbital. They repel each other strongly, and this strong repulsion offsets the greater nuclear charge. Another contribution to the difference is the lower energy of the O^+ ion on account of its having a $2\mathrm{s}^2 2\mathrm{p}^3$ configuration: as we have seen, a half-filled subshell has a relatively low energy (Fig. 1.25). Additionally, the half-filled shell of p orbitals of nitrogen is a particularly stable configuration.

When considering F and Ne on the right of Period 2, the last electrons enter orbitals that are already half full, and continue the trend from O towards higher ionization energy. The higher values of the ionization energies of these two elements reflect the high value of Z_{eff}. The value of I_1 falls back sharply from Ne to Na as the outermost electron occupies the next shell with an increased principal quantum number and is therefore further from the nucleus.

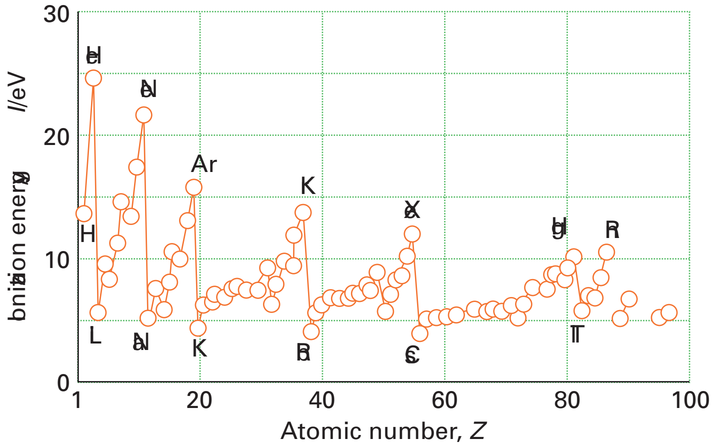

Figure 1.25 The periodic variation of first ionization energies.

EXAMPLE 1.8 Accounting for a variation in ionization energy

Account for the decrease in first ionization energy between phosphorus and sulfur.

Answer We approach this question by considering the ground-state configurations of the two atoms:

P $[\mathrm{Ne}]3s^2 3p_x^1 3p_y^1 3p_z^1$ S $[\mathrm{Ne}]3s^2 3p_x^2 3p_y^1 3p_z^1$

As in the analogous case of N and O, in the ground state of S, two electrons are present in a single 3p orbital. They are so close together that they repel each other strongly, and this increased repulsion offsets the effect of the greater nuclear charge of S compared with P. As in the difference between N and O, the half-filled subshell of S^+ also contributes to the lowering of energy of the ion and hence to the smaller ionization energy.

Self-test 1.8 Account for the decrease in first ionization energy between fluorine and chlorine.

Another important pattern is that successive ionizations of an element require increasingly higher energies (Fig. 1.26). Thus, the second ionization energy of an element E (the energy needed to remove an electron from the cation E^+) is higher than its first ionization energy, and its third ionization energy (the energy needed to remove an electron from E^{2+}) is higher still. The explanation is that the higher the positive charge of a species, the greater the electrostatic attraction experienced by the electron being removed. Moreover, when an electron is removed, Z_{eff} increases and the atom contracts. It is then even more difficult to remove an electron from this smaller, more compact, cation. The difference in ionization energy is greatly magnified when the electron is removed from a closed shell of the atom (as is the case for the second ionization energy of Li and any of its congeners) because the electron must then be extracted from a compact orbital in which it interacts strongly with the nucleus. The first ionization energy of Li, for instance, is 513 kJ mol^{-1}, but its second ionization energy is 7297 kJ mol^{-1}, more than ten times greater.

The pattern of successive ionization energies down a group is far from simple. Figure 1.26 shows the first, second, and third ionization energies of the members of Group 13. Although they lie in the expected order $I_1 < I_2 < I_3$, there is no simple trend. The lesson to be drawn is that whenever an argument hangs on trends in small differences in ionization energies, it is always best to refer to actual numerical values rather than to guess a likely outcome.

