Nanoscale Science and Technology

Edited by

Robert W. Kelsall
The University of Leeds, UK

Ian W. Hamley
The University of Leeds, UK

and

Mark Geoghegan
The University of Sheffield, UK

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Contents

List of contributors xii
Preface xiv
Chapter authors xvi

1 Generic methodologies for nanotechnology: classification and fabrication 1
  1.1 Introduction and classification 1
    1.1.1 What is nanotechnology? 1
    1.1.2 Classification of nanostructures 1
    1.1.3 Nanoscale architecture 4
  1.2 Summary of the electronic properties of atoms and solids 5
    1.2.1 The isolated atom 5
    1.2.2 Bonding between atoms 8
    1.2.3 Giant molecular solids 11
    1.2.4 The free electron model and energy bands 12
    1.2.5 Crystalline solids 14
    1.2.6 Periodicity of crystal lattices 14
    1.2.7 Electronic conduction 16
  1.3 Effects of the nanometre length scale 19
    1.3.1 Changes to the system total energy 20
    1.3.2 Changes to the system structure 20
    1.3.3 How nanoscale dimensions affect properties 24
  1.4 Fabrication methods 32
    1.4.1 Top-down processes 32
    1.4.2 Bottom-up processes 37
    1.4.3 Methods for templating the growth of nanomaterials 49
    1.4.4 Ordering of nanosystems 51
  1.5 Preparation, safety and storage issues 54
Bibliography 54

2 Generic methodologies for nanotechnology: characterization 56
  2.1 General classification of characterization methods 56
    2.1.1 Analytical and imaging techniques 57
    2.1.2 Some scattering physics 58
  2.2 Microscopy techniques 62
    2.2.1 General considerations for imaging 64

Bibliography
2.2.2 Image magnification and resolution 65
2.2.3 Other considerations for imaging 67
2.2.4 Light microscopy 68
2.3 Electron microscopy 69
2.3.1 General aspects of electron optics 69
2.3.2 Electron beam generation 70
2.3.3 Electron–specimen interactions 70
2.3.4 Scanning electron microscopy 72
2.3.5 Transmission electron microscopy 76
2.3.6 Scanning transmission electron microscopy 82
2.4 Field ion microscopy 83
2.5 Scanning probe techniques 85
2.5.1 Scanning tunnelling microscopy 85
2.5.2 Atomic force microscopy 87
2.5.3 Other scanning probe techniques 92
2.6 Diffraction techniques 92
2.6.1 Bulk diffraction techniques 92
2.6.2 Surface diffraction techniques 96
2.7 Spectroscopy techniques 97
2.7.1 Photon spectroscopy 98
2.7.2 Radio frequency spectroscopy 105
2.7.3 Electron spectroscopy 108
2.8 Surface analysis and depth profiling 113
2.8.1 Electron spectroscopy of surfaces 114
2.8.2 Mass spectrometry of surfaces 117
2.8.3 Ion beam analysis 119
2.8.4 Reflectometry 120
2.9 Summary of techniques for property measurement 122
2.9.1 Mechanical properties 122
2.9.2 Electron transport properties 124
2.9.3 Magnetic properties 126
2.9.4 Thermal properties 127
Bibliography 128

3 Inorganic semiconductor nanostructures 130
3.1 Introduction 130
3.2 Overview of relevant semiconductor physics 131
3.2.1 What is a semiconductor? 131
3.2.2 Doping 132
3.2.3 The concept of effective mass 133
3.2.4 Carrier transport, mobility and electrical conductivity 133
3.2.5 Optical properties of semiconductors 134
3.2.6 Excitons 135
3.2.7 The pn junction 136
3.2.8 Phonons 137
3.2.9 Types of semiconductor 137
3.3 Quantum confinement in semiconductor nanostructures 138
   3.3.1 Quantum confinement in one dimension: quantum wells 139
   3.3.2 Quantum confinement in two dimensions: quantum wires 142
   3.3.3 Quantum confinement in three dimensions: quantum dots 142
   3.3.4 Superlattices 143
   3.3.5 Band offsets 144

3.4 The electronic density of states 144

3.5 Fabrication techniques 145
   3.5.1 Requirements for an ideal semiconductor nanostructure 146
   3.5.2 The epitaxial growth of quantum wells 147
   3.5.3 Lithography and etching 147
   3.5.4 Cleaved-edge overgrowth 147
   3.5.5 Growth on vicinal substrates 148
   3.5.6 Strain-induced dots and wires 149
   3.5.7 Electrostatically induced dots and wires 150
   3.5.8 Quantum well width fluctuations 150
   3.5.9 Thermally annealed quantum wells 151
   3.5.10 Semiconductor nanocrystals 151
   3.5.11 Colloidal quantum dots 151
   3.5.12 Self-assembly techniques 152
   3.5.13 Summary of fabrication techniques 158

