

CHAPTER 3 – ATOMIC STRUCTURE AND PROPERTIES

Introduction

The nuclear atom and quantum theory are the accepted theories for the atom. In this chapter, we demonstrate their utility by using them to explain trends in atomic properties.

3.1 Valence Electrons

Introduction

Most of the properties of an atom are related to the nature of its electron cloud and how strongly the electrons interact with the nucleus. In this section, we identify the electrons that are most important in determining atomic properties.

Prerequisites

- 2.7 Electron Configurations (Write electron configurations for atoms.)

Objectives

- Distinguish between core and valence electrons.
- Determine the number of valence electrons in an atom.
- Write valence electron configurations of main group atoms.

3.1-1. Valence Electrons Video

A video or simulation is available online.

3.1-2. Valence Electron Definition

Valence electrons consist of those electrons in the outermost s sublevel and those in any unfilled sublevel.

The electrons in an atom can be divided into two groups:

- **Core electrons** are the tightly bound electrons that are unaffected by chemical reactions. **Core electrons reside in filled sublevels** and form a spherical shell of negative charge around the nucleus that affects the amount of nuclear charge that the outermost electrons experience.
- **Valence electrons** are those outermost electrons that dictate the properties of the atom and are involved in chemical bonding. **The valence electrons are those in the outermost s sublevel and any unfilled sublevels.**

The number of valence electrons in an atom equals the group number of the atom.

3.1-3. Valence Electron Configurations of Main Group Elements

All of the elements in a group have the same number of valence electrons (Group number), and their valence electron configurations are the same except for the value of the n quantum number (the period). Thus, the periodicity of chemical properties is due to the periodicity of the valence electron configurations. The table shows the generic valence electron configurations of the elements in each group of the main group elements and the specific configurations of the second period.

Group	1A	2A	3A	4A	5A	6A	7A
Configuration	ns^1	ns^2	ns^2np^1	ns^2np^2	ns^2np^3	ns^2np^4	ns^2np^5
2 nd Period Element	Li	Be	B	C	N	O	F
Configuration	$2s^1$	$2s^2$	$2s^22p^1$	$2s^22p^2$	$2s^22p^3$	$2s^22p^4$	$2s^22p^5$

Table 3.1: Valence Electron Configurations

3.1-4. Valence Electron Configurations of Transition Elements

The valence electron configuration of the first row transition elements has the form $4s^23d^b$, where b is the position of the element in the d block. Cr and Cu are the two exceptions because they each promote one of their 4s electrons into the 3d sublevel to obtain half-filled and completely filled 3d sublevels. Zinc is often considered a transition element because of its location, but its d sublevel is full, and its chemistry is more like that of a Group 2A metal than a transition metal. Thus, its valence electron configuration is $4s^2$, in keeping with its Group number of 2B. Similarly, Cu is $4s^13d^{10}$, and the fact that it is a 1B element would lead you to think that its valence electron configuration should be $4s^1$. However, unlike zinc, copper does use its d orbitals in bonding. Indeed, the most common ion formed by copper is the Cu^{2+} ion. Thus, copper's chemistry is dictated by its d electrons, and its valence electron configuration is $4s^13d^{10}$.

3.1-5. Practice with Valence Electrons

Valence electrons and valence electron configurations are very important in chemistry. Practice determining the valence electron configurations for atoms and then check your answer by clicking on the element in the periodic table available online.

3.1-6. Core vs. Valence Electrons Exercise

EXERCISE 3.1:

Use the facts that all of the electrons in an atom are either core or valence electrons, and the number of valence equals the group number of the element to determine the number of valence and core electrons in each of the following atoms.

O

Valence = _____

Core = _____

Ca

Valence = _____

Core = _____

Sn

Valence = _____

Core = _____

3.1-7. Main Group Valence Configurations Exercise

EXERCISE 3.2:

Write the valence electron configuration of each of the following main group elements.

Si ($Z = 14$) _____

K ($Z = 19$) _____

Tl ($Z = 81$) _____

Br ($Z = 35$) _____

3.1-8. Transition Metal Valence Configurations Exercise

EXERCISE 3.3:

Write the valence electron configuration for each of the following transition elements.

Ti _____

Fe _____

Cu _____

3.1-9. More Valence Electron Configuration Exercises

EXERCISE 3.4:

Use the periodic table to help you write valence electron configurations for the following atoms.

