

Chapter Four

Energy Levels of Atoms and Ions

This chapter reviews the energy-level structure of atoms and ions, together with the nomenclature for referring to those levels. It is probably an understatement to say that the material in this chapter is not electrically exciting; it should be regarded as reference material that can be returned to as needed.

Atomic spectroscopists customarily identify the different ionization stages of the elements by roman numerals, with I corresponding to the neutral atom, II to singly ionized, III to doubly ionized, and so on. Thus atomic hydrogen is referred to as H I, ionized hydrogen (H^+) as H II, and five-times ionized oxygen (O^{+5}) as O VI.

We now consider the disposition of the electrons.

4.1 Single-Electron Orbitals

According to the quantum mechanical theory of multielectron atoms, it is a good first approximation to think of the electrons as occupying “single-electron” orbitals characterized by integer quantum numbers n and ℓ : $n = 1, 2, 3, \dots$ is the “principal” quantum number (the electron wave function has $n - 1$ radial nodes), and ℓ is the orbital angular momentum in units of \hbar . For a given principal quantum number n , the possible values of ℓ are $0 \leq \ell < n$.

The letters s, p, d, f are used to designate orbitals with $\ell = 0, 1, 2, 3$. In addition to the quantum numbers n and ℓ , there is a third quantum number characterizing the orbital: m_z , the projection of the orbital angular momentum/ \hbar onto the z axis. Thus m_z can take on $2\ell + 1$ different values: $-\ell, \dots, -1, 0, 1, \dots, \ell$. If there is no applied magnetic field, the energy of the orbital is independent of m_z .

Electrons are spin $1/2$ particles, and the projection of the electron spin onto the z axis can take on only 2 values: $-\hbar/2$ or $+\hbar/2$. Again, if there is no applied field, these two states are degenerate.

Thus a given pair of quantum numbers $n\ell$ actually refers to $2(2\ell + 1)$ distinct electronic wave functions.

4.2 Configurations

An atom or ion with a single electron can have its electron in any of the allowed orbitals or wave functions. When an atom or ion has more than one electron, the

Pauli exclusion principle forbids two electrons from sharing the same wave function. Therefore, there can be at most $2(2\ell + 1)$ electrons in a given **subshell** $n\ell$: s subshells can contain at most 2 electrons, p subshells can contain at most 6 electrons, and d subshells can contain up to 10 electrons.

The orbitals, in order of increasing energy, are $1s$, $2s$, $2p$, $3s$, $3p$, $4s$, $3d$, $4p$, $5s$, and so on. Thus atomic carbon, with 6 electrons, has a ground state **configuration** with 2 electrons in the $1s$ subshell, 2 electrons in the $2s$ subshell, and the remaining 2 electrons in the $2p$ subshell. The number of electrons in each subshell is designated by a superscript: the ground state configuration for neutral carbon is written $1s^2 2s^2 2p^2$. Neutral sodium, with 11 electrons, has ground state configuration $1s^2 2s^2 2p^6 3s$.

4.3 Spectroscopic Terms

Each electron has orbital angular momentum $\ell\hbar$ and spin angular momentum $\hbar/2$. If an orbital has more than one and less than $4\ell + 1$ electrons (for the np subshell, this means 2, 3, or 4 electrons), then there is more than one way in which the orbital and spin angular momentum vectors of the electrons in the partially filled shell can add. In the so-called “L-S coupling” approximation, the orbital angular momenta add (vectorially) to give a total orbital angular momentum $L\hbar$, and the individual spin angular momenta similarly add to give a total spin angular momentum $S\hbar$; the wave functions of course must obey the Pauli exclusion principle. Each allowed (L, S) combination is referred to as a **term**.¹ Terms are designated by $^{2S+1}\mathcal{L}$, where $\mathcal{L} = S, P, D, F$ for orbital angular momentum $L = 0, 1, 2, 3$.