3.6 Physical processes in semiconductor nanostructures 158
   3.6.1 Modulation doping 158
   3.6.2 The quantum Hall effect 161
   3.6.3 Resonant tunnelling 162
   3.6.4 Charging effects 164
   3.6.5 Ballistic carrier transport 166
   3.6.6 Interband absorption in semiconductor nanostructures 168
   3.6.7 Intraband absorption in semiconductor nanostructures 170
   3.6.8 Light emission processes in nanostructures 171
   3.6.9 The phonon bottleneck in quantum dots 174
   3.6.10 The quantum confined Stark effect 175
   3.6.11 Non-linear effects 176
   3.6.12 Coherence and dephasing processes 177

3.7 The characterisation of semiconductor nanostructures 177
   3.7.1 Optical and electrical characterisation 178
   3.7.2 Structural characterisation 182

3.8 Applications of semiconductor nanostructures 184
   3.8.1 Injection lasers 184
   3.8.2 Quantum cascade lasers 188
   3.8.3 Single-photon sources 190
   3.8.4 Biological tagging 191
   3.8.5 Optical memories 191
   3.8.6 Impact of nanotechnology on conventional electronics 192
   3.8.7 Coulomb blockade devices 197
   3.8.8 Photonic structures 198
3.9 Summary and outlook 200
Bibliography 201

4 Nanomagnetic materials and devices 203
4.1 Magnetism 203
  4.1.1 Magnetostatics 203
  4.1.2 Diamagnetism, paramagnetism and ferromagnetism 204
  4.1.3 Magnetic anisotropy 206
  4.1.4 Domains and domain walls 209
  4.1.5 The magnetization process 212
4.2 Nanomagnetic materials 212
  4.2.1 Particulate nanomagnets 213
  4.2.2 Geometrical nanomagnets 219
4.3 Magnetoresistance 221
  4.3.1 Contributions to resistivity in metals 221
  4.3.2 Giant magnetoresistance 222
  4.3.3 Spin valves 227
  4.3.4 Tunnelling magnetoresistance 229
4.4 Probing nanomagnetic materials 231
4.5 Nanomagnetism in technology 233
4.6 The challenges facing nanomagnetism 234
Bibliography 235

5 Processing and properties of inorganic nanomaterials 237
5.1 Introduction 237
  5.1.1 Classification 238
5.2 The thermodynamics and kinetics of phase transformations 238
  5.2.1 Thermodynamics 238
  5.2.2 Homogeneous nucleation 241
  5.2.3 Heterogeneous nucleation 244
  5.2.4 Growth 245
  5.2.5 Overall transformation rate 246
5.3 Synthesis methods 246
  5.3.1 Rapid solidification processing from the liquid state 247
  5.3.2 Devitrification 247
  5.3.3 Inert gas condensation 249
  5.3.4 Electrodeposition 252
  5.3.5 Mechanical methods 254
5.4 Structure 258
  5.4.1 Microstructure 259
  5.4.2 Grain boundary structure 260
  5.4.3 Structural metastability 260
5.5 Microstructural stability 261
  5.5.1 Diffusion 261
  5.5.2 Grain growth 263
7 Self-assembling nanostructured molecular materials and devices 343
  7.1 Introduction 343
  7.2 Building blocks 344
    7.2.1 Synthetic 344
    7.2.2 Biological 345
  7.3 Principles of self-assembly 348
    7.3.1 Non-covalent interactions 349
    7.3.2 Intermolecular packing 350
    7.3.3 Biological self-assembly 353
    7.3.4 Nanomotors 355
  7.4 Self-assembly methods to prepare and pattern nanoparticles 356
    7.4.1 Nanoparticles from micellar and vesicular polymerization 356
    7.4.2 Functionalized nanoparticles 357
    7.4.3 Colloidal nanoparticle crystals 358
    7.4.4 Self-organizing inorganic nanoparticles 360
    7.4.5 Liquid crystal nanodroplets 362
    7.4.6 Bionanoparticles 363
    7.4.7 Nano-objects 365
  7.5 Templated nanostructures 365
    7.5.1 Mesoporous silica 365
    7.5.2 Biominalization 366
    7.5.3 Nanostructures templated by block copolymer self-assembly 368
  7.6 Liquid crystal mesophases 368
    7.6.1 Micelles and vesicles 368
    7.6.2 Lamellar phase 369
    7.6.3 ABC triblock structures 370
    7.6.4 Smectic and nematic liquid crystals 370
    7.6.5 Discotic liquid crystals 373
  7.7 Summary and outlook 373
Bibliography 374

