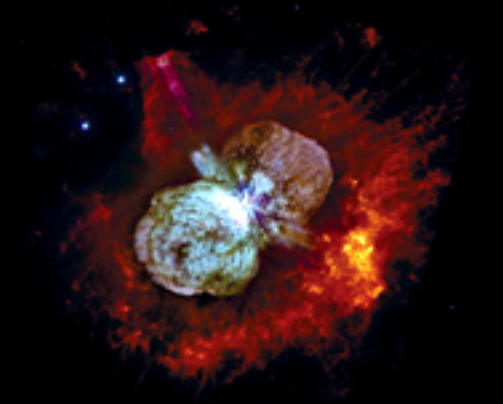




Atomic Astrophysics and Spectroscopy

Anil K. Pradhan and Sultana N. Nahar

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Atomic Astrophysics and Spectroscopy

Spectroscopy allows the precise study of astronomical objects and phenomena. Bridging the gap between physics and astronomy, this is the first integrated graduate-level textbook on atomic astrophysics. It covers the basics of atomic physics and astrophysics, including state-of-the-art research applications, methods and tools.

The content is evenly balanced between the physical foundations of spectroscopy and their applications to astronomical objects and cosmology. An undergraduate knowledge of physics is assumed, and relevant basic material is summarised at the beginning of each chapter.

The material is completely self-contained and contains sufficient background information for self-study. Advanced users will find it useful for spectroscopic studies. Websites hosted by the authors contain updates, corrections, exercises and solutions, and news items from physics and astronomy related to spectroscopy. Links to these can be found at www.cambridge.org/9780521825368.

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and

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Preface

This text is aimed at students and researchers in both astronomy and physics. Spectroscopy links the two disciplines; one as the point of application and the other as the basis. However, it is not only students but also advanced researchers engaged in astronomical observations and analysis who often find themselves rather at a loss to interpret the vast array of spectral information that routinely confronts them. It is not readily feasible to reach all the way back into the fundamentals of spectroscopy, while one is involved in detailed and painstaking analysis of an individual spectrum of a given astrophysical object. At the same time (and from the other end of the spectrum, so to speak) physics graduate students are not often exposed to basic astronomy and astrophysics at a level that they are quite capable of understanding, and, indeed, that they may contribute to if so enabled.

Therefore, we feel the need for a textbook that lays out steps that link the mature field of atomic physics, established and developed for well over a century, to the latest areas of research in astronomy. *The challenge is recurring and persistent: high-resolution observations made with great effort and cost require high-precision analytical tools, verified and validated theoretically and experimentally.*

Historically, the flow of information has been both ways: astrophysics played a leading role in the development of atomic physics, and as one of the first great applications of quantum physics. As such, it is with basic quantum mechanics that we begin the study of astrophysical spectroscopy. The atomic physics and the astrophysics content are intended to be complementary, and attempt to provide a working knowledge in the two areas, as necessary for spectral analysis and modelling. The emphasis is on the introductory theoretical basics, leading up to a practical framework for applications of atomic spectroscopy. While we limit ourselves to atomic physics, we have attempted to highlight and delineate its reach into the main areas of astronomy.

The link between basic-to-advanced atomic physics and spectral analysis is increasingly important in ever

more sophisticated astrophysical models. But the challenge of writing a book such as this one has been to find a balance between basic physics treatment that is not superficial, and state-of-the-art astrophysical applications that are not too technical. Though that defined and delimited the scope, it was still clear from the outset that the material should encompass a wide variety of topics. But what is essential and what is superfluous is, to some extent, a matter of subjective judgement. The level of depth and breadth of each topic is subject to these constraints. However, owing to the objective needs before us, we have tried to be as comprehensive as possible (limited by our own expertise, of course).

The text is evenly divided into atomic physics and astrophysics. The first seven chapters form the foundational elements of atomic processes and spectroscopy. The next seven chapters deal with astrophysical applications to specific objects and physical conditions. Each chapter follows the same plan. We begin with the essentials that all readers should be able to follow easily. However, towards the end of each chapter we outline some of the more advanced or specialized areas. The subject matter is broadly divided into ‘basic’ material in both areas, and ‘advanced’ material that incorporates state-of-the-art methods and results. The underlying atomic physics is intended as an introduction to more specialized areas, such as spectral diagnostics, astrophysical models, radiative transfer, plasma opacities, etc.

Emphasizing the unifying and connecting themes, the text is planned as follows. Following the Introduction, the next six chapters cover ‘basic’ collisional and radiative atomic structure and processes. The second part of the text, the other seven chapters, are the ‘applications’ of the physical framework developed in the first part. Chapters 8 and 9 describe the interaction of radiation with matter and spectral formation. The remainder of the text, Chapters 10–14, deals with descriptions of astronomical sources: stars, nebulae, active galactic nuclei and cosmology. A special chapter is devoted to a description of

the largest single application of atomic physics to astronomy: stellar opacities (Chapter 11). However, the content of these chapters is *not* designed to be exhaustive, but mainly to exemplify spectral formation in astrophysical environments. Each of Chapters 10–14 contains tables and sample spectra characteristic of the particular astrophysical source(s). The appendices provide some of the tools, and some of the atomic data, needed in spectral modelling. However, they are not comprehensive and readers are advised to consult the websites described below.

Supplementary to the present text are the authors' websites.¹ They will provide continual updates and revisions related to atomic data and developments in atomic astrophysics. Eventually, this facility is designed to be user-interactive, with features such as on-line calculation of spectral line intensities and ratios, model calculations of ionization fractions, etc., using up-to-date atomic data.

¹ www.astronomy.ohio-state.edu/~pradhan and
www.astronomy.ohio-state.edu/~nahar.

Acknowledgements

The material in this book is partially based on several courses that Anil Pradhan has taught over the years. First of all, it is from a course on Theoretical Spectroscopy taught to astronomy graduate students at the Ohio State University every alternate year for nearly 20 years. Some of the material is also derived from graduate courses taught on atomic structure at the University of Windsor, scattering theory at the University of Colorado, and advanced undergraduate courses on stellar astrophysics at Ohio State. In addition, teaching introductory astronomy courses to non-science majors at Ohio State has been a valuable exercise in learning that, in addition to the discovery of wondrous new objects, some of the most basic and common phenomena in the Universe remain poorly understood (and *that* is the fun and *raison d'être* for doing astronomy!).

But it is in the inspiration derived from our teachers and mentors wherein lies the foundation. The first acknowledgement – indeed a debt of gratitude – is due to Mike Seaton, advisor and mentor for over three decades. Mike was among the foremost pioneers who developed atomic astrophysics into the discipline it is today. Although he was not aware of this effort, and, regretably, would not see it, Mike's monumental contributions are self-evident throughout the text. Nearly a decade ago, Dimitri Mihalas first suggested to Anil Pradhan the need for a book such as this. Dimitri has since then encouraged and advised on several aspects of the presentation, so well exemplified in his classic *Stellar Atmospheres*. From the observational side, Don Osterbrock continually pointed out over many years the specific needs for astrophysical diagnostics that could be fulfilled by the state-of-the-art atomic physics he appreciated so well. We also regret

that Don is no more to see the fruit of his inspiration, howsoever imperfect this may be.

A number of our colleagues have read parts of the material and made numerous suggestions. We are especially grateful to our long-time collaborator, Werner Eissner, for revisions of the chapter on atomic structure. Special thanks are due to former student, postdoc, and now a valued colleague, Max Montenegro, for expertly and patiently (re-)drawing most of the figures in the book. Among the several colleagues who reviewed the material, Gerry Newsom and Bob Wing made particularly valuable comments on the chapters on stars, emission lines and nebulae. We also thank Dirk Grupe, Hong Lin Zhang, Prajaval Shastri, Bob Williams, Belinda Wilkes and David Branch, who read and suggested many corrections or improvements. But although all the material in the text has been reviewed by at least one of them, any errors, omissions and inaccuracies are entirely our responsibility. All we can say is that, fortunately, we have the electronic means to correct or revise any material, and would greatly appreciate readers pointing those things out to us. We shall endeavour to post all updates on the special website meant for this book (with due acknowledgement).

Finally, we would like to acknowledge the immense support and motivation derived from our families, to whom this work is dedicated. Anil Pradhan would like to thank his wife, Indira, and children, Alka and Vivek, his mother, Sarojini (who is no more), grandparents, Lakshman Swarup and Phoolmati Pradhan, and parents Mahesh Chandra and Kunj Bala Pradhan. Sultana Nahar is grateful for inspiration from parents, Abdul Razzaq and Shamsun Nahar, teachers and family, especially her son, Alburuj R. Rahman.

I Introduction

1.1 Atomic astrophysics and spectroscopy

Spectroscopy is the science of light–matter interaction. It is one of the most powerful scientific tools for studying nature. Spectroscopy is dependent on, and therefore reveals, the inherent as well as the extrinsic properties of matter. Confining ourselves to the present context, it forms the link that connects astronomy with fundamental physics at atomic and molecular levels. In the broadest sense, spectroscopy explains all that we see. It underlies vision itself, such as the distinction between colours. It enables the study of matter and light through the wavelengths of radiation (‘colours’) emitted or absorbed uniquely by each element. Atomic astrophysics is atomic physics and plasma physics applied to astronomy, and it underpins astrophysical spectroscopy. Historically, astrophysical spectroscopy is older than modern astrophysics itself. One may recall Newton’s experiments in the seventeenth century on the dispersion of sunlight by a prism into the natural rainbow colours as an identification of the visible band of radiation. More specifically, we may trace the beginning of astrophysical spectroscopy in the early nineteenth century to the discovery of dark lines in the solar spectrum by Wollaston in 1802 and Fraunhofer in 1815. The dark lines at discrete wavelengths arise from removal or absorption of energy by atoms or ions in the solar atmosphere. Fraunhofer observed hundreds of such features that we now associate with several constituent elements in the Sun, such as the *sodium D lines*.

Figure 1.1 shows the *Fraunhofer lines*. Fraunhofer himself did not associate the lines with specific elements; that had to await several other crucial developments, including laboratory experiments, and eventually quantum theory. He labelled the lines alphabetically, starting from A in the far red towards shorter wavelengths. It is instructive to revisit the proper identification of these historic

lines. Going from right to left in Fig. 1.1, the first two lines A (7594 Å) and B (6867 Å) do not originate in the Sun but are due to absorption by oxygen in the terrestrial atmosphere. The line C at 6563 Å is due to absorption by hydrogen (the same transition in *emission* is a bright red line). The three lines A, B and C lie towards the red end of the visible spectrum. In the middle region of the spectrum are the two orange lines D1 and D2 (5896, 5890 Å, respectively) that are the characteristic ‘doublet’ lines of sodium (sodium lamps have an orange hue, owing to emission in the very same transitions). Towards the blue end we have the strong line E at 5270 Å, due to absorption by neutral iron, and another line, F (4861 Å), due to hydrogen. The molecular G band of CH lies around 4300 Å. Farther into the blue, there are the H and K lines (3968, 3934 Å, respectively) from singly ionized calcium, which are among the strongest absorption lines in the solar spectrum. Although the letters have no physical meaning, this historic notation is carried through to the present day. Much of early astrophysics consisted of the identification of spectral lines, according to the presence of various atomic species in stars and nebulae.

The lightest and most abundant element in the Universe is hydrogen, chemical symbol H. The abundances and line intensities of other elements are expressed relative to H, which has the most common spectroscopic features in most astronomical sources. Observed line wavelengths led to an early grasp of specific spectra, but it needed the advent of quantum mechanics to understand the underlying structure. The pioneering exploration of the hydrogen spectrum and of alkali atoms by Rydberg was the first systematic attempt to analyze the pattern of spectral lines. We shall see later how useful simple variants of the empirical Rydberg formula can be in the analysis of astrophysical spectra.

Spectroscopy also predates quantum mechanics. In spite of the empirical work and analysis, a quantitative understanding of spectroscopy had to await the quantum

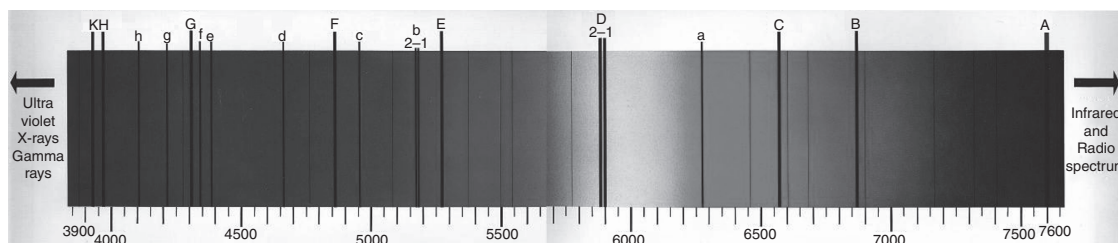


FIGURE 1.1 The Fraunhofer lines (Courtesy *Institute for Astronomy*, University of Hawaii, www.harmsy.freeuk.com).

theory of the atom. Schrödinger's success in finding the right equation that would reproduce the observed hydro-genic energy levels according to the Bohr model and the Rydberg formula was the crucial development. Mathematically, Schrödinger's equation is a rather straightforward second-order differential equation, well-known in mathematical analysis as Whittaker's equation [1]. It was the connection of its eigenvalues with the energy levels of the hydrogen atom that established basic quantum theory. In the next chapter, we shall retrace the derivation that leads to the quantization of apparently continuous variables such as energy. However, with the exception of the hydrogen atom, the main problem was (and to a significant extent still is!) that atomic physics gets complicated very fast as soon as one moves on to non-hydrogenic systems, starting with the very next element, helium. This is not unexpected, since only hydrogen (or the hydrogenic system) is a two-body problem amenable to an exact mathematical solution. All others are three-body or many-body problems that mainly have numerical solutions obtained on solving generalized forms of the Schrödinger's equation. With modern-day supercomputers, however, non-hydrogenic systems, particularly those of interest in astronomy, are being studied with increasing accuracy. A discussion of the methods and results is one of the main topics of this book.

Nearly all astronomy papers in the literature identify atomic transitions by wavelengths, and not by the spectral states involved in the transitions. The reason for neglecting basic spectroscopic information is because it is thought to be either too tedious or irrelevant to empirical analysis of spectra. Neither is quite true. But whereas the lines of hydrogen are well-known from undergraduate quantum mechanics, lines of more complicated species require more detailed knowledge. Strict rules, most notably the Pauli exclusion principle, govern the formation of atomic states. But their application is not straightforward, and the full algebraic scheme must be followed, in order to derive and understand which states are allowed by nature to exist, and which are not. Moreover, spectroscopic information for a given atom can

be immensely valuable in correlating with other similar atomic species.