Different terms (e.g., for an np^2 configuration, the three possible terms 3P , 1D , and 1S) will differ in energy by a significant fraction of the total binding energy of

¹ Determining what terms can be constructed for a given electron configuration can become involved, but it may be helpful to look at one example: two p electrons, i.e., np^2 . Each of the p electrons has orbital quantum number $\ell = 1$ and spin quantum number $s = 1/2$. With three possible values of $m_\ell = -1, 0, 1$, and two possible values of $m_s = -1/2, 1/2$, there are $3 \times 2 = 6$ possible one-electron states. The exclusion principle says that both electrons cannot share the same one-electron state, giving $(6 \times 5)/2 = 15$ possible different states for the two indistinguishable electrons:

1. Both electrons could have $m_\ell = 1$, giving $L_z = 2$, but this would require that one electron be spin up and one spin down, so that $S = 0$. Having $L_z = 2$ requires $L \geq 2$. For two $\ell = 1$ orbitals, the maximum possible value of $L = 2$. Thus it is evident that one of the allowed terms has $S = 0$ and $L = 2$, i.e., 1D . With multiplicity $(2S + 1)(2L + 1) = 1 \times 5$, this accounts for 5 of the 15 possible quantum states.
2. Both electrons could have $m_s = +1/2$, and $S = 1$. One electron could have $m_\ell = 1$ and one have $m_\ell = 0$, so that $L_z = 1$ is possible, requiring this state to have $L \geq 1$. We have seen earlier that the only way to have $L > 1$ is to have $S = 0$; therefore, this term must have $L = 1$. With degeneracy $(2S + 1)(2L + 1) = 3 \times 3$, this 3P term accounts for 9 quantum states.
3. We have thus far accounted for $5+9=14$ of the 15 quantum states. Therefore there can be only one remaining term, and it must be a singlet, with $S = 0$ and $L = 0$: 1S .

Thus a $2p^2$ configuration gives rise to 3 different terms: 1D , 3P , and 1S . The term with the largest possible values of S and L usually has the lowest Coulomb energy. In this case the 3P term has the lowest energy.

the electrons in the partially filled subshell. Thus for atoms and low-ionization ions, the energy differences between different terms of the ground state configuration will be of order a few eV.

Table 4.1 lists the terms for the ground state configurations of atoms and ions where the outermost subshell is ns or np .

Higher energy states can be constructed by taking one of the electrons out of the ground state configuration and putting it into a higher orbital. For example, in the case of atomic carbon, this can be done by removing one of the $2s$ electrons and promoting it to a $2p$ orbital, giving $1s^2 2s^1 2p^3$ – the electrons in this configuration can also be organized into different terms.

When $L > 0$ and $S > 0$, there is more than one way to add \mathbf{L} and \mathbf{S} to get the total angular momentum $\mathbf{J} = \mathbf{L} + \mathbf{S}$. For given L and S , the allowed values of J range from $|L - S|$ to $L + S$. Thus the 3P term can have $J = 0, 1, 2$, with the spin-orbit interaction leading to “fine-structure” splitting between the three different fine-structure levels of the term: 3P_0 , 3P_1 , and 3P_2 .

Because of the possibility of multiple J values for a given L and S , the terms are also referred to as **multiplets**. A term with $L = 0$ or $S = 0$ can have only one possible value of J , and is therefore referred to as **singlet**. Terms with two, three, four, ... possible values of J are referred to as **doublet**, **triplet**, **quartet**, and so on.

4.4 Fine Structure: Spin-Orbit Interaction

As mentioned earlier, when a configuration has $L > 0$ and $S > 0$, there are different ways the orbital and spin angular momenta can add to give total angular momentum J . Each will have different value of $\mathbf{L} \cdot \mathbf{S}$, and will differ in energy due to **spin-orbit coupling**. The fractional energy shifts are of order $\sim 10^{-2}$ eV. This splitting of energy levels is referred to as **fine structure**.

4.5 Designation of Energy Levels for Atoms and Ions: Spectroscopic Notation

If

$$L = (\text{total orbital angular momentum})/\hbar ,$$

$$S = (\text{total spin angular momentum})/\hbar ,$$

$$J = (\text{total electronic angular momentum})/\hbar ,$$

then the energy levels (including fine structure splitting) are designated by spectroscopic notation:

$$^{2S+1}\mathcal{L}_J^p ,$$

$$\begin{aligned}
&\text{where } \mathcal{L} = S, P, D, F, \dots \\
&\quad \text{for } L = 0, 1, 2, 3, \dots \\
&\text{and } p = \begin{cases} \text{blank} & \text{for state of **even** parity} \\ o & \text{for state of **odd** parity} \end{cases} .
\end{aligned}$$