8 Macromolecules at interfaces and structured organic films 377
  8.1 Macromolecules at interfaces 377
  8.2 The principles of interface science 379
    8.2.1 Surface and interface energies 379
  8.3 The analysis of wet interfaces 381
  8.4 Modifying interfaces 382
    8.4.1 Adsorption and surfactancy 382
    8.4.2 Polymer adsorption 383
    8.4.3 The chemistry of grafting 384
    8.4.4 Physical properties of grafted polymer layers 387
    8.4.5 Nanostructured organic coatings by soft lithography and other techniques 390
  8.5 Making thin organic films 391
    8.5.1 Spin-coating of polymers and colloids 392
    8.5.2 Making organic multilayers 393
8.6 Surface effects on phase separation
  8.6.1 Polymer blends 397
  8.6.2 Block copolymers 400
8.7 Nanopatterning surfaces by self-assembly
  8.7.1 Patterns produced on heterogeneous substrates 405
  8.7.2 Topographically patterned surfaces 406
  8.7.3 Patterns produced by thin film dewetting 409
8.8 Practical nanoscale devices exploiting macromolecules at interfaces
  8.8.1 Molecular and macromolecular electronics 411
  8.8.2 Nanofluidics 413
  8.8.3 Filtration and sorting 415
Bibliography 418

9 Bionanotechnology 419
  9.1 New tools for investigating biological systems 419
    9.1.1 Scanning probe microscopy for biomolecular imaging 419
    9.1.2 Force measurement in biological systems 423
    9.1.3 Miniaturisation and analysis 428
    9.1.4 Organisation of biomolecular structure at the nanometre scale 432
  9.2 Biomimetic nanotechnology 435
    9.2.1 DNA as a nanotechnology building block 435
    9.2.2 Molecular motors 439
    9.2.3 Artificial photosynthesis 442
  9.3 Conclusions 444
Bibliography 445

Index 446
List of contributors

EDITORS

Dr Robert W. Kelsall
Institute of Microwaves and Photonics
School of Electronic and Electrical Engineering
University of Leeds
Leeds LS2 9JT
United Kingdom
r.w.kelsall@leeds.ac.uk

Dr Ian W. Hamley
Centre for Self Organising Molecular Systems
University of Leeds
Leeds LS2 9JT
United Kingdom
I.W.Hamley@chemistry.leeds.ac.uk

Dr Mark Geoghegan
Department of Physics and Astronomy
University of Sheffield
Sheffield S3 7RH
United Kingdom
mark.geoghegan@sheffield.ac.uk

Prof. Mike R. J. Gibbs
Department of Engineering Materials
University of Sheffield
Sheffield S1 3JD
United Kingdom
M.R.Gibbs@Sheffield.ac.uk

Dr Martin Grell
Department of Physics and Astronomy
University of Sheffield
Sheffield S3 7RH
United Kingdom
m.grell@sheffield.ac.uk

Dr Chris Hammond
Institute for Materials Research
School of Process, Environmental and Materials Engineering
University of Leeds
Leeds LS2 9JT
United Kingdom
c.hammond@leeds.ac.uk

AUTHORS

Dr Rik Brydson
Institute for Materials Research
School of Process, Environmental and Materials Engineering
University of Leeds
Leeds LS2 9JT
United Kingdom
mtlrmdb@leeds.ac.uk

Prof. Richard Jones
Department of Physics and Astronomy
Hicks Building
University of Sheffield
Sheffield S3 7HF
United Kingdom
r.a.l.jones@sheffield.ac.uk
LIST OF CONTRIBUTORS

Prof. Graham Leggett
Department of Chemistry
University of Sheffield
Sheffield S3 7HF
United Kingdom
graham.leggett@umist.ac.uk

Dr Iain Todd
Department of Engineering Materials
University of Sheffield
Sheffield S1 3JD
United Kingdom
i.todd@sheffield.ac.uk

Dr David Mowbray
Department of Physics and Astronomy
University of Sheffield
Sheffield S3 7RH
United Kingdom
d.mowbray@sheffield.ac.uk
Preface

In the two years since we first started planning this book, so much has been written about nanotechnology that the subject really needs no introduction. Nanotechnology has been one of the first major new technologies to develop in the internet age, and as such has been the topic of thousands of unregulated, unrefereed websites, discussion sites and the like. In other words, much has been written, but not all is necessarily true. The press has also made its own, unique contribution: ‘nanotechnology will turn us all into grey goo’ makes for a good story (in some newspapers at least), and then there’s the 1960s image of nanotechnology, still present today, of Raquel Welch transported in a nanosubmarine through the bloodstream of an unsuspecting patient. This book isn’t about any of that! One thing that the recent press coverage of nanotechnology has achieved is to draw attention to the possible hazards which accompany any new technology and to pose relevant questions about the likely impact of the various facets of nanotechnology on our society. Whilst we would certainly encourage investigation and discussion of such issues, they do not fall within the remit of this book.

Nanoscale Science and Technology has been designed as an educational text, aimed primarily at graduate students enrolled on masters or PhD programmes, or indeed, at final year undergraduate or diploma students studying nanotechnology modules or projects. We should also mention that the book has been designed for students of the physical sciences, rather than the life sciences. It is based largely on our own masters course, the Nanoscale Science and Technology MSc, which has been running since 2001 and was one of the first postgraduate taught courses in Europe in this subject area. The course is delivered jointly by the Universities of Leeds and Sheffield, and was designed primarily by several of the authors of this book. As in designing the course, so in designing the book have we sought to present the breadth of scientific topics and disciplines which contribute to nanotechnology. The scope of the text is bounded by two main criteria. Firstly, we saw no need to repeat the fine details of established principles and techniques which are adequately covered elsewhere, and secondly, as a textbook, Nanoscale Science and Technology is intended to be read, in its entirety, over a period of one year. In consideration of the first of these criteria, each chapter has a bibliography indicating where more details of particular topics can be found.