While we shall explore atomic structure in detail in the next chapter, even a brief historical sketch of atomic astrophysics would be incomplete without the noteworthy connection to stellar spectroscopy. In a classic paper in 1925 [2], Russell and Saunders implemented the then new science of quantum mechanics, in one of its first major applications, to derive the algebraic rules for recoupling total spin and angular momenta S and L of all electrons in an atom. The so-called *Russell–Saunders coupling* or *LS coupling* scheme thereby laid the basis for spectral identification of the states of an atom – and hence the foundation of much of atomic physics itself. Hertzsprung and Russell then went on to develop an extremely useful phenomenological description of stellar spectra based on spectral type (defined by atomic lines) vs. temperature or colour. The so-called *Hertzsprung–Russell (HR) diagram* that plots luminosity versus spectral type or temperature is the starting point for the classification of all stars (Chapter 10).

In this introductory chapter, we lay out certain salient properties and features of astrophysical sources.

1.2 Chemical and physical properties of elements

There are similarities and distinctions between the *chemical* and the *physical* properties of elements in the periodic table (Appendix 1). Both are based on the electronic arrangements in shells in atoms, divided in *rows* with increasing atomic number Z . The electrons, with principal quantum number n and orbital angular momentum ℓ , are arranged in *configurations* according to shells (n) and subshells (nl), denoted as $1s, 2s, 2p, 3s, 3p, 3d \dots$ (the number of electrons in each subshell is designated as the exponent). The chemical properties of elements are well-known. Noble gases, such as helium, neon and argon, have low chemical reactivity owing to the tightly bound closed shell electronic structure: $1s^2$ (He, $Z = 2$) $1s^2 2s^2 2p^6$ (Ne, $Z = 10$) and $1s^2 2s^2 2p^6 3s^2 3p^6$ (argon, $Z = 18$). The

alkalis, lithium (Li, $Z = 3$), sodium (Na, $Z = 11$), potassium (K, $Z = 19$), etc., have relatively high chemical reactivity owing to the single valence electron ns outside a closed shell configuration, e.g., $1s^2 2s^1$ (Li) (see Chapter 2 for a detailed discussion). Chemical reactivity is responsible for molecular formation and processes. Sodium or potassium atoms combine easily with chlorine, a halogen with a vacancy in the $3p$ electronic orbit ($1s^2 2s^2 2p^6 3s^2 3p^5$), to form NaCl or KCl (common salts); the pairing is through an ionic bond, reflecting the fact that the Na atom ‘donates’ an electron, while the chlorine atom gains an electron to fill the ‘vacancy’ to close the outer shell. The chemical properties involving valence electrons and the reactivity of an element are determined by the *electron affinity*, the energy required to remove valence electrons. Atoms with more than one valence electron in an open shell form molecular bonds in a similar manner. The carbon atom has two valence electrons in the $2p$ shell, which can accommodate six electrons as a closed shell. The four vacancies can be filled by single electrons from four H atoms to form one of the most common molecular compounds in nature, CH_4 (methane), which, for instance, is probably the predominant constituent of ‘oceans’ on Saturn’s moon Titan. Carbon monoxide, CO, is one of the most abundant molecular species in astronomical sources. Its stability lies in the match between the two valence electrons in the carbon atom and the two vacancies in the oxygen atom, which has four electrons in the $2p$ shell. In general, the chemical properties of elements are concerned with valence electrons and shells of atoms.

On the other hand, by physical properties of elements, we refer largely to spectroscopic and atomic processes, such as energy level structure, radiative transitions, excitations, ionization and more. Of course, these are also based on the electronic structure of atoms and ions but in a different manner than those of chemical processes. To begin with, the physical and chemical properties are expected to be similar for elements along the *columns* of the periodic table, since the electronic structures are similar (discussed in detail in Chapter 2). For example, boron (B) and aluminium (Al) both have a single valence electron in the p shell, preceded by an inner two-electron filled s shell: $1s^2 2s^2 2p^1$ (B) and $1s^2 2s^2 2p^6 3s^2 3p^1$ (Al). Therefore, the energy-level structure and processes involving those levels are usually similar. Both boron and aluminium display two-level fine structure splitting of the ground state $np(^2P_{1/2}^o - ^2P_{3/2}^o)$. Transitions between these two levels generate a weak ‘forbidden’ spectroscopic line in both the elements. Likewise, the atoms of fluorine and

chlorine in the halogen column have energy-level structures and spectral features similar to B and Al, owing to the fact that a single-vacancy p shell has the same spectral composition as a single-valence p electron: $1s^2 2s^2 2p^5$ (F) and $1s^2 2s^2 2p^6 3s^2 3p^5$ (Cl); both atoms also have the same ground state as B and Al, $^2P^o$, and the same type of forbidden transition.

From the point of view of atomic and astrophysical spectroscopy one of the most important manifestations of physical properties is for ions along an *isoelectronic sequence*: ions of different elements and atomic number Z , but with the same number N of electrons. For example, the helium isoelectronic sequence consists of the ions of all elements of the periodic table stripped down to two electrons: $1s^2$ in the ground state (*He-like ions*). The columns of the periodic table already provide a guide to similarity of physical properties, for if similar electronic structure leads to similar properties, then the same electronic structure should do so also. For example, the singly charged carbon ion (expressed by C^+ or C II) has five electrons, isoelectronic with boron; similarly the nitrogen ion N III , the oxygen ion O IV and each ion of an element ($Z > 5$) with five electrons belongs to the boron sequence. However, there is a crucial physical difference with neutral elements along a column in the periodic table: not only is the atomic number Z different, but also the charge on each ion $+z = Z - N$ in the isoelectronic sequence is different. Therefore, the atomic physics, which depends basically on the electromagnetic potential in the atom or ion, is different for each ion. As Z increases, the attractive electron–nucleus Coulomb potential increases, resulting in higher-speed electrons. When the velocities are sufficiently high, relativistic effects become important. The energy-level splittings and processes dependent on relativistic and inter-electron interactions lead to significant differences in spectral formation for ions within the same isoelectronic sequence. We shall discuss a number of aspects of isoelectronic sequences in much more detail in later chapters.

Physical properties of elements also refer to interaction of radiation with matter on the atomic scale, which brings forth some physical processes not usually within the realm of chemistry, such as excitation and ionization of electrons.¹ Finally, physical phenomena are dependent

¹ To some extent the distinction between physical and chemical processes, as we have drawn here, is superficial from a fundamental viewpoint. But we do so purposefully to emphasize the physical nature of elemental species as they lead to atomic and astrophysical spectroscopy.

on environmental properties, primarily the temperature and density of the ambient plasma medium. The diversity of astrophysical environments makes it necessary to consider the intrinsic physical properties of atoms in conjunction with extrinsic plasma parameters. This book is concerned with the physical properties of elements in various ionization stages, particularly from an astrophysical perspective.

1.3 Electromagnetic spectrum and observatories

Astrophysical observations using state-of-the-art spectrometers on-board space missions and on ground-based telescopes are revealing spectral features at very high resolution in all wavelength ranges. Indeed, one may view astronomical sources as ‘astrophysical laboratories’ for atomic physics – a reversal of roles that greatly enhances the reach of both disciplines, atomic physics and astronomy.

Radiation emission from astronomical objects ranges over the whole electromagnetic spectrum from radio waves to gamma rays. The photon energy $h\nu$ and wavelength λ corresponding to each type of radiation are related inversely as

$$\nu = c/\lambda. \quad (1.1)$$

The least energetic radio wave photons have the longest wavelength $\lambda > 1$ m, and the most energetic gamma rays have wavelengths more than ten orders of magnitude smaller, $\lambda < 0.1$ Å. (Note that $1 \text{ Å} = 10^{-10} \text{ m} = 10^{-4} \mu\text{m} = 0.1 \text{ nm}$, where a μm is also referred to as *micron* and ‘nm’ refers to nano-metre.)

Figure 1.2 is a schematic representation of the different regions of the electromagnetic spectrum of solar radiation transmitting through the terrestrial atmosphere. The atmosphere blocks out most regions of the spectrum (shaded area), except the optical or visible (vis), the near infrared (NIR), and the radio waves. The visible band is,

in fact, a very narrow range in wavelength, but of course the one most accessible. The shaded regions are opaque to an observer on the ground, owing to higher atmospheric opacity. For example, water vapour in the atmosphere is very effective in blocking out IR radiation, owing to absorption by H_2O molecules, except in a few ‘windows’ or bands around 100–1000 nm or 1–10 μm (discussed later). This atmospheric ‘blanketing’ is also beneficial to us since it not only retains the re-radiated energy from the Earth (the greenhouse effect), but also absorbs the more energetic radiation from the Sun. Even a little more of the Sun’s ultraviolet (UV) radiation could be biologically disastrous, not to mention the effect of high energy particles and other cosmic radiation of shorter wavelengths, which, although some do get through, are largely blocked out by the atmosphere. The use of ground-based telescopes is, therefore, confined to the wavelength ranges accessible from the Earth, after propagation of radiation through the atmosphere. For all other wavelengths we need to go into Outer Space.

Figure 1.2 also shows the general division of the electromagnetic spectrum for the Earth-based and space-based telescopes. Satellite-based space observatories make observations in the opaque regions. Some recent space observatories are the Compton Gamma-Ray Observatory (GRO), the X-ray Multi-Mirror Mission-Newton (XMM-Newton), the Chandra X-ray Observatory (CXO), Hubble Space Telescope (HST), Spitzer Infra-red Observatory, etc., respectively named after famous scientists: Arthur Compton, Isaac Newton, Subrahmanyan Chandrasekhar, Edwin Hubble and Lyman Spitzer. Another current mission includes the multi-wavelength X-ray– γ -ray NASA satellite Swift, to study gamma-ray bursts that are found to occur all across the sky, and X-ray observations from active galactic nuclei and other sources.

There is significant overlap in the approximate wavelength ranges given, depending on the detectors and instrumentation. Ground-based telescopes have sensitive spectrometers that can range somewhat outside the range

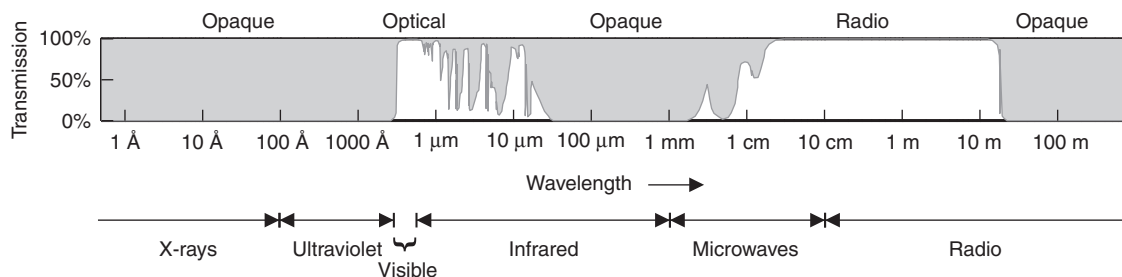


FIGURE 1.2 The electromagnetic spectrum of transmitted radiation through the Earth’s atmosphere (<http://imagine.gsfc.nasa.gov>).

visible to the human eye, 4000–7000 Å. Optical CCDs (charge-coupled devices) can detect radiation from near UV to near IR, 3000–10 000 Å. The detector capability, measured in terms of the percentage of photons detected, called the *quantum efficiency*, deteriorates rapidly near the edges of some spectral windows. Subsequent chapters on astronomical objects will describe the prominent atomic species and spectral features. Atomic and molecular processes play the dominant role at all wavelengths except gamma-rays due to nuclear processes and electron–positron annihilation or synchrotron radiation.

Exercise 1.1 Compile a list of current major ground and space observatories with spectroscopic instruments and corresponding wavelength ranges.

1.4 Astrophysical and laboratory plasmas

Ionized materials in astrophysical plasmas constitute over 99% of the observed matter in the Universe – that is, all the matter in stars, nebulae and interstellar matter, which comprise observable galaxies.² As we mentioned, the analysis of characteristic light is the science of spectroscopy, and nearly all information on observable matter is derived from spectroscopy. This is how we really see the Universe in all its glory. Observable matter spans a huge range in density–temperature parameter space. Whereas the interstellar medium may be cold and thin, down to a few K and to less than one particle per cm³, highly energetic plasmas in the vicinity of black holes at centres of galaxies may approach a thousand million K and immense (as yet unknown) densities. An important set

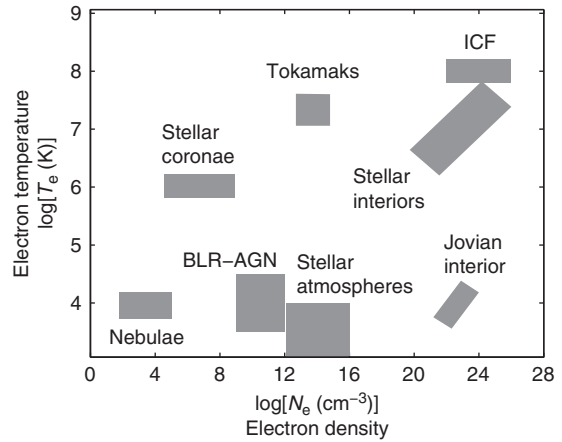


FIGURE 1.3 Temperature–density regimes of plasmas in astrophysical objects, compared with laboratory plasmas in magnetic confinement fusion devices, such as tokamaks, and inertial confinement fusion (ICF) devices, such as Z-pinch machines and high-powered laser facilities. BLR-AGN refers to ‘broad-line regions in active galactic nuclei’, where many spectral features associated with the central massive black hole activity manifest themselves.

of temperature–density combinations is the one in stellar cores: exceeding ten million K and 100 g cm^{−3}, conditions required for hydrogen nuclear fusion that provides most of stellar energy.

Figure 1.3 shows astrophysical and laboratory plasma sources and their approximate temperatures and densities. As one might see, the astrophysical objects correspond to several regimes of electron temperature T_e and density n_e . Often, only some parts of a source are observed. Ordinary stars, for instance, range from a temperature $T \sim 2000\text{--}3000$ K in their outer atmospheres to $>10^7$ K in the core, where thermonuclear fusion creates their energy. The directly observable parts of a star are its *photosphere*, from which most of its radiation is emitted, and the hot highly ionized gas in the *corona*, a tenuous but extended region surrounding the main body of the star. In an extreme manifestation of temperature ranges, a stellar condition called supernova begins with an explosive plasma ball of some thousand million degrees, to less than 10^3 K after a few years of expansion into a ‘nebular’ remnant of the diffuse ionized plasma. It contains mainly H II and the material ejected from the progenitor star, as well as matter swept up from the interstellar medium. The detailed temperature–density–abundance–ionization structure of objects is revealed by spectral analysis of the observable regions of each type of object in different wavelength ranges, as discussed in individual chapters.

