THE QUANTUM IN CHEMISTRY:
An Experimentalist’s View

Roger Grinter

School of Chemical Sciences and Pharmacy
University of East Anglia

John Wiley & Sons, Ltd
THE QUANTUM IN CHEMISTRY:

An Experimentalist’s View
THE QUANTUM IN CHEMISTRY:
An Experimentalist’s View

Roger Grinter

School of Chemical Sciences and Pharmacy
University of East Anglia

John Wiley & Sons, Ltd
Contents

Preface ........................................................................................................... xiii

Chapter 1  The Role of Theory in the Physical Sciences ......................... 1
  1.0 Introduction ......................................................................................... 1
  1.1 What is the role of theory in science? .............................................. 1
  1.2 The gas laws of Boyle and Gay-Lussac .......................................... 3
  1.3 An absolute zero of temperature .................................................... 4
  1.4 The gas equation of Van der Waals ................................................ 5
  1.5 Physical laws .................................................................................... 5
  1.6 Laws, postulates, hypotheses, etc. ................................................... 6
  1.7 Theory at the end of the 19th century ............................................. 7
  1.8 Bibliography and further reading ................................................... 8

Chapter 2  From Classical to Quantum Mechanics .............................. 9
  2.0 Introduction ....................................................................................... 9
  2.1 The motion of the planets: Tycho Brahe and Kepler ..................... 10
  2.2 Newton, Lagrange and Hamilton ................................................... 11
  2.3 The power of classical mechanics ................................................... 12
  2.4 The failure of classical physics ....................................................... 12
  2.5 The black-body radiator and Planck’s quantum hypothesis .......... 13
    2.5.1 Planck’s solution to the black-body radiation problem .......... 15
    2.5.2 A qualitative interpretation of the form of the black-body emission curve in the light of Planck’s hypothesis ................. 16
    2.5.3 Quantisation in classical mechanics ....................................... 18
  2.6 The photoelectric effect ................................................................ 20
    2.6.1 Einstein’s theory of the photoelectric effect confirmed experimentally ............................................................... 22
  2.7 The emission spectra of atoms ...................................................... 23
    2.7.1 Bohr’s theory of the structure of the hydrogen atom ............ 24
    2.7.2 Comparison of Bohr’s model with experiment ...................... 26
    2.7.3 Further development of Bohr’s theory .................................... 26
  2.8 de Broglie’s proposal ....................................................................... 26
  2.9 The Schrödinger equation .............................................................. 28
    2.9.1 Eigenfunctions and eigenvalues .............................................. 29
Chapter 3  The Application of Quantum Mechanics          37

3.0 Introduction ................................................. 38
3.1 Observables, operators, eigenfunctions and eigenvalues .......... 38
3.2 The Schrödinger method ....................................... 39
3.3 An electron on a ring .......................................... 40
   3.3.1 The Hamiltonian operator for the electron on a ring ........ 40
   3.3.2 Solution of the Schrödinger equation .................... 41
   3.3.3 The acceptable eigenfunctions ........................... 41
3.4 Hückel’s \((4N + 2)\) rule: aromaticity ........................ 44
3.5 Normalisation and orthogonality .............................. 46
3.6 An electron in a linear box ................................... 46
   3.6.1 The Hamiltonian operator for an electron in a linear box . 46
   3.6.2 The acceptable eigenfunctions ........................... 47
   3.6.3 Boundary conditions ..................................... 48
3.7 The linear and angular momenta of electrons confined within a  
   one-dimensional box or on a ring ................................ 48
   3.7.1 The linear momentum of an electron in a box .............. 49
   3.7.2 The angular momentum of an electron on a ring ........... 50
3.8 The eigenfunctions of different operators ........................ 52
3.9 Eigenfunctions, eigenvalues and experimental measurements ..... 53
3.10 More about measurement: the Heisenberg uncertainty principle . 55
3.11 The commutation of operators .................................. 57
3.12 Combinations of eigenfunctions and the superposition of states . 58
3.13 Operators and their formulation ................................ 59
   3.13.1 Position or co-ordinate, \(\hat{x}\) .......................... 59
   3.13.2 Potential energy, \(\hat{V}\) ................................ 59
   3.13.3 Linear momentum, \(\hat{p}_x\) .............................. 60
   3.13.4 Kinetic energy, \(\hat{W}\) ................................ 60
   3.13.5 Angular momentum, \(\hat{L}\) .............................. 60
3.14 Summary ....................................................... 60
3.15 Bibliography and further reading ................................ 61
Problems for Chapter 3 ............................................. 71

Chapter 4  Angular Momentum .................................... 73

4.0 Introduction .................................................... 73
4.1 Angular momentum in classical mechanics .......................... 73
4.2 The conservation of angular momentum ............................ 75
Contents

4.3 Angular momentum as a vector quantity ............................................. 75
4.4 Orbital angular momentum in quantum mechanics ................................. 76
  4.4.1 The vector model .......................................................................... 77
4.5 Spin angular momentum ....................................................................... 78
4.6 Total angular momentum ..................................................................... 78
  4.6.1 The addition and conservation of angular momentum in quantum mechanics .................................................................................................. 79
  4.6.2 The laws of quantum-mechanical angular momentum ...................... 81
4.7 Angular momentum operators and eigenfunctions ................................. 82
  4.7.1 The raising and lowering, shift or ladder operators .......................... 82
4.8 Notation ............................................................................................... 83
4.9 Some examples ..................................................................................... 84
4.10 Bibliography and further reading .......................................................... 86
Problems for Chapter 4 ........................................................................... 93

Chapter 5  The Structure and Spectroscopy of the Atom ............................ 95

  5.0 Introduction ....................................................................................... 96
  5.1 The eigenvalues of the hydrogen atom ............................................... 96
  5.2 The wave functions of the hydrogen atom ........................................... 97
    5.2.1 The radial function, \( R_{n,l}(r) \) .................................................. 98
    5.2.2 The angular functions, \( \Theta_{l,m}(\theta) \) and \( \Phi_{m}(\phi) \) .............. 99
  5.3 Polar diagrams of the angular functions ............................................. 100
    5.3.1 The \( s \)-functions .................................................................... 101
    5.3.2 The \( p \)-functions .................................................................... 101
    5.3.3 The \( d \)-functions .................................................................... 103
  5.4 The complete orbital wave functions .................................................. 104
  5.5 Other one-electron atoms ................................................................... 104
  5.6 Electron spin ..................................................................................... 105
  5.7 Atoms and ions with more than one electron ........................................ 105
    5.7.1 The self-consistent field ............................................................ 106
    5.7.2 Electron correlation ................................................................... 106
    5.7.3 The periodic table of the elements ............................................. 107
  5.8 The electronic states of the atom ....................................................... 107
    5.8.1 The five quantum numbers of a single electron ............................ 108
    5.8.2 Quantum numbers for the many-electron atom ............................ 108
    5.8.3 The assignment of term symbols ............................................... 108
    5.8.4 Term energies and Hund’s rules ............................................... 110
  5.9 Spin-orbit coupling ........................................................................... 111
    5.9.1 Russell–Saunders or \( LS \) coupling ............................................. 111
    5.9.2 \( jj \) coupling ........................................................................... 112
    5.9.3 Intermediate coupling ................................................................ 113
    5.9.4 Inter-electronic spin-orbit coupling ........................................... 115
  5.10 Selection rules in atomic spectroscopy ................................................ 115
    5.10.1 Angular momentum ................................................................. 115
    5.10.2 Parity ...................................................................................... 116
## Contents

