

Many-Electron Atoms

What distinguished Mendeleev was not only genius, but a passion for the elements. They became his personal friends; he knew every quirk and detail of their behavior.

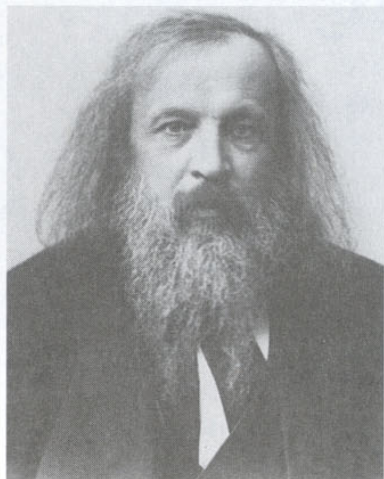
J. Bronowski

We began our study of atomic physics in the previous chapter with a study of the hydrogen atom. Now we will examine more complex atoms with multiple electrons. The highlight of this chapter is the understanding of how quantum mechanics explains the periodic table of the chemical elements. We shall also discover how even a qualitative understanding of atomic structure allows us to explain some of the physical and chemical properties of the elements.

8.1 Atomic Structure and the Periodic Table

We now have a good basis for understanding the hydrogen atom. How do we proceed to understand atoms with more than one electron? The obvious procedure is to add one more electron (helium atom) to the Schrödinger equation and solve for the wave functions. We soon run into formidable mathematical problems. Not only do we now have a nucleus with charge $+2e$ attracting two electrons, we also have the interaction of the two electrons repelling one another. The energy level obtained previously for the hydrogen atom for the first electron will be changed because of these new interactions. In general the problem of many-electron atoms cannot be solved exactly with the Schrödinger equation because of the complex potential interactions. However, with modern computers great progress has been made, and numerical calculations can be carried out with great precision. If we cannot solve exactly for the wave functions, then what can we learn about many-electron atoms?

Let us see how far we can go toward explaining experimental results without actually computing the wave functions of many-electron atoms. Physicists and chemists have been studying the properties of the elements for centuries. We



Dmitri Ivanovich Mendeleev (1834–1907), a Russian chemist, studied and was a professor at the University of St. Petersburg where he developed the periodic table. He successfully predicted the properties of several elements and discovered gallium (1875), scandium (1879), and germanium (1886). *AIP Emilio Segrè Visual Archives, W. F. Meggers collection.*



Wolfgang Pauli (1900–1958) was born in Austria, studied at Munich, and spent brief periods at Göttingen, Copenhagen, and Hamburg before accepting an appointment at Zurich in 1925 where he remained, except for brief periods at American universities including Princeton University during World War II. Pauli was a brilliant theoretical physicist who received the Nobel Prize in 1945. *Photo taken by S. A. Goudsmidt, AIP/Niels Bohr Library.*

know much about atomic sizes, chemical behavior, ionization energies, magnetic moments, and spectroscopic properties, including x-ray spectra. In 1869 the Russian chemist Dmitri Mendeleev arranged the elements into a periodic table that systematized many of their chemical properties. Mendeleev predicted several hitherto unknown elements that were ultimately discovered (most notably, germanium). The elucidation of the underlying physical basis of this (empirical) periodic table became one of the outstanding goals of physics. This goal was attained by the end of the 1920s.

The rise of quantum physics was accompanied by a vast accumulation of precise atomic spectroscopic data for optical frequencies. Attempting to understand these data, Wolfgang Pauli (Nobel Prize, 1945) proposed in 1925 his famous **exclusion principle**:

Pauli Exclusion Principle: No two electrons in an atom may have the same set of quantum numbers (n, ℓ, m_ℓ, m_s).

This principle has far-reaching implications. Using it we can describe in a reasonable, precise fashion the organization of atomic electrons into shells and subshells. Pauli's exclusion principle applies to all particles of half-integer spin which are called *fermions* and can be generalized to include particles in the nucleus, where it is crucial to nuclear structure because neutrons and protons are both fermions.

The atomic electron structure* leading to the observed ordering of the periodic table can be understood by the application of two rules:

1. The electrons in an atom tend to occupy the lowest energy levels available to them.
 2. Only one electron can be in a state with a given (complete) set of quantum numbers (Pauli exclusion principle).
- (8.1)

Let us apply these rules to the first few atoms in the periodic table. Hydrogen has quantum numbers (n, ℓ, m_ℓ, m_s) equal to $(1, 0, 0, \pm 1/2)$ in its lowest energy state (ground state). In the absence of a magnetic field, the $m_s = 1/2$ state is degenerate with the $m_s = -1/2$ state. In neutral helium the quantum numbers must be different for the two electrons, so if the quantum numbers are $(1, 0, 0, 1/2)$ for the first electron, those for the second electron must be $(1, 0, 0, -1/2)$. Direct experimental evidence shows that the two electrons in the He atom have their spins antialigned (spin angular momentum opposed) rather than aligned (spin angular momentum aligned). This supports the Pauli exclusion principle. These two electrons form a rather strong bond with their spin angular momentum antialigned. We speak of the electrons as being *paired*, and the total spin is zero.

The principal quantum number n has also been given letter codes:

$$\begin{aligned} n &= 1 & 2 & 3 & 4 & \dots \\ \text{Letter} &= \text{K} & \text{L} & \text{M} & \text{N} & \dots \end{aligned} \quad (8.2)$$

Because the binding energies depend mainly on n , the electrons for a given n are said to be in **shells**. We speak of the K shell, L shell, and so on (recall from Chapter 4 that this was nomenclature used to describe Moseley's x-ray results). The $n\ell$ descriptions are called **subshells**. We have $1s, 2p, 3d$ subshells. Both electrons in

*The use of hydrogenic quantum numbers for other atoms implies a hydrogenlike central field for the outer electrons of these atoms.

the He atom are in the K shell and 1s subshell (which is a shell in itself). We use a superscript to denote the number of electrons in each subshell. The hydrogen atom description is $1s^1$ or $1s$ (the superscript 1 is sometimes omitted), and the helium atom is $1s^2$.

The next atom in the table is lithium. There is no more space in the K shell because only two electrons are allowed. The next shell is the L shell ($n = 2$), and the possible subshells are $2s$ and $2p$. Rule 1 says the electrons will occupy the state with the lowest energy. Remember that semiclassically the $2s$ state (with zero angular momentum) has an orbit through the nucleus, whereas the $2p$ state has a more nearly circular orbit. An electron in the $2p$ subshell (Li) will experience a $+3e$ nuclear charge, but the positive nuclear charge will be partially screened* by the two electrons in the $1s$ shell. The effective charge that the $2p$ electron sees (or feels) will therefore be $Z_{\text{eff}} \sim +1e$. The $2s$ electron, on the other hand, spends more time than a $2p$ electron actually passing near the nucleus, hence the effective charge it experiences will be $Z_{\text{eff}} > +1e$. Therefore, an electron in the $2s$ subshell will experience a more attractive potential than a $2p$ electron and will thus lie lower in energy. The electronic structure of Li is $1s^2 2s^1$. The third electron has the quantum numbers $(2, 0, 0, \pm 1/2)$.

How many electrons may be in each subshell in order not to violate the Pauli exclusion principle?

	<u>Total</u>
For each m_ℓ : two values of m_s	2
For each ℓ : $(2\ell + 1)$ values of m_ℓ	$2(2\ell + 1)$

Thus each $n\ell$ subshell can have $2(2\ell + 1)$ electrons. The $1s, 2s, 3s, 4s$ subshells may have only two electrons. The $2p, 3p, 4p$ subshells may have up to six. The $3d, 4d, 5d$ subshells may have up to ten.

We can now describe the electronic configurations of many-electron atoms. Although there are effects due to internal magnetic fields, in the absence of external magnetic fields the m_ℓ and m_s quantum numbers do not affect the atom's total energy. Thus, the different states available within the same subshell are nearly degenerate. For a qualitative understanding we need only refer to $n\ell$.

The filling of electrons in an atom generally proceeds until each subshell is full. When a subshell has its maximum number of electrons, we say it is *closed* or *filled*. Electrons with lower ℓ values spend more time inside the (inner) closed shells. Classically, we understand this result, because the lower ℓ values have more elliptical orbits than the higher ℓ values. The electrons with higher ℓ values are therefore more shielded from the nuclear charge $+Ze$, feel less Coulomb attraction, and lie higher in energy than those with lower ℓ values. For a given n the subshells fill in the order s, p, d, f, g, \dots . This shielding effect becomes so pronounced that the $4s$ subshell actually fills before the $3d$ subshell even though it has a larger n . This happens often as the higher-lying shells fill with electrons. Experimental evidence shows that the order of subshell filling given in Table 8.1 is generally correct. There are some important variations from this order, which produce the rare earth lanthanides and actinides. A schematic diagram of the subshell energy levels is shown in Figure 8.1.

One nomenclature for identifying atoms is ${}_Z X$ where Z is the atomic number of the element (the number of protons), and X is the chemical symbol that

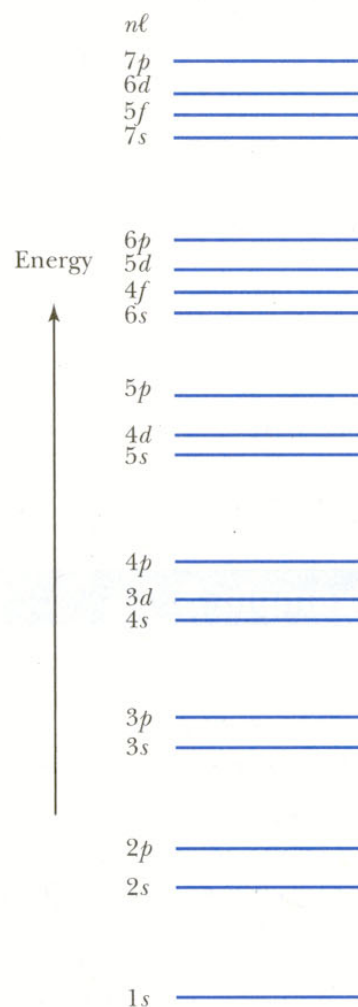


FIGURE 8.1 Approximate energy ordering of the subshells for the outermost electron in an atom. This representation assumes that the given subshell is receiving its first electron and that all lower subshells are full and all higher subshells are empty.

*"Screened" in this case means the electron will react to both the $+3e$ nucleus charge and $-2e$ electron charge within its own orbit.

TABLE 8.1
Order of Electron Filling in Atomic Subshells

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

identifies the element. The number of electrons in a neutral atom is Z . The Z is superfluous because every element has a unique Z . For example, ${}_8\text{O}$ and O stand for the same element, because oxygen has $Z = 8$. In Chapter 12 we will discuss isotopes of elements in which the mass number of the element may vary because the number of neutrons in the nucleus may be different.