1A 2A												3A 4A 5A 6A 7A 8A					
s block												p block					
1	2											1	2	3	4	5	He
Li	Be	d block										B	C	N	O	F	Ne
Na	Mg	1	2	3	4	5	6	7	8	9	10	Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Ac	Rf	Db	Sg	Bh	Hs	Mt									
		f block															
		1	2	3	4	5	6	7	8	9	10	11	12	13	14		
		Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu		
		Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr		

Sc _____

N _____

Co _____

Bi _____

Sr _____

Mn _____

3.2 Shielding and Effective Nuclear Charge

Introduction

In this section, you will learn how to predict the relative strengths with which the valence electrons interact with the nucleus.

3.2-1. Effective Nuclear Charge Video

A video or simulation is available online.

3.2-2. Shielding and Effective Nuclear Charge

Core electrons shield valence electrons better than do other valence electrons.

The nuclear charge experienced by an electron affects the size and energy of its orbitals, so it is an important factor in determining the properties of the valence electrons and orbitals. However, a valence electron is not attracted by the full positive charge of the nucleus because it is shielded by the other electrons, mainly the core electrons. The nuclear charge that is actually experienced by a valence electron is called the **effective nuclear charge**, Z_{eff} . 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).

$$Z_{\text{eff}} = Z - \sigma \quad \text{Effective Nuclear Charge} \quad (3.1)$$

σ is the **shielding** of the other electrons.

A valence electron is screened both by the core electrons and other valence electrons. However, core electrons are closer to the nucleus, so **core electrons shield valence electrons better than do other valence electrons**. This important fact will be used to explain the trends of atomic properties within a period.



Figure 3.1a In the absence of any electrons, the full nuclear charge (as shown by the red color) is observed. The nuclear charge is $+Z$, where Z is the atomic number (the number of protons in the nucleus). If this were a calcium nucleus, the resulting charge would be $+20$.



Figure 3.1b The nuclear charge is shielded by the negative charge of the core electrons (yellow sphere). Thus, only a portion of the nuclear charge can be felt through the core electrons as shown by the fact that the red color is greatly reduced by the yellow sphere. If this were a Group 2A element, the charge that would result would be $+2$ as the two valence electrons are not included. Thus, the charge has been reduced from $+40$ to $+2$ by the core electrons.



Figure 3.1c Addition of the valence electrons (green sphere) results in the atom. Essentially none of the nuclear charge is felt outside the neutral atom.

3.2-3. Trends in Z_{eff}

Effective nuclear charge increases going from left to right in a period.

Trends within a period: The charge of the nucleus increases by a full unit of positive charge in going from one element to the next in a period, but the additional electrons are valence electrons, which do not shield with a full negative charge. Consequently, **effective nuclear charge increases going from left to right in a period**. This effect is very important because it explains many trends within a period.

Consider the following comparison of Li and F:

- 1 $Z = 3$ for Li, which is $1s^2 2s^1$. $Z_{\text{eff}} \sim 1$ according to Figure 3.2. Thus, the two $1s$ electrons exert a shielding of $\sigma \sim 3 - 1 = 2$.
- 2 $Z = 9$ for F, which is $1s^2 2s^2 2p^5$, but $Z_{\text{eff}} \sim 5$. Thus, the shielding is $\sigma \sim 9 - 5 = 4$.

Although F has five more electrons than Li, they increase the shielding by only 2 (from 2 in Li to 4 in F). This is because they are valence electrons, which do not shield very well.

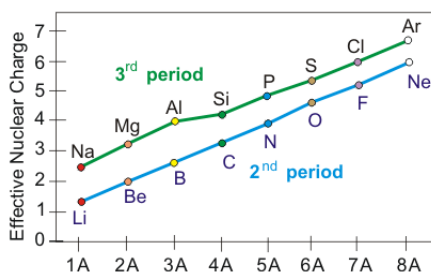


Figure 3.2 Effective Nuclear Charges of the Elements in the 2nd and 3rd Periods

Trends within a group: The shielding ability of the core electrons decreases as their n quantum number increases. As a result, the effective nuclear charge experienced by the valence electrons within a group increases with the n quantum number of the valence level. Consequently, effective nuclear charge increases going down a group. For example, the $2s$ electron on Li experiences an effective nuclear charge of ~ 1 , while the $3s$ electron on Na experiences a charge of ~ 2 , which shows that the $n = 2$ electrons do not shield as well as the $n = 1$ electrons.

