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|      | Ac| Th| Pa| U | Np| Pu| Am| Cm| Bk| Cf |Es | Fm |Md |No |    |    |    |    |

Notes:
- Each element is represented by its atomic number (Z) and atomic weight (M).
- Periods and groups are indicated on the left and top edges respectively.
- The periodic table includes the noble gases in the outermost period.
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For Anne
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Preface to the Second Edition

In this edition the structure of the First Edition has been retained. However, in the intervening years an enormous number of new experimental and theoretical studies have appeared in the literature, and although this is an introductory text, many of these new studies merit reporting. The additions are spread throughout the text, but can be roughly divided into four groups. The first area is computational science and engineering. Computer simulations of the behaviour of solids, from the engineering of large-scale structures using finite element analysis, via atomistic simulation and molecular dynamics, used to study features such as elastic behaviour and dislocation movement, through to the calculation of the electronic properties of solids via density functional theory, are used routinely in almost all disciplines that are related to the subject matter of this book. The computer calculation of phase diagrams (CALPHAD) also comes into this category. An indication of the principles underlying these programmes of work is given to underpin the computational “black boxes” available (Chapters 1, 2, 4 and 10).

Another area of change is that concerned with nanoscale properties. Here, not only is the primary literature growing rapidly but there are a rapidly increasing number of specialised books that deal with the subject. Some of the properties that are affected by small scales are described, including the magnetic and ferroelectric properties of thin films and superlattices (Chapters 11 and 12) and nanoparticle colours (Chapter 14).

Point defects are key components for the manipulation of the physical properties of solids, and this area has been supplemented. The universally used Kroger-Vink notation for point defects has been defined (Chapter 3). The interplay between defect populations and ionic conductivity (Chapter 7), relaxor ferroelectrics (Chapter 11), the electronic and magnetic properties of cobaltites and manganites, including colossal magnetoresistance (Chapter 12, 13), cuprate superconductors (Chapter 13) and thermoelectric properties (Chapter 15) are described.

New text has also been added to cover a number of important crystallographically related topics. These include quasicrystals (Chapter 3), phase transformations including first- and second-order transitions, displacive versus reconstructive transitions and order–disorder transitions, and martensitic transitions (Chapter 9), and coverage of crystal symmetry with respect to piezoelectricity (Chapter 11).

Other new topics include lithium-air batteries (Chapter 8), increased discussion of elastic moduli and their measurement using ultrasonic waves (Chapter 10), the newly appreciated physical property of flexoelectricity (Chapter 11), crystal field effects, the magnetic properties of garnets and photoinduced magnetism (Chapter 12), dye-sensitized solar cells (Chapter 14), zero thermal expanding solids (Chapter 15), increased discussion of nuclear stability and radioisotope dating (Chapter 16).

The text on all these topics is necessarily compact, but can be supplemented by reference to extensive additional sources listed in the Further Reading sections.

Because of this expansion of material, of necessity some sections of the original have had to be excised. For the same reason, much of the supplementary information in the first edition has been
removed or incorporated into the relevant chapters. In making these changes, all the material has been rewritten and rearranged to the extent that no single page of this edition is identical to any in the first edition. In addition, all figures have been redrawn in colour. These, together with the solutions to the Introductory Questions and Problems and Exercises, are to be found on a companion web site (http://www.wiley.com/go/tilleysolids2e).

It is a pleasure to acknowledge the help from the staff at John Wiley, including Rebecca Stubbs, Emma Strickland and Sarah Tilley, all of whom were enthusiastic about this project and fielded my many queries efficiently. The staff of the Trevithick library in Cardiff University provided, as always, help in tracking down obscure references. Professor F.S. Stone and Dr D.F. Klemperer were generous in their encouragement. Finally I must acknowledge my wife Anne, who has continually supported and helped in more ways that it is possible to record.

R.J.D. Tilley
August 2012
Preface to the First Edition

This book originated in lectures to undergraduate students in materials science, which were later extended to geology, physics and engineering students. The subject matter is concerned with the structures and properties of solids. The material is presented with a science bias, and is aimed not only at students taking traditional materials science and engineering courses, but also courses in the rapidly expanding fields of materials chemistry and physics. The coverage aims to be complementary to established books in materials science and engineering. The level is designed to be introductory in nature, and as far as is practical, the book is self-contained. The chapters are provided with questions designed to reinforce the concepts presented. These are in two parts. A multiple choice ‘Quick Quiz’ is designed to be tackled rapidly, and aims to uncover weaknesses in a student’s grasp of the fundamental concepts described. The ‘Calculations and Questions’ are more traditional, containing numerical examples to test the understanding of formulae, and derivations that are not carried out in the main body of the text. Many chapters contain one or more appendices that bear directly upon the material, but which would disrupt the flow of the subject matter if included within the chapter itself. These are meant to provide more depth than is possible otherwise. Further Reading allows students to take matters a little further. With only one exception, the references are to printed information. In general, it would be expected that a student would initially turn to the Internet for information. Sources here are rapidly located and this avenue of exploration has been left to the student.

