## **Chapter 7**

## **Electron Configurations and the Properties of Atoms**

#### In this Chapter...

In the last chapter we introduced and explored the concept of orbitals, which define the shapes electrons take around the nucleus of an atom. In this chapter we expand this description to atoms that contain more than one electron and compare atoms that differ in their numbers of protons in the nucleus and electrons surrounding that nucleus. Much of what we know and can predict about the properties of an atom can be derived from the number and arrangement of its electrons and the energies of its orbitals, including its size, and the types and number of bonds it will form, among many other properties.

## **Chapter Outline**

- 7.1 Electron Spin and Magnetism
- 7.2 Orbital Energy
- 7.3 Electron Configuration of Elements
- 7.4 Properties of Atoms
- 7.5 Formation and Electron Configuration of Ions

Chapter Summary
Chapter Summary Assignment

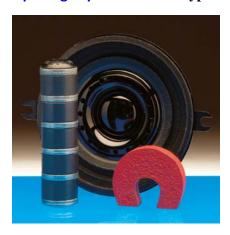
## 7.1 Electron Spin and Magnetism

#### **Section Outline**

- 7.1a Electron Spin and the Spin Quantum Number, ms
- 7.1b Types of Magnetic Materials Section Summary Assignment

In this section, we introduce the concept of electron spin and the spin quantum number,  $m_s$ . The idea of electron spin was first proposed in the 1920s and was supported by experiments that further supported the quantum theory of the atom described in the previous chapter.

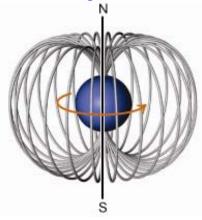
## **Opening Exploration 7.1** Types of Magnets



## 7.1a Electron Spin and the Spin Quantum Number, ms

Although electrons are too small to observe directly, we can detect the magnetic field that they exert. This magnetic field is generated by **electron spin**, the negatively charged electron spinning on an axis (**Interactive Figure 7.1.1**).

**Interactive Figure 7.1.1:** Relate electron spin and magnetic properties.



Electron spin and magnetic field

The magnetic field produced by an electron occurs in one of two directions, indicating that electron spin is quantized. That is, an electron has only two possible **spin states**. In one spin state, the electron produces a magnetic field with the North pole in one direction. In the other spin state, the North pole is in the opposite direction (**Figure 7.1.2**).

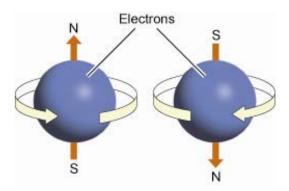


Figure 7.1.2 Electron spin and magnetic fields.

Spin states are defined by a fourth quantum number, the **spin quantum number**,  $m_s$ . Because there are two different spin states,  $m_s$  has two possible values:  $+\frac{1}{2}$  or  $-\frac{1}{2}$ . The sign of  $m_s$  is used to indicate the fact that the two spin states are in opposite directions and should not be confused with the negative charge on the electron.

**Symbolizing Electron Spin** We saw in the previous chapter that lines or boxes can be used to depict orbitals. Electrons in orbitals are shown using arrows, where the direction of the arrow indicates the spin state of the electron. For example, in the diagram that follows, the upward  $(\uparrow)$  and downward  $(\downarrow)$  arrows indicate electrons in different spin states.



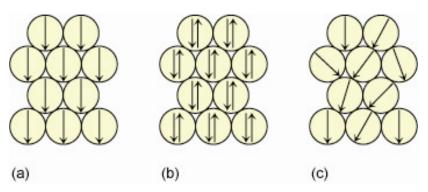
In this text, we will arbitrarily assign  $m_s = +\frac{1}{2}$  to electrons represented with an upward arrow (also called "spin up" electrons) and  $m_s = -\frac{1}{2}$  to electrons represented with a downward arrow (also called "spin down" electrons).

# **7.1b Types of Magnetic Materials**

Magnetic materials derive their magnetic behavior from the magnetic properties of their electrons. Because all electrons produce a magnetic field, you might ask the question, "Why aren't all materials magnetic?" The answer lies in the fact that the magnetic fields generated by electrons with opposite spin (in a single atom, molecule, or ion) directly counteract and cancel each other. Therefore, any atom or molecule with half spin up electrons and half spin down electrons will have a net magnetic field of zero. Two electrons with opposite spin are said to be spin paired and produce no net magnetic field. An uneven number of electrons leaves unpaired electrons. Materials with unpaired electrons are magnetic.

The magnetism of most materials can be categorized as being diamagnetic, paramagnetic, or ferromagnetic. In a **diamagnetic** material (**Interactive Figure 7.1.3(a**)), all electrons are spin paired and the material does not have a net magnetic field. These materials are slightly repelled by the magnetic field of a strong magnet.

**Interactive Figure 7.1.3:** Use spin states to predict magnetic properties.



Electron spin representations of a material with (a) diamagnetic, (b) paramagnetic, and (c) ferromagnetic properties.

**Paramagnetic** materials (**Interactive Figure 7.1.3(b)**) contain atoms, molecules, or ions with unpaired electrons. In the absence of an external, strong magnetic field, the magnetic fields generated by the individual particles are arranged in random directions and the magnetism produced by each atom or molecule can be cancelled by the magnetic fields around it. This results in a magnetic material, but one with a weak net magnetic field. However, the presence of strong, external magnet causes the individual spins to align so that the material is attracted to the magnet.

**Ferromagnetic** materials (**Interactive Figure 7.1.3(c**)), like paramagnetic materials, contain particles with unpaired electrons. In these materials, however, the individual magnetic fields align naturally and produce a strong, permanent magnetic field. The common magnets you are familiar with are ferromagnets.

## 7.2 Orbital Energy

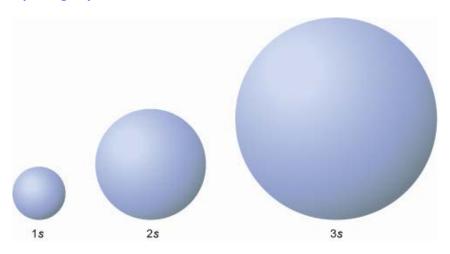
## **Section Outline**

7.2a Orbital Energies in Single- and Multielectron Species

Section Summary Assignment

In the previous chapter, we observed that the energy of an orbital in a hydrogen atom is related to its size: the larger the orbital, the higher the energy of an electron in that orbital. The size of the orbital was also shown to be dependent on the principal quantum number, n. In this section, we explore the energy of orbitals in single- and multielectron atoms.

## **Opening Exploration 7.2**



# 7.2 Orbital Energies in Single- and Multielectron Species

The relationship between the principal quantum number, n, and orbital energy is shown in an orbital energy diagram (**Figure 7.2.1**).

