AUCHE 230 - STRUCTURE AND BONDING



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AUCHE 230 - Structure and Bonding

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Licensing

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CHAPTER OVERVIEW

1: Review

1.1: The Structure of Atoms
1.2: Nuclei of Atoms
1.3: Lewis Symbols and Structures
1.4: Formal Charges and Resonance
1.5: Molecular Structure and Polarity

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1.1: The Structure of Atoms

Learning Objectives

- Describe the three main subatomic particles.
- State how the subatomic particles are arranged in atoms.

There have been several minor but important modifications to Dalton's atomic theory. For one thing, Dalton considered atoms to be indivisible. We know now that atoms not only can be divided but also are composed of three different kinds of particle, *subatomic particles*, with their own properties that are different from the chemical properties of atoms.

Subatomic Particles

The first subatomic particle was identified in 1897 and called the electron. It is an extremely tiny particle, with a mass of about 9.109×10^{-31} kg. Experiments with magnetic fields showed that the electron has a negative electrical charge. By 1920, experimental evidence indicated the existence of a second particle. A proton has the same amount of charge as an electron, but its charge is positive, not negative. Another major difference between a proton and an electron is mass. Although still incredibly small, the mass of a proton is 1.673×10^{-27} kg, which is almost 2,000 times greater than the mass of an electron. Because opposite charges attract each other (while like charges repel each other), protons attract electrons (and vice versa).

Finally, additional experiments pointed to the existence of a third particle. Evidence produced in 1932 established the existence of the neutron, a particle with about the same mass as a proton but with no electrical charge, it is *neutral*. We understand now that all atoms can be broken down into subatomic particles: protons, neutrons, and electrons. Table 1.1.1 lists some of their important characteristics and the symbols used to represent each particle.

Table 1.1.1: Properties of the Subatomic Particles

Particle	Symbol	Mass (kg)	Relative Mass (proton = 1)	Relative Charge
proton	p^+	1.673×10^{-27}	1	+1
neutron	n^0	1.675×10^{-27}	1	0
electron	e^-	9.109×10^{-31}	0.00055	−1

The Nucleus

How are these subatomic particles arranged? Between 1909 and 1911, Ernest Rutherford, a Cambridge physicist, and his associates Hans Geiger and Ernest Marsden performed experiments that provided strong evidence concerning the internal structure of an atom. They took a very thin metal foil, such as gold or platinum, and aimed a beam of positively charged particles (called alpha particles, which are combinations of two protons and two neutrons) from a radioactive source toward the foil. Surrounding the foil was a detector—either a scintillator (a material that glows when hit by such particles) or some unexposed film (which is exposed where the particles hit it). The detector allowed the scientists to determine the distribution of the alpha particles after they interacted with the foil. Figure 1.1.1 shows a diagram of the experimental setup.

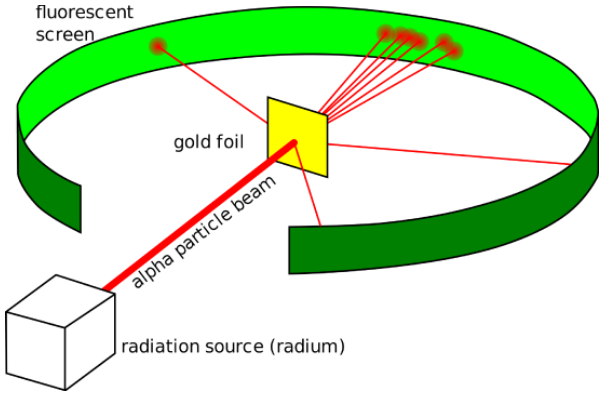


Figure 1.1.1: The Geiger-Marsden Experimental Setup. Experiments using this setup were used to investigate the structure of atoms. In this experiment, most of the particles traveled straight through the foil, but some alpha particles were deflected off to one side. Some were even deflected back toward the source. This was unexpected. Rutherford once said, "It was almost as incredible as if you fired a 15-inch shell at a piece of tissue paper and it came back and hit you." (CC SA-BY 3.0; Kurzon).

Rutherford proposed the following model to explain these experimental results. Protons and neutrons are concentrated in a central region he called the nucleus (plural, *nuclei*) of the atom. Electrons are outside the nucleus and orbit about it because they are attracted to the positive charge in the nucleus. Most of the mass of an atom is in the nucleus, while the orbiting electrons account for an atom's size. As a result, an atom consists largely of empty space. Rutherford called his description the "planetary model" of the atom. Figure 1.1.2 shows how this model explains the experimental results.

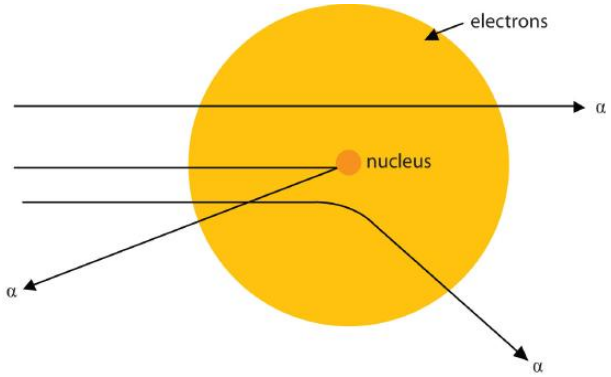


Figure 1.1.2: Rutherford's Metal Foil Experiments. Rutherford explained the results of the metal foil experiments by proposing that most of the mass and the positive charge of an atom are located in its nucleus, while the relatively low-mass electrons orbit about the nucleus. Most alpha particles go straight through the empty space, a few particles are deflected, and fewer still ricochet back toward the source. The nucleus is much smaller proportionately than depicted here.

> *The planetary model of the atom replaced the plum pudding model, which had electrons floating around aimlessly like plums in a "pudding" of positive charge.*

Rutherford's model is essentially the same model that we use today to describe atoms but with one important modification. The planetary model suggests that electrons occupy certain specific, circular orbits about the nucleus. We know now that this model is overly simplistic. A better description is that electrons form fuzzy clouds around nuclei. Figure 1.1.3 shows a more modern version of our understanding of atomic structure.

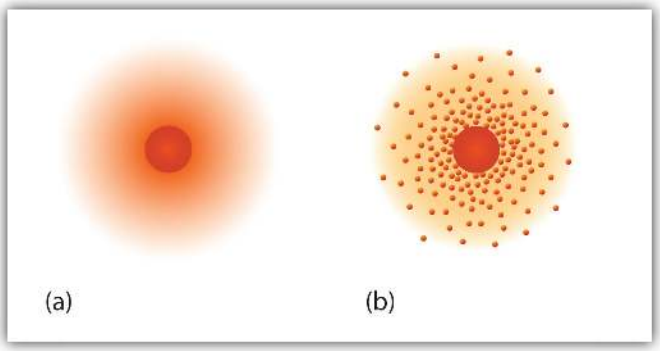


Figure 1.1.3: A Modern Depiction of Atomic Structure. A more modern understanding of atoms, reflected in these representations of the electron in a hydrogen atom, is that electrons occupy regions of space about the nucleus; they are not in discrete orbits like planets around the sun. (a) The darker the color, the higher the probability that an electron will be at that point. (b) In a two-dimensional cross section of the electron in a hydrogen atom, the more crowded the dots, the higher the probability that an electron will be at that point. In both (a) and (b), the nucleus is in the center of the diagram.

Concept Review Exercises

1. What are the charges and the relative masses of the three subatomic particles?
2. Describe the structure of an atom in terms of its protons, neutrons, and electrons.

Answers

1. proton: +1, large; neutron: 0, large; electron: −1, small
2. Protons and neutrons are located in a central nucleus, while electrons orbit about the nucleus.

Key Takeaways

- Atoms are composed of three main subatomic particles: protons, neutrons, and electrons.
- Protons and neutrons are grouped together in the nucleus of an atom, while electrons orbit about the nucleus.

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1.2: Nuclei of Atoms

Learning Objectives

- Define and differentiate between the atomic number and the mass number of an element.
- Explain how isotopes differ from one another.

Now that we know how atoms are generally constructed, what do atoms of any particular element look like? How many protons, neutrons, and electrons are in a specific kind of atom? First, if an atom is electrically neutral overall, then the number of protons equals the number of electrons. Because these particles have the same but opposite charges, equal numbers cancel out, producing a neutral atom.

Atomic Number

In the 1910s, experiments with x-rays led to this useful conclusion: the magnitude of the positive charge in the nucleus of every atom of a particular element is the same. In other words, all atoms of the same element have the same number of protons. Furthermore, different elements have a different number of protons in their nuclei, so the number of protons in the nucleus of an atom is characteristic of a particular element. This discovery was so important to our understanding of atoms that the number of protons in the nucleus of an atom is called the atomic number (Z).

For example, hydrogen has the atomic number 1; all hydrogen atoms have 1 proton in their nuclei. Helium has the atomic number 2; all helium atoms have 2 protons in their nuclei. There is no such thing as a hydrogen atom with 2 protons in its nucleus; a nucleus with 2 protons would be a helium atom. The atomic number *defines* an element. Table 1.2.1 lists some common elements and their atomic numbers. Based on its **atomic number**, you can determine the **number of protons in the nucleus** of an atom. The largest atoms have over 100 protons in their nuclei.

Table 1.2.1: Some Common Elements and Their Atomic Numbers

Element	Atomic Number	Element	Atomic Nmbers
aluminum (Al)	13	magnesium (Mg)	12
americium (Am)	95	manganese (Mn)	25
argon (Ar)	18	mercury (Hg)	80
barium (Ba)	56	neon (Ne)	10
beryllium (Be)	4	nickel (Ni)	28
bromine (Br)	35	nitrogen (N)	7
calcium (Ca)	20	oxygen (O)	8
carbon (C)	6	phosphorus (P)	15
chlorine (Cl)	17	platinum (Pt)	78
chromium (Cr)	24	potassium (K)	19
cesium (Cs)	55	radon (Rn)	86
fluorine (F)	9	silver (Ag)	47
gallium (Ga)	31	sodium (Na)	11
gold (Au)	79	strontium (Sr)	38
helium (He)	2	sulfur (S)	16
hydrogen (H)	1	titanium (Ti)	22

Element	Atomic Number	Element	Atomic Nmbers
iron (Fe)	26	tungsten (W)	74
iodine (I)	53	uranium (U)	92
lead (Pb)	82	zinc (Zn)	30
lithium (Li)	3	zirconium (Zr)	40

Example 1.2.1

What is the number of protons in the nucleus of each element?

a. aluminum
b. iron
c. carbon

Answer a

According to Table 2.4.1, aluminum has an atomic number of 13. Therefore, every aluminum atom has 13 protons in its nucleus.

Answer b

Iron has an atomic number of 26. Therefore, every iron atom has 26 protons in its nucleus.

Answer c

Carbon has an atomic number of 6. Therefore, every carbon atom has 6 protons in its nucleus.

Exercise 1.2.1

What is the number of protons in the nucleus of each element? Use Table 2.4.1.

a. sodium
b. oxygen
c. chlorine

Answer a

Sodium has 11 protons in its nucleus.

Answer b

Oxygen has 8 protons in its nucleus.

Answer c

Chlorine has 17 protons in its nucleus

How many electrons are in an atom? Previously we said that for an electrically neutral atom, the **number of electrons equals the number of protons**, so the total opposite charges cancel. Thus, the **atomic number** of an element also gives the **number of electrons** in an atom of that element. (Later we will find that some elements may gain or lose electrons from their atoms, so those atoms will no longer be electrically neutral. Thus we will need a way to differentiate the number of electrons for those elements.)

Example 1.2.2

How many electrons are present in the atoms of each element?

a. sulfur
b. tungsten

c. argon

Answer a

The atomic number of sulfur is 16. Therefore, in a neutral atom of sulfur, there are 16 electrons.

Answer b

The atomic number of tungsten is 74. Therefore, in a neutral atom of tungsten, there are 74 electrons.

Answer c

The atomic number of argon is 18. Therefore, in a neutral atom of argon, there are 18 electrons.

? Exercise 1.2.2

How many electrons are present in the atoms of each element?

a. magnesium
b. potassium
c. iodine

Answer a

Mg has 12 electrons.

Answer b

K has 19 electrons.

Answer c

I has 53 electrons.

Isotopes

How many neutrons are in atoms of a particular element? At first it was thought that the number of neutrons in a nucleus was also characteristic of an element. However, it was found that atoms of the same element can have *different* numbers of neutrons. Atoms of the same element (i.e., same atomic number, Z) that have different numbers of neutrons are called isotopes. For example, 99% of the carbon atoms on Earth have 6 neutrons and 6 protons in their nuclei; about 1% of the carbon atoms have 7 neutrons in their nuclei. Naturally occurring carbon on Earth, therefore, is actually a mixture of isotopes, albeit a mixture that is 99% carbon with 6 neutrons in each nucleus.

An important series of isotopes is found with hydrogen atoms. Most hydrogen atoms have a nucleus with only a single proton. About 1 in 10,000 hydrogen nuclei, however, also has a neutron; this particular isotope is called *deuterium*. An extremely rare hydrogen isotope, *tritium*, has 1 proton and 2 neutrons in its nucleus. Figure 1.2.1 compares the three isotopes of hydrogen.