The subject matter is divided into five sections. Part 1 covers the building blocks of solids. Here the topics centre upon atoms and bonding, and the patterns of structure that result. In this section, the important concepts of microstructure and macrostructure are developed, leading naturally to an understanding of why nanostructures possess unique properties. Defects that are of importance are also described here. Part 2 is concerned with the traditional triumvirate of metals, ceramics and polymers, together with a brief introduction to composite materials. The subject is condensed into a single chapter. It provides an overview of a comparative nature, focused upon giving a broad appreciation of why the fundamental groups of materials appear to differ so much, and laying the foundations for why some, such as ceramic superconductors, seem to behave so differently from their congeners. Part 3 has a more chemical bias, and describes reactions and transformations. The principles of diffusion are outlined in Chapter 7; electrochemical ideas, which lead naturally to batteries, corrosion and electroplating, are described in Chapter 8. Solid-state transformations, which impinge upon areas as diverse as shape memory alloys, semiconductor doping and sintering, are introduced in Chapter 9. Part 4 is a description of the physical properties of solids, and complements the chemical aspects detailed in Part 3. The topics covered are those of importance to both science and technology, mechanical, Chapter 10, insulators, Chapter 11, magnetic, Chapter 12, electronic, Chapter 13, optical, Chapter 14, and thermal, Chapter 15. Part 5 is concerned with radioactivity. This topic is of enormous importance, and
in particular the disposal of nuclear waste in solid form is of pressing concern.

The material in all of the later sections is founded upon the concepts presented in Part 1, that is, properties are explained as arising naturally from the atomic constituents, the chemical bonding, the microstructures and defects present in the solid. This leads naturally to an understanding of why nanostructures have seemingly different properties from bulk solids. Because of this, nanostructures are not gathered together in one section, but considered throughout the book, in the context of the better-known macroscopic properties of the material.

It is a pleasure to acknowledge the help of Dr A. Slade and Mrs Celia Carden of John Wiley, who have given continual encouragement and assistance to this venture. Ms Rachael Catt read the complete manuscript with meticulous care, exposed ambiguities and inconsistencies in both text and figures, and added materially to the final version. Mr Allan Coughlin read large parts of earlier drafts, clarified many obscurities and suggested many improvements. Mr Rolfe Jones has provided information and micrographs of solids whenever called upon. As always, my family has been ever-supportive during the writing of this book, and my wife Anne has endured the hours of being a computer widow without complaint. To all of these, my heartfelt thanks.
PART 1

Structures and microstructures
1

The electron structure of atoms

- What is a wavefunction?
- What is an atomic term?
- How are the energy levels of atoms labelled?

An atom of any element is made up of a small massive nucleus, in which almost all of the mass resides, surrounded by an electron cloud. Each element is differentiated from all others by the amount of positive charge on the nucleus, called the proton number or atomic number, Z. The proton number is an integer specifying the number of protons in the nucleus, each of which carries one unit of positive charge. In a neutral atom, the nuclear charge is exactly balanced by Z electrons in the outer electron cloud, each of which carries one unit of negative charge. Variants of atoms that have slightly more or fewer electrons than are required for charge neutrality are called ions; those which have lost electrons have an overall positive charge and those that have gained electrons have an overall negative charge. Positively charged ions are sometimes called cations and negatively charged ions are sometimes called anions.

The electrons associated with the chemical elements in a material (whether in the form of a gas, liquid or solid) control the chemical and physical properties of the atoms. The energies and regions of space occupied by electrons in an atom may be calculated using quantum theory.

1.1 The hydrogen atom

1.1.1 The quantum mechanical description

A hydrogen atom is the simplest of atoms. It consists of a nucleus consisting of a single proton carrying one unit of positive charge, together with a single bound electron carrying one unit of negative charge. Hydrogenic or hydrogen-like atoms or ions are very similar, in that they can be analysed in terms of a single electron bound to a nucleus with an apparent charge different from unity. Information about the electron can be obtained by solving the Schrödinger equation, in which the electron is represented as a wave. The permitted solutions to this equation, called wavefunctions, describe the energy and probability of location of the electron in any region around the nucleus. Each of the solutions contains three integer terms called quantum numbers. They are n, the principal quantum number, l, the orbital angular momentum quantum number, and m\textsubscript{l}, the magnetic quantum number. The names of the last two quantum numbers pre-date modern
quantum chemistry. They are best regarded as labels rather than representing classical concepts such as the angular momentum of a solid body. The quantum numbers define the state of a system.