Figure 7.2.1 Identify Orbital Energies in Single-Electron Species



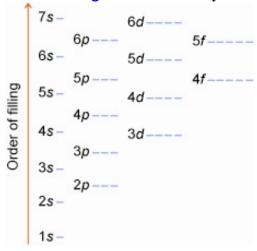
Orbital energies (n = 1 to n = 4) in a single-electron species

For a single-electron species such as a hydrogen atom, the energy of the atomic orbitals depends only on the value of n. For example, a 2p orbital in a hydrogen atom has the same energy as a 2s orbital. The energy of an orbital in a single-electron system depends only on the degree of attraction

between the electron in that orbital and the nucleus. This is mainly a function of the average distance of the electron from the nucleus, which is controlled by the principal quantum number, n.

In multielectron species such as helium atoms or sodium ions, the orbital energies depend both on the principal quantum number, n, and the type of orbital, given by the angular momentum quantum number,  $\ell$  (Interactive Figure 7.2.2). Multielectron atoms are more complex because the energy of the electron depends on both how close an electron is to the nucleus and the degree to which it experiences repulsive forces with the other electrons present in the atom or ion.

## **Interactive Figure 7.2.2:** Identify orbital energies in multi-electron species.



## Orbital energies in a multielectron species

As shown in Interactive Figure 7.2.2, subshell energies increase with increasing  $\ell$  (in a given energy level, s ).

Using Interactive Figure 7.2.2 as a reference, we can make several generalizations about orbital energies in multielectron species.

- As *n* increases, orbital energy increases for orbitals of the same type. A 4*s* orbital is higher in energy than a 3*s* orbital.
- As  $\ell$  increases, orbital energy increases. In the n = 3 shell, 3s < 3p < 3d.
- As *n* increases, the subshell energies become more closely spaced and overlapping occurs. The 4*f* orbital is higher in energy than the 5*s* orbital, despite its lower *n* value.

## 7.3 Electron Configuration of Elements

## **Section Outline**

- 7.3a The Pauli Exclusion Principle
- 7.3b Electron Configurations for Elements in Periods 1–3
- 7.3c Electron Configurations for Elements in Periods 4–7
- 7.3d Electron Configurations and the Periodic Table

Section Summary Assignment

The **electron configuration** of an element shows how electrons are distributed in orbitals—which ones are filled and which ones remain vacant. We can predict the electron configuration of

most elements, and we can use electron configurations to predict physical and chemical properties of the elements.

**Opening Exploration 7.3 Electron Configurations** 



Sulfur electron configuration:



# 7.3a The Pauli Exclusion Principle

To predict the electron configuration for an atom's **ground state**, the lowest energy state for an atom, electrons are put into the orbitals with the lowest energy possible, placing no more than two electrons in an orbital.

The order of subshell filling is related to n, the principal quantum number, and  $\ell$ , the angular momentum quantum number. In general,

- electrons fill orbitals in order of increasing  $(n + \ell)$  and
- when two or more subshells have the same  $(n + \ell)$  value, electrons fill the orbital with the lower n value.

These general rules result in the following orbital filling order:

The **Pauli exclusion principle** states that no two electrons within an atom can have the same set of four quantum numbers  $(n, \ell, m_1, \text{ and } m_s)$ . The limits on possible values for the four quantum numbers means that a single orbital can accommodate no more than two electrons, and when an orbital contains two electrons, those electrons must have opposite spins (**Figure 7.3.1**).

Figure 7.3.1 Apply the Pauli Exclusion Principle

(a) (b)

Electron arrangements in an orbital that are (a) allowed and (b) not allowed



Q1: Which orbital fills first, 4d or 5s?

4*d* 5*s* 

Q2: Is the following electron arrangement allowed or not allowed?

allowed not allowed

# 7.3b Electron Configurations for Elements in Periods 1–3

**Hydrogen and Helium** Hydrogen has a single electron that occupies the orbital with the lowest energy, the 1s orbital. Two methods are used to represent this electron configuration. The spdf **notation** (also called spectroscopic notation) has the general format  $n\ell^{\#}$ , where subshells are listed in the order in which they are filled and the number of electrons occupying each subshell is shown to the right of the subshell as a superscript. The spdf notation for hydrogen is

H: 1s<sup>1</sup> (pronounced "one-ess-one")

**Orbital box notation** uses boxes or horizontal lines to represent orbitals and arrows to represent electrons. The electron configuration of hydrogen in orbital box notation is

H: 1s

Helium has two electrons, and both occupy the lowest-energy 1s orbital. The electron configuration of helium in *spdf* notation and orbital box notation is therefore

He: 
$$1s^2$$
 (pronounced "one-ess-two") 
$$1s = 1, \ \ell = 0, \ m_\ell = 0, \ m_s = +\frac{1}{2}$$

$$1s = 1, \ \ell = 0, \ m_\ell = 0, \ m_s = -\frac{1}{2}$$

Each electron in helium has a unique set of four quantum numbers, as required by the Pauli exclusion principle. Notice that hydrogen and helium are in the first row of the periodic table and both elements fill orbitals in the first energy level (1s).

Orbital box notations provide information about the number of paired and unpaired electrons in an atom, and that information can be used to determine whether the atoms are paramagnetic or diamagnetic. Hydrogen has one unpaired electron and is a paramagnetic species, whereas helium's electrons are paired and it is diamagnetic.

**Lithium to Neon** Lithium has three electrons, two in the 1s orbital and one that is in an orbital in the second energy level. As shown previously, the 2s orbital is lower in energy than the 2p orbitals, so the electron configuration of lithium in spdf notation and orbital box notation is

Li: 
$$1s^2 2s^1$$
 1s 2s

Notice that it would be more correct to draw the orbital box notation electron configuration of lithium as shown below because the 2s orbital is higher in energy than the 1s orbital.

2s

However, it is common to show all orbitals on a horizontal line when writing orbital box notation electron configurations in order to make more efficient use of space.

Beryllium has two electrons in the 1s and the 2s orbitals.

Boron has five electrons. Four electrons fill the 1s and 2s orbitals, and the fifth electron is in a 2p orbital. Notice that the orbital box diagram shows all three 2p orbitals even though only one of the 2p orbitals is occupied.

Carbon has six electrons, four in the 1s and 2s orbitals and two in the 2p orbitals. When electrons occupy a subshell with multiple orbitals such as 2p, **Hund's rule of maximum multiplicity** applies. This rule states that the lowest-energy electron configuration is the one where the maximum number of electrons is unpaired. In the case of carbon, this means that the two 2p electrons each occupy a different 2p orbital (**Interactive Figure 7.3.2**).