² It is worth mentioning how astronomers currently view matter and energy. There is considerable evidence that observable matter comprises only 4% of the Universe. About 22% is so-called ‘dark matter’ that apparently does not interact with electromagnetic radiation to emit or absorb light, and is therefore not observed. The existence of dark matter may be inferred by its gravitational influence on objects. For example, the rotation rate of matter within galaxies is observed *not* to decrease with increasing distance from the centre as expected, but rather remains roughly constant to very large distances. This implies that there is unseen matter in and beyond the observable halo of galaxies. Some of the matter may also be hidden in hot and highly ionized gas in the intergalactic medium, which is indicated by X-ray spectroscopy. The remaining 74% constituent is called *dark energy*, if one interprets the observed acceleration in the expansion rate of the Universe as part of the gravitational mass–energy balance. We discuss these topics in detail in Chapter 14.

1.4.1 Laboratory astrophysics

Is it possible to create conditions in the laboratory that simulate those in astrophysical sources? If yes, then it would be possible to study precisely the physical processes at play as well as measure the basic physical quantities that would enable modelling or numerical simulation of the source plasma in general. As we have seen, owing to the vast range of conditions prevailing in astrophysical sources, that is only possible under the restricted conditions available in a laboratory. In fact, experimental conditions are often quite stringent. The temperatures, densities and particle energies must be precisely measurable to obtain meaningful results for physical parameters of interest, such as cross sections and rates. Nevertheless, such experiments constitute what is called *laboratory astrophysics*. Laboratory devices need to create and maintain a plasma for sufficiently long periods of time for measurements to be carried out. This is quite difficult, especially for measuring *absolute* cross sections with high accuracy, since the results need to be calibrated relative to some independent criterion.

Essentially, the experimental techniques are designed to enable electrons and photons to interact with atoms or ions. This is accomplished either by *colliding* or *merging* beams of interacting particles, or in devices that confine an (electron + ion) plasma. Among these instruments for high-resolution measurements are *electron beam ion traps* (EBIT), which create a trapped plasma of ions interacting with an electron beam of controlled energy within some beam width, *ion storage rings*, where ions are magnetically trapped for long periods of time in a ring-like structure, enabling electron-ion experiments, and *advanced light sources* (ALS) of photons mounted on synchrotron accelerators for targeting the ‘stored’ ions and measuring photoionization cross sections. We will describe these experiments later, while discussing benchmarking and validation of theoretical results.

Laboratory plasma sources, while quite different from astrophysical sources in spatial and temporal behaviour, also span a wide range of temperature–density regimes. Most of the spectral diagnostics and atomic data we describe in this text also apply to laboratory plasmas. In particular, two classes of device for controlled thermonuclear fusion are shown in Fig. 1.3: (i) magnetically confined plasma reactors, called *tokamaks*, and (ii) *inertial confinement fusion* (ICF) devices. The ICF machines are essentially of two types. The first kind is based on laser-induced fusion, wherein an arrangement of symmetrically directed and powerful lasers is fired at a small deuterium-tritium pellet (heavy isotopes of hydrogen containing

either one or two neutrons respectively), causing it to implode. The second kind are the so-called Z-pinch³ machines, wherein a very high electrical discharge passes through wires of a heavy element, arranged cylindrically, which explode and emit X-rays that are directed towards the pellet. The fusion pellet is placed inside the cylindrical formation or cavity, which is called the *hohlraum*. At high temperatures, heavy elements exist in many ionization stages and emit copious amount of radiation; gold ($Z = 79$) is the common choice for hohlraum wires.

1.4.2 Astrophysical plasma composition and abundances

Astronomical objects are generally electrically neutral, i.e., an equal number of negative (electrons) and positive (protons and other ions) charges exists. The electrons are the dominant and most ‘active’ constituents, since their velocities compared with those of protons are $v_e/v_p = \sqrt{m_p/m_e} = 42.85$. In astronomical plasmas, typical proton densities are $\sim 80\%$ of n_e , and other heavier ions, such as helium nuclei (α particles), and partially or fully stripped ions of heavier elements constitute the rest of the positively charged particles. In astrophysical nomenclature, all elements heavier than helium are called ‘metals’. Cosmic plasma compositions denote the H-abundance as ‘X’, He-abundance as ‘Y’, and all other metals combined as ‘Z’. For instance, the solar elemental composition by mass is $X = 0.70$, $Y = 0.28$, $Z = 0.02$. Although metals constitute only 2% of the plasma, they are responsible for most of the spectral features, and they crucially determine properties, such as the plasma opacity that governs the transfer of radiation through the source (Chapter 10). Further study of plasmas in various situations requires us to consider the fundamental bulk properties associated with this most prevalent state of matter.

1.5 Particle distributions

A plasma of charged particles and a radiation field of photons can be treated with certain distribution functions.

³ The ‘Z’ here refers *not* to the atomic number but the fact that a current passing along the z-axis through a wire creates a surrounding magnetic field, which acts naturally to constrain or ‘pinch’ the exploding plasma; the wires are indeed made of high-Z material!

1.5.1 Fermions and bosons

Concepts of indistinguishability and symmetry play a fundamental role in quantum mechanics. All particles of a given kind; electrons, protons, photons, etc., have the same observational property of being indistinguishable from other particles of the same kind. This universal fact is of profound importance and is known as the *principle of indistinguishability* [3]. Quantum mechanically, all observable quantities are expressed in terms of probabilities derived from a wavefunction formed for each kind of particle in terms of its spatial and spin coordinates. But the probabilities are related to the *squares* of the wavefunctions. That introduces an ambiguity in the actual sign of the wavefunction, which can be ‘+’ or ‘−’. The total wavefunction of an ensemble of identical particles is therefore fixed by nature into two kinds. The first kind, *bosons*, refers to a *symmetric* total wavefunction, corresponding to the fact that interchange of coordinates of any two particles leaves the sign of the wavefunction unchanged. The second kind are called *fermions*, which correspond to an *antisymmetric* total wavefunction that changes sign upon interchange of coordinates.⁴ The spin is a special ‘coordinate’, and has a value that is either integral (or zero), or half-integral. Bosons are particles of zero or integral spin, and fermions possess half-integral intrinsic angular momentum. Bosons and fermions obey different statistical mechanics: *Bose–Einstein statistics* in the case of bosons, and *Fermi–Dirac statistics* for fermions, both discussed in the next section.

1.5.2 Temperature: Maxwellian and Planck functions

The concept of ‘temperature’, which gives a measure of hot and cold in general sense, needs a more precise description in astronomy. For a given system of particles, say photons or electrons, the temperature has a meaning if and only if it corresponds to a distinct radiation (photon) or particle (electron) energy *distribution*. In the ordinary sense, the ‘temperature’ of a photon or an electron, or even a photon or electron beam, is meaningless. But the root-mean-square (rms) particle energy may be simply related to the *kinetic* temperature according to

$$E = h\nu \sim kT, \text{ and } E = 1/2 mv^2. \quad (1.2)$$

With three-dimensional components of the velocity,

$$\begin{aligned} \frac{1}{2}mv^2 &= \frac{3}{2}kT, \quad k = 8.6171 \times 10^{-5} \text{ eV K}^{-1} \\ &= 1.38062 \times 10^{-16} \text{ erg K}^{-1} \end{aligned} \quad (1.3)$$

where k is the Boltzmann constant. Consider a star ionizing a molecular cloud into a gaseous nebula. *Nebulae* are a class of so-called H II regions where the principal ionic species is ionized hydrogen (protons). The two distinct objects, the star and the nebula, have different temperatures; one refers to the energy of the radiation emitted by the star, and the other to the energy of electrons in the surrounding ionized gas heated by the star.

1.5.2.1 Black-body radiation and the Sun

The total energy emitted by an object per unit area per unit time is related to its temperature by the *Stefan–Boltzmann Law*

$$E = \sigma T^4, \text{ where } \sigma = 5.67 \times 10^{-8} \text{ W (m}^{-2} \text{ K}^{-4}) \quad (1.4)$$

is known as the Stefan constant. The Stefan–Boltzmann relation holds for a body in *thermal equilibrium*. The term *black body* expresses black colour or rather the lack of any preferred colour, absorbing radiation most efficiently at *all* wavelengths. *Kirchhoff’s law* states that the emissivity of a black body is related to its absorptivity; a black body is also the most efficient radiator (emitter) at all wavelengths (discussed further in Chapter 10). At any temperature, a black body emits energy in the form of electromagnetic radiation at *all* wavelengths or frequencies. However, the distribution of emitted radiation changes with temperature such that the peak value and form of the distribution function defines a unique temperature for the object (black body), as discussed in the next section. The total *luminosity* L of a spherical black body of radius R , such as a star, integrated over all frequencies, is called the *bolometric luminosity*,

$$L = 4\pi R^2 \sigma T^4. \quad (1.5)$$

The radiation field of a star, considered to be a black body, is given by the Planck distribution function,⁵ which defines the energy–frequency relationship at a given temperature:

$$B_\nu(T_*) = \frac{2h\nu^3}{c^2} \frac{1}{\exp(h\nu/kT_*) - 1}, \quad (1.6)$$

where T_* is the *radiation temperature* of the star and ν is the frequency of the photons. In terms of wavelengths it reads

⁴ A simple and elegant ‘proof’ is given in the classic textbook by E. U. Condon and G. H. Shortley [3].

⁵ This is the underlying radiation field, which is attenuated by spectral features, such as lines and bands particular to the star.

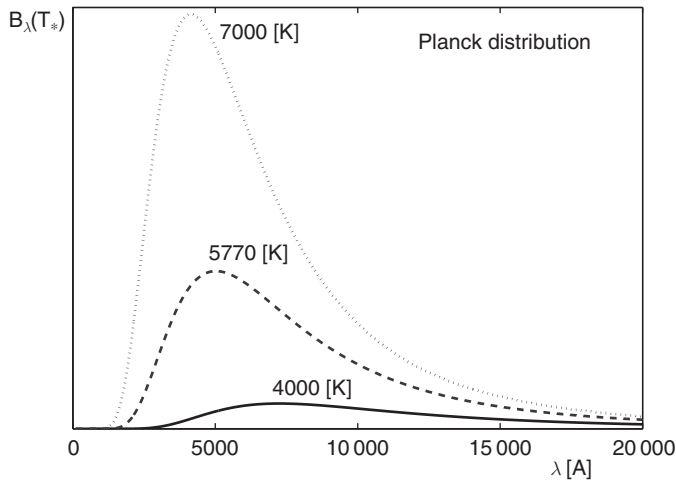


FIGURE 1.4 Planck distributions of photon intensity vs. wavelength at radiation temperatures T_* of various stars. Light from the Sun corresponds to $T_* = 5770$ K, which peaks at wavelengths around yellow; stars with higher(lower) temperature are bluer (redder). The Planck function B_λ is discussed in the text.

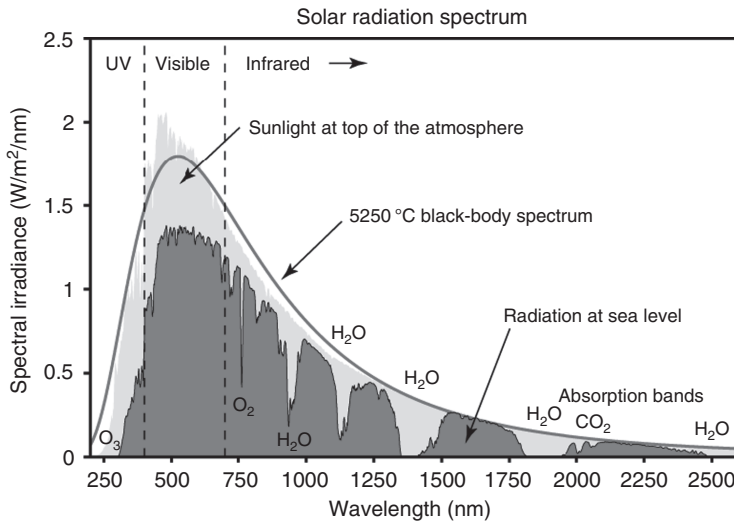


FIGURE 1.5 Sunlight as received at the top of the atmosphere and at sea level after attenuation by atmospheric constituents, primarily ozone, oxygen, water and carbon dioxide. (Courtesy Robert A. Rhode, http://globalwarmingart.com/wiki/Image:Solar_Spectrum.png).

$$B_\lambda(T_*) = \frac{2hc^2}{\lambda^5} \frac{1}{\exp(hc/\lambda k T_*) - 1}. \quad (1.7)$$

A surface temperature of $T_* = 5770$ K corresponds to the peak emission of a black body in the characteristic colour of the Sun – yellow – around 5500 Å . Hotter stars radiate more in the blue or ultraviolet and are ‘bluer’; cooler stars radiate a greater fraction in the infrared and are ‘redder’ than the Sun. Figure 1.4 shows the black-body curves for several temperatures T_* representative of stars. *Wien’s law* states that the black body distribution $B_\lambda(T)$ peaks at

$$\lambda_p = \frac{2.8978 \times 10^7 \text{ Å}}{T/\text{K}}, \quad (1.8)$$

thus peaking at $\frac{2.898 \times 10^3 \text{ Å}}{T/10000 \text{ K}}$ or 2900 Å at 10000 K .

We have already noted the historical relevance of the spectrum of the Sun. But, of course, the Sun is of great

importance otherwise. It is therefore instructive to introduce a few salient features of solar spectra, some of which we shall deal with in later chapters.

Figure 1.5 illustrates several aspects of ‘sunlight’ as received on the Earth. First, following the discussion above about black-body curves associated with the radiation of stars, Fig. 1.5 is fitted to a black body at a slightly lower temperature, 5250 K , than at the surface of the Sun. The best fitting Planck function corresponds to a somewhat lower temperature than the actual spectrum observed *above* the atmosphere (light grey). The spectrum at *sea level* (dark grey) is seen to be significantly attenuated by absorption by the constituents of the atmosphere, primarily molecular bands due to water, oxygen and ozone. Figure 1.5 also shows that, although the peak of Sun’s radiation is in the visible, there is a long tail indicating significant flux in the infrared. Water vapour in the

atmosphere absorbs much of the longer wavelength ($\lambda > 1000 \text{ nm} = 10\,000 \text{ \AA} = 1 \mu\text{m}$) IR radiation via molecular transitions in H_2O .⁶ But water also allows a considerable amount of solar radiation to be transmitted through the atmosphere through what are referred to as ‘windows’ in certain wavelength bands where H_2O has inefficient absorption (weak molecular transitions). Three of these windows are of particular importance, since they enable astronomical observations to be made from ground level in these IR bands, referred to as the *J, H and K bands*⁷ centred around $1.2 \mu\text{m}$, $1.6 \mu\text{m}$ and $2.2 \mu\text{m}$, respectively.