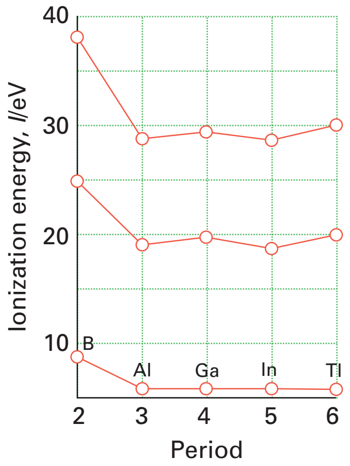

Figure 1.26 The first, second, and third ionization energies of the elements of Group 13. Successive ionization energies increase, but there is no clear pattern of ionization energies down the group.

(c) Electron affinity

Key point: Electron affinities are highest for elements near fluorine in the periodic table.

The **electron-gain enthalpy**, $\Delta_{\mathrm{eg}}H^{\ominus}$, is the change in standard molar enthalpy when a gaseous atom gains an electron:

$$\mathrm{A(g)} + \mathrm{e^-(g)} \rightarrow \mathrm{A^-(g)}$$

EXAMPLE 1.9 Accounting for values of successive energies of ionization

Rationalize the following values for successive ionization energies of boron, where $\Delta_{\text{ion}}H(N)$ is the Nth enthalpy of ionization:

N	1	2	3	4	5
$\Delta_{\text{ion}}H(N)/(\text{kJ mol}^{-1})$	807	2433	3666	25033	32834

Answer When considering trends in ionization energy, a sensible starting point is the electron configurations of the atoms. The electron configuration of B is $1s^2 2s^2 2p^1$. The first ionization energy corresponds to removal of the electron in the 2p orbital. This electron is shielded from nuclear charge by the core and the full 2s orbital. The second value corresponds to removal of a 2s electron from the B^+ cation. This electron is more difficult to remove on account of the increased effective nuclear charge. The effective nuclear charge increases further on removal of this electron, resulting in an increase between $\Delta_{\text{ion}}H(2)$ and $\Delta_{\text{ion}}H(3)$. There is a large increase between $\Delta_{\text{ion}}H(3)$ and $\Delta_{\text{ion}}H(4)$ because the 1s shell lies at very low energy as it experiences almost the full nuclear charge and also has $n = 1$. The final electron to be removed experiences no shielding of nuclear charge so $\Delta_{\text{ion}}H(5)$ is very high, and is given by $hcRZ^2$ with $Z = 5$, corresponding to (13.6 eV) $\times$ 25 = 340 eV (32.8 MJ mol^{-1}).

Self-test 1.9 Study the values listed below of the first five ionization energies of an element and deduce to which group of the periodic table the element belongs. Give your reasoning.

N	1	2	3	4	5
$\Delta_{\text{ion}}H(N)/(\text{kJ mol}^{-1})$	1093	2359	4627	6229	37838

Electron gain may be either exothermic or endothermic. Although the electron-gain enthalpy is the thermodynamically appropriate term, much of inorganic chemistry is discussed in terms of a closely related property, the **electron affinity**, E_a, of an element (Table 1.6), which is the difference in energy between the gaseous atoms and the gaseous ions at $T = 0$.

$$E_a = E(\text{A,g}) - E(\text{A}^-,\text{g}) \tag{1.9}$$

Although the precise relation is $\Delta_{\text{eg}}H^{\ominus} = -E_a - \frac{5}{2}RT$, the contribution $\frac{5}{2}RT$ is commonly ignored. A positive electron affinity indicates that the ion A^- has a lower, more negative energy than the neutral atom, A. The second electron-gain enthalpy, the enthalpy change for the attachment of a second electron to an initially neutral atom, is invariably positive because the electron repulsion outweighs the nuclear attraction.