5.11 The Zeeman effect ........................................ 117
  5.11.1 The normal Zeeman effect ............................ 118
  5.11.2 The anomalous Zeeman effect ......................... 120
5.12 Bibliography and further reading .......................... 121

Problems for Chapter 5 ........................................ 129

Chapter 6 The Covalent Chemical Bond ...................... 131

  6.0 Introduction ............................................ 132
  6.1 The binding energy of the hydrogen molecule .......... 133
  6.2 The Hamiltonian operator for the hydrogen molecule . 134
  6.3 The Born–Oppenheimer approximation .................... 136
  6.4 Heitler and London: The valence bond (VB) model .... 137
  6.5 Hund and Mulliken: the molecular orbital (MO) model 139
  6.6 Improving the wave functions ............................ 140
    6.6.1 The value of Z .................................... 140
    6.6.2 Polarisation ...................................... 140
  6.7 Unification: Ionic structures and configuration interaction . 141
  6.8 Electron correlation ...................................... 143
  6.9 Bonding and antibonding MOs ............................. 145
  6.10 Why is there no He–He Bond? .......................... 146
  6.11 Atomic orbital overlap ................................... 146
    6.11.1 $\sigma$ (sigma) overlap ............................. 147
    6.11.2 $\pi$ (pi) overlap .................................. 147
    6.11.3 $\delta$ (delta) overlap ............................... 148
    6.11.4 Non-bonding overlap ................................. 148
  6.12 The Homonuclear diatomic molecules from lithium to fluorine 149
  6.13 Heteronuclear diatomic molecules ....................... 151
  6.14 Charge distribution ...................................... 153
  6.15 Hybridisation and resonance ............................ 153
    6.15.1 Hybridisation: Pauling 1931 ......................... 153
    6.15.2 Hybridisation and the valence bond theory ......... 156
    6.15.3 Hybridisation of carbon AOs ......................... 156
    6.15.4 The choice of hybrid orbitals ....................... 161
    6.15.5 The properties of hybrid-orbital bonds ............ 162
  6.16 Resonance and the valence bond theory .................. 163
  6.17 Molecular geometry ...................................... 163
    6.17.1 The valence-shell electron-pair repulsion (VSEPR) model . 164
    6.17.2 The VSEPR model and multiple bonds ............... 165
  6.18 Computational developments ................................ 167
  6.19 Bibliography and further reading ....................... 168

Problems for Chapter 6 ........................................ 176

Chapter 7 Bonding, Spectroscopy and Magnetism in Transition-Metal Complexes .......................... 181

  7.0 Introduction ............................................ 181
<table>
<thead>
<tr>
<th>Chapter 9</th>
<th>Nuclear Magnetic Resonance Spectroscopy</th>
<th>261</th>
</tr>
</thead>
<tbody>
<tr>
<td>9.0</td>
<td>Introduction</td>
<td>261</td>
</tr>
<tr>
<td>9.1</td>
<td>The magnetic properties of atomic nuclei</td>
<td>262</td>
</tr>
<tr>
<td>9.2</td>
<td>The frequency region of NMR spectroscopy</td>
<td>264</td>
</tr>
<tr>
<td>9.3</td>
<td>The NMR selection rule</td>
<td>264</td>
</tr>
<tr>
<td>9.4</td>
<td>The chemical shift</td>
<td>267</td>
</tr>
<tr>
<td>9.4.1</td>
<td>The delta (δ) scale</td>
<td>268</td>
</tr>
<tr>
<td>9.4.2</td>
<td>The shielding constant, σ (sigma)</td>
<td>270</td>
</tr>
<tr>
<td>9.5</td>
<td>Nuclear spin–spin coupling</td>
<td>270</td>
</tr>
<tr>
<td>9.6</td>
<td>The energy levels of a nuclear spin system</td>
<td>273</td>
</tr>
<tr>
<td>9.6.1</td>
<td>First order spectra</td>
<td>274</td>
</tr>
<tr>
<td>9.6.2</td>
<td>Second order spectra</td>
<td>275</td>
</tr>
<tr>
<td>9.7</td>
<td>The intensities of NMR spectral lines</td>
<td>276</td>
</tr>
<tr>
<td>9.8</td>
<td>Quantum mechanics and NMR spectroscopy</td>
<td>277</td>
</tr>
<tr>
<td>9.9</td>
<td>Bibliography and further reading</td>
<td>278</td>
</tr>
<tr>
<td>Problems</td>
<td>for Chapter 9</td>
<td>287</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Chapter 10</th>
<th>Infrared Spectroscopy</th>
<th>289</th>
</tr>
</thead>
<tbody>
<tr>
<td>10.0</td>
<td>Introduction</td>
<td>289</td>
</tr>
<tr>
<td>10.1</td>
<td>The origin of the infrared spectra of molecules</td>
<td>290</td>
</tr>
<tr>
<td>10.2</td>
<td>Simple harmonic motion</td>
<td>290</td>
</tr>
<tr>
<td>10.3</td>
<td>The quantum-mechanical harmonic oscillator</td>
<td>293</td>
</tr>
<tr>
<td>10.3.1</td>
<td>Quantisation of the energy</td>
<td>293</td>
</tr>
<tr>
<td>10.3.2</td>
<td>Zero-point energy</td>
<td>294</td>
</tr>
<tr>
<td>10.3.3</td>
<td>Vibrational eigenfunctions</td>
<td>294</td>
</tr>
<tr>
<td>10.4</td>
<td>Rotation of a diatomic molecule</td>
<td>294</td>
</tr>
<tr>
<td>10.4.1</td>
<td>Eigenfunctions of the rigid rotator</td>
<td>297</td>
</tr>
<tr>
<td>10.5</td>
<td>Selection rules for vibrational and rotational transitions</td>
<td>297</td>
</tr>
<tr>
<td>10.5.1</td>
<td>A semi-classical view of the selection rules</td>
<td>301</td>
</tr>
<tr>
<td>10.5.2</td>
<td>Infrared intensities</td>
<td>301</td>
</tr>
<tr>
<td>10.6</td>
<td>Real diatomic molecules</td>
<td>302</td>
</tr>
<tr>
<td>10.7</td>
<td>Polyatomic molecules</td>
<td>303</td>
</tr>
<tr>
<td>10.7.1</td>
<td>Normal co-ordinates, normal vibrations, vibrational eigenfunctions and eigenvalues</td>
<td>303</td>
</tr>
<tr>
<td>10.7.2</td>
<td>Vibrations of real polyatomic molecules</td>
<td>305</td>
</tr>
<tr>
<td>10.7.3</td>
<td>Characteristic group frequencies</td>
<td>308</td>
</tr>
<tr>
<td>10.7.4</td>
<td>Large molecules</td>
<td>308</td>
</tr>
<tr>
<td>10.8</td>
<td>Anharmonicity</td>
<td>309</td>
</tr>
<tr>
<td>10.8.1</td>
<td>Fermi resonance</td>
<td>309</td>
</tr>
<tr>
<td>10.8.2</td>
<td>Vibrational angular momentum and the Coriolis interaction</td>
<td>311</td>
</tr>
<tr>
<td>10.9</td>
<td>The \textit{ab-initio} calculation of IR spectra</td>
<td>316</td>
</tr>
</tbody>
</table>
### Chapter 11  Electronic Spectroscopy