Example 8.1

Give the electron configuration and the $n\ell$ value of the last electrons in the subshell (called *valence electrons*) for the following atoms: ${}_{11}\text{Na}$, ${}_{18}\text{Ar}$, ${}_{20}\text{Ca}$, ${}_{35}\text{Br}$.

Solution: ${}_{11}\text{Na}$: Sodium has 11 electrons, 10 of which are in the filled $1s^2 2s^2 2p^6$ subshells, which is called the *core* because it is filled. According to the order of filling given in Table 8.1, the extra electron must be in the $3s$ subshell with $n = 3$, $\ell = 0$. The electronic configuration is then $1s^2 2s^2 2p^6 3s^1$. The chemical properties of Na are determined almost exclusively by this one extra electron outside the core. The core is rather inert with the orbital and intrinsic angular momenta of the electrons paired to zero.

${}_{18}\text{Ar}$: From Table 8.1 we see that 18 electrons complete the $3p$ subshell, so the last electron has $n = 3$, $\ell = 1$, and the electronic configuration is $1s^2 2s^2 2p^6 3s^2 3p^6$. Argon has completely closed subshells and no extra (valence) electrons.

This is the reason argon, one of the inert gases, is chemically inactive.

${}_{20}\text{Ca}$: After Ar the next two electrons go into the $4s$ subshell, so $n = 4$, $\ell = 0$, and the electronic configuration for calcium is $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$. There is a rather large energy gap between the $3p$ subshell and the $4s$ and $3d$ subshells (see Figure 8.1). The two electrons in the $4s$ subshell are situated rather precariously outside the inert core of Ar and can react strongly with other atoms.

${}_{35}\text{Br}$: One more electron past ${}_{35}\text{Br}$ finishes the $4p$ subshell and makes the strongly inert gas krypton. The last electron in ${}_{35}\text{Br}$ has $n = 4$ and $\ell = 1$, and the electronic configuration of the last few subshells is $3p^6 4s^2 3d^{10} 4p^5$. Bromine badly needs one more electron to complete its subshell and is very active chemically with a high electron affinity—searching for that last electron to fill its $4p$ subshell.

It is now relatively easy to understand the structure of the periodic table shown in Figure 8.2. The ordering of electrons into subshells follows from the two rules of Equation (8.1). In Figure 8.2 the horizontal groupings are according to separate subshells. Atomic electron configurations are often denoted by only the last subshell, and all previous subshells are assumed to be filled. In

Periodic Table of Elements

Closed shells	Alkaline earths		Transition elements										Rare Halogens gases						
Groups:	1	2											13	14	15	16	17	18	
	1																		2
	H																		He
	$1s$																		$1s^2$
	3	4											5	6	7	8	9	10	
$1s^2$	Li	Be											B	C	N	O	F	Ne	
	$2s^1$	$2s^2$											$2s^2 2p^1$	$2s^2 2p^2$	$2s^2 2p^3$	$2s^2 2p^4$	$2s^2 2p^5$	$2s^2 2p^6$	
	11	12											13	14	15	16	17	18	
$2s^2 2p^6$	Na	Mg											Al	Si	P	S	Cl	Ar	
	$3s^1$	$3s^2$											$3s^2 3p^1$	$3s^2 3p^2$	$3s^2 3p^3$	$3s^2 3p^4$	$3s^2 3p^5$	$3s^2 3p^6$	
	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	
$3s^2 3p^6$	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr	
	$4s^1$	$4s^2$	$3d^1 4s^2$	$3d^2 4s^2$	$3d^3 4s^2$	$3d^5 4s^1$	$3d^5 4s^2$	$3d^6 4s^2$	$3d^7 4s^2$	$3d^8 4s^2$	$3d^{10} 4s^1$	$3d^{10} 4s^2$	$3d^{10} 4s^2$	$3d^{10} 4s^2$	$3d^{10} 4s^2$	$3d^{10} 4s^2$	$3d^{10} 4s^2$	$3d^{10} 4s^2$	
	37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54	
$3d^{10} 4s^2 4p^6$	Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe	
	$5s^1$	$5s^2$	$4d^1 5s^2$	$4d^2 5s^2$	$4d^4 5s^1$	$4d^5 5s^1$	$4d^6 5s^1$	$4d^7 5s^1$	$4d^8 5s^1$	$4d^{10}$	$4d^{10} 5s^1$	$4d^{10} 5s^2$	$4d^{10} 5s^2$	$4d^{10} 5s^2$	$4d^{10} 5s^2$	$4d^{10} 5s^2$	$4d^{10} 5s^2$	$4d^{10} 5s^2$	
	55	56	57	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86	
$4d^{10} 5s^2 5p^6$	Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn	
	$6s^1$	$6s^2$	$5d^1 6s^2$	$4f^{14} 5d^2 6s^2$	$4f^{14} 5d^3 6s^2$	$4f^{14} 5d^4 6s^2$	$4f^{14} 5d^5 6s^2$	$4f^{14} 5d^6 6s^2$	$4f^{14} 5d^7 6s^1$	$4f^{14} 5d^9 6s^1$	$4f^{14} 5d^{10} 6s^1$	$4f^{14} 5d^{10} 6s^2$	$4f^{14} 5d^{10} 6s^2 6p^1$	$4f^{14} 5d^{10} 6s^2 6p^2$	$4f^{14} 5d^{10} 6s^2 6p^3$	$4f^{14} 5d^{10} 6s^2 6p^4$	$4f^{14} 5d^{10} 6s^2 6p^5$	$4f^{14} 5d^{10} 6s^2 6p^6$	
	87	88	89	104	105	106	107	108	109	110	111	112							
$4f^{14} 5d^{10} 6s^2 6p^6$	Fr	Ra	Ac	Rf	Db	Sg	Bh	Hs	Mt										
	$7s^1$	$7s^2$	$6d^1 7s^2$	$5f^{14} 6d^2 7s^2$	$5f^{14} 6d^3 7s^2$	$5f^{14} 6d^4 7s^2$	$5f^{14} 6d^5 7s^2$	$5f^{14} 6d^6 7s^2$	$5f^{14} 6d^7 7s^2$	$5f^{14} 6d^9 7s^1$	$5f^{14} 6d^{10} 7s^1$	$5f^{14} 6d^{10} 7s^2$							
			Lanthanides																
			58	59	60	61	62	63	64	65	66	67	68	69	70	71			
			Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu			
			$4f^2 6s^2$	$4f^3 6s^2$	$4f^4 6s^2$	$4f^5 6s^2$	$4f^6 6s^2$	$4f^7 6s^2$	$4f^7 6s^2$	$4f^9 6s^2$	$4f^{10} 6s^2$	$4f^{11} 6s^2$	$4f^{12} 6s^2$	$4f^{13} 6s^2$	$4f^{14} 6s^2$	$4f^{14} 5d^1 6s^2$			
					Actinides														
			90	91	92	93	94	95	96	97	98	99	100	101	102	103			
			Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr			
			$6d^2 7s^2$	$5f^2 6d^1 7s^2$	$5f^3 6d^1 7s^2$	$5f^4 6d^1 7s^2$	$5f^6 7s^2$	$5f^7 7s^2$	$5f^7 6d^1 7s^2$	$5f^8 6d^1 7s^2$	$5f^{10} 7s^2$	$5f^{11} 7s^2$	$5f^{12} 7s^2$	$5f^{13} 7s^2$	$5f^{14} 7s^2$	$5f^{14} 6d^1 7s^2$			

FIGURE 8.2 The atomic number and element symbol are given in the top of each box. The electron configuration for each element is specified by giving the values of the principal quantum numbers n , the angular momentum quantum numbers ℓ (s , p , d , or f), and the number of electrons outside closed shells. The configuration of some of the closed shells is given on the left.

Figure 8.2 only the last unfilled subshell configurations are shown. There are occasions when a smooth order doesn't occur. For example, ${}_{40}\text{Zr}$ has $5s^24d^2$, that is, the $5s$ subshell is filled, but the next element, ${}_{41}\text{Nb}$, has the structure $5s^14d^4$. An electron has been taken from the $5s$ subshell and placed in the $4d$ subshell with an additional electron to make a total of four electrons in the $4d$ subshell. There are several such unusual cases as the atomic number increases. These details reflect the complex electron–electron interactions in a system of many particles.

Groups and periods

Let us briefly review some of the special arrangements of the periodic table. The vertical columns (or **groups**) have similar chemical and physical properties. This occurs because they have the same valence electron structure—that is, they have the same number of electrons in an ℓ orbit and can form similar chemical bonds. The horizontal rows are called **periods**, and they correspond to filling of the subshells. For example, in the fourth row the $4s$ subshell is filled first with 2 electrons, next the $3d$ subshell is filled with 10 electrons, and finally the $4p$ subshell is filled with 6 electrons. The fourth row consists of 18 elements and the filling of the $4s$, $3d$, and $4p$ subshells.

FIGURE 8.3 The ionization energies of the elements are shown versus the atomic numbers. The element symbols are shown for the peaks and valleys with the subshell closure in parentheses where appropriate. When a single electron is added to the p and d subshells, the ionization energy significantly decreases indicating the shell effects of atomic structure.