This effect opposes that of changing the n quantum number because increasing n increases the energy of the valence levels, but increasing the effective nuclear charge lowers the energy of the valence levels. The effect of increasing n is the more important because the energies of the valence levels do increase going down a group.

3.2-4. Effective Nuclear Charge Exercise

EXERCISE 3.5:

Select the electron in each pair that experiences the greater effective nuclear charge.

2p in Cl

3p in Cl

4p in Br

5s in Rb

2p in F

3p in P

4s in Br

4s in K

3.3 Relative Atomic Size

Introduction

Atoms are not hard spheres with well defined boundaries, so the term “atomic radius” is somewhat vague and there are several definitions of what the atomic radius is. Consequently, atomic radii are not measured directly. Rather, they are inferred from the distances between atoms in molecules, which can be readily determined with several techniques. However, a discussion of how atomic radii are defined requires an understanding of chemical bonding and the solid state, so a detailed discussion of the different types of radii and their values is postponed until Chapter 8. In this section, we restrict our discussion to trends in the relative sizes of atoms.

Prerequisites

- 1.8 Electromagnetism and Coulomb’s Law
- 1.11 Dimitri Mendeleev and The Periodic Law
- 2.3 Bohr Model (Use the Bohr model to relate the size of an orbital to its n quantum number and atomic number.)

Objectives

- Explain the periodicity in the size of valence orbitals.
- Determine the relative sizes of atoms based on their positions in the periodic table.

3.3-1. The Bohr Model and Atomic Size

The size of the atom is given by the size of its valence electron clouds. Although the orbits of fixed radii suggested in the Bohr model are not correct, the conclusions of the model can still be used to gain a qualitative understanding of *trends* in atomic radii by substituting the effective nuclear charge for the atomic number in Equation 2.4 to obtain the following:

$$r_n \propto \frac{n^2}{Z_{\text{eff}}}$$

- The average size of an orbital increases as its n quantum number increases.
- The size of the electron cloud decreases as the effective nuclear charge it experiences increases.

3.3-2. Atomic Size

Atomic radii increase going down a group and decrease going across a period.

The size of an atom is defined by the size of the valence orbitals. Using the Bohr model as discussed above, we conclude that

- atomic radii increase going down a group because the n quantum number of the outermost orbitals increases, and

- atomic radii decrease going from left to right in a period because Z_{eff} increases.

Note that the atomic radii of H and Rb are 0.37 Å and 2.11 Å, respectively.

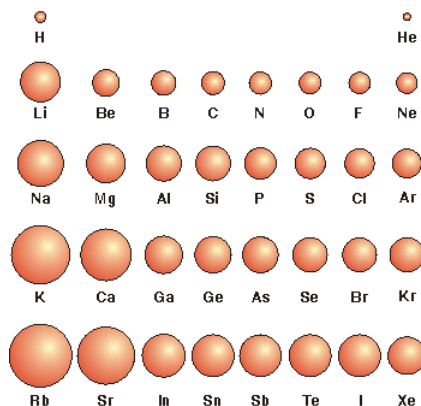


Figure 3.3 Relative Atomic Radii

3.3-3. Atomic Size Exercise

EXERCISE 3.6:

Use only a periodic table to determine the **largest** atom in each group.

Cl

Na

Br

F

S

K

I

Al

Ge

3.4 Relative Orbital Energies

Introduction

The relative energy of the valence orbitals in an atom is an important characteristic of the atom as it dictates both properties of the atom and the manner and strength of its interaction with other atoms. Indeed, we will invoke relative orbital energies in making predictions about chemical processes throughout the remainder of this course. In this section, we use the Bohr model to predict the relative energies of the valence orbitals in some small atoms.

Prerequisites

- 1.8 Electromagnetism and Coulomb's Law
- 1.11 Dimitri Mendeleev and The Periodic Law
- 2.3 Bohr Model (Use the Bohr model to relate the energy of an orbital to its n quantum number and atomic number.)

Objectives

- Determine the relative energies of electrons based on their n quantum number and the effective nuclear charge they experience.

3.4-1. Orbital Energies Video

A video or simulation is available online.

