3.0 INTRODUCTION

In the previous chapters, we constructed a model of the atom. However, for this model to be useful, it must be able to account for atomic properties, and it must form a basis upon which predictions can be made. In this chapter, we test some predictions based on the quantum model and discuss atomic properties in terms of quantum theory.

THE OBJECTIVES OF CHAPTER 3 ARE TO USE THE QUANTUM THEORY DEVELOPED IN CHAPTER 2 TO:

- explain the periodicity in the chemical properties of the elements;
- predict relative sizes of atoms;
- predict relative orbital energies;
- predict the relative ability of atoms to lose or gain electrons; and
- describe the magnetic properties of atoms.

3.1 VALENCE ELECTRONS

Most of the remainder of this text is concerned more with molecules than with atoms. However, molecules are built from atoms that bond to one another through an exchange or sharing of electrons. Indeed, most atomic properties are dictated by the nature of the electron cloud and how strongly the electrons interact with the nucleus. Sublevels that are full are generally very stable and closer to the nucleus, so electrons can neither be added to nor removed from them. The outermost s sublevel is the only exception: electrons can be removed from a filled, outermost s sublevel because it is very high in energy and contains only two electrons. Consequently, electrons in filled sublevels (other than the outermost s) are not involved in bonding and are referred to as core electrons. The chemical properties of an atom are dictated by the electrons and orbitals that are involved in bonding. These high-energy electrons are called valence electrons, and the orbitals they occupy are called valence orbitals.
The valence electrons are those in the outermost s and in any partially filled sublevels.

Valence electrons can be donated to or shared with other atoms to produce bonds, while the valence orbitals are used to accept electrons from or to share electrons with other atoms. Thus, the number and location of the valence electrons are important characteristics of the atom, and they are given in an atom’s valence electron configuration. As shown in Table 3.1, the number of valence electrons of a main group element is equal to its group number, so valence electron configurations vary periodically through the periodic table. Indeed, the periodicity of the chemical properties of the elements is the result of the periodicity of their valence electron configurations.

The valence electrons are frequently, but not always, those electrons beyond the previous noble gas. For example, the electron configuration of Al is [Ne]3s\(^2\)3p\(^1\), and its valence electron configuration is 3s\(^2\)3p\(^1\). However, electrons in filled d sublevels are not valence electrons even though they come after the previous noble gas and the outermost s electrons in the electron configuration. Thus, the valence electron configurations of elements in the p block (Groups 3A - 7A) do not include the d electrons. For example, the electron configuration of Ga is [Ar]4s\(^2\)3d\(^10\)4p\(^1\), but the 3d sublevel is full so the 3d electrons are not valence electrons. The valence electron configuration of gallium is 4s\(^2\)4p\(^1\), consistent with the fact that it is a Group 3A nonmetal with three valence electrons.

The valence electrons of the transition metals are in the outermost s and d sublevels, so their valence electron configurations are typically of the form ns\(^2\)(n - 1)d\(^x\) where n is the period and x is usually determined from the position of the element in the transition metal block. For example, the valence electron configuration of Mn, the fifth element in the block is 4s\(^2\)3d\(^5\). However, there are three transition elements in the first d block that can be confusing. In Section 2.8, we saw that the electron configurations of Cr and Cu were exceptions and those exceptions are found in their valence electron configurations.

- Cr is 4s\(^1\)3d\(^5\)
- Cu is 4s\(^1\)3d\(^10\). The 3d sublevel of copper is full and Cu is in Group 1B, so it would be easy to omit the 3d electrons. However, much of copper’s chemistry involves its 3d orbitals, so they are considered to be valence orbitals.
- Zn is 4s\(^2\). The 3d sublevel of Zn is filled and not used in bonding. This is not an exception, it is pointed out here only because Zn has no d electrons even though it is in the d-block.

We now apply our knowledge of the electronic structure of the atoms to the valence electrons in order to predict those atomic properties that will help us in our study of chemical bonding.