The **parity** of an energy level is “even” or “odd” depending on whether the electronic wave function changes sign under reflection of all of the electron positions through the origin. If ℓ_i are the orbital angular momenta of the individual electron orbitals, then

$$\text{parity is } \begin{cases} \text{even} & \text{if } \prod_i (-1)^{\ell_i} = 1 \quad (\text{i.e., } \sum_i \ell_i \text{ is even}) \\ \text{odd} & \text{if } \prod_i (-1)^{\ell_i} = -1 \quad (\text{i.e., } \sum_i \ell_i \text{ is odd}) \end{cases} .$$

Note that the adopted notation for designating energy levels overlooks possible hyperfine structure arising from interaction of the electrons with the magnetic moment of the nucleus.

4.5.1 Multiplicity and Degeneracy

Because the total spin **S** and total orbital angular momentum **L** are vectors, they can point in different directions. The **multiplicity** of a term with total spin S and orbital angular momentum L is $g = (2S + 1) \times (2L + 1)$. Thus the 3P term, with $S = 1$ and $L = 1$, has multiplicity $3 \times 3 = 9$. When spin-orbit coupling is taken into consideration, these states are split into distinct fine-structure levels, each with a definite value of J and a **degeneracy** $g = 2J + 1$: $g = 1, 3$, and 5 for $^3P_0, ^3P_1$, and 3P_2 .

4.5.2 Example: Six-electron System

Consider a six-electron system (e.g., C I, N II, O III, F IV, Ne V). The ground configuration $1s^2 2s^2 2p^2$ has *even* parity. The $1s^2$ and $2s^2$ electrons form filled subshells, whereas the $2p$ subshell is only partially filled.

There are three different ways that the two $2p$ electron orbits and spins can be organized into an overall wave function that is antisymmetric under electron exchange, as required by the Pauli exclusion principle – see footnote 1 or, e.g., Bransden & Joachain (2003): 3P (i.e., $L = 1, S = 1$), 1D (i.e., $L = 2, S = 0$), and 1S (i.e., $L = 0, S = 0$). The term with the lowest energy is 3P . With nonzero S and nonzero L , the 3P term splits into 3 fine structure levels: $^3P_{0,1,2}$. The first excited term is 1D – this is a singlet because it has spin 0, so that the only fine-structure level has $J = L = 2$. The remaining term, 1S , is also a singlet. The energy-level diagram for the ground configuration is shown for N II and O III in Figure 4.1.

Table 4.1 lists the terms corresponding to the ground configuration for atoms or ions where the outermost subshell is either ns or np .

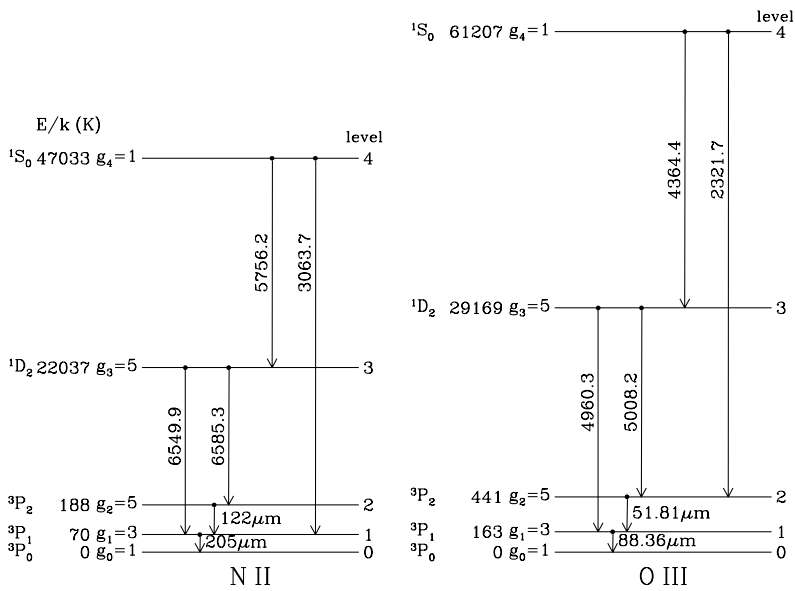


Figure 4.1 Energy-level diagram for the ground configuration of the $2p^2$ ions N II and O III. (Fine-structure splitting is exaggerated for clarity.) Forbidden transitions connecting these levels are shown, with wavelengths in vacuo.