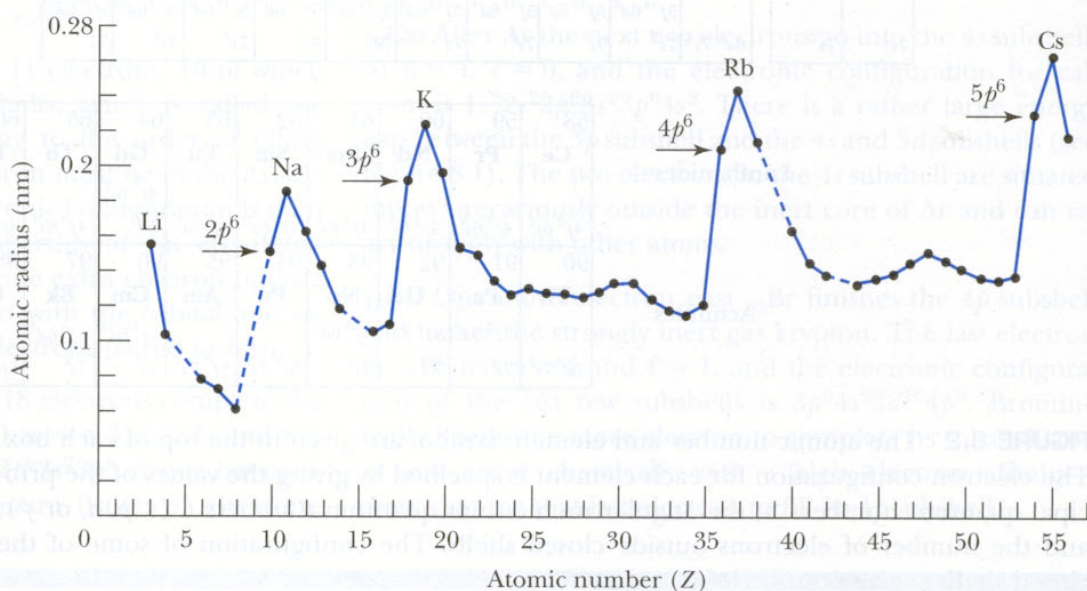
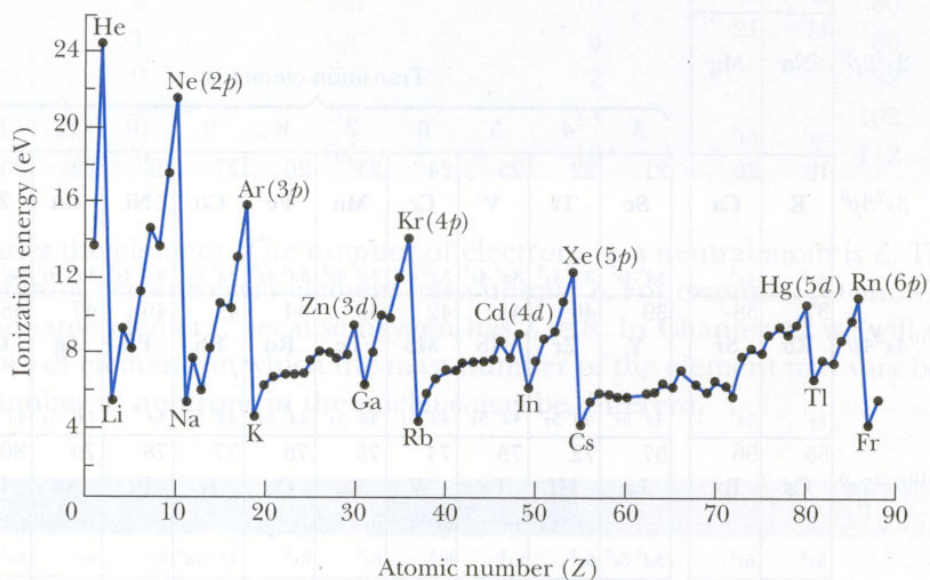


FIGURE 8.4 Atomic radii from ionic crystal atomic data. The radii are the smallest when the subshells are filled.

In order to compare some properties of elements we show the ionization energies of elements in Figure 8.3 and atomic radii in Figure 8.4. (The ionization energy is the energy required to remove the most weakly bound electron, forming a positive ion.) The electrical conductivity and resistivity also show subshell effects. Good electrical conductors need free electrons that are only weakly bound to their nuclei. In Chapter 10 we shall see similar patterns in superconducting properties. The differences according to subshells are remarkable.

Inert Gases

The last group of the periodic table is the inert gases. They are unique in that they all have closed subshells, a p subshell except for helium. They have no valence electrons, and the p subshell is tightly bound. These elements therefore are inert chemically. They do not easily form chemical bonds with other atoms. They have zero net spins, large ionization energies (Figure 8.3), and poor electrical conductivities. Their boiling points are quite low, and at room temperature they are monoatomic gases, because their atoms interact so weakly with each other.

Alkalis

Hydrogen and the alkali metals (Li, Na, K, etc.) form Group 1 of the periodic table. They have a single s electron outside an inert core. This electron can be easily removed, so the alkalis easily form positive ions with a charge $+1e$. Therefore, we say that their *valence* is $+1$. Figure 8.3 shows that the alkali metals have the lowest ionization energies. The drop in ionization energies between the inert gases and the alkalis is precipitous. The alkali metals are relatively good electrical conductors, because the valence electrons are free to move around from one atom to another.

Alkaline Earths

The alkaline earths are in Group 2 of the periodic table. These elements (Be, Mg, Ca, Sr, etc.) have two s electrons in their outer subshell, and although these subshells are filled, the s electrons can extend rather far from the nucleus and can be relatively easily removed. The alkali metals and alkaline earths have the largest atomic radii (Figure 8.4), because of their loosely bound s electrons. The ionization energies (Figure 8.3) of the alkaline earths are also low, but their electrical conductivity is high. The valence of these elements is $+2$, and they are rather active chemically.

Halogens

Immediately to the left of the inert gases, Group 17 lacks one electron from having a filled outermost subshell. These elements (F, Cl, Br, I, etc.) all have a valence of -1 and are chemically very active. They form strong ionic bonds (for example, NaCl) with the alkalis (valence $+1$) by gaining the electron given up easily by the alkali atom. In effect, a compound such as NaCl consists of a Na^+ and a Cl^- ion strongly bound by their mutual Coulomb interaction. The groups to the immediate left of the halogens have fewer electrons in the p shell. In Figure 8.4 it is apparent that the radii of the p subshell decrease as electrons are added. A more stable configuration occurs in the p subshell as it is filled, resulting in a more tightly bound atom.

Transition Metals

The three rows of elements in which the $3d$, $4d$, and $5d$ subshells are being filled are called the *transition elements* or *transition metals*. Their chemical properties are similar—primarily determined by the s electrons, rather than by the d subshell being filled. This occurs because the s electrons, with higher n values, tend to have greater radii than the d electrons. The filling of the $3d$ subshell leads to some important characteristics for elements in the middle of the period. These elements (Fe, Co, and Ni) have several d -shell electrons with unpaired spins (as dictated by Hund's rules, see Section 8.2). The spins of neighboring atoms in a crystal lattice align themselves, producing large magnetic moments and the ferromagnetic properties of these elements (see Section 10.4). As the d subshell is filled, the electron spins eventually pair off, and the magnetic moments, as well as the tendency for neighboring atoms to align spins, are reduced.

Lanthanides

The lanthanides ($_{58}\text{Ce}$ to $_{71}\text{Lu}$), also called the *rare earths*, all have similar chemical properties. This occurs because they all have the outside $6s^2$ subshell completed while the smaller $4f$ subshell is being filled. The ionization energies (see Figure 8.3) are similar for the lanthanides. As occurs in the $3d$ subshell, the electrons in the $4f$ subshell often have unpaired electrons. These unpaired electrons align themselves, and because there can be so many electrons in the f subshell, large magnetic moments may occur. The large orbital angular momentum ($\ell = 3$) also helps the large ferromagnetic effects that some of the lanthanides have. The element holmium can have an extremely large internal magnetic field at low temperatures, much larger than even that of iron.

Actinides

The actinides ($_{90}\text{Th}$ to $_{103}\text{Lr}$) are similar to the lanthanides in that inner subshells are being filled while the $7s^2$ subshell is complete. It is difficult to obtain reliable chemical data for these elements, because they are all radioactive. It is possible to keep significant quantities of a few actinide isotopes, which have sufficiently long half-lives. Examples of these are thorium-232, uranium-235, and uranium-238, which occur naturally, and neptunium-237 and plutonium-239, which are produced in the laboratory.

Example 8.2

Copper and silver have the two highest electrical conductivities. Explain how the electronic configurations of copper and silver can account for their very high electrical conductivities.

Solution: We need to refer to Figure 8.2 to investigate their electron configurations. We see that $_{28}\text{Ni}$ has the structure $3d^84s^2$, but $_{29}\text{Cu}$ has the structure $3d^{10}4s^1$ and the next element, $_{30}\text{Zn}$, has $3d^{10}4s^2$. Copper is unique in that one

electron from the $4s$ subshell has changed to the $3d$ subshell. The remaining $4s$ electron is very weakly bound—in fact it is almost free.

Something similar happens to $_{47}\text{Ag}$ in the next period. The elements on either side have completed the $4d^{10}$ subshell, and for $_{47}\text{Ag}$ the $5s$ electron is only weakly bound. The elements $_{41}\text{Nb}$ through $_{45}\text{Rh}$ have an unpaired $5s$ electron, but incomplete $4d$ subshells, and so less screening—their $5s$ electrons are less free to wander than that of $_{47}\text{Ag}$.

8.2 Total Angular Momentum

If an atom has an orbital angular momentum and a spin angular momentum due to one or more of its electrons, we expect that, as is true classically, these angular momenta combine to produce a **total angular momentum**. We learned previously, in Section 7.5, that an interaction between the orbital and spin angular momenta in one-electron atoms causes splitting of energy levels into doublets, even in the absence of external magnetic fields. In this section we shall examine how the orbital and spin angular momenta combine and see how this results in energy-level splittings.

Single-Electron Atoms

We discuss initially only atoms having a single electron outside an inert core (for example, the alkalis). For an atom with orbital angular momentum \mathbf{L} and spin angular momentum \mathbf{S} , the total angular momentum \mathbf{J} is given by

$$\mathbf{J} = \mathbf{L} + \mathbf{S} \quad (8.3)$$

Because L , L_z , S , and S_z are quantized, the total angular momentum and its z component J_z are also quantized. If j and m_j are the appropriate quantum numbers for the single electron we are considering, quantized values of J and J_z are, in analogy with the single electron of the hydrogen atom,

$$J = \sqrt{j(j+1)} \hbar \quad (8.4a)$$

$$J_z = m_j \hbar \quad (8.4b)$$

Because m_ℓ is integral and m_s is half-integral, m_j will always be half-integral. Just as the value of m_ℓ ranges from $-\ell$ to ℓ , the value of m_j ranges from $-j$ to j , and therefore j will be half-integral.

The quantizations of the magnitudes of \mathbf{L} , \mathbf{S} , and \mathbf{J} are all similar.

$$\begin{aligned} L &= \sqrt{\ell(\ell+1)} \hbar \\ S &= \sqrt{s(s+1)} \hbar \\ J &= \sqrt{j(j+1)} \hbar \end{aligned} \quad (8.5)$$

The total angular momentum quantum number for the single electron can only have the values

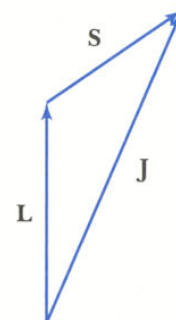
$$j = \ell \pm s \quad (8.6)$$

which, because $s = 1/2$, can only be $\ell + 1/2$ or $\ell - 1/2$ (but j must be $1/2$ if $\ell = 0$). The relationships of \mathbf{J} , \mathbf{L} , and \mathbf{S} are shown in Figure 8.5. For an ℓ value of 1, the quantum number j is $3/2$ or $1/2$, depending on whether \mathbf{L} and \mathbf{S} are aligned or antialigned. The notation commonly used to describe these states is

$$nL_j \quad (8.7)$$

where n is the principal quantum number, j the total angular momentum quantum number, and L is an uppercase letter (S , P , D , etc.) representing the orbital angular momentum quantum number.

Total angular momentum



$$\begin{aligned} j &= \ell + s \\ &= 1 + \frac{1}{2} = \frac{3}{2} \end{aligned}$$



$$\begin{aligned} j &= \ell - s \\ &= 1 - \frac{1}{2} = \frac{1}{2} \end{aligned}$$

FIGURE 8.5 When forming the total angular momentum from the orbital and spin angular momenta, the addition must be done vectorially, $\mathbf{J} = \mathbf{L} + \mathbf{S}$. We show schematically the addition of \mathbf{L} and \mathbf{S} with $\ell = 1$ and $s = 1/2$ to form vectors \mathbf{J} with quantum numbers $j = 1/2$ and $3/2$.