The expertise of the authors ranges from electronic engineering, physics and materials science to chemistry and biochemistry, which we believe has helped us achieve both breadth and balance. That said, this book is inevitably our take on nanotechnology, and any other group of authors would almost certainly have a different opinion on what should be included and what should be emphasised. Also, in such a rapidly developing
field, our reporting is in danger of fast becoming out of date (one of our co-authors, who was the most efficient in composing his text, paid the rather undeserved penalty of having to make at least two sets of revisions simply to update facts and figures to reflect new progress in research). We should certainly be grateful to receive any information on errors or omissions.

Although most of the chapters have been written by different authors, we were keen that, to better fulfil its role as a textbook, this volume should read as one coherent whole rather than as a collection of individual monographs. To this end, not only have we as editors made numerous adjustments to improve consistency, and avoid duplication and omission, but in some places we have also made more substantial editorial changes. We should like to acknowledge the tolerance of our co-authors throughout this process. We are all still on speaking terms – just! It is not really necessary for us to tabulate in detail exactly who contributed what to each chapter in the final manuscript, except that we note that the nanostructured carbon section in Chapter 6 was provided by Rob Kelsall. Finally, we should like to acknowledge Terry Bambrook, who composed virtually all of the figures for chapters 1 and 2.

Robert W. Kelsall, Ian W. Hamley and Mark Geoghegan

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Chapter authors

Chapter 1. Generic methodologies for nanotechnology: classification and fabrication
Rik M. Brydson and Chris Hammond

Chapter 2. Generic methodologies for nanotechnology: characterisation
Rik M. Brydson and Chris Hammond

Chapter 3. Inorganic semiconductor nanostructures
David Mowbray

Chapter 4. Nanomagnetic materials and devices
Mike R. J. Gibbs

Chapter 5. Processing and properties of inorganic nanomaterials
Iain Todd

Chapter 6. Electronic and electro-optic molecular materials and devices
Martin Grell

Chapter 7. Self-assembling nanostructured molecular materials and devices
Ian W. Hamley

Chapter 8. Macromolecules at interfaces and structured organic films
Mark Geoghegan and Richard A. L. Jones

Chapter 9. Bionanotechnology
Graham J. Leggett and Richard A. L. Jones
Generic methodologies for nanotechnology: classification and fabrication

1.1 INTRODUCTION AND CLASSIFICATION

1.1.1 What is nanotechnology?

Nanotechnology is the term used to cover the design, construction and utilization of functional structures with at least one characteristic dimension measured in nanometres. Such materials and systems can be designed to exhibit novel and significantly improved physical, chemical and biological properties, phenomena and processes as a result of the limited size of their constituent particles or molecules. The reason for such interesting and very useful behaviour is that when characteristic structural features are intermediate in extent between isolated atoms and bulk macroscopic materials; i.e., in the range of about $10^{-9}$ m to $10^{-7}$ m (1 to 100 nm), the objects may display physical attributes substantially different from those displayed by either atoms or bulk materials. Ultimately this can lead to new technological opportunities as well as new challenges.

1.1.2 Classification of nanostructures

As we have indicated above, a reduction in the spatial dimension, or confinement of particles or quasiparticles in a particular crystallographic direction within a structure generally leads to changes in physical properties of the system in that direction. Hence one classification of nanostructured materials and systems essentially depends on the number of dimensions which lie within the nanometre range, as shown in Figure 1.1: (a) systems confined in three dimensions, (b) systems confined in two dimensions, (c) systems confined in one dimension.
Nanoparticles and nanopores exhibit three-dimensional confinement (note that historically pores below about 100 nm in dimension are often sometimes confusingly referred to as micropores). In semiconductor terminology such systems are often called quasi-zero dimensional, as the structure does not permit free particle motion in any dimension.

Nanoparticles may have a random arrangement of the constituent atoms or molecules (e.g., an amorphous or glassy material) or the individual atomic or molecular units may be ordered into a regular, periodic crystalline structure which may not necessarily be the same as that which is observed in a much larger system (Section 1.3.1). If crystalline, each nanoparticle may be either a single crystal or itself composed of a number of different crystalline regions or grains of differing crystallographic orientations (i.e., polycrystalline) giving rise to the presence of associated grain boundaries within the nanoparticle.