Table 4.1 Terms for ns and np Subshells

Ground configuration	Terms (in order of increasing energy)	Examples
$\dots ns^1$	$^2S_{1/2}$	HI, He II, C IV, N V, O VI
$\dots ns^2$	1S_0	He I, C III, N IV, O V
$\dots np^1$	$^2P_{1/2,3/2}^o$	C II, N III, O IV
$\dots np^2$	$^3P_{0,1,2}^o, ^1D_2, ^1S_0$	C I, N II, O III, Ne V, S III
$\dots np^3$	$^4S_{3/2}^o, ^2D_{3/2,5/2}^o, ^2P_{1/2,3/2}^o$	NI, O II, Ne IV, S II, Ar IV
$\dots np^4$	$^3P_{2,1,0}, ^1D_2, ^1S_0$	O I, Ne III, Mg V, Ar III
$\dots np^5$	$^2P_{3/2,1/2}^o$	Ne II, Na III, Mg IV, Ar IV
$\dots np^6$	1S_0	Ne I, Na II, Mg III, Ar III

4.6 Hyperfine Structure: Interaction with Nuclear Spin

If the nucleus has nonzero spin, it will have a nonzero magnetic moment. If the nucleus has a magnetic moment, then fine-structure levels with nonzero electronic angular momentum can themselves be split due to interaction of the electrons with the magnetic field produced by the nucleus. This “hyperfine” splitting is typically of order 10^{-6} eV. Hyperfine splitting is usually difficult to observe in optical spectra due to Doppler broadening, but it needs to be taken into account if precise

modeling of line profiles is required.

It is customary to let

$$\begin{aligned} J &\equiv [\text{electronic angular momentum}]/\hbar, \\ I &\equiv [\text{nuclear angular momentum}]/\hbar, \text{ and} \\ F &\equiv [\text{total angular momentum}]/\hbar. \end{aligned}$$

The best-known example of hyperfine splitting is the hydrogen atom, where the ground electronic state $1s\ ^2S_{1/2}$ has $J = 1/2$ and the proton has $I = 1/2$. The $1s\ ^2S_{1/2}$ state is split into two levels: The lower level has the electron and proton spins antiparallel, with total angular momentum $F = 0$. The hyperfine excited state has the proton and electron spins parallel, and $F = 1$. The levels are split by $\Delta E = 6.7 \times 10^{-6}$ eV, giving rise to the astronomically important 21-cm transition.

4.7 Zeeman Effect

When a static magnetic field \mathbf{B}_0 is applied, each of the fine-structure levels \mathcal{L}_J splits into $2J+1$ energy levels, with energies depending on the value of $\mathbf{J} \cdot \mathbf{B}_0$. The energy splittings are small, of order $\mu_B B_0 \approx 5.78 \times 10^{-15} (B_0/\mu\text{G})$ eV, where $\mu_B \equiv e\hbar/2m_e c$ is the **Bohr magneton**. Interstellar magnetic field strengths are of order $1 - 100\ \mu\text{G}$, and therefore the Zeeman shifts are too small to be measured for transitions in the sub-mm or shortward ($h\nu \gtrsim 10^{-4}$ eV).

However, in the case of atomic hydrogen, the hyperfine splitting gives rise to the 21-cm transition, with an energy $h\nu = 5.9 \times 10^{-6}$ eV, and, therefore, an applied field of order $10\ \mu\text{G}$ shifts the frequency by about one part in 10^8 . This shift is much smaller than the frequency shift $v/c \sim 10^{-5}$ due to a radial velocity of a few km s^{-1} , and it would be nearly impossible to detect, except that it leads to a shift in frequency between the two circular polarization modes. The Zeeman effect in HI 21-cm can therefore be detected by taking the *difference* of the two circular polarization signals. This technique has been used to measure the magnetic field strength in a number of HI regions.

4.8 Further Reading

Bransden & Joachain (2003) provide a comprehensive discussion of the spectroscopy of atoms and ions.