Biophysics

An Introduction

Rodney M. J. Cotterill
Danish Technical University, Denmark

JOHN WILEY & SONS, LTD

Biophysics

An Introduction

Biophysics

An Introduction

Rodney M. J. Cotterill
Danish Technical University, Denmark

JOHN WILEY & SONS, LTD

Published by John Wiley & Sons Ltd,
Baffins Lane, Chichester,
West Sussex PO19 1UD, England

National 01243 779777
International (+44) 1243 779777

e-mail (for orders and customer service enquiries):
cs-books@wiley.co.uk
Visit our Home Page on http://www.wiley.co.uk
or http://www.wiley.com

Other Wiley Editorial Offices

John Wiley & Sons, Inc., 605 Third Avenue,
New York, NY 10158-0012, USA

Wiley-VCH Verlag GmbH, Pappelallee 3,
D-69469 Weinheim, Germany

John Wiley & Sons (Australia) Ltd, 33 Park Road, Milton,
Queensland 4064, Australia

John Wiley & Sons (Asia) Pte Ltd, 2 Clementi Loop #02-01,
Jin Xing Distripark, Singapore 0512

John Wiley & Sons (Canada) Ltd, 22 Worcester Road,
Rexdale, Ontario M9W 1L1, Canada

Library of Congress Cataloging-in-Publication Data

Cotterill, Rodney, 1933–
Biophysics : an introduction/Rodney Cotterill.
p. cm.
Includes bibliographical references and index.
ISBN 0–471–48537–3 (acid-free paper)—ISBN 0–471–48538–1 (pbk. : acid-free paper)
1. Biophysics. I. Title.

QH505 C64 2002
571.4—dc21

2002069134

British Library Cataloguing in Publication Data

A catalogue record for this book is available from the British Library

ISBN 0 471-485373 (Hardback) 0-471 48538 1 (Paperback)

Typeset in 10.5/13 pt Times by Kolam Information Services Pvt. Ltd, Pondicherry, India
Printed and bound in Great Britain by TJ International Ltd, Padstow, Cornwall
This book is printed on acid-free paper responsibly manufactured from sustainable forestry, in which at least two trees are planted for each one used for paper production.

For my teacher, Herbert C. Daw, and for my biophysics students – past, present and future

Contents

Preface xi

1 Introduction 1
Exercises 6
Further reading 6

2 Chemical Binding 7
2.1 Quantum Mechanics 7
2.2 Pauli Exclusion Principle 9
2.3 Ionization Energy, Electron Affinity and Chemical Binding 10
2.4 Electronegativity and Strong Bonds 15
2.5 Secondary Bonds 21
Exercises 22
Further reading 22

3 Energies, Forces and Bonds 23
3.1 Interatomic Potentials for Strong Bonds 23
3.2 Interatomic Potentials for Weak Bonds 29
3.3 Non-central Forces 32
3.4 Bond Energies 33
3.5 Spring Constants 39
Exercises 40
Further reading 41

4 Rates of Reaction 43
4.1 Free Energy 43
4.2 Internal Energy 45
4.3 Thermodynamics and Statistical Mechanics 46
4.4 Reaction Kinetics 55
4.5 Water, Acids, Bases and Aqueous Reactions 59
4.6 Radiation Energy 65
Exercises 67
Further reading 68

5 Transport Processes **69**
5.1 Diffusion 69
5.2 Viscosity 76
5.3 Thermal Conduction 80
Exercises 81
Further reading 81

6 Some Techniques and Methods **83**
6.1 X-Ray Diffraction and Molecular Structure 83
6.2 Nuclear Magnetic Resonance 93
6.3 Scanning Tunnelling Microscopy 98
6.4 Atomic Force Microscopy 101
6.5 Optical Tweezers 103
6.6 Patch Clamping 108
6.7 Molecular Dynamics 112
6.8 Potential Energy Contour Tracing 115
Exercises 118
Further reading 119

7 Biological Polymers **123**
7.1 Nucleic Acids 124
7.2 Nucleic Acid Conformation: DNA 129
7.3 Nucleic Acid Conformation: RNA 132
7.4 Proteins 134
7.5 Protein Folding 151
Exercises 157
Further reading 158

8 Biological Membranes **161**
8.1 Historical Background 161
8.2 Membrane Chemistry and Structure 166
8.3 Membrane Physics 174
Exercises 185
Further reading 185

9 Biological Energy **187**
9.1 Energy Consumption 187
9.2 Respiration 188
9.3 Photosynthesis 190
9.4 ATP Synthesis 199
Exercises 206
Further reading 207

10 Movement of Organisms **209**
10.1 Bacterial Motion 209
10.2 Chemical Memory in Primitive Organisms 218

10.3 Muscular Movement 220
10.4 Human Performance 233
Exercises 235
Further reading 235

11 Excitable Membranes 237
11.1 Diffusion and Mobility of Ions 237
11.2 Resting Potential 240
Exercises 246
Further reading 246

12 Nerve Signals 249
12.1 Passive Response 249
12.2 Nerve Impulses (Action Potentials) 256
12.3 The Nervous System 268
Exercises 275
Further reading 275

13 Memory 277
13.1 Hebbian Learning 277
13.2 Neural Networks 281
13.3 Auto-association 288
Exercises 293
Further reading 294

14 Control of Movement 297
14.1 The Primacy of Movement 297
14.2 Ballistic Control in a Simplified Visual System 299
14.3 More Sophisticated Modes of Control 304
14.4 The Heterogeneous Structure of Muscle Fibres 305
14.5 Central Pattern Generators 307
14.6 Conditioned Reflexes 311
14.7 Volition and Free Will 314
14.8 What Purpose Does Consciousness Serve? 320
14.9 Passive versus Active in Mental Processing 325
14.10 The Relevant Anatomy and Physiology 328
14.11 Intelligence and Creativity 335
14.12 A Final Word 338
Exercises 339
Further reading 339

Appendix A: Elements of Quantum Mechanics 343
A.1 Quantization of Energy 343
A.2 Atomic Structure 345
A.3 The Wave Equation 347
A.4 Quantum Mechanical Tunnelling 350