3.4-2. The Bohr Model and Orbital/Electron Energy

The ease with which an electron is lost from an atom is given by how strongly the electron is bound to the atom, which, in turn, is given by the energy of the electron in the atom. We again use the conclusions of the Bohr model in a qualitative way to understand *trends* in valence electron energies by substituting the effective nuclear charge for the atomic number in Equation 2.5 to obtain Equation 3.2.

$$E_x \propto -\frac{Z_{\text{eff}}^2}{n^2} \quad \text{Electron/Orbital Energy Approximation} \quad (3.2)$$

E_x is the energy of a valence orbital on atom X, and n is the principle quantum number of its valence shell. While Equation 3.2 is only a very rough approximation, it is useful in demonstrating how the **relative** orbital energies of the valence electrons in the atoms of the first three periods are related. We conclude that

- 1 The energy of an electron increases (becomes less negative and is bound less tightly) as its n quantum number increases.
- 2 The energy of an electron decreases (becomes more negative and is bound more tightly) as the effective nuclear charge increases.

3.4-3. Relative Energies, an Example

The valence orbitals of nonmetals are relatively low in energy, while those of metals are relatively high.

A video or simulation is available online.

We now determine the relative valence orbital energies of Li, C, and F as shown in Figure 3.4. We use the fact that they are each in the second period to get n and Figure 3.2 to obtain values of Z_{eff} and construct the table shown in Figure 3.4. We use Equation 3.2 and the values in the table to conclude the following.

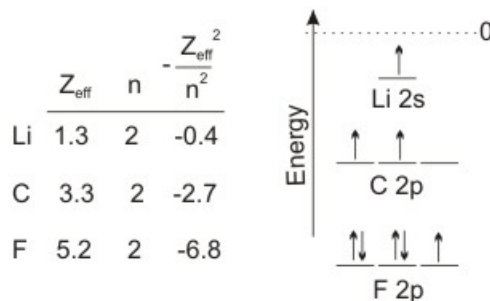


Figure 3.4

- The five 2p valence electrons of fluorine experience a highly positive effective nuclear charge of 5.2 and a very low n quantum number, so the value for $\frac{Z_{\text{eff}}^2}{n^2}$ is quite large. Thus, the energy of the valence orbitals of fluorine is very low. Indeed, they are the lowest-energy valence orbitals of any atom. Nonmetals are all characterized by low-energy valence orbitals.
- The two 2p electrons of carbon experience an effective nuclear charge of +3.3 and the same n quantum number as fluorine, so the value of $\frac{Z_{\text{eff}}^2}{n^2}$ is less than that of fluorine. Thus, the valence electrons of carbon are not bound as tightly as those on fluorine and the carbon valence orbitals are higher in energy than those of fluorine. However, carbon is a nonmetal, and the energy of its valence orbitals is still relatively low.
- Lithium is a metal, and its 2s valence electron experiences an effective nuclear charge of only +1.3, which produces a very low value for Z_{eff} squared over n squared. Consequently, the valence electron on a lithium atom is bound only weakly, and its valence orbital energy is quite high. Indeed, metals are all characterized by high-energy valence orbitals.

3.4-4. Predicting Relative Energy Exercise

EXERCISE 3.7:

Use the effective nuclear charges (Figure 3.2) and the n quantum number of the valence electrons of chlorine, oxygen, sulfur, and silicon in Equation 3.2 to predict the relative energies of their valence orbitals. Compare to the values of $\frac{Z_{\text{eff}}^2}{n^2}$ to those for Li (0.4), C (2.7), and F (6.8).

Chlorine ($Z_{\text{eff}} = 6.1$)
 above Li
 Li - - - - -
 between Li and C
 C - - - - -
 between C and F
 F - - - - -
 below F

Sulfur ($Z_{\text{eff}} = 5.5$)
 above Li
 Li - - - - -
 between Li and C
 C - - - - -
 between C and F
 F - - - - -
 below F

Oxygen ($Z_{\text{eff}} = 4.6$)
 above Li
 Li - - - - -
 between Li and C
 C - - - - -
 between C and F
 F - - - - -
 below F

Silicon ($Z_{\text{eff}} = 4.3$)
 above Li
 Li - - - - -
 between Li and C
 C - - - - -
 between C and F
 F - - - - -
 below F

3.4-5. Relative Valence Orbital Energies for Several Atoms

Before leaving our discussion of relative orbital energies, we add H ($Z_{\text{eff}} = 1$) and O ($Z_{\text{eff}} = 4.5$) to our energy diagram to obtain the following diagram that contains eight elements of the first three periods.