### Table 3.1 Valence electron configurations of the elements by chemical group and examples from the 2nd period

<table>
<thead>
<tr>
<th>Group</th>
<th>1A</th>
<th>2A</th>
<th>3A</th>
<th>4A</th>
<th>5A</th>
<th>6A</th>
<th>7A</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li</td>
<td>2s(^1)</td>
<td>(\text{ns}^2)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Be</td>
<td>2s(^2)</td>
<td>(\text{ns}^2)</td>
<td>(\text{np}^1)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>2s(^2)</td>
<td>(\text{ns}^2)</td>
<td>(\text{np}^2)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>2s(^2)</td>
<td>(\text{ns}^2)</td>
<td>(\text{np}^3)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>N</td>
<td>2s(^2)</td>
<td>(\text{ns}^2)</td>
<td>(\text{np}^4)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>O</td>
<td>2s(^2)</td>
<td>(\text{ns}^2)</td>
<td>(\text{np}^5)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>F</td>
<td>2s(^2)</td>
<td>(\text{ns}^2)</td>
<td>(\text{np}^5)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

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3.2 SHIELDING AND EFFECTIVE NUCLEAR CHARGE

The nuclear charge experienced by the valence electrons helps determine the atomic properties because the greater the nuclear charge a valence electron experiences, the more tightly it is bound to the atom and the lower is its energy. However, a valence electron is not exposed to the full positive charge of the nucleus because it is shielded or screened from the nuclear charge by intervening electrons, mainly the core electrons (Figure 3.1). Consider the case of Li (1s<sup>2</sup>2s<sup>1</sup>). The nuclear charge is +3, but the 2s valence electron experiences a nuclear charge of only +1.3 because most of the electron density of the 1s core electrons lies between it and the nucleus. Thus, the 1s electrons shield the 2s electron from over half of the nuclear charge. The nuclear charge that is actually experienced by a valence electron is called the effective nuclear charge, Z<sub>eff</sub>. The effective nuclear charge experienced by an electron is equal to the charge of the nucleus (Z) minus that portion of the nuclear charge that is shielded by the other electrons (σ) or

\[
Z_{\text{eff}} = Z - \sigma
\]

Eq. 3.1

We can apply Equation 3.1 to the 2s electron in Li and write 1.3 = 3 - σ, or σ = 1.7. Thus, the two 1s electrons shield with only 85% of their full charge of -2.

Core electrons are closer to the nucleus, so they shield valence electrons better than do other valence electrons. Thus, in going from one atom to the next in a period, Z increases by one as one proton is added, but σ increases by less than one because the additional valence electron does not shield with its full charge. Therefore, as shown in Figure 3.2, the effective nuclear charge experienced by the outermost electrons increases from left to right in a period. As a result, Z<sub>eff</sub> is low for metals and high for nonmetals.

Screening is the reason that the energy of an electron in a multi-electron atom depends upon both the n and l quantum numbers, while the energy of a one-electron atom or ion depends only upon n (Equation 2.5). An electron in an orbital screens other electrons best when its electron density is closer to the nucleus. Each nodal plane in an orbital reduces the electron density at the nucleus, and the number of nodal planes is equal to the l quantum number. Consequently, the shielding ability of electrons in a level decreases as their l quantum number increases; i.e., within a level, the screening ability of the electrons is s > p > d > f. For example, Z<sub>eff</sub> = 6.12 for the 3p electrons of chlorine, but it is 7.07 for the 3s electrons. The greater effective nuclear charge experienced by the 3s electrons lowers their energy to below that of the 3p electrons. Thus, orbital energies increase with the l quantum number because increasing l decreases Z<sub>eff</sub>.

![Figure 3.1 Shielding nuclear charge](image1)

(a) The unshielded positive charge of the nucleus. (b) The negative charge of core electrons shields much of the nuclear charge. (c) The nuclear charge experienced by the outermost electrons is greatly reduced because it is shielded by both the core electrons and the other valence electrons.

