Chapter 7. Atomic Physics

Notes:

- *Most of the material in this chapter is taken from Thornton and Rex, Chapter 8.*

7.1 The Pauli Exclusion Principle

We saw in the previous chapter that the hydrogen atom could be precisely understood by considering the Schrödinger equation, including the electrostatic potential energy that accounts for the interaction between the nucleus and the electron. We then discovered that the family of stationary states, which are the solutions of the Schrödinger equation can be completely characterized by three quantum numbers $n, \ell,$ and m. However, we also found that the state of the electron is further characterized by its intrinsic spin, which acts in a way akin to the angular momentum in that it provides an extra magnetic moment and is quantized similarly. But comparisons between the $\hat{\mathbf{S}}$ and $\hat{\mathbf{L}}$ operators should probably not be pushed too far, as for the electron the spin is half-integer with $s = 1/2$ independent of any other parameter, while $0 \le \ell \le n-1$ and always an integer. As a result, the states of the hydrogen can only be fully specified by combining the previous three quantum numbers for the solutions of the Schrödinger equation and the magnetic spin quantum number m_s, forming the (n,ℓ,m,m_s) foursome. As we will now discover there is another very important aspect of the spin that is absolutely essential for understanding the structure of many-electron atoms.

Although it would be in principle possible to solve the Schrödinger equation for more complicated atoms, the presence of several interaction terms between the different electrons makes the problem analytically intractable and basically impossible to solve. The exact determination of the stationary states, their energy, angular momentum, etc. must then be accomplished using computers. It is, however, possible to qualitatively understand the structure of many-electron atoms using the results obtain for the study of the hydrogen atom and another fundamental principle that we owe to the Austrian physicist **Wolfgang Pauli** (1900-1958).

The so-called *Pauli exclusion principle*, which stems from Pauli's efforts to explain the structure of the periodic table, can be stated as follows

Two identical fermions cannot occupy the same state.

Remember that fermions have half-integer spins; the electron with $s = 1/2$ is therefore one. As Pauli initial enunciation of his principle in 1925 happened as he was studying the atomic structure, it can then stated more specifically for atomic electrons with

No two electrons in an atom can share the same set of quantum numbers (n,ℓ,m,m_s).

The structure of atoms and that of the periodic table can be explained with this principle and the further assumption that *atomic electrons tend to occupy the lowest available energy states*.

To see how this works, let us consider the next simplest atom after hydrogen, i.e., helium. The helium atom (He) is composed of a nucleus made of two protons and two neutrons for a total charge of $+2e$ (a neutron has the same mass as a proton but no charge) and two electrons. As was the case for the hydrogen atom we can expect that the lowest energy state for an electron will consists of a 1s wave function with the electron spin quantum number either $1/2$ or $-1/2$, i.e., $(n,\ell,m,m_s)=(1,0,0,\pm 1/2)$. The second electron is also likely to occupy a similar state, but because of the Pauli exclusion principle, which forbids two electrons from occupying the exact same state, the quantum numbers can only be $(n,\ell,m,m_s)=(1,0,0,\mp 1/2)$; note the opposite sign of m_s for the two electrons. We are thus left with the picture of the helium atom having its two electrons in 1s states, where one electron has its spin "up" and the other its spin "down." The complete ground state of the helium atom is then denoted by $1s^2$, where the ending superscript specifies the number of electrons in the given state (in this case, 1s).

What would be the electronic structure for the next simplest atom, i.e., Lithium (Li), which contains three electrons (and a nucleus made of three protons and four neutron)? It should now be clear that the Pauli exclusion principle will forbid the lowest atomic state to be something like $1s^3$, since this would imply that two electrons would have to share the same m_s number (i.e., the ending superscript cannot be greater than two for a ns orbital). To minimize energy two electrons will still occupy the inner *shell* $1s^2$, while the third one will reside on the next unoccupied orbital with favourable energy. In this case the next available lowest-energy electron state is 2s. The lithium atom ground state is therefore $1s^2 2s^1$. One would be justified to ask why couldn't the ground configuration be $1s^2 2p^1$ instead? Indeed, this appears to be supported by the fact that our solution for the hydrogen atom asserted that s and p orbitals for a given n number have the same energy E_n. The answer lies with the consideration of the precise shapes of the different orbitals. An s orbital is said to be more *penetrating* than a p orbital. That is, the radial wave function for $\ell=0$ is more concentrated closer to the nucleus than that for $\ell=1$. This implies that an electron on a 2p orbital in the lithium atom is more likely to have the nuclear charge of $+3e$ *screened* by the two electrons on the 1s orbitals and "feel" an effective charge of $\sim +e$. On the other hand, an electron on the more penetrating 2s orbital is not as screened and will see more of the nuclear charge (i.e., the effective charge is greater than $+e$), which results in a lower potential energy due to its stronger interaction with the nucleus. The $1s^2 2s^1$ state is thus of lower energy than the $1s^2 2p^1$ state and the correct choice for the ground state of lithium.