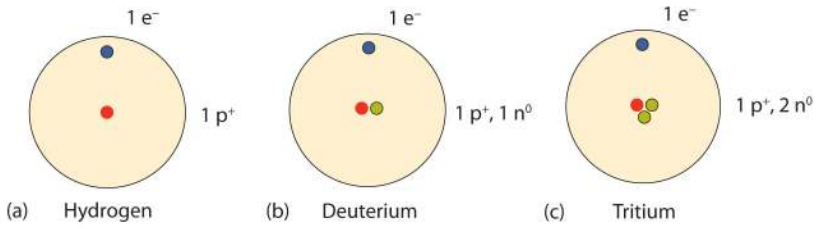


Figure 1.2.1: Isotopes of Hydrogen. Most hydrogen atoms have only a proton in the nucleus (a). A small amount of hydrogen exists as the isotope deuterium, which has one proton and one neutron in its nucleus (b). A tiny amount of the hydrogen isotope tritium, with one proton and two neutrons in its nucleus, also exists on Earth (c). The nuclei and electrons are proportionately much smaller than depicted here.

The discovery of isotopes required a minor change in Dalton's atomic theory. Dalton thought that all atoms of the same element were exactly the same.

Most elements exist as mixtures of isotopes. In fact, there are currently over 3,500 isotopes known for all the elements. When scientists discuss individual isotopes, they need an efficient way to specify the number of neutrons in any particular nucleus. The *mass number* (A) of an atom is the sum of the numbers of protons and neutrons in the nucleus. Given the mass number for a nucleus (and knowing the atomic number of that particular atom), you can determine the number of neutrons by subtracting the atomic number from the mass number.

A simple way of indicating the mass number of a particular isotope is to list it as a superscript on the left side of an element's symbol. Atomic numbers are often listed as a subscript on the left side of an element's symbol. Thus, we might see

$$\begin{matrix}\text{mass number}\longrightarrow\\ \text{atomic number}\longrightarrow\end{matrix}{}^{56}_{26}\text{Fe} \tag{1.2.1}$$

which indicates a particular isotope of iron. The 26 is the atomic number (which is the same for all iron atoms), while the 56 is the mass number of the isotope. To determine the number of neutrons in this isotope, we subtract 26 from 56: 56 − 26 = 30, so there are 30 neutrons in this atom.

Example 1.2.3

How many protons and neutrons are in each atom?

a. $^{35}_{17}\text{Cl}$
b. $^{127}_{53}\text{I}$

Answer a

In $^{35}_{17}\text{Cl}$ there are 17 protons, and 35 − 17 = 18 neutrons in each nucleus.

Answer b

In $^{127}_{53}\text{I}$ there are 53 protons, and 127 − 53 = 74 neutrons in each nucleus.

Exercise 1.2.3

How many protons and neutrons are in each atom?

a. $^{197}_{79}\text{Au}$
b. $^{23}_{11}\text{Na}$

Answer a

In $^{197}_{79}\text{Au}$ there are 79 protons, and 197 − 79 = 118 neutrons in each nucleus.

Answer b

In $^{23}_{11}\text{Na}$ there are 11 protons, and 23 − 11 = 12 neutrons in each nucleus.

It is not absolutely necessary to indicate the atomic number as a subscript because each element has its own unique atomic number. Many isotopes are indicated with a superscript only, such as ^{13}C or ^{235}U. You may also see isotopes represented in print as, for example, carbon-13 or uranium-235.

Summary

The atom consists of discrete particles that govern its chemical and physical behavior. Each atom of an element contains the same number of protons, which is the **atomic number (Z)**. Neutral atoms have the same number of electrons and protons. Atoms of an element that contain different numbers of neutrons are called **isotopes**. Each isotope of a given element has the same atomic number but a different **mass number (A)**, which is the **sum of the numbers of protons and neutrons**.

Almost all of the mass of an atom is from the total protons and neutrons contained within a tiny (and therefore very dense) nucleus. The majority of the volume of an atom is the surrounding space in which the electrons reside. A representation of a carbon-12 atom is shown below in Figure 1.2.2.

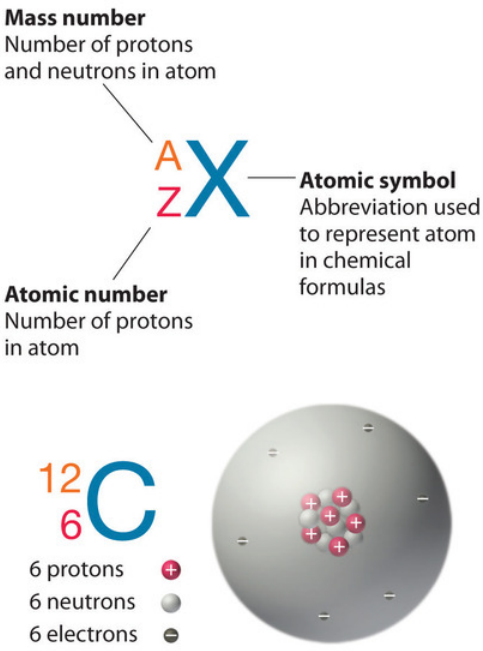


Figure 1.2.2: Formalism used for identifying specific nuclide (any particular kind of nucleus)

The atomic symbol, X, is the abbreviation used to represent an atom in chemical formulas. The mass number, A, is the number of protons and neutrons in the atom, which is to the left of the X. The atomic number, Z, is the number of protons in the atom, which is to the left of the X and below the A.

Concept Review Exercises

1. Why is the atomic number so important to the identity of an atom?
2. What is the relationship between the number of protons and the number of electrons in an atom?
3. How do isotopes of an element differ from each other?
4. What is the mass number of an element?

Answers

1. The atomic number defines the identity of an element. It describes the number of protons in the nucleus.
2. In an electrically neutral atom, the number of protons equals the number of electrons.
3. Isotopes of an element have the same number of protons but have different numbers of neutrons in their nuclei.
4. The mass number is the sum of the numbers of protons and neutrons in the nucleus of an atom.

Key Takeaways

- Each element is identified by its atomic number. The atomic number provides the element's location on the periodic table
- The isotopes of an element have different masses and are identified by their mass numbers.

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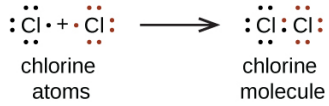
1.3: Lewis Symbols and Structures

Learning Objectives

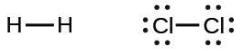
- Draw Lewis structures depicting the bonding in simple molecules

Lewis Structures

We also use Lewis symbols to indicate the formation of covalent bonds, which are shown in Lewis structures, drawings that describe the bonding in molecules and polyatomic ions. For example, when two chlorine atoms form a chlorine molecule, they share one pair of electrons:



The Lewis structure indicates that each Cl atom has three pairs of electrons that are not used in bonding (called lone pairs) and one shared pair of electrons (written between the atoms). A dash (or line) is usually used to indicate a shared pair of electrons:



In the Lewis model, a single shared pair of electrons is a single bond. Each Cl atom interacts with eight valence electrons total: the six in the lone pairs and the two in the single bond.

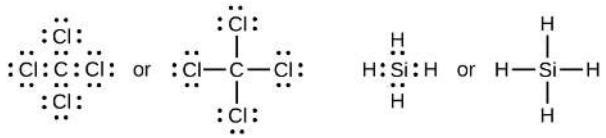


Lewis Structure of Molecules: https://youtu.be/xWiFCqA9Ur0

The Octet Rule

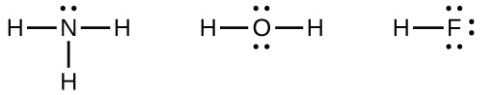
The other halogen molecules (F_2, Br_2, I_2, and At_2) form bonds like those in the chlorine molecule: one single bond between atoms and three lone pairs of electrons per atom. This allows each halogen atom to have a noble gas electron configuration. The tendency of main group atoms to form enough bonds to obtain eight valence electrons is known as the octet rule.

The number of bonds that an atom can form can often be predicted from the number of electrons needed to reach an octet (eight valence electrons); this is especially true of the nonmetals of the second period of the periodic table (C, N, O, and F). For example, each atom of a group 14 element has four electrons in its outermost shell and therefore requires four more electrons to reach an octet. These four electrons can be gained by forming four covalent bonds, as illustrated here for carbon in CCl_4 (carbon tetrachloride) and silicon in SiH_4 (silane). Because hydrogen only needs two electrons to fill its valence shell, it is an exception to the octet rule and only needs to form one bond. The transition elements and inner transition elements also do not follow the octet rule since they have d and f electrons involved in their valence shells.



carbon tetrachloride silane

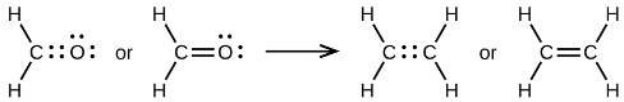
Group 15 elements such as nitrogen have five valence electrons in the atomic Lewis symbol: one lone pair and three unpaired electrons. To obtain an octet, these atoms form three covalent bonds, as in NH_3 (ammonia). Oxygen and other atoms in group 16 obtain an octet by forming two covalent bonds:



ammonia Water hydrogen fluoride

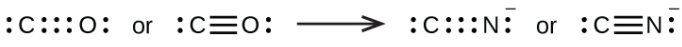
Double and Triple Bonds

As previously mentioned, when a pair of atoms shares one pair of electrons, we call this a single bond. However, a pair of atoms may need to share more than one pair of electrons in order to achieve the requisite octet. A double bond forms when two pairs of electrons are shared between a pair of atoms, as between the carbon and oxygen atoms in CH_2O (formaldehyde) and between the two carbon atoms in C_2H_4 (ethylene):



formaldehyde ethylene

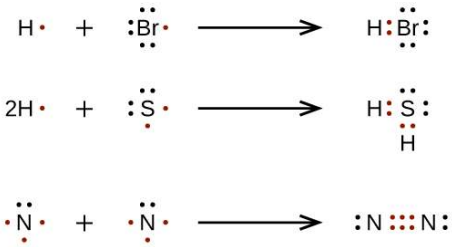
A triple bond forms when three electron pairs are shared by a pair of atoms, as in carbon monoxide (CO) and the cyanide ion (CN^-):



carbon monoxide cyanide ion

Writing Lewis Structures with the Octet Rule

For very simple molecules and molecular ions, we can write the Lewis structures by merely pairing up the unpaired electrons on the constituent atoms. See these examples:



For more complicated molecules and molecular ions, it is helpful to follow the step-by-step procedure outlined here:

1. Determine the total number of valence (outer shell) electrons among all the atoms. For cations, subtract one electron for each positive charge. For anions, add one electron for each negative charge.
2. Draw a skeleton structure of the molecule or ion, arranging the atoms around a central atom. (Generally, the least electronegative element should be placed in the center.) Connect each atom to the central atom with a single bond (one electron pair).
3. Distribute the remaining electrons as lone pairs on the terminal atoms (except hydrogen), completing an octet around each atom.

4. Place all remaining electrons on the central atom.
5. Rearrange the electrons of the outer atoms to make multiple bonds with the central atom in order to obtain octets wherever possible.

Let us determine the Lewis structures of SiH_4, CHO_2^-, NO^+, and OF_2 as examples in following this procedure:

1. Determine the total number of valence (outer shell) electrons in the molecule or ion.
   - For a molecule, we add the number of valence electrons on each atom in the molecule:

$$\begin{aligned} &SiH_4 && (1.3.1)\\ &\text{Si: } 4 \text{ valence electrons/atom} \times 1 \text{ atom} = 4 && (1.3.2)\\ &+\text{H: } 1 \text{ valence electron/atom} \times 4 \text{ atoms} = 4 && (1.3.3)\\ &\qquad\qquad = 8 \text{ valence electrons} && (1.3.4)\end{aligned}$$

   - For a *negative ion*, such as CHO_2^-, we add the number of valence electrons on the atoms to the number of negative charges on the ion (one electron is gained for each single negative charge):

$$\begin{aligned} &CHO_2^-\\ &\text{C: } 4 \text{ valence electrons/atom} \times 1 \text{ atom} = 4\\ &\text{H: } 1 \text{ valence electron/atom} \times 1 \text{ atom} = 1\\ &\text{O: } 6 \text{ valence electrons/atom} \times 2 \text{ atoms} = 12\\ &+ \qquad\qquad 1 \text{ additional electron} = 1\\ &\qquad\qquad = 18 \text{ valence electrons}\end{aligned}$$

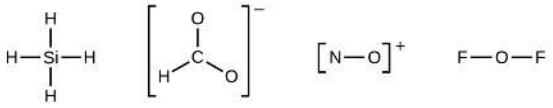
   - For a *positive ion*, such as NO^+, we add the number of valence electrons on the atoms in the ion and then subtract the number of positive charges on the ion (one electron is lost for each single positive charge) from the total number of valence electrons:

$$\begin{aligned} &NO^+\\ &\text{N: } 5 \text{ valence electrons/atom} \times 1 \text{ atom} = 5\\ &\text{O: } 6 \text{ valence electron/atom} \times 1 \text{ atom} = 6\\ &+ -1 \text{ electron (positive charge)} = -1\\ &\qquad\qquad = 10 \text{ valence electrons}\end{aligned}$$