1.1.2 The energy of the electron

The principal quantum number, \( n \), defines the energy of the electron. It can take integer values 1, 2, 3 \ldots to infinity. The energy of the electron is lowest for \( n = 1 \) and this represents the most stable or ground state of the hydrogen atom. The next lowest energy is given by \( n = 2 \), then by \( n = 3 \), and so on. The energy of each state is given by the simple formula:

\[
E = -\frac{A}{n^2} \tag{1.1}
\]

where \( A \) is a constant equal to \( 2.179 \times 10^{-18} \) J \((13.6\,\text{eV})\), and \( E \) is the energy of the level with principal quantum number \( n \). The negative sign in the equation indicates that the energy of the electron is chosen as zero when \( n \) is infinite, that is to say, when the electron is no longer bound to the nucleus.

There is only one wavefunction for the lowest energy, \( n = 1 \), state. The states of higher energy each have \( n^2 \) different wavefunctions, all of which have the same energy, that is, there are four different wavefunctions corresponding to \( n = 2 \), nine different wavefunctions for \( n = 3 \), and so on. These wavefunctions are differentiated from each other by different values of the quantum numbers \( l \) and \( m_l \), as explained below. Wavefunctions with the same energy are said to be degenerate.

It is often convenient to represent the energy associated with each value of the principal quantum number, \( n \), as a series of steps or energy levels (Figure 1.1). It is important to be aware of the fact that the electron can only take the exact energy values given by equation (1.1). When an electron gains energy, it jumps from an energy level with a lower value of \( n \) to a level with a higher value of \( n \). When an electron loses energy, it drops from an energy level with a higher value of \( n \) to an energy level with a lower value. The discrete packets of energy given out or taken up in this way are photons of electromagnetic radiation (Chapter 14). The energy of a photon needed to excite an electron from energy \( E_1 \), corresponding to an energy level \( n_1 \), to energy \( E_2 \), corresponding to an energy level \( n_2 \), is given by:

\[
E = E_1 - E_2 = -2.179 \times 10^{-18} \left[ \frac{1}{n_1^2} - \frac{1}{n_2^2} \right] \, \text{J}
\]

\[
= -13.6 \left[ \frac{1}{n_1^2} - \frac{1}{n_2^2} \right] \, \text{eV} \tag{1.2}
\]

The energy of the photon emitted when the electron falls back from \( E_2 \) to \( E_1 \) is the same. The frequency, \( \nu \) (or the equivalent wavelength, \( \lambda \)), of the photons that are either emitted or absorbed during these energy changes is given by the equation:

\[
E = h\nu = \frac{hc}{\lambda} \tag{1.3}
\]

where \( h \) is the Planck constant. (Note that this equation applies to the transition between any two

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{energy_levels}
\caption{The energy levels available to an electron in a hydrogen atom.}
\end{figure}

\footnote{The unit of energy, electron volt, \( \text{eV} \), is frequently used for atomic processes. \( 1\,\text{eV} = 1.602 \times 10^{-19} \) J.}
energy levels on any atom, not just between energy levels on hydrogen or a hydrogenic atom.) The energy needed to free the electron completely from the proton, which is called the ionisation energy of the hydrogen atom, is given by putting \( n_1 = 1 \) and \( n_2 = \infty \) in equation (1.2). The ionisation energy is \( 13.6 \text{ eV} \ (2.179 \times 10^{-18} \text{ J}) \).

In the case of a single electron attracted to a nucleus of charge \( +Ze \), the energy levels are given by:

\[
E = \frac{-AZ^2}{n^2}
\]  

(1.4)

This shows that the energy levels are much lower than in hydrogen, and that the ionisation energy of such atoms is considerably higher.

### 1.1.3 Electron orbitals

The principal quantum number is not sufficient to determine the location of the electron in a hydrogen atom. In addition, the two other interdependent quantum numbers, \( l \) and \( m_l \), are needed.