Exercises 352
Further reading 352

Appendix B: The Hydrogen Atom 353
B.1 The Hamiltonian 353
B.2 The Hydrogen Atom 353
B.3 Solution of the Φ Equation 356
B.4 Solution of the Θ Equation 357
B.5 Solution of the *R* Equation 358
B.6 Quantum Numbers and Energy Levels 360
B.7 Wave Functions 360
Exercises 364
Further reading 364

Appendix C: Thermal Motion 365
C.1 Ideal Gases 365
C.2 Liquids 369
Exercises 371
Further reading 371

Appendix D: Probability Distributions 373
D.1 Bernoulli Trials and the Binomial Distribution 373
D.2 The Poisson Approximation 373
D.3 The Normal, or Gaussian, Distribution 375
Further reading 376

Appendix E: Differential Equations 377
Further reading 379

Name Index 381
Subject Index 385

Preface

This book is based on the course in biophysics that I have taught for the past two decades at the Danish Technical University, and it should be suitable for similar courses at other places of higher education.

I originally delivered the lectures in Danish and Henrik Jørgensen, one of my first students, recorded my words in shorthand and then collaborated with my secretary, Carolyn Hallinger, to produce a set of Danish notes. I updated these from time to time, and ultimately translated them into English. There were two subsequent expansions of the text before it acquired the form reproduced here. Meanwhile Ove Broo Sørensen and Bjørn Nielsen provided valuable help with many of the illustrations.

The course now attracts so many students that I have needed the backing of two assistant teachers, in connection with the weekly homework assignments. Henrik Bohr and Bjørn Nielsen have provided this service with great skill and diligence, and it is a pleasure to acknowledge their contribution to the enterprise.

The cause of biophysics at this university has benefited greatly from the support provided by colleagues in other departments, and most notably by Robert Djurtoft, Ole Mouritsen, Knud Særmark and Jens Ulstrup, together with whom I set up what came to be known as the Biophysics Initiative. Professors Mouritsen and Særmark were formerly my departmental colleagues, and I enjoyed close interactions with both of them.

The interest and encouragement of the wider Danish biophysics community has also been invaluable, and I would especially like to mention Salim Abdali, Preben Alstrøm, Olaf Sparre Andersen, Svend Olav Andersen, Christen Bak, Per Bak, Rogert Bauer, Klaus Bechgaard, Kirstine Berg-Sørensen, Myer Bloom, Jacob Bohr, Tomas Bohr, John Clark, Jens Peder Dahl, Tom Duke, Henrik Flyvberg, Christian Frøjær-Jensen, Sonia Grego, John Hjort Ipsen, Karl Jalkanen, Mogens Høgh Jensen, Kent Jørgensen, Carsten Knudsen, Bent Kofoed, Morten Kringelbach, Erik Hviid Larsen, Signe Larsen, Jens Jørgen Led, Per Anker Lindegaard, Jens Ulrik Madsen, Axel Michelsen, Erik Mosekilde, Knud Mørch, Claus Nielsen, Simon Nørrelykke, Lene Oddershede,

Niels Berg Olsen, Steffen Petersen, Flemming Poulsen, Christian Rischel, Jens Christian Skou, Kim Sneppen, Ove Sten-Knusen, Maria Sperotto, Stig Steenstrup, Thomas Zeuthen and Martin Zuckerman.

Solutions for the exercises can be found on my website:
http://info.fysik.dtu.dk/Brainscience/rodney.html

Rodney Cotterill

1 Introduction

It is probably no exaggeration to say that many regard biophysics as a discipline still waiting to be adequately defined. This conclusion appears to be endorsed by the considerable differences between several of the publications on the subject cited at the end of this chapter. Indeed, in terms of the items they discuss, these barely overlap with each other. But this should be taken as an indication of the sheer multiplicity of things that now belong under the biophysics banner; no single author could reasonably be expected to cover them all. If one considers what these books and articles describe *collectively*, a unified picture does in fact emerge.

Biophysics is simply the application of physics to biology, with a view to furthering the understanding of biological systems. There is a related activity in which methods developed originally for purely physical challenges have been applied to biological (and in some cases medical) issues. Biophysics tends to be studied by those who have a background in physics, and who may thus be bringing useful expertise to the investigation of living things. But there have also been examples of biologists acquiring the requisite knowledge of physics and then using this to solve a specific problem.

Biophysics is not a young subject, but its emphasis has gradually changed over the years. In the first part of the 20th century, biophysicists primarily concerned themselves with things quite closely related to medicine, and many large hospitals had a resident member of this fraternity. The issues of interest were the flow of blood through pumps and the associated tubing (drawing on the work of George Stokes, among others), the monitoring of heart function through the related electrical activity, and later of brain activity with much the same instrumentation (with valuable input from Hans Berger), and also the fracture of bone (with a borrowing of the ideas developed by Alan Griffith, in a quite different context).

Around the same time, the field was gradually acquiring a new type of activity related to processes at the atomic level, this having been provoked by Wilhelm Röntgen's discovery of X-rays. His astonishment at discovering their power of penetrating human tissue, but apparently not bone, soon led to the use of X-rays for diagnostic purposes, of course. Only later did it emerge that there are grave dangers associated with such radiation, and physicists then

found their advice being sought in connection with the monitoring of X-ray doses. Through their efforts, recording by film was supplemented by recording with electronic devices. One of the pioneering theoretical efforts in understanding the interaction of radiation with matter was published by Niels Bohr, who had earlier put forward the first successful picture of the atom.

These developments were of obvious importance to medicine, but another use of X-rays, originally confined to the inorganic domain, was later going to have an enormous impact on all of biology, and through this on medicine itself. Max von Laue and his colleagues, Walter Friedrich and Paul Knipping, had discovered the diffraction of X-rays, and William Bragg and Lawrence Bragg were soon applying the phenomenon to the determination of crystal structures. The latter Bragg, William's son, encouraged the extension of the technique to the biological realm, and researchers such as William Astbury, John Bernal, Peter Debye and Max Perutz soon took up the challenge. The early work in the area, before the Second World War, contributed to the determination of the sizes of protein molecules, and within twenty years it was producing pictures of proteins at the atomic level.