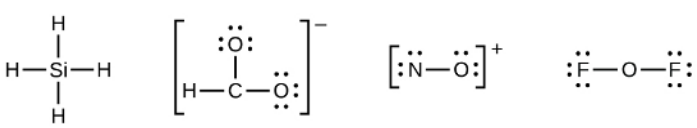
   - Since OF_2 is a neutral molecule, we simply add the number of valence electrons:

$$\begin{aligned} &OF_2\\ &\text{O: } 6 \text{ valence electrons/atom} \times 1 \text{ atom} = 6\\ &+\text{F: } 7 \text{ valence electrons/atom} \times 2 \text{ atoms} = 14\\ &\qquad\qquad = 20 \text{ valence electrons}\end{aligned}$$

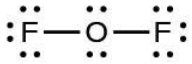
2. Draw a skeleton structure of the molecule or ion, arranging the atoms around a central atom and connecting each atom to the central atom with a single (one electron pair) bond. (Note that we denote ions with brackets around the structure, indicating the charge outside the brackets:)



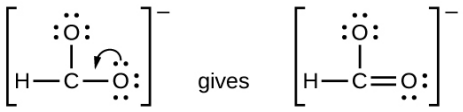
3. When several arrangements of atoms are possible, as for CHO_2^-, we must use experimental evidence to choose the correct one. In general, the less electronegative elements are more likely to be central atoms. In CHO_2^-, the less electronegative carbon atom occupies the central position with the oxygen and hydrogen atoms surrounding it. Other examples include P in $POCl_3$, S in SO_2, and Cl in ClO_4^-. An exception is that hydrogen is almost never a central atom. As the most electronegative element, fluorine also cannot be a central atom.
4. Distribute the remaining electrons as lone pairs on the terminal atoms (except hydrogen) to complete their valence shells with an octet of electrons.
   - There are no remaining electrons on SiH_4, so it is unchanged:



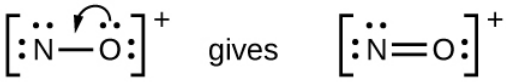
5. Place all remaining electrons on the central atom.
   - For SiH_4, CHO_2^-, and NO^+, there are no remaining electrons; we already placed all of the electrons determined in Step 1.
   - For OF_2, we had 16 electrons remaining in Step 3, and we placed 12, leaving 4 to be placed on the central atom:



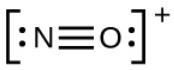
6. Rearrange the electrons of the outer atoms to make multiple bonds with the central atom in order to obtain octets wherever possible.
   - SiH_4: Si already has an octet, so nothing needs to be done.
   - CHO_2^-: We have distributed the valence electrons as lone pairs on the oxygen atoms, but the carbon atom lacks an octet:



- NO^+: For this ion, we added eight outer electrons, but neither atom has an octet. We cannot add any more electrons since we have already used the total that we found in Step 1, so we must move electrons to form a multiple bond:



- This still does not produce an octet, so we must move another pair, forming a triple bond:



- In OF_2, each atom has an octet as drawn, so nothing changes.

Example 1.3.1: Writing Lewis Structures

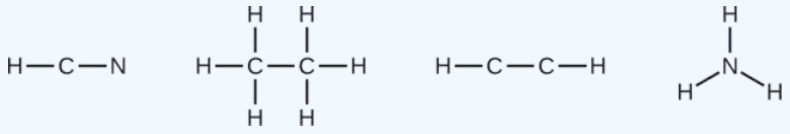
NASA's Cassini-Huygens mission detected a large cloud of toxic hydrogen cyanide (HCN) on Titan, one of Saturn's moons. Titan also contains ethane (H_3CCH_3), acetylene (HCCH), and ammonia (NH_3). What are the Lewis structures of these molecules?

Solution

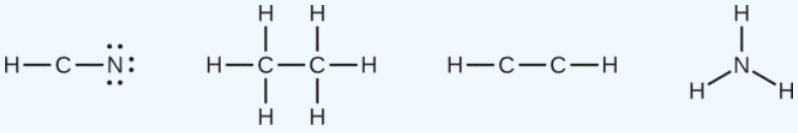
Calculate the number of valence electrons.

- HCN: (1 × 1) + (4 × 1) + (5 × 1) = 10
- H_3CCH_3: (1 × 3) + (2 × 4) + (1 × 3) = 14
- HCCH: (1 × 1) + (2 × 4) + (1 × 1) = 10
- NH_3: (5 × 1) + (3 × 1) = 8

Draw a skeleton and connect the atoms with single bonds. Remember that H is never a central atom:



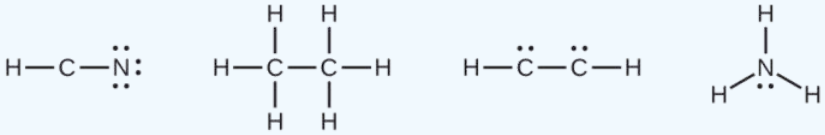
Where needed, distribute electrons to the terminal atoms:



- HCN: six electrons placed on N
- H_3CCH_3: no electrons remain

- HCCH: no terminal atoms capable of accepting electrons
- NH_3: no terminal atoms capable of accepting electrons

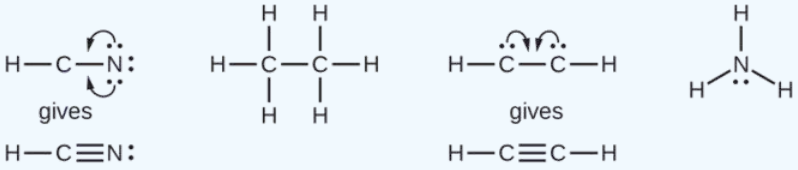
Where needed, place remaining electrons on the central atom:



- HCN: no electrons remain
- H_3CCH_3: no electrons remain
- HCCH: four electrons placed on carbon
- NH_3: two electrons placed on nitrogen

Where needed, rearrange electrons to form multiple bonds in order to obtain an octet on each atom:

- HCN: form two more C–N bonds
- H_3CCH_3: all atoms have the correct number of electrons
- HCCH: form a triple bond between the two carbon atoms
- NH_3: all atoms have the correct number of electrons



? Exercise 1.3.1

Both carbon monoxide, CO, and carbon dioxide, CO_2, are products of the combustion of fossil fuels. Both of these gases also cause problems: CO is toxic and CO_2 has been implicated in global climate change. What are the Lewis structures of these two molecules?

Answer



Exceptions to the Octet Rule

Many covalent molecules have central atoms that do not have eight electrons in their Lewis structures. These molecules fall into three categories:

- Odd-electron molecules have an odd number of valence electrons, and therefore have an unpaired electron.
- Electron-deficient molecules have a central atom that has fewer electrons than needed for a noble gas configuration.
- Hypervalent molecules have a central atom that has more electrons than needed for a noble gas configuration.

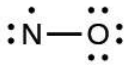
Odd-electron Molecules

We call molecules that contain an odd number of electrons free radicals. Nitric oxide, NO, is an example of an odd-electron molecule; it is produced in internal combustion engines when oxygen and nitrogen react at high temperatures.

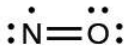
To draw the Lewis structure for an odd-electron molecule like NO, we follow the same five steps we would for other molecules, but with a few minor changes:

1. *Determine the total number of valence (outer shell) electrons*. The sum of the valence electrons is 5 (from N) + 6 (from O) = 11. The odd number immediately tells us that we have a free radical, so we know that not every atom can have eight electrons in its valence shell.
2. *Draw a skeleton structure of the molecule*. We can easily draw a skeleton with an N–O single bond: N–O

3. *Distribute the remaining electrons as lone pairs on the terminal atoms*. In this case, there is no central atom, so we distribute the electrons around both atoms. We give eight electrons to the more electronegative atom in these situations; thus oxygen has the filled valence shell:

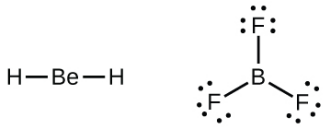


4. *Place all remaining electrons on the central atom*. Since there are no remaining electrons, this step does not apply.
5. *Rearrange the electrons to make multiple bonds with the central atom in order to obtain octets wherever possible.* We know that an odd-electron molecule cannot have an octet for every atom, but we want to get each atom as close to an octet as possible. In this case, nitrogen has only five electrons around it. To move closer to an octet for nitrogen, we take one of the lone pairs from oxygen and use it to form a NO double bond. (We cannot take another lone pair of electrons on oxygen and form a triple bond because nitrogen would then have nine electrons:)

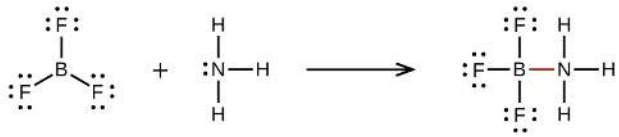


Electron-deficient Molecules

We will also encounter a few molecules that contain central atoms that do not have a filled valence shell. Generally, these are molecules with central atoms from groups 2 and 13 and outer atoms that are hydrogen or other atoms that do not form multiple bonds. For example, in the Lewis structures of beryllium dihydride, BeH_2, and boron trifluoride, BF_3, the beryllium and boron atoms each have only four and six electrons, respectively. It is possible to draw a structure with a double bond between a boron atom and a fluorine atom in BF_3, satisfying the octet rule, but experimental evidence indicates the bond lengths are closer to that expected for B–F single bonds. This suggests the best Lewis structure has three B–F single bonds and an electron deficient boron. The reactivity of the compound is also consistent with an electron deficient boron. However, the B–F bonds are slightly shorter than what is actually expected for B–F single bonds, indicating that some double bond character is found in the actual molecule.



An atom like the boron atom in BF_3, which does not have eight electrons, is very reactive. It readily combines with a molecule containing an atom with a lone pair of electrons. For example, NH_3 reacts with BF_3 because the lone pair on nitrogen can be shared with the boron atom:



Hypervalent Molecules

Elements in the second period of the periodic table ($n = 2$) can accommodate only eight electrons in their valence shell orbitals because they have only four valence orbitals (one 2*s* and three 2*p* orbitals). Elements in the third and higher periods ($n \geq 3$) have more than four valence orbitals and can share more than four pairs of electrons with other atoms because they have empty *d* orbitals in the same shell. Molecules formed from these elements are sometimes called hypervalent molecules.Table 1.3.5 shows the Lewis structures for two hypervalent molecules, PCl_5 and SF_6.

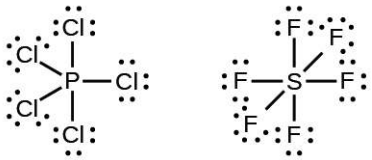
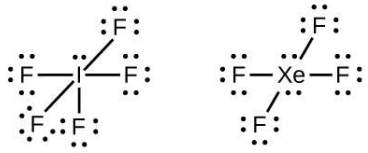


Table **1.3.5***: In PCl_5, the central atom phosphorus shares five pairs of electrons. In SF_6, sulfur shares six pairs of electrons.*

In some hypervalent molecules, such as IF_5 and XeF_4, some of the electrons in the outer shell of the central atom are lone pairs:



When we write the Lewis structures for these molecules, we find that we have electrons left over after filling the valence shells of the outer atoms with eight electrons. These additional electrons must be assigned to the central atom.

Example 1.3.2: Octet Rule Violations

Xenon is a noble gas, but it forms a number of stable compounds. We examined XeF_4 earlier. What are the Lewis structures of XeF_2 and XeF_6?

Solution

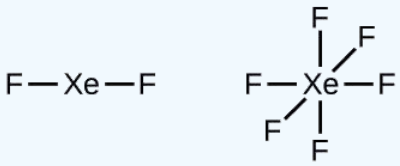
We can draw the Lewis structure of any covalent molecule by following the six steps discussed earlier. In this case, we can condense the last few steps, since not all of them apply.

Step 1: Calculate the number of valence electrons:

$$XeF_2: 8 + (2 \times 7) = 22$$

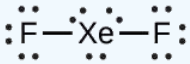
$$XeF_6: 8 + (6 \times 7) = 50$$

***Step 2: Draw a skeleton joining the atoms by single bonds.* Xenon will be the central atom because fluorine cannot be a central atom:**

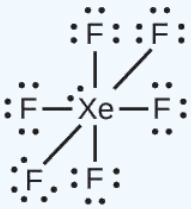


Step 3: Distribute the remaining electrons.

XeF_2: We place three lone pairs of electrons around each F atom, accounting for 12 electrons and giving each F atom 8 electrons. Thus, six electrons (three lone pairs) remain. These lone pairs must be placed on the Xe atom. This is acceptable because Xe atoms have empty valence shell *d* orbitals and can accommodate more than eight electrons. The Lewis structure of XeF_2 shows two bonding pairs and three lone pairs of electrons around the Xe atom:



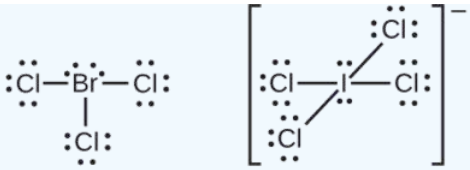
XeF_6: We place three lone pairs of electrons around each F atom, accounting for 36 electrons. Two electrons remain, and this lone pair is placed on the Xe atom:



Exercise 1.3.2: interhalogens

The halogens form a class of compounds called the interhalogens, in which halogen atoms covalently bond to each other. Write the Lewis structures for the interhalogens $BrCl_3$ and ICl_4^-.