11.0 Introduction ................................................. 327
11.1 Atomic and molecular orbitals .......................... 328
11.2 The spectra of covalent molecules ..................... 329
    11.2.1 $\pi \rightarrow \pi^*$ transitions ..................... 329
    11.2.2 $n \rightarrow \pi^*$ transitions ..................... 330
    11.2.3 Transition-metal complexes ..................... 330
11.3 Charge transfer (CT) spectra .......................... 330
11.4 Many-electron wave functions .......................... 332
11.5 The $1s^12s^1$ configuration of the helium atom; singlet and triplet states 333
    11.5.1 The energies of the $1s \rightarrow 2s$ excited states of the helium atom 335
    11.5.2 The one-electron energies; operator
        \[-\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - 2/r_1 - 2/r_2\] 335
    11.5.3 The two-electron, i.e. electron-repulsion, energy; operator $1/r_{12}$ 336
    11.5.4 The total energies of singlet and triplet state 338
    11.5.5 Electron repulsion in the triplet and singlet states of the excited
        helium atom: a diagrammatic illustration ............. 339
    11.5.6 Summary of Section 11.5 .......................... 341
11.6 The $\pi$-electron spectrum of benzene ................ 341
11.7 Selection rules ............................................. 344
    11.7.1 Electron spin (multiplicity) and transition probability 344
    11.7.2 Spatial aspects of transition probability for an allowed electronic
        transition ........................................... 346
    11.7.3 The vibrational factor in the transition probability 347
11.8 Slater determinants (Appendix 6) ...................... 348
11.9 Bibliography and further reading ........................ 348
Problems for Chapter 11 ............................... 348

### Chapter 12  Some Special Topics

12.0 Introduction ................................................ 352
12.1 The Hückel molecular orbital (HMO) theory ............. 352
    12.1.1 The basis of Hückel’s approach ................. 352
    12.1.2 The method ........................................ 353
    12.1.3 Hückel’s assumptions ............................ 354
    12.1.4 Determination of HMO energies and AO coefficients 354
    12.1.5 Applications of HMO energies .................. 357
    12.1.6 Applications of HMO coefficients ............... 361
    12.1.7 Some final comments on the Hückel theory .... 362
12.2 Magnetism in chemistry .................................. 363
    12.2.1 Magnetic susceptibility: diamagnetism and paramagnetism 364
## Contents

12.2.2 Magnetic susceptibility: ferromagnetism and antiferromagnetism 365  
12.2.3 Magnetic fields and dipoles: some definitions 365  
12.2.4 The magnetic effect of electronic orbital motion 366  
12.2.5 The consequences of chemical bonding 368  
12.2.6 The magnetic effect of electron spin 369  
12.2.7 Magnetism in practice 370  
12.2.8 Systems of interacting molecular magnets 374  
12.2.9 A note of warning 376  
12.2.10 An application 377  

12.3 The band theory of solids 378  
12.3.1 The tight binding approximation 378  
12.3.2 The electron–gas (free-electron) approximation 381  
12.3.3 Molecular and ionic solids 386  
12.3.4 Applications 387  
12.3.5 Metals, insulators and semiconductors 387  
12.3.6 Optical properties of solids 390  
12.3.7 Mechanical properties of solids 390  

12.4 Bibliography and further reading 390  
Problems for Chapter 12 397  

### Appendices

1 Fundamental Constants and Atomic Units 401  
2 The Variation Method and the Secular Equations 403  
3 Energies and Wave Functions by Matrix Diagonalisation 411  
4 Perturbation Theory 417  
5 The Spherical Harmonics and Hydrogen Atom Wave Functions 425  
6 Slater Determinants 429  
7 Spherical Polar Co-ordinates 431  
8 Numbers: Real, Imaginary and Complex 433  
9 Dipole and Transition Dipole Moments 435  
10 Wave Functions for the $^3F$ States of $d^2$ using Shift Operators 439  

### Index

443
Preface

In his prologue to ‘The Go-Between’ L.P. Hartley wrote: ‘The past is a foreign country: they do things differently there.’ He might have been describing quantum mechanics, which goes some way to explaining why it is normally only the denizens of that strange land, the theoreticians, who dare to enter into print about it. So what is a self-confessed experimentalist doing there?

Of the many factors that have influenced the development of chemistry in the second half of the 20th century, none has been more important than the inexorable diffusion across the traditional subject boundaries of concepts, which have their origins in theoretical physics. Students of chemistry and research scientists alike, not only in chemistry, are under continual pressure to assimilate and apply these ideas; quantum mechanics forms a central part of many of them. But the learning is hard, and although there are many excellent books they tend to be written by authors who are by nature theoreticians and whose approach to the subject differs from that of the experimentalist in many ways. I know, because I have been in this position all my working life.

My original motivation, which has not changed with the years, was to interpret myself, in as exact a way as I was able, the experimental observations that I as a spectroscopist was making. In the course of my studies I spent a lot of time with most of the classic texts on the subject which are directed at chemists and some intended for physicists. Those in the English language that is. However, as excellent as they mostly are, two aspects of them often failed to satisfy me. Firstly, their authors are very good mathematicians and do not always make allowances for the lesser experience and ability in those realms of people like me. This also has the unfortunate side effect of encouraging students at all levels to believe that their difficulties are attributable to a lack of mathematical expertise when they are, in fact, more commonly due to a failure to grasp some essential quantum-mechanical concept. In my experience, once the concept has been grasped, the mathematical expression of it is much easier to understand. Secondly, expositions of quantum mechanics frequently lack examples of chemical applications. I am of the view that a real example, even when it is much simplified and gives a result which does not agree well with experiment, is always better than no example at all. The texts which do contain examples are usually those directed at a particular branch of experimental measurement, a particular branch of spectroscopy for example, and they, naturally, cannot concern themselves with a broader view of the quantum mechanics which they apply. In this book I have tried to bring the basic quantum-mechanical theory closer to real chemical examples and to make the inevitable mathematics involved subordinate to the understanding of the principles.

