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Mark Fox
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Part I

Fundamental Principles

1

Preliminary Concepts

Atomic physics is the subject that studies the inner workings of the atom. It remains one of the most important testing grounds for quantum theory and is therefore a very active area of research, both for its contribution to fundamental physics and to technology. Furthermore, many other branches of science rely heavily on atomic physics, especially astrophysics, laser physics, solid-state physics, quantum information science, and chemistry. So much so, that Richard Feynman once wrote (1964):

> If, in some cataclysm, all scientific knowledge were to be destroyed, and only one sentence passed on to the next generation of creatures, what statement would contain the most information in the fewest words? I believe it is the *atomic hypothesis* (or atomic fact, or whatever you wish to call it) that *all things are made of atoms – little particles that move around in perpetual motion, attracting each other when they are a little distance apart, but repelling upon being squeezed into one another*. In that one sentence you will see an *enormous* amount of information about the world, if just a little imagination and thinking are applied.

The task of atomic physics is to understand the structure of atoms, and hence to explain experimental observations such as the wavelengths of spectral lines. For all elements apart from hydrogen, we have to deal with a complicated many-body problem consisting of a nucleus and more than one electron. Atomic physics proceeds by a series of approximations that make this problem tractable. Before we set about this task, it is first necessary to cover a number of important basic concepts and definitions.

1.1 Quantized Energy States in Atoms

The first basic concept we need is that of **bound states**. Atoms are held together by the attractive force between the positively charged nucleus and

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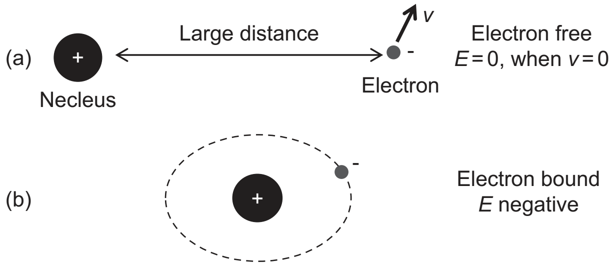

Figure 1.1 (a) Unbound state with the electron far from the nucleus. The electron moves freely with velocity ($\boldsymbol{v}$) independent of the presence of the nucleus. (b) Bound electron state with negative energy.

the negatively charged electrons: the electrons are *bound* to the atom, rather than being *free* to move though space. In the limit where the electron is very far away from the nucleus, the attractive force is negligible; the electron is free to move with velocity ($\boldsymbol{v}$) without any influence from the nucleus, as illustrated schematically in Figure 1.1(a). It is natural to define the energy (E) of this free (or *unbound*) state as being zero when $\boldsymbol{v} = 0$. When the electron moves closer to the nucleus, it begins to experience an attractive force, leading to the formation of a stable bound state as illustrated in Figure 1.1(b). The energy of the bound state is lower than that of the free electron since it requires energy to pull the electron away from the nucleus. The amount of energy required is called the **binding energy** of the electron. With our definition of $E = 0$ corresponding to the unbound state, the absolute energy (E) of the bound state must be negative, with the binding energy equal to $-E = |E|$.

The early understanding of the atom was built around the solar system analogy, that the planets orbit around the sun under the influence of the attractive gravitational force. While it will not be appropriate to push this analogy too far on account of the need to use quantum mechanics rather than Newtonian mechanics to describe the motion, it does provide a useful starting point. In the same way that the planets arrange themselves into orbits at varying radii from the sun, the electrons in an atom are arranged in a series of quantized states around the nucleus. The planets nearest the sun are very strongly bound and have small radii with fast periods. The outer planets, by contrast, are less strongly bound, and have large radii and long periods. Similarly, the electrons are arranged into orbital **shells** around the nucleus. The electrons nearest the nucleus are very strongly bound, while those further away are more weakly bound. The arrangement of the electrons within these quantized shells around the nucleus is the basis of the **shell model** of the atom discussed in Chapter 4.

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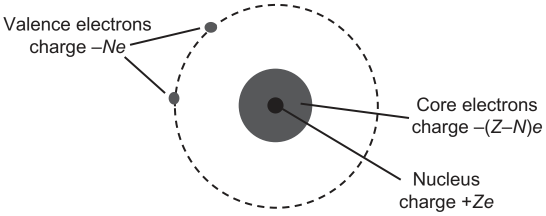

Figure 1.2 Arrangement of electrons into core and valence shells within a neutral atom of atomic number Z with N valence electrons.