Mention of molecular size serves as a reminder that it would be easy to overlook the importance of methods developed for separating different molecular species, and their consequent contribution to biology. These methods would not have emerged had it not been for the prior work on the underlying physics. So the development of techniques such as ultra-centrifugation (invented by Thé Svedberg), electrophoresis (by Arne Tiselius) and partition chromatography (by Archer Martin and Richard Synge) owes much to the earlier efforts of George Stokes, Albert Einstein and Irving Langmuir.

But to return to structure determination by means of X-ray diffraction, this approach reached its zenith around the middle of the 20th century. Max Perutz and John Kendrew set about determining the structures of the oxygen-transporting proteins myoglobin and its larger cousin haemoglobin. Meanwhile, Maurice Wilkins, Rosalind Franklin and Raymond Gosling had turned their attention to deoxyribonucleic acid (DNA). Within a decade, the secrets of these key structures had been exposed, important input having come from the knowledge acquired of the bonding between atoms, thanks to the efforts of physicists.

Another spectacular success for physics was the invention of the electron microscope by Ernst Ruska (following important efforts by Denis Gabor). This played a vital role in the study of the microstructure of muscle, by Hugh Huxley and his colleagues, and of viruses, by Aaron Klug and Robert Horne, and their respective colleagues. And there was still good mileage to be had from X-rays because Allan Cormack and Godfrey Hounsfield applied these to the study of brain tissue, by computer assisted tomography (CAT scanning). This fine lead was subsequently augmented by development of such other brain-probing techniques as positron emission tomography (PET) and functional magnetic resonance imaging (fMRI). And while on the subject of the brain, we

have magnetoencephalography (MEG), which owes its existence to something which started as speculation in the purest of physics, namely the work of Brian Josephson on quantum mechanical tunnelling between superconductors.

So the current growth in the application of physics to biology can point to many respectable antecedents. To the names already quoted of physicists who turned their talents to biology we could add Francis Crick (who has latterly shifted his attention from matters molecular to matters mental), Max Delbrück, Walter Gilbert, Salvador Luria and Rosalyn Yalow. These researchers, and many others like them, have brought to biology the quantitative discipline that is the hallmark of physics.

But we should not overlook the unwitting contributions to biology made by physicists of an earlier era – physicists who had probably never even heard of the word biophysics. And in this respect, no advance can quite compete with that which came from the seemingly esoteric study of gaseous discharge. In 1855, Heinrich Geissler devised a vacuum pump based on a column of mercury which functioned as a piston. He and Julius Plücker used this to remove most of the air from a glass tube into which they had sealed two electrical leads, and they used this simple apparatus to study electrical discharges in gases. Their experiments, and related ones performed by Michael Faraday and John Gassiot, probed the influences of electric and magnetic fields on the glow discharge, and it was established that the light was emitted when 'negative rays' struck the glass tube. The discharge tube underwent a succession of design modifications, by William Crookes, Philipp Lenard and Jean Perrin, and this activity culminated with Wilhelm Röntgen's discovery of X-rays in 1895 and Joseph (J. J.) Thomson's discovery of the electron, two years later. These landmarks led, respectively, to the investigations of atomic arrangement mentioned above, and explanations of the forces through which the atoms interact.

These advances were to prove pivotal in the study of biological systems. Moreover, we should not overlook the instruments that owe their existence to those early investigations of the influences of various fields on an electron beam. These led to the cathode ray oscilloscope, with which Edgar Adrian was able to discover the all-or-nothing nature of the nerve impulse. The precision with which that instrument enables one to determine the temporal characteristics of the impulse was vital to Alan Hodgkin and Andrew Huxley's explanation of nerve conduction. The cathode ray oscilloscope presaged the emergence of electron microscopy, which was referred to above.

We should add one more name to the list, because it is nearly always overlooked: John Atanasoff. In the 1930s, confronted with a data analysis problem in his research in solid-state physics, he hit upon the idea of automating his calculations with an electronic machine. This was, indeed, the first electronic digital computer, and the descendants of that device have been indispensable to many of the techniques mentioned above. It would not be eccentric, therefore, to call Atanasoff one of the unsung heroes of biophysics.

Biophysics, then, is an activity that operates within biology, and it contributes to the tackling of some of the major mysteries in that realm. Even though there may be some dispute as to which are the main issues at the current time, few would dispute the claim that protein folding, tissue differentiation, speciation, microscopic recognition and (not the least) consciousness and intelligence are amongst the greatest challenges of our era. It is certainly the case that when we fully understand the physical principles underlying these phenomena, biology as a whole will be very much more advanced than it is today.

Let us briefly consider the nature of these challenges. First, the protein-folding problem has been referred to as the second half of the genetic code. It has long been known that the sequence of bases in the DNA molecule determines the sequence of amino acids in a protein, that is to say the protein's primary structure. It is also well known that the primary structure dictates the final three-dimensional conformation of the protein molecule, but we are unable at the present time to predict that structure, working solely from the primary sequence. The best that one can do is to predict, with a reasonable degree of reliability, certain sub-structural motifs that are frequently observed to be present in the three-dimensional structure. Although this is a notable achievement in its own right, it still falls far short of the desired ability to predict any protein's structure from the primary sequence, and this is an obvious obstacle to full realization of the potential inherent in genetic manipulation. If one were able to overcome that hurdle, this would open up the possibility of tailoring proteins to fulfil specific tasks, for the fact is that what a protein does is determined by its three-dimensional structure.

The tissue-differentiation problem arises from the fact that every cell in a multi-cellular organism contains an identical set of genetic instructions, but for some reason only part of the message is expressed in any one type of cell. In our own bodies, for example, it is this fact that determines that there are different cellular structures in our various parts, and that the same distribution of these bits and pieces is observed in every normal individual. It has long been clear that the differentiation mechanism depends upon the interaction of proteins and nucleic acids, and that it thus hinges on the forces between the constituent atoms. It has also emerged that the differentiation process depends upon the diffusion of certain molecular species in the growing embryo. Biophysics can thus contribute to this topic, through elucidating the microscopic factors that influence the diffusion.

Speciation deals with the questions of why and how a single species occasionally gives rise to two distinct evolutionary branches. It has long been clear that modification of the genetic message lies at the heart of this phenomenon, but the details are still lacking. After all, no two humans have identical sets of genes (unless they happen to be clones or identical twins, triplets, etc.), but we nevertheless all belong to the same species. Here, too, interaction between molecules is of the essence.