Answer





Expanded Valence Shell Bonding: https://youtu.be/Y4fBdOJBSHI

Summary

Valence electronic structures can be visualized by drawing Lewis symbols (for atoms and monatomic ions) and Lewis structures (for molecules and polyatomic ions). Lone pairs, unpaired electrons, and single, double, or triple bonds are used to indicate where the valence electrons are located around each atom in a Lewis structure. Most structures—especially those containing second row elements—obey the octet rule, in which every atom (except H) is surrounded by eight electrons. Exceptions to the octet rule occur for odd-electron molecules (free radicals), electron-deficient molecules, and hypervalent molecules.

Glossary

double bond
covalent bond in which two pairs of electrons are shared between two atoms

free radical
molecule that contains an odd number of electrons

hypervalent molecule
molecule containing at least one main group element that has more than eight electrons in its valence shell

Lewis structure
diagram showing lone pairs and bonding pairs of electrons in a molecule or an ion

Lewis symbol
symbol for an element or monatomic ion that uses a dot to represent each valence electron in the element or ion

lone pair
two (a pair of) valence electrons that are not used to form a covalent bond

octet rule

guideline that states main group atoms will form structures in which eight valence electrons interact with each nucleus, counting bonding electrons as interacting with both atoms connected by the bond

single bond

bond in which a single pair of electrons is shared between two atoms

triple bond

bond in which three pairs of electrons are shared between two atoms

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1.4: Formal Charges and Resonance

Learning Objectives

- Compute formal charges for atoms in any Lewis structure
- Use formal charges to identify the most reasonable Lewis structure for a given molecule
- Explain the concept of resonance and draw Lewis structures representing resonance forms for a given molecule

Previously, we discussed how to write Lewis structures for molecules and polyatomic ions. In some cases, however, there is seemingly more than one valid structure for a molecule. We can use the concept of formal charges to help us predict the most appropriate Lewis structure when more than one is reasonable.

Calculating Formal Charge

The formal charge of an atom in a molecule is the *hypothetical* charge the atom would have if we could redistribute the electrons in the bonds evenly between the atoms. Another way of saying this is that formal charge results when we take the number of valence electrons of a neutral atom, subtract the nonbonding electrons, and then subtract the number of bonds connected to that atom in the Lewis structure.

Thus, we calculate formal charge as follows:

$$\text{formal charge} = \#\text{ valence shell electrons (free atom)} - \#\text{ lone pair electrons} - \frac{1}{2}\#\text{ bonding electrons}$$

We can double-check formal charge calculations by determining the sum of the formal charges for the whole structure. The sum of the formal charges of all atoms in a molecule must be zero; the sum of the formal charges in an ion should equal the charge of the ion.

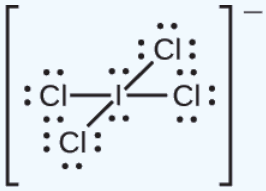
We must remember that the formal charge calculated for an atom is not the *actual* charge of the atom in the molecule. Formal charge is only a useful bookkeeping procedure; it does not indicate the presence of actual charges.

Example 1.4.1: Calculating Formal Charge from Lewis Structures

Assign formal charges to each atom in the interhalogen ion $\mathrm{ICl_4^-}$.

Solution

We divide the bonding electron pairs equally for all I– Cl bonds:



We assign lone pairs of electrons to their atoms. Each Cl atom now has seven electrons assigned to it, and the I atom has eight.

Subtract this number from the number of valence electrons for the neutral atom:

- I: 7 – 8 = –1
- Cl: 7 – 7 = 0

The sum of the formal charges of all the atoms equals –1, which is identical to the charge of the ion (–1).

Exercise 1.4.1

Calculate the formal charge for each atom in the carbon monoxide molecule:



Answer

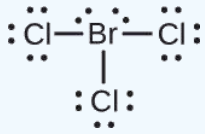
C −1, O +1

Example 1.4.2: Calculating Formal Charge from Lewis Structures

Assign formal charges to each atom in the interhalogen molecule $BrCl_3$.

Solution

Assign one of the electrons in each Br–Cl bond to the Br atom and one to the Cl atom in that bond:



Assign the lone pairs to their atom. Now each Cl atom has seven electrons and the Br atom has seven electrons.

Subtract this number from the number of valence electrons for the neutral atom. This gives the formal charge:

- Br: 7 – 7 = 0
- Cl: 7 – 7 = 0

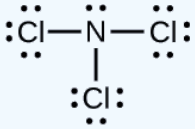
All atoms in $BrCl_3$ have a formal charge of zero, and the sum of the formal charges totals zero, as it must in a neutral molecule.

Exercise 1.4.2

Determine the formal charge for each atom in NCl_3.

Answer

N: 0; all three Cl atoms: 0



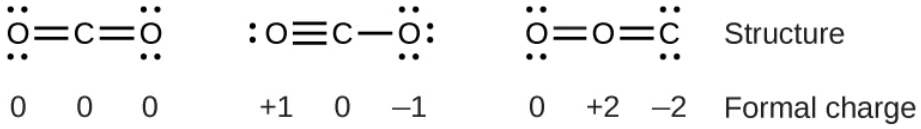
Using Formal Charge to Predict Molecular Structure

The arrangement of atoms in a molecule or ion is called its molecular structure. In many cases, following the steps for writing Lewis structures may lead to more than one possible molecular structure—different multiple bond and lone-pair electron placements or different arrangements of atoms, for instance. A few guidelines involving formal charge can be helpful in deciding which of the possible structures is most likely for a particular molecule or ion.

Predicting Molecular Structure Guidelines

1. A molecular structure in which all formal charges are zero is preferable to one in which some formal charges are not zero.
2. If the Lewis structure must have nonzero formal charges, the arrangement with the smallest nonzero formal charges is preferable.
3. Lewis structures are preferable when adjacent formal charges are zero or of the opposite sign.
4. When we must choose among several Lewis structures with similar distributions of formal charges, the structure with the negative formal charges on the more electronegative atoms is preferable.

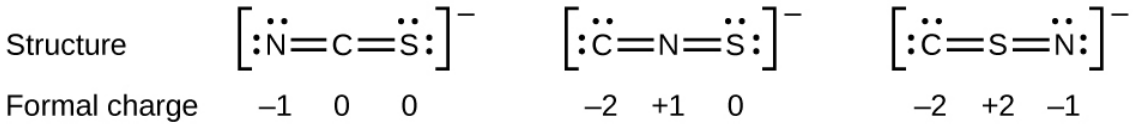
To see how these guidelines apply, let us consider some possible structures for carbon dioxide, CO_2. We know from our previous discussion that the less electronegative atom typically occupies the central position, but formal charges allow us to understand *why* this occurs. We can draw three possibilities for the structure: carbon in the center and double bonds, carbon in the center with a single and triple bond, and oxygen in the center with double bonds:



Three Lewis structures are shown. The left and right structures show a carbon atom double bonded to two oxygen atoms, each of which has two lone pairs of electrons. The center structure shows a carbon atom that is triple bonded to an oxygen atom with one lone pair of electrons and single bonded to an oxygen atom with three lone pairs of electrons. The third structure shows an oxygen atom double bonded to another oxygen atom with to lone pairs of electrons. The first oxygen atom is also double bonded to a carbon atom with two lone pairs of electrons.

Comparing the three formal charges, we can definitively identify the structure on the left as preferable because it has only formal charges of zero (Guideline 1).

As another example, the thiocyanate ion, an ion formed from a carbon atom, a nitrogen atom, and a sulfur atom, could have three different molecular structures: CNS^-, NCS^-, or CSN^-. The formal charges present in each of these molecular structures can help us pick the most likely arrangement of atoms. Possible Lewis structures and the formal charges for each of the three possible structures for the thiocyanate ion are shown here:

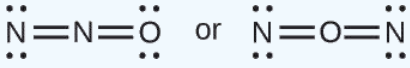


Two rows of structures and numbers are shown. The top row is labeled, “Structure” and depicts three Lewis structures and the bottom row is labeled, “Formal charge.” The left structure shows a carbon atom double bonded to a nitrogen atom with two lone electron pairs on one side and double bonded to a sulfur atom with two lone electron pairs on the other. The structure is surrounded by brackets and has a superscripted negative sign. Below this structure are the numbers negative one, zero, and zero. The middle structure shows a carbon atom with two lone pairs of electrons double bonded to a nitrogen atom that is double bonded to a sulfur atom with two lone electron pairs. The structure is surrounded by brackets and has a superscripted negative sign. Below this structure are the numbers negative two, positive one, and zero. The right structure shows a carbon atom with two lone electron pairs double bonded to a sulfur atom that is double bonded to a nitrogen atom with two lone electron pairs. The structure is surrounded by brackets and has a superscripted negative sign. Below this structure are the numbers negative two, positive two, and one.

Note that the sum of the formal charges in each case is equal to the charge of the ion (–1). However, the first arrangement of atoms is preferred because it has the lowest number of atoms with nonzero formal charges (Guideline 2). Also, it places the least electronegative atom in the center, and the negative charge on the more electronegative element (Guideline 4).

Example 1.4.3: Using Formal Charge to Determine Molecular Structure

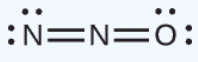
Nitrous oxide, N_2O, commonly known as laughing gas, is used as an anesthetic in minor surgeries, such as the routine extraction of wisdom teeth. Which is the likely structure for nitrous oxide?



Solution Determining formal charge yields the following:



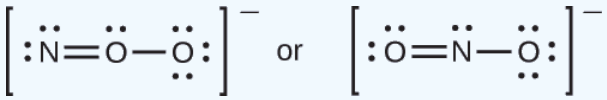
The structure with a terminal oxygen atom best satisfies the criteria for the most stable distribution of formal charge:



The number of atoms with formal charges are minimized (Guideline 2), and there is no formal charge larger than one (Guideline 2). This is again consistent with the preference for having the less electronegative atom in the central position.

? Exercise 1.4.3

Which is the most likely molecular structure for the nitrite (NO_2^-) ion?



Answer

ONO^-

Resonance

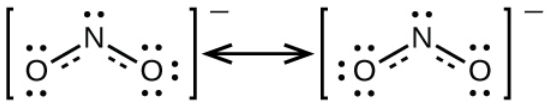
You may have noticed that the nitrite anion in Example 1.4.3 can have two possible structures with the atoms in the same positions. The electrons involved in the N–O double bond, however, are in different positions:



Two Lewis structures are shown. The left structure shows an oxygen atom with three lone pairs of electrons single bonded to a nitrogen atom with one lone pair of electrons that is double bonded to an oxygen with two lone pairs of electrons. Brackets surround this structure, and there is a superscripted negative sign. The right structure shows an oxygen atom with two lone pairs of electrons double bonded to a nitrogen atom with one lone pair of electrons that is single bonded to an oxygen atom with three lone pairs of electrons. Brackets surround this structure, and there is a superscripted negative sign.

If nitrite ions do indeed contain a single and a double bond, we would expect for the two bond lengths to be different. A double bond between two atoms is shorter (and stronger) than a single bond between the same two atoms. Experiments show, however, that both N–O bonds in NO_2^- have the same strength and length, and are identical in all other properties.

It is not possible to write a single Lewis structure for NO_2^- in which nitrogen has an octet and both bonds are equivalent. Instead, we use the concept of resonance: if two or more Lewis structures with the same arrangement of atoms can be written for a molecule or ion, the actual distribution of electrons is an *average* of that shown by the various Lewis structures. The actual distribution of electrons in each of the nitrogen-oxygen bonds in NO_2^- is the average of a double bond and a single bond. We call the individual Lewis structures resonance forms. The actual electronic structure of the molecule (the average of the resonance forms) is called a resonance hybrid of the individual resonance forms. A double-headed arrow between Lewis structures indicates that they are resonance forms. Thus, the electronic structure of the NO_2^- ion is shown as:

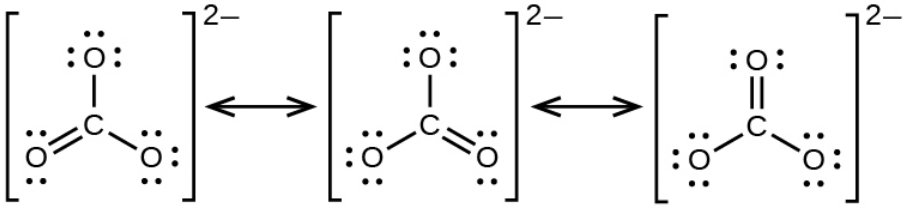


Two Lewis structures are shown with a double headed arrow drawn between them. The left structure shows an oxygen atom with two lone pairs of electrons double bonded to a nitrogen atom with one lone pair of electrons that is single bonded to an oxygen atom with three lone pairs of electrons. Brackets surround this structure, and there is a superscripted negative sign. The right structure shows an oxygen atom with three lone pairs of electrons single bonded to a nitrogen atom with one lone pair of electrons that is double bonded to an oxygen atom with two lone pairs of electrons. Brackets surround this structure, and there is a superscripted negative sign.