Spin-orbit coupling

In Section 7.5 we briefly mentioned that the single electron of the hydrogen atom can feel an internal magnetic field $\mathbf{B}_{\text{internal}}$ due to the proton, which in the rest system of the electron appears to be circling it (see Figure 7.10). A careful examination of this effect shows that the spin of the electron and the orbital angular momentum can be coupled, an effect called *spin-orbit coupling*. The potential energy $V_{s\ell}$ will be equal to $-\boldsymbol{\mu}_s \cdot \mathbf{B}_{\text{internal}}$. The spin magnetic moment is proportional to $-\mathbf{S}$, and $\mathbf{B}_{\text{internal}}$ is proportional to \mathbf{L} , so that $V_{s\ell} \sim \mathbf{S} \cdot \mathbf{L} = SL \cos \alpha$, where α is the angle between \mathbf{S} and \mathbf{L} . The result of this effect is to make the states with $j = \ell - 1/2$ slightly lower in energy than for $j = \ell + 1/2$, because α is smaller when $j = \ell + 1/2$. The same applies for the atom when placed in an external magnetic field. The same effect leads us to accept j and m_j as better quantum numbers than m_ℓ and m_s , even for single-electron atoms like hydrogen. We mean “better” in this case, because j and m_j are more directly related to a physical observable. A given state having a definite energy can no longer be assigned a definite L_z and S_z , but it can have a definite J_z . The wave functions will now depend on n , ℓ , j , and m_j . The spin-orbit interaction splits the $2P$ level into two states, $2P_{3/2}$ and $2P_{1/2}$, with $2P_{1/2}$ being lower in energy. There are additional relativistic effects, which will not be discussed here, that give corrections to the spin-orbit effect.

In the absence of an external magnetic field, the total angular momentum is conserved in *magnitude and direction*. The effect of the internal magnetic field is to cause \mathbf{L} and \mathbf{S} to precess about \mathbf{J} . In an external magnetic field, however, \mathbf{J} will precess about \mathbf{B}_{ext} , while \mathbf{L} and \mathbf{S} still precess about \mathbf{J} . The motion of \mathbf{L} and \mathbf{S} then becomes quite complicated.

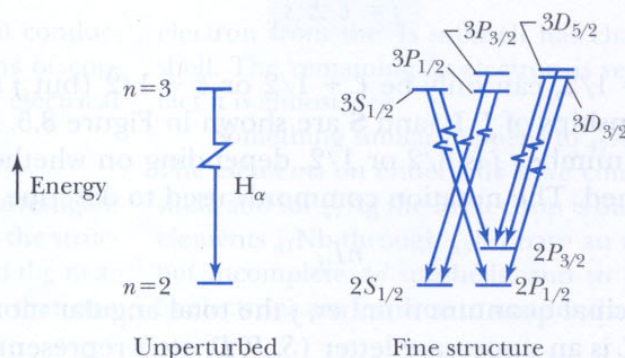
Optical spectra are due to transitions between different energy levels. We have already discussed transitions for the hydrogen atom in Section 7.6 and gave the rules listed in Equation (7.36). For single-electron atoms, we now add the selection rules for Δj . The restriction of $\Delta \ell = \pm 1$ will require $\Delta j = \pm 1$ or 0. The allowed transitions for a single-electron atom are

$$\begin{aligned} \Delta n &= \text{anything} & \Delta \ell &= \pm 1 \\ \Delta m_j &= 0, \pm 1 & \Delta j &= 0, \pm 1 \end{aligned} \quad (8.8)$$

The selection rule for Δm_j follows from our results for Δm_ℓ in Equation (7.36) and from the result that $m_j = m_\ell + m_s$, where m_s is not affected.

Figure 7.10 presented an energy-level diagram for hydrogen showing many possible transitions. We show in Figure 8.6 a highly exaggerated portion of the hydrogen energy-level diagram for $n = 2$ and $n = 3$ levels showing the spin-orbit splitting. All of the states (except for the s states) are split into doublets. What appeared in Figure 7.10 to be one transition is now actually seven different

FIGURE 8.6 At the left the unperturbed H_α line is shown due to a transition between the $n = 3$ and $n = 2$ shells of the hydrogen atom. At right is shown the more detailed level structure (not to scale) of the hydrogen atom that leads to optical fine structure. The spin-orbit interaction splits each of the $\ell \neq 0$ states.



transitions. The splitting is quite small, but measurable—typically on the order of 10^{-5} eV in hydrogen. For example, the splitting between the $2P_{3/2}$ and $2P_{1/2}$ levels has been found to be 4.5×10^{-5} eV.

We show in Figure 8.7 the energy levels of a single-electron atom, sodium, compared with that of hydrogen. The single electron in sodium is $3s^1$, and the energy levels of sodium should be similar to that of $n = 3$ and above for hydrogen. However, the strong attraction of the electrons with small ℓ causes those energy levels to be considerably lower than for higher ℓ . Notice in Figure 8.7 that the $5f$ and $6f$ energy levels of sodium closely approach the hydrogen energy levels, but the $3s$ energy level of sodium is considerably lower. The transitions between the energy levels of sodium displayed in Figure 8.7 are consistent with the selection rules of Equation (8.8).

The fine splitting of the levels for different j are too small to be seen in Figure 8.7. Nevertheless these splittings are important, and they are easily detected in the optical spectra of sodium. The energy levels $3P_{3/2}$ and $3P_{1/2}$ are separated by about 2×10^{-3} eV, for example. This splits the $3p \rightarrow 3s$ (~ 2.1 eV) optical line into a doublet: the famous yellow sodium doublet, with $\lambda = 589.0$ nm and 589.6 nm (see also Example 8.6).

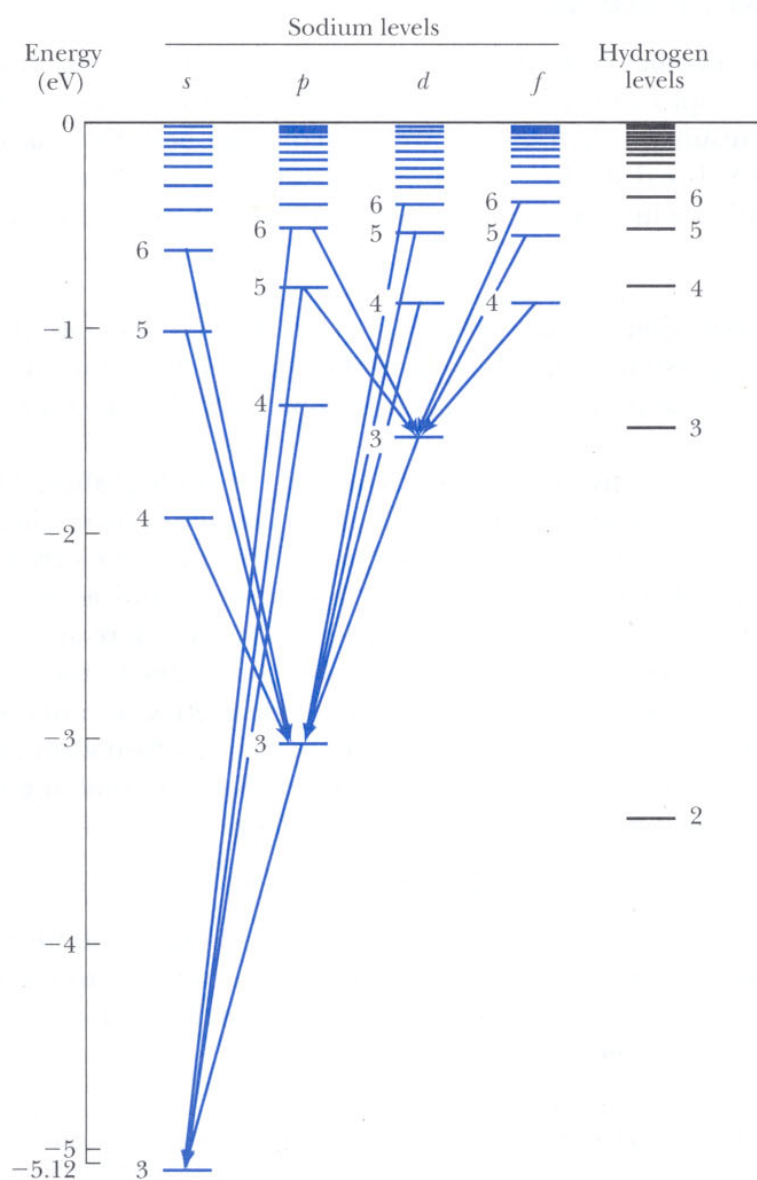


FIGURE 8.7 The energy-level diagram of sodium (single electron outside inert core) is compared to that of hydrogen. Coulomb effects cause the lower ℓ states of sodium to be lower than the corresponding levels of hydrogen. Several allowed transitions are shown for sodium.

Example 8.3

Show that an energy difference of 2×10^{-3} eV for the $3p$ subshell of sodium accounts for the 0.6-nm splitting of a spectral line at 589.3 nm.

Solution: The wavelength λ of a photon is related to the energy of a transition by

$$E = \frac{hc}{\lambda}$$

For a small splitting, we approximate by using a differential,

$$dE = \frac{-hc}{\lambda^2} d\lambda$$

Then, letting $\Delta E = dE$ and $\Delta\lambda = d\lambda$ and taking absolute values yields

$$|\Delta E| = \frac{hc}{\lambda^2} |\Delta\lambda| \quad \text{or} \quad |\Delta\lambda| = \frac{\lambda^2}{hc} |\Delta E|$$

$$|\Delta\lambda| = \frac{(589.3 \text{ nm})^2 (2 \times 10^{-3} \text{ eV})}{1.240 \times 10^3 \text{ eV} \cdot \text{nm}} = 0.6 \text{ nm}$$

Many-Electron Atoms

The situation becomes formidable for more than two electrons outside an inert core. Various empirical rules (for example, Hund's rules) help in applying the quantization results to such atoms. We will consider here the case of two electrons outside a closed shell (for example, helium and the alkaline earths.)*

The order in which a given subshell is filled is governed by Hund's rules, which state that

Hund's rules

1. The total spin angular momentum S should be maximized to the extent possible without violating the Pauli exclusion principle.
2. Insofar as Rule 1 is not violated, L should also be maximized.

For example, the first five electrons to occupy a d subshell should all have the same value of m_s . This requires that each one has a different m_ℓ (because the allowed m_ℓ values are $-2, -1, 0, 1, 2$). By Rule 2 the first two electrons to occupy a d subshell should have $m_\ell = 2$ and $m_\ell = 1$ or $m_\ell = -2$ and $m_\ell = -1$.