**Interactive Figure 7.3.2:** Apply Hund's rule of maximum multiplicity.

Carbon's electron configuration has two unpaired electrons in the 2p orbitals.

The electron configurations of nitrogen, oxygen, fluorine, and neon are shown here. Notice that the highest-energy orbital for all second-row elements is in the second energy level (2s or 2p).

**Sodium to Argon** The elements in the third row of the periodic table have electrons that occupy orbitals in the third energy level, as shown.





When electron configurations for multielectron species are written, **noble gas notation** is often used to represent filled shells (these filled shells are also called **core electrons**). In noble gas notation, the symbol for a noble gas is written within square brackets in front of the *spdf* or orbital box notation representing additional, noncore electrons. For example, the electron configuration for chlorine is written using noble gas notation as shown here.

CI: [Ne]
$$3s^23p^5$$
 [Ne] 1 1 1 1 3 3 3 3 p

The symbol [Ne] represents the 10 lowest-energy electrons  $(1s^22s^22p^6)$  in the electron configuration.

## **EXAMPLE PROBLEM: Write electron configurations for period 1–3 elements.**

Write the electron configuration for phosphorus using orbital box notation.

#### **SOLUTION:**

You are asked to write the electron configuration for an element in orbital box notation.

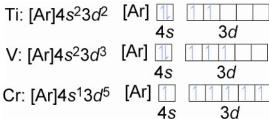
You are given the identity of the element.

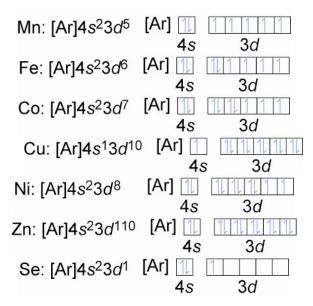
# 7.3.1T: Tutorial Assignment 7.3.1: Mastery Assignment

# 7.3c Electron Configurations for Elements in Periods 4–7

Both potassium and calcium have electron configurations similar to those of other elements in Groups 1A and 2A.

Scandium is the first transition element, and it is the first element to fill the 3d orbitals. The electron configurations of the transition elements follow Hund's rule:





Both chromium and copper have electron configurations that do not follow the general filling order, for reasons that are complex and related to the similar energies of the 4s and 3d orbitals in multielectron atoms. The electron configurations for these elements should be memorized. The electron configurations for all elements are shown in **Interactive Table 7.3.1**. There are a few exceptions to the general filling order in the heavier elements, but most elements follow the general guidelines that we have used to write electron configurations.

**Interactive Table 7.3.1** Electron Configurations of Atoms in the Ground State

Z	Element	Configuration	Z	Element	Configuration	Z	Element	Configuration
1	Н	$1s^1$	41	Nb	$[Kr]5s^14d^4$	81	Tl	$[\text{Xe}]6s^25d^{10}4f^{14}6p^1$
2	He	$1s^2$	42	Mo	$[Kr]5s^14d^5$	82	Pb	$[Xe]6s^25d^{10}4f^{14}6p^2$
3	Li	$[He]2s^1$	43	Tc	$[Kr]5s^24d^9$	83	Bi	$[Xe]6s^25d^{10}4f^{14}6p^3$
4	Be	$[He]2s^2$	44	Ru	$[Kr]5s^{1}4d^{7}$	84	Po	[Xe] $6s^25d^{10}4f^{14}6p^4$
5	В	$[He]2s^22p^1$	45	Rh	$[Kr]5s^{1}4d^{8}$	85	At	[Xe] $6s^25d^{10}4f^{14}6p^5$
6	C	[He] $2s^22p^2$	46	Pd	[Kr] $4d^{10}$	86	Rn	$[Xe]6s^25d^{10}4f^{14}6p^6$
7	N	[He] $2s^22p^3$	47	Ag	$[Kr]5s^{1}4d^{10}$	87	Fr	$[Rn]7s^1$
8	O	[He] $2s^22p^4$	48	Cd	$[Kr]5s^24d^{10}$	88	Ra	$[Rn]7s^2$
9	F	[He] $2s^22p^5$	49	In	$[Kr]5s^24d^{10}5p^1$	89	Ac	$[Rn]7s^26d^1$
10	Ne	[He] $2s^22p^6$	50	Sn	$[Kr]5s^24d^{10}5p^2$	90	Th	$[Rn]7s^26d^2$
11	Na	$[Ne]3s^1$	51	Sb	$[Kr]5s^24d^{10}5p^3$	91	Pa	$[Rn]7s^26d^15f^2$
12	Mg	$[Ne]3s^2$	52	Te	$[Kr]5s^24d^{10}5p^4$	92	U	$[Rn]7s^26d^15f^3$
13	Al	$[\text{Ne}]3s^23p^1$	53	I	$[Kr]5s^24d^{10}5p^5$	93	Np	$[Rn]7s^26d^15f^4$
14	Si	[Ne] $3s^23p^2$	54	Xe	$[Kr]5s^24d^{10}5p^6$	94	Pu	$[Rn]7s^25f^6$
15	P	$[\text{Ne}]3s^23p^3$	55	Cs	$[Xe]6s^1$	95	Am	$[Rn]7s^25f^7$
16	S	[Ne] $3s^23p^4$	56	Ba	$[Xe]6s^2$	96	Cm	$[Rn]7s^26d^15f^7$
17	Cl	[Ne] $3s^23p^5$	57	La	$[Xe]6s^25d^1$	97	Bk	$[Rn]7s^25f^9$
18	Ar	$[Ne]3s^23p^6$	58	Ce	$[Xe]6s^25d^14f^1$	98	Cf	$[Rn]7s^25f^{10}$
19	K	$[Ar]4s^1$	59	Pr	$[Xe]6s^24f^3$	99	Es	$[Rn]7s^25f^{11}$
20	Ca	$[Ar]4s^2$	60	Nd	$[Xe]6s^24f^4$	100	Fm	$[Rn]7s^25f^{12}$
21	Sc	$[Ar]4s^23d^1$	61	Pm	[Xe] $6s^24f^5$	101	Md	$[Rn]7s^25f^{13}$
22	Ti	$[Ar]4s^23d^2$	62	Sm	$[Xe]6s^24f^6$	102	No	$[Rn]7s^25f^{14}$
23	V	$[Ar]4s^23d^3$	63	Eu	$[Xe]6s^24f^7$	103	Lr	$[Rn]7s^26d^15f^{14}$
24	Cr	$[Ar]4s^13d^5$	64	Gd	$[Xe]6s^25d^14f^7$	104	Rf	$[Rn]7s^26d^25f^{14}$
25	Mn	$[Ar]4s^23d^5$	65	Tb	$[Xe]6s^24f^9$	105	Db	$[Rn]7s^26d^35f^{14}$
26	Fe	$[Ar]4s^23d^6$	66	Dy	$[Xe]6s^24f^{10}$	106	Sg	$[Rn]7s^26d^45f^{14}$
27	Co	$[Ar]4s^23d^7$	67	Но	$[Xe]6s^24f^{11}$	107	Bh	$[Rn]7s^26d^55f^{14}$
28	Ni	$[Ar]4s^23d^8$	68	Er	$[Xe]6s^24f^{12}$	108	Hs	$[Rn]7s^26d^65f^{14}$
29	Cu	$[Ar]4s^{1}3d^{10}$	69	Tm	[Xe] $6s^24f^{13}$	109	Mt	$[Rn]7s^26d^75f^{14}$
30	Zn	$[Ar]4s^23d^{10}$	70	Yb	$[Xe]6s^24f^{14}$	110	Ds	$[Rn]7s^26d^85f^{14}$
31	Ga	$[Ar]4s^23d^{10}4p^1$	71	Lu	[Xe] $6s^25d^14f^{14}$	111	Rg	$[Rn]7s^26d^95f^{14}$
32	Ge	$[Ar]4s^23d^{10}4p^2$	72	Hf	[Xe] $6s^25d^24f^{14}$	112	Cn	$[Rn]7s^26d^{10}5f^{14}$
33	As	$[Ar]4s^23d^{10}4p^3$	73	Ta	$[Xe]6s^25d^34f^{14}$	113		$[Rn]7s^26d^{10}5f^{14}7p^1$
34	Se	$[Ar]4s^23d^{10}4p^4$	74	W	$[Xe]6s^25d^44f^{14}$	114		$[Rn]7s^26d^{10}5f^{14}7p^2$
35	Br	$[Ar]4s^23d^{10}4p^5$	75	Re	$[Xe]6s^25d^54f^{14}$	115		$[Rn]7s^26d^{10}5f^{14}7p^3$
36	Kr	$[Ar]4s^23d^{10}4p^6$	76	Os	[Xe] $6s^25d^64f^{14}$	116		$[Rn]7s^26d^{10}5f^{14}7p^4$
37	Rb	$[Kr]5s^1$	77	Ir	$[Xe]6s^25d^74f^{14}$	117		$[Rn]7s^26d^{10}5f^{14}7p^5$
38	Sr	$[Kr]5s^2$	78	Pt	[Xe] $6s^15d^94f^{14}$	118		$[Rn]7s^26d^{10}5f^{14}7p^6$
39	Y	$[Kr]5s^24d^1$	79	Au	$[Xe]6s^{1}5d^{10}4f^{14}$			
40	Zr	$[Kr]5s^24d^2$	80	Hg	[Xe] $6s^25d^{10}4f^{14}$			