![Figure 3.2 Effective nuclear charge](image2)

The effective nuclear charge experienced by the outermost electrons of the second and third period elements.
3.3 RELATIVE SIZES OF ATOMICS

The size of an atom is represented by the size of its outermost (valence) shell, but electrons clouds are not hard spheres with well-defined boundaries, so the term “atomic radius” is somewhat vague. As a result, there are several definitions of the atomic radius, which are inferred from the distances between atoms in molecules or metals. Although these distances can be readily determined with several techniques, their determination requires knowledge of chemical bonding and the solid state. Consequently, we postpone a detailed discussion of atomic radii until Chapter 8. However, knowledge of relative atomic size will aid our discussion in future chapters, so we now apply our knowledge of the Bohr model, quantum theory, and effective nuclear charge to determine qualitative trends in atomic sizes. Although the idea of a fixed radius given in the Bohr model is incorrect, the Bohr equation for the radius (Equation 2.4) does reflect the appropriate terms. Thus, we will assume that \( r_n \propto \frac{n^2 Z_{\text{eff}}}{Z_{\text{eff}}} \), so the size of an atom depends upon two factors:

- **n quantum number**: The average distance between an electron and the nucleus increases with its principle quantum number. The n quantum number of the valence electrons is constant within a period, but it increases in going down a group. We conclude that the sizes of the atoms increase in going down a group due to an increase in their n quantum number.

- **Z_{\text{eff}}**: An electron cloud is contracted by high effective nuclear charge, so increases in Z_{\text{eff}} result in smaller atomic radii. Z_{\text{eff}} increases in going across a period, so we conclude that the sizes of the atoms decrease in going left to right in a period due to an increase in Z_{\text{eff}}.

Rb (large \( n \), low \( Z_{\text{eff}} \)) is a very large atom, while F (low \( n \), high \( Z_{\text{eff}} \)) is very small. Figure 3.3 shows the relative atomic sizes of the main group elements.

3.4 ORBITAL ENERGY

Two important properties of an atom that are discussed in the following sections are the ease with which it gains and loses electrons. However, both depend upon the energy of the orbital from which it is removed or added, so we begin our discussion with a treatment of relative orbital energies.

The Bohr equation for the energy of an electron (Equation 2.5) does not apply to multi-electron atoms because it neglects interactions between electrons. However, it can provide insight into trends in atomic properties if the effective nuclear charge is used instead of the atomic number. Therefore, we use Equation 3.2 in our discussion.

\[
E_x \propto \frac{Z_{\text{eff}}^2}{n^2}
\]

Eq 3.2

* As shown in Figure 3.3, Z_{\text{eff}} also changes within a group, but the differences in the properties of the elements within a group are dominated by the differences in the n quantum number.
Ex is the energy of a valence orbital on atom X, and n is the n quantum number of its valence shell. Equation 3.2 is only a very rough approximation and will be used only to order the orbital energies not to determine what the energies are. We begin by ordering the valence orbital energies of the following elements of the second period. They are in the second period, so n = 2, and Z_{eff}, which is obtained from Figure 3.2, is given in parenthesis after each element. Li (1.3), C (3.3), O (4.6), and F (5.2). Equation 3.2 produces the following: $E_{\text{Li}} \propto -0.4$; $E_{\text{C}} \propto -2.7$; $E_{\text{O}} \propto -5.3$, and $E_{\text{F}} \propto -6.8$. Based on these numbers, we conclude that the 2s orbital of lithium is the highest energy (least negative) orbital of the four, while the 2p orbitals of carbon, oxygen, and fluorine follow in order. These four atoms demonstrate one important rule:

Orbital energies decrease going across a period because the effective nuclear charge increases while the n quantum number of the valence electrons is unchanged.

Example 3.1

a) Use Equation 3.2 and Figure 3.2 to determine the relative energies of the third period elements silicon, sulfur, and chlorine.

n = 3 for all four atoms, and Figure 3.2 shows that $Z_{\text{eff}} \approx 4.3$ for Si, 5.5 for S, and 6.1 for Cl. Substitution into Equation 3.2 yields $E_{\text{Si}} \propto -2.1$, $E_{\text{S}} \propto -3.4$, and $E_{\text{Cl}} \propto -4.1$. The 3p orbital of silicon is the highest and the 3p orbital of Cl is the lowest in energy of the three.

b) What is $E_{\text{H}}$, the relative position of the hydrogen orbital?

Hydrogen is a one-electron atom, so Equation 2.5 can be used: $E_{\text{H}} \propto -(1^2/1^2) = -1$.

c) Draw an energy diagram that shows the relative energies of the valence orbitals of the seven elements discussed thus far.