Besides the spin-orbit interaction already discussed, there are now spin-spin and orbital-orbital interactions. There are also effects due to the spin of the nucleus that lead to *hyperfine* structure, but the nuclear effect is much smaller than the ones we are presently considering. For the two-electron atom, we label the electrons 1 and 2 so that we have $\mathbf{L}_1, \mathbf{S}_1$ and $\mathbf{L}_2, \mathbf{S}_2$. The total angular momentum \mathbf{J} is the vector sum of the four angular momenta:

$$\mathbf{J} = \mathbf{L}_1 + \mathbf{L}_2 + \mathbf{S}_1 + \mathbf{S}_2 \quad (8.9)$$

There are two schemes, called *LS coupling* and *jj coupling*, for combining the four angular momenta to form J . The decision of which scheme to use depends on relative strengths of the various interactions. We shall see that *jj coupling* predominates for heavier elements.

*The reader is referred to H. G. Kuhn's *Atomic Spectra* 2nd ed. New York: Academic Press, 1969, or H. E. White's *Introduction to Atomic Spectra* New York: McGraw-Hill, 1934 for further study.

LS, or Russell-Saunders, Coupling

The LS coupling scheme is used for most atoms when the magnetic field is weak. The orbital angular momenta \mathbf{L}_1 and \mathbf{L}_2 combine to form a total orbital angular momentum \mathbf{L} and similarly for \mathbf{S} .

$$\mathbf{L} = \mathbf{L}_1 + \mathbf{L}_2 \quad (8.10)$$

$$\mathbf{S} = \mathbf{S}_1 + \mathbf{S}_2 \quad (8.11)$$

Then \mathbf{L} and \mathbf{S} combine to form the total angular momentum.

$$\mathbf{J} = \mathbf{L} + \mathbf{S} \quad (8.12)$$

One of Hund's rules states that the electron spins combine to make \mathbf{S} a maximum. Physically this occurs because of the mutual repulsion of the electrons, which want to be as far away from each other as possible in order to have the lowest energy. If two electrons in the same subshell have the same m_s , they must then have different m_ℓ , normally indicating different spatial distributions. Similarly, the lowest energy states normally occur with a maximum \mathbf{L} . We can understand this physically, because the electrons would revolve around the nucleus in the same direction if aligned, thus staying as far apart as possible. If \mathbf{L}_1 and \mathbf{L}_2 were antialigned, they would pass each other more often, tending to have a higher interaction energy.

For the case of two electrons the total spin angular momentum quantum number* may be $S = 0$ or 1 depending on whether the spins are antiparallel or parallel. For a given value of L , there are $2S + 1$ values of J , because J goes from $L - S$ to $L + S$ (for $L > S$). For $L < S$ there are fewer than $2S + 1$ possible values of J (see Examples 8.4 and 8.5). The value of $2S + 1$ is called the **multiplicity** of the state.

The notation nL_j discussed before for a single-electron atom becomes

$$n^{2S+1}L_j \quad (8.13)$$

This code is called *spectroscopic* or *term symbols*. For two electrons we have **singlet** states ($S = 0$) and **triplet** states ($S = 1$), which refer to the multiplicity $2S + 1$. Recall that a single-electron state (with $s = 1/2$) is a doublet, with $2s + 1 = 2$.

Consider two electrons: One is in the $4p$ and one is in the $4d$ subshell. We have the following possibilities ($S_1 = 1/2$, $S_2 = 1/2$, $L_1 = 1$, and $L_2 = 2$) for the atomic states shown in Table 8.2. A schematic diagram showing the relative energies of these states is shown in Figure 8.8. The spin-spin interaction breaks the unperturbed state into the singlet and triplet states. The Coulomb effect, due to the electrons, orders the highest L value for each of these states to be lowest in energy. Finally, the spin-orbit splitting causes the lowest J value to be lowest in energy (\mathbf{L} and \mathbf{S} antialigned).

As an example of the optical spectra obtained from two-electron atoms, we consider the energy-level diagram of magnesium in Figure 8.9. The most obvious characteristic of this figure is that we have separated the energy levels according to whether they are $S = 0$ or $S = 1$. This is because *allowed* transitions must have

*It is customary to use capital letters, L , S , and J for the angular momentum quantum numbers of many-electron atoms. This can lead to confusion, because we are accustomed to thinking, for example, $S = |\mathbf{S}|$. To avoid confusion, remember that the magnitude of an angular momentum vector is always some number times \hbar , while the new angular momentum quantum numbers, L , S , and J are simply integers or half-integers.

Multiplicity

Spectroscopic symbols

Singlet and triplet states

TABLE 8.2
Spectroscopic Symbols for Two Electrons: One in 4*p* and One in 4*d*

<i>S</i>	<i>L</i>	<i>J</i>	Spectroscopic Symbol
0 (singlet)	1	1	4 ¹ P ₁
	2	2	4 ¹ D ₂
	3	3	4 ¹ F ₃
1 (triplet)	1	2	4 ³ P ₂
		1	4 ³ P ₁
		0	4 ³ P ₀
	2	3	4 ³ D ₃
1 (triplet)	2	2	4 ³ D ₂
		1	4 ³ D ₁
	3	4	4 ³ F ₄
1 (triplet)	3	3	4 ³ F ₃
		2	4 ³ F ₂

$\Delta S = 0$, and no allowed transitions are possible between singlet and triplet states. This does not mean that it is impossible for such transitions to occur. Remember that *forbidden* transitions occur, but with much lower probability than allowed transitions.

The two electrons in magnesium outside the closed 2*p* subshell are 3*s*². Therefore, the ground state of magnesium is 3¹S₀ (*S* = 0, *L* = 0, and *J* = 0). The 3³S₁ state (*S* = 1, *J* = 1) cannot exist because *m_s* = 1/2 for both electrons in order to have *S* = 1, and this is forbidden by the exclusion principle. A 3³S₁ state is

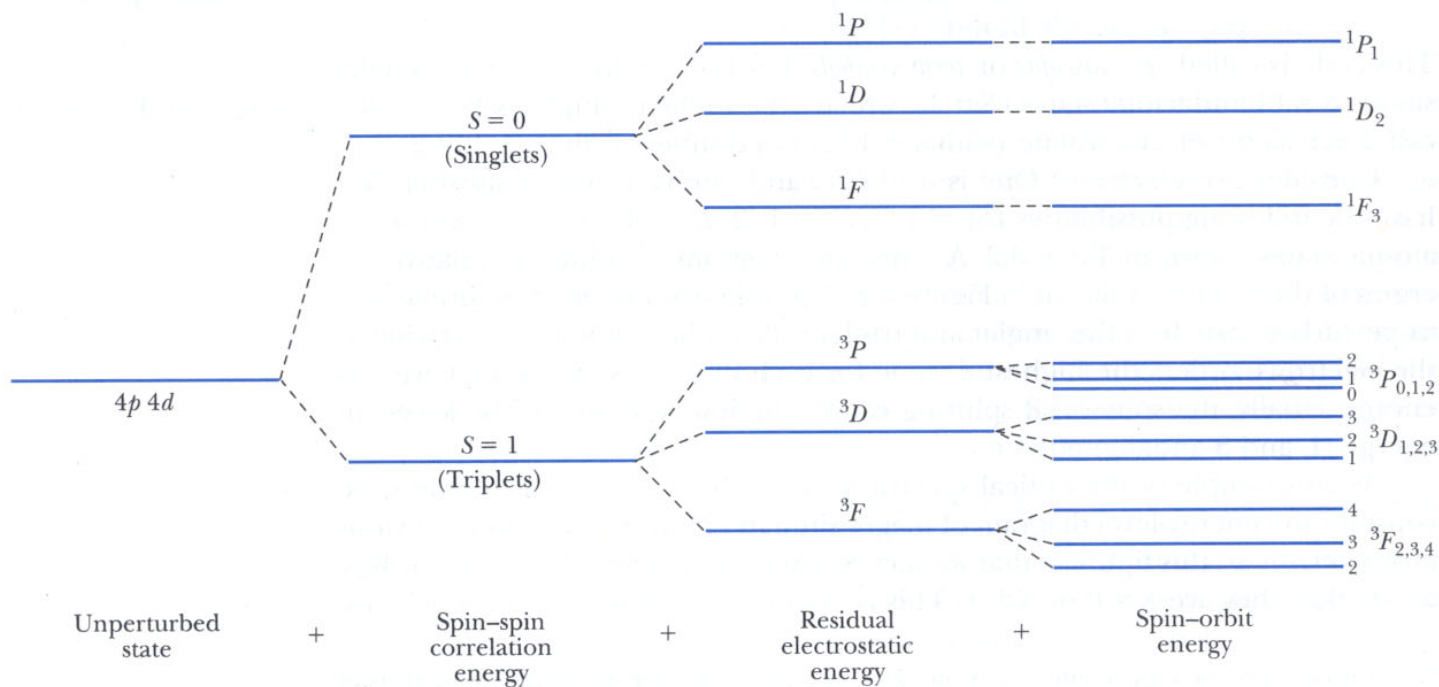


FIGURE 8.8 Schematic diagram indicating the increasing fine structure splitting due to different effects. This case is for an atom having two valence electrons, one in the 4*p* and the other in the 4*d* state. The energy is not to scale. From R. B. Leighton, *Principles of Modern Physics*, New York: McGraw-Hill, 1959, p. 261.