We should remember that a molecule described as a resonance hybrid *never* possesses an electronic structure described by either resonance form. It does not fluctuate between resonance forms; rather, the actual electronic structure is *always* the average of that shown by all resonance forms. George Wheland, one of the pioneers of resonance theory, used a historical analogy to describe the relationship between resonance forms and resonance hybrids. A medieval traveler, having never before seen a rhinoceros, described it as a hybrid of a dragon and a unicorn because it had many properties in common with both. Just as a rhinoceros is neither a

dragon sometimes nor a unicorn at other times, a resonance hybrid is neither of its resonance forms at any given time. Like a rhinoceros, it is a real entity that experimental evidence has shown to exist. It has some characteristics in common with its resonance forms, but the resonance forms themselves are convenient, imaginary images (like the unicorn and the dragon).

The carbonate anion, CO_3^{2-}, provides a second example of resonance:



Three Lewis structures are shown with double headed arrows in between. Each structure is surrounded by brackets, and each has a superscripted two negative sign. The left structure depicts a carbon atom bonded to three oxygen atoms. It is single bonded to two of these oxygen atoms, each of which has three lone pairs of electrons, and double bonded to the third, which has two lone pairs of electrons. The double bond is located between the lower left oxygen atom and the carbon atom. The central and right structures are the same as the first, but the position of the double bonded oxygen has moved to the lower right oxygen in the central structure and to the top oxygen in the right structure.

One oxygen atom must have a double bond to carbon to complete the octet on the central atom. All oxygen atoms, however, are equivalent, and the double bond could form from any one of the three atoms. This gives rise to three resonance forms of the carbonate ion. Because we can write three identical resonance structures, we know that the actual arrangement of electrons in the carbonate ion is the average of the three structures. Again, experiments show that all three C–O bonds are exactly the same.

Summary

In a Lewis structure, formal charges can be assigned to each atom by treating each bond as if one-half of the electrons are assigned to each atom. These hypothetical formal charges are a guide to determining the most appropriate Lewis structure. A structure in which the formal charges are as close to zero as possible is preferred. Resonance occurs in cases where two or more Lewis structures with identical arrangements of atoms but different distributions of electrons can be written. The actual distribution of electrons (the resonance hybrid) is an average of the distribution indicated by the individual Lewis structures (the resonance forms).

Key Equations

- $\text{formal charge} = \#\text{ valence shell electrons (free atom)} - \#\text{ one pair electrons} - \frac{1}{2}\#\text{ bonding electrons}$

Glossary

formal charge

charge that would result on an atom by taking the number of valence electrons on the neutral atom and subtracting the nonbonding electrons and the number of bonds (one-half of the bonding electrons)

molecular structure

arrangement of atoms in a molecule or ion

resonance

situation in which one Lewis structure is insufficient to describe the bonding in a molecule and the average of multiple structures is observed

resonance forms

two or more Lewis structures that have the same arrangement of atoms but different arrangements of electrons

resonance hybrid

average of the resonance forms shown by the individual Lewis structures

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1.5: Molecular Structure and Polarity

Learning Objectives

- Predict the structures of small molecules using valence shell electron pair repulsion (VSEPR) theory
- Explain the concepts of polar covalent bonds and molecular polarity
- Assess the polarity of a molecule based on its bonding and structure

Thus far, we have used two-dimensional Lewis structures to represent molecules. However, molecular structure is actually three-dimensional, and it is important to be able to describe molecular bonds in terms of their distances, angles, and relative arrangements in space (Figure 1.5.1). A bond angle is the angle between any two bonds that include a common atom, usually measured in degrees. A bond distance (or bond length) is the distance between the nuclei of two bonded atoms along the straight line joining the nuclei. Bond distances are measured in Ångstroms (1 Å = 10^{-10} m) or picometers (1 pm = 10^{-12} m, 100 pm = 1 Å).

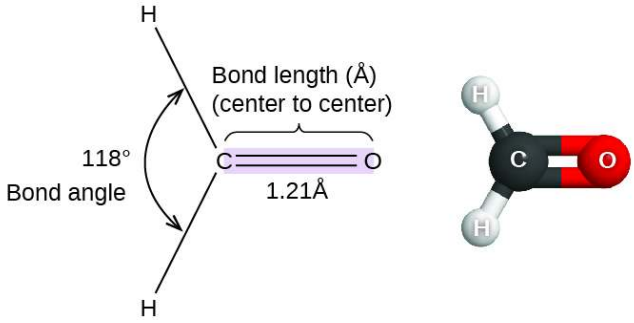


Figure 1.5.1: Bond distances (lengths) and angles are shown for the formaldehyde molecule, H_2CO.

A pair of images are shown. The left image shows a carbon atom with three atoms bonded in a triangular arrangement around it. There are two hydrogen atoms bonded on the left side of the carbon and the angle between them is labeled, “118 degrees” and, “Bond angle.” The carbon is also double bonded to an oxygen atom. The double bond is shaded and there is a bracket which labels the bond, “Bond length (angstrom), (center to center),” and, “1.21 angstrom.” The right image shows a ball-and-stick model of the same elements. The hydrogen atoms are white, the carbon atom is black, and the oxygen atom is red."

VSEPR Theory

Valence shell electron-pair repulsion theory (VSEPR theory) enables us to predict the molecular structure, including approximate bond angles around a central atom, of a molecule from an examination of the number of bonds and lone electron pairs in its Lewis structure. The VSEPR model assumes that electron pairs in the valence shell of a central atom will adopt an arrangement that minimizes repulsions between these electron pairs by maximizing the distance between them. The electrons in the valence shell of a central atom form either bonding pairs of electrons, located primarily between bonded atoms, or lone pairs. The electrostatic repulsion of these electrons is reduced when the various regions of high electron density assume positions as far from each other as possible.

VSEPR theory predicts the arrangement of electron pairs around each central atom and, usually, the correct arrangement of atoms in a molecule. We should understand, however, that the theory only considers electron-pair repulsions. Other interactions, such as nuclear-nuclear repulsions and nuclear-electron attractions, are also involved in the final arrangement that atoms adopt in a particular molecular structure.

As a simple example of VSEPR theory, let us predict the structure of a gaseous BeF_2 molecule. The Lewis structure of BeF_2 (Figure 1.5.2) shows only two electron pairs around the central beryllium atom. With two bonds and no lone pairs of electrons on the central atom, the bonds are as far apart as possible, and the electrostatic repulsion between these regions of high electron density is reduced to a minimum when they are on opposite sides of the central atom. The bond angle is 180° (Figure 1.5.2).

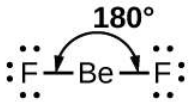


Figure 1.5.2: The BeF_2 molecule adopts a linear structure in which the two bonds are as far apart as possible, on opposite sides of the Be atom.

A Lewis structure is shown. A fluorine atom with three lone pairs of electrons is single bonded to a beryllium atom which is single bonded to a fluorine atom with three lone pairs of electrons. The angle of the bonds between the two fluorine atoms and the beryllium atom is labeled, “180 degrees.”

Figure 1.5.3 illustrates this and other electron-pair geometries that minimize the repulsions among regions of high electron density (bonds and/or lone pairs). Two regions of electron density around a central atom in a molecule form a linear geometry; three regions form a trigonal planar geometry; four regions form a tetrahedral geometry; five regions form a trigonal bipyramidal geometry; and six regions form an octahedral geometry.

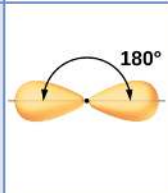
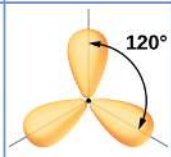
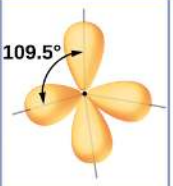
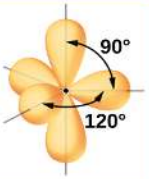
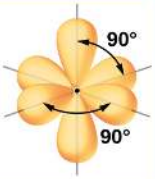
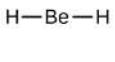
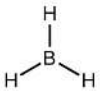
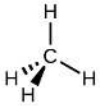
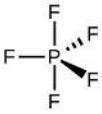
Number of regions	Two regions of high electron density (bonds and/or unshared pairs)	Three regions of high electron density (bonds and/or unshared pairs)	Four regions of high electron density (bonds and/or unshared pairs)	Five regions of high electron density (bonds and/or unshared pairs)	Six regions of high electron density (bonds and/or unshared pairs)
Spatial arrangement					
Line-dash-wedge notation					
Electron pair geometry	Linear; 180° angle	Trigonal planar; all angles 120°	Tetrahedral; all angles 109.5°	Trigonal bipyramidal; angles of 90° or 120° An attached atom may be equatorial (in the plane of the triangle) or axial (above or below the plane of the triangle).	Octahedral; all angles 90° or 180°

Figure 1.5.3: The basic electron-pair geometries predicted by VSEPR theory maximize the space around any region of electron density (bonds or lone pairs).

A table with four rows and six columns is shown. The header column contains the phrases, “Number of regions,” “Spatial arrangement,” “Wedge/dash Notation,” and “Electron pair Geometry.” The first row reads: “Two regions of high electron density (bonds and/or unshared pairs)”, “Three regions of high electron density (bonds and/or unshared pairs),” “Four regions of high electron density (bonds and/or unshared pairs),” “Five regions of high electron density (bonds and/or unshared pairs),” and “Six regions of high electron density (bonds and/or unshared pairs).” The second row shows diagrams of orbitals. The first image shows two oval-shaped orbs with an arrow indicating an angle of 180 degrees. The second image shows three oval-shaped orbs with an arrow indicating an angle of 120 degrees. The third image shows four oval-shaped orbs with an arrow indicating an angle of 109.5 degrees. The fourth image shows five oval-shaped orbs with an arrow indicating an angle of 90 and 120 degrees. The fifth image shows six oval-shaped orbs with an arrow indicating an angle of 90 degrees. The third row contains Lewis structures. The first structure shows a beryllium atom single bonded to two hydrogen atoms. The second structure shows a boron atom single bonded to three hydrogen atoms. The third structure shows a carbon atom single bonded to four hydrogen atoms. The fourth structure shows a phosphorus atom single bonded to five fluorine atoms. The fifth structure shows a sulfur atom single bonded to six fluorine atoms. The fourth row contains the phrases “Linear; 180 degree angle,” Trigonal Planar; all angles 120 degrees,” “Tetrahedral; all angles 109.5 degrees,” “Trigonal bipyramidal; angles of 90 degrees and 120 degrees. An attached atom may be equatorial, (in the plane of the triangle), or axial, (above the plane of the triangle),” and “Octahedral; 90 degrees or 180 degrees.”

Electron-pair Geometry versus Molecular Structure

It is important to note that electron-pair geometry around a central atom is *not* the same thing as its molecular structure. The electron-pair geometries shown in Figure 1.5.3 describe all regions where electrons are located, bonds as well as lone pairs. Molecular structure describes the location of the *atoms*, not the electrons.

We differentiate between these two situations by naming the geometry that includes *all* electron pairs the electron-pair geometry. The structure that includes only the placement of the atoms in the molecule is called the molecular structure. The electron-pair geometries will be the same as the molecular structures when there are no lone electron pairs around the central atom, but they will be different when there are lone pairs present on the central atom.

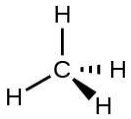


Figure 1.5.4: The molecular structure of the methane molecule, CH_4, is shown with a tetrahedral arrangement of the hydrogen atoms. VSEPR structures like this one are often drawn using the wedge and dash notation, in which solid lines represent bonds in the plane of the page, solid wedges represent bonds coming up out of the plane, and dashed lines represent bonds going down into the plane.

A Lewis structure shows a carbon atom single bonded to four hydrogen atoms. This structure uses wedges and dashes to give it a three dimensional appearance.

For example, the methane molecule, CH_4, which is the major component of natural gas, has four bonding pairs of electrons around the central carbon atom; the electron-pair geometry is tetrahedral, as is the molecular structure (Figure 1.5.4). On the other hand, the ammonia molecule, NH_3, also has four electron pairs associated with the nitrogen atom, and thus has a tetrahedral electron-pair geometry. One of these regions, however, is a lone pair, which is not included in the molecular structure, and this lone pair influences the shape of the molecule (Figure 1.5.5).

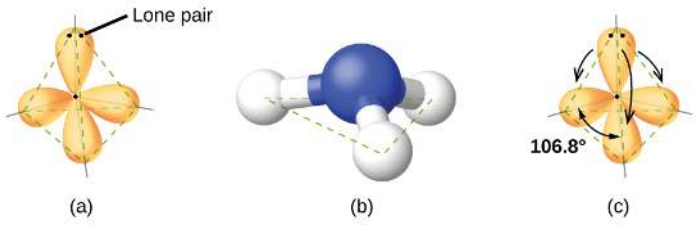


Figure 1.5.5: (a) The electron-pair geometry for the ammonia molecule is tetrahedral with one lone pair and three single bonds. (b) The trigonal pyramidal molecular structure is determined from the electron-pair geometry. (c) The actual bond angles deviate slightly from the idealized angles because the lone pair takes up a larger region of space than do the single bonds, causing the HNH angle to be slightly smaller than 109.5°.