$E_{\text{Li}}$ is the least negative, so the 2s valence orbital of Li is the highest energy orbital considered. Hydrogen follows with $E_{\text{H}} \propto -1.0$. Arranging the other elements in descending order, we arrive at Figure 3.4, which shows the relative orbital energies. Note that the orbital energy of hydrogen is higher than the other nonmetals, but it is lower than the metals. The fact that the valence orbital of H lies between those of the metals and the nonmetals is an important one that we will use in several of the later chapters.

Comparing the results of Equation 3.2 for the second and third periods, we note that the 3p orbital of sulfur is higher in energy than the 2p orbital of oxygen even though the effective nuclear charge experienced by the electrons is greater in sulfur. Similar conclusions can be drawn from comparisons of carbon and silicon and from fluorine and
chlorine. We conclude the following important rule

Orbital energies increase (become less negative) going down a group due to increases in the n quantum number even though the effective nuclear charge also increases slightly.

The energies of the valence orbitals of all atoms lie in a relatively narrow range due to the periodicity in $Z_{\text{eff}}$ and an increasing n quantum number. Core electrons, on the other hand, continue to drop in energy as the number of protons increases because they are not shielded very efficiently by the valence electrons. Thus, the valence 2p orbitals of oxygen are at lower energy than the valence 3p valence orbitals on sulfur because valence orbital energies increase going down a group, but the 2p electrons in oxygen are much higher in energy than the 2p electrons on sulfur because sulfur has 16 protons while oxygen has only eight.

Example 3.2

Select the orbital at lower energy in each pair.

... the 2p orbital on N or the 2s orbital on N

$n+1$ is less for a 2s than for a 2p, so the 2s orbital is lower in energy. The reason is that s orbitals have no nodal planes, while p orbitals have one. Consequently, the s electrons screen the p electrons better than the p electrons screen the s.

... the 2p orbital on Br or the 2p orbital on F

$n = 2$ for both orbitals, but $Z_{\text{eff}}$ is much greater in the vicinity of the 35 protons of a Br atom than around the nine protons of a F atom. Using Equation 3.2 and the relative magnitudes of $Z_{\text{eff}}$, we conclude that the 2p orbital of Br is much lower in energy. The 2p electrons in Br are core electrons, while those in F are valence electrons, and core electrons are always lower in energy than valence electrons.*

... the 2p orbital on N or the 2p orbital on O

$n = 2$ for both orbitals, but $Z_{\text{eff}}$ increases in going from left to right in a period, so it is greater for O than for N. Thus, the 2p orbital on O is lower in energy because electrons in an O orbital experience a greater effective nuclear charge.

* The valence 2p electrons of F are lower in energy than the valence 4p electrons of Br due to the difference between the n quantum numbers and the number of shielding electrons.
3.5 IONIZATION ENERGY

Ionization energy (IE) is the energy required to remove the outermost electron from an atom or ion in the gaseous state. The process for atom A is described by the following:

\[ A + \text{IE} \rightarrow A^{+\ast} + e_{1}^{-\ast} \]

The ionization energy is a measure of how tightly the electron is bound to the atom, so it measures essentially the same thing as does the orbital energy. We conclude that

The ionization energy is approximately equal to the negative of the orbital energy of the removed electron.

Thus, trends in ionization energies should be similar to those for orbital energies given in the previous section. Consider the cases for Li, C, O, and F shown in Figure 3.5. The order of their ionization energies is the same as that for their orbital energies given in Figure 3.4. Li is a 1A metal with a low \( Z_{\text{eff}} \) and a relatively high valence orbital energy, so it has a relatively low ionization energy of 520 kJ/mol. This places the energy of the 2s orbital in lithium at about -520 kJ/mol. Metals are characterized by low ionization energies, which means that they lose their valence electrons relatively easily, which is why they corrode. Oxygen and fluoride are nonmetals with high \( Z_{\text{eff}} \), so their 2p orbitals are very low in energy, and their ionization energies are quite high. Indeed, the ionization energy of a fluorine atom, 1681 kJ/mol, is the highest ionization energy of any atom other than the noble gases. The energy of the 2p orbital in fluorine is approximately -1681 kJ/mol, which is the lowest energy valence orbital of any atom. Carbon lies between Li and O in the periodic table and in Figure 3.4, and its ionization energy also lies between those of Li and O.