## **EXAMPLE PROBLEM: Write electron configurations for period 4–7 elements.**

Write electron configurations for the following elements, in *spdf* notation and orbital box notation. Identify the element as paramagnetic or diamagnetic.

(a) Zn (Do not use the noble gas notation.)

(b) Sm (Use the noble gas notation.)

## **SOLUTION:**

**You are asked** to write electron configurations in both *spdf* and orbital box notation and to identify the element as paramagnetic or diamagnetic.

You are given the identity of the element.

(a) Zinc is element 30. Use the filling order to write the electron configuration, keeping in mind the maximum number of electrons that can be accommodated in a subshell.

*spdf* notation:  $1s^22s^22p^63s^23p^64s^23d^{10}$ 

Zinc is diamagnetic because its electron configuration shows no unpaired electrons.

(b) Samarium is element 62. Use the symbol [Xe] to represent the first 54 electrons in the electron configuration.

*spdf* notation: [Xe] $6s^24f^6$ 

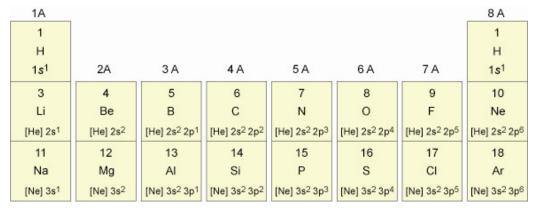
< Samarium is paramagnetic because its electron configuration shows six unpaired electrons.

7.3.2T: Tutorial Assignment 7.3.2: Mastery Assignment

# 7.3d Electron Configurations and the Periodic Table

**Interactive Figure 7.3.3** shows the electron configurations for the elements in periods 1–3, written using *spdf* notation and noble gas notation.

**Interactive Figure 7.3.3:** Relate electron configuration and the periodic table.



Electron configurations, periods 1-3

Notice that elements within a group have the following in common:

• They have the same number of electrons beyond the core electrons (represented by noble gas notation) and similar electron configurations. For example, both Li and Na have one electron

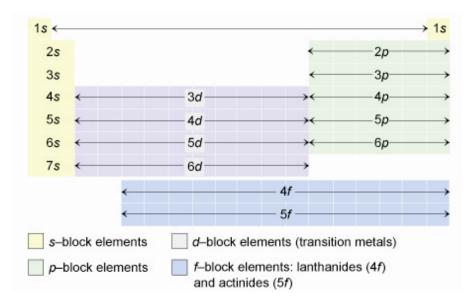
in addition to the core electrons, and both elements have the general electron configuration [noble gas] $ns^1$ .

• The number of electrons beyond the core electrons is equal to the group number (with the exception of He).

The electrons beyond the core electrons are the **valence electrons** for an element. The valence electrons are the highest-energy electrons and are the electrons least strongly attracted to the nucleus. It is these electrons that are involved in chemical reactions and the formation of chemical bonds. As shown in **Interactive Figure 7.3.3** for the Group A elements, the number of valence electrons is equal to the group number of the element. The fact that elements within a group have similar electron configurations and the same number of valence electrons suggests that elements within a group have similar properties, something we will investigate later in this chapter.

The orbital filling order is related to the structure of the periodic table, as shown in Interactive Figure 7.3.4.

# **Interactive Figure 7.3.4:** Identify electron configuration and valence electrons for element using the periodic table.



#### Subshells and the periodic table

The periodic table can be divided into four blocks, indicated by color in **Interactive Figure 7.3.4**, each of which represents the type of subshell that is filled with the highest-energy electrons for the elements in that block. Elements in Groups 1A and 2A constitute the ns-block because the highest-energy electron is assigned to the ns orbital. Groups 3A through 8A make up the np-block, where np subshells are filled last. The s-block and p-block elements are the Group A elements in the periodic table and are commonly called the main-group elements. The transition elements sit within the (n-1)d-block, and the lanthanide and actinide elements make up the (n-2)f-block.