Elements are identified by their atomic number Z, which defines the number of protons in the nucleus. Since the charge of the proton is $+e$, where e is the magnitude of the electron charge, the charge of the nucleus is equal to $+Ze$. Free atoms are normally found in a neutral electrical state, which means that they have Z bound electrons (charged atoms are discussed in Section 1.2). The electrons in the outermost shell are called **valence electrons**. It is these valence electrons that take part in chemical bonding, with their number N determining the chemical valency of the atom. The remaining $(Z - N)$ electrons are in inner shells, and are called **core electrons**, as illustrated in Figure 1.2. These core electrons are very strongly bound and can only be accessed by using high-energy (e.g., X-ray) photons, as discussed in Section 4.4.3. The optical spectra of the atom are determined by the valence electrons, which are, therefore, the main focus of atomic physics.

The energies of bound states in atoms are frequently quoted in **electron volt** (eV) units. One electron volt is the energy acquired by an electron when it is accelerated by a voltage of 1 volt. Thus 1 eV = e J, where $-e \approx -1.6 \times 10^{-19}$ C is the charge of the electron. This is a convenient unit, because the binding energies of the valence electrons in atoms are typically a few eV. The core electrons, however, have much larger binding energies, typically in the keV range for atoms with large Z.

1.2 Ionization States and Spectroscopic Notation

In the previous section, we considered the case of a neutral atom in which Z electrons are bound to a nucleus containing Z protons. Charged atoms also exist in which the number of electrons is different to Z. Such charged atoms are called **ions**. In atomic physics, we deal almost exclusively with positively charged ions, in which the number of bound electrons is less than Z.

In chemistry, however, it is also necessary to consider negative ions, in which the atom binds more than Z electrons.

The **ionization energy** of an atom (also sometimes called the **ionization potential**) is defined as the lowest energy required to remove an electron. The electrons are bound to the atom in shells with different quantized binding energies, and the ionization energy is equal to the binding energy of the least strongly bound electron. In practice, this will be one of the valence electrons.

Hydrogen is the first element and has $Z = 1$. Since it only binds one electron, it only has one ionization energy. All other atoms have more than one bound electron, and therefore have more than one ionization energy. An atom with atomic number Z has Z **ionization states**, and hence Z ionization energies. The nth ionization energy is defined as the energy required to remove the nth electron from the atom, according to the following sequence:

$$\begin{array}{lcll} \mathrm{A} & \rightarrow & \mathrm{A}^{+} + \mathrm{e}^{-} & \text{first ionization energy} \\ \mathrm{A}^{+} & \rightarrow & \mathrm{A}^{2+} + \mathrm{e}^{-} & \text{second ionization energy} \\ & \vdots & & \qquad\vdots \\ \mathrm{A}^{(Z-1)+} & \rightarrow & \mathrm{A}^{Z+} + \mathrm{e}^{-} & Z\text{th ionization energy,} \end{array}$$

where A^{n+} represents an atom, A, that has lost n electrons from the neutral state, with A^{Z+} corresponding to an isolated nucleus. Each ionization state has a unique spectrum, which allows the atom to be identified from analysis of its spectral lines.

In normal laboratory conditions at temperature T (with $T \sim 300\,\mathrm{K}$), the thermal energy $k_{\mathrm{B}}T$ is significantly smaller than the first ionization energy of the atom. This means that atoms are normally in the neutral state. In order to study ions, we either have to raise the temperature significantly (e.g., in a flame), or we have to deliberately strip off the electrons (e.g., in a collision with another charged particle in a discharge tube). In astrophysics, however, we study the spectra of atoms in stars, where the temperature is always very high and highly ionized states are routinely found.

Astronomers have been studying the spectra of atoms and ions for a long time, using the characteristic spectral lines of the elements to determine the composition of stars. In order to categorize the spectral lines, **spectroscopic notation** was introduced to identify the different ionization states of the atoms. In this notation, the nth ionization state of atom A is written A (n+1), where (n+1) is written in capital Roman numerals. Thus, A I is the neutral state of the atom, A II is the first ionization state A^{+}, and so on. Spectroscopic notation is widely used in astrophysics and also in important databases of atomic physics (see Section 1.5). Table 1.1 shows how the notation is applied to the element sodium (chemical symbol Na), which has an atomic number of 11.