Figure 1.1 Classification of nanostructures. (a) Nanoparticles and nanopores (nanosized in three dimensions): (i) high-resolution TEM image of magnetic iron oxide nanoparticle, (ii) TEM image of ferritin nanoparticles in a liver biopsy specimen, and (iii) high-resolution TEM image of nanoporosity in an activated carbon. (b) Nanotubes and nanofilaments (nanosized in two dimensions): (i) TEM image of single-walled carbon nanotubes prepared by chemical vapour deposition, (ii) TEM image of ordered block copolymer film, and (iii) SEM image of silica nanotube formed via templating on a tartaric acid crystal. (c) Nanolayers and nanofilms (nanosized in one dimension): (i) TEM image of a ferroelectric thin film on an electrode, (ii) TEM image of cementite (carbide) layers in a carbon steel, and (iii) high-resolution TEM image of glassy grain boundary film in an alumina polycrystal. Images courtesy of Andy Brown, Zabeada Aslam, Sarah Pan, Manoch Naksata and John Harrington, IMR, Leeds
Figure 1.1  Continued
Nanoparticles may also be quasi-crystalline, the atoms being packed together in an icosahedral arrangement and showing non-crystalline symmetry characteristics. Such quasi-crystals are generally only stable at the nanometre or, at most, the micrometre scale.

Nanoparticles may be present within another medium, such as nanometre-sized precipitates in a surrounding matrix material. These nanoprecipitates will have a specific morphology (e.g., spherical, needle-shaped or plate-shaped) and may possess certain crystallographic orientation relationships with the atomic arrangement of the matrix depending on the nature (coherency) of the interface which may lead to coherency strains in the particle and the matrix. One such example is the case of self-assembled semiconductor quantum dots, which form due to lattice mismatch strain relative to the surrounding layers and whose geometry is determined by the details of the strain field (Chapter 3). Another feature which may be of importance for the overall transport properties of the composite system is the connectivity of such nanometre-sized regions or, in the case of a nanoporous material, nanopore connectivity.

In three dimensions we also have to consider collections of consolidated nanoparticles; e.g., a nanocrystalline solid consisting of nanometre-sized crystalline grains each in a specific crystallographic orientation. As the grain size $d$ of the solid decreases the proportion of atoms located at or near grain boundaries, relative to those within the interior of a crystalline grain, scales as $1/d$. This has important implications for properties in ultrafine-grained materials which will be principally controlled by interfacial properties rather than those of the bulk.

Systems confined in two dimensions, or quasi-1D systems, include nanowires, nanorods, nanofilaments and nanotubes: again these could either be amorphous, single-crystalline or polycrystalline (with nanometre-sized grains). The term ‘nanoropes’ is often employed to describe bundles of nanowires or nanotubes.

Systems confined in one dimension, or quasi-2D systems, include discs or platelets, ultrathin films on a surface and multilayered materials; the films themselves could be amorphous, single-crystalline or nanocrystalline.

Table 1.1 gives examples of nanostructured systems which fall into each of the three categories described above. It can be argued that self-assembled monolayers and multilayered Langmuir–Blodgett films (Section 1.4.3.1) represent a special case in that they represent a quasi-2D system with a further nanodimensional scale within the surface film caused by the molecular self-organization.

### 1.1.3 Nanoscale architecture

Nanotechnology is the design, fabrication and use of nanostructured systems, and the growing, shaping or assembling of such systems either mechanically, chemically or biologically to form nanoscale architectures, systems and devices. The original vision of Richard Feynman\(^1\) was of the ‘bottom-up’ approach of fabricating materials and devices at the atomic or molecular scale, possibly using methods of self-organization and self-assembly of the individual building blocks. An alternative ‘top-down’ approach is the

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ultramiiniaturization or etching/milling of smaller structures from larger ones. These methods are reviewed in Section 1.4. Both approaches require a means of visualizing, measuring and manipulating the properties of nanostructures; computer-based simulations of the behaviour of materials at these length scales are also necessary. This chapter provides a general introduction to the preparation and properties of nanostructures, whilst the subsequent chapters give greater detail on specific topics.

### 1.2 SUMMARY OF THE ELECTRONIC PROPERTIES OF ATOMS AND SOLIDS

To understand the effects of dimensionality in nanosystems, it is useful to review certain topics associated with the constitution of matter, ranging from the structure of the isolated atom through to that of an extended solid.

#### 1.2.1 The isolated atom

The structure of the atom arises as a direct result of the wave–particle duality of electrons, which is summarized in the de Broglie relationship, \( \lambda = \frac{\hbar}{m_e v} \), where \( \lambda \) is the (electron) wavelength, \( m_e \) is the (electron) mass, \( v \) is the velocity and...
The wave–particle duality of the electron means that an electron behaves both as a wave (i.e., it is extended over space and has a wavelength and hence undergoes wave-like phenomena such as diffraction) and a particle (i.e., it is localized in space and has a position, a velocity and a kinetic energy). This is conveniently summarized in the idea of a wave packet a localized wave that is effectively the summation of a number of different waves of slightly differing wavelengths.