I owe a great deal to many friends with whom I have worked. My interest in the interpretation of physical–chemical measurements was first aroused by Stephen Mason and continued by Edgar Heilbronner. When I arrived at the University of East Anglia
I had the great good fortune of entering into a period of collaborative research with Andrew Thomson who was as determined as I to learn some quantum mechanics. Together with some excellent post-doctoral fellows and graduate students, we spent many a lunch hour chewing literally on our packed lunches and figuratively on the theory of groups, ligand fields, angular momentum, irreducible tensors etc. This was for me a learning experience like no other and I am in debt to all who took part in the struggle; especially to Andrew.

Then, as this book began to grow, I was most grateful to Norman Sheppard when he expressed an interest in reading several of the early chapters and commenting on them with his usual, meticulous care. I have also benefited from discussions of particular problems with many other colleagues here at UEA. Positive and encouraging suggestions made by reviewers of sample chapters were also much appreciated and I have tried to take account of them.

In spite of the help I have received, it is too much to hope that no errors and/or misconceptions remain and I would like to expand a little on that subject. No error in a book from which a reader is trying to learn something can be trivial; even typographical errors can seriously mislead a student who is insecure in his/her knowledge of the subject. Readers will surely detect such errors and I would be most grateful if they would inform me of them. But misconceptions are an altogether more serious problem and in this connection I make a special appeal. In attempting to make quantum mechanics more approachable I have not hesitated to simplify and to draw on classical analogies wherever possible. In so doing I fear that I may have ventured out on a number of limbs too weak to support the weight which I have placed upon them. I hope that readers who detect this type of problem or who feel uneasy about statements which I have made will be good enough to point their concerns out to me.

A final word of thanks must go to four people. To my parents who, though they themselves had only elementary educations, did everything they could to further mine. And to my wife, Charlotte, and daughter, Rebecca, who have given me so much support and encouragement in my scientific endeavours. I trust that they will feel that this book was a worthwhile enterprise.

I also wish to thank Ivan Rodwell for provision of the three cartoons in this book.

Roger Grinter

http://www.grinter.org/quantum.html/
CHAPTER 1
The Role of Theory in the Physical Sciences

1.0 INTRODUCTION

In this chapter we shall consider the role of theory in science and enquire what is meant when we speak of a ‘law’ in the physical sciences. We shall ask: what are these laws, how do they arise and what is their value or purpose within science? There are two reasons for approaching the subject of the quantum in chemistry in this way. Firstly, these are questions of interest in their own right to which, in my view, insufficient attention is paid in the teaching of science. This can result in a degree of confusion, especially in a subject as inherently complex as quantum theory, where newcomers to the subject are apt to think that if only they knew more mathematics they could derive results which, in fact, cannot be and never were derived. This leads to an undesirable focus of attention upon the mathematical rather than the conceptual aspects of the problem. Thus, the second reason for discussing scientific laws is an attempt to place the laws of quantum theory in a perspective in which their origin, value and meaning can be better appreciated by beginners in the field.

1.1 WHAT IS THE ROLE OF THEORY IN SCIENCE?

It is a matter of historical fact that man has been observing the natural world, and recording his observations, since ancient times. We may safely conclude that the verbal communication of observation is even older, as the times and routes of migrating animals, birds
and fish are of crucial importance to people who live by hunting, while a knowledge of the seasons, of rainfall etc. is essential to food gatherers.\(^1\) The importance of these and other natural phenomena made those whose knowledge of them was most extensive the leaders of their communities and exceptional status was accorded to those who had, or were believed to have, the ability to predict such events.

Historically, prediction has been attempted either through an appeal to the supernatural or by means of a reasoned extrapolation of facts already known. These two approaches to the same problem are not as different as they might appear. If an observed fact, the annual flooding of a river for example, is believed to be under the direct and immediate control of the gods, then it is quite rational to consult those gods about such events. Nor does the involvement of the supernatural necessarily conflict with the making and recording of observations. It has been suggested that a preoccupation with astrology may well account for the fact that the Mesopotamians of the first millennium BC excelled in astronomy.\(^2\) Thus, the ancient fascination with the prediction of the future led not only to the use of rite and ritual but also to the recording and ordering of observations, a tendency which also received support from the widespread belief that there must be a system or order in the universe. The challenge of finding this system, and of demonstrating that one has found it by predicting the results of observations yet to be made, is the driving force of science and necessitates not only the collection of data but also the arrangement of that data within some conceptual framework that makes it easier to remember, understand and use.

We can distinguish two broad categories of such conceptual frameworks, or models. The first comprises models of an essentially descriptive nature in which the phenomenon in question is likened to objects of our everyday experience. An example of this type of model would be the description of the fundamental constituents of matter given by Lucretius, a Roman of the first century BC. In his view, all substances were composed of indestructible atoms and . . . "Things that seem to us to be hard and stiff must be composed of deeply indented and hooked atoms held firmly by their intertangling branches. . . . Liquids, on the other hand, must owe their fluid consistency to component atoms that are hard and round, for poppy seed can be poured as easily as if it were water . . . ."\(^3\) The molecular models used by modern chemists fall into this category; atoms are represented by coloured spheres and bonds by metal rods.

The second category of model is the mathematical model in which natural phenomena are represented by a set of symbols, the meanings of which have been defined, and which obey some particular rules of mathematical manipulation. A differential equation, for example, may be used to model a chemical reaction by providing a description of the rates of change with time of the concentrations of the reagents involved in the reaction. It is this kind of model to which we refer when we speak of the theoretical structure of the natural sciences. It is the type of model which is most useful to us when we are comparing numerical experimental data with theoretical predictions, i.e. in quantitative work.

A theoretical structure is essential to all the natural sciences. It provides the framework into which the pieces of the jigsaw of experimental data are fitted, thus revealing their inter-relationships and exposing gaps in our knowledge which need to be filled with the results of new experiments. In filling these gaps theory plays a leading role; it not only shows where new measurements are required but also tells the experimentalist what to expect when the experiments in question are performed. This is very important since,
clearly, the apparatus must be designed so that it is capable of measuring the phenomena to be studied and the quantities used must be appropriate to the equipment.