Another interesting feature of Fig. 1.5 is the difference in radiation above and below the atmosphere on the UV side where, unlike the IR, the solar UV flux drops off rapidly. This is the *ozone effect*, as O_3 prevents the harmful UV radiation from reaching the Earth and thereby makes life as we know it possible.

1.5.2.2 Maxwellian particle distribution

Using old quantum theory (before the invention of wave mechanics), Einstein proposed an explanation of the *photoelectric effect* that relates Planck’s quantum of energy $h\nu$ to absorption by an atom with the ejection of an electron. For instance, if the atom is surrounded by other atoms as in a metal, then a certain amount of energy is needed for the electron to escape. Hence the kinetic energy of the photoelectron is obtained as

$$\frac{1}{2}mv^2 = h\nu - W, \quad (1.9)$$

where W is called a *work function*. In the process of photoionization, where an atom or ion is ionized by absorbing a photon, W may be thought of as the *ionization energy* E_I of a bound electron.

The charged particles in the plasma ionized by a star in an H II region have an *electron temperature* T_e associated with the mean kinetic energy of the electrons given by Eq. 1.2. But it makes little sense to refer to the temperature of a single particle. Hence an averaged kinetic energy over a specified distribution of particle velocities is

⁶ The basic composition of the Earth’s atmospheric gases by volume at sea level is $\text{N}_2 \sim 78\%$, $\text{O}_2 \sim 21\%$. Note that these two gases alone comprise $\sim 99\%$ of the dry atmosphere. But there are variations, allowing for $\text{H}_2\text{O} < 4\%$ and $\text{CO}_2 \sim 0.036\%$, and some other trace gases. Both H_2O and CO_2 are greenhouse gases that regulate the greenhouse effect on Earth. Although the CO_2 concentration is usually only about one hundredth of that of H_2O , it can be pivotal in global warming, since it is directly affected by life on Earth and carbon-based fossil fuels.

⁷ Not to be confused with the H and K lines of ionized calcium.

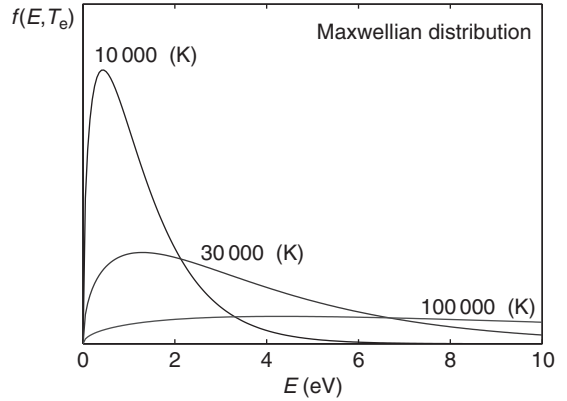


FIGURE 1.6 Maxwellian distributions, $f(E, T_e)$ of free electron energies at three bulk plasma kinetic temperatures T_e .

defined. In most astrophysical sources the fractional probability of electrons as a function of velocity or energy is characterized by a Maxwellian distribution of electrons at temperature T_e as

$$f(v) = \frac{4}{\sqrt{\pi}} \left(\frac{m}{2kT} \right)^{3/2} v^2 \exp \left(-\frac{mv^2}{2kT} \right). \quad (1.10)$$

Figure 1.6 shows the general form of the Maxwellian distribution functions at a few characteristic temperatures T_e . An example of the distinction, as well as the physical connection, between the Planck function and the Maxwellian function is found in H II regions. They are ionized by the hottest stars with black-body temperatures of $T_* \approx 30\,000\text{--}40\,000 \text{ K}$. The resulting ionization of hydrogen in a molecular cloud (see Chapter 12) creates a plasma with electron kinetic energies that can be described by a Maxwellian distribution at $T_e \approx 10\,000\text{--}20\,000 \text{ K}$. Since $1 \text{ eV} \equiv 11\,600 \text{ K}$ (see Eq. 1.3), the electron temperature is of the order of 1 eV in H II regions.

Plasmas need not always have a Maxwellian distribution; electron velocity (energy) distributions may not be given by Eq. 1.10. For example, in the expanding ejecta of supernovae, solar flares or laboratory fusion devices, some electrons may be accelerated to very high velocities. Such non-Maxwellian components or high-energy ‘tails’ may co-exist in a source otherwise characterized by a Maxwellian plasma that defines the bulk kinetic temperature. Another example is that of mono-energetic beams used in laboratory experiments; the beam widths may be described by the well-known Gaussian distribution centred around a given energy. It should be noted that often the subscripts on temperature T are omitted, and it is the context that determines whether the reference is to radiation or the electron temperature, T_* or T_e . The kinetic

temperature of other particle constituents in a plasma, such as protons or other ions (T_p , T_i), is also characterized in terms of a Maxwellian. However, it may happen that $T_e \neq T_p$ or T_i , if there are bulk motions or processes that separate electrons from protons or ions.

1.6 Quantum statistics

Free particles, such as fermions and bosons, usually obey the Maxwellian or Planckian distributions associated with a temperature. When particles congregate to form structures like atoms, molecules, etc., they do so in accordance with laws of quantum mechanics described by energy levels quantized in energy and other variables such as momentum. The statistical mechanics of quantum distribution of particles among those levels is *quantum statistics*. There are three statistical distributions that relate to plasma sources. Once again, temperature is the crucial variable that determines the energies of particles and the levels they can occupy, subject to the principle of indistinguishability (and hence their fundamental classification as fermions or bosons) and quantum mechanical rules, such as the *Pauli exclusion principle*.

1.6.1 Maxwell–Boltzmann statistics

In thermal equilibrium, temperature determines the energy available for particles to be excited to higher levels, and the population distribution among them. Assuming a temperature T and a given excited energy level E_i , the distribution of the number of particles in level i relative to the total is

$$\frac{N_i}{N} = \frac{g_i e^{-E_i/kT}}{\sum_j g_j e^{-E_j/kT}}. \quad (1.11)$$

Here, g_i is the statistical weight for level i or its maximum possible occupancy number. The Maxwell–Boltzmann distribution is the one most frequently used to evaluate the number of electrons in excited levels of an atom or ion. The denominator in Eq. 1.11 is referred to as the *partition function*,

$$U = \sum_i g_i e^{-E_i/kT}. \quad (1.12)$$

It is related to what is known as the *equation-of-state* for a plasma and is discussed in detail in Chapter 10.

1.6.2 Fermi–Dirac statistics

What happens as $T \rightarrow 0$? In that limit, the distribution of particles depends on their basic nature; fermions or

bosons. Since fermions are particles with half-integral spin they must occupy discrete states in accordance with the Pauli exclusion principle, which states that no two fermions can occupy the same quantum mechanical state. This basic fact leads to atomic structure, corresponding to the states of the atom defined by the couplings of angular and spin momenta of all electrons (Chapter 2). As the temperature approaches absolute zero, the electrons have no energy to be excited into higher levels. But not all atomic electrons can occupy the same quantum mechanical state, in particular the ground state, since that would violate the exclusion principle. So they occupy the next available higher levels, until a highest level, called the *Fermi level*, with energy E_F . The Fermi–Dirac probability distribution is given by

$$f(E_i, T) = \frac{1}{\exp[(E_i - E_F)/kT] + 1}. \quad (1.13)$$

At $T = 0$, we have probabilities $f(E, T) = 1$ if $E \leq E_F$ and $f(E, T) = 0$ otherwise. We may visualize the situation as in Fig. 1.7. All levels up to the Fermi level are filled at absolute temperature zero, constituting an ensemble of fermions called the *Fermi sea*. As T increases, particles get excited to higher levels, out of the Fermi sea. Eventually, for sufficiently high temperature and $kT \gg E$, the Fermi–Dirac distribution approaches the Maxwell–Boltzmann distribution characterized by the exponentially decaying probability as $\exp(-E/kT)$ in Eq. 1.11. The probability (Eq. 1.13) is related to the actual number of particles in an energy level i as

$$N_i(\text{FD}) = \frac{g_i}{\exp[(E_i - E_F)/kT] + 1}. \quad (1.14)$$

Thus far we have considered only the temperature as the primary physical quantity. But in fact the density of the plasma plays an equally important role. Intuitively one can see that for sufficiently high densities, at any temperature, particles may be forced together so that the exclusion principle applies. In such a situation one can think of a ‘quantum degeneracy pressure’ owing to the fact that no two electrons with all the same quantum numbers can be forced into the same state. When that happens, all accessible levels would again be occupied at the given temperature *and* density. The foremost example of Fermi–Dirac distribution in astrophysics is that of *white dwarfs* (Chapter 10). These are stellar remnants of ordinary stars, like the Sun, but at the end of stellar evolution after the nuclear fuel (fusion of H, He, etc.) that powers the star runs out. The white dwarfs have extremely high densities, about a million times that of the Sun. The electrons in white dwarfs experience degeneracy pressure, which in fact prevents their gravitational collapse by forcing the

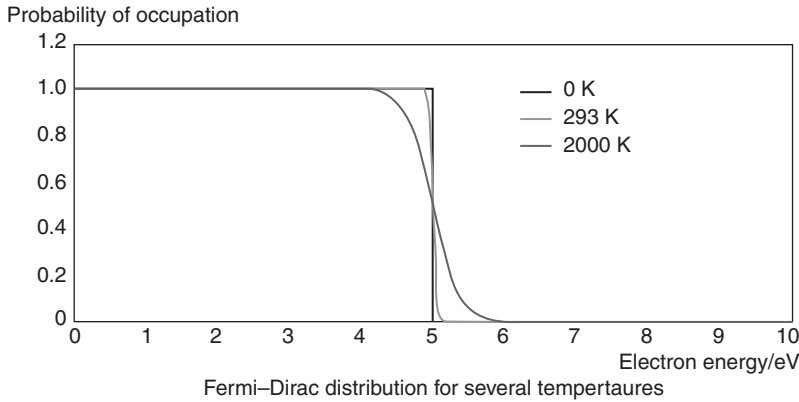


FIGURE 1.7 Fermi-Dirac distribution.

electrons to remain apart (up to a certain limit, as we shall see in Chapter 10).

following gravitational collapse, has been contemplated. That, if observed, would be complementary to known objects, such as neutron stars, made of fermions.

I.6.3 Bose-Einstein statistics

Zero-spin or integral-spin particles are unaffected by the Pauli exclusion principle and any number may occupy any energy level. They follow the Bose-Einstein probability distribution for the number of particles

$$N_i(BE) = \frac{g_i}{\exp E_i/kT - 1} \quad (1.15)$$

All bosons at absolute zero tend to congregate in the same quantum mechanical state, in what must be the ground state. The Bose-Einstein distribution also approaches the Maxwell-Boltzmann distribution for $kT \gg E_i$.

Bosons might be not only single particles, such as photons (spin 0), but also a system of atomic particles with the total spin of all electrons, protons and neutrons adding up to an integral value or zero in each atom. Atoms of alkali elements, such as rubidium, are examples of bosons, which have been experimentally shown to undergo condensation into the same structure-less state. As an alkali, rubidium atoms have an unpaired electron and an odd-atomic numbered nucleus, both of which have a spin quantum number of $1/2$ that, in the lowest state, corresponds to a total spin of 0. The so-called Bose-Einstein condensation (BEC) is achieved by lowering the kinetic temperature to practically zero by slowing down the atomic velocities through laser impact (*laser cooling*). Recall the simple kinetic theory expression (Eq. 1.2), which relates velocity to temperature; bringing the atoms in a gas to a virtual standstill occurs in the μK range. At such a temperature the atoms coalesce into a *Bose-Einstein condensate*. There is very little hard scientific evidence on any astrophysical entity that would be a boson condensate. But the hypothesis of a ‘boson star’, perhaps

I.7 Spectroscopy and photometry

Spectroscopy and imaging of astrophysical sources, i.e., spectra and ‘pictures’, complement each other in astrophysical studies. In between the two lies *photometry*, or the calibrated measurement of brightness in a given wavelength band (or ‘colour’). The division between spectroscopy and photometry rests essentially on the study of energy *at* a given wavelength of spectroscopy or *in* a given wavelength region of photometry. Finer divisions between the two rest on resolution, techniques and instruments.

I.7.1 Photometry and imaging

Photometry involves measurement and calibration of brightness in certain wavelength ranges or bands, e.g. in the optical. As already mentioned, the general division between spectroscopy and photometry is that, while the former refers to the study of energy emitted in the continuum and lines, the latter concerns total emission across a region in the electromagnetic spectrum. However, the difference may be thought of simply in terms of resolution: photometry measures spectral energy with low resolution, and spectroscopy determines the division of energy with high resolution at specific wavelengths (usually associated with atomic and molecular transitions).

Photometric observations correspond to integrated energy (brightness) in a wavelength band weighted by the response function of the filter or the detector. Around the visible region of the spectrum, transmitted through the atmosphere and observable from the ground, the main wavelength bands are denoted as ultraviolet, violet, blue,

green, red and infrared regions. There are a number of systems in observational use for the exact division of wavelengths. One of the more common schemes is as follows. The approximate peak wavelengths are, in Å: 3650 (ultraviolet), 4800 (blue), 5500 (green), 7000 (red), and 8800 (infrared). In addition the near-IR bands are divided into three parts, corresponding to atmospheric transmission windows (Figs 1.2 and 1.5): 12000 (J), 16000 (H) and 22000 (K). Astronomical photometry forms the basis of ‘colour-magnitude’ diagrams of stars and galaxies that relate the bulk energy emitted to temperature, luminosity and other physical properties. Thus photometry is useful for information on a macroscopic scale, such as size, location or surroundings of an astronomical object, whereas spectroscopy yields more detailed information on microscopic physical processes.

1.7.2 Spectroscopy

The formation of the spectrum from an astrophysical plasma depends on atomic processes that emit or absorb radiation. The astrophysical plasma constituents are in general electrons, protons and trace elements in various ionization stages. Also, there is often an external radiation field, for example, from another star or galactic nucleus, interacting with the plasma. The radiative and collisional interactions, in turn, depend on the prevailing density, temperature and radiation source. A variety of atomic interactions, mainly between the electrons and ions, determine the observed spectral features that are divided into the primary components of a typical spectrum: (i) a continuum defining the background radiation, if present, and (ii) a superposition of lines that add or subtract energy to or from the continuum, characterized by emission or absorption, respectively. The relative magnitudes of intensities of the continuum and the lines is a function of the densities, temperatures, radiation field and abundances of elements in the source. Atomic astrophysics seeks to study the qualitative and quantitative nature of the microscopic atomic interactions and the observed spectra.