Example 3.3

Use the relative orbital energies given in Figure 3.4 to order the ionization energies of silicon, sulfur, and chlorine.

The valence orbitals of silicon are higher than those of sulfur and chlorine, which means that the electrons are not bound as tightly. Therefore, the ionization energy of silicon is the lowest. The valence orbitals of chlorine are the lowest of the three, so they are bound most tightly. Consequently, chlorine has the highest ionization energy. We conclude that \( IE_{\text{Si}} < IE_{\text{S}} < IE_{\text{Cl}} \). The observed ionization energies are 786, 999, and 1256 kJ·mol\(^{-1}\), respectively. Comparing these values with those of C, O, and F, we conclude that ionization energies decrease in going down a group.

Figure 3.5 Ionization energy and orbital energy

The ionization energy is approximately equal to the negative of the orbital energy. The ionization energies of Li, C, O, and F are 520, 1086, 1314, and 1681 kJ/mol, respectively.
Figure 3.6 shows the periodic trend in ionization energies of the main group elements. Note that the rise in the ionization energies from left to right within a period follows that of the effective nuclear charge, while the steady decrease within a group is due to an increase in the n quantum number. In general,

Metals have low ionization energies because they have low effective nuclear charges. Consequently, they readily lose valence electrons to form cations. Nonmetals have high ionization energies, so they do not form cations in chemical processes.

Electron configurations in which sublevels are filled (Groups 2A and 8A) or half-filled (Group 5A) are unusually stable, so removing an electron from these elements is more difficult and results in deviations from the expected periodicity. For example, the effective nuclear charge of B is greater than that of Be, but the ionization energy of Be is greater than that of B because the electron must be removed from a filled 2s sublevel in Be. Similarly, the ionization energy of N is greater than that of O because the 2p sublevel of N is half-filled.

3.6 ELECTRONEGATIVITY

Electronegativity ($\chi$) is a measure of an atom's ability to attract bonding electrons, so electron density in a bond accumulates near those atoms with higher electronegativities. Bonding electrons reside in orbitals involving the valence orbitals of the atoms, especially those that are unfilled, and electrons seek to minimize their energy, so an atom that is highly electronegative is simply one whose valence orbitals, especially those that are unfilled, are low in energy. $E_n \propto -(Z_{\text{eff}})^2/n^2$, so atoms with large $Z_{\text{eff}}$ (nonmetals) and valence orbitals with low n quantum numbers have high electronegativities.

Electronegativity depends upon the energy of the valence orbitals. It increases as the energy of the valence orbitals decreases.

Consider the orbital energies of Li, C, and F shown in Figure 3.7. Li is a metal with a low $Z_{\text{eff}}$, so its orbital energy is high. The electron in it is readily lost (low ionization energy), but bonding electrons are not drawn to the high-energy orbital, so Li has a very low electronegativity. F is a nonmetal with a high $Z_{\text{eff}}$, so its orbital energy is low. Thus, it is very difficult to remove a 2p electron from F (high ionization energy), but bonding electrons are drawn to the low energy unfilled orbital, so F is highly electronegative. The 2p orbital energy of C is about half way between the valence orbital energies of Li and F, and its electronegativity is also about half way between these two extremes in the period.
Example 3.4

a) Use the relative orbital energies given in Figure 3.4 to order the electronegativities of silicon, sulfur, and chlorine.

Silicon has the highest energy valence orbitals of the three, so it is the least electronegative, while the valence orbitals of chlorine are the lowest in energy, so Cl is the most electronegative: $\chi_{Si} < \chi_{S} < \chi_{Cl}$. Orbital energies increase going down a group, so we also predict the following: $\chi_{Si} < \chi_{C} < \chi_{O} < \chi_{Cl} < \chi_{F}$.