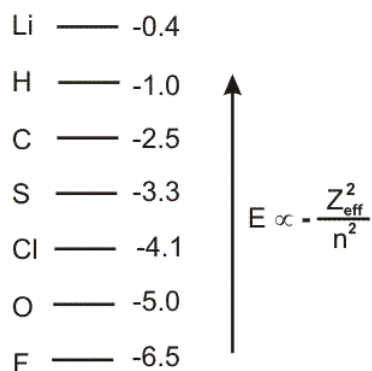


Figure 3.5 The relative energies of the valence orbitals of some atoms studied in the first three periods. Values of $-\frac{Z_{\text{eff}}^2}{n^2}$ are given to the right.

We draw the following two conclusions based on the diagram:

- 1 Orbital energies decrease (become more negative) going across a period because Z_{eff} increases. Thus, $\text{Li} > \text{C} > \text{O} > \text{F}$.
- 2 Orbital energies increase (become less negative) going down a group because n increases. Thus, $\text{Si} > \text{C}$; $\text{S} > \text{O}$; and $\text{Cl} > \text{F}$.

3.4-6. Orbital Energy Exercise

EXERCISE 3.8:

Consider the following valence orbital energy diagram that we have constructed to this point.

a
Li (-0.4)
b
H (-1.0)
c
Si (-2.0)
d
C (-2.5)
e
S (-3.3)
f
Cl (-4.2)
g
O (-5.0)
h
F (-6.5)

Where would the valence orbitals of the following atoms be placed? Give the letter of the location.

(a) N ($Z_{\text{eff}} = 3.83$)

a
b
c
d
e
f
g
h

(b) P ($Z_{\text{eff}} = 4.89$)

a
b
c
d
e
f
g
h

3.4-7. Core vs. Valence Orbital Energies Exercise

The energies of the valence orbitals of all atoms lie in a relatively narrow range due to the periodicity in Z_{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.

EXERCISE 3.9:

Select the orbital that is at lower energy in each pair.

2p on N
2s on N

2p on Br
2p on F

2p on N
2p on O

3.5 Ionization Energy

Introduction

One of the properties of an atom that is important in dictating the chemical properties of the atom is the ease with which the atom loses one or more of its valence electrons. This property of an atom is given by the atom's ionization energy or ionization potential, the topic of this section.

Prerequisites

- 1.8 Electromagnetism and Coulomb's Law
- 1.11 Dimitri Mendeleev and The Periodic Law
- 2.3 Bohr Model (Use the Bohr model to relate the energy of an orbital to its n quantum number and atomic number.)

Objectives

- Predict the relative ionization energies of atoms based on their positions in the periodic table or the relative energies of their occupied valence orbitals.

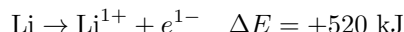
3.5-1. Ionization Energy Video

A video or simulation is available online.

3.5-2. Ionization Energy and Orbital Energy

Ionization energies measure the energy of the highest energy electron.

The **ionization energy** (IE) of an atom is the energy required to remove the highest energy electron. The ionization energy of lithium is 520 kJ/mol, which means that the electrons in a mole of lithium atoms can be removed by the input of 520 kJ. The ionization process is

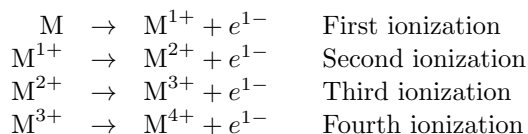


where $\Delta E = IE$, the ionization energy. The energy change results because the energy of the electron in the initial state is different than in the final state. In the initial state, the electron is in an orbital of energy E_n , but in the final state, it is a free electron with no potential energy. The relationship between the ionization energy and the orbital energy is obtained as follows:

$$\begin{aligned} IE &= E_{\text{final}} - E_{\text{initial}} \\ IE &= \text{free electron energy} - \text{orbital energy} \\ IE &= 0 - E_n \end{aligned}$$

Thus, $IE = -E_n$. The orbital energy of the highest energy electron can be approximated as the negative of the ionization energy of the atom.

In the above discussion, we have considered the removal of only the highest energy electron, but as shown in the following, other electrons can also be removed by successive ionizations. Thus, the energy required to remove the first electron is the first ionization energy and that required to remove the second electron is the second ionization energy, and so forth. Consider the case of the metal M.