For example, suppose we wish to determine the amount of silver in the waste solution from a photographic processing laboratory by precipitating insoluble silver chloride with hydrochloric acid and weighing it. Our theory is embodied in the chemical equation:

$$\text{AgX (in solution)} + \text{HCl} \rightarrow \text{AgCl (precipitated)} + \text{HX}$$

The formula AgCl in this equation provides the information whereby the amount of silver in the precipitated silver chloride can be determined; provided, of course, that we know the relative atomic masses of silver and chlorine. The whole equation allows us to calculate how much silver chloride will be formed for a given amount of silver in the aqueous mixture. This information is required not only to determine the amount of silver, but also to plan the experiment in such a way that the precipitate to be weighed is of a mass appropriate for the chemical balance with which we propose to weigh it. To do this we may need to make a preliminary estimate of the amount of silver in the waste.

When, using a more elaborate example, we say that the length of the O–H bond in the water molecule is $95.7 \times 10^{-12}$ m and the HOH bond angle $104.5^\circ$, then these figures have been obtained using a theory, quantum mechanics in fact, which relates the measured absorption by water vapour of electromagnetic radiation in the microwave region (wavelengths of the order of 1–2 cm) to the masses of the nuclei and the molecular geometry. Theory is not simply a substitute for experiment, it is a vital adjunct to it.

But theory is always a suggestion or hypothesis, the correctness, or otherwise, of which can only be tested against experimental fact. Therefore, theory must always be subordinate to experiment. If, after thorough checking for errors, the results of an experiment are found to differ from those predicted by theoretical calculations, then the theory must be amended, or perhaps even discarded. Thus, although the theoretical framework of science is an essential aspect which guides our progress towards a deeper understanding, we must always recognise that a current theory may one day prove to be inadequate and require replacement. These points can be illustrated by means of the gas laws.

1.2 THE GAS LAWS OF BOYLE AND GAY-LUSSAC

In 1662 Robert Boyle (1627–1691) published the results of a series of experiments on the compression of air in the closed, short arm of a J-shaped tube. Boyle observed that as the pressure, $P$, measured by the difference of height of the columns of mercury in the two arms of the tube, increased, the volume, $V$, of air in the closed end of the tube decreased. Further, he noted that at constant temperature the volume is inversely proportional to the pressure, a quantitative result which could be expressed in the simple equation:

$$P \propto \frac{1}{V} \text{ or } PV = \text{constant} \quad (1.2.1)$$

The words in italics and Equation (1.2.1) are both expressions of what we now know as Boyle’s law, and in answer to two of the questions posed above we may say that Boyle’s law arose from a series of experiments and that it expresses the results of those experiments in a convenient and precise mathematical form.

The dependence of the volume of a gas upon temperature, $t$, at constant pressure was studied by four French scientists, Guillaume Amontons (1663–1705), Jacques Charles
(1746–1823), Joseph Gay-Lussac (1778–1850) and Henri Regnault (1810–1878). The
result of their labours is known as the law of Gay-Lussac, which was published in 1847 by
Regnault. He refined the earlier experimental methods and expressed the law in the form:

\[ V = V_0 (1 + t/273) \]  \hspace{1cm} (1.2.2)

Where \( V_0 \) is the volume of the gas at 0°C. Here again we have a law which has been
discovered by experimental measurements and, if we consider it carefully, we find that it
says that, at constant pressure, the volume of a gas increases by 1/273 of its volume at 0°C
for every degree rise in temperature. Clearly, Equations (1.2.1) and (1.2.2) are of great
practical value. They can, for example, be used to calculate the volumes and pressures of
gases at high temperatures. Such calculations are essential in the design of industrial plant
for chemical processes, many of which take place at very high temperatures and pressures.

1.3 AN ABSOLUTE ZERO OF TEMPERATURE

But Equation (1.2.2) carries a far more fundamental message, as Amontons had realised.
As we decrease the temperature of the gas below 0°C, i.e. when \( t \) becomes negative, the
volume of the gas decreases. But this process must have a limit, since there is no such
thing as a negative volume, and it is clear from Equation (1.2.2) that the limit of zero
volume is reached at \( t = -273 \) °C. Therefore, \(-273 \) °C must be the lowest temperature
which can be achieved. We are forced to a remarkable conclusion; although we can go
up in temperature indefinitely, there is a clear lower limit. This surprising result has been
substantiated experimentally and a more exact figure for the absolute zero of temperature
is \(-273.15 \) °C, which is the origin of the scale of absolute temperature where temperature,
\( T \), is measured in degrees Kelvin or K:

\[ T(K) = t(°C) + 273.15 \]  \hspace{1cm} (1.3.1)

It is interesting to note here the importance of the accuracy of experimental data in
formulating scientific laws. The mere observation that the volume of a fixed quantity of

![Figure 1.1](image-url) Exponential and linear temperature-volume relationships for a gas
gas decreased when the temperature was lowered might not have led to the concept of an absolute zero of temperature, much less to a value for it. Changes in physical quantities are frequently described by an exponential function and in Figure 1.1 it is shown that the equation:

\[ V = V_0 \exp(t/273) \]  

(1.3.2)
gives a temperature–volume relationship which is very similar to that given by Equation (1.2.2) in the region of temperature readily accessible to early researchers, i.e. −20 to +100 °C. But according to Equation (1.3.2), the volume of the gas never reaches zero, no matter how low the temperature. So it was vitally important that the accuracy of Regnault’s experimental measurements showed clearly that the relationship between the temperature and the volume of a gas was a linear rather than an exponential one.

1.4 THE GAS EQUATION OF VAN DER WAALS

Attempts to study Gay-Lussac’s law down to very low temperatures failed because the gases all liquefied long before the absolute zero was reached. And, indeed, many gases were found to show marked deviations from the pressure–volume–temperature (PVT) behaviour described by Boyle and Gay-Lussac for what became known as ideal gases which obeyed the combined equation:

\[ PV = nRT \]  

(1.4.1)
where \( R \) is the ideal gas constant which has a value of 8.31 J K\(^{-1}\) mol\(^{-1}\) and \( n \) is the number of moles of gas in the sample (1 mole of gas contains 6.022 \times 10^{23} \) molecules. These deviations of the PVT behaviour of real gases from the ideal could be represented by more complex gas laws such as that proposed by Johannes Diderik Van der Waals (1837–1923) in 1873:

\[ (P + a/V^2)(V - b) = nRT \]  

(1.4.2)
in which \( a \) and \( b \) respectively are parameters that allow for the attraction between the molecules and for the finite volumes of the molecules themselves. They have different values for different gases which are found by comparing the experimentally determined PVT behaviour of the gas with the Equation (1.4.2).

But to describe Van der Waals’ equation in detail would deviate too far from the central theme of this book and we therefore turn to a summary of the answers to the questions about physical laws posed in Section 1.0.