The periodic behavior of electronegativity is shown in Figure 3.8. Electronegativity increases left to right in a period due to an increase in effective nuclear charge and decreases going down a group due to an increase in the $n$ quantum number. Consequently, fluorine (high $Z_{eff}$ and low $n$) is the most electronegative atom, while cesium (low $Z_{eff}$ and high $n$) is the least electronegative element shown in Figure 3.8. In summary, nonmetals have high electronegativities, so they tend to gain electrons to form anions, but metals have low electronegativities, so they do not gain electrons to become anions.

b) Use Figure 3.4 to predict which is more electronegative, oxygen or chlorine.

The valence orbitals of oxygen are lower than those of chlorine, so oxygen is more electronegative.

An exception to the above generality about the electronegativities of metals arises from the fact that d and f electrons do not shield very well because they contain two and three nodal planes, respectively. Therefore, the effective nuclear charge experienced by the valence orbitals in late metals (metals that lie on the right side of the Periodic Table) can be quite large. For example, Pb has 27 more protons and electrons than does Cs, but 24 of those electrons are d and f electrons, which do not shield the 27 additional protons very well. Thus, the 6p electrons in Tl and Pb experience relatively high $Z_{eff}$ (12.25 and 12.39, respectively), which makes both of these metals fairly electronegative. Indeed, the electronegativity of Pb is much greater than that of Si even though they are in the same Group, and the valence orbitals in Pb have a much higher $n$ quantum number. We conclude that due to their high effective nuclear charges, late metals have unusually high electronegativities (Table 3.2), which impacts significantly on their chemical properties.

### Table 3.2 Electronegativities of some late metals*

<table>
<thead>
<tr>
<th>Metal</th>
<th>Electronegativity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag</td>
<td>1.9</td>
</tr>
<tr>
<td>Sn</td>
<td>2.0</td>
</tr>
<tr>
<td>Hg</td>
<td>2.0</td>
</tr>
<tr>
<td>Tl</td>
<td>2.0</td>
</tr>
<tr>
<td>Pb</td>
<td>2.3</td>
</tr>
</tbody>
</table>

* Late metals, such as those listed in Table 3.2, are those that lie on the right side of the periodic table. Early metals, such as the Group 1A and 2A metals, lie on the left side of the table.
Example 3.5

Use the energy level diagram for the valence orbitals of atoms X and Y in the margin to answer the following:

a) Which atom has the lower ionization energy?

The atom with the lower ionization energy is the one with the higher energy electrons. The two electrons on atom Y are at higher energy, which means that they are not attracted to the nucleus as strongly. Thus, atom Y has the lower ionization energy.

b) Which atom is more electronegative?

The more electronegative atom is the one whose valence orbitals are at lower energy. The valence orbitals on Atom X are much lower in energy than those on atom Y, so atom X is much more electronegative than atom Y.

3.7 MAGNETIC PROPERTIES

Magnetic phenomena have been known since ancient times. For example, early Chinese, Greeks and Romans knew that the mineral lodestone or magnetite, Fe₃O₄, has the property of attracting other iron particles. When lodestone is rubbed against a piece of iron, the iron acquires a similar ability to attract other magnetized materials. The magnets produced in this manner have two ends, the north (N) and south (S) poles. Furthermore, like-poles (N-N and S-S) repel one another, and unlike-poles (N-S) attract. Thus, by the 13th century, magnets were used to make directional compasses, which interacted with the earth’s magnetic field.

In 1819, the Danish physicist Hans Christian Oersted found that a magnetic needle is deflected by an electric current flowing through a wire. In 1831, the English scientist Michael Faraday showed that electricity and magnetism were related when he discovered that moving a magnet near a wire induced an electric current in that wire.

In the 20th century, investigations on magnetism turned toward an understanding of its origins at an atomic-level. The origin of magnetism became apparent in the work of two American physicists, Samuel Goudsmit and George Uhlenbeck, who showed that the electron itself had spin, and the spinning electron behaved like a magnet (Section 2.5). Indeed, all magnetic properties are due to the magnetic fields caused by spinning electrons. However, no magnetic field is generated by paired electrons because the two different electron spins are opposed and their magnetic fields cancel. Consequently, the magnetic properties of an atom are due solely to its unpaired electrons. There are two
magnetic classifications for atoms:

1. **Paramagnetic atoms** have unpaired electrons and are attracted by an applied magnetic field. The attraction is due to the interaction of the magnetic fields of the unpaired electrons with the applied magnetic field. *The greater the number of unpaired electrons, the more paramagnetic is the atom.*

2. **Diamagnetic atoms** have no unpaired electrons and are not attracted by an applied magnetic field.*

Although magnetism is the result of unpaired electrons, it is a bulk property of the material; that is, magnetism is a property of large groups of atoms rather than individual atoms. It is important to realize that individual atoms typically occur only as gases because they interact with one another in the solid state so strongly that they lose their atomic identity and become part of a material. Thus, carbon is a paramagnetic atom with two unpaired electrons (valence electron configuration: $2s^22p^2$), but graphite and diamond, the common forms of elemental carbon, are diamagnetic because of the manner in which the carbon atoms interact in the solid. Iron atoms are also paramagnetic with four unpaired electrons ($4s^23d^6$), and they interact with one another in the solid. However, some of the unpaired electrons in iron align over many iron atoms to make iron a magnetic material. We discuss magnetic materials in more detail in Chapter 14.

3.8 **CHAPTER SUMMARY AND OBJECTIVES**

Valence electrons and orbitals, which are those in the outermost s sublevel and any unfilled sublevels, are involved in bonding and determine the chemical properties of the element. Indeed, the periodicity of chemical properties is a result of the periodicity of valence electron configurations. The size and energy of a valence orbital both depend upon the $n$ quantum number and the nuclear charge that it experiences, which is called the effective nuclear charge. The effective nuclear charge increases in going from left to right in the periodic table, while the $n$ quantum number increases in going down a group. Thus, atoms that lie on the right side of the periodic table (nonmetals) at the top of their groups have low energy valence orbitals that are closer to the nucleus, while atoms on the left side (metals) and at the bottom of their group have high energy electrons that are far from the nucleus. Ionization energy is the energy that is required to remove an electron, so atoms on the left side of the periodic table (metals) have low ionization energies and lose their valence electrons easily. Electronegativity is a measure of an atom’s ability to attract bonding electrons. Atoms with unfilled orbitals at low energy are highly electronegative,

* Diamagnetic atoms are actually repelled slightly by an applied field, but the reasons for the repulsion are beyond the scope of this discussion.
so nonmetals have high electronegativities because they have high effective nuclear charges. The trends in atomic size, ionization energies, and electronegativities are summarized in Figure 3.9. Paramagnetic atoms are attracted by magnetic fields because they have unpaired electrons. In contrast, diamagnetic atoms are not attracted by magnetic fields because all of their electrons are paired.

After studying the material presented in this chapter, you should be able to:

1. distinguish between valence and core electrons (Section 3.1);
2. determine the number of valence electrons present in an atom (Section 3.1);
3. predict valence electron configurations (Section 3.1);
4. explain shielding and effective nuclear charge (Section 3.2);
5. predict trends in atomic radii from the periodic table (Section 3.3);
6. predict relative valence orbital energies of atoms (Section 3.4)
7. define ionization energy and predict trends in it from the periodic table (Section 3.5);
8. define electronegativity and predict trends in it from the periodic table (Section 3.6); and
9. predict whether an atom is paramagnetic or diamagnetic (Section 3.7).
3.9 EXERCISES

1. Write valence electron configurations for each of the following:
   a) carbon  b) cobalt  c) chlorine  d) magnesium

2. Write valence electron configurations for each of the following:
   a) copper  b) calcium  c) sulfur  d) phosphorus

3. Which electron experiences the greater nuclear charge? Explain your reasoning in each case.
   a) a 5p electron of In or a 5p electron of Sb?
   b) a 5s electron of Sn or a 5p electron of Sn?