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Table 1.1 *Ionization states of the element sodium (chemical symbol Na), which has an atomic number of 11.*

Atom/ion	Spectroscopic notation	Number of electrons
Na	Na I	11
Na^+	Na II	10
Na^{2+}	Na III	9
⋮	⋮	⋮
Na^{11+}	Na XII	0

1.3 Ground States and Excited States

A neutral atom with atomic number Z has Z electrons bound to the nucleus. As mentioned in Section 1.1 and discussed in detail in Chapter 4, the quantized electron states are arranged in shells around the nucleus. The Pauli exclusion principle, which will be discussed in Chapters 4 and 6, dictates that each shell can only hold a specific number of electrons. The electrons therefore fill up the shells in sequence of increasing energy, moving to a higher energy shell once the lower energy shell is full. Eventually, all the electrons have been bound. The final state of the atom with its electrons filling up the lowest available energy shells in accordance with the Pauli exclusion principle is called the **ground state** of the atom.

The ground state of a typical atom is shown schematically in Figure 1.3. As before, we assume that there are N valence electrons, and therefore $(Z-N)$ core electrons. The diagram is drawn for the specific case of the neutral magnesium atom, where $Z = 12$ and $N = 2$. Each horizontal line indicates a quantized energy state, and the vertical axis is energy. The zero of energy is defined as the point at which the electron is free and all the quantized bound states have negative energy, as discussed in Section 1.1. The shading for the free states indicates that the energy is not quantized: the electron is free to move with arbitrary kinetic energy, and so can have any positive energy. The free states are therefore said to form a **continuum**: there is a continuous spectrum of energies that are possible, with no breaks due to quantization.

It is important to note that the energy axis in Figure 1.3 is not linear. The core shell states have very large negative energies, and should really be way off the bottom of the page. Since the core electrons play no part in the optical spectra, they are usually omitted from atomic energy-level diagrams; this will be the policy adopted from here onward, unless we are specifically considering the core electrons (as we do in Section 4.4.3).

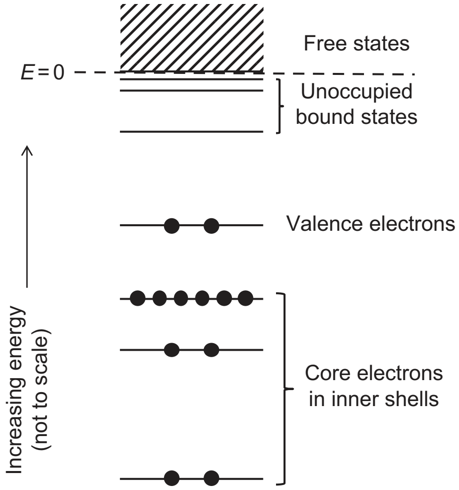

Figure 1.3 Arrangement of the electrons in the ground state of an atom. The electrons fill up the atomic shells in order of increasing energy until all the electrons have been accounted. The shading for the free states indicates that the energy is not quantized: it forms a continuum. The diagram is drawn for the case of the neutral Mg atom ($Z = 12$), which has 12 electrons. Note that the energy scale is not linear. The core shells are very strongly bound, and their large negative energies would be way off the page on a linear scale. These core electron states are usually omitted from atomic energy-level diagrams.

There are an infinite number of quantized bound states in an atom, but only a small number (the ones with lowest energy) are occupied in the ground state configuration of the atom. All of the other states lie at higher energy. The **excited states** of the atom are obtained by promoting valence electrons to these unoccupied states at higher energy. If there is more than one valence electron, then the excited states are obtained by promoting just *one* of the valence electrons to a higher energy state, as shown in Figure 1.4. Despite the large number of these excited states, we usually only need to consider the first few to explain the most important features of the optical spectra. The large number of other excited states at higher energies are increasingly weakly bound, and eventually merge into the continuum of free states available to unbound electrons. This means that the infinitieth excited state corresponds to the ionization limit, which provides a method to define the energy of the ground state electron configuration. This energy is identified in Figure 1.4, and can be determined experimentally by measuring the first ionization energy of the atom.

The energy gap between the ground state of an atom and its first excited state is typically much larger than the thermal energy $k_B T$ at room temperature.

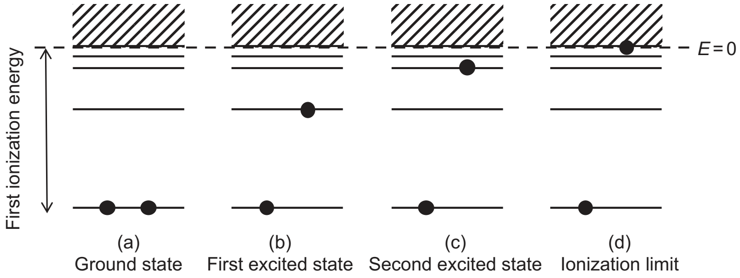

Figure 1.4 Ground and excited states of an atom with two valence electrons. (a) Ground state. (b) First excited state. (c) Second excited state. (d) Ionization limit, equivalent to the infinitieth excited state. Note that the ground state is the same as in Figure 1.3, except that the core electrons are no longer shown.