1.5 PHYSICAL LAWS

A physical law expresses, either in words or in algebraic form, the result which is to be expected of a particular experiment. Thus, Equation (1.2.2) tells us what volume of gas we would have at any temperature, \( t \), if its volume at 0 °C is \( V_0 \). From Equation (1.2.1) we can calculate either pressure or volume, though we must first perform an experiment to determine the value of the constant for the particular gas. If it is an ideal gas then the constant is \( nRT \), where \( n \) is the number of moles of gas in the sample (Equation (1.4.1)).
Laws arise, are discovered or deduced as a result of experimental observations. They are not derived by pure mathematical reasoning though they may be, and indeed very frequently are, expressed in an algebraic form. It follows from this that since laws are found as a result of experimentation they must also stand or fall by the results of any other experiments to which they relate. Thus the ideal gas law (Equation (1.4.1)) failed the test of application to all gases, especially in the region of low temperatures and/or high pressures. The law is therefore of limited applicability. But it is not useless and there are many circumstances in which it can provide valuable results.

A group of one or more laws normally underlies a theoretical model of some aspect of the real world as it is seen by science. Thus, the three laws of thermodynamics are the foundation stones, discovered by experiment, which allow us to describe quantitatively the inter-conversion of the various forms of energy; of heat into mechanical work for example. Together they form a mathematical model of all such processes. Newton’s three laws perform the same function for mechanics, the study of motion; in the next chapter we shall examine them in more detail.

The value of laws to science and technology applies at various levels. At the most simple, but highly significant in applied science, there is the practical use of a law to predict a quantity which cannot be readily measured; the gas pressure in a novel chemical plant which is still at the planning stage, for example. A law also establishes the framework into which experimental results may be fitted as they become available. This not only provides the means of interpreting the results but also alerts the experimentalist when a new result cannot be reconciled with the current structure of the theory. This may mean that an experimental error has been made or that the law is flawed. At a deeper level, laws reveal new concepts which were not suspected at the time when the measurements which gave rise to the law were made. We may safely assume that the concept of an absolute zero of temperature was not the idea which stimulated the first experiments of Amontons; but it arose directly from them. Here lies the great importance of laws for the development of the natural sciences. As the full significance of the quantities related in a law is appreciated, scientists are led to a deeper understanding of their subject and to the formulation of new experiments to test the law at the more fundamental level. If the law fails, such a test it must be regarded as flawed and of limited use, but not necessarily totally useless. The important point is that experiment is the only test of the validity of a law. Laws summarise the results of a wealth of experimental data and present them in a condensed form suitable for application or for further study. But they are always subordinate to experiment.

1.6 LAWS, POSTULATES, HYPOTHESES, ETC.

The waters of the present discussion are sometimes muddied by the variety of terms used to describe the same thing. We speak, for example, of the gas laws, Planck’s quantum hypothesis, the Pauli principle and the postulates of quantum mechanics. Each term highlighted in italics has essentially the same meaning; it is a statement, which we have here called a law, or a set of such statements, that summarises the results of experimental measurements. The different words express different aspects of the meaning of that statement. The terms law and principle emphasise the power and immutability; postulate and hypothesis the fact that this is a suggestion or a proposal which may later require
modification. But in this book we shall regard all such expressions, and some others, as meaning laws.

1.7 THEORY AT THE END OF THE 19TH CENTURY

As the 19th century drew to a close the theoretical basis of the physical sciences appeared to be very mature and powerful. In particular, the three great structures of Maxwell’s equations, which describe the behaviour of electromagnetic radiation, thermodynamics and mechanics, were remarkably successful in interpreting the experimental facts then known. Three examples show the range and power of these laws.

The laws of mechanics had been formulated by Isaac Newton (1643–1727) to model the motions of the planets and described these motions with remarkable accuracy. During the 1860s James Clerk Maxwell (1831–1879) and Ludwig Edward Boltzmann (1844–1906) used Newtonian mechanics to describe the motion of molecules in a gas, developing what we now call the kinetic theory of gases. The theory is in excellent agreement with the extensive experimental data encapsulated in the gas laws of Boyle and Gay-Lussac. The many deviations from the experimentally observed behaviour of real gases are due to the failure of other assumptions in the theory; that there is no attractive force between the molecules for example. Newtonian mechanics was thus shown to be applicable to bodies ranging in mass between $10^{-25}$ and $10^{+25}$ kg.

In the area of thermodynamics, the frequency of the chirping of the tree cricket, Oecanthus, has been found to depend upon the absolute temperature in strict conformity with the equation first put forward by Svante August Arrhenius (1859–1927).\(^4\) The logarithm of the frequency of chirping is inversely proportional to the absolute temperature, showing that the tree cricket’s chirping is quite involuntary and is controlled by its body chemistry which, in turn, is subject to the laws of thermodynamics. The same is true of the autonomous functions of the higher mammals; the human heart beat for example, though the temperature range available to the experimentalist is rather small in this case.

Our final example concerns electricity, magnetism and light. Michael Faraday (1791–1867) had shown that an electric current flowing in a coil produces a magnet and that when polarised light passes through a glass plate surrounded by the magnetic coil the plane of polarisation of the light is rotated. Thus, electricity, magnetism and light are related. An electric current can be measured by determining the magnetism it produces; the units of this measurement are called electromagnetic units, emu. An electric current can also be measured in terms of the flow of charge; the units of this type of measurement are electrostatic units, esu. In 1857, Gustav Kirchoff (1824–1887) showed experimentally that the ratio of the emu to the esu was equal to the velocity of light. These relationships between electricity, magnetism and light and between the emu and the esu were brilliantly and quantitatively interpreted by Maxwell with his mathematical model of electromagnetic radiation published in 1873. Maxwell’s model, which is always referred to as Maxwell’s equations, though they might equally well be called Maxwell’s laws, showed that light and all wavelengths of electromagnetic radiation could be described in terms of a magnetic and an electric field that are orientated at right-angles to each other and oscillate with the frequency of the radiation. This led to the prediction that an oscillating electric spark would generate electromagnetic radiation, a prediction which was beautifully confirmed by Heinrich Hertz (1857–1894) in a series of experiments reported in 1886–1888. We shall
explore Maxwell’s description of electromagnetic radiation and the properties of polarised light further in Chapter 8.

With successes like these to its credit it seems scarcely surprising that some physicists apparently thought that there was little more to do in the field of theory other than to dot some i’s and cross a few t’s. Nevertheless, there were a small number of experiments the results of which defied interpretation in terms of the theories, i.e. laws, then available. It was the search for solutions to these problems which led to the revolutionary ideas of Max Planck (1858–1947) and Albert Einstein (1879–1955), and to quantum mechanics. In the next chapter we shall follow the history of mechanics to illustrate further the role which theory plays in science and to see how, early in the 20th century, some of the foundations of the structure of theoretical physics were found to be by no means as secure as they had once appeared.