Microscopic recognition has to do with the molecular processes that dictate the manner in which different cells mutually interact. Such interactions are important for all the body's cells, but they are particularly important in the case of those that belong to the immune system. The great importance of this system is reflected in the fact that over 1% of a person's body weight is represented by such cells. They must distinguish between those things that belong to the body's tissues and outsiders that might threaten the organism's integrity. So, yet again, one has a mechanism that ultimately depends upon interactions between atoms.

Finally, there is the great mystery of consciousness and the related issue of intelligence. Although there are those who prefer to make a clear distinction between mind and body, there is a growing feeling that it might soon be possible to understand how such ephemeral things as consciousness and the mind arise from the physiological processes that occur in the nervous system. It is by no means clear that adumbration of the physical basis of consciousness would also further our understanding of what underlies intelligence, but it does not appear too optimistic to believe that this could be the case.

It might seem that this list of problems overlooks other pressing issues in the biological domain. One might be tempted to ask why the major scourges of cancer and AIDS have not been included. The fact is, however, that they are implicit in two of the above five categories, because cancer is merely one aspect of the wider issue of tissue differentiation, and AIDS is caused by the human immune deficiency virus (HIV), which undermines the immune system, the latter being categorized under the general heading of microscopic recognition.

The challenging problems identified above have not been listed in an arbitrary order. On the contrary, they show a natural progression from the level of a single molecule, as in the case of the protein-folding issue, to properties of the organism that derive from the behaviour of millions of individual cells. In much the same way, the subject matter in this book follows a logical sequence in which processes at the atomic level are dealt with first, while relevant properties of the nervous system appear toward the end of the book. In between those extremes, the sequence roughly follows that of increasing size. Thus the discussion of molecules leads on logically to properties of organelles, and this in turn is followed by a brief treatment of entire cells. Finally, the issue of neural signalling is discussed, both at the level of the single neuron and ultimately with reference to the functioning of the entire brain. Important items in this latter part of the book are membrane excitability, which underlies that signalling, the changes at the sub-cellular level involved in the laying down of memories, and the process of cognition. On the other hand, no chapters specifically address the three central items in the above list. These are nevertheless mentioned in the relevant places, and representative items in the scientific literature are cited in the Further Reading sections.

There are approximately 10^{12} individual cells in the adult human body. Hopefully, the following chapters will enable the reader to get a good impression of the processes which occur on a number of different size scales, and which lead to the overall functioning of the body. The things described herein should serve to confirm that the quantitative approach has much to recommend it when one is trying to work out how the body's component structures and systems acquire their wonderful functions. Finally, this book aims to endorse what Philip Anderson noted concerning biological phenomena. These are ultimately dependent on Nature's fundamental forces, of course, but the existence of higher levels of organization in living matter implies that there must also be other laws at work. As one makes the transition to each higher level of organization, one must anticipate the emergence of new principles that could not have been predicted on the basis of what was seen at the lower level.

Exercises

1.1 Write an essay on the following question. Will biophysics become one of the major scientific disciplines in the 21st century?

1.2 Max Perutz once referred to 1953 as the *annus mirabilis* of molecular biology. What did he have in mind?

Further reading

Anderson, P. W., (1972). More is different. *Science*, **177**, 393–396.
Cerdonio, M. and Noble, R. W., (1986). *Introductory Biophysics* World Scientific, Singapore.
Cotterill, R. M. J., (2003). *The Material World* Cambridge University Press, Cambridge.
Elsasser, W. M., (1958). *The Physical Foundation of Biology* Clarendon Press, Oxford.
Flyvbjerg, H., *et al.*, eds., (1997). *Physics of Biological Systems: From Molecules to Species* Springer, Berlin.
Glaser, R., (2001). *Biophysics* Springer, Berlin.
Nossal, R. J. and Lecar, H., (1991). *Molecular and Cell Biophysics* Addison-Wesley, Redwood City, CA.
Parak, F. G., (2001). Biological physics hits the high life. *Physics World* **14**(10), 28–29.
Parisi, G., (1993). Statistical physics and biology. *Physics World*, **6**, 42–47.
Parsegian, V. A., (1997). Harness the hubris: useful things physicists could do in biology. *Physics Today*, 23–27, July issue.
Schrödinger, E., (1944). *What is Life?* Cambridge University Press, London.
Setlow, R. B. and Pollard, E. C., (1962). *Molecular Biophysics*. Addeson-Wesley, Reading, MA.
Sybesma, C., (1989). *Biophysics: An Introduction* Kluwer Academic, Dordrecht.

2 Chemical Binding

In this chapter, a *qualitative* account of the electronic structure of atoms will be given (see Appendices A and B), partly because a mathematically precise analysis of groups of atoms is still not possible, but mainly because a qualitative treatment is usually sufficient to provide an understanding of the way in which atoms bind together to form molecules. We thus begin by taking a brief look at an isolated atom.

2.1 Quantum Mechanics

Through his own experimental work on the atomic nucleus, Ernest Rutherford put forward a picture of the atom in which the heavy nucleus is located at the centre, while the electrons, discovered by Joseph (J. J.) Thomson, move in the surrounding space, their characteristic distances from the nucleus being of the order of 0.1 nm (i.e. a tenth of a nanometer, or 1 Ångström unit). The major developments in the theory of atomic structure thereafter were due to Niels Bohr, who realized that only certain energy states would be permitted by the quantum principle postulated by Max Planck in 1900; by Louis de Broglie, who advocated that a dual attitude be adopted toward sub-atomic particles, such that they are regarded as simultaneously having both particle and wave natures (see Appendix A); and by Erwin Schrödinger, whose equation showed how to derive the allowed states of electrons, both regarding their permitted energies and their spatial distribution with respect to the nucleus.