Among the first quantities to be obtained from spectroscopy is the temperature, which generally determines the wavelength range of the resulting spectra, as well as a measure of the total energy output of the source (such as a star). Another useful parameter derived from spectroscopy of an astronomical object is its gross composition in terms of the amount of ‘metals’ present or its *metallicity*. But the metallicity is generally measured not with respect to all the metals in the source but to iron, which is one of the most abundant elements. Iron often provides hundreds,

if not thousands, of observable spectral lines. Metallicity is therefore the ratio of iron to hydrogen, Fe/H, and is denoted relative to the same ratio in the Sun (defined in Chapter 10). In practice the Fe/H ratio is determined from a few lines of neutral or singly ionized iron.

Sometimes it is difficult to carry out spectroscopic studies, especially in the case of faint objects that may be far away (at high redshift for instance). In other cases a broad classification involving the total emission in two or more wavelength ranges is sufficient. Therefore, astronomers avail themselves of whatever energy they can collect and measure, as described in the next section.

1.7.3 Spectrophotometry

Spectroscopy and photometry may be combined as *spectrophotometry*, which refers to calibrated spectral energy distribution. It is also useful to carry out narrow-band or single-line imaging of a given source, say at a specific wavelength, e.g., the well-known 5007 green line from O III (Chapter 9). The advantage of such a combination of observations is that one can ascertain the spatial distribution, as well as the emission, from plasma in an extended source such as a nebula. For instance, the λ 5007 line may indicate the temperature distribution in the source, e.g., a supernova remnant in a late phase that resembles a gaseous nebula.

An example of measurements that lie in between photometry and spectroscopy is that of *photometric redshifts* of distant objects, now being derived observationally. The redshift of a spectral line, usually the strongest line Ly α , indicates the distance of the source at the present epoch due to the cosmological expansion of the Universe (Chapter 14). A similar redshift also occurs in the entire wavelength region, since all photons from the receding source undergo the same redshift. If spectroscopic observations are not possible or difficult owing to the large distance of an object, photometric redshifts may be derived from the much larger photon flux that can be detected in a wavelength region as opposed to a single wavelength.

1.8 Spectroscopic notation

A Roman numeral or a numerical superscript after the chemical symbol of the element denotes its ionization state: I or 0 for neutral, II or + for singly ionized, and so on; e.g., Li I or Li⁰, Li II or Li⁺, and Li III or Li²⁺. The last ionization state, the fully stripped bare ion, has a numeral equal to Z , the atomic (proton) number in

the nucleus. These are the common notations in atomic physics and spectroscopy. However, the astronomy usage can vary according to context in a sometimes confusing manner. While the spectroscopic notation with the numeral refers to an ionization state, the superscript notation may refer to the *abundance* of an element. For example, Fe II refers to singly ionized iron, but Fe⁺ refers to its abundance when written as, e.g., O⁺/Fe⁺, which means the abundance by number of O II ions relative to Fe II.

1.9 Units and dimensions

Until one turns to routine calculations, in particular to computers, which have no concept of physical quantities and, apart from logical and bookkeeping operations, are good only for *number* crunching, one stays with *physical* equations. Being invariant to choice and change of ‘yardsticks’, the outcome of Eq. 1.7, for instance, remains unaltered if one measures the wavelength λ in units of Å, km or, if one prefers, units bigger than parsecs or smaller than fm (femtometres, 10⁻¹⁵ metres).⁸ The electric and magnetic interactions are controlled by the dimensionless *electromagnetic coupling parameter*

$$\alpha = \frac{e^2}{\hbar c} = 1 / 137.0360, \quad (1.16)$$

often referred to as the *fine-structure constant*. In the atomic shell environment, energies are most naturally measured in units of

$$1 \text{ Ry} = \frac{\alpha^2}{2} mc^2 = 13.6 \text{ eV}, \quad (1.17)$$

the ionization energy of a hydrogen atom out of its ground state.

Strict observance of *phase invariance* for canonical pairs of observables fixes the unit of time:

$$\tau_0 = \hbar / \text{Ry} = 4.8378 \times 10^{-17} \text{ s}, \quad (1.18)$$

the ‘Rydberg’ time of around 50 as (attosecond, 10⁻¹⁸ s, lasts as long as it takes a hydrogen electron in its ground state with velocity $c \cdot \alpha$ to traverse the diameter of the

atom, whose radius a_0 of about 0.5 Å we pick as the unit of length:

$$a_0 = \frac{\hbar}{mc} / \alpha = \lambda^C / (2\pi \alpha) = 0.529177 \times 10^{-8} \text{ cm}. \quad (1.19)$$

Again it is a ‘mechanical’ property of the electron, now its Compton wavelength, that leads to the Bohr radius a_0 ; momentum mc rather than $\lambda^C = h/(mc)$. This fixes the unit of linear momentum $p = \hbar k$ or wavenumber k , such that

$$k \rightarrow k \cdot a_0 \quad (1.20)$$

secures an invariant phase (kr) if $r \rightarrow r/a_0$.

The third canonical pair of observables in atomic physics is a familiar affair, which in a sense started atomic physics and spectroscopy; the uncertainty relation for angular momentum d ,

$$\Delta d \cdot \Delta \varphi = \hbar, \quad (1.21)$$

yields $\hbar/(2\pi) = \hbar$ as the natural unit of angular momentum, because the angle φ is uncertain by 2π in a closed orbit.

For convenience, one uses less natural units, such as for energy the Hartree (H) and Rydberg units (also referred to as *atomic units* (au))

$$1 \text{ H} = 2 \text{ Ry} = 27.21 \text{ eV}, \quad (1.22)$$

which implies $\tau^{\text{H}} = \tau_0/2$,

The atomic units are arrived at technically on *dropping* the quantities $\hbar$, m and e (or equivalently setting them equal to unity), while the physical units are *derived* from the equation of motion. This is akin to saying that in the MKS (metre–kilogram–second) system a day lasts 86 400 MKS or the equator spans 4×10^7 MKS. We rather focus on (conjugate pairs of) observables. Notably the elementary electric charge e is not an observable: it enters atomic structure by way of coupling with an external electromagnetic field.⁹ The assignments in Eqs 1.17 and 1.19 conceptually define its role via

$$e^2 = 2 a_0 \text{ Ry}. \quad (1.23)$$

⁸ Physical quantities are the product of a ‘quality’ (a yardstick) and an ‘intensity’ (the measure taken with it), and as one factor in the product increases, the other decreases (e.g., in Eq. 2.40). Turning from *scale invariance* to calculations involving the atomic shell, ‘qualities’ that keep the intensities within a convenient range are as described herein.

⁹ As W. Eissner points out, only via approaches such as Millikan’s experiment, followed by the long [hi]story of QED. Historically, Sommerfeld named α the fine-structure constant before its primary role in QED could be appreciated. The square e^2 does appear in the equations of motion, but only as the electromagnetic coupling parameter α with the two other *universal structure constants* (Eq. 1.16). In Chapter 14, we address the issue of *variation* of fundamental natural constants, which of course would alter phase space and physical relations such as the Heisenberg uncertainty principle and, in fact, lead to a different Universe or an *evolution* thereof.

Rydberg's constant began in spectroscopy as

$$\mathcal{R}_\infty = \frac{\text{Ry}}{\hbar c} = 109\,737.32\,\text{cm}^{-1}, \quad (1.24)$$

or rather in a form corrected along

$$1\,\mathcal{R}_M = \frac{M}{M + m_e} \mathcal{R}_\infty \quad (1.25)$$

for the finite mass $M \approx 1820\,m_e$ of the hydrogen nucleus:

$$\mathcal{R}_H = 109\,677.576\,\text{cm}^{-1}. \quad (1.26)$$

The wavenumber $\mathcal{R}$ readily translates into the (vacuum) wave length λ of a photon needed to ionize the ground state $1s^2S$:

$$\lambda_H^{\text{PI}} = 1/\mathcal{R} = 911.76\,\text{\AA}. \quad (1.27)$$

The equivalent temperature of 1 Ry follows from Eqs 1.17 and 1.3 as

$$1\,\text{Ry} \equiv 157\,885\,\text{K}. \quad (1.28)$$

It is interesting that atomic sizes of all elements are remarkably similar. Given the Bohr radius (Eq. 1.19) of the electron orbit in the hydrogen atom the size (diameter) of the H atom is $\sim 1\,\text{\AA}$. One might think that heavier

atoms would increase in size according to atomic number along the periodic table (see Appendix A). But this is not so when one examines the calculated radii of atoms of various elements. All atoms lie in the narrow range $\sim 1\text{--}3\,\text{\AA}$. This is because the inner electrons are pulled in closer to the nucleus as Z increases. Nonetheless, it is remarkable that atomic size is constant to within a factor of three for all elements, though Z varies by nearly a factor of 100. Of course, the size of atomic *ions* varies significantly from these values since for ions the size depends on both Z and the number of electrons N in the ion, i.e., the ion charge $z \equiv Z - N + 1$.

A table of physical constants useful in atomic physics and astronomy is given in Appendix A.

Exercise 1.2 Write a program to compute and plot the Maxwellian and Planck functions corresponding to a range of T_e and T_* , respectively.

Exercise 1.3 Plot the black-body function (a) at the effective temperature of the Sun, $T_* = 5700\,\text{K}$, and (b) at $T_* = 2.73\,\text{K}$, the microwave background temperature of the Universe; compare the latter with data obtained by space satellites, such as the Cosmic Background Explorer (COBE). The Universe would be a perfect black body, provided one ignored all the matter in it!

2 Atomic structure

As mentioned in the first chapter, astrophysical applications played a crucial role in the development of atomic physics. In their 1925 paper, Russell and Saunders [2] derived the rules for spectroscopic designations of various atomic states based on the coupling of orbital angular momenta of all electrons into a total L , and the coupling of all spin momenta into a total S , called the LS coupling scheme. Each atomic state is thus labelled according to the total L and S .

Atomic structure refers to the organization of electrons in various shells and subshells. Theoretically it means the determinations of electron energies and wavefunctions of bound (and quasi-bound) states of all electrons in the atom, ion or atomic system (such as electron–ion). As fermions, unlike bosons, electrons form *structured* arrangements bound by the attractive potential of the nucleus. Different atomic states arise from quantization of motion, orbital and spin angular momenta of all electrons. Transitions among those states involve photons, and are seen as lines in observed spectra.

This chapter first describes the quantization of individual electron orbital and spin angular momenta as quantum numbers l and s , and the principal quantum number n , related to the total energy E of the hydrogen atom. The dynamic state of an atom or ion is described by the Schrödinger equation. For hydrogen, the total energy is the sum of electron kinetic energy and the potential energy in the electric field of the proton.

For multi-electron atoms the combination of individual l and s follows strict coupling rules for the total angular momenta, which define the *symmetry of atomic levels*. In a given atom or ion, the rules constitute the angular algebra for all possible atomic states to be determined *independently* of dynamical variables in any effective atomic potential. The orbital spin and the dynamical parts are separately quantized and therefore separable in the Hamiltonian. With a given spin-orbital nl , the dynamical quantities determine the *stationary*

states and expectation values, such as the mean radius of each orbital $\langle r_{nl} \rangle$. These concepts are introduced here through the simplest atomic system, hydrogen. It is the most abundant element in the Universe (90% by number and 70% by mass). The series of spectral lines due to absorption or emission of photons by hydrogen lie in the ultraviolet (UV), optical and infrared (IR) wavelength ranges in the spectra of nearly all astrophysical objects.

Subsequent sections discuss the atomic structure for multi-electron atoms, beginning with the two electrons atom, helium. For a multi-electron atomic system, electron–electron correlation interactions are to be added, introducing complexity in determining the energies and wavefunctions. An approximate treatment of a multi-electron atom, in analogy with the central potential field in an H-atom, comprises the *central-field approximation*. The most common and complete treatment is the generalization of the Schrödinger equation into the *Hartree–Fock equations*.

In addition, if the velocity of the electrons in the atom is significant compared with c , such as in heavy elements or highly charged ions, relativistic effects come into play. The primary effect is the explicit consideration of fine structure, in addition to the total LS scheme, and consequent splitting of LS states or terms into fine-structure levels J . The atomic levels are then designated as LSJ . The fully relativistic version of the equation of motion of an electron is described by the Dirac equation. However, relativistic effects may be incorporated in successively complex approximations, depending on the nuclear charge or *atomic number* Z , to varying extent, that are *intermediate* between the non-relativistic Schrödinger equation and the Dirac equation. The intermediate methods form a class of *Breit–Pauli approximations* appropriate for most atomic systems of astrophysical importance up to the iron group elements.

Finally, the behaviour of energy levels along *isoelectronic sequences*, that is, ions with the same number of electrons but different number Z of protons in the nucleus, illustrates a number of practical useful features of atomic spectroscopy.

2.1 The hydrogen atom

The study of the hydrogen atom underpins the basic concepts of atomic spectroscopy. Therefore the quantum mechanical treatment for this atom is discussed in some detail, leading up to the Rydberg series of levels that define the series of spectral lines.

The classical equation of motion of an electron with mass m moving in the central field of a heavy nucleus with electric charge number Z is

$$\frac{\mathbf{p}^2}{2m} - \frac{Ze^2}{r} = \frac{p_r^2 + p_\perp^2}{2m} - \frac{Ze^2}{r} = E, \quad (2.1)$$

with $\mathbf{p}$ split as indicated by subscripts. The quantum mechanical analogue is obtained on replacing the momentum and energy differential operators $\mathbf{p} \rightarrow -i\hbar\nabla$ and $E \rightarrow i\hbar\partial/\partial t$ to obtain the Schrödinger form,

$$\left[-\frac{\hbar^2}{2m} (\nabla^2) + V(r) \right] \Psi = E \Psi \quad (2.2)$$

$$\left[-\frac{\hbar^2}{2m} (\nabla_r^2 + \nabla_\perp^2) + V(r) \right] \Psi = E \Psi, \quad (2.3)$$

$$\text{specifically } V(r) = -\frac{Ze^2}{r} = -\frac{2Z}{r/a_0} \text{ Ry.} \quad (2.4)$$

In standard notation for spherical coordinates we have

$$\nabla_r^2 = \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) \quad (2.5)$$

$$\begin{aligned} \nabla_\perp^2 &= \frac{1}{r^2 \sin \vartheta} \frac{\partial}{\partial \vartheta} \left(\sin \vartheta \frac{\partial}{\partial \vartheta} \right) \\ &+ \frac{1}{r^2 \sin^2 \vartheta} \frac{\partial^2}{\partial \varphi^2} \end{aligned} \quad (2.6)$$

$$\Psi(r, \vartheta, \varphi) = R(r) Y(\vartheta, \varphi),$$

as the wavefunction factorizes accordingly. Substitution into the Schrödinger equation gives

$$\frac{1}{R} \frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) + \frac{2mr^2}{\hbar^2} [E - V(r)] \quad (2.7)$$

$$= -\frac{1}{Y} \left[\frac{1}{\sin \vartheta} \frac{\partial}{\partial \vartheta} \left(\sin \vartheta \frac{\partial Y}{\partial \vartheta} \right) + \frac{1}{\sin^2 \vartheta} \frac{\partial^2 Y}{\partial \varphi^2} \right]. \quad (2.8)$$

Since the left-hand side depends only on r and the right only on the two spherical angles, both sides must equal some constant λ . Dealing with the angular equation first

conveniently leads to the radial problem, as in the following subsections.