Three images are shown and labeled, “a,” “b,” and “c.” Image a shows a nitrogen atom single bonded to three hydrogen atoms. There are four oval-shaped orbs that surround each hydrogen and one facing away from the rest of the molecule. These orbs are located in a tetrahedral arrangement. Image b shows a ball-and-stick model of the nitrogen single bonded to the three hydrogen atoms. Image c is the same as image a, but there are four curved, double headed arrows that circle the molecule and are labeled, “106.8 degrees.”

Small distortions from the ideal angles in Figure 1.5.5 can result from differences in repulsion between various regions of electron density. VSEPR theory predicts these distortions by establishing an order of repulsions and an order of the amount of space occupied by different kinds of electron pairs. The order of electron-pair repulsions from greatest to least repulsion is:

lone pair-lone pair > lone pair-bonding pair > bonding pair-bonding pair

This order of repulsions determines the amount of space occupied by different regions of electrons. A lone pair of electrons occupies a larger region of space than the electrons in a triple bond; in turn, electrons in a triple bond occupy more space than those in a double bond, and so on. The order of sizes from largest to smallest is:

lone pair > triple bond > double bond > single bond

Consider formaldehyde, H_2CO, which is used as a preservative for biological and anatomical specimens. This molecule has regions of high electron density that consist of two single bonds and one double bond. The basic geometry is trigonal planar with 120° bond angles, but we see that the double bond causes slightly larger angles (121°), and the angle between the single bonds is slightly smaller (118°).

In the ammonia molecule, the three hydrogen atoms attached to the central nitrogen are not arranged in a flat, trigonal planar molecular structure, but rather in a three-dimensional trigonal pyramid (Figure 1.5.6) with the nitrogen atom at the apex and the three hydrogen atoms forming the base. The ideal bond angles in a trigonal pyramid are based on the tetrahedral electron pair geometry. Again, there are slight deviations from the ideal because lone pairs occupy larger regions of space than do bonding electrons. The H–N–H bond angles in NH_3 are slightly smaller than the 109.5° angle in a regular tetrahedron (Figure 1.5.6) because the lone pair-bonding pair repulsion is greater than the bonding pair-bonding pair repulsion. The ideal molecular structures are predicted based on the electron-pair geometries for various combinations of lone pairs and bonding pairs.

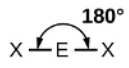
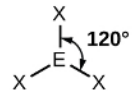
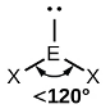
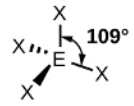
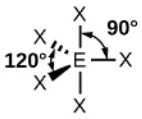
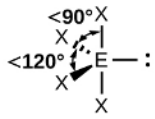
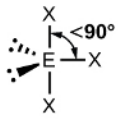
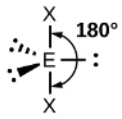
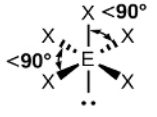
Number of electron pairs	Electron pair geometries: 0 lone pair	1 lone pair	2 lone pairs	3 lone pairs	4 lone pairs
2	 Linear				
3	 Trigonal planar	 Bent or angular			
4	 Tetrahedral	 Trigonal pyramid	 Bent or angular		
5	 Trigonal bipyramid	 Sawhorse or seesaw	 T-shape	 Linear	
6	 Octahedral	 Square pyramid	 Square planar	 T-shape	 Linear

Figure 1.5.6: The molecular structures are identical to the electron-pair geometries when there are no lone pairs present (first column). For a particular number of electron pairs (row), the molecular structures for one or more lone pairs are determined based on modifications of the corresponding electron-pair geometry.

A table is shown that is comprised of six rows and six columns. The header row reads: “Number of Electron Pairs,” “Electron pair geometries; 0 lone pair,” “1 lone pair,” “2 lone pairs,” “3 lone pairs,” and “4 lone pairs.” The first column contains the numbers 2, 3, 4, 5, and 6. The first space in the second column contains a structure in which the letter E is single bonded to the letter X on each side. The angle of the bonds is labeled with a curved, double headed arrow and the value, “180 degrees.” The structure is labeled, “Linear.” The second space in the second column contains a structure in which the letter E is single bonded to the letter X on three sides. The angle between the bonds is labeled with a curved, double headed arrow and the value, “120 degrees.” The structure is labeled, “Trigonal planar.” The third space in the second column contains a structure in which the letter E is single bonded to the letter X four times. The angle between the bonds is labeled with a curved, double headed arrow and the value, “109 degrees.” The structure is labeled, “Tetrahedral.” The fourth space in the second column contains a structure in which the letter E is single bonded to the letter X on five sides. The angle between the bonds is labeled with a curved, double headed arrow and the values “90 and 120 degrees.” The structure is labeled, “Trigonal bipyramid.” The fifth space in the second column contains a structure in which the letter E is single bonded to the letter X on six sides. The angle between the bonds is labeled with a curved, double headed arrow and the value, “90 degrees.” The structure is labeled, “Octahedral.” The first space in the third column is empty while the second contains a structure in which the letter E is single bonded to the letter X on each side and has a lone pair of electrons. The angle between the bonds is labeled with a curved, double headed arrow and the value, “less than 120 degrees.” The structure is labeled, “Bent or angular.” The third space in the third column contains a structure in which the letter E is single bonded to the letter X three times and to a lone pair of electrons. It is labeled with a curved, double headed arrow and the value, “less than 109 degrees.” The structure is labeled, “Trigonal pyramid.” The fourth space in the third column contains a structure in which the letter E is single bonded to the letter X on four sides and has a lone pair of electrons. The bond angle is labeled with a curved, double headed arrow and the values, “less than 90 and less than 120 degrees.” The structure is labeled, “Sawhorse or seesaw.” The fifth space in the third column contains a structure in which the letter E is single bonded to the letter X on five sides and has a lone pair of electrons. The bond angle is labeled with a curved, double headed arrow and the value, “less than 90 degrees.” The structure is labeled, “Square pyramidal.” The first and second spaces in the fourth column are empty while the third contains a structure in which the letter E is single bonded to the letter X on each side and has two lone pairs of electrons. The bond angle is labeled with a curved, double headed arrow and the value, “less than less than 109 degrees.” The structure is labeled, “Bent or angular.” The fourth space in the fourth column contains a structure in which the letter E is single bonded to the letter X three times and to two lone pairs of electrons. The bond angle is labeled with a curved, double headed arrow and the value, “less than 90 degrees.” The structure is labeled, “T - shape.” The fifth space in the fourth column contains a structure in which the letter E is single bonded to the letter X on four sides and has two lone pairs of electrons. The bond angle is labeled with a curved, double headed arrow and the value “90 degrees.” The structure is labeled, “Square planar.” The first, second and third spaces in the fifth column are empty while the fourth contains a structure in which the letter E is single bonded to the letter X on each side and has three lone pairs of electrons. The

bond angle is labeled with a curved, double headed arrow and the value, “180 degrees.” The structure is labeled, “Linear.” The fifth space in the fifth column contains a structure in which the letter E is single bonded to the letter X three times and to three lone pairs of electrons. The bond angle is labeled with a curved, double headed arrow and the value, “less than 90 degrees.” The structure is labeled, “T - shape.” The first, second, third, and fourth spaces in the sixth column are empty while the fifth contains a structure in which the letter E is single bonded to the letter X on each side and has four lone pairs of electrons. The bond angle is labeled with a curved, double headed arrow and the value “180 degrees.” The structure is labeled, “Linear.” All the structures use wedges and dashes to give them three dimensional appearances.

According to VSEPR theory, the terminal atom locations (Xs in Figure 1.5.7) are equivalent within the linear, trigonal planar, and tetrahedral electron-pair geometries (the first three rows of the table). It does not matter which X is replaced with a lone pair because the molecules can be rotated to convert positions. For trigonal bipyramidal electron-pair geometries, however, there are two distinct X positions (Figure 1.5.7a): an axial position (if we hold a model of a trigonal bipyramid by the two axial positions, we have an axis around which we can rotate the model) and an equatorial position (three positions form an equator around the middle of the molecule). The axial position is surrounded by bond angles of 90°, whereas the equatorial position has more space available because of the 120° bond angles. In a trigonal bipyramidal electron-pair geometry, lone pairs always occupy equatorial positions because these more spacious positions can more easily accommodate the larger lone pairs.

Theoretically, we can come up with three possible arrangements for the three bonds and two lone pairs for the ClF_3 molecule (Figure 1.5.7). The stable structure is the one that puts the lone pairs in equatorial locations, giving a T-shaped molecular structure.

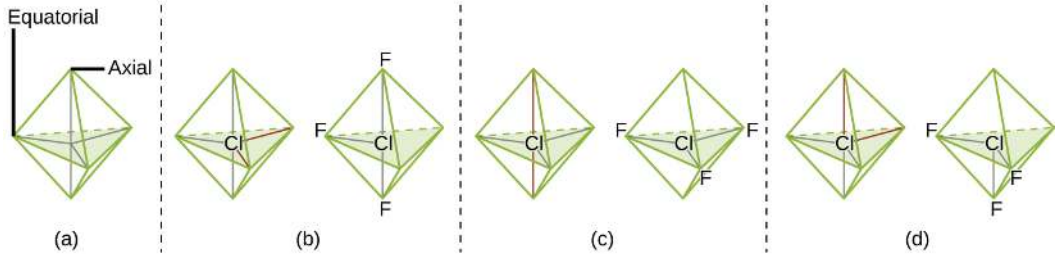


Figure 1.5.7: (a) In a trigonal bipyramid, the two axial positions are located directly across from one another, whereas the three equatorial positions are located in a triangular arrangement. (b–d) The two lone pairs (red lines) in ClF_3 have several possible arrangements, but the T-shaped molecular structure (b) is the one actually observed, consistent with the larger lone pairs both occupying equatorial positions.

Four sets of images are shown and labeled, “a,” “b,” “c,” and “d.” Each image is separated by a dashed vertical line. Image a shows a six-faced, bi-pyramidal structure where the central vertical axis is labeled, “Axial,” and the horizontal plane is labeled, “Equatorial.” Image b shows a pair of diagrams in the same shape as image a, but in these diagrams, the left has a chlorine atom in the center while the right has a chlorine atom in the center, two fluorine atoms on the upper and lower ends, and one fluorine in the left horizontal position. Image c shows a pair of diagrams in the same shape as image a, but in these diagrams, the left has a chlorine atom in the center while the right has a chlorine atom in the center and three fluorine atoms in each horizontal position. Image d shows a pair of diagrams in the same shape as image a, but in these diagrams, the left has a chlorine atom in the center while the right has a chlorine atom in the center, two fluorine atoms in the horizontal positions, and one in the axial bottom position.

When a central atom has two lone electron pairs and four bonding regions, we have an octahedral electron-pair geometry. The two lone pairs are on opposite sides of the octahedron (180° apart), giving a square planar molecular structure that minimizes lone pair-lone pair repulsions.

Predicting Electron Pair Geometry and Molecular Structure

The following procedure uses VSEPR theory to determine the electron pair geometries and the molecular structures:

1. Write the Lewis structure of the molecule or polyatomic ion.
2. Count the number of regions of electron density (lone pairs and bonds) around the central atom. A single, double, or triple bond counts as one region of electron density.
3. Identify the electron-pair geometry based on the number of regions of electron density: linear, trigonal planar, tetrahedral, trigonal bipyramidal, or octahedral (Figure 1.5.7, first column).
4. Use the number of lone pairs to determine the molecular structure (Figure 1.5.7). If more than one arrangement of lone pairs and chemical bonds is possible, choose the one that will minimize repulsions, remembering that lone pairs occupy more space than multiple bonds, which occupy more space than single bonds. In trigonal bipyramidal arrangements, repulsion is minimized when every lone pair is in an equatorial position. In an octahedral arrangement with two lone pairs, repulsion is minimized when the lone pairs are on opposite sides of the central atom.

The following examples illustrate the use of VSEPR theory to predict the molecular structure of molecules or ions that have no lone pairs of electrons. In this case, the molecular structure is identical to the electron pair geometry.

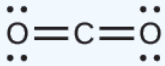
Example 1.5.1: Predicting Electron-pair Geometry and Molecular Structure

Predict the electron-pair geometry and molecular structure for each of the following:

a. carbon dioxide, CO_2, a molecule produced by the combustion of fossil fuels
b. boron trichloride, BCl_3, an important industrial chemical

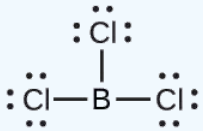
Solution

(a) We write the Lewis structure of CO_2 as:

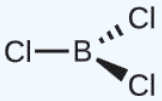


This shows us two regions of high electron density around the carbon atom—each double bond counts as one region, and there are no lone pairs on the carbon atom. Using VSEPR theory, we predict that the two regions of electron density arrange themselves on opposite sides of the central atom with a bond angle of 180°. The electron-pair geometry and molecular structure are identical, and CO_2 molecules are linear.