Using these ideas we come to our first model of the atom, the Rutherford–Bohr model. Here the small central nucleus of the atom consists of positively charged protons and (neutral) neutrons. Electrons orbit the nucleus in stable orbits. The allowed, stable orbits are those in which the electron wavelength, given by the de Broglie formula, is an integral multiple \( n \) of the circumference of the orbit \( r \):

\[
2\pi r = n\lambda = \frac{n\hbar}{m_e v}.
\]

This implies that

\[
m_e v r = \frac{n\hbar}{2\pi},
\]

in other words, the angular momentum \( m_e v r \) is quantized in that it is an integral multiple of \( \hbar/2\pi \).

The Bohr model leads to the idea that only certain electron orbits or shells are allowed by this quantization of angular momentum (i.e., the value of \( n \)). The Bohr shells in an atom are labelled according to the quantum number, \( n \), and are given the spectroscopic labels K, L, M, N, etc. (where \( n = 1, 2, 3, 4, \ldots \)). To understand the form of the periodic table of elements, it is necessary to assume that each Bohr shell can contain \( 2n^2 \) electrons. For instance, a K shell (\( n = 1 \)) can contain 2 electrons, whereas an L shell (\( n = 2 \)) can accommodate 8 electrons. As well as having a distinct form and occupancy, each shell also has a corresponding well-defined energy. It is usual to define the zero of the energy scale (known as the vacuum level) as the potential energy of a free electron far from the atom. In order to correspond with atomic emission spectra measured experimentally, the energies of these levels \( E_n \) are then negative (i.e., the electrons are bound to the atom) and are proportional to \( 1/n^2 \). Such a simplified picture of the structure of an isolated Mg atom and the associated energy level diagram are shown in Figure 1.2.

A much more sophisticated model of the atom considers the wave-like nature of the electrons from the very beginning. This uses wave mechanics or quantum mechanics.
Here each electron is described by a wavefunction $\psi$ which is a function of spatial position $(x,y,z)$ and, in general, of time. Physically $|\psi|^2$ represents the probability of finding the electron at any point. To work out the energy of each electron, we need to solve the Schrödinger equation which, in the time-independent case, takes the form

$$-\frac{\hbar^2}{2m_e} \nabla^2 \psi + V(x,y,z)\psi = E\psi,$$  \hspace{1cm} (1.3)

where $V(x,y,z)$ describes the potential energy function in the environment of the electron. Solution of the Schrödinger equation, under certain boundary conditions, leads to a set of solutions for the allowed wavefunctions $\psi_n$ of the atomic electrons together with their associated energies $E_n$.

This equation can only be solved analytically for the case of the hydrogen atom, where there is only one electron moving in the potential of a single proton, the hydrogen nucleus. Only a certain set of electronic wavefunctions and associated energy levels fulfill this Schrödinger equation. The wavefunctions may be expressed as a radial part, governing the spatial extent of the wavefunction, multiplied by a spherical harmonic function which determines the shape. The allowed wavefunctions form the electron orbitals, which we term 1s, 2s, 2p, 3s, 3p, 3d, etc. (here 1, 2, 3, \ldots are alternative labels for K, L, M, \ldots). These allowed wavefunctions now depend on not just one quantum number but four: $n$, $l$, $m$ and $s$. These numbers may be summarized as follows:

- $n$ is the principal quantum number; it is like the quantum number used for the case of Bohr shells ($n = 1, 2, 3, \ldots$).

- $l$ is the angular momentum quantum number; it can vary from $l = 0, 1, 2, \ldots, (n - 1)$. The value of $l$ governs the orbital shape of the subshell: $l = 0$ is an s orbital, which is spherical; $l = 1$ is a p orbital, which has a dumbbell shape; while $l = 2$ is a d orbital, which has a more complex shape such as a double dumbbell.

- $m$ is the magnetic quantum number; it can vary from $m = 0, \pm 1, \ldots, \pm l$. The value of $m$ governs the spatial orientation of the different orbitals within a subshell; i.e., there are three p orbitals ($l = 1$) $p_x$, $p_y$, and $p_z$ corresponding to the three values of $m$ which are 0, $\pm 1$ and $-1$. In the absence of a magnetic field, all these orbitals within a particular subshell will have the same energy.

- $s$ is the spin quantum number which, for an electron, can take the values $\pm 1/2$. Each $(n, l, m)$ orbital can contain two electrons of opposite spin due to the Pauli exclusion principle, which states that no two electrons can have the same four quantum numbers.

Using this identification in terms of the quantum numbers, each electron orbital in an atom therefore has a distinct combination of energy, shape and direction $(x, y, z)$ and can contain a maximum of two electrons of opposite spin.

In an isolated atom, these localized electronic states are known as Rydberg states and may be described in terms of simple Bohr shells or as combinations of the three quantum numbers $n$, $l$ and $m$ known as electron orbitals. The Bohr shells (designated K, L, M, \ldots) correspond to the principal quantum numbers $n$ equal to 1, 2, 3, etc. Within each of these shells, the electrons may exist in $(n - 1)$ subshells (i.e., s, p, d, or f subshells, for which the angular momentum quantum number $l$ equals 0, 1, 2, 3, respectively).
The occupation of the electronic energy levels depends on the total number of electrons in the atom. In the hydrogen atom, which contains only one electron, the set of Rydberg states is almost entirely empty except for the lowest-energy 1s level which is half full. As we go to higher energies, the energy spacing between these states becomes smaller and smaller and eventually converges to a value known as the vacuum level \((n = \infty)\), which corresponds to the ionization of the inner-shell electron. Above this energy the electron is free of the atom and this is represented by a continuum of empty electronic states. In fact, the critical energy to ionize a single isolated hydrogen atom is equal to 13.61 eV and this quantity is the Rydberg constant.