This means that the atom will normally be in its ground state. In order to promote the atom to its excited states, energy must be imparted to it. This is typically done by placing the atom in a discharge tube, and applying voltage to cause collisions with electrons flowing down the tube. The atom can also be promoted to a specific excited state by absorption of a photon (see section 1.4).

For atoms that have two or more valence electrons, it is reasonable to ask why we only consider excited states in which only one electron is promoted to higher energy. For example, in Figure 1.4, the second excited state has one electron in the lowest level and the other in the third, rather than both electrons in the second level. We only consider these states because it costs more energy to promote both electrons than to completely remove the first electron: the ionized state has a lower energy than the unionized one with two electrons in higher levels. It is therefore easier to ionize the atom than to excite both electrons simultaneously.

The state of the atom after one electron has been removed corresponds to the singly charged ion A^+. The method of defining a ground state and excited states starts again for this ion, with the ground state of the ion corresponding to the ionization state of the neutral atom. For example, the ionization limit of the neutral helium atom ($Z = 2$) corresponds to the ground state of the He^+ ion. (See discussion of Figure 6.2 in Chapter 6.) If the atom has more than two electrons, this process keeps repeating itself, with the ground state of the ion A^{n+} corresponding to the ionization limit of the ion $\mathrm{A}^{(n-1)+}$. Each ionization state has its own characteristic sequence of energy levels, which can be determined by analysis of the optical spectra, as discussed in section 1.4.

The correspondence between the ionization limit of one ionization state and the ground state of the next one is shown in Figure 1.5. It is apparent from this

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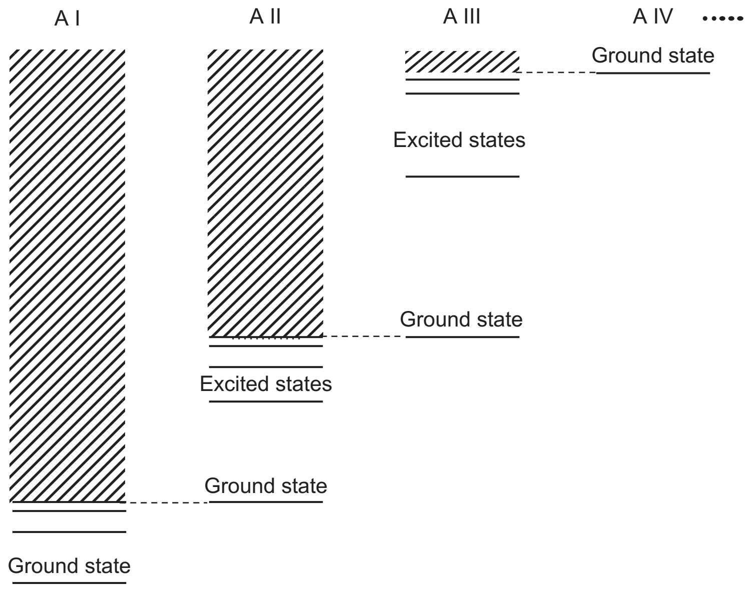

Figure 1.5 Correspondence between the ionization limit of an atom or ion and the ground state of the next ion in the sequence. Spectroscopic notation is used for the different ionization states: A I indicates the neutral atom, A II the singly charged ion, A III the doubly charged ion, and A IV the triply charged ion.

diagram that the definition of $E = 0$ is a *relative* one: $E = 0$ for one ionization state corresponds to a negative energy for the next one. (This distinction does not apply, of course, to hydrogen, as it only has one electron.) In absolute terms, the true zero of energy should be defined as the state with all Z electrons stripped from the nucleus. For a multi-electron atom, this would mean that the ground state of the neutral atom, together with its excited states, all have large negative energies in absolute terms. However, since the energies of the core electrons remain constant while the valence electrons are excited, it makes sense to subtract them and define the zero of energy for each ionization state as the energy to remove the first valence electron.

1.4 Atomic Spectroscopy

We can gain a great deal of knowledge about atoms from studying the way they interact with light, and in particular from measuring atomic spectra. The extreme precision with which optical spectral lines can be measured