1.8 BIBLIOGRAPHY AND FURTHER READING

Chapter 2
From Classical to Quantum Mechanics

2.0 Introduction ................................................................. 9
2.1 The motion of the planets: Tycho Brahe and Kepler ................ 10
2.2 Newton, Lagrange and Hamilton ..................................... 11
2.3 The power of classical mechanics .................................... 12
2.4 The failure of classical physics ........................................ 12
2.5 The black-body radiator and Planck’s quantum hypothesis ...... 13
  2.5.1 Planck’s solution to the black-body radiation problem ...... 15
  2.5.2 A qualitative interpretation of the form of the black-body emission curve in the light of Planck’s hypothesis .......... 16
  2.5.3 Quantisation in classical mechanics ............................ 18
2.6 The photoelectric effect .................................................. 20
  2.6.1 Einstein’s theory of the photoelectric effect confirmed experimentally .................................................. 22
2.7 The emission spectra of atoms ......................................... 23
  2.7.1 Bohr’s theory of the structure of the hydrogen atom ....... 24
  2.7.2 Comparison of Bohr’s model with experiment ............... 26
  2.7.3 Further development of Bohr’s theory .......................... 26
2.8 de Broglie’s proposal ..................................................... 26
2.9 The Schrödinger equation .............................................. 28
  2.9.1 Eigenfunctions and eigenvalues ................................. 29
2.10 Bibliography and further reading ................................... 30
Problems for Chapter 2 ....................................................... 34

2.0 INTRODUCTION

In this chapter we shall first follow the historical course of the development of Newtonian or classical mechanics. We do this not only because classical mechanics is a limiting case of quantum mechanics, but also because the story of how classical mechanics developed is an excellent illustration of how a set of laws and the theoretical model which they sustain develops as a result of the interplay between experiment and theory. Having arrived with classical mechanics at the end of the 19th century, we shall investigate some particularly important experimental results which the laws of thermodynamics, mechanics and
electromagnetic radiation that were available at that time were quite unable to interpret, despite their outstanding successes in many other applications. Finally, we shall see how Erwin Schrödinger and Werner Heisenberg cut the Gordian knot with the introduction of a new mechanics—quantum mechanics.

2.1 THE MOTION OF THE PLANETS: TYCHO BRAHE AND KEPLER

Before there can be any theory there must be experimental observations to be interpreted by the theory. (This proposition is not self-evident; the ancient Greeks developed theoretical concepts almost entirely without appeal to experimental evidence.) The collection of the experimental data which formed the basis for the first theory of mechanics may be traced back to the astronomical observations made, without a telescope, by the Danish nobleman Tycho Brahe (1546–1601), whose measurements were the most important and accurate of early modern times. Tycho, who is usually known by this latinised version of his Danish name, Tyge, was renowned for his fiery temperament and for most of his life he wore an artificial silver nose to replace the original appendage which had been sliced off in a duel at the age of 19. It is interesting to note that he thought it was not possible to make observations without the guidance of a theoretical system of the world, and he adopted a modified earth-centred system, now of course, known to be false. But the idea that measurements should be made in the light of a theory which, it is believed, can interpret them and fit them into the framework of our existing knowledge, is an important part of the modern scientific method; a point discussed in Chapter 1.

In 1599, Tycho Brahe moved from Copenhagen to Prague, where he was joined by German mathematical astronomer Johannes Kepler (1571–1630) in 1600. When he died in 1601, Tycho bequeathed his collection of data to Kepler who found, after many years of exacting work, that the observations of the planets could be interpreted in terms of the following three laws.

Kepler’s Laws of Planetary Motion

1. The orbits of the planets are ellipses with the sun at one focus.
2. The line drawn from the sun to the planet sweeps out equal areas in equal times.
3. The square of the time required for a planet to complete its orbit is proportional to the cube of its mean distance from the sun, i.e. the length of the semi-major axis of the ellipse.

These laws are illustrated graphically in Figure 2.1.

In formulating his laws, Kepler brought the science of mechanics from the data-collection phase to the next important stage through which any developed scientific theory must pass. This is the stage at which the known experimental data are unified, in that it is shown that the data can be interpreted in terms of a small number of fundamental concepts: the laws. Clearly, if the laws are soundly based they have predictive power, i.e. the results of experiments or observations not yet made can be foretold. This is the only convincing test of the laws. A set of laws constitutes a theory, and when a theory fails systematically to predict correctly the result of experiments, then that theory must be amended or, in extreme cases, abandoned.
p–q is the major and r–s the minor axis of the ellipse which the path of the planet traces around the sun. The orbits of the planets of our solar system are much more like circles than that shown here which more closely resembles that of an asteroid, e.g. Icarus.

If the planet takes equal times to move from a to b and from c to d then the areas of the two sectors, a–sun–b and c–sun–d, of the ellipse are equal.

Figure 2.1 Kepler’s laws of planetary motion

The predictive power of Kepler’s laws is illustrated by his tables of astronomical data, published in 1627, which he calculated by means of his three laws and named the Rudolphine Tables in honour of his patron, the emperor Rudolph II. The planets Mercury and Venus, which have orbits of radius less than that of Earth, sometimes pass between the earth and the sun. At such times the planet in question, viewed from the earth, can be seen to move across the face of the sun. This is known as a transit of the planet. With the aid of his tables, Kepler correctly predicted the transits of Mercury (7th November, 1631) and of Venus (4th December, 1639 and 6th June, 1671) across the sun’s disc. All these events actually took place as Kepler had said they would; but not before he died in 1630.

The next stage in this brief history of classical mechanics concerns a further phase through which scientific theories often pass; a phase in which a more fundamental, and hence more widely applicable, set of laws is sought. Kepler’s laws described the motions of the planets – but why did they move in that way? An answer to that question might reveal that the motions of other bodies were governed by similar laws.

2.2 NEWTON, LAGRANGE AND HAMILTON

Isaac Newton (1643–1727) was not the only man of his time to grapple with this problem. His answer to it, together with accounts of many of his other scientific and mathematical achievements, appeared in his Philosophiae Naturalis Principia Mathematica in 1687. The four laws upon which he based his analysis were clearly of a much more fundamental, and therefore more general, nature than Kepler’s.

Newton’s Laws of Motion

1. A particle moves with a constant (perhaps zero) velocity (and therefore in a straight line) unless it is acted upon by a force.
2. A particle acted upon by a force \( F \) will move with an acceleration \( a \) proportional to that force, the constant of proportionality being the inverse of its mass \( m \).

\[ a = \frac{F}{m} \quad (2.2.1) \]

3. When two particles act upon one another, the two forces acting on the particles are equal and opposite to one another and are directed along the line joining the two particles.

4. The gravitational force of attraction between two bodies is proportional to the product of their masses \( m_1 \) and \( m_2 \) and inversely proportional to the square of the distance \( r \) between them. The constant of proportionality is the gravitational constant \( G \).

\[ F = G \times \left( \frac{m_1 m_2}{r^2} \right) \quad (2.2.2) \]

The items or postulates 1 to 3 constitute the laws of what we now know as classical mechanics. During the following two centuries other formulations based on different postulates were developed, notably by Joseph-Louis Lagrange (1736–1813) and William Rowan Hamilton (1805–1865). However, these later formulations of classical mechanics were entirely consistent with Newton’s and with each other; any one version could be derived mathematically from any other. The Lagrangian and Hamiltonian formulations found acceptance because they were more elegant in certain applications and the theory as a whole scored many truly remarkable successes.