The loss of an electron reduces the screening of the remaining electrons, so the remaining electrons experience greater nuclear charge and are more difficult to remove. Thus, each successive ionization energy is greater than the preceding. We use the term ionization energy to refer to the first ionization energy in the remainder of the chapter.

3.5-3. Putting Numbers to Orbital Energies

The energy required to remove one 2p electron from each atom in a mole of F atoms to produce a mole of F^{1+} ions is 1681 kJ, so the ionization energy of fluorine is 1681 kJ/mol. In addition, 1681 kJ/mole are released in the reverse process, so we conclude that the 2p orbital energy is -1681 kJ/mol. Nonmetals are characterized by high ionization energies and low valence orbital energies because they have high effective nuclear charges.

The ionization energy of carbon is 1086 kJ/mol, so the orbital energy of a 2p orbital in carbon is -1086 kJ/mol.

The ionization energy of lithium is only 520 kJ/mol, so the orbital energy of its 2s orbital is -520 kJ/mol. The valence orbitals of metals are characterized by low ionization energies and high valence orbital energies because they have low effective nuclear charges.

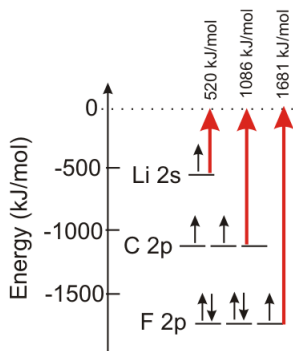


Figure 3.6 Ionization Energy and Orbital Energy

3.5-4. Ionization Energy Trends

Ionization energies increase going up a group and going from left to right in a period.

Ionization energy is the energy required to remove the highest energy electron from an atom, which can be estimated with the assumption that $IE = -E_n$; i.e., that the ionization energy equals the negative of the orbital energy of the electron. E_n can be estimated with Equation 3.2, so we conclude that ionization energies

- increase moving up a group due to the decrease in the n quantum number, and
- increase from left to right in a period due to the increase in Z_{eff} .

This trend is shown in Figure 3.7, which shows the ionization energies of the atoms in order of atomic number. However, there are some apparent exceptions that arise because **electron configurations in which sublevels are filled (Groups 2A and 8A) or half-filled (Group 5A) are unusually stable, so removing an electron from an element in one of these groups 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.

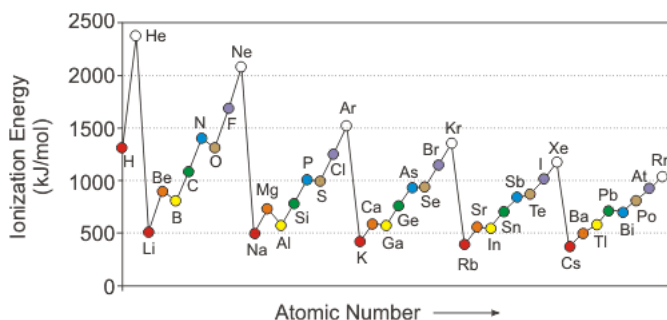


Figure 3.7 First Ionization Energies of the Main Group Elements: Circles of the same color represent elements of the same group. For example, all Group 1A elements are shown as red circles.

Summary

- **Metals** are characterized by low effective nuclear charge, so they all have low ionization energies. Consequently, **metals tend to lose electrons**, and the farther to the left of the Periodic Table, the more easily the electrons are lost. Thus, the 1A elements lose their valence electron very easily. The ionization energy also decreases going down a family, so Cs (high n and low Z_{eff}) loses its valence electron so easily that it must be stored in oil because it gives up its 6s electron to water or oxygen when exposed to the air.

- **Nonmetals** have high effective nuclear charges, so they have relatively high ionization energies. Thus, nonmetals do not lose their electrons very easily. Excluding the noble gases, F (low n and high Z_{eff}) has the highest ionization energy of any atom, which means that the valence electrons of fluorine are very tightly bound.

3.5-5. Ionization Energy Exercise

EXERCISE 3.10:

Use only a Periodic Table to determine the atom in each group with the **greatest** ionization energy.

Cl	Na	Br	Si
F	S	K	P
I	Al	Ge	S

3.6 Electronegativity

Introduction

The electrons in a bond can lower their potential energy by residing closer to the atom in the bond that has the valence orbital at lower energy. The ability of an atom to attract the bonding electrons to itself is called its **electronegativity** (χ). Atoms are most electronegative when their valence orbitals are low in energy. Electronegativity is the topic of this section.