- \( l \) takes values of 0, 1, 2 \ldots (\( n - 1 \))
- \( m_l \) takes values of 0, \( \pm 1, \pm 2 \ldots \pm l \)

Each set of quantum numbers defines the state of the system and is associated with a wavefunction. For a value of \( n = 1 \), there is only one wavefunction, corresponding to \( n = 1, l = 0 \) and \( m_l = 0 \). For \( n = 2 \), \( l \) can take values of 0 and 1, and \( m_l \) can then take values of 0, associated with \( l = 0 \), and \( -1, 0 \) and \( +1 \), associated with \( l = 1 \). For \( n = 3 \), \( l \) can take values of 0, 1 and 2, and \( m_l \) then can take values of 0, associated with \( l = 0 \), \( -1, 0 \) and \( +1 \), associated with \( l = 1 \), and \( -2, -1, 0, +1, +2 \), associated with \( l = 2 \). These states are referred to as orbitals and for historical reasons they are given letter symbols. Orbitals with \( l = 0 \) are called s orbitals, those with \( l = 1 \) are called p orbitals, those with \( l = 2 \) are called d orbitals, and those with \( l = 3 \) are called f orbitals (Table 1.1).

The set of orbitals derived from a single value of the principal quantum number form a shell. The lowest energy shell is called the K shell, and corresponds to \( n = 1 \). The other shells are labelled alphabetically (Table 1.1). For example, the L shell corresponds to the four orbitals associated with \( n = 2 \).

There is only one s orbital in any shell, labelled 1s, 2s and so on. There are three p orbitals in all shells from \( n = 2 \) upwards, collectively called 3p, 4p and so on. There are five d orbitals in the shells from \( n = 3 \) upwards, collectively called 3d, 4d, 5d and so on. There are seven f orbitals in the shells from \( n = 4 \) upwards, collectively called 4f, 5f and so on.

### 1.1.4 Orbital shapes

The probability of encountering the electron in a certain small volume of space surrounding a point with coordinates \( x \), \( y \) and \( z \) is proportional to the square of the wavefunction at that point. With this information, it is possible to map out regions around the nucleus where the electron density is greatest.

The probability of encountering an electron in an s orbital does not depend upon direction but does vary with distance from the nucleus (Figure 1.2a,b,c). This probability peaks at a radial distance of 0.05292 nm for a 1s orbital – equal to the distance calculated by Bohr as the minimum allowed radius of an orbiting ‘planetary’ electron around a proton, and called the Bohr radius. As the electron is promoted to the 2s, 3s, 4s orbitals, the maximum probability peaks further and further from the nucleus. Thus a high-energy electron is most likely to be found far from the

<table>
<thead>
<tr>
<th>( n )</th>
<th>( l )</th>
<th>( m_l )</th>
<th>Orbital</th>
<th>Shell</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>0</td>
<td>1s</td>
<td>K</td>
</tr>
<tr>
<td>2</td>
<td>0</td>
<td>0</td>
<td>2s</td>
<td>L</td>
</tr>
<tr>
<td>1</td>
<td>-1, 0 +1</td>
<td>2p (3 orbitals)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>0</td>
<td>0</td>
<td>3s</td>
<td>M</td>
</tr>
<tr>
<td>1</td>
<td>-1, 0 +1</td>
<td>3p (3 orbitals)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>-2, -1, 0 +1, +2</td>
<td>3d (5 orbitals)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>0</td>
<td>0</td>
<td>4s</td>
<td>N</td>
</tr>
<tr>
<td>1</td>
<td>-1, 0 +1</td>
<td>4p (3 orbitals)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>-2, -1, 0 +1, +2</td>
<td>4d (5 orbitals)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>-3, -2, -1,0, +1, +2</td>
<td>4f (7 orbitals)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

(Table 1.1).
Generally, s orbitals are drawn as spherical boundary surfaces that enclose an arbitrary volume in which there is a high probability, say 95%, that the electron will be found (Figure 1.2d,e).

All other wavefunctions are specified by three quantum numbers and can be divided into two parts: a radial part, with similar probability shapes to those shown in Figure 1.2, multiplied by an angular part. The maximum probability of finding the electron depends upon both the radial and angular parts of the wavefunction, and the resulting boundary surfaces have complex shapes. For many purposes, however, it is sufficient to describe only the angular part of the wavefunction.

The boundary surfaces of the angular parts of the three p orbitals are approximately dumbbell-shaped, each consisting of two lobes. These lie along three mutually perpendicular directions, which it is natural to equate to x, y and z-axes (Figure 1.3). The corresponding orbitals are labelled npₓ, npᵧ and np₂, for

**Figure 1.2** The probability of finding an electron at a distance r from the nucleus: (a) 1s; (b) 2s; (c) 3s. The boundary surfaces of the orbitals: (d) 1s; (e) 2s.