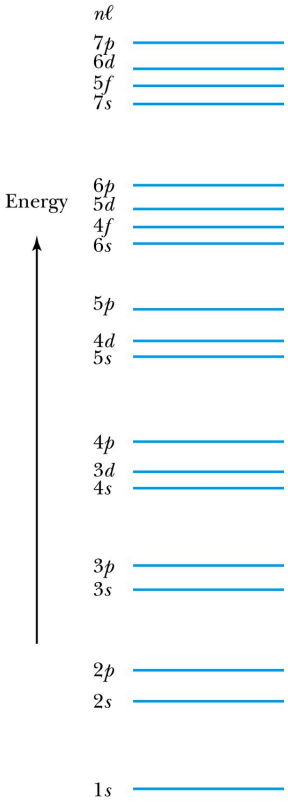
Just as the orbitals are designated by letters depending on the values of the ℓ quantum number, e.g., s, p, d, f, etc., *shells* are associated to the different values of the principal quantum number n. More precisely, levels of $n=1,2,3,4,\ldots$ are given the capital letters K, L, M, N, … The aforementioned $n\ell$ orbitals are then called *subshells*. It

follows that both electrons of the helium atom occupy the K shell, which is then *filled* or *closed*, while lithium has two electrons in the K shell and one *lone* electron in the L shell on the 2s subshell. Two electrons occupying the same orbital, as for the 1s subshell of the K shell for helium and lithium, as said to be *paired*. We could then continue to "build up" atoms by adding and pairing electrons in the L shell in the same manner. We would then readily find the following configurations: $1s^2 2s^2$ for beryllium (Be, 4 protons and 5 neutrons), $1s^2 2s^2 2p^1$ for boron (B, 5 protons and 6 neutrons), $1s^2 2s^2 2p^2$ for carbon (C, 6 protons and 6 neutrons), $1s^2 2s^2 2p^3$ for nitrogen (N, 7 protons and 7 neutrons), and so on until we fill the 2p subshell and L shell for neon (Ne, 10 protons and 10 neutrons) at $1s^2 2s^2 2p^6$. We note that the $n\ell$ subshell can harbour at most $2(2\ell+1)$ electrons, where the leading factor of two accounts the two spin states available to an electron.

Before we go too far with this process and consider atoms with increasing numbers of electrons, we must recognize that our discussion is quantitative and does not account for several internal interactions and couplings that affect the energy levels of atomic orbitals. For example, the magnetic moments stemming from orbital angular momenta and spins can interact through *spin-orbit coupling* and contribute to the energy of a given state. Such effects are not accounted in our treatment of the hydrogen atom, which underlies much of our discussion. The energy ordering of subshells within a single shell or between adjacent shells does not follow a simple s, p, d, etc., listing. A careful analysis reveals the ordering given in Table 8.1 below.

Table 8.1 Order of Electron Filling in Atomic Subshells

n	ℓ	Subshell	Subshell Capacity	Total Electrons in All Subshells
1	0	1*s*	2	2
2	0	2*s*	2	4
2	1	2*p*	6	10
3	0	3*s*	2	12
3	1	3*p*	6	18
4	0	4*s*	2	20
3	2	3*d*	10	30
4	1	4*p*	6	36
5	0	5*s*	2	38
4	2	4*d*	10	48
5	1	5*p*	6	54
6	0	6*s*	2	56
4	3	4*f*	14	70
5	2	5*d*	10	80
6	1	6*p*	6	86
7	0	7*s*	2	88
5	3	5*f*	14	102
6	2	6*d*	10	112



Exercises

1. Use Table 8.1 to determine the ground state configuration of potassium (K, consisting of 19 protons and 20 neutrons).

Solution.

Potassium has 19 electrons, which we must place in subshells of increasing energy. The K and L shells are successively filled without interruption and will use up $(2)+(2+6)=10$ electrons (for the $\left(1s^2\right)+\left(2s^2+2p^6\right)$ subshells). Likewise, the next 8 electrons will occupy the $3s^2$ and $3p^6$ subshells, but Table 8.1 tells us that final *lone* electron does not go to a 3d but a 4s orbital. The ground state configuration for potassium is therefore $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$.