4. Which orbital is at higher energy? Explain your reasoning in each case.
   a) a 4p orbital of Se or a 3d orbital of Se
   b) a 3s orbital of S or a 3s orbital of Se
   c) a 2p orbital of C or a 2p orbital of O

5. Use ionization energies to explain why +4 ions are very rare.

6. Use only the Periodic Table to order the elements in each of the following groups by increasing atomic radius.
   a) N, F, B  b) Ge, Pb, Sn  c) K, Na, Li  d) As, Sn, S

7. Use only the Periodic Table to order the elements in each of the following groups by decreasing atomic radius.
   a) Na, K, Cl  b) Al, C, B  c) C, Ge, Sn  d) Cs, Zn, O

8. Order the elements in each group of Exercise 6 by increasing first ionization energy.

9. Order the elements in each group of Exercise 7 by decreasing first ionization energy.

10. Order the elements in each group of Exercise 6 by increasing electronegativity.

11. Order the elements in each group of Exercise 7 by decreasing electronegativity.

12. Which is the largest atom in each of the following groups?
   a) C, N, P, S  b) N, O, F  c) F, Cl, Br

13. Which is the most electronegative atom in each of the following groups?
   a) N, O, P  b) O, S, Se  c) Si, P, S

Refer to the following diagrams showing the highest energy electrons and lowest energy empty orbitals of some atoms to answer Exercises 14-16

Exercise 14  Exercise 15  Exercise 16

14. For atoms A, B, and C,
    a) list the atoms in order of increasing ionization energy,
    b) list the atoms in order of decreasing electronegativity, and
    c) identify each atom as either paramagnetic or diamagnetic.

15. For atoms D, E, and F,
    a) list the atoms in order of increasing ionization energy,
    b) list the atoms in order of decreasing electronegativity, and
    d) identify each atom as either paramagnetic or diamagnetic.

16. For atoms G, H, and K,
    a) list the atoms in order of increasing ionization energy,
    b) list the atoms in order of decreasing electronegativity, and
    e) identify each atom as either paramagnetic or diamagnetic.
17. The relative energies of the highest occupied orbitals of H, Li, and F are given to the right.
   a) Identify each atom as X, Y, or Z.
   b) Where would the energies of the 3p orbital of Cl and the 4s orbital of K be placed? (Below X, between X and Y, between Y and Z, or above Z)

18. How many of the electrons in each of the following are core electrons and how many are valence electrons?
   a) Na   b) Xe   c) S   d) Ga

19. Use Equation 3.2 to explain why first ionization energies decrease going down a group and why electronegativities increase going from left to right in a period.

20. The first ionization energy of magnesium is 738 kJ/mol; its second ionization energy is 1451 kJ/mol; and its third ionization energy is 7733 kJ/mol.
   a) Write the chemical equations for the processes to which these numbers apply.
   b) Why is the second ionization energy so much greater than the first?
   c) Suggest a reason why the third ionization energy is over five times greater than the second, but the second is less than twice the first.

21. Use the following effective nuclear charges experienced by the outermost electrons to order their outermost orbitals from lowest to highest energy:

<table>
<thead>
<tr>
<th>Element</th>
<th>Zeff</th>
</tr>
</thead>
<tbody>
<tr>
<td>P</td>
<td>4.89</td>
</tr>
<tr>
<td>Al</td>
<td>4.07</td>
</tr>
<tr>
<td>Br</td>
<td>9.03</td>
</tr>
<tr>
<td>Pb</td>
<td>12.39</td>
</tr>
</tbody>
</table>

22. Given the following n quantum numbers of the valence shells, and the effective nuclear charges experienced by their valence electrons:

<table>
<thead>
<tr>
<th>Element</th>
<th>n</th>
<th>Zeff</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>2</td>
<td>3.1</td>
</tr>
<tr>
<td>B</td>
<td>4</td>
<td>3.5</td>
</tr>
<tr>
<td>C</td>
<td>5</td>
<td>11.6</td>
</tr>
</tbody>
</table>

Arrange the elements in increasing electronegativity and size. The elements belong to Groups 1A, 4A, and 7A. To which group does each element belong?

23. Use Equation 3.2 to determine where in Figure 3.4 the energy of the valence orbitals of nitrogen (Zeff = 3.9) would be found? Is the location consistent with its electronegativity of 3.04? … with its ionization energy of 1402 kJ/mol? If not, explain why.

24. Use Equation 3.2 to determine where in Figure 3.4 the energy of the valence orbitals of boron (Zeff = 2.6) would be found. Is the location consistent with its electronegativity of 2.04 and its ionization energy of 800 kJ/mol? If not, explain why.