Schrödinger's time-independent equation reads

$$\mathcal{H} \cdot \Psi = \mathscr{E} \cdot \Psi \tag{2.1}$$

where $\mathcal{H}$ is the Hamiltonian operator, $\mathscr{E}$ is the energy and Ψ is the wave function, the latter being a function of position with respect to the nucleus. This equation appears to be remarkably simple, but one must bear in mind that the Hamiltonian itself will usually be a composite of several terms, while the wave function will include components describable only in terms of complex

numbers. The solution of the Schrödinger equation for the very important case of the hydrogen atom is given in Appendix B.

Max Born hit upon the correct interpretation of the distribution yielded by the Schrödinger equation when he suggested that $\Psi\Psi^*$ (where Ψ^* is the complex conjugate of Ψ) gives the probability that an electron will be located at that position. (For our purposes here, $\Psi\Psi^*$ can be regarded as simply being the square of the amplitude of the wave function.) Just as the vibrations of a (one-dimensional) guitar string and the (two-dimensional) skin of a drum can be characterized by a set of numbers which refer to the positions and multiplicity of the nodal points (i.e. positions where the amplitude is zero), so it is with the electron probability distribution around a nucleus. Although we need not go into the details here, different quantum states of an electron in the vicinity of an atomic nucleus are characterized by different spherical and non-spherical probability distributions. Although other factors also come into play, as we will see later, it is the shapes of these distributions that determine the shapes of the molecules formed when two or more atoms form a reasonably permanent mutual liaison.

In the case of the one-dimensional guitar string, the situation can be characterized by a single number, which is related to the number of nodal points located along the string. In the case of the vibrating skin of a drum, two different numbers are required in order to fully characterize the situation: one of these refers to nodal points whereas the other refers to nodal lines (which may be curved). In the three-dimensional space around an atomic nucleus, therefore, it is not surprising that three different numbers are required for a full description of the spatial arrangement of the probability distribution for each electron, there now being nodal points, nodal lines and nodal surfaces. It turns out that a further number is required, because the electron possesses what is known as spin, which is very roughly analogous to the spin of a planet, as it describes its orbit around the sun. Just as the spin of such a planet may be either in a left-handed or a right-handed direction, so too the spin of an electron has one of just two possibilities. The spin quantum number of an electron is usually designated by the letter s, and the other quantum numbers by the letters n, l, and m (see Appendix B). Figure 2.1 shows the spatial distribution of the squared probability amplitude for a number of different situations which can apply to an electron in orbit around an atomic nucleus. These are indeed usually referred to as orbitals.

The lowest energy (ground) state for a hydrogen atom, the $1s$ state, is characterized by a spherically-symmetric wave intensity with a single spherical nodal surface at infinity. The lowest energy excited state is the $2s$, and this has an additional spherical nodal surface centred on the nucleus. The $2p$ states, which have slightly higher energy, have nodal surfaces which pass through the nucleus. There are three of them, corresponding to the three possible values of the magnetic quantum number m. States with lobes extending along one of the

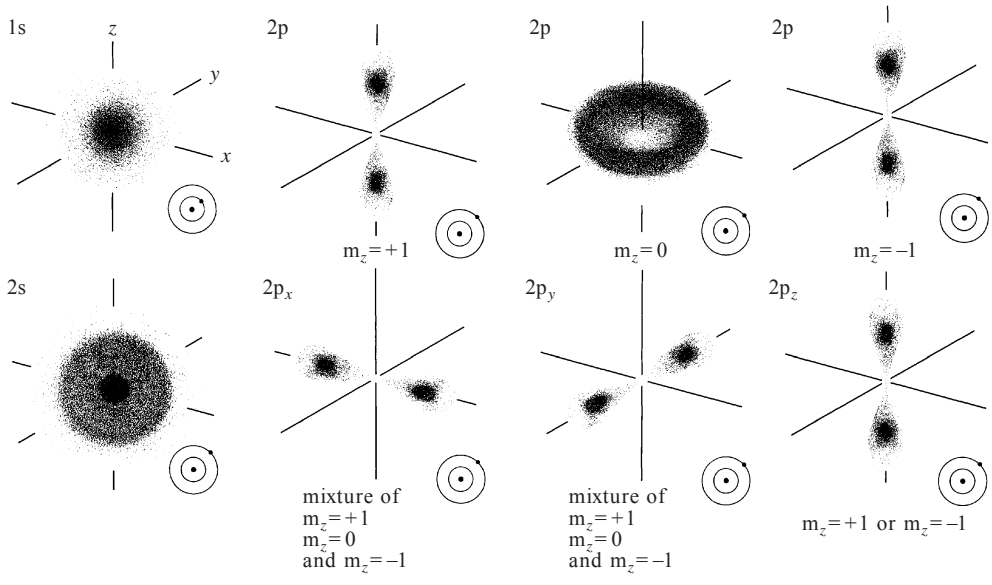

Figure 2.1 Spatial distribution of the squared probability amplitude for a number of different situations which can apply to an electron in orbit around an atomic nucleus

Cartesian axes can be obtained by mixing the three 2*p* states in the correct proportions. The insets in Figure 2.1 and later diagrams indicate schematically the equivalent Bohr orbits.

2.2 Pauli Exclusion Principle

Although we do not need to go into all the details here, there are certain rules which are useful when considering situations in which there is more than one electron present in an atom. For a start, no two electrons can be associated with the same atomic nucleus and have precisely the same values for all four of the quantum numbers. This is known as the Pauli Exclusion Principle (after Wolfgang Pauli), and it is a particularly potent factor when two similar atoms lie sufficiently close to one another. Regarding the actual shapes of the orbitals, the *s* types all have spherical symmetry, whereas the *p* types show elongation along an axis (see Figure 2.1). (The *s* used to designate one type of orbital should not be confused with the symbol for the spin quantum number; see Appendix B.) When all the *p* orbitals are fully occupied by their permitted complement of electrons, however, these collectively also display spherical symmetry. This is particularly noticeable in the noble gas atoms, which indeed possess only such full shells. Another important property of electron orbitals is

that a linear combination of different possible wave functions is also a possible solution of the time-independent Schrödinger equation.