The electron affinity of an element is largely determined by the energy of the *lowest unfilled* (or half-filled) orbital of the ground-state atom. This orbital is one of the two **frontier orbitals** of an atom, the other one being the *highest filled* atomic orbital. The frontier orbitals are the sites of many of the changes in electron distributions when bonds form,

Table 1.6 First electron affinities of the main-group elements, $E_a/(\text{kJ mol}^{-1})$*

H							He
72							−48
Li	Be	B	C	N	O	F	Ne
60	≤ 0	27	122	−8	141	328	−116
					−780		
Na	Mg	Al	Si	P	S	Cl	Ar
53	≤ 0	43	134	72	200	349	−96
					−492		
K	Ca	Ga	Ge	As	Se	Br	Kr
48	2	29	116	78	195	325	−96
Rb	Sr	In	Sn	Sb	Te	I	Xe
47	5	29	116	103	190	295	−77

* The first values refer to the formation of the ion X^- from the neutral atom; the second value to the formation of X^{2-} from X^-.

EXAMPLE 1.10 Accounting for the variation in electron affinity

Account for the large decrease in electron affinity between Li and Be despite the increase in nuclear charge.

Answer When considering trends in electron affinities, as in the case of ionization energies, a sensible starting point is the electron configurations of the atoms. The electron configurations of Li and Be are [He]$2s^1$ and [He]$2s^2$, respectively. The additional electron enters the 2s orbital of Li but it enters the 2p orbital of Be, and hence is much less tightly bound. In fact, the nuclear charge is so well shielded in Be that electron gain is endothermic.

Self-test 1.10 Account for the decrease in electron affinity between C and N.

and we shall see more of their importance as the text progresses. An element has a high electron affinity if the additional electron can enter a shell where it experiences a strong effective nuclear charge. This is the case for elements towards the top right of the periodic table, as we have already explained. Therefore, elements close to fluorine (specifically O and Cl, but not the noble gases) can be expected to have the highest electron affinities as their Z_{eff} is large and it is possible to add electrons to the valence shell. Nitrogen has very low electron affinity because there is a high electron repulsion when the incoming electron enters an orbital that is already half full.

A note on good practice Be alert to the fact that some people use the terms 'electron affinity' and 'electron-gain enthalpy' interchangeably. In such cases, a positive electron affinity could indicate that A^- has a higher energy than A.

(d) Electronegativity

Key points: The electronegativity of an element is the power of an atom of the element to attract electrons when it is part of a compound; there is a general increase in electronegativity across a period and a general decrease down a group.

The **electronegativity**, χ (chi), of an element is the power of an atom of the element to attract electrons to itself when it is part of a compound. If an atom has a strong tendency to acquire electrons, it is said to be highly electronegative (like the elements close to fluorine). Electronegativity is a very useful concept in chemistry and has numerous applications, which include a rationalization of bond energies and the types of reactions that substances undergo and the prediction of the polarities of bonds and molecules (Chapter 2).

Periodic trends in electronegativity can be related to the size of the atoms and electron configuration. If an atom is small and has an almost closed shell of electrons, then it is more likely to attract an electron to itself than a large atom with few valence electrons. Consequently, the electronegativities of the elements typically increase left to right across a period and decrease down a group.

Quantitative measures of electronegativity have been defined in many different ways. Linus Pauling's original formulation (which results in the values denoted χ_P in Table 1.7) draws on concepts relating to the energetics of bond formation, which will be dealt with in Chapter 2.[2] A definition more in the spirit of this chapter, in the sense that it is based on the properties of individual atoms, was proposed by Robert Mulliken. He observed that, if an atom has a high ionization energy, I, and a high electron affinity, E_a, then it will be likely to acquire rather than lose electrons when it is part of a compound, and hence be classified as highly electronegative. Conversely, if its ionization energy and electron affinity are both low, then the atom will tend to lose electrons rather than gain them, and hence be classified as electropositive. These observations motivate the definition of the **Mulliken electronegativity**, χ_M, as the average value of the ionization energy and the electron affinity of the element (both expressed in electronvolts):

$$\chi_M = \tfrac{1}{2}(I + E_a) \tag{1.10}$$

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[2] Pauling values of electronegativity are used throughout the following chapters.