The number of elements in each horizontal row within a block is related to the number of orbitals within that block and the number of electrons that can fill that subshell. For example, the d-block is 10 elements across because the d subshell contains five d orbitals and can accommodate a maximum of 10 electrons.

The periodic table can be used to generate electron configurations by "counting up" from hydrogen to the desired element. Each element represents the addition of one electron to an orbital. For

example, arsenic, As, is a p-block element. To "count up" to As, you begin with the first-row elements, H and He, each of which represents an electron in the 1s orbital  $(1s^2)$ . Next, Li and Be represent  $2s^2$  and B through Ne represent  $2p^6$ . Similarly, Na and Mg represent  $3s^2$  and Al through Ar represent  $3p^6$ . In the fourth row of the periodic table, K and Ca represent  $4s^2$ , Sc through Zn represent  $3d^{10}$ , and Ga through As represent three electrons in the 4p orbital,  $4p^3$ . The electron configuration of arsenic is

As:  $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^3$  [Ar] $4s^2 3d^{10} 4p^3$ 

## **7.4 Properties of Atoms**

#### **Section Outline**

7.4a Trends in Orbital Energies

7.4b Atomic Size

7.4c Ionization Energy

7.4d Electron Affinity

Section Summary Assignment

Electron configurations play a large role in determining the properties of atoms. Some of the key factors that influence atomic properties include the size of the largest occupied orbitals, the energy of the highest-energy orbitals, the number of orbital vacancies, and the number of electrons in the highest-energy orbitals. Most atomic properties can be related to the degree of attraction between the outermost electrons to the nucleus, and the number of electrons in the outermost electron shell, the number of valence electrons.

## **Opening Exploration 7.4** Orbital Energies and Atomic Properties



## 7.4a Trends in Orbital Energies

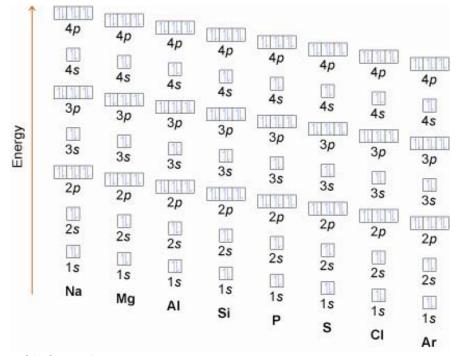
As shown in the previous section, the organization of the periodic table is closely related to electron configurations. The energy of atomic orbitals is also related to the structure of the periodic table.

As you move down within a group, the energy of highest-energy occupied orbitals increases. Likewise, the elements have greater numbers of electrons, and they occupy orbitals with higher n. As the value of n increases from element to element, the orbitals are larger, the electrons in these orbitals

are farther from the nucleus, and the electrons in these high-energy orbitals experience weaker electron–nucleus attractions.

Similarly, as you move left to right across the periodic table within a period, the energy of all atomic orbitals of the elements decreases. Consider the elements in the third period, Na through Ar, for example (Interactive Figure 7.4.1).



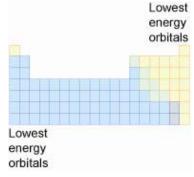


#### Orbital energies, Na-Ar

When moving from Na to Mg, two factors affect the energy of the atomic orbitals. First, the Mg nucleus has one more proton than the Na nucleus, which increases the nucleus—electron attractive forces. This will lower the energy of atomic orbitals. Second, Mg has one more electron than Na, which increases the electron—electron repulsions. This will increase the energy of atomic orbitals.

As shown in **Interactive Figure 7.4.1**, the Mg atomic orbitals are lower in energy than the Na atomic orbitals. This suggests that the attractive forces that result from additional protons in the nucleus are more important than the repulsive forces from the additional electrons. In general, when moving across a period from left to right, the attractive forces between the electrons and the nucleus increase and thus the orbital energies decrease.

Figure 7.4.2 Relative Orbital Energy of the Elements



**Effective Nuclear Charge** The combination of attractive forces between electrons and the nucleus and electron–electron repulsive forces is called the **effective nuclear charge** and is given the symbol  $Z^*$ . The effective nuclear charge for the highest-energy electrons in an atom is the nuclear charge felt by those electrons, taking into account the electron–electron repulsive forces between high-energy electrons and core electrons. A simplified method for calculating  $Z^*$  for the highest-energy electrons in an atom is

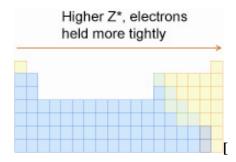
$$Z^* = Z - [number of core electrons]$$

Using this simplified method, we can calculate values of Z and  $Z^*$  for Na through Ar:

	Na	$\mathbf{M}\mathbf{g}$	Al	Si	P	$\mathbf{S}$	Cl	Ar
Z	11	12	13	14	15	16	17	18
$Z^*$	1	2	3	4	5	6	7	8

As  $Z^*$  increases, the electrons feel a strong attractive force from the nucleus. This has the effect of decreasing the energy of the atomic orbitals. As the energy of the atomic orbitals decreases, the electrons are held closer to the nucleus and are held more tightly to the nucleus

## **Interactive Figure 7.4.3:** Explore effective nuclear charge.



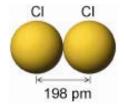
## Relative effective nuclear charge for the elements

This general trend in orbital energies controls most of the observed trends we see in atomic properties, as we will explore in the rest of this chapter.

## 7.4b Atomic Size

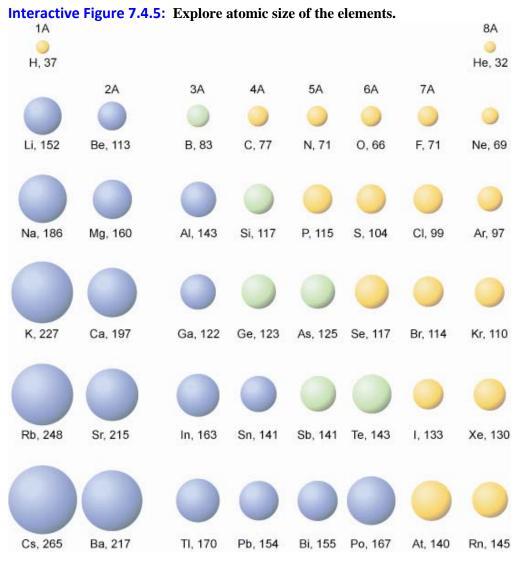
The size of an atom is controlled by the size of its orbitals, but orbitals are boundless, with no defined outer limit. Chemists use many different definitions for the size of an atom. The **covalent radius** of an element is the distance between the nuclei of two atoms of that element when they are held together by a single bond. For example, the distance between two bonded Cl atoms in Cl<sub>2</sub> is 198 pm (**Figure 7.4.4**). Therefore, the covalent radius of each Cl atom is 99.0 pm. Other covalent radii are determined from atom distances in molecules. Because distances between bonded atoms vary from molecule to molecule, tables of covalent radii show average values.