Suppose that Ψ_1 and Ψ_2 are two such possible wave functions. We will then have that

$$\mathcal{H} \cdot \Psi_1 = \mathscr{E} \cdot \Psi_1$$

and

$$\mathcal{H} \cdot \Psi_2 = \mathscr{E} \cdot \Psi_2$$

If we now multiply the first of these equations by the coefficient C_1 and the second by C_2, and add the two results, we obtain

$$\mathcal{H} \cdot (C_1 \cdot \Psi_1 + C_2 \cdot \Psi_2) = \mathscr{E} \cdot (C_1 \cdot \Psi_1 + C_2 \cdot \Psi_2) \tag{2.2}$$

This is an equally valid version of the time-independent Schrödinger equation.

We can now proceed to discuss what happens when two atoms approach each other. It is clear that they must exert a force upon each other, and a moment's reflection reveals that these forces may be either attractive or repulsive. This conclusion comes from the dual facts that matter does not spontaneously explode or implode. In other words, one meets with resistance if an attempt is made to squeeze a piece of condensed matter (i.e. a solid or a liquid) into a smaller volume. Likewise, resistance is encountered if one tries to stretch a piece of material beyond its quiescent dimensions. This indicates that the interatomic potential is repulsive at sufficiently short range and attractive at sufficiently long range, and the implication is thus that there must be an intermediate distance at which there is neither repulsion nor attraction. This will correspond to an interatomic separation for which the forces are precisely balanced, and it is this characteristic distance that essentially determines the density of a piece of material.

2.3 Ionization Energy, Electron Affinity and Chemical Binding

It is interesting to note that these considerations were well appreciated even before it had been unequivocally demonstrated that atoms actually exist. It is not surprising, therefore, that the arguments do not take into account possible redistribution of the subatomic particles when two atoms approach one another sufficiently closely. In general, there will be a rearrangement of the electrons between the two atoms, the notable exception being the case where both atoms are of the noble gas type. Two quantities are of importance when considering what might happen in the two-atom case, these being the ionization energy

and the electron affinity. The ionization energy, E_I, is the minimum energy required to remove an electron from an otherwise neutral atom. The situation is described by

$$A \rightarrow A^+ + e^- \tag{2.3}$$

A denotes the neutral atom, A^+ a positively charged ion, and e^- the electron. The electron affinity, E_A, is the energy gained when a neutral atom acquires an additional electron. This other situation is described by

$$A + e^- \rightarrow A^- \tag{2.4}$$

A^- denotes the negatively charged atom that results from this process. It is very important to note that these two equations are *not* merely mutual opposites, because the product of the first reaction is a positive ion and a negative electron, whereas the participants in the second reaction are a *neutral* atom and a negative electron.

A good example is seen in the compound lithium fluoride, in which a lithium atom readily donates one of its electrons to a fluorine atom, the latter thereby acquiring an electron structure which resembles that of a noble gas atom, with all of its electron orbitals having the maximum number of permitted electrons (see Table 2.1). The separation of the electron from the lithium atom requires an amount of energy equal to the ionization energy, E_I. When the fluorine

Table 2.1 The electronic characteristics of the elements

Atomic Number	Element	Orbital electronic configuration	E_I(aJ)	E_A(aJ)
1	H	$1s$	2.178	0.120
2	He	$1s^2$	3.938	
3	Li	[He]$2s$	0.863	0.087
4	Be	[He]$2s^2$	1.493	−0.096
5	B	[He]$2s^2 2p$	1.329	0.032
6	C	[He]$2s^2 2p^2$	1.804	0.200
7	N	[He]$2s^2 2p^3$	2.329	−0.016
8	O	[He]$2s^2 2p^4$	2.181	0.235
9	F	[He]$2s^2 2p^5$	2.791	0.553
10	Ne	[He]$2s^2 2p^6$	3.454	
11	Na	[Ne]$3s$	0.823	0.119
12	Mg	[Ne]$3s^2$	1.225	−0.048
13	Al	[Ne]$3s^2 3p$	0.959	0.096
14	Si	[Ne]$3s^2 3p^2$	1.305	0.261
15	P	[Ne]$3s^2 3p^3$	1.762	0.112

continues overleaf

Table 2.1 (*continued*)

Atomic Number	Element	Orbital electronic configuration	E_I(aJ)	E_A(aJ)
16	S	[Ne]$3s^2 3p^4$	1.659	0.332
17	Cl	[Ne]$3s^2 3p^5$	2.084	0.578
18	Ar	[Ne]$3s^2 3p^6$	2.524	
19	K	[Ar]$4s$	0.695	
20	Ca	[Ar]$4s^2$	0.979	
21	Sc	[Ar]$4s^2 3d$	1.051	
22	Ti	[Ar]$4s^2 3d^2$	1.094	
23	V	[Ar]$4s^2 3d^3$	1.080	
24	Cr	[Ar]$4s 3d^5$	1.083	
25	Mn	[Ar]$4s^2 3d^5$	1.191	
26	Fe	[Ar]$4s^2 3d^6$	1.266	
27	Co	[Ar]$4s^2 3d^7$	1.259	
28	Ni	[Ar]$4s^2 3d^8$	1.223	
29	Cu	[Ar]$4s 3d^{10}$	1.237	
30	Zn	[Ar]$4s^2 3d^{10}$	1.504	−0.144
31	Ga	[Ar]$4s^2 3d^{10} 4p$	0.961	0.029
32	Ge	[Ar]$4s^2 3d^{10} 4p^2$	1.262	0.192
33	As	[Ar]$4s^2 3d^{10} 4p^3$	1.572	0.096
34	Se	[Ar]$4s^2 3d^{10} 4p^4$	1.562	0.272
35	Br	[Ar]$4s^2 3d^{10} 4p^5$	1.897	0.538
36	Kr	[Ar]$4s^2 3d^{10} 4p^6$	2.242	
37	Rb	[Kr]$5s$	0.669	
38	Sr	[Kr]$5s^2$	0.912	
39	Y	[Kr]$5s^2 4d$	1.041	
40	Zr	[Kr]$5s^2 4d^2$	1.113	
41	Nb	[Kr]$5s 4d^4$	1.085	
42	Mo	[Kr]$5s 4d^5$	1.137	
43	Tc	[Kr]$5s^2 4d^5$	1.166	
44	Ru	[Kr]$5s 4d^7$	1.180	
45	Rh	[Kr]$5s 4d^8$	1.195	
46	Pd	[Kr]$4d^{10}$	1.334	
47	Ag	[Kr]$5s 4d^{10}$	1.213	
48	Cd	[Kr]$5s^2 4d^{10}$	1.440	−0.096
49	In	[Kr]$5s^2 4d^{10} 5p$	0.927	0.032
50	Sn	[Kr]$5s^2 4d^{10} 5p^2$	1.176	
51	Sb	[Kr]$5s^2 4d^{10} 5p^3$	1.384	
52	Te	[Kr]$5s^2 4d^{10} 5p^4$	1.443	0.352
53	I	[Kr]$5s^2 4d^{10} 5p^5$	1.675	0.490
54	Xe	[Kr]$5s^2 4d^{10} 5p^6$	1.943	
55	Cs	[Xe]$6s$	0.624	
56	Ba	[Xe]$6s^2$	0.835	
57	La	[Xe]$6s^2 5d$	0.899	
58	Ce	[Xe]$6s^2 4f 5d$	1.107	
59	Pr	[Xe]$6s^2 4f^3$	0.923	
60	Nd	[Xe]$6s^2 4f^4$	1.011	