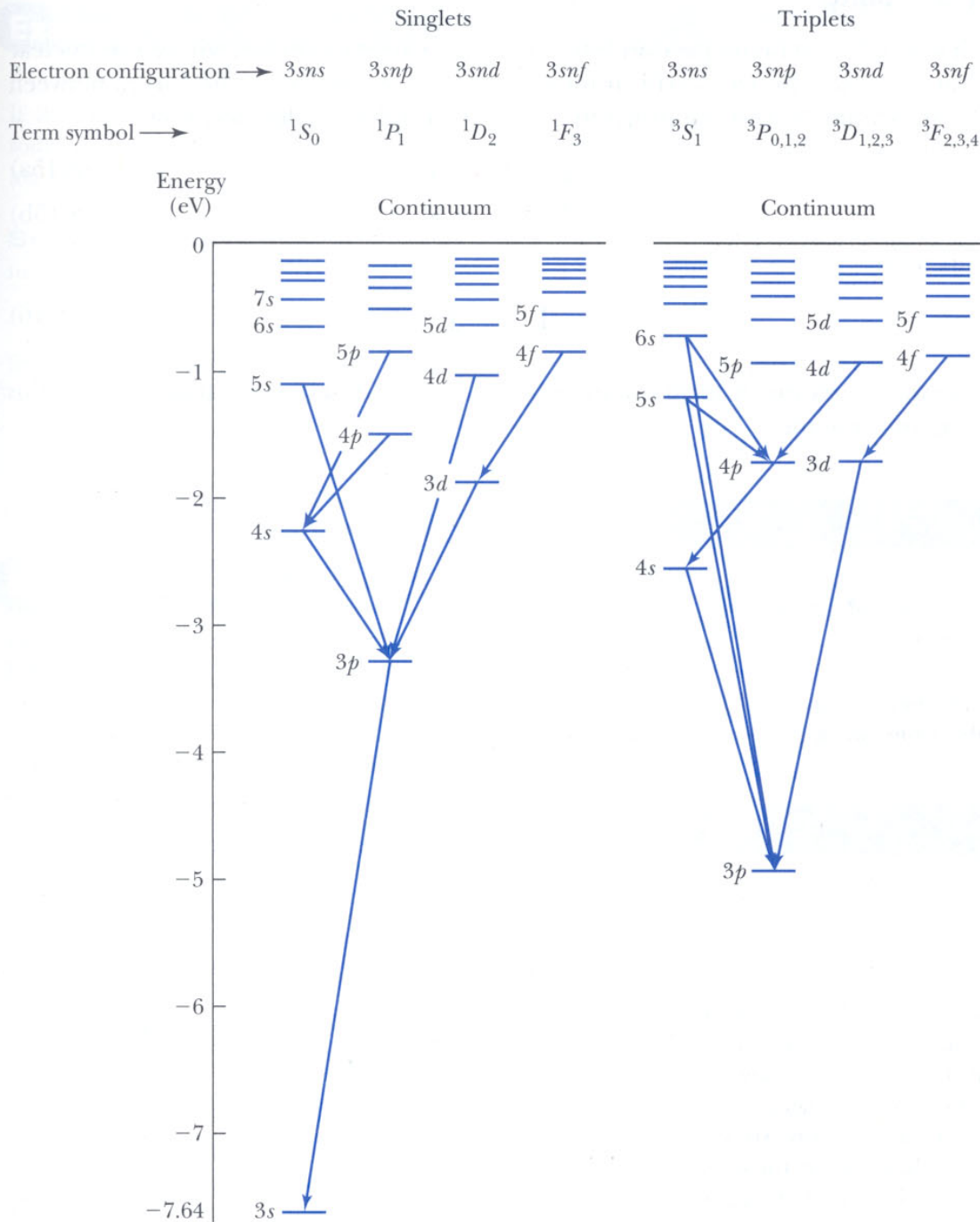


FIGURE 8.9 Energy-level diagram for magnesium with one electron in the $3s$ subshell and the other electron (two-electron atom) excited into the nl subshell indicated. The singlet and triplet states are separated, because transitions between them are not allowed by the $\Delta S = 0$ selection rule. Several allowed transitions are indicated.

allowed if one of the electrons is in a higher n shell. The energy-level diagram of Figure 8.9 is generated by one electron remaining in the $3s$ subshell while the other electron is promoted to the subshell indicated on the diagram. The allowed transitions (for the LS coupling scheme) are

$$\begin{aligned}
 \Delta L &= \pm 1 & \Delta S &= 0 \\
 \Delta J &= 0, \pm 1 & (J = 0 \rightarrow J = 0 \text{ is forbidden})
 \end{aligned}
 \tag{8.14}$$

A magnesium atom excited to the $3s3p$ triplet state has no lower triplet state to which it can decay. The only state lower in energy is the $3s3s$ ground state, which is singlet. Such an excited triplet state may exist for a relatively long time ($\gg 10^{-8}$ s) before it finally decays to the ground state as a forbidden transition. Such a $3s3p$ triplet state is called **metastable**, because it lives for such a long time on the atomic scale.

Metastable states

jj Coupling

This coupling scheme predominates for the heavier elements, where the nuclear charge causes the spin-orbit interactions to be as strong as the forces between the individual \mathbf{S}_i and the individual \mathbf{L}_i . The coupling order becomes

$$\mathbf{J}_1 = \mathbf{L}_1 + \mathbf{S}_1 \quad (8.15a)$$

$$\mathbf{J}_2 = \mathbf{L}_2 + \mathbf{S}_2 \quad (8.15b)$$

and then

$$\mathbf{J} = \sum_i \mathbf{J}_i \quad (8.16)$$

The spectroscopic or term notation is also used to describe the final states in this coupling scheme.

Example 8.4

What are the total angular momentum and the spectroscopic notation for the ground state of helium?

Solution: The two electrons for helium are both $1s$ electrons. Because helium is a light atom, we will use the

LS coupling scheme. We have $L_1 = 0$ and $L_2 = 0$, and therefore $L = 0$. We can have $S = 0$ or 1 for two electrons, but not in the same subshell. The spins must be antialigned and $S = 0$. Therefore $J = 0$ also. The ground state spectroscopic symbol for helium is 1^1S_0 .

Example 8.5

What are the L , S , and J values of the first few excited states of helium?

Solution: The lowest excited states of helium must be $1s^1 2s^1$ or $1s^1 2p^1$ —that is, one electron is promoted to either the $2s^1$ or $2p^1$ subshell. It turns out that *all* excited states of helium are single-electron states, because to excite both electrons requires more than the ionization energy. We expect the excited states of $1s^1 2s^1$ to be lower in energy than those of $1s^1 2p^1$, because the subshell $2s^1$ is lower in energy than the $2p^1$ subshell. The possibilities are:

$$1s^1 2s^1 \quad L = 0$$

$$\text{if } S = 0, \text{ then } J = 0$$

$$\text{if } S = 1, \text{ then } J = 1$$

with $S = 1$ being lowest in energy. The lowest excited state is 3S_1 and then comes 1S_0 .

$$1s^1 2p^1 \quad L = 1$$

$$\text{if } S = 0, \text{ then } J = 1$$

$$\text{if } S = 1, \text{ then } J = 0, 1, 2$$

The state 3P_0 has the lowest energy of these states, followed by 3P_1 , 3P_2 , and 1P_1 .

The energy-level diagram for helium is shown in Figure 8.10.

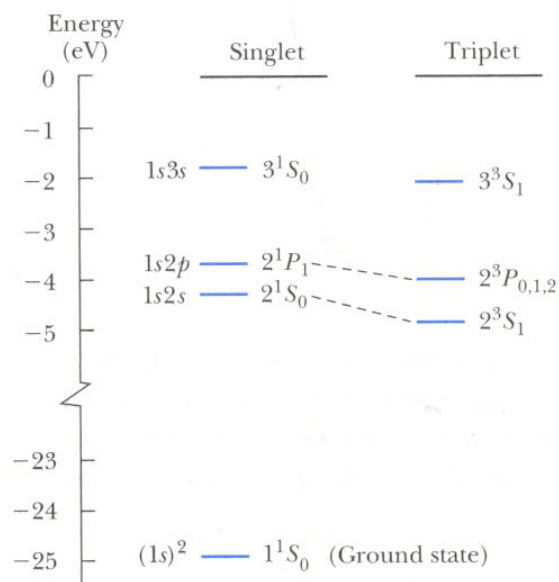


FIGURE 8.10 The low-lying atomic states of helium are shown. The ground state (1S_0) is some 20 eV below the grouping of the lowest excited states. The level indicated by $^3P_{0,1,2}$ is actually three states (3P_0 , 3P_1 , 3P_2), but the separations are too small to be indicated.

Example 8.6

If the spin-orbit splitting of the $3P_{3/2}$ and $3P_{1/2}$ states of sodium is 0.002 eV, what is the internal magnetic field causing the splitting?

Solution: The potential energy due to the spin magnetic moment is

$$V = -\boldsymbol{\mu}_s \cdot \mathbf{B} \quad (8.17)$$

By analogy with Equation (7.34), the z component of the total magnetic moment is

$$\mu_z = -g_s \left(\frac{e\hbar}{2m} \right) \frac{J_z}{\hbar} \quad (8.18)$$

where we have used the gyromagnetic ratio $g_s = 2$, because this splitting is actually due to spin. The difference in spins between the $3P_{3/2}$ and $3P_{1/2}$ states is \hbar so that

$$\Delta E = g_s \left(\frac{e\hbar}{2m} \right) \frac{\hbar}{\hbar} B = \frac{e\hbar}{m} B$$

Then

$$B = \frac{m\Delta E}{e\hbar} = \frac{(9.11 \times 10^{-31} \text{ kg})(0.002 \text{ eV})}{(1.6 \times 10^{-19} \text{ C})(6.58 \times 10^{-16} \text{ eV} \cdot \text{s})} \\ = 17 \text{ T, a large magnetic field}$$

Example 8.7

What are the possible energy states for atomic carbon?

Solution: The element carbon has two $2p$ subshell electrons outside the closed $2s^2$ subshell. Both electrons have $\ell = 1$, so we can have $L = 0, 1$, or 2 using the LS coupling scheme. The spin angular momentum is $S = 0$ or 1 . We list the possible states:

S	L	J	Spectroscopic Notation	
0	0	0	1S_0	
	1	1	1P_1	not allowed
	2	2	1D_2	
1	0	1	3S_1	not allowed
	1	0, 1, 2	$^3P_{0,1,2}$	
	2	1, 2, 3	$^3D_{1,2,3}$	not allowed

The 3S_1 state is not allowed by the Pauli exclusion principle, because both electrons in the $2p^2$ subshell would have $m_s = +1/2$ and $m_\ell = 0$. Similarly, the $^3D_{1,2,3}$ states are not allowed, because both electrons would have $m_s = +1/2$ and

$m_\ell = 1$. According to Hund's rules, the triplet states $S = 1$ will be lowest in energy, so the ground state will be one of the $^3P_{0,1,2}$ states. The spin-orbit interaction then indicates the 3P_0 state to be the ground state; the others are excited states.

The fact that the 1P_1 state is not allowed is a result of the antisymmetrization of the wave function, which we have not discussed. This rule, which requires electrons to have antisymmetric wave functions, is basically an extension of the Pauli exclusion principle for this example, and it allows the states in which the m_ℓ of the two electrons are equal to combine only with $S = 0$ states. The m_ℓ values for the electrons forming the $S = 1$ state must be unequal. This rule is the theoretical basis for Hund's rules, described previously. It precludes the 1P , 3S , and 3D states from existing for $2p^2$ electrons. The states with one electron having $m_\ell = 1$, $m_s = +1/2$ and the other with $m_\ell = 0$, $m_s = -1/2$ still exist, but they can be included in the 1D_2 state, for example, because $m_s = 0$ and $m_L = 2, 1, 0, -1, -2$.

The low-lying excited states of carbon are then 3P_1 , 3P_2 , 1D_2 , and 1S_0 .

8.3 Anomalous Zeeman Effect

In Section 7.4 we discussed the normal Zeeman effect and showed that the splitting of an optical spectral line into three components in the presence of an external magnetic field could be understood by considering the interaction ($\boldsymbol{\mu}_\ell \cdot \mathbf{B}_{\text{ext}}$) of the orbital angular momentum magnetic moment m_ℓ and the external magnetic field. Soon after the discovery of this effect by Zeeman in 1896, it was found that often more than the three closely spaced optical lines were observed. This observation was called the *anomalous* Zeeman effect. We are now

able to explain both Zeeman effects. We shall see that the anomalous effect depends on the effects of electron intrinsic spin.