Table 1.7 Pauling χ_P, Mulliken, χ_M, and Allred–Rochow, χ_{AR}, electronegativities

H							He
2.20							5.5
3.06							
2.20							
Li	Be	B	C	N	O	F	Ne
0.98	1.57	2.04	2.55	3.04	3.44	3.98	
1.28	1.99	1.83	2.67	3.08	3.22	4.43	4.60
0.97	1.47	2.01	2.50	3.07	3.50	4.10	5.10
Na	Mg	Al	Si	P	S	Cl	Ar
0.93	1.31	1.61	1.90	2.19	2.58	3.16	
1.21	1.63	1.37	2.03	2.39	2.65	3.54	3.36
1.01	1.23	1.47	1.74	2.06	2.44	2.83	3.30
K	Ca	Ga	Ge	As	Se	Br	Kr
0.82	1.00	1.81	2.01	2.18	2.55	2.96	3.0
1.03	1.30	1.34	1.95	2.26	2.51	3.24	2.98
0.91	1.04	1.82	2.02	2.20	2.48	2.74	3.10
Rb	Sr	In	Sn	Sb	Te	I	Xe
0.82	0.95	1.78	1.96	2.05	2.10	2.66	2.6
0.99	1.21	1.30	1.83	2.06	2.34	2.88	2.59
0.89	0.99	1.49	1.72	1.82	2.01	2.21	2.40
Cs	Ba	Tl	Pb	Bi			
0.79	0.89	2.04	2.33	2.02			
0.70	0.90	1.80	1.90	1.90			
0.86	0.97	1.44	1.55	1.67			

The hidden complication in the apparently simple definition of the Mulliken electronegativity is that the ionization energy and electron affinity in the definition relate to the **valence state**, the electron configuration the atom is supposed to have when it is part of a molecule. Hence, some calculation is required because the ionization energy and electron affinity to be used in calculating χ_M are mixtures of values for various actual spectroscopically observable states of the atom. We need not go into the calculation, but the resulting values given in Table 1.7 may be compared with the Pauling values (Fig. 1.27). The two

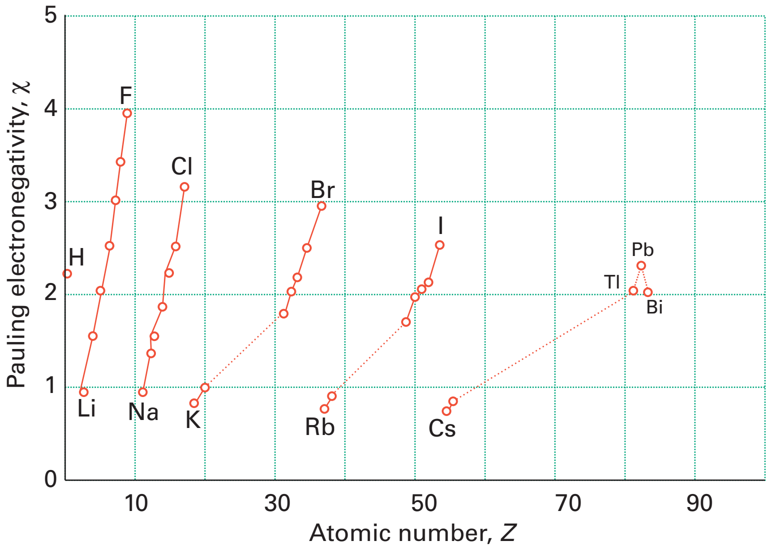

Figure 1.27 The periodic variation of Pauling electronegativities.

scales give similar values and show the same trends. One reasonably reliable conversion between the two is

$$\chi_P = 1.35\chi_M^{1/2} - 1.37 \tag{1.11}$$

Because the elements near F (other than the noble gases) have high ionization energies and appreciable electron affinities, these elements have the highest Mulliken electronegativities. Because χ_M depends on atomic energy levels—and in particular on the location of the highest filled and lowest empty orbitals—the electronegativity of an element is high if the two frontier orbitals of its atoms are low in energy.