Table 2.1 (*continued*)

Atomic Number	Element	Orbital electronic configuration	E_I(aJ)	E_A(aJ)
61	Pm	$[Xe]6s^2 4f^5$		
62	Sm	$[Xe]6s^2 4f^6$	0.897	
63	Eu	$[Xe]6s^2 4f^7$	0.908	
64	Gd	$[Xe]6s^2 4f^7 5d$	0.987	
65	Tb	$[Xe]6s^2 4f^9$	1.080	
66	Dy	$[Xe]6s^2 4f^{10}$	1.093	
67	Ho	$[Xe]6s^2 4f^{11}$		
68	Er	$[Xe]6s^2 4f^{12}$	0.974	
69	Tm	$[Xe]6s^2 4f^{13}$	0.931	
70	Yb	$[Xe]6s^2 4f^{14}$	0.993	
71	Lu	$[Xe]6s^2 4f^{14} 5d$	0.801	
72	Hf	$[Xe]6s^2 4f^{14} 5d^2$		
73	Ta	$[Xe]6s^2 4f^{14} 5d^3$	1.262	
74	W	$[Xe]6s^2 4f^{14} 5d^4$	1.278	
75	Re	$[Xe]6s^2 4f^{14} 5d^5$	1.261	
76	Os	$[Xe]6s^2 4f^{14} 5d^6$	1.394	
77	Ir	$[Xe]6s^2 4f^{14} 5d^7$	1.442	
78	Pt	$[Xe]6s 4f^{14} 5d^9$	1.442	
79	Au	$[Xe]6s 4f^{14} 5d^{10}$	1.477	
80	Hg	$[Xe]6s^2 4f^{14} 5d^{10}$	1.671	
81	TI	$[Xe]6s^2 4f^{14} 5d^{10} 6p$	0.978	
82	Pb	$[Xe]6s^2 4f^{14} 5d^{10} 6p^2$	1.188	
83	Bi	$[Xe]6s^2 4f^{14} 5d^{10} 6p^3$	1.167	
84	Po	$[Xe]6s^2 4f^{14} 5d^{10} 6p^4$	1.350	
85	At	$[Xe]6s^2 4f^{14} 5d^{10} 6p^5$		
86	Rn	$[Xe]6s^2 4f^{14} 5d^{10} 6p^6$	1.722	
87	Fr	$[Rn]7s$		
88	Ra	$[Rn]7s^2$	0.851	
89	Ac	$[Rn]7s^2 6d$		
90	Th	$[Rn]7s^2 6d^2$	1.121	
91	Pa	$[Rn]7s^2 5f^2 6d$		
92	U	$[Rn]7s^2 5f^3 6d$	0.984	
93	Np	$[Rn]7s^2 5f^4 6d$		
94	Pu	$[Rn]7s^2 5f^6$	0.823	
95	Am	$[Rn]7s^2 5f^7$	0.968	
96	Cm	$[Rn]7s^2 5f^7 6d$		
97	Bk	$[Rn]7s^2 5f^9$		
98	Cf	$[Rn]7s^2 5f^{10}$		
99	Es	$[Rn]7s^2 5f^{11}$		
100	Fm	$[Rn]7s^2 5f^{12}$		
101	Md	$[Rn]7s^2 5f^{13}$		
102	No	$[Rn]7s^2 5f^{14}$		
103	Lr	$[Rn]7s^2 5f^{14} 6d$		

atom subsequently acquires that same electron, and thereby develops an electron structure resembling that of neon, the overall system gains an amount of energy equal to the electron affinity, E_A. Because E_I is usually larger than E_A, this electron transfer process might seem to require a net input of energy (see Table 2.2). However, we must remember that the situation does not involve two atoms that are well separated. On the contrary, they remain in the vicinity of each other, and so there are other energy contributions to be taken into account. It transpires that the Coulomb interaction (named for Charles de Coulomb) fully compensates for the above net energy input, so there will indeed be chemical binding between the two atoms involved. The situation is illustrated in Figure 2.2, and one notes that the binding is purely electrostatic in nature; there is no directionality in the binding. This interaction is, of course, a classical example of ionic bonding.

In ionic bonding, electropositive and electronegative atoms combine through the electric attraction between ions that are produced by electron transfer. Good examples are provided by the alkali halides such as LiF. Each neutral (electropositive) lithium atom loses its 2*s* electron and thereby becomes a positive ion, somewhat resembling a positively-charged helium atom. Each neutral (electronegative) fluorine atom gains an extra 2*p* electron and becomes a negative ion, resembling a negatively-charged neon atom.