This description is strictly only true for hydrogen; however, other heavier atoms are found to have similar wavefunction (hydrogenic-like) solutions, which ultimately leads to the concept of the periodic table of elements, as each atom has more and more electrons which progressively fill the allowed energy levels. This is shown for a magnesium atom in Figure 1.2. The chemical properties of each atom are then principally determined by the number of valence electrons in the outermost electron shell which are relatively loosely bound and available for chemical reaction with other atomic species.

### 1.2.2 Bonding between atoms

One way to picture the bonding between atoms is to use the concept of Molecular Orbital (MO) Theory. MO theory considers the electron wavefunctions of the individual atoms combining to form molecular wavefunctions (or molecular orbitals as they are known). These orbitals, which are now delocalized over the whole molecule, are then occupied by all the available electrons from all the constituent atoms in the molecule. Molecular orbitals are really only formed by the wavefunctions of the electrons in the outermost shells (the valence electrons); i.e., those which significantly overlap in space as atoms become progressively closer together; the inner electrons remain in what are essentially atomic orbitals bound to the individual atoms.

A simple one-electron molecule is the \(\text{H}_2^+\) ion, where we have to consider the interactions (both attractive and repulsive) between the single electron and two nucleii. The Born–Oppenheimer approximation regards the nuclei as fixed and this simplifies the Hamiltonian used in the Schrödinger equation for the molecular system. For a one-electron molecule, the equation can be solved mathematically, leading to a set of molecular wavefunctions \(\psi\) which describe molecular orbitals and depend on a quantum number \(\lambda\) which specifies the angular momentum about the internuclear axis. Analogous to the classification of atomic orbitals (AOs) in terms of angular momentum \(l\) as s, p, d, etc., the MOs may be classified as \(\sigma, \pi, \delta\) depending on the value of \(\lambda\) (\(\lambda = 0, 1, 2, \) respectively). Very simply a \(\sigma\) MO is formed from the overlap (actually a linear combination) of AOs parallel to the bond axis, whereas a \(\pi\) MO results from the overlap of AOs perpendicular to the bond axis. For the \(\text{H}_2^+\) ion, the two lowest-energy solutions are known as \(1s\sigma_g\) and \(1s\sigma_u\). Here 1s refers to the original atomic orbitals; the subscripts \(g\) and \(u\) refer to whether the MO is either symmetrical or non-symmetrical with respect to inversion about a line drawn between the nucleii (viz. an even or odd mathematical function). This is shown in figure 1.3.
As can be seen, the electron density is concentrated between the nuclei for the $1s\sigma_g$ MO, which is known as a bonding orbital since the energy of the molecular wavefunction is lower (i.e., more stable) than the corresponding isolated atomic wavefunctions. Conversely, the electron density is diminished between the nuclei for $1s\sigma_u$, which is known as an antibonding orbital since the energy of the molecular wavefunction is higher (i.e., less stable) than the corresponding isolated atomic wavefunction.

More generally, it is necessary to be able to solve the Schrödinger equation for molecules containing more than one electron. One way to do this is to use approximate
solutions similar to those obtained for the hydrogen atom, since when an electron is near a particular nucleus it will have a hydrogen-like form. Using this approach we can then construct a set of molecular orbitals from a linear combination of atomic orbitals (LCAO). For instance, as shown in Figure 1.4, the $1s_{\sigma_g}$ bonding MO is formed from the in-phase overlap (i.e., addition) of two $1s$ atomic orbitals, whereas the $1s_{\sigma_u}$ antibonding MO is formed from the out-of-phase overlap (i.e., subtraction) of two $1s$ atomic orbitals. Similar considerations apply to overlap of $p$ orbitals, although now these may form both $\sigma$ and $\pi$ bonding and antibonding MOs.

The stability of simple diatomic molecules such as $H_2$, $H_2^-$, and $He_2$ depends on the relative filling of the bonding and antibonding MOs; e.g., $H_2^-$ contains three electrons, two of which fill the bonding MO ($1s_{\sigma_g}$ level) while the third enters the antibonding MO ($1s_{\sigma_u}$ level); consequently, the overall bond strength is approximately half that in $H_2$. Meanwhile $He_2$ is unstable as there are an equal number of electrons in bonding MOs as in antibonding MOs. The same principles apply to more complicated diatomic molecules. However, if the atoms are different then the energy levels of the electrons associated with the constituent atoms will also be different and this will lead to an asymmetry in the MO energy level diagram.