Figure 7.4.4 The Distance Between Two Cl Atoms in Cl<sub>2</sub> is 198 pm



The **metallic radius** of an element is the distance between the nuclei of two atoms in a metallic crystal. Tables of atomic radii generally report covalent radii for nonmetals and metallic radii for metals.

The size of an atom is closely related to its electron configuration. Recall that the lower an orbital's energy, the more tightly an electron in that orbital is held to the nucleus and the smaller the orbital. Therefore, the trend in atomic size follows that of orbital energies, with the smallest atoms in the top right of the periodic table and the largest atoms in the lower left (**Interactive Figure 7.4.5**).



Atom radii (pm)

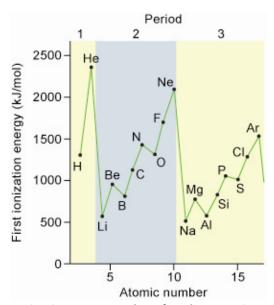
## 7.4c Ionization Energy

**Ionization energy** is the amount of energy required to remove an electron from a gaseous atom.

$$X(g) \rightarrow X^{+}(g) + e^{-}(g)$$
  $\Delta E = \text{ionization energy}$ 

All atoms require energy to remove an electron, and therefore ionization energy values are positive. The trends in ionization energies follow that expected based on orbital energies (**Interactive Figure 7.4.6**).

### **Interactive Figure 7.4.6:** Explore ionization energy values.



Ionization energy values for elements in periods 1-3

Notice that the elements farther down within a group, for example, moving from H to Li to Na, have decreased ionization energy. This trend is related to orbital energies. The electron removed from sodium occupies a 3s orbital, which is higher in energy than the electron lost by lithium (2s), which in turn is higher than the energy of the electron lost by hydrogen (1s).

Ionization energy generally increases when moving left to right across a period. This trend is related both to orbital energies and to effective nuclear charge,  $Z^*$ . Orbital energies decrease and  $Z^*$  increases in the elements as you move left to right across a period. Therefore, the farther right an element is, the more strongly the outermost electrons are attracted to the nucleus and the higher the ionization energies are, in general, a large, positive ionization energy value indicates that an element is more stable as a neutral atom than as a cation.

Notice that Interactive Figure 7.4.4 shows two areas where there are exceptions to the general trend in ionization energy values: at the Group 3A elements and at the Group 6A elements. In both cases, elements have ionization energy values that are lower than would be predicted based on the general trend.

The lower-than-expected ionization energy values for the Group 3A elements can be explained by examining electron configurations of the Group 2A and 3A elements.

Group 2A: [noble gas] $ns^2$  Group 3A: [noble gas] $ns^2np^1$ 

The *np* electron removed from a Group 3A element has higher energy than the *ns* electron removed from a Group 2A element. The *np* electron is easier to remove than the *ns* electron, resulting in ionization energies for the Group 3A elements that are lower than predicted.

The lower-than-expected ionization energy values for the Group 6A elements can be explained by examining electron configurations of the Group 5A and 6A elements.

The electron removed from a Group 6A element is in a filled *np* orbital. Electron–electron repulsive forces make it easier to remove this paired electron than the unpaired *np* electron removed from a Group 5A element; therefore, Group 6A elements have ionization energies that are lower than predicted.

# 7.4d Electron Affinity

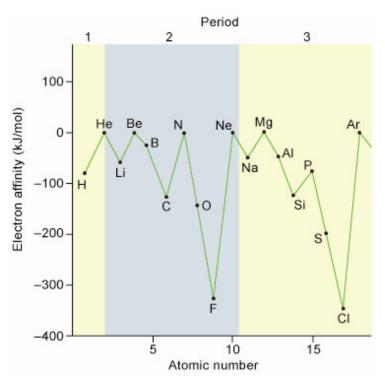
**Electron affinity** is the energy change when a gaseous atom gains an electron.

$$X(g) + e^{-}(g) \rightarrow X^{-}(g)$$

 $\Delta E$  = electron affinity

Although most elements have negative electron affinity values, some are slightly positive or close to zero. Keep in mind that a negative electron affinity value indicates that energy is released when an electron is added to a gaseous atom and that a large, negative electron affinity value indicates that an element is more stable as an anion than as a neutral atom. Not all atoms have a measurable electron affinity. Despite this, the trends in electron affinities generally follow those of the other periodic properties we have examined thus far (with numerous exceptions) (**Interactive Figure 7.4.7**).

## **Interactive Figure 7.4.7:** Explore electron affinity values.



Electron affinity values for elements in periods 1-3

Elements lower in a group generally have less negative electron affinity values than those higher in a group.

H: -72.8 kJ/mol

Li: -59.6 kJ/mol

Na: -52.9 kJ/mol

K: -48.4 kJ/mol

As atomic size increases down a group, the orbital that is occupied by the new electron increases in energy. As the orbital energy increases, the attractive forces between the new electron and the nucleus decrease, so electron affinity becomes less negative. In general, adding electrons becomes less favorable the farther down a group the element is.

Electron affinity values generally are more negative in elements farther to the right across a period. There are some notable exceptions, however, at the Group 2A and 5A elements.

Group 2A: [noble gas] ns

Group 5A: [noble gas] ns

ns

np

The Group 2A elements have electron affinities that are very close to zero because the added electron occupies the *np* orbital. Adding an electron to this higher-energy orbital requires energy, so the electron affinity is much lower (less negative) than predicted from general trends. The Group 5A elements have low (less negative) electron affinity values because the added electron occupies a half-filled *np* orbital and introduces new electron–electron repulsion forces.

Notice that the Group 8A elements also have electron affinity values that are close to zero. An electron added to a noble gas element would occupy the (n + 1)s orbital in a higher-energy level. Thus, the noble gases generally do not form anions.

## 7.5 Formation and Electron Configuration of Ions

#### **Section Outline**

7.5a Cations

7.5b Anions

7.5c Ion Size

Section Summary Assignment

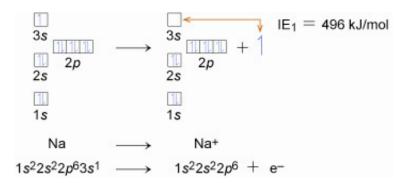
As you saw in Chapter 2, ions form when atoms gain or lose electrons. Whether an atom gains or loses electrons is related to orbital energy and atomic electron configuration. Recall from Section 7.4 and Interactive Figure 7.4.x that the energy of the highest-energy occupied orbitals increases in each element as you move down within a group and the energy of all atomic orbitals decreases in each element as you move left to right across the periodic table.