7.2 The Periodic Table

With the understanding of the electronic structure of atoms we acquired it is now relatively easy to understand the structure of the periodic table, which was first introduced by the Russian chemist **Dmitri Ivanovich Mendeleev** (1834-1907) in 1869 (well before the advent of quantum mechanics). Figure 1 shows the table, with the electronic configuration specified for every element.

The periodic table is organized in *groups*, along the different columns, for elements sharing the same chemical properties. A careful look of any given column will show that the corresponding elements all have the same or similar subshell status. That is, they all have the same number of electrons occupying a given ℓ subshell, irrespective of the n number. The rows are known as *periods* and correspond to the filling of subshells. As one goes from the first element on the left to the last on the right of a period, one or more than one subshell can be successively filled. Periods are characterized by the number of shells (or energy levels) of electrons surrounding the nucleus. Here is a brief description of some important groups.

Group 1 - Alkalis

This group, to which hydrogen belongs, are characterized by having one s electron in the outer subshell. Since s electrons tend to extend relatively far from the nucleus and, furthermore, can easily be stripped off the atom (thus forming a positive ion of charge $+1e$) these elements are highly reactive. Because of this tendency to give or share an electron it is said that alkalis have a *valence* of +1. This also results in them being good electrical conductors. All elements in this group, except hydrogen, are refereed to as *alkali metals*.

Group 2 - Alkaline Earths

Alkaline earths elements have their outer s subshell filled. Although we might assume that they would then be more stable than alkalis, the fact that s orbitals are extended and

their electrons easily removed render them quite chemically reactive. They have a valence of $+2$ and are good electrical conductors.

Groups 3 to 12 – Transition Metals (or Transition Elements)

The three rows where the 3d, 4d, and 5d subshells are being filled (i.e., elements 21-30, 39-48, and 72-80) form the transition metals group. Several of these atoms (e.g., iron (Fe), cobalt (Co), and nickel (Ni)) have strong magnetic moments due to the presence of unpaired electrons in the d subshell. These electrons will see their spins aligned therefore producing the ferromagnetic properties of the elements.

The *rare earths elements* consisting of the *lanthanides* (elements 58-71) and *actinides* (elements 90-103) can also be included in this group. This is because these elements have unpaired electrons in the f subshells (for $n = 4$ and $n = 5$, respectively) leading also to large magnetic moments.

Group 17 - Halogens

All elements of this group have five electrons in their outer p subshell, and therefore have a valence of -1. This characteristic renders them very chemically reactive; Fluorine (F) is the most reactive element in existence. Halogens will especially bond efficiently with alkalis, which have a valence of $+1$, to form compound such as NaCl.

Atoms in groups 13 to 16 are composed of *metals* (e.g., aluminum (Al), tin (Sn), and bismuth (Bi)), *non-metals* (carbon (C), nitrogen (N), and oxygen (O)), and *metalloids* (often semiconductors) exhibiting some properties of metals and non-metals (e.g., boron (B), silicon (Si), Arsenic (As), and tellurium (Te)).

7.3 The Combination of Angular Momenta

We saw that transitions metals have high magnetic moments because of the effect of unpaired electron's spin. To understand how this comes about we must first understand how angular momenta, orbital and intrinsic spin, combine or add up to form the total angular momentum $\hat{\mathbf{J}}$. We will consider the simple case for the combination of the spin $\hat{\mathbf{S}}$ and orbital angular momentum $\hat{\mathbf{L}}$ of a single electron. We first note that the two momenta add vectorially

$$\hat{\mathbf{J}} = \hat{\mathbf{L}} + \hat{\mathbf{S}}. \tag{7.1}$$

We remember that both the orbital and spin angular momenta are quantized such that

$$\begin{aligned} L &= \sqrt{\ell(\ell+1)}\hbar, \quad L_z = m_\ell \hbar \\ S &= \sqrt{s(s+1)}\hbar, \quad S_z = m_s \hbar \end{aligned} \tag{7.2}$$