2.1.1 Angular equation

The expression 2.8 leads to the angular equation

$$\frac{1}{\sin \vartheta} \frac{\partial}{\partial \vartheta} \left(\sin \vartheta \frac{\partial Y}{\partial \vartheta} \right) + \frac{1}{\sin^2 \vartheta} \frac{\partial^2 Y}{\partial \varphi^2} + \lambda Y = 0, \quad (2.9)$$

with solutions $Y(\vartheta, \varphi)$, known as spherical harmonics.¹ The equation can be expressed in the convenient form

$$L^2 Y(\vartheta, \varphi) = \lambda Y(\vartheta, \varphi), \quad (2.10)$$

with an angular momentum operator L . Writing the solution as

$$Y(\vartheta, \varphi) = \Theta(\vartheta) \Phi(\varphi) \quad (2.11)$$

and substituting in Eq. 2.9, the equation separates to the form

$$\frac{d^2 \Phi}{d\varphi^2} + \nu \Phi = 0, \quad (2.12)$$

$$\frac{1}{\sin \vartheta} \frac{d}{d\vartheta} \left(\sin \vartheta \frac{d\Theta}{d\vartheta} \right) + \left(\lambda - \frac{\nu}{\sin^2 \vartheta} \right) \Theta = 0, \quad (2.13)$$

where ν is another constant. If ν is the square of an integer, i.e., $\nu = m^2$, Φ and its derivative $d\Phi/d\varphi$ are finite and continuous in the domain 0 to 2π :

$$\Phi(\varphi) = (2\pi)^{-1/2} e^{im\varphi}; \quad (2.14)$$

m is called the *magnetic angular quantum number* and equals 0, ± 1 , ± 2 , ... On replacing ϑ by $w = \cos \vartheta$ the equation for Θ reads

$$\frac{d}{dw} \left[(1 - w^2) \frac{d\Theta}{dw} \right] + \left[\lambda - \frac{m^2}{1 - w^2} \right] \Theta(w) = 0. \quad (2.15)$$

A finite solution Θ requires

$$\lambda = l(l + 1), \quad (2.16)$$

with positive integers $l = 0, 1, 2, \dots$. The solutions are associated Legendre polynomials of order l and m ,

$$P_l^m(w) = (1 - w^2)^{|m|/2} \frac{d^{|m|}}{dw^{|m|}} P_l(w), \quad (2.17)$$

¹ Like sin, exp and other standard mathematical functions, Y is set in *roman* type since it is taken for a filter or operator that creates a *value* from arguments or *variables*, which appear in *italic* type in scientific notation. In this sense, non-standard functions are taken for variables as a whole. Thus the Legendre polynomials $P(\cos \vartheta)$ appear in *roman* type, so there is no notation clash with radial functions $P(r)$ in the next sections.

where $m = l, l-1, \dots, -l$. For $m = 0$ the function $P_l(w)$ is a Legendre polynomial of order l . The angular solution of normalized spherical harmonic is (e.g. [4])

$$Y_{lm}(\vartheta, \varphi) = N_{lm} P_l^m(\cos \vartheta) e^{im\varphi}, \quad (2.18)$$

where

$$N_{lm} = \epsilon \left[\frac{2l+1}{4\pi} \frac{(l-|m|)!}{(l+|m|)!} \right]^{1/2}, \quad (2.19)$$

with $\epsilon = (-1)^m$ for $m > 0$ and $\epsilon = 1$ for $m \leq 0$. Spherical harmonics satisfy the orthogonality condition,

$$\begin{aligned} \int_{\varphi=0}^{2\pi} \int_{\vartheta=0}^{\pi} Y_{l_1 m_1}^*(\vartheta, \varphi) Y_{l_2 m_2}(\vartheta, \varphi) \sin \vartheta \, d\vartheta \, d\varphi \\ = \delta_{l_1, l_2} \delta_{m_1, m_2}. \end{aligned} \quad (2.20)$$

The equation with angular momentum operator can now be written as

$$L^2 Y_l^m(\vartheta, \varphi) = l(l+1) \hbar^2 Y_l^m(\vartheta, \varphi) \quad (2.21)$$

and

$$m = l, l-1, \dots, -l. \quad (2.22)$$

With angular momentum $L = mvr = mwr^2$ the angular frequency $w = L/mr^2$, the centripetal force is $mw^2r = L^2/mr^3$ and the corresponding potential energy is

$$\frac{1}{2}mw^2r^2 = \frac{L^2}{2mr^2}. \quad (2.23)$$

This is similar to the second potential term of hydrogen, provided

$$L^2 = l(l+1)\hbar^2. \quad (2.24)$$

2.1.2 Radial equation

We now turn to the radial coordinate representing the dynamical motion of the electron in the atom. Equation 2.7 leads to the radial equation

$$\left[\frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{d}{dr} \right) + \frac{2m}{\hbar^2} (E - V(r)) - \frac{\lambda}{r^2} \right] R(r) = 0, \quad (2.25)$$

λ being established in Eq. 2.24. It simplifies on substituting $R(r) = P(r)/r$:

$$\left[\frac{\hbar^2}{2m} \frac{d^2}{dr^2} - V(r) - \frac{l(l+1)\hbar^2}{2mr^2} + E \right] P(r) = 0. \quad (2.26)$$

Using atomic units we write ($e = m_e = a_0 = \hbar = 1$)²

$$\left[\frac{d^2}{dr^2} - V(r) - \frac{l(l+1)}{r^2} + E \right] P(r) = 0, \quad (2.27)$$

2.1.3 Rydberg states and hydrogenic energy levels

It may appear that it is easier to express the radial equation than its angular counterpart, but its solution is not only more difficult: it is *always* approximate, with the outstanding exception of the single electron. The angular algebra embodied in the angular equation can be evaluated *exactly* for an atomic transition matrix element, but the solution of the radial equation entails the use of an effective potential, constructed in various approximations, as described in Chapter 4. For hydrogenic systems this is the well-known Coulomb potential Ze^2/r , as discussed below.

Equation 2.27 can be solved on specifying boundary conditions. The bound electron moves in the attractive potential of the nucleus, which behaves as $\lim_{r \rightarrow \infty} V(r) = 0$. Let us look for solutions at two limiting cases of the electron motion: (i) r at infinity and (ii) r near $r = 0$.

For case (i) with $r \rightarrow \infty$ the radial *number* equation reduces to

$$\left[\frac{d^2}{dr^2} + E \right] P(r) = 0, \quad (2.28)$$

which has solutions

$$P(r) = e^{\pm ar}, \quad a = \sqrt{-E}. \quad (2.29)$$

Taking $E < 0$, implying bound states, a runaway solution $e^{ar} \rightarrow \infty$ for $r \rightarrow \infty$ is not acceptable. On the other hand, $\lim_{r \rightarrow \infty} e^{-ar} = 0$ is a possible solution, and is also valid for $E > 0$ when a becomes imaginary, implying free spherical waves. We concentrate on $E < 0$.

² The radial motion displayed in this equation is reminiscent of the one-dimensional motion of a particle in a potential, namely

$$V(r) + \frac{l(l+1)\hbar^2}{2mr^2},$$

where the last term is a centrifugal potential. Moving away from physics for a moment to computers, which know nothing about physics but can deal superbly with mere numbers, we divide Eq. 2.26 with $V(r)$ from Eq. (1.23) by 1 Ry as expressed in Eq. 1.17:

$$\left[\frac{d^2}{d(r/a_0)^2} + \frac{2Z}{r/a_0} - \frac{l(l+1)}{(r/a_0)^2} + E/\text{Ry} \right] P(r) = 0$$

This is a pure *number equation*, having exploited a_0 from Eq. 1.19.

The asymptotic behaviour suggests that the solution $P(r)$ should have the form

$$P(r) = e^{-ar} f(r) \quad (2.30)$$

subject to the condition $\lim_{r \rightarrow 0} f(r) = 0$. On substitution, the radial number Eq. 2.27 leads to

$$\frac{d^2 f}{dr^2} - 2a \frac{df}{dr} + \left[\frac{2Z}{r} - \frac{l(l+1)}{r^2} \right] f(r) = 0 \quad (2.31)$$

for a hydrogen-like ion with one electron and a positively charged nucleus with Z protons. If $r \ll 1$, the solution $f(r)$ may be expressed as a power series

$$f(r) = r^s [A_0 + A_1 r + A_2 r^2 + \dots]. \quad (2.32)$$

For f to be finite as $r \rightarrow 0$, consistent with the behaviour of an orbital nl 'bound' at the nucleus, requires $s > 0$ for the exponent.

Exercise 2.1 Use a power series expansion in the radial equation to show that

$$s = l + 1 > 0, \quad (2.33)$$

i.e., $\lim_{r \rightarrow 0} P(r) \sim r^{l+1}$. Prove that the coefficients A obey the recursion relation

$$\frac{A_k}{A_{k-1}} = \frac{2[(l+k)a - Z]}{k^2 + (2l+1)k}, \quad (2.34)$$

$$\lim_{k \rightarrow \infty} \frac{A_k}{A_{k-1}} = \frac{2a}{k}. \quad (2.35)$$

We note that the exponential e^{2ar} has the following expansion:

$$e^{2ar} = 1 + 2ar + \frac{(2ar)^2}{2!} + \dots + \frac{(2ar)^k}{k!} + \dots, \quad (2.36)$$

$$\frac{(2a)^k / k!}{(2a)^{k-1} / (k-1)!} = \frac{2a}{k}. \quad (2.37)$$

Equation 2.32 indicates that the radial solution f behaves as $r^s e^{2ar}$ for large k . Therefore,

$$P(r) = f(r) e^{-ar} \approx r^{l+1} e^{ar} \quad (2.38)$$

at large distances r .

The above solution diverges at infinity, i.e., $P(r) \rightarrow \infty$ for $r \rightarrow \infty$ unless the series terminates at some finite values of k . Eq. 2.34, along with a from Eq. 2.29, shows that the coefficient A_k vanishes if the following condition is met:

$$(l+k)\sqrt{-E} - Z = 0 \quad (2.39)$$

or, reverting E to energies from shorthand for numbers E/Ry ,

$$E = -\frac{Z^2}{n^2} \times \text{Ry}; \quad (2.40)$$

One may also replace Ry with 'Hartrees/2' or 'au/2' in atomic units. The boundary conditions on the radial wavefunctions have forced the bound states to be discrete with integer n . The equation gives an infinite number of discrete energy levels $-Z^2/n^2$ asymptotically approaching zero for any finite charge number Z . It also shows that the energy is degenerate with respect to l and m . *Degeneracy* in energy or state is defined as the number of eigenfunctions associated with a particular energy.

2.1.4 Hydrogenic wavefunctions

The full series solution for the hydrogen radial function $P(r)$ may be expressed in terms of Laguerre polynomials (e.g., [4])

$$L_{n+l}^{2l+1}(r) = C_0 + C_1 r + C_2 r^2 + \dots + C_{n-l-1} E q \cdot r^{n-l-1}, \quad (2.41)$$

where

$$C_{n-l-1} = (-1)^{n-l} \frac{(n+l)!}{(n-l-1)!}. \quad (2.42)$$

For C_{n-l-1} to remain finite, $n-l-1$ must be zero or a positive integer (note that $0! = 1$ and $n! = \pm\infty$ for a negative integer value of n). Hence

$$n = l + 1, l + 2, \dots \quad (2.43)$$

The radial function then becomes

$$P_{nl}(r) = \sqrt{\frac{(n-l-1)!Z}{n^2[(n+l)!]^3 a_0}} \left[\frac{2Zr}{na_0} \right]^{l+1} \times e^{-Zr/na_0} L_{n+l}^{2l+1} \left(\frac{2Zr}{na_0} \right), \quad (2.44)$$

where the Laguerre polynomial is given by

$$L_{n+l}^{2l+1}(\rho) = \sum_{k=0}^{n-l-1} (-1)^{k+2l+1} \times \frac{[(n+l)!]^2 \rho^k}{(n-l-1-k)!(2l+1+k)!k!}. \quad (2.45)$$

The orthogonality condition of the radial function is

$$\int_0^\infty P_{nl}(r) P_{n'l}(r) dr = \delta_{nn'}, \quad (2.46)$$

$\sqrt{1/a_0}$ of Eq. 2.44 securing scale invariance. In *bra-ket* notation, the complete solution for the bound states of hydrogen may now be written as

$$\begin{aligned}\langle r|nlm\rangle &\equiv \psi_{nlm}(r, \vartheta, \varphi) = R_{nl}(r)Y_{lm}(\vartheta, \varphi) \\ &= \frac{1}{r} P_{nl}(r)Y_{lm}(\vartheta, \varphi),\end{aligned}\quad (2.47)$$

which satisfies the orthogonality condition

$$\begin{aligned}\langle nlm|n'l'm'\rangle &= \int \psi_{nlm}^*(r, \vartheta, \varphi) \psi_{n'l'm'}(r, \vartheta, \varphi) d\tau \\ &= \delta_{nn'} \delta_{ll'} \delta_{mm'}.\end{aligned}\quad (2.48)$$

where $d\tau = r^2 dr \sin \vartheta d\vartheta d\varphi$.