The interaction that splits the energy levels in an external magnetic field \mathbf{B}_{ext} is still caused by the $\boldsymbol{\mu} \cdot \mathbf{B}$ interaction. However, the magnetic moment is due not only to the orbital contribution $\boldsymbol{\mu}_\ell$, it must depend on the spin magnetic moment $\boldsymbol{\mu}_s$ as well. The $2J + 1$ degeneracy (due to m_j) for a given total angular momentum state J is removed by the effect of the external magnetic field. If the external field \mathbf{B}_{ext} is small in comparison with the internal magnetic field (say $B_{\text{ext}} < 0.1 \text{ T}$), then \mathbf{L} and \mathbf{S} (using the LS coupling scheme) precess about \mathbf{J} while \mathbf{J} precesses *slowly* about \mathbf{B}_{ext} .

We can see this more easily by calculating $\boldsymbol{\mu}$ in terms of \mathbf{L} , \mathbf{S} , and \mathbf{J} . The total magnetic moment $\boldsymbol{\mu}$ is

$$\boldsymbol{\mu} = \boldsymbol{\mu}_\ell + \boldsymbol{\mu}_s \tag{8.19}$$

$$= -\frac{e}{2m} \mathbf{L} - \frac{e}{m} \mathbf{S} \tag{8.20}$$

where $\boldsymbol{\mu}_\ell$ is obtained from Equation (7.26) and $\boldsymbol{\mu}_s$ from Section 7.5.

$$\boldsymbol{\mu} = -\frac{e}{2m} (\mathbf{L} + 2\mathbf{S}) = -\frac{e}{2m} (\mathbf{J} + \mathbf{S}) \tag{8.21}$$

The vectors $-\boldsymbol{\mu}$ and \mathbf{J} are along the same direction only when $S = 0$. We show schematically in Figure 8.11 what is happening. The \mathbf{B}_{ext} defines the z direction. We plot $-\boldsymbol{\mu}$ instead of $+\boldsymbol{\mu}$ in order to emphasize the relationship between $\boldsymbol{\mu}$ and \mathbf{J} . In a weak magnetic field the precession of $\boldsymbol{\mu}$ around \mathbf{J} is much faster than the precession of \mathbf{J} around \mathbf{B}_{ext} . Therefore, we first find the average $\boldsymbol{\mu}_{\text{av}}$ about \mathbf{J} and then find the interaction energy of $\boldsymbol{\mu}_{\text{av}}$ with \mathbf{B}_{ext} . We leave this as an exercise for the student (see Problem 29). The result is

$$V = \frac{e\hbar B_{\text{ext}}}{2m} g m_j = \mu_B B_{\text{ext}} g m_j \tag{8.22}$$

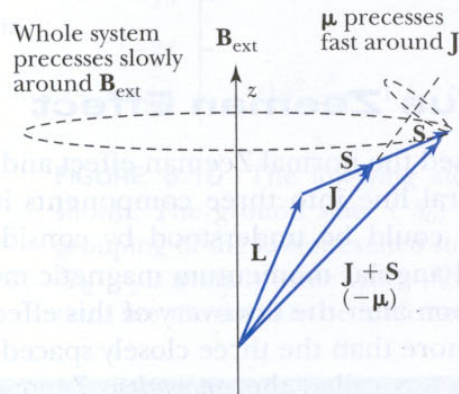
where μ_B is the Bohr magneton and

Landé g factor

$$g = 1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)} \tag{8.23}$$

is a dimensionless number called the **Landé g factor**. The magnetic total angular momentum numbers m_j range from $-J$ to J in integral steps. The external field \mathbf{B}_{ext} splits each state J into $2J + 1$ equally spaced levels separated by $\Delta E = V$, with V determined in Equation (8.22), each level being described by a different m_j .

FIGURE 8.11 Relationships between \mathbf{S} , \mathbf{L} , \mathbf{J} , and $\boldsymbol{\mu}$ are indicated. The \mathbf{B}_{ext} is the z direction. The magnetic moment $\boldsymbol{\mu}$ precesses fast around \mathbf{J} as \mathbf{J} precesses more slowly around the weak \mathbf{B}_{ext} . After J. D. McGervey, *Introduction to Modern Physics*. New York: Academic Press, 1983, p. 329.



In addition to the previous selection rules [Equation (8.14)] for photon transitions between energy levels, we must now add one for m_j :

$$\Delta m_j = \pm 1, 0 \quad (8.24)$$

but $m_{j_1} = 0 \rightarrow m_{j_2} = 0$ is forbidden when $\Delta J = 0$.

Example 8.8

Show that the normal Zeeman effect should be observed for transitions between the 1D_2 and 1P_1 states.

Solution: Because $2S + 1 = 1$ for both states, then $S = 0$ and $J = L$. The g factor from Equation (8.23) is equal to 1 (as it always will be for $S = 0$). The 1D_2 state splits into five equally spaced levels, and the 1P_1 state splits into three (see Figure 8.12). Using the selection rules from Equations (8.14) and (8.24), there are only nine allowed transi-

tions between the two states as labeled in Figure 8.12. The other transitions are disallowed by the selection rule for Δm_j . Even though there are nine different transitions, there are only three possible energies for emitted or absorbed photons, because transition energies labeled 1, 3, 6 are identical, as are 2, 5, 8, and also 4, 7, 9. Thus the three equally spaced transitions of the normal Zeeman effect are observed whenever $S = 0$.

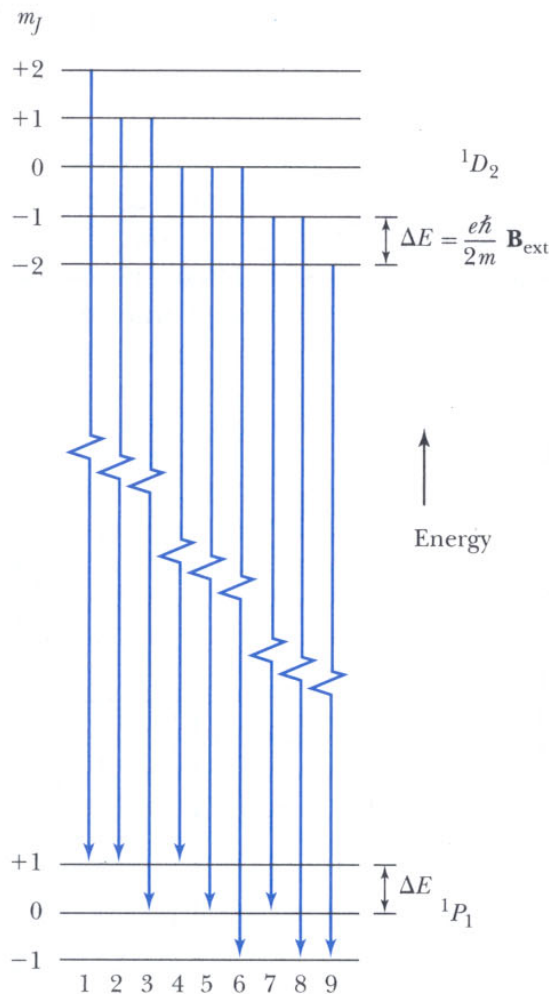


FIGURE 8.12 Examples of transitions for the normal Zeeman effect. The nine possible transitions are labeled, but there are only three distinctly different energies because the split energy levels are equally spaced (ΔE) for both the 1D_2 and 1P_1 states.

The anomalous Zeeman effect is a direct result of intrinsic spin. Let us consider transitions between the 2P and 2S states of sodium as shown in Figure 8.13. In a completely unperturbed state the ${}^2P_{3/2}$ and ${}^2P_{1/2}$ states are degenerate. However, the internal spin-orbit interaction splits them, with ${}^2P_{1/2}$ being lower in energy. The ${}^2S_{1/2}$ state is not split by the spin-orbit interaction because $\ell = L = 0$.

When sodium is placed in an external magnetic field, all three states are split into $2J + 1$ levels with different m_j (see Figure 8.13). The appropriate Landé g factors are

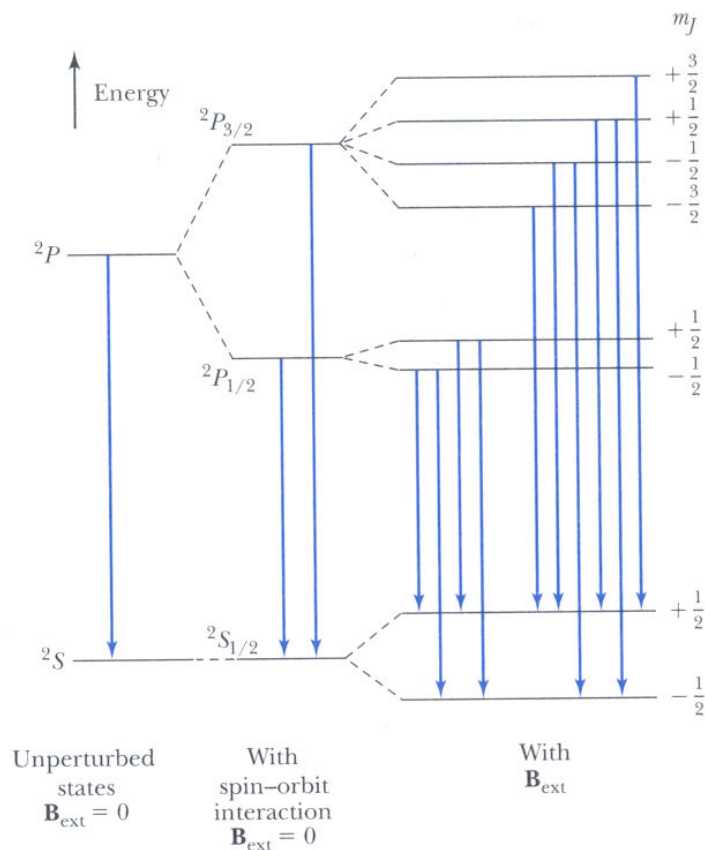
$${}^2S_{1/2} \quad g = 1 + \frac{\frac{1}{2}\left(\frac{1}{2} + 1\right) + \frac{1}{2}\left(\frac{1}{2} + 1\right)}{2 \cdot \frac{1}{2}\left(\frac{1}{2} + 1\right)} = 2$$

$${}^2P_{1/2} \quad g = 1 + \frac{\frac{1}{2}\left(\frac{1}{2} + 1\right) + \frac{1}{2}\left(\frac{1}{2} + 1\right) - 1(1 + 1)}{2 \cdot \frac{1}{2}\left(\frac{1}{2} + 1\right)} = 0.67$$

$${}^2P_{3/2} \quad g = 1 + \frac{\frac{3}{2}\left(\frac{3}{2} + 1\right) + \frac{1}{2}\left(\frac{1}{2} + 1\right) - 1(1 + 1)}{2 \cdot \frac{3}{2}\left(\frac{3}{2} + 1\right)} = 1.33$$

All g factors are different, and the energy-splitting ΔE calculated using Equation (8.22) for the three states will be different. By using the selection rules, the allowed transitions are shown in Figure 8.13. There are four different energy transitions for ${}^2P_{1/2} \rightarrow {}^2S_{1/2}$ and six different energy transitions for ${}^2P_{3/2} \rightarrow {}^2S_{1/2}$.