Prerequisites

- 1.8 Electromagnetism and Coulomb's Law
- 1.11 Dimitri Mendeleev and The Periodic Law
- 2.3 Bohr Model (Use the Bohr model to relate the energy of an orbital to its n quantum number and atomic number.)

Objectives

- Predict the relative electronegativities of atoms based on their positions in the periodic table or the relative energies of their unfilled valence orbitals.
- Explain the differences between metals and nonmetals that arise from the differences in their ionization energies and electronegativities.

3.6-1. Electronegativity Video

A video or simulation is available online.

3.6-2. Electronegativity and Orbital Energy

Atoms with low-energy valence orbitals are highly electronegative.

Electronegativity (χ) 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.

EXAMPLE:

$E_n = -\frac{(Z_{\text{eff}})^2}{n^2}$, so the valence orbitals of atoms with high electronegativities have

- 1 large Z_{eff} (nonmetals) and
- 2 low n quantum numbers (high in the periodic table).

Consider the orbital energies of Li, C, and F shown in Figure 3.8. Li is a metal with a low Z_{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_{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 halfway between the valence orbital energies of Li and F, and its electronegativity is also about half way between these two extremes in the period.

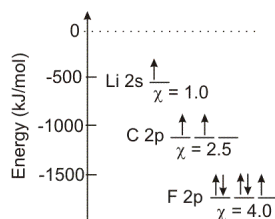


Figure 3.8 Electronegativity and Orbital Energy

3.6-3. The Meaning of Electronegativity

The electronegativity difference between two atoms dictates the type of bond that forms between them. Refer to Figure 3.9 for the following discussion.

- 1 The electronegativities of two fluorine atoms are identical, so the bonding electrons are shared equally by the two atoms. Bonds in which the bonding electrons are shared equally are called covalent bonds.
- 2 Fluorine is more electronegative than carbon, so the bonding electrons in a C-F bond reside closer to the fluorine atom. The excess of electron density close to the fluorine atom gives it a partial negative charge. A Greek delta (δ) is used to indicate that it is only a partial charge as the carbon still experiences some of the negative charge of the bonding electrons.
- 3 The electronegativity difference between Li and F is so great that the bonding electrons reside almost exclusively on the fluorine to give it a full negative charge. Bonds in which the bonding electrons are not shared but reside on one atom are called ionic bonds.

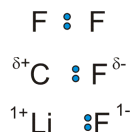


Figure 3.9

Ionic bonds are the topic of Chapter 4, and covalent bonds are discussed in Chapters 5 and 6.

3.6-4. Electronegativity Trends

Electronegativities decrease going down a group and increase going across a period.

We use the Bohr model to approximate the energy of the lowest energy empty orbital $-E_n$ and conclude that

- electronegativities decrease going down a group because n increases, which causes the orbital energies to increase, and

- electronegativities increase going from left to right in a period because Z_{eff} increases, which causes the orbital energies to decrease (become more negative).

Consequently,

- **Nonmetals** are characterized by high Z_{eff} , so their valence orbitals are low in energy. Consequently, **nonmetals are highly electronegative** (2.0 to 4.0).
- **Main group metals** have low effective nuclear charges and are characterized by high energy valence orbitals. Thus, **main group metals have very low electronegativities** (0.7 to 1.5).

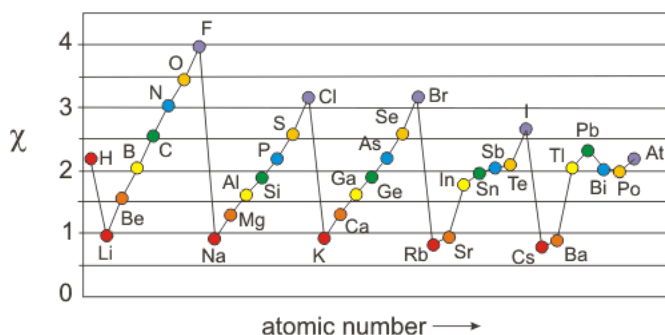


Figure 3.10 Electronegativities of the Main Group Elements: Circles of the same color represent elements of the same group. For example, all Group 1A elements are shown as red circles.

3.6-5. Late Metals

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 (see Table 3.2), which impacts significantly on their chemical properties.