**Figure 1.4** Formation of molecular orbitals from a linear combination of atomic orbitals; the + and − signs indicate the signs (phases) of the wavefunctions.
For polyatomic molecules such as BF₃ a greater variety of molecular orbitals can be formed. MO theory emphasizes the delocalized nature of the electron distribution, so in general these MOs are extended over not just two, but all the constituent atoms. The total number of MOs (bonding, antibonding or non-bonding) is equal to the number of valence atomic orbitals used to construct them.

1.2.3 Giant molecular solids

When atoms come into close proximity with other atoms in a solid, most of the electrons remain localized and may be considered to remain associated with a particular atom. However, some outer electrons will become involved in bonding with neighbouring atoms. Upon bonding the atomic energy level diagram is modified. Briefly, the well-defined outer electron states of the atom overlap with those on neighbouring atoms and become broadened into energy bands. One convenient way of picturing this is to envisage the solid as a large molecule. Figure 1.5 shows the effect of increasing the number of atoms on the electronic energy levels of a one-dimensional solid (a linear chain of atoms).

For a simple diatomic molecule, as discussed previously, the two outermost atomic orbitals (AOs) overlap to produce two molecular orbitals (MOs) which can be viewed as a linear combination of the two constituent atomic orbitals. As before, the bonding MO is formed from the in-phase overlap of the AOs and is lower in energy than the corresponding AOs, whereas the other MO, formed from the out-of-phase overlap, is higher in energy than the corresponding AOs and is termed an antibonding MO. Progressively increasing the length of the molecular chain increases the total number of MOs, and gradually these overlap to form bands of allowed energy levels which are separated by forbidden energy regions (band gaps). These band gaps may be thought of as arising from the original energy gaps between the various atomic orbitals of the isolated atoms.

Note that the broadening of atomic orbitals into energy bands as the atoms are brought closer together to form a giant molecular solid can sometimes result in the overlapping of energy bands to give bands of mixed (atomic) character. The degree to which the orbitals are concentrated at a particular energy is reflected in a quantity known as the density of states (DOS) \( N(E) \), where \( N(E) \, dE \) is the number of allowed

![Figure 1.5](image-url)  
*Electron energy level diagram for a progressively larger linear chain of atoms showing the broadening of molecular orbitals into energy bands for a one-dimensional solid*
energy levels per unit volume of the solid in the energy range between $E$ and $E + dE$. As in a simple molecule, each MO energy level in the energy band can accommodate two electrons of opposite spin. The total number of electrons from all the interacting atomic orbitals in the large molecule fill this set of MOs, the highest occupied energy level being known as the Fermi level $E_F$. The sum of the energies of all the individual electrons in the large molecule gives the total energy of the system, which gives a measure of the stability of the atomic arrangement in terms of the system free energy.

1.2.4 The free electron model and energy bands

An alternative view of the electronic band structure of solids is to consider the electron waves in a periodic crystalline potential. The starting point for this approach is the Drude–Lorentz free electron model for metals. In this model a metallic solid is considered as consisting of a close packed lattice of positive cations surrounded by an electron sea or cloud formed from the ionization of the outer shell (valence) electrons. We can then treat the valence electrons as if they were a gas inside a container and use classical kinetic gas theory. This works best for the electropositive metals of Groups I and II as well as aluminium (the so-called free electron metals) and can explain many of the fundamental properties of metals such as high electrical and thermal conductivities, optical opacity, reflectivity, ductility and alloying properties.

However, a more realistic approach is to treat the free electrons in metals quantum mechanically and consider their wave-like properties. Here the free valence electrons are assumed to be constrained within a potential well which essentially stops them from leaving the metal (the ‘particle-in-a-box’ model). The box boundary conditions require the wavefunctions to vanish at the edges of the crystal (or ‘box’). The allowed wavefunctions given by the Schrödinger equation then correspond to certain wavelengths as shown in Figure 1.6. For a one-dimensional box of length $L$, the permitted wavelengths are $\lambda_n = 2L/n$, where $n = 1, 2, 3 \ldots$ is the quantum number of the state; the permitted wavevectors $k_n = 2\pi/\lambda$ are given by $k_n = n\pi/L$.

This simple particle-in-a-box model results in a set of wavefunctions given by

$$\psi_n = (2/L)^{1/2} \sin(n\pi x/L),$$

where $n = 1, 2, 3 \ldots$, and for each $n$ the corresponding energy of the electronic level is

$$E_n = \frac{n^2 \hbar^2}{8mL^2}.$$  (1.5)

$E_n$ represents solely kinetic energy since the potential energy is assumed to be zero within the box. Thus there is a parabolic relationship between $E_n$ and $n$, and therefore between $E_n$ and $k$ since $k$ depends directly on $n$ as described above. The permitted energy levels on this parabola are discrete (i.e., quantized); however in principle the size of $L$ for most metal crystals (ranging from microns to millimetres or even centimetres) means that the separation between levels is very small compared with the thermal energy $k_BT$. 