Various alternative 'atomic' definitions of electronegativity have been proposed. A widely used scale, suggested by A.L. Allred and E. Rochow, is based on the view that electronegativity is determined by the electric field at the surface of an atom. As we have seen, an electron in an atom experiences an effective nuclear charge Z_{eff}. The Coulombic potential at the surface of such an atom is proportional to Z_{eff}/r, and the electric field there is proportional to Z_{eff}/r^2. In the **Allred–Rochow definition** of electronegativity, χ_{AR} is assumed to be proportional to this field, with r taken to be the covalent radius of the atom:

$$\chi_{AR} = 0.744 + \frac{35.90 Z_{\text{eff}}}{(r/\text{pm})^2} \tag{1.12}$$

The numerical constants have been chosen to give values comparable to Pauling electronegativities. According to the Allred–Rochow definition, elements with high electronegativity are those with high effective nuclear charge and the small covalent radius: such elements lie close to F. The Allred–Rochow values parallel closely those of the Pauling electronegativities and are useful for discussing the electron distributions in compounds.

(e) Polarizability

Key points: **A polarizable atom or ion is one with orbitals that lie close in energy; large, heavy atoms and ions tend to be highly polarizable.**

The **polarizability**, α, of an atom is its ability to be distorted by an electric field (such as that of a neighbouring ion). An atom or ion (most commonly, an anion) is highly **polarizable** if its electron distribution can be distorted readily, which is the case if unfilled atomic orbitals lie close to the highest-energy filled orbitals. That is, the polarizability is likely to be high if the separation of the frontier orbitals is small and the polarizability will be low if the separation of the frontier orbitals is large (Fig. 1.28). Closely separated frontier orbitals are typically found for large, heavy atoms and ions, such as the atoms and ions of the heavier alkali metals and the heavier halogens, so these atoms and ions are the most polarizable. Small, light atoms, such as the atoms and ions near fluorine, typically have widely spaced energy levels, so these atoms and ions are least polarizable. Species that effectively distort the electron distribution of a neighbouring atom or anion are described as having **polarizing ability**.

We shall see the consequences of polarizability when considering the nature of bonding in Section 2.2, but it is appropriate to anticipate here that extensive polarization leads to covalency. **Fajan's rules** summarize the factors that affect polarization:

- Small, highly charged cations have polarizing ability.
- Large, highly charged anions are easily polarized.
- Cations that do not have a noble-gas electron configuration are easily polarized.

The last rule is particularly important for the d-block elements.

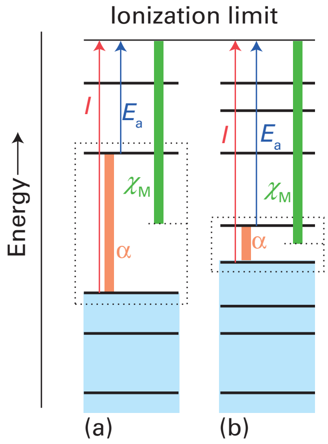

Figure 1.28 The interpretation of the electronegativity and polarizability of an element in terms of the energies of the frontier orbitals (the highest filled and lowest unfilled atomic orbitals). (a) Low electronegativity and polarizability; (b) high electronegativity and polarizability.

EXAMPLE 1.11 Identifying polarizable species

Which would be the more polarizable, an F^- ion or an I^- ion?

Answer We can make use of the fact that polarizable anions are typically large and highly charged. An F^- ion is small and singly charged. An I^- ion has the same charge but is large. Therefore, an I^- ion is likely to be the more polarizable.

Self-test 1.11 Which would be more polarizing, Na^+ or Cs^+?