## **Opening Exploration 7.5** Electron Configurations of Ions

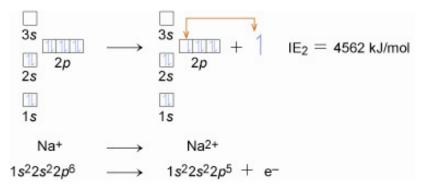


## 7.5a Cations

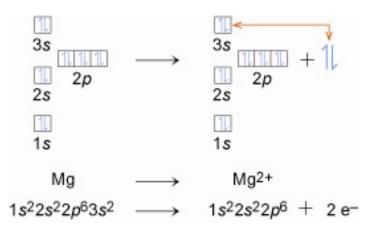
A cation forms when an atom loses one or more electrons. Metals have low ionization energy values, so metals generally form cations. For example, sodium, a Group 1A element, loses one electron to form the sodium cation, Na<sup>+</sup>. Examination of the Na electron configuration shows that the highest-energy electron occupies the 3s orbital. This is the sodium *valence electron*, and it is this electron that is lost upon formation of Na<sup>+</sup>.



The energy required to remove a second electron from an atom is the second ionization energy,  $IE_2$ . For any atom,  $IE_2 > IE_1$ . Sodium does not normally form a +2 cation because the second electron is removed from the 2p subshell, which is much lower in energy than the 3s subshell. Removing an electron from an inner energy shell requires a great deal of energy, in this case almost 10 times as much as is required to remove the 3s valence electron.



Magnesium, a Group 2A element, loses both of its valence electrons to form a +2 cation.

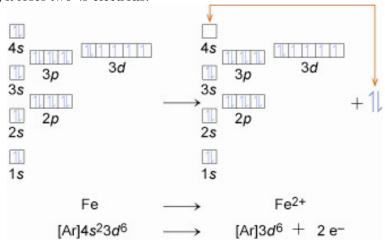


Like sodium, magnesium is expected to easily lose its valence electrons, but not an electron from a lower-energy shell. As shown in Table 7.5.1, the first and second ionization energies for Mg are relatively low, but the third ionization energy ( $IE_3$ ) is more than 10 times greater than  $IE_1$ .

Table 7.5.1 First, Second, and Third IE values for Mg

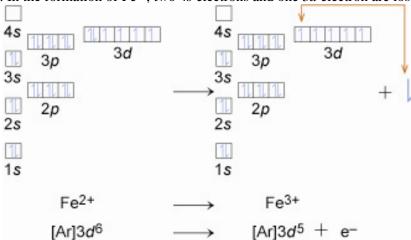
$Mg(g) \rightarrow Mg^{+}(g) + e^{-}$	$IE_1 = 738 \text{ kJ/mol}$
$Mg^2(g) \rightarrow Mg^{2+}(g) + e^-$	$IE_2 = 1451 \text{ kJ/mol}$
$Mg^{2+}(g) \to Mg^{3+}(g) + e^{-}$	$IE_3 = 7733 \text{ kJ/mol}$

In general, when metals form cations, they lose electrons from the highest-energy occupied orbitals, those with the highest n value. Transition metals have valence electrons in ns, (n-1)d, and in the case of lanthanides and actinides, (n-2)f orbitals. When a transition metal forms a cation, electrons are first lost from the outermost occupied orbital (the orbital with highest n). For example, when iron forms a +2 cation, it loses two 4s electrons.



Recall that the 4s orbital is filled before the 3d orbitals are filled. However, electrons are removed from the highest-energy orbitals because those electrons feel the weakest attractive "pull" from the positively charged nucleus.

Transition metals often form more than one cation. Iron is commonly found in both the 2+ and 3+ oxidation states. In the formation of Fe<sup>3+</sup>, two 4s electrons and one 3d electron are lost.



Notice that the electron removed to form  $Fe^{3+}$  from  $Fe^{2+}$  is taken from a filled 3d orbital, not a half-filled orbital. This minimizes the repulsive forces between electrons.

## **EXAMPLE PROBLEM: Write electron configurations for cations.**

Write electron configurations for the following ions in *spdf* and orbital box notation.

- (a) Al<sup>3+</sup> (Do not use noble gas notation.)
- (b)  $Cr^{2+}$  (Use noble gas notation.)

## **SOLUTION:**

You are asked to write an electron configuration for a cation using *spdf* and orbital box notation.

You are given the identity of the cation.

(a) Aluminum is element 13. The element loses three electrons from its highest-energy orbitals to form the  $Al^{3+}$  ion.

(b) Chromium is element 24. The element loses two electrons from its highest-energy orbitals to form the  $Cr^{2+}$  ion.

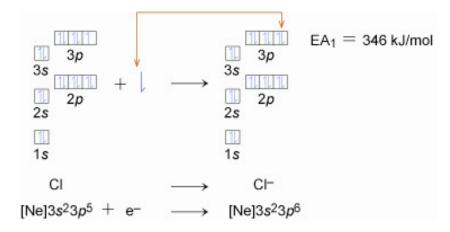
$$Cr^{2+}$$
: [Ar] $3d^4$  [Ar]  $\boxed{\phantom{a}}$   $\boxed{\phantom{a}}$ 

$$Cr^{2+}$$
: [Ar]  $3d^4$  [Ar]  $4s$   $3d$ 

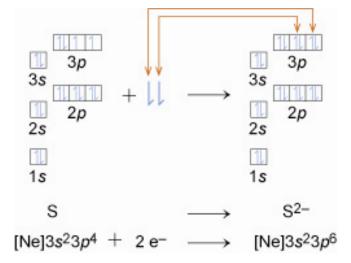
7.5.1T: Tutorial Assignment 7.5.1: Mastery Assignment

## 7.5b Anions

An anion forms when an atom gains one or more electrons. Nonmetals have relatively large, negative electron affinity values, so nonmetals generally form anions. For example, chlorine gains one electron to form the chloride ion, Cl<sup>-</sup>. Examination of the Cl electron configuration shows that the 3*p* subshell in Cl contains a single vacancy. Cl therefore gains a single electron in a 3*p* orbital to form Cl<sup>-</sup>.



Sulfur has two 3p orbital vacancies and can therefore gain two electrons.



The total number of electrons gained when an element forms an anion is related to the electron configuration of the element. In the case of Cl, only one electron is gained because a second electron would occupy the higher-energy 4s orbital. An electron in this orbital is farther from the nucleus and therefore feels less attractive "pull" from the nucleus. For the same reason, sulfur is often found as a 2– anion and not a 3– anion.