It is no coincidence that it is the lithium atom in the above reaction that loses an electron. Of the two elements involved, it is lithium that has a lone electron outside shells that are fully occupied. The fluorine atom, on the other hand, has an outermost shell that lacks only one electron. This difference is clearly revealed in the first ionization energies of the two atoms (that is to say the energy which must be expended in removing one electron from the neutral atom). As can be seen in Table 2.1, the first ionization energy of lithium is 0.863 aJ, whereas the first ionization energy of fluorine is 2.791 aJ. Indeed, to find ionization

Table 2.2 Comparison of electronegativity with the sum of ionization energy and electron affinity. All values are for 25°C

	E_I	E_A	Sum	e_N
F	2.8	0.6	3.4	4.0
Cl	2.1	0.6	2.7	3.0
Br	1.9	0.5	2.4	2.8
I	1.7	0.5	2.2	2.5
H	2.2	0.1	2.3	2.1
Li	0.9	0.1	1.0	1.0
Na	0.8	0.1	0.9	0.9
K	0.7	0	0.7	0.8
Rb	0.7	0	0.7	0.8
Cs	0.6	0	0.6	0.7

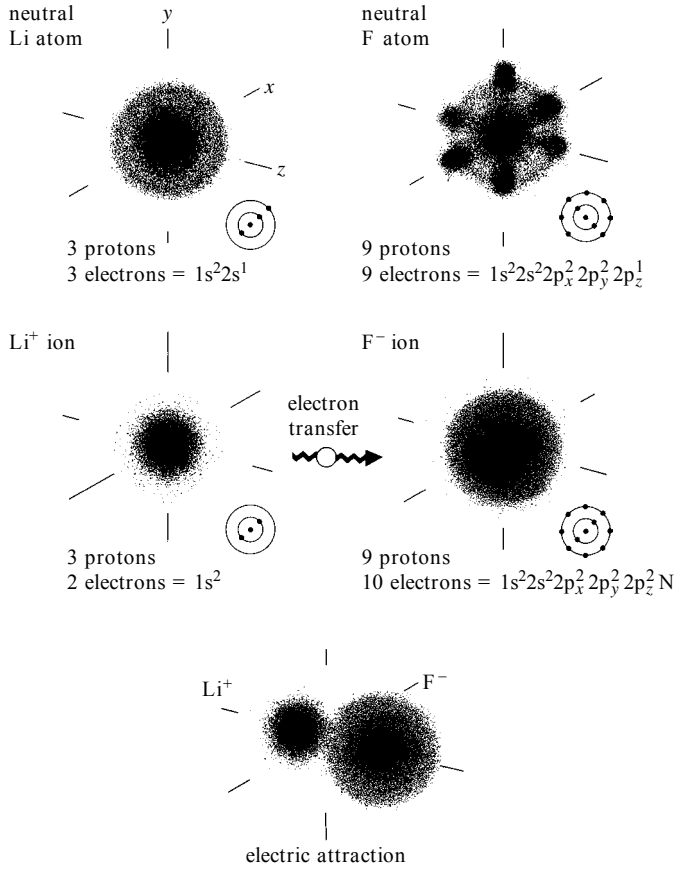

Figure 2.2 An illustration of ionic bonding in the case of LiF

energies larger than that exhibited by the fluorine atom, one would have to go to the noble gases themselves, with their fully occupied electron orbitals.

2.4 Electronegativity and Strong Bonds

Although the propensity that a given atomic species displays for losing or gaining electrons is determined by the dual factors of ionization potential and electron affinity, an adequate qualitative measure of the same thing is provided by a single parameter known as the electronegativity, e_N. Atoms with large electronegativities tend to capture electrons, whereas the opposite is the case for atoms with small electronegativities (these being said to be electropositive). A reliable scale of electronegativity has been derived by Linus Pauling and it is, as indicated above, a dual measure of ionization energy and electron affinity. Typical values are given in Table 2.2.

If the difference in the electronegativities of two atoms is quite small, there will be no clear tendency for one to lose an electron while the other gains this subatomic particle. There is thus no basis for ionic binding in such a situation. Instead, one has either covalent bonding or metallic bonding, the first of these occurring if the two atoms are both electronegative, and the latter arising when they are both electropositive. An example of covalent bonding is seen if the two atoms involved are both fluorine. The nine electrons in an atom of this element are arranged in such a way that there are two in the 1*s* orbital, two in the 2*s* orbital, two in each of the $2p_x$ and $2p_y$ orbitals, and finally a single electron in the $2p_z$ orbital. It is only the latter orbital, therefore, which lacks an electron and, as we saw in the case of ionic bonding, it can fulfil this need by acquiring an electron from another atom. However, in the case of the covalent bond, it does this not by completely removing an electron from that other atom, but rather by entering into a mutual sharing of atoms, in which the unfilled orbitals of both atoms are filled by the other's lone $2p_z$ electron.

One sees from Figure 2.3, which depicts the situation in a hydrogen fluoride molecule, that the $2p_z$ orbitals alone are involved in the binding. Although the interatomic bond is highly directional, as mentioned earlier, it possesses rotational symmetry and there is very little resistance to rotation of one of the atoms with respect to the other, about the *z*-axis. This form of covalent bonding is known as a σ-bond (sigma bond) and numerous examples are

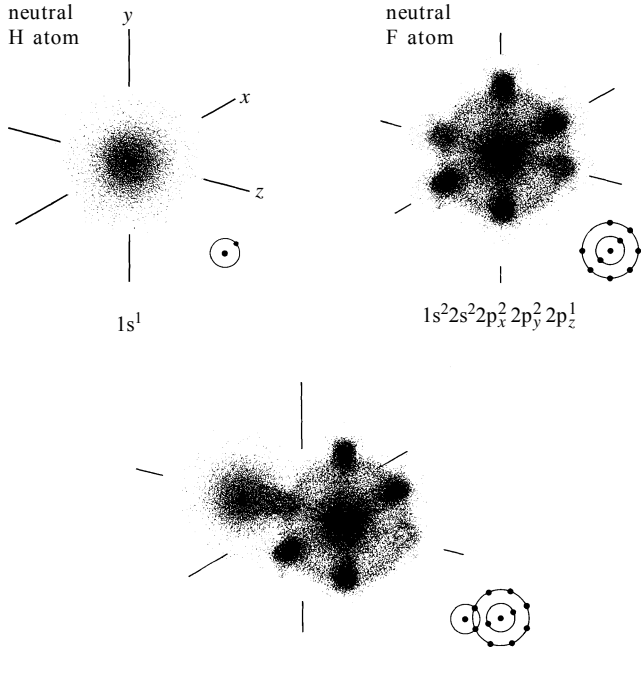

Figure 2.3 A simple example of covalent bonding which occurs in the HF molecule