Metal	χ
Ag	1.9
Sn	2.0
Hg	2.0
Tl	2.0
Pb	2.3

Table 3.2: Electronegativities of Late Metals

3.6-6. Metals vs. Nonmetals

Metals have low ionization energies and nonmetals have high electronegativities.

Metals are characterized by lower effective nuclear charges, so they have

- relatively large atomic radii
- lower ionization energies
- lower electronegativities

Nonmetals are characterized by high effective nuclear charges, so they have

- relatively small atomic radii
- higher ionization energies

- higher electronegativities

Thus, **metals tend to lose electrons (low ionization energy), while nonmetals tend to gain electrons (high electronegativities).**

3.6-7. Electronegativity Exercise

EXERCISE 3.11:

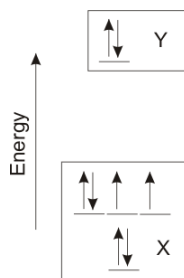
Use only a Periodic Table to determine the atom in each group with the **greatest** electronegativity.

Cl	Na	Br	Al
F	S	K	Tl
I	Al	Ge	Ga

3.6-8. Orbital Energy and Atomic Properties Exercise

EXERCISE 3.12:

Use what you have learned about the relationships between orbital energies and ionization energies and electronegativities and the valence orbital occupancies of atoms X and Y given below to answer the following questions about atoms X and Y.



The atom with the lower ionization energy:

X
Y

The atom with the higher electronegativity:

X
Y

The group of the periodic table to which each atom belongs:

X _____

Y _____

3.7 Magnetic Properties

Introduction

All magnetic properties are due to the magnetic fields caused by electron spin. 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. In this section, we give a brief introduction into the magnetic properties of atoms and materials.

Prerequisites

- 2.5 The Quantum Numbers (Explain the meaning of the m_s quantum number.)

Objectives

- Explain the origin of magnetism.
- Distinguish between paramagnetic and diamagnetic atoms.
- Explain why magnetic atoms are not always magnetic materials.

3.7-1. Paramagnetism and Diamagnetism

The paramagnetism of an atom increases with the number of unpaired electrons.

Atoms with unpaired electrons are **paramagnetic**. Paramagnetic atoms align in magnetic fields due to the presence of the unpaired electrons. The more unpaired electrons an atom has, the more paramagnetic it is. Both Li and N have unfilled valence subshells, so both have unpaired electrons and are paramagnetic. N has three unpaired electrons while Li has only one, so N is more paramagnetic than Li.

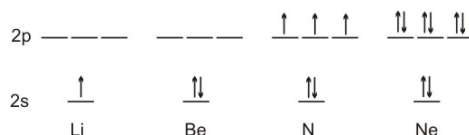


Figure 3.11

Atoms with no unpaired electrons are **diamagnetic**. Diamagnetic atoms do not align in magnetic fields because they have no unpaired electrons. Neither Be nor Ne has any unfilled valence shells, so both are diamagnetic.

3.7-2. Ferromagnetism

Ferromagnetism is a measure of the bulk magnetism of a material, while paramagnetism is a measure of the magnetism of individual atoms.

Paramagnetism and diamagnetism are atomic properties, not bulk properties. Thus, N and Li are paramagnetic atoms, but nitrogen gas and lithium metal are not magnetic because the unpaired electrons on the atoms pair with one another to form materials that are not magnetic. The magnetism you are familiar with is called **ferromagnetism**. It is a **bulk property** because it requires unpaired electrons in a material, not just in an isolated atom. Iron is the best known example. Fe atoms have four unpaired electrons, so Fe atoms are paramagnetic. When Fe atoms bond to form iron metal, there is electron pairing in the solid, but not all four electrons pair. Consequently, iron metal is magnetic and iron is a ferromagnet.

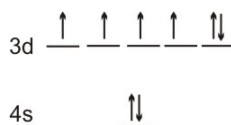


Figure 3.12 Valence orbital occupancy of Fe. It is both paramagnetic and ferromagnetic.

3.7-3. Paramagnetism Exercise

EXERCISE 3.13:

Use a Periodic Table to determine the more paramagnetic atom in each pair.

O
N

Na
Mg

Cr
Fe

3.8 Exercises and Solutions

Links to view either the end-of-chapter exercises or the solutions to the odd exercises are available in the HTML version of the chapter.