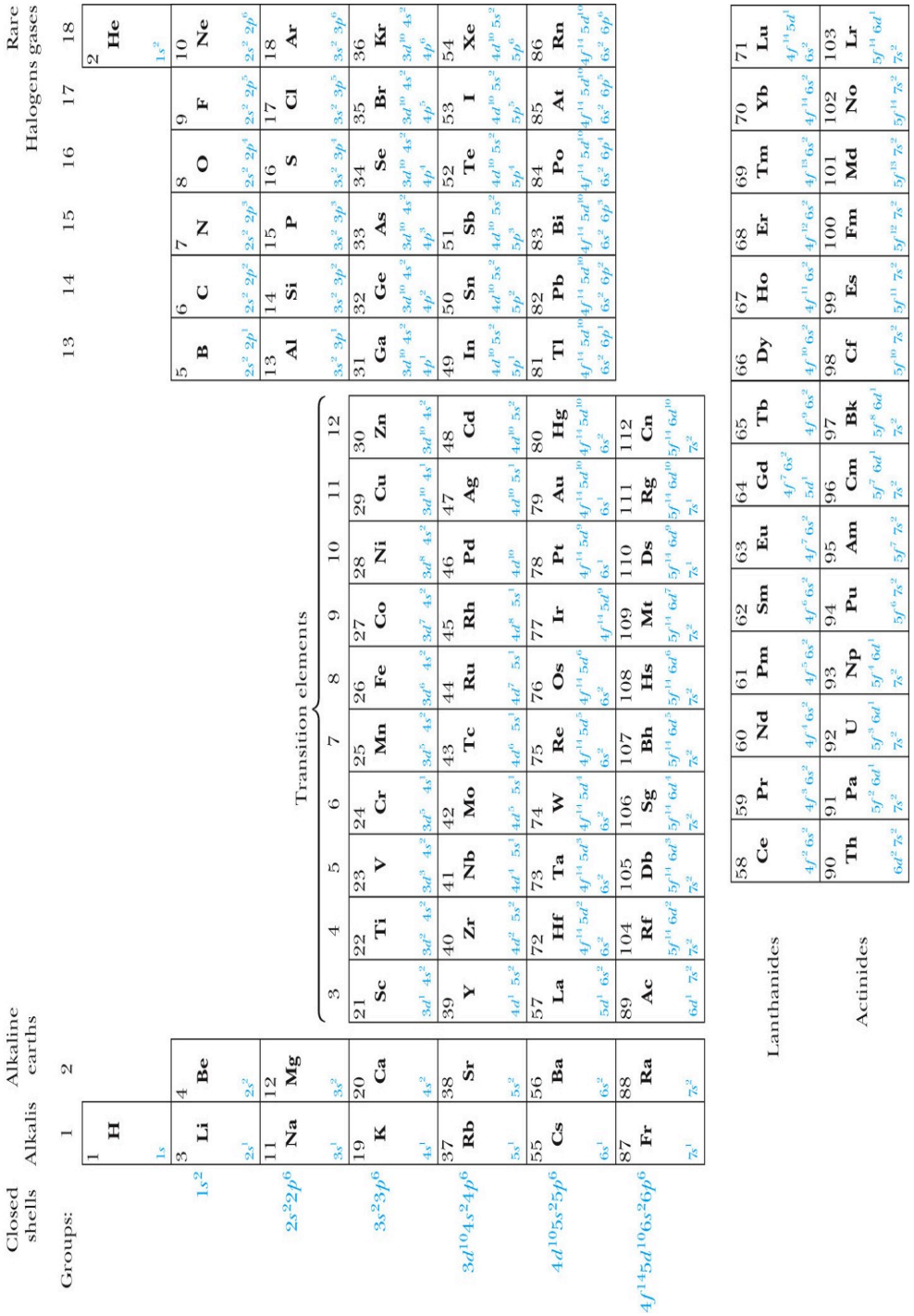


Figure 1 – The periodic table, with the electronic configuration specified for every element.

where $|m_\ell| \le \ell$ and $|m_s| \le s$. We therefore expect that the total angular momentum will also be quantized in a similar manner with

$$J = \sqrt{j(j+1)}\hbar$$
$$J_z = m_j \hbar, \tag{7.3}$$

and $|m_j| \leq j$. From equations (7.2) and (7.3) we can write

$$J_z = (m_\ell + m_s)\hbar, \tag{7.4}$$

or $m_j = m_\ell + m_s$. It is important to realize that different values for m_ℓ, m_s, or m_j imply a different orientation for the corresponding vectors. We therefore expect that there will be several possibilities for both the orientation of the total angular momentum $\hat{\mathbf{J}}$ as well as its magnitude J.