**Figure 1.3** The boundary surfaces of the p orbitals: (a) pₓ; (b) pᵧ; (c) p₂.
example, 2pₓ, 2pᵧ and 2pᵣ. Note that the electron occupies both lobes of the p orbital. The probability of encountering a p electron on the perpendicular plane that separates the two halves of the dumbbell is zero, and this plane is called a **nodal plane**. The sign of the wavefunction is of importance when orbitals overlap to form bonds. The two lobes of each p orbital are labelled as + and −, and the sign changes as a nodal plane is crossed. The radial probability of encountering an electron in a p orbital is zero at the nucleus, and increases with distance from the nucleus. The maximum probability is further from the nucleus for an electron in a 3p orbital than a 2p orbital, and so on, so that 3p orbitals have a greater extension in space than 2p orbitals.

The distribution of the electron in either the d or f orbitals is more complicated than those of the p orbitals. There are five d orbitals, and seven f orbitals. Three of the 3d set of wavefunctions have lobes lying between pairs of axes, dₓᵧ between the x- and y-axes, dₓz between the x- and z-axes, and dᵧz between the y- and z-axes. The other two orbitals have lobes along the axes, dₓ²₋ᵧ² pointing along x and y, and dₓz pointing along the z-axis (Figure 1.4). Except for the dₓz orbital, two perpendicular planar nodes separate the lobes and intersect at the nucleus. In the dₓz orbital, the nodes are conical surfaces.

### 1.2 Many-electron atoms

#### 1.2.1 The orbital approximation

If we want to know the energy levels and electron distribution of an atom with a nuclear charge of +Z surrounded by Z electrons, it is necessary to write out a more extended form of the Schrödinger equation that takes into account not only the attraction of the nucleus for each electron, but also the repulsive interactions between the electrons themselves. The resulting equation has proved impossible to solve analytically, but increasingly accurate numerical solutions have been available for many years.

The simplest level of approximation, called the **orbital approximation**, supposes that an electron moves in a potential due to the nucleus and the average field of all the other electrons present in the atom. This means that the electron experiences an **effective nuclear charge**, Zₑff, which is considered to be located as a point charge at the nucleus of the atom. In this approximation the orbital shapes are the same as for hydrogen, but the energy levels of all of the orbitals drop sharply as Zₑff increases (Figure 1.5). When one reaches lithium, Z = 3, the 1s orbital energy has already decreased so much that it forms a chemically unreactive shell. This is translated into the concept of an atom as consisting of unreactive **core electrons**, surrounded by a small number of outermost **valence electrons**, which are of chemical significance. Moreover, the change of energy as Z increases justifies the approximation that the valence electrons of all atoms are at similar energies.

Although **shapes** of the orbitals are not changed from the shapes found for hydrogen, the radial part of the wave function is altered, and the **extension** of the orbitals increases as the effective nuclear charge increases. This corresponds to the idea that heavy atoms are larger than light atoms. In addition, a different effective nuclear charge is experienced by electrons in differing orbitals. This has the effect of separating the energy of the ns, np, nd and nf orbitals that are identical in hydrogen. It is found that for any value of n, the s orbitals have lowest energy, the three p orbitals have equal and slightly higher energy, the five d orbitals have equal and slightly higher energy again, and the seven f orbitals have equal and slightly higher energy again (Figure 1.6). However, the energy differences between the higher energy orbitals are very small, and this simple ordering is not followed exactly for heavier atoms.

#### 1.2.2 Electron spin and electron configuration

The results presented so far, derived from solutions to the simplest form of the Schrödinger equation, do not explain the observed properties of atoms exactly. In order to account for the discrepancy the electron is allocated a fourth quantum number called the **spin quantum number**, s. The spin quantum number has a value of ½. The spin of an electron on an atom
can adopt one of two different directions, represented by a quantum number, $m_s$, which takes values of $+\frac{1}{2}$ or $-\frac{1}{2}$. These two spin directions have considerable significance in chemistry and physics and are frequently represented by $\uparrow$, spin up, or $\alpha$, and $\downarrow$, spin down or $\beta$. Although the spin quantum number was originally postulated to account for certain experimental observations, it arises naturally in more sophisticated formulations of the Schrödinger equation that take into account the effects of relativity.

The electron configuration of an atom is the description of the number of electrons in each orbital, based upon the orbital model. This is usually given for the lowest energy possible, called the ground state. To obtain the electron configuration