### 2.3 THE POWER OF CLASSICAL MECHANICS

In Section 1.7 attention was drawn to the way in which Maxwell and Boltzmann developed the kinetic theory of gases by applying Newton’s laws to the motion of the molecules of a gas, thereby obtaining a deeper understanding of the gas laws of Boyle, Charles and Gay-Lussac. The gas laws were to the study of gases what Kepler’s laws were to mechanics; the first attempt to unify a mass of experimental data in a mathematical formalism. The work of Newton, Maxwell and Boltzmann brought these two strands of theoretical physics together and classical mechanics was thus shown to be largely applicable to bodies ranging in mass from \( 10^{-25} \) to \( 10^{+25} \) kg. Other examples of the ability of theory to interpret very diverse experimental observations have been cited in Chapter 1. Theoretical physicists at the end of the 19th century were fully justified in feeling that their science, which we may term classical theoretical physics, was capable of meeting any challenge the experimentalist might throw down. And yet experimental measurements already on record, or soon to be made, would be shown to be fundamentally at variance with the laws of classical physics and would, in due course, trigger a complete revolution in the subject. What were those measurements?

### 2.4 THE FAILURE OF CLASSICAL PHYSICS

It goes without saying that so cogent and successful a structure as classical physics did not fall easily or rapidly. If the laws are thought of as the belt of the structure then the blows that brought it down fell below that belt, striking at fundamental assumptions
which were embodied in the laws but never explicitly stated. The fact that the structure needed to be replaced rather than simply repaired took many years to gain acceptance, and the replacement was scarcely viable until the late 1920s. The first 30 years of the 20th century was at one and the same time a period of turmoil and of intense excitement and creativity in the scientific world. It witnessed some of mankind’s most outstanding intellectual achievements.

There was one major blow which we shall not discuss here. It fell in 1905 when Albert Einstein (1879–1955) showed that, because of the finite velocity of light, to say that two events take place simultaneously only has meaning if the events occur at the same place, and the concepts of space and time cannot therefore be separated as they are in classical physics. Einstein demonstrated that the velocity of light was a limiting velocity and that, although Newtonian mechanics was quite adequate for bodies moving with velocities only a fraction of that of light, it was not applicable to bodies moving at velocities approaching that limit. Nevertheless, we would not think of using relativistic mechanics to calculate the orbit of a communications satellite for example. Newtonian mechanics is much easier to apply and, for such a system, gives answers which are in practice quite indistinguishable from the relativistic results. This illustrates a very important point; although we know that classical mechanics is of limited applicability, it is still extremely useful and very widely used.

From the point of view of the development of quantum mechanics, a more important event had taken place four years before Einstein proposed his theory of relativity. In 1901 Max Karl Ernst Ludwig Planck (1858–1947) proposed a similarly radical solution to a problem that had been plaguing theoreticians throughout the 1890s; the energy spectrum of the black-body radiator.

### 2.5 THE BLACK-BODY RADIATOR AND PLANCK’S QUANTUM HYPOTHESIS

Any body at a temperature above the absolute zero emits electromagnetic radiation over a range of wavelengths. The energy required to produce this radiation, which is known as thermal radiation, comes from the thermal agitation of the particles of which the body is composed and, if the temperature of the body is above that of its surroundings, then, as the radiation is emitted, the body cools down. When the body reaches the temperature of its surroundings equilibrium is established and the body absorbs and emits radiation at exactly the same rates. Both the emission and the absorption processes are of interest to us. In 1879 Josef Stefan (1835–1893) discovered experimentally that the total energy per second \( I_T \) emitted from the surface of a body over all frequencies is proportional to the fourth power of its absolute temperature \( T \):

\[
I_T \propto T^4
\]

In 1884 Boltzmann deduced the constant of proportionality from thermodynamic principles and wrote the equation in the form:

\[
I_T = \sigma eT^4
\]

(2.5.1)

where \( \sigma \) is the Stefan-Boltzmann constant \((\sigma = 5.67 \times 10^{-8} \text{ W m}^{-2} \text{K}^{-4})\) and \( e \) is a dimensionless constant called the emissivity, which lies between 0 and 1, depending upon the nature of the emitting surface.
The ability of a body to absorb electromagnetic radiation is defined by its absorptivity, $a$, which is the ratio of the total radiant energy falling upon its surface to the total energy absorbed by the surface. Gustav Kirchhoff showed by a powerful thermodynamic argument that $e$ was equal to $a$, and this equality has also been substantiated by experiment. Thus, good absorbers of radiation are also good emitters, and vice versa. A body which is both a perfect emitter and a perfect absorber, i.e. one for which $e = a = 1.0$ is called a black body and is of particular interest. The best experimental realisation of a black body surface is a small hole in a cavity furnace with blackened inner walls. Radiation passing in through the hole has effectively no chance of being reflected back through it, so $a = 1.0$ and therefore $e = 1.0$ also.

The reason for the great interest in the properties of the perfectly emitting and absorbing black body can be seen by setting $e = 1.0$ in Equation (2.5.1). The total energy emitted is found to be dependent on the Stefan-Boltzmann constant and the fourth power of the absolute temperature but not upon any aspect of the body itself. Clearly, black-body radiation is a very fundamental phenomenon which demands an interpretation. Accurate experimental data were provided in 1899 by Otto Richard Lummer (1860–1925) and Ernst Pringsheim (1859–1917). They used a device not unlike a spectrometer to measure the way in which the intensity of the emitted radiation, $I(\lambda)$, depended upon the wavelength of that radiation, $\lambda$, and found curves such as those shown in Figure 2.2. The ordinate of Figure 2.2 is not $I(\lambda)$ but $\rho(\lambda)$, the energy density inside the cavity, which is equal to $4I(\lambda)/c$ where $c$ is the velocity of light. More precisely, $\rho(\lambda)$ is the energy of the radiation in the wavelength interval $\lambda$ to $\lambda + d\lambda$ in 1 m$^3$ of the cavity. Note how the peak of the curve moves to shorter wavelengths as the temperature is increased. This phenomenon is observed when the filament of an electric fire goes from dull red to almost white as the fire heats up. For a particular temperature, the total energy emitted, $I_T$, is proportional to the area under the curve and one can see how rapidly this rises with temperature, as is required by the factor $T^4$ in Equation (2.5.1).

Even before Lummer and Pringsheim’s accurate data became available, the essential form of the relationship between energy and wavelength was known and had stimulated

![Figure 2.2 The emission spectra of a black-body radiator](image-url)