2.1.5 Charge density and expectation values

$R_{nl}^2(r)$ is the *radial charge density* describing the distribution of electrons of different symmetries (ℓ values) at a distance r from the nucleus. One can compute the charge density, that is the probability of finding an electron in volume element $d\tau$ as

$$\psi^* \psi d\tau = \frac{1}{r^2} P_{nl}^2(r) Y_{lm}^*(\vartheta, \varphi) Y_{lm}(\vartheta, \varphi) d\tau. \quad (2.49)$$

One may obtain the *expectation values* $\langle nl|r^k|nl\rangle$ to moments of order k :

$$\langle r^k \rangle = \int_0^\infty P_{nl}^2(r) r^k dr = \int_0^\infty R_{nl}^2 r^{k+2} dr, \quad (2.50)$$

for example

$$\begin{aligned}\langle r \rangle &= \frac{a_0}{2Z} [3n^2 - l(l+1)], \\ \langle r^2 \rangle &= \frac{a_0^2}{Z^2} \frac{n^2}{2} [5n^2 + 1 - 3l(l+1)], \\ \left\langle \frac{1}{r} \right\rangle_{nl} &= \frac{Z}{n^2 a_0}, \\ \left\langle \frac{1}{r^2} \right\rangle_{nl} &= \frac{Z^2}{n^2 \left(l + \frac{1}{2}\right) a_0^2}, \\ \left\langle \frac{1}{r^3} \right\rangle_{nl} &= \frac{Z^3}{n^3 l \left(l + \frac{1}{2}\right) (l+1) a_0^3}.\end{aligned}\quad (2.51)$$

These relations are useful in atomic structure calculations of matrix elements comprising radial integrals over wavefunctions.

States with $E > 0$, in contrast to $E < 0$, form a continuum instead of a discrete spectrum, because their orbits are not closed and thus not quantized. A continuum state is a free state, except that it is designated with an angular momentum (and either box or flux normalization).

Exercise 2.2 Obtain from the full expression for $P_{nl}(r)$ in terms of Laguerre polynomials, the radial functions for the $1s$ and the $2p$ orbitals.

2.2 Quantum numbers and parity

Atomic structure depends on quantization of continuous variables (r , E), ϑ , and φ . They are associated with discrete quantum numbers as

$$\begin{aligned}r, E &\rightarrow n \text{ (principal quantum number)} \\ &= 1, 2, 3, \dots \infty \\ \vartheta &\rightarrow l \text{ (orbital quantum number)} \\ &= 0, 1, 2, \dots (n-1) \\ \varphi &\rightarrow m_\ell \text{ (magnetic quantum number)} \\ &= 0, \pm 1, \pm 2, \dots \pm l,\end{aligned}\quad (2.52)$$

where n represents a shell consisting of ℓ number of subshells, or $n\ell$ orbitals, which further subdivide into m_ℓ suborbitals.

The shells with $n = 1, 2, 3, 4, 5, 6, \dots$ are referred to as K, L, M, N, O, P, $\dots$ — as *values* set in *roman* type. Each shell can accommodate a maximum number of $2n^2$ electrons. A shell is *closed* when full, i.e., all $n\ell m$ orbitals are fully occupied, and *open* when there are vacancies. By long-standing convention, angular momenta l are represented by alphabetic characters s, p, d, f, g, h, i, k, $\dots$ for $l = 0, 1, 2, 3, 4, 5, 6, 7, \dots$ (note that there is no value j; scientific notation aims to avoid confusion with *variables* like spin momentum s , linear momentum p , angular momentum l or oscillator strength f). Thus, an electron in an orbital of $nl = 1s$ is in the first or K-shell ($n = 1$) and in an orbit with $l = 0$ (s orbital). The total angular momentum L for more than one electron follows the same alphabetic character notation, but in the upper case. For example, $L = 0$ is denoted as S, and the higher values are $L = 1, 2, 3, 4, 5, 6, 7$, etc., are P, D, F, G, H, I, K, etc. (note again the absence of 'J'). The orbital magnetic quantum number m depends on l and is written as m_l . For ions with more than one electron, the total orbital magnetic angular momentum can be obtained as $M_L = \sum_i m_{li}$ where L is the total orbital angular momentum. There are $2L + 1$ possible values of M_l for the same L and this is called the angular momentum multiplicity of L .

These quantum numbers reflect the shape and symmetry of the density distribution through the angular function $P_l^m(\vartheta, \varphi)$ and the radial function $R_{nl}(r)$. The latter exhibits nodes (intersecting zeros along the radius vector), the former exhibits nodes at well-defined angles. The higher the value of n , the looser the binding and the greater

the number of nodes in R_{nl} for a given value of l . There are $n - l - 1$ nodes in the wavefunction of an electron labelled nl , counting the sloping one far out and the one at the (pointlike) nucleus as one. Hence for a 2s orbital, the number of nodes is $2 - 0 - 1 = 1$; for a 3d orbital, it is $3 - 2 - 1 = 0$, etc.

The intrinsic angular momentum s of the electron manifests itself via the associated magnetic *Bohr* moment μ_B : as orbitals $l > 0$ create a magnetic field, this moment aligns in quantized positions of s , which leads to term splitting and Pauli's ad-hoc theory. It was overtaken by the Dirac equation, where both s and μ_B rather miraculously appear (it took a while to see why). The spin is separately quantized in non-relativistic quantum mechanics. The associated spin quantum number S is defined such that S^2 commutes with all dynamical variables and, similar to L^2 , the eigenvalue S^2 is $S(S+1)\hbar^2$, that is,

$$S^2\psi_s = \hbar^2 S(S+1)\psi_s. \quad (2.53)$$

However, spin s can be an integer or half an odd integer. For a single electron, $s = 1/2$. While s refers to spin angular momentum of a single electron, S refers to the total or net spin angular momentum. As m is related to l , the spin magnetic quantum number m_s is related to S such that its values vary from $-S$ to $+S$, differing by unity. Hence for a particle with $S = 1/2$, m_s has two values, $-1/2$, $1/2$, describing spin down and spin up. The spin multiplicity of an LS state is given by $2S + 1$, and is labelled singlet, doublet, triplet, quartet, quintet, sextet, septet, octet, etc., for $2S + 1 = 1, 2, 3, 4, 5, 6, 7, 8$, etc.

We noted that non-relativistic hydrogenic energies depend only on the principal quantum number n and are degenerate with respect to both l and m_l . For a given n the value of l can vary from 0 to $n - 1$, and for each l , m_l between $-l$ to l , the eigenfunctions are $(2l + 1)$ degenerate in energy. The total degeneracy of the energy level E_n is

$$\sum_{l=0}^{n-1} (2l + 1) = n^2. \quad (2.54)$$

This degeneracy for a one-electron atom is said to be 'accidental', and is a consequence of the form Z/r of the Coulomb potential. Because it depends only on radial distance, the hydrogenic Hamiltonian is not affected by angular factors, rendering it invariant under rotations. Including the two-spin states that nature distinguishes along some axis, the total number of degenerate levels for a given n is $2n^2$.

Finally, we define the *parity* π of an atomic state. It refers to the symmetry of the state in spatial coordinates. It expresses the phase factor that describes the behaviour of the wavefunction, either positive or negative, with respect to its mirror image or flipping of the distance coordinate. Considering the sum of the integer values l , one speaks of 'even' parity π is $+1$, of 'odd' parity otherwise:

$$\pi = (-1)^{\sum_i l_i} = \begin{cases} +1, & \text{even} \\ -1, & \text{odd,} \end{cases} \quad (2.55)$$

where i is the index of (valence) electrons. Typically odd parity is expressed as superscript 'o' (in roman type since a value or label, not a variable), while even parity is either not marked or denoted by a superscript 'e'. Parity change is a crucial criterion for dipole allowed transitions between two atomic states (Chapter 9).

2.3 Spectral lines and the Rydberg formula

Photons are emitted or absorbed as electrons jump down or up between two energy levels and produce spectral lines. The energy *difference* between two levels is also expressed in terms of frequencies or wavelengths of the spectral lines. For a hydrogen atom, the wavenumber of the spectral line is given by

$$\Delta\mathcal{E}_{n,n'} = \mathcal{R}_H \left[\frac{1}{n'^2} - \frac{1}{n^2} \right] \quad (n' > n), \quad (2.56)$$

where $\mathcal{R}_H$ is the Rydberg constant of Eq. 1.26; finite atomic masses of elements often introduce very small but spectroscopically significant corrections in wavenumbers and lengths.

The Rydberg formula (Eq. 2.56) yields series of spectral lines, each corresponding to a fixed initial n and final $n < n' \leq \infty$, as seen in Fig. 2.1. The first five series are

- (i) $\Delta\mathcal{E}_{n,n'} = \mathcal{R}_H \left[1 - \frac{1}{n'^2} \right]$, $n' = 2, 3, 4, \dots$ Lyman (Ly),
- (ii) $\Delta\mathcal{E}_{n,n'} = \mathcal{R}_H \left[\frac{1}{2^2} - \frac{1}{n'^2} \right]$, $n' = 3, 4, 5, \dots$ Balmer (Ba),
- (iii) $\Delta\mathcal{E}_{n,n'} = \mathcal{R}_H \left[\frac{1}{3^2} - \frac{1}{n'^2} \right]$, $n' = 4, 5, 6, \dots$ Paschen (Pa),
- (iv) $\Delta\mathcal{E}_{n,n'} = \mathcal{R}_H \left[\frac{1}{4^2} - \frac{1}{n'^2} \right]$, $n' = 5, 6, 7, \dots$ Brackett (Br),

$$(v) \Delta \mathcal{E}_{n,n'} = \mathcal{R}_H \left[\frac{1}{5^2} - \frac{1}{n'^2} \right], \quad n' = 6, 7, 8, \dots \quad \text{Pfund (Pf).}$$

The computer delivers numbers for energies, typically in Rydberg units, whereas an observer measures (Fabry–Perot) wavenumbers $\mathcal{E} = E/(\hbar c)$, in particular Eq. 1.26 for ionizing hydrogen out of its ground state, i.e.,

$$\mathcal{R}_H = 109,677.576 \text{ cm}^{-1} = \frac{1}{911.76 \text{ Å}},$$

or its inverse, namely wavelengths in angstroms:

$$\lambda = \frac{911.76 \text{ Å}}{\Delta \mathcal{E}/\mathcal{R}_y}. \quad (2.57)$$

The Lyman, Balmer, Paschen, and other series of H-lines are found to lie in distinct bands of the *electromagnetic spectrum*, as shown in Fig. 2.1. In particular, the Lyman series from 1215–912 Å lies in the far ultraviolet (FUV), the Balmer series from 6564–3646 Å in the optical and near ultraviolet regions, and the Paschen series from 18 751–8204 Å in the infrared (IR). The sequence of transitions in each series is denoted as $\alpha, \beta, \gamma, \delta$, etc., such that the first transition ($\Delta n = 1$) is α , the second ($\Delta n = 2$) is β , and so on. The wavelengths in the Lyman series are (Fig. 2.1): Ly α (1215.67 Å), Ly β (1025.72 Å), Ly γ (972.537 Å), ..., Ly $_{\infty}$ (911.76 Å). The Ly α line is the resonance line in hydrogen, i.e., it corresponds to a (2p–1s) transition, that is, from the first excited level to the ground level. Historically, the Balmer series in the visible (optical) range, readily accessible to ground-based telescopes, has been associated explicitly with hydrogen, and labelled as H α (6562.8 Å), H β (4861.33 Å), H γ (4340.48 Å), H δ (4101.73 Å), and so on, towards shorter wavelengths.

Spectral lines of H and other elements had been identified in astronomical objects long before their quantum mechanical interpretation, such as the Fraunhofer absorption lines from the Sun, which have been observed since 1814.

Exercise 2.3 (a) Use the formulae above to show for which series the hydrogen spectral lines overlap. (b) Calculate the Ly α transitions in H-like ions of all elements from C to Fe. [Hint: all wavelengths should lie in the X-ray range $\lambda < 40 \text{ Å}$.] (c) Give examples of transitions in H-like ions that may lie in the extreme ultraviolet (EUV) wavelength range $100 \text{ Å} < \lambda < 600 \text{ Å}$.

2.4 Spectroscopic designation

Before we describe the details of atomic calculations to determine the energy levels of a multi-electron atom, it

is useful to describe its angular momenta as a guide to multi-electron structures.

A multi-electron system is described by its configuration and a defined spectroscopic state. The *electronic configuration* of an atomic system describes the arrangement of electrons in shells and orbitals, and is expressed as $n l^q$. In the case of a helium atom, the ground configuration is $1s^2$, where the superscript gives the occupancy number or the number of electrons in orbital $1s$. For carbon with six electrons the configuration is $1s^2 2s^2 2p^2$, that is, two electrons in the $1s$ shell, two in $2s$ and two in $2p$ orbitals (when both s shells are full). The angular momenta of an atom depend on its electronic configuration.

The spectroscopic state of the atom is described by the total orbital angular momentum L , which is the vector sum of the individual angular momenta of all electrons. Likewise, the total spin angular momentum S is the vector sum over spin quantum numbers of all electrons. However, the state is not unique, and depends on physical factors, such as the number of electrons in the atom and its nuclear charge. The spectroscopic identification is based on the coupling of angular and spin quantum numbers of all electrons in the atom. The basic scheme is known as *LS* coupling or Russell–Saunders coupling, mentioned earlier. The main point is that in *LS* coupling the orbital motion of the electron is not strongly coupled to the spin momentum. Therefore, the orbital momenta of all electrons can be added together separately to yield a total L for the whole atom, and the spin momenta can likewise be added together to give total S . More precisely, both L and S are treated as separate constants of motion. The Hamiltonian is then *diagonal* in L^2 and S^2 operators, as both angular quantities commute with H :

$$[H, L^2] = 0 = [H, S^2]. \quad (2.58)$$

This secures *simultaneous* eigenfunctions $|LSM_L M_S\rangle$ of the operators L^2 and S^2 , and of the component L_z and S_z .

Vector addition of angular momenta means that the total is a set of all possible positive numbers with a difference of unity ranging from the simple addition and subtraction of the component momenta. Hence, vector addition of L_1 and L_2 is the set of positive values from $|L_2 - L_1|, |L_2 - L_1 + 1|, \dots, |L_2 + L_1|$. Similar addition holds for spin S . These can be added for the total angular momentum, $J = L + S$. These sums, along with the Bohr atomic model and the Pauli exclusion principle, which states that no two electrons in an atom can be in the same level, determine the total final number of possible states of the atomic system.