(b) We write the Lewis structure of BCl_3 as:



Thus we see that BCl_3 contains three bonds, and there are no lone pairs of electrons on boron. The arrangement of three regions of high electron density gives a trigonal planar electron-pair geometry. The B–Cl bonds lie in a plane with 120° angles between them. BCl_3 also has a trigonal planar molecular structure.



The electron-pair geometry and molecular structure of BCl_3 are both trigonal planar. Note that the VSEPR geometry indicates the correct bond angles (120°), unlike the Lewis structure shown above.

Exercise 1.5.1

Carbonate, CO_3^{2-}, is a common polyatomic ion found in various materials from eggshells to antacids. What are the electron-pair geometry and molecular structure of this polyatomic ion?

Answer

The electron-pair geometry is trigonal planar and the molecular structure is trigonal planar. Due to resonance, all three C–O bonds are identical. Whether they are single, double, or an average of the two, each bond counts as one region of electron density.

Example 1.5.2: Predicting Electron-pair Geometry and Molecular Structure

Two of the top 50 chemicals produced in the United States, ammonium nitrate and ammonium sulfate, both used as fertilizers, contain the ammonium ion. Predict the electron-pair geometry and molecular structure of the NH_4^+ cation.

Solution

We write the Lewis structure of NH_4^+ as:

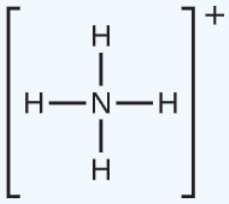


Figure 1.5.7).

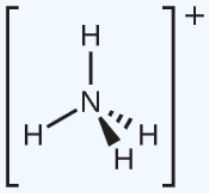


Figure 1.5.8: *The ammonium ion displays a tetrahedral electron-pair geometry as well as a tetrahedral molecular structure.*

Exercise 1.5.2

Identify a molecule with trigonal bipyramidal molecular structure.

Answer

Any molecule with five electron pairs around the central atoms including no lone pairs will be trigonal bipyramidal. PF_5 is a common example

The next several examples illustrate the effect of lone pairs of electrons on molecular structure.

Example 1.5.3: Lone Pairs on the Central Atom

Predict the electron-pair geometry and molecular structure of a water molecule.

Solution

The Lewis structure of H_2O indicates that there are four regions of high electron density around the oxygen atom: two lone pairs and two chemical bonds:

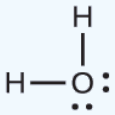


Figure 1.5.9. Thus, the electron-pair geometry is tetrahedral and the molecular structure is bent with an angle slightly less than 109.5°. In fact, the bond angle is 104.5°.

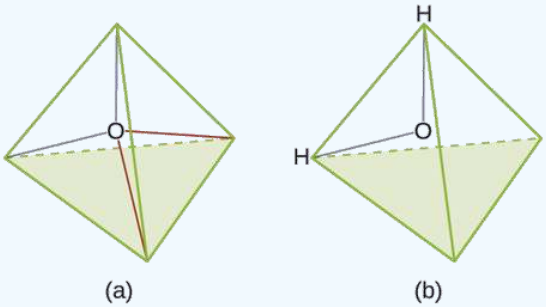


Figure 1.5.9: (a) H_2O has four regions of electron density around the central atom, so it has a tetrahedral electron-pair geometry. (b) Two of the electron regions are lone pairs, so the molecular structure is bent.

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Exercise 1.5.3

The hydronium ion, H_3O^+, forms when acids are dissolved in water. Predict the electron-pair geometry and molecular structure of this cation.

Answer

electron pair geometry: tetrahedral; molecular structure: trigonal pyramidal

Example 1.5.4: SF_4 Sulfur tetrafluoride,

Predicting Electron-pair Geometry and Molecular Structure: SF_4, is extremely valuable for the preparation of fluorine-containing compounds used as herbicides (i.e., SF_4 is used as a fluorinating agent). Predict the electron-pair geometry and molecular structure of a SF_4 molecule.

Solution

The Lewis structure of SF_4 indicates five regions of electron density around the sulfur atom: one lone pair and four bonding pairs:

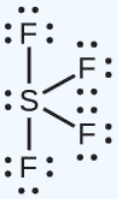


Figure 1.5.10).

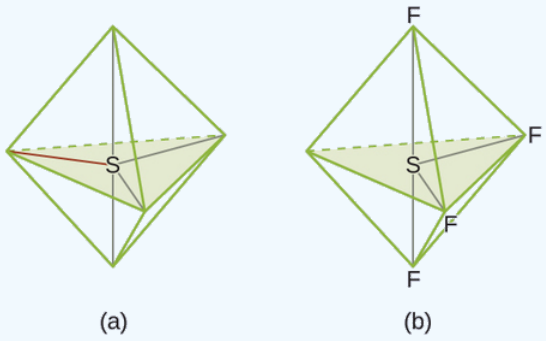


Figure 1.5.10: (a) SF_4 has a trigonal bipyramidal arrangement of the five regions of electron density. (b) One of the regions is a lone pair, which results in a seesaw-shaped molecular structure.

Exercise 1.5.4

Predict the electron pair geometry and molecular structure for molecules of XeF_2.

Answer

The electron-pair geometry is trigonal bipyramidal. The molecular structure is linear.

Example 1.5.4: XeF_4

Of all the noble gases, xenon is the most reactive, frequently reacting with elements such as oxygen and fluorine. Predict the electron-pair geometry and molecular structure of the XeF_4 molecule.

Solution

The Lewis structure of XeF_4 indicates six regions of high electron density around the xenon atom: two lone pairs and four bonds:

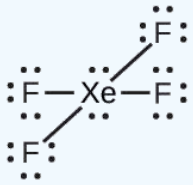


Figure 1.5.11: The five atoms are all in the same plane and have a square planar molecular structure.

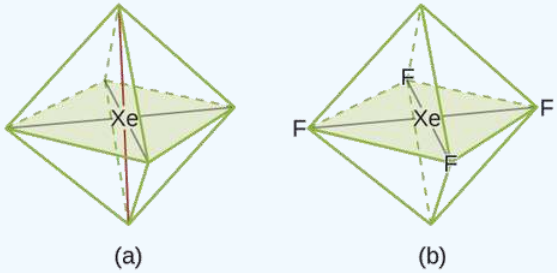


Figure 1.5.11: (a) XeF_4 adopts an octahedral arrangement with two lone pairs (red lines) and four bonds in the electron-pair geometry. (b) The molecular structure is square planar with the lone pairs directly across from one another.

? Exercise 1.5.4

In a certain molecule, the central atom has three lone pairs and two bonds. What will the electron pair geometry and molecular structure be?

Answer

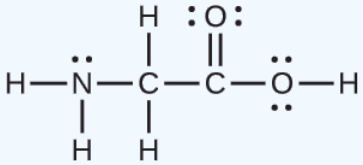
electron pair geometry: trigonal bipyramidal; molecular structure: linear

Molecular Structure for Multicenter Molecules

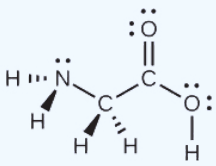
When a molecule or polyatomic ion has only one central atom, the molecular structure completely describes the shape of the molecule. Larger molecules do not have a single central atom, but are connected by a chain of interior atoms that each possess a "local" geometry. The way these local structures are oriented with respect to each other also influences the molecular shape, but such considerations are largely beyond the scope of this introductory discussion. For our purposes, we will only focus on determining the local structures.

✔ Example 1.5.5: Predicting Structure in Multicenter Molecules

The Lewis structure for the simplest amino acid, glycine, $H_2NCH_2CO_2H$, is shown here. Predict the local geometry for the nitrogen atom, the two carbon atoms, and the oxygen atom with a hydrogen atom attached:



Solution



Consider each central atom independently. The electron-pair geometries:

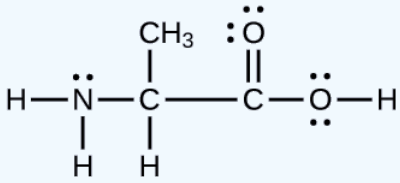
- nitrogen—four regions of electron density; tetrahedral
- carbon ($\underline{C}H_2$)—four regions of electron density; tetrahedral
- carbon ($\underline{C}O_2$)—three regions of electron density; trigonal planar
- oxygen ($\underline{O}H$)—four regions of electron density; tetrahedral

The local structures:

- nitrogen—three bonds, one lone pair; trigonal pyramidal
- carbon ($\underline{C}H_2$)—four bonds, no lone pairs; tetrahedral
- carbon ($\underline{C}O_2$)—three bonds (double bond counts as one bond), no lone pairs; trigonal planar
- oxygen ($\underline{O}H$)—two bonds, two lone pairs; bent (109°)

Exercise 1.5.5

Another amino acid is alanine, which has the Lewis structure shown here. Predict the electron-pair geometry and local structure of the nitrogen atom, the three carbon atoms, and the oxygen atom with hydrogen attached:



Answer

electron-pair geometries: nitrogen—tetrahedral; carbon ($\underline{C}H$)—tetrahedral; carbon ($\underline{C}H_3$)—tetrahedral; carbon ($\underline{C}O_2$)—trigonal planar; oxygen ($\underline{O}H$)—tetrahedral; local structures: nitrogen—trigonal pyramidal; carbon ($\underline{C}H$)—tetrahedral; carbon ($\underline{C}H_3$)—tetrahedral; carbon ($\underline{C}O_2$)—trigonal planar; oxygen ($\underline{O}H$)—bent (109°)

Example 1.5.6: Molecular Simulation

Using this molecular shape simulator allows us to control whether bond angles and/or lone pairs are displayed by checking or unchecking the boxes under “Options” on the right. We can also use the “Name” checkboxes at bottom-left to display or hide the electron pair geometry (called “electron geometry” in the simulator) and/or molecular structure (called “molecular shape” in the simulator).

Build the molecule HCN in the simulator based on the following Lewis structure:

$$H\text{–}C\equiv N$$

Click on each bond type or lone pair at right to add that group to the central atom. Once you have the complete molecule, rotate it to examine the predicted molecular structure. What molecular structure is this?

Solution

The molecular structure is linear.

Exercise 1.5.6

Build a more complex molecule in the simulator. Identify the electron-group geometry, molecular structure, and bond angles. Then try to find a chemical formula that would match the structure you have drawn.

Answer

Answers will vary. For example, an atom with four single bonds, a double bond, and a lone pair has an octahedral electron-group geometry and a square pyramidal molecular structure. $XeOF_4$ is a molecule that adopts this structure.

Molecular Polarity and Dipole Moment

As discussed previously, polar covalent bonds connect two atoms with differing electronegativities, leaving one atom with a partial positive charge (δ+) and the other atom with a partial negative charge (δ–), as the electrons are pulled toward the more electronegative atom. This separation of charge gives rise to a bond dipole moment. The magnitude of a bond dipole moment is represented by the Greek letter mu (μ) and is given by

$$\mu = Qr \tag{1.5.1}$$

where

- Q is the magnitude of the partial charges (determined by the electronegativity difference) and
- r is the distance between the charges:

This bond moment can be represented as a vector, a quantity having both direction and magnitude (Figure 1.5.12). Dipole vectors are shown as arrows pointing along the bond from the less electronegative atom toward the more electronegative atom. A small plus sign is drawn on the less electronegative end to indicate the partially positive end of the bond. The length of the arrow is proportional to the magnitude of the electronegativity difference between the two atoms.

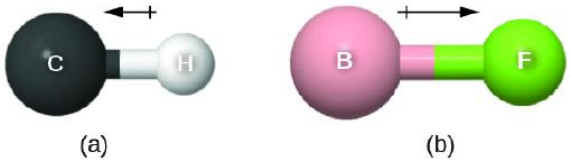


Figure 1.5.12: (a) There is a small difference in electronegativity between C and H, represented as a short vector. (b) The electronegativity difference between B and F is much larger, so the vector representing the bond moment is much longer.

A whole molecule may also have a separation of charge, depending on its molecular structure and the polarity of each of its bonds. If such a charge separation exists, the molecule is said to be a polar molecule (or dipole); otherwise the molecule is said to be nonpolar. The dipole moment measures the extent of net charge separation in the molecule as a whole. We determine the dipole moment by adding the bond moments in three-dimensional space, taking into account the molecular structure.

For diatomic molecules, there is only one bond, so its bond dipole moment determines the molecular polarity. Homonuclear diatomic molecules such as Br_2 and N_2 have no difference in electronegativity, so their dipole moment is zero. For heteronuclear molecules such as CO, there is a small dipole moment. For HF, there is a larger dipole moment because there is a larger difference in electronegativity.

When a molecule contains more than one bond, the geometry must be taken into account. If the bonds in a molecule are arranged such that their bond moments cancel (vector sum equals zero), then the molecule is nonpolar. This is the situation in CO_2 (Figure 1.5.13*A*). Each of the bonds is polar, but the molecule as a whole is nonpolar. From the Lewis structure, and using VSEPR theory, we determine that the CO_2 molecule is linear with polar C=O bonds on opposite sides of the carbon atom. The bond moments cancel because they are pointed in opposite directions. In the case of the water molecule (Figure 1.5.13*B*), the Lewis structure again shows that there are two bonds to a central atom, and the electronegativity difference again shows that each of these bonds has a nonzero bond moment. In this case, however, the molecular structure is bent because of the lone pairs on O, and the two bond moments do not cancel. Therefore, water does have a net dipole moment and is a polar molecule (dipole).