FIGURE 8.13 Schematic diagram of anomalous Zeeman effect for sodium (energy levels not to scale). With $\mathbf{B}_{\text{ext}} = 0$ for the unperturbed states, there is only one transition. With the spin-orbit interaction splitting the 2P state into 2 states, there are two possible transitions when $\mathbf{B}_{\text{ext}} = 0$. Finally, the \mathbf{B}_{ext} splits J into $2J + 1$ components, each with a different m_j . The energy splitting ΔE for each major state is different because $\Delta E = g m_j (e\hbar/2m) B_{\text{ext}}$ and the Landé g factor for $g[\Delta E({}^2S_{1/2})] > g[\Delta E({}^2P_{3/2})] > g[\Delta E({}^2P_{1/2})]$. All allowed transitions are shown.



If the external magnetic field is increased, then \mathbf{L} and \mathbf{S} precess too rapidly about \mathbf{B}_{ext} and our averaging procedure for $\boldsymbol{\mu}$ around \mathbf{B}_{ext} breaks down. In that case, the equations developed in this section are incorrect. This occurrence, called the *Paschen-Back effect*, must be analyzed differently. We will not pursue this calculation further.*

*See H. E. White's, *Introduction to Atomic Spectra*. New York: McGraw-Hill, 1934 for more information.

Summary

The Pauli exclusion principle states that no two electrons in an atom may have the same set of quantum numbers (n, ℓ, m_ℓ, m_s). Because electrons normally occupy the lowest energy state available, the Pauli exclusion principle may be used to produce the periodic table and understand many properties of the elements.

The total angular momentum \mathbf{J} is the vector sum of \mathbf{L} and \mathbf{S} , $\mathbf{J} = \mathbf{L} + \mathbf{S}$. The coupling of \mathbf{S} and \mathbf{L} , called the *spin-orbit interaction*, leads to lower energies for smaller values of J . For two or more electrons in an atom we can couple the \mathbf{L}_i and \mathbf{S}_i of the valence electrons by either *LS* or *jj* coupling. The spectroscopic notation for an atomic state is $n^{2S+1}L_J$.

The allowed transitions now have

$$\begin{aligned} \Delta L &= \pm 1 & \Delta S &= 0 \\ \Delta J &= 0, \pm 1 & (J = 0 \rightarrow J = 0 \text{ is forbidden}) \end{aligned} \quad (8.14)$$

The anomalous Zeeman effect is explained by the removal of the $2J + 1$ degeneracy when an atom is placed in a weak magnetic field. Each state has a different m_J , which has the selection rule for transitions of $\Delta m_J = \pm 1, 0$ (with exceptions). The normal Zeeman effect (three spectral lines) occurs when $S = 0$.

Questions

1. Explain in terms of the electron shell configuration why it is dangerous to throw sodium into water.
2. Why are the inert gases in gaseous form at room temperature?
3. Which groups of elements have the best and which the poorest electrical conductivities? Explain.
4. Why are the elements with good electrical conductivities also generally good thermal conductors?
5. Boron, carbon, and aluminum are not part of the alkalis or alkaline earths, yet they are generally good electrical conductors. Explain.
6. The alkali metals have the lowest ionization energies (Figure 8.3), yet they have the largest atomic radii (Figure 8.4). Is this consistent? Explain.
7. List four compounds that you believe should be strongly bound. Explain why.
8. Explain why the transition metals have good thermal and electrical conductivities.
9. Why do the alkaline earths have low resistivities?
10. Why is there no spin-orbit splitting for the ground state of hydrogen?
11. Is it possible for both atoms in a hydrogen molecule to be in the $(1, 0, 0, -1/2)$ state? Explain.
12. Discuss in your own words the differences between \mathbf{L} and ℓ , between m_ℓ and m_s , and between J_z and m_j .

Problems

8.1 Atomic Structure and the Periodic Table

1. A lithium atom has three electrons. Allow the electrons to interact with each other and the nucleus. Label each electron's spin and angular momentum. List all the possible interactions.
2. For all the elements through neon list the electron descriptions of these elements in their ground state using $n\ell$ notation (for example, helium is $1s^2$).
3. How many subshells are there in the following shells: L, N, and O?

- What electron configuration would you expect ($n\ell$) for the first excited state of argon and krypton?
- Using Table 8.1 and Figure 8.2 write down the electron configuration ($n\ell$ notation) of the following elements: potassium, vanadium, selenium, zirconium, samarium, and uranium.
- Using Figure 8.2 list all the (a) inert gases, (b) alkalis, and (c) alkaline earths.
- The $3s$ state of Na has an energy of -5.14 eV. Determine the effective nuclear charge.
- List the quantum numbers (n, ℓ, m_ℓ, m_s) for all the electrons in a nitrogen atom.
- What atoms have the configuration (a) $1s^2 2s^2 2p$, (b) $1s^2 2s^2 2p^6 3s$, (c) $3s^2 3p^6$?

8.2 Total Angular Momentum

- If the zirconium atom ground state has $S = 1$ and $L = 3$, what are the permissible values of J ? Write the spectroscopic notation for these possible values of S , L , and J . Which one of these is likely to represent the ground state?
- Using the information in Table 8.2, determine the ground state spectroscopic symbol for gallium.
- List all the elements through calcium that you would expect not to have a spin-orbit interaction that splits the ground state energy. Explain.
- For the hydrogen atom in the $3d$ excited state find the possible values of ℓ, m_ℓ, j, s, m_s , and m_j . Give the term notation for each possible configuration.
- What are S, L , and J for the following states: $^1S_0, ^2D_{5/2}, ^5F_1, ^3F_4$?
- What are the possible values of J_z for the $8^2G_{7/2}$ state?
- (a) What are the possible values of J_z for the $6^2F_{7/2}$ state? (b) Determine the minimum angle between the total angular momentum vector and the z axis for this state.
- Explain why the spectroscopic term symbol for lithium in the ground state is $^2S_{1/2}$.
- What is the spectroscopic term symbol for aluminum in its ground state? Explain.
- The $4P$ state in potassium is split by its spin-orbit interaction into the $4P_{3/2}$ ($\lambda = 766.41$ nm) and $4P_{1/2}$ ($\lambda = 769.90$ nm) states (the wavelengths are for the transitions to the ground state). Calculate the spin-orbit energy splitting and the internal magnetic field causing the splitting.
- Draw the energy-level diagram for the states of carbon discussed in Example 8.7. Draw lines between states that have allowed transitions and list $\Delta L, \Delta S$, and ΔJ .
- An $n = 2$ shell (L shell) has a $2s$ state and two $2p$ states split by the spin-orbit interaction. Careful measurements of the K_α x ray ($n = 2 \rightarrow n = 1$ transition) reveal only two spectral lines. Explain.
- What is the energy difference between a spin-up state and spin-down state for an electron in an s state if the magnetic field is 1.7 T?
- Which of the following elements can have either (or both) singlet and triplet states and which have neither: He, Al, Ca, Sr? Explain.
- If the minimum angle between the total angular momentum vector and the z axis is 32.3° (in a single-electron atom), what is the total angular momentum quantum number?
- Use the Biot-Savart law to find the magnetic field in the frame of an electron circling a nucleus of charge Ze . If the velocity of the electron around the nucleus is \mathbf{v} and the position vector of the proton with respect to the electron is \mathbf{r} , show that the magnetic field at the electron is

$$\mathbf{B} = \frac{Ze}{4\pi\epsilon_0} \frac{\mathbf{L}}{mc^2 r^3}$$
 where m is the electron mass and \mathbf{L} is the angular momentum, $\mathbf{L} = m\mathbf{r} \times \mathbf{v}$.
- Using the internal magnetic field of the previous problem show that the potential energy of the spin magnetic moment μ_s interacting with $\mathbf{B}_{\text{internal}}$ is given by

$$V_{se} = \frac{Ze^2}{4\pi\epsilon_0} \frac{\mathbf{S} \cdot \mathbf{L}}{m^2 c^2 r^3}$$
 There is an additional factor of $1/2$ to be added from relativistic effects called the *Thomas factor*.
- The difference between the $2P_{3/2}$ and $2P_{1/2}$ doublet in hydrogen due to the spin-orbit splitting is 4.5×10^{-5} eV. (a) Compare this with the potential energy given in the previous problem. (b) Compare this with a more complete calculation giving the potential energy term V as

$$V = -\frac{Z^4 \alpha^4}{2n^3} mc^2 \left(\frac{2}{2j+1} - \frac{3}{4n} \right)$$
 where α is the fine-structure constant, $\alpha = 1/137$.

8.3 Anomalous Zeeman Effect

- For which L and S values does an atom exhibit the normal Zeeman effect? Does this apply to both ground and excited states? Can an atom exhibit both the normal and anomalous Zeeman effects?
- Derive Equations (8.22) and (8.23). First find the average value of μ and \mathbf{J} . Use

$$\mu_{\text{av}} = (\mu \cdot \mathbf{J}) \frac{\mathbf{J}}{\mathbf{J} \cdot \mathbf{J}} \quad \text{and} \quad V = -\mu_{\text{av}} \cdot \mathbf{B}$$
 (Remember $|\mathbf{J}|^2 = J(J+1)\hbar^2$.)

30. In the early 1900s the normal Zeeman effect was useful to determine the electron's e/m if Planck's constant was assumed known. Calcium is an element that exhibits the normal Zeeman effect. The difference between adjacent components of the spectral lines is observed to be 0.013 nm for $\lambda = 422.7$ nm when calcium is placed in a magnetic field of 1.5 T. From these data calculate the value of $e\hbar/m$ and compare with the accepted value today. Calculate e/m assuming the known value of \hbar .
31. Calculate the Landé g factor for an atom with a single (a) s electron, (b) p electron, (d) d electron.
32. An atom with the states ${}^2G_{9/2}$ and ${}^2H_{11/2}$ is placed in a weak magnetic field. Draw the energy levels and indicate the possible allowed transitions between the two states.
33. Repeat the previous problem for 3P_1 and 3D_2 states.
34. With no magnetic field, the spectral line representing the transition from the ${}^2P_{1/2}$ state to the ${}^2S_{1/2}$ state in sodium has the wavelength 589.76 nm (see Figure 8.13). This is one of the two strong yellow lines in sodium. Calculate the difference in wavelength between the shortest and longest wavelength between these two states when placed in a magnetic field of 0.5 T.
35. When sodium in the ${}^2P_{3/2}$ state is placed in a magnetic field of 0.5 T, the energy level splits into four levels (see Figure 8.13). Calculate the energy difference between these levels.