Finally, not all main-group elements commonly form ions. The Group 1A, 2A, and 3A metals lose lone, two, and three electrons, respectively, to form cations where the charge on the cation is equal to the group number. The Group 5A, 6A, and 7A nonmetals gain three, two, and one electrons, respectively, to form anions where the charge on the anion is equal to (8 – the group number). The Group 4A elements, however, are not commonly found as +4 or -4 ions because the gain or loss of four electrons requires a great deal of energy.

## **EXAMPLE PROBLEM: Write electron configurations for anions.**

Write electron configurations for the following ions in *spdf* and orbital box notation.

- a) O<sup>2-</sup> (Do not use noble gas notation.)
- (b) I<sup>-</sup> (Use noble gas notation.)

#### **SOLUTION:**

7.5.2T: Tutorial Assignment 7.5.2: Mastery Assignment

## 7.5c Ion Size

The size of an ion is related both to the size of the atom from which it is formed and the ion charge. In Interactive Figure 7.5.1, notice that

- cations are smaller than the atoms from which they are formed;
- anions are larger than the atoms from which they are formed; and
- anions are generally larger than cations.

**Interactive Figure 7.5.1:** Explore relative sizes of neutral atoms, cations and anions.

[Figure ID #7-77]

Ionic radii

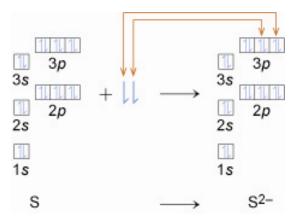
Cations are smaller than the atoms from which they are formed primarily because they have fewer electrons. For example, magnesium has 12 electrons and loses 2 of them to form the  $Mg^{2+}$  cation.



A  $Mg^{2+}$  ion is smaller than a Mg atom because the highest-energy occupied orbital has changed from 3s to 2p. The 2p orbital is smaller than the 3s orbital, so the radius of the cation is smaller than the

radius of the Mg atom. In addition, the fact that Mg<sup>2+</sup> has fewer electrons than Mg minimizes electron repulsion forces, also decreasing the size of the cation.

Anions are larger than the atoms from which they are formed primarily because of their added electrons. Consider formation of the sulfide ion,  $S^{2-}$ , from a sulfur atom. The sulfide ion has 18 electrons, 2 more than a sulfur atom. The additional electrons occupy the 3p subshell, which was already partially occupied in a sulfur atom.



The added electrons increase to the existing repulsive forces between electrons in the 3p subshell, causing the electrons to move away from one another. This in turn leads to an expansion of the electron cloud and an anion that is larger than the neutral atom.

Consider the following **isoelectronic** series, species with the same number of electrons but different numbers of protons.

	Protons	Electrons	Electron	Ion Radius
			Configuration	
$O^{2-}$	8	10	$1s^2 2s^2 2p^6$	140 pm
$F^-$	9	10	$1s^22s^22p^6$	133 pm
$Na^+$	11	10	$1s^22s^22p^6$	102 pm
$\mathrm{Mg}^{2+}$	12	10	$1s^22s^22p^6$	66 pm

The ion with the largest radius in this isoelectronic series is  $O^{2-}$ , and the smallest ion is  $Mg^{2+}$ . The oxide ion has only 8 protons to attract its 10 electrons, whereas the magnesium ion has 12 protons and thus more strongly attracts its 10 electrons.

## **Chapter Review**

## **Key Concepts**

#### 7.1 Electron Spin and Magnetism

- Electrons exert a magnetic field due to electron spin (7.1a).
- An electron has two possible spin states, indicated by the spin quantum number  $(m_s = +\frac{1}{2})$  or  $-\frac{1}{2}$  (7.1a).
- Materials with unpaired electrons are magnetic (7.1b).

• The magnetic nature of a material can be categorized as diamagnetic, paramagnetic, or ferromagnetic (7.1b).

## 7.2 Orbital Energy

- In a single-electron atom, the energy of an orbital is directly related to n, the principal quantum number (7.2a).
- In multielectron atoms, orbital energy depends on both n and  $\ell$  (7.2a).

## 7.3 Electron Configuration of Elements

- The electron configuration of an element shows how electrons are distributed in orbitals (7.3).
- An atom's ground state is the lowest-energy electron configuration for that atom (7.3a).
- The Pauli exclusion principle states that no two electrons within an atom can have the same set of four quantum numbers (7.3a).
- Electron configurations are written using *spdf* and orbital box notatin (7.3b).
- Hund's rule of maximum multiplicity states that the lowest-energy electron configuration is the one where the maximum number of electrons is unpaired (7.3b).
- Noble gas notation is a shortcut used when writing electron configurations, where a noble gas symbol is used to represent core electrons (7.3b).
- Valence electrons are the electrons beyond the core electrons (7.3d).

#### 7.4 Properties of Atoms

- Orbital energy increases in elements as you move left to right across the periodic table and down within a periodic group (7.4a).
- The effective nuclear charge for the highest-energy electrons in an atom is the nuclear charge felt by those electrons, taking into account the attractive forces between electrons and the nucleus and the repulsive forces between electrons (7.4a).
- Effective nuclear change generally increases in elements as you move left to right across the periodic table (7.4a).
- The covalent radius of an element is the distance between the nuclei of two atoms of that element when they are held together by a single bond (7.4b).
- Metallic radius is the distance between two atoms in a metallic crystal (7.4b).
- Atom size generally decreases in each element as you move left to right across the periodic table and increases as you move down within a periodic group (7.4b).
- Ionization energy is the amount of energy required to remove an electron from a gaseous atom (7.4c).
- Ionization energy generally increases in each element as you move left to right across the periodic table and decreases as you move down within a periodic group (7.4c).
- Electron affinity is the energy change when an electron is added to a gaseous atom (7.4d).
- Electron affinity values generally become more negative in each element as you move left to right across the periodic table and become less negative (more positive) as you move down within a periodic group (7.4d).

#### 7.5 Formation and Electron Configuration of Ions

- Metals generally form cations by losing their highest-energy valence electrons (7.5a).
- Nonmetals generally form anions by gaining electrons in their highest-energy orbitals (7.5b).

- Cations are generally smaller than the atom from which they are formed, and anions are generally larger than the atoms from which they are formed (7.5c).
- Isoelectronic ions have the same number of electrons but different numbers of protons (7.5c).

# **Key Terms**

7.1 Electron Spin and Magnetism electron spin spin states spin quantum number,  $m_s$  diamagnetic paramagnetic ferromagnetic

7.3 Electron Configuration of Elements electron configuration ground state
Pauli exclusion principle spdf notation orbital box notation
Hund's rule of maximum multiplicity noble gas notation core electrons valence electrons

7.4 Properties of Atoms effective nuclear charge covalent radius metallic radius ionization energy electron affinity

7.5 Formation and Electron Configuration of Ions isoelectronic