To get a better sense of this let us consider the case where $\ell = 1$, $m_\ell = -1, 0,$ and 1, and $s = 1/2$, $m_s = -1/2$ and $1/2$. Considering equation (7.4) tells us that the following values for m_j are realized

$$m_j = \underbrace{3/2, 1/2}_{\substack{m_\ell=1 \\ m_s=\pm\frac{1}{2}}}, \underbrace{1/2, -1/2}_{\substack{m_\ell=0 \\ m_s=\pm\frac{1}{2}}}, \underbrace{-1/2, -3/2}_{\substack{m_\ell=-1 \\ m_s=\pm\frac{1}{2}}}. \tag{7.5}$$

These values for the magnetic total quantum number can be grouped as follows to find the realized values for j according to equation (7.3)

$$\begin{aligned} j &= \frac{3}{2}, \quad m_j = \frac{3}{2}, \frac{1}{2}, -\frac{1}{2}, -\frac{3}{2} \\ j &= \frac{1}{2}, \quad m_j = \frac{1}{2}, -\frac{1}{2}. \end{aligned} \tag{7.6}$$

This result can be generalized to any pair of angular momenta of any kind (i.e., any mixture of orbital, spin, or "intermediate" total angular momenta) with

$$\begin{aligned} \hat{\mathbf{J}} &= \hat{\mathbf{J}}_1 + \hat{\mathbf{J}}_2 \\ |j_1 - j_2| \leq j &\leq |j_1 + j_2| \\ |m_j| &\leq j, \end{aligned} \tag{7.7}$$

where successive values for J differ by 1. It can easily be verified that equations (7.6) are verified when $\hat{\mathbf{J}}_1 = \hat{\mathbf{L}}_1$ and $\hat{\mathbf{J}}_2 = \hat{\mathbf{S}}_1$.

Let us now come back to the case of a transition metal atom and see if we can better understand its high magnetic moment relative to elements of other groups. For example, we consider the case of titanium (Ti), which has the $[\mathrm{Ar}]3\mathrm{d}^2 4\mathrm{s}^2$ electronic configuration ($[\mathrm{Ar}]$ means that the inner core of titanium corresponds to the *filled* electronic configuration of argon, which is $1\mathrm{s}^2 2\mathrm{s}^2 2\mathrm{p}^6 3\mathrm{s}^2 3\mathrm{p}^6$). The d subshell of titanium is thus

incomplete with only two electrons. For reasons that we will not discuss here, the ground state for such an atom with two unpaired electron on an outer subshell is realized when *i)* the spin is maximized, *ii)* the orbital angular momentum is also maximized, and *iii)* the total angular momentum is minimized, while always keeping in mind that the Pauli exclusion principle must be verified. The total spin is then $\hat{\mathbf{S}} = \hat{\mathbf{S}}_1 + \hat{\mathbf{S}}_2$, which implies that $s = 0$ or 1. Because of the first rule above we choose $s = 1$. Likewise, the total orbital angular momentum is $\hat{\mathbf{L}} = \hat{\mathbf{L}}_1 + \hat{\mathbf{L}}_2$ with $\ell_1 = \ell_2 = 2$ and therefore $\ell = 0, 1, 2, 3,$ and 4. We may be tempted to choose $\ell = 4$ in order to maximize the orbital momentum, but this would go against the Pauli exclusion principle since it implies that $m_{\ell_1} = m_{\ell_2} = 2$ (remember that $\ell_1 = \ell_2$ and $s_1 = s_2$). We must therefore settle for $\ell = 3$, which in turn implies that the total angular momentum $\hat{\mathbf{J}} = \hat{\mathbf{L}} + \hat{\mathbf{S}}$ can span the values $j = 2, 3,$ and 4. Evidently, $\hat{\mathbf{J}}$ is minimized for $j = 2$, which is a state possessing a significant magnetic moment for $m_j \neq 0$.

Finally, the state (or configuration) of an atom is expressed with the following notation

$$^{2s+1}L_j, \tag{7.8}$$

where $2s+1$ is called the *multiplicity* of the state, and L is a capital letter used for the orbital corresponding to ℓ. For example, the ground state of titanium we determined earlier is defined with $^3F_2$.

Exercise

2. Determined the notation for the ground state of carbon given that its configuration is $1s^2 2s^2 2p^2$.

Solution.

We have two unpaired p electrons for which we maximize the spin with $s = 1$. The possible values for the total orbital angular momentum are $\ell = 0, 1,$ and 2, with the maximum allowed by the Pauli exclusion principle of $\ell = 1$. It follows that $j = 0, 1,$ and 2, for a minimum of $j = 0$ and a ground state denoted by $^3P_0$.