The total *symmetry of an atomic state* is specified by L, S and the parity. The *LS* coupling designation of

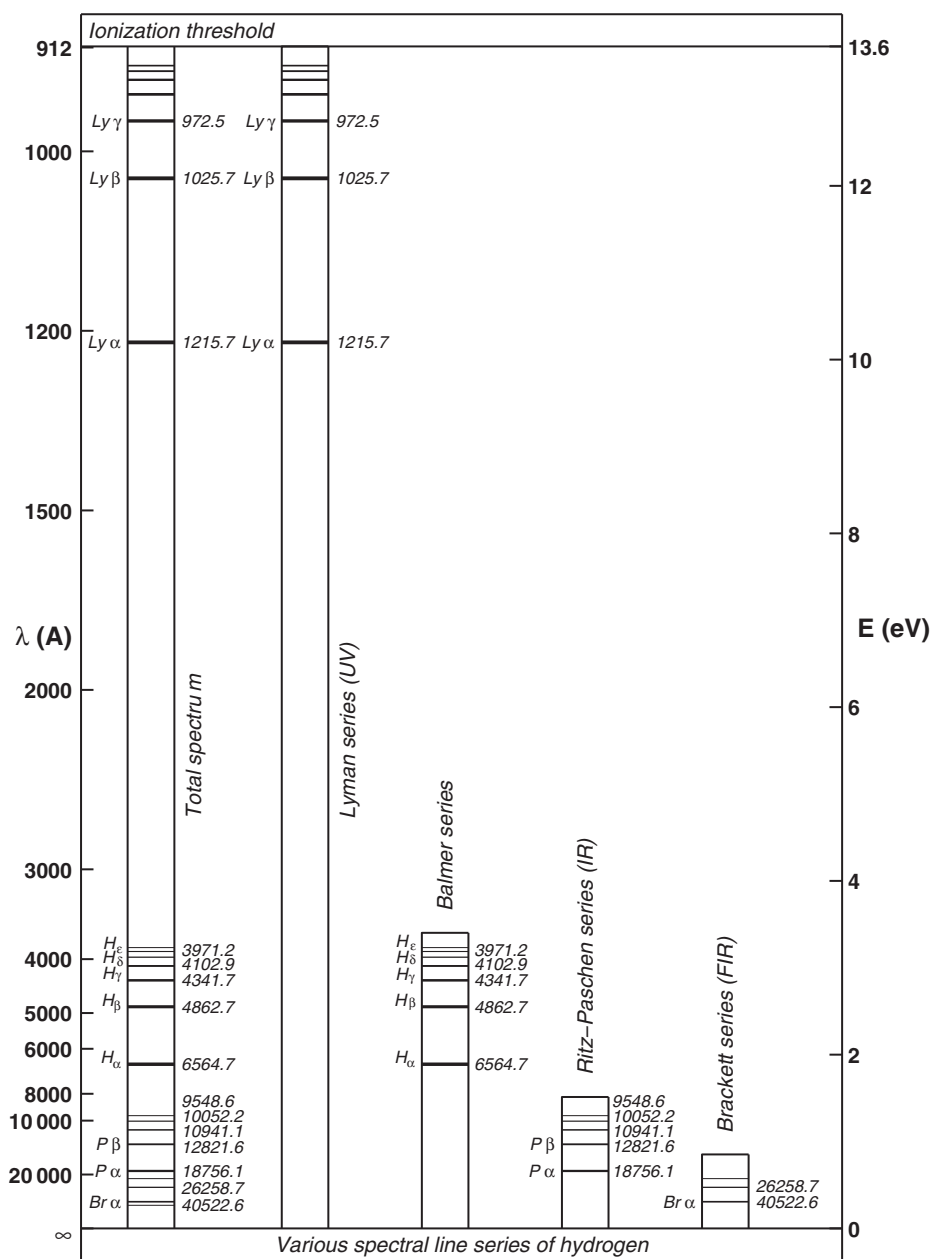


FIGURE 2.1 The hydrogen spectrum and energy levels. The Lyman series lies in the UV, the Balmer series in the optical, the Paschen series in the near IR, and the Brackett series in the far IR.

an atomic state is conventionally expressed as $(2S+1)L^\pi$ and is called LS term. For a single-electron system, i.e., hydrogen, total $L = \ell$ and total $S = s = 1/2$. Since the spin multiplicity $(2S + 1) = 2$, the $1s$ ground state term with $L = 0$ and even parity is designated as 2S . Similarly the excited state of $2p$ electron with its odd parity $[(-1)^1]$ is $^2P^o$, of $3d$ is 2D , and so on. Thus, all LS terms of hydrogen have doublet spin multiplicity and are denoted $^2L^\pi$.

Now consider two electrons with $l_1 = 1$ and $l_2 = 2$. Vector addition of these two gives three total L ; 1, 2, 3, from $|l_2 - l_1|$ to $l_1 + l_2$. The spin quantum number s is always $1/2$. So the vector addition gives two possible total spin S ; $s_1 - s_2 = 0$ and $s_1 + s_2 = 1$. Therefore, all two-electron states, such as of helium, are either singlets or triplets since $(2S + 1) = 1$ and 3 , respectively. Generally, the LS coupling designation of an atomic state is referred

to as an *LS term*. To emphasize: *LS* coupling is applicable when relativistic effects are not important enough to couple individual orbital and spin angular momenta together (this is discussed later).

2.5 The ground state of multi-electron systems

As mentioned above, the Bohr atomic model and the Pauli exclusion principle play crucial roles in structuring electrons in multi-electron systems. The $n = 1$ or K-shell has two levels, since $m_l = 0$ ($l = 0$) and $m_s = \pm 1/2$ (spin up and down). Hence, with occupancy number 2 of the K-shell, we can write

$$\text{K-shell: } n = 1, \ell = 0, m_\ell = 0, m_s = \pm \frac{1}{2}.$$

The ground configuration of the two electrons in helium is $1s^2$ with opposite spins, that is total sum $S = 0$, and the spin multiplicity is $(2S + 1) = 1$. Since both are s-electrons with $\ell = 0$, therefore $L = 0$ and parity is even. Hence, the helium ground state is 1S . With both $L = 0 = S$ for the filled K-shell $1s^2$ (1S), the helium ‘core’ will not add to the total L and S of the electronic configurations of elements with more than two electrons.

The situation gets a bit complicated with the next L-shell for which

$$\text{L-shell: } n = 2, \ell = 0, 1, m_\ell = 0, \pm 1, m_s = \pm \frac{1}{2}. \quad (2.59)$$

The electrons can fill up the orbitals, giving electronic configurations of various elements as

$$\begin{aligned} [\ell = 0, m_\ell = 0] &\rightarrow 1s^2 2s^1 (\text{Li}), 1s^2 2s^2 (\text{Be}), \\ [\ell = 1, m_\ell = 0, \pm 1] &\rightarrow (1s^2 2s^2) + 2p^1 (\text{B}), \\ &\quad + 2p^2 (\text{C}), + 2p^3 (\text{N}), \\ &\quad + 2p^4 (\text{O}), + 2p^5 (\text{F}), \\ &\quad + 2p^6 (\text{Ne}). \end{aligned}$$

The lithium ground state *LS* depends only on the single 2s-electron, i.e., in analogy with hydrogen, the Li ground terms must be $1s^2 2s$ (2S). With core $1s^2$ all other excited terms of helium must be of the form 2L , where $L = \ell$, the orbital angular momentum of the outer valence electron. The beryllium ground state is $1s^2 2s^2$ (1S) since the 2s subshell is also filled (paired spins and orbital momenta), in analogy with helium.

Moving on to the $\ell = 1$ open subshell, the ground *LS* term for boron is simple: $1s^2 2s^2 2p^1$ ($^2P^0$); again, the analogy with hydrogen may be invoked since the closed Be-like electronic core $1s^2 2s^2$ does not contribute to total L or S . But the *LS* assignment by inspection breaks down

for carbon, and all other open L-shell elements, since we now have more than one electron in the p-shell and it is no longer obvious how the exclusion principle allows the *LS* designation of possible atomic states. Furthermore, if we consider not just the ground configuration but also excited configurations then we have (with the exception of hydrogen) a myriad of couplings of spin and orbital angular momenta of two or more electrons.

The general question then is: what are the spectroscopic *LS* terms for a given electronic configuration with open-shell non-equivalent electrons (single electron in outer orbit), e.g., $n \ell n' \ell'$ ($n \neq n'$), and equivalent electrons $n\ell^q$ with the same n and ℓ in a configuration with occupancy number q ? We need not consider the closed shells or subshells, since their total $L = 0 = S$, do not affect the *LS* states of open-shells.

The exclusion principle states that no two electrons in an atom may have the same four quantum numbers ($n, \ell, m_{\ell i}, m_{s i}$). At first sight, it appears straightforward to apply this rule to construct a list of allowed *LS* terms. However, it turns out to be rather involved in terms of bookkeeping, related to combinations of total M_L, M_S , consistent with the four quantum numbers of all electrons in a configuration. They are illustrated next.

2.5.1 Non-equivalent electron states

The *LS* coupling is simple for non-equivalent electrons since the n are different and the exclusion principle is not invoked; that is, terms of all possible L and S values are allowed. The possible values are simply vectorial sums of the individual ℓ and s values. The easiest example is that of two s-electrons, i.e., $ns n's$ of an excited configuration of helium. The total $L = 0$, since both electrons have $\ell = 0$. But the spins $\pm \frac{1}{2}$ can now add up to $S = 1$ or 0 , i.e., the multiplicity $(2S + 1)$ can be 3 or 1, respectively. Therefore, we have two $ns n's$ ($^1S, ^3S$) *LS* terms, e.g., the first two excited terms in helium; similarly the next two higher terms are $1s 2p$ ($^3P, ^1P$). We ignore the parity for the time being, since it is easy to determine even or odd parity from summed l (Eq. 2.55). For more than two electrons we can couple L and S in a straightforward manner; say for three electrons,

$$\begin{aligned} ns n'p (^1P) n''d &\rightarrow ^2P, ^2D, ^2F, \\ ns n'p (^3P) n''d &\rightarrow (^{2,4})P, D, F. \end{aligned}$$

The couplings are the same for any three electrons *spd*. The first two electrons s and p give $sp(^1P, ^3P)$ terms, which couple to the d electron as above. The singlet 1P parent term ($S = 0$) yields only the doublet ($S = 1/2$) terms, but the triplet 3P term ($S = 1$) gives both doublets ($S = 1/2$)

TABLE 2.1 Six possible combinations for a p-electron.

m_l	m_s	1	1/2	0	1/2	-1	1/2	1	-1/2	0	-1/2	-1	-1/2
Notation		1^+		0^+		-1^+		1^-		0^-		-1^-	

TABLE 2.2 Twenty possible distributions for the np^3 -electrons.

M_L	2	1	0	-1	-2
M_S					
3/2			$1^+ 0^+ - 1^+$		
1/2	$1^+ 0^+ 1^-$	$1^+ 0^+ 0^-$	$1^+ 0^+ - 1^-$	$1^+ - 1^+ - 1^-$	$0^+ - 1^+ - 1^-$
1/2		$1^+ - 1^+ 1^-$	$1^+ - 1^+ 0^-$	$0^+ - 1^+ 0^-$	
1/2			$0^+ - 1^+ 1^-$		
-1/2	$1^+ 1^- 0^-$	$1^+ - 1^- 1^-$	$1^+ - 1^- 0^-$	$0^+ 0^- - 1^-$	$-1^+ 0^- - 1^-$
-1/2		$0^+ 1^- 0^-$	$0^+ 1^- - 1^-$	$-1^+ 1^- - 1^-$	
-1/2			$-1^+ 1^- 0^-$		
-3/2			$1^- 0^- - 1^-$		

and quartets ($S=3/2$) when coupled to the third d-electron. It is clear that one obtains the same coupled LS terms regardless of the order in which the terms are coupled, i.e., same for pds, dsp, etc.

Similarly, for three non-equivalent p-electrons we can write down the LS terms as follows. Dropping the n prefix, assuming that $n \neq n' \neq n''$, we have pp' (1S , 1P , 1D , 3S , 3P , 3D) as the parent terms, which yield

$$\begin{aligned}
 (^1S) p'' &\rightarrow ^2P, \\
 (^1P) p'' &\rightarrow ^2(S, P, D), \\
 (^1D) p'' &\rightarrow ^2(P, D, F), \\
 (^3S) p'' &\rightarrow ^{(2,4)}P, \\
 (^3P) p'' &\rightarrow ^{(2,4)}(S, P, D), \\
 (^3D) p'' &\rightarrow ^{(2,4)}(P, D, F).
 \end{aligned}$$

2.5.2 Equivalent electron states

For equivalent electron configurations nl^q , both the vector addition of angular and spin momenta and the Pauli exclusion principle are to be considered. The exclusion principle disallows certain LS terms, and requires an explicit evaluation of all possible combinations of (m_{li}, m_{si}) for the q equivalent electrons to form the *allowed* values of total (M_L, M_S) .

Consider the equivalent electron configuration np^3 . As seen above for non-equivalent electrons not subject to the exclusion principle, the six possible LS states are: $^2,^4S$, $^2,^4P$, $^2,^4D$ and $^2,^4F$. But many of these states are eliminated by the exclusion principle. To wit: no $L = 3$ or F terms can be allowed since two of the three electrons

will have the same (m_{li}, m_{si}) . But we must do the book-keeping systematically as follows. The p subshell can have

$$m_l = 1, 0, -1; \quad m_s = 1/2, -1/2, \quad (2.60)$$

Hence, with common values of n and $l(=1)$ but differing in m_l and m_s , there are six possible combinations of m_l and m_s , or cells, as given in Table 2.1.

Now the combination of three $2p$ electrons can be expressed as all possible distributions of the type $(1^+ 0^+ 1^+)$, $(1^+ 1^- 1^+)$, etc. (Do we detect a problem with these combinations?) A distribution in the cell $(1^+ 0^+ 1^-)$ is associated with values $M_L = 2$ and $M_S = \frac{1}{2}$. Since electrons are indistinguishable, they may be permuted without affecting the distribution; thus $(1^+ 0^+ 1^-)$, $(0^+ 1^+ 1^-)$ are the same. These electrons are grouped according to their respective values of M_L and M_S . Since

$$M_L = \sum_i m_{li}; \quad M_S = \sum_i m_{si}, \quad (2.61)$$

each LS term must have a cell with the highest $M_L = L$ or $M_S = S$. The rule is that *the highest M_L or M_S must have a cell with $M_L - 1, M_L - 2, \dots, -M_L$ and $M_S - 1, M_S - 2, \dots, -M_S$* . The number of independent distributions of three indistinguishable electrons in six orbitals is $(6 \times 5 \times 4)/3! = 20$. The combined electronic cells are now grouped according to M_L and M_S in Table 2.2. A distribution of $(1^+ 0^+ 1^-)$ has the values $M_L = 2$ and $M_S = 1/2$. Table 2.2 shows all 20 possible distributions of (m_l, m_s) , following the exclusion principle.