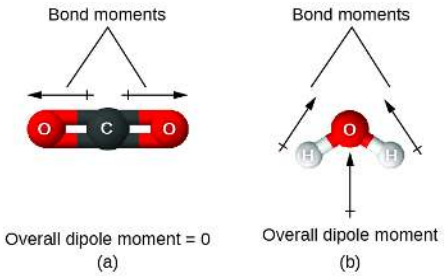
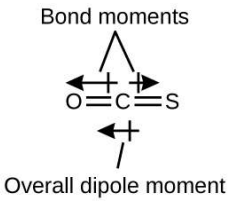


Figure 1.5.13: The overall dipole moment of a molecule depends on the individual bond dipole moments and how they are arranged. (a) Each CO bond has a bond dipole moment, but they point in opposite directions so that the net CO_2 molecule is nonpolar. (b) In contrast, water is polar because the OH bond moments do not cancel out.

The OCS molecule has a structure similar to CO_2, but a sulfur atom has replaced one of the oxygen atoms. To determine if this molecule is polar, we draw the molecular structure. VSEPR theory predicts a linear molecule:

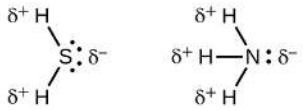


The C–O bond is considerably polar. Although C and S have very similar electronegativity values, S is slightly more electronegative than C, and so the C-S bond is just slightly polar. Because oxygen is more electronegative than sulfur, the oxygen end of the molecule is the negative end.

Chloromethane, CH_3Cl, is another example of a polar molecule. Although the polar C–Cl and C–H bonds are arranged in a tetrahedral geometry, the C–Cl bonds have a larger bond moment than the C–H bond, and the bond moments do not completely cancel each other. All of the dipoles have a upward component in the orientation shown, since carbon is more electronegative than hydrogen and less electronegative than chlorine:



When we examine the highly symmetrical molecules BF_3 (trigonal planar), CH_4 (tetrahedral), PF_5 (trigonal bipyramidal), and SF_6 (octahedral), in which all the polar bonds are identical, the molecules are nonpolar. The bonds in these molecules are arranged such that their dipoles cancel. However, just because a molecule contains identical bonds does not mean that the dipoles will always cancel. Many molecules that have identical bonds and lone pairs on the central atoms have bond dipoles that do not cancel. Examples include H_2S and NH_3. A hydrogen atom is at the positive end and a nitrogen or sulfur atom is at the negative end of the polar bonds in these molecules:



To summarize, to be polar, a molecule must:

1. Contain at least one polar covalent bond.
2. Have a molecular structure such that the sum of the vectors of each bond dipole moment does not cancel.

Properties of Polar Molecules

Polar molecules tend to align when placed in an electric field with the positive end of the molecule oriented toward the negative plate and the negative end toward the positive plate (Figure 1.5.14). We can use an electrically charged object to attract polar molecules, but nonpolar molecules are not attracted. Also, polar solvents are better at dissolving polar substances, and nonpolar solvents are better at dissolving nonpolar substances.

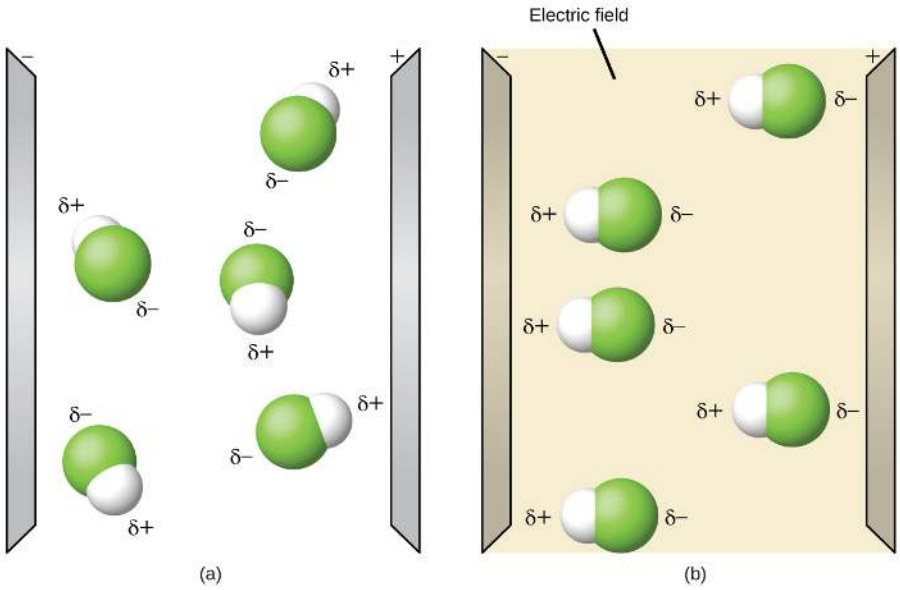


Figure 1.5.14: (a) Molecules are always randomly distributed in the liquid state in the absence of an electric field. (b) When an electric field is applied, polar molecules like HF will align to the dipoles with the field direction.

Example 1.5.7: Polarity Simulations

Open the molecule polarity simulation and select the "Three Atoms" tab at the top. This should display a molecule ABC with three electronegativity adjustors. You can display or hide the bond moments, molecular dipoles, and partial charges at the right. Turning on the Electric Field will show whether the molecule moves when exposed to a field, similar to Figure 1.5.14

Use the electronegativity controls to determine how the molecular dipole will look for the starting bent molecule if:

a. A and C are very electronegative and B is in the middle of the range.
b. A is very electronegative, and B and C are not.

Solution

a. Molecular dipole moment points immediately between A and C.
b. Molecular dipole moment points along the A–B bond, toward A.

Exercise 1.5.7

Determine the partial charges that will give the largest possible bond dipoles.

Answer

The largest bond moments will occur with the largest partial charges. The two solutions above represent how unevenly the electrons are shared in the bond. The bond moments will be maximized when the electronegativity difference is greatest. The controls for A and C should be set to one extreme, and B should be set to the opposite extreme. Although the magnitude of the bond moment will not change based on whether B is the most electronegative or the least, the direction of the bond moment will.

Summary

VSEPR theory predicts the three-dimensional arrangement of atoms in a molecule. It states that valence electrons will assume an electron-pair geometry that minimizes repulsions between areas of high electron density (bonds and/or lone pairs). Molecular structure, which refers only to the placement of atoms in a molecule and not the electrons, is equivalent to electron-pair geometry only when there are no lone electron pairs around the central atom. A dipole moment measures a separation of charge. For one bond, the bond dipole moment is determined by the difference in electronegativity between the two atoms. For a molecule, the

overall dipole moment is determined by both the individual bond moments and how these dipoles are arranged in the molecular structure. Polar molecules (those with an appreciable dipole moment) interact with electric fields, whereas nonpolar molecules do not.

Glossary

axial position
location in a trigonal bipyramidal geometry in which there is another atom at a 180° angle and the equatorial positions are at a 90° angle

bond angle
angle between any two covalent bonds that share a common atom

bond distance
(also, bond length) distance between the nuclei of two bonded atoms

bond dipole moment
separation of charge in a bond that depends on the difference in electronegativity and the bond distance represented by partial charges or a vector

dipole moment
property of a molecule that describes the separation of charge determined by the sum of the individual bond moments based on the molecular structure

electron-pair geometry
arrangement around a central atom of all regions of electron density (bonds, lone pairs, or unpaired electrons)

equatorial position
one of the three positions in a trigonal bipyramidal geometry with 120° angles between them; the axial positions are located at a 90° angle

linear
shape in which two outside groups are placed on opposite sides of a central atom

molecular structure
structure that includes only the placement of the atoms in the molecule

octahedral
shape in which six outside groups are placed around a central atom such that a three-dimensional shape is generated with four groups forming a square and the other two forming the apex of two pyramids, one above and one below the square plane

polar molecule
(also, dipole) molecule with an overall dipole moment

tetrahedral
shape in which four outside groups are placed around a central atom such that a three-dimensional shape is generated with four corners and 109.5° angles between each pair and the central atom

trigonal bipyramidal
shape in which five outside groups are placed around a central atom such that three form a flat triangle with 120° angles between each pair and the central atom, and the other two form the apex of two pyramids, one above and one below the triangular plane

trigonal planar

shape in which three outside groups are placed in a flat triangle around a central atom with 120° angles between each pair and the central atom

valence shell electron-pair repulsion theory (VSEPR)

theory used to predict the bond angles in a molecule based on positioning regions of high electron density as far apart as possible to minimize electrostatic repulsion

vector

quantity having magnitude and direction

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CHAPTER OVERVIEW

2: Atomic Orbitals

2.1: The Wave Behavior of Matter
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2.1: The Wave Behavior of Matter

The Wave Character of Matter

In the ground-breaking work by Einstein on the photoelectric effect, he initially assumed that photons had zero mass, which made them a peculiar sort of particle indeed. In 1905, however, he published his special theory of relativity, which related energy and mass according to the following equation:

$$E = h\nu = h\frac{c}{\lambda} = mc^2 \tag{1.4.1}$$

According to this theory, a photon of wavelength λ and frequency ν has a nonzero mass, which is given as follows:

$$m = \frac{E}{c^2} = \frac{h\nu}{c^2} = \frac{h}{\lambda c} \tag{1.4.2}$$

That is, light, which had always been regarded as a wave, also has properties typical of particles, a condition known as wave–particle duality (a principle that matter and energy have properties typical of both waves and particles). Depending on conditions, light could be viewed as either a wave or a particle.

In 1922, the American physicist Arthur Compton (1892–1962) reported the results of experiments involving the collision of x-rays and electrons that supported the particle nature of light. At about the same time, a young French physics student, Louis de Broglie (1892–1972), began to wonder whether the converse was true: Could particles exhibit the properties of waves? In his PhD dissertation submitted to the Sorbonne in 1924, de Broglie proposed that a particle such as an electron could be described by a wave whose wavelength is given by

$$\lambda = \frac{h}{mv} \tag{1.4.3}$$

where

- h is Planck's constant,
- *m* is the mass of the particle, and
- *v* is the velocity of the particle.

This revolutionary idea was quickly confirmed by American physicists Clinton Davisson (1881–1958) and Lester Germer (1896–1971), who showed that beams of electrons, regarded as particles, were diffracted by a sodium chloride crystal in the same manner as x-rays, which were regarded as waves. It was proven experimentally that electrons do exhibit the properties of waves. For his work, de Broglie received the Nobel Prize in Physics in 1929.

If particles exhibit the properties of waves, why had no one observed them before? The answer lies in the numerator of de Broglie's equation, which is an extremely small number. As you will calculate in Example 1.4.1, Planck's constant (6.63×10^{-34} J•s) is so small that the wavelength of a particle with a large mass is too short (less than the diameter of an atomic nucleus) to be noticeable.

Example 1.4.1

Calculate the wavelength of a baseball, which has a mass of 149 g and a speed of 100 mi/h.

Given: mass and speed of object

Asked for: wavelength

Strategy:

A. Convert the speed of the baseball to the appropriate SI units: meters per second.
B. Substitute values into Equation 6.4.3 and solve for the wavelength.

Solution:

A) The wavelength of a particle is given by λ = *h*/*mv*. We know that *m* = 0.149 kg, so all we need to find is the speed of the baseball:

$$v = \left(\frac{100\ \cancel{mi}}{\cancel{h}}\right)\left(\frac{1\ \cancel{h}}{60\ \cancel{min}}\right)\left(\frac{1.609\ \cancel{km}}{\cancel{mi}}\right)\left(\frac{1000\ m}{\cancel{km}}\right)$$

B) Recall that the joule is a derived unit, whose units are (kg•m^2)/s^2. Thus the wavelength of the baseball is

$$\lambda = \frac{6.626 \times 10^{-34}\ J \cdot s}{(0.149\ kg)\,(44.69\ m \cdot s)} = \frac{6.626 \times 10^{-34}\ \cancel{kg} \cdot m^{\cancel{2}} \cdot \cancel{s}^{\cancel{-2}} \cdot \cancel{s}}{\left(0.149\ \cancel{kg}\right)\left(44.69\ \cancel{m} \cdot \cancel{s^{-1}}\right)} = 9.95 \times 10^{-35}\ m \qquad (2.1.1)$$

(You should verify that the units cancel to give the wavelength in meters.) Given that the diameter of the nucleus of an atom is approximately 10^{-14} m, the wavelength of the baseball is almost unimaginably small.

? Exercise 1.4.1

Calculate the wavelength of a neutron that is moving at 3.00 × 10^3 m/s.

Answer:

1.32 Å, or 132 pm

As you calculated in Example 1.4.1, objects such as a baseball or a neutron have such short wavelengths that they are best regarded primarily as particles. In contrast, objects with very small masses (such as photons) have large wavelengths and can be viewed primarily as waves. Objects with intermediate masses, such as electrons, exhibit the properties of both particles and waves. Although we still usually think of electrons as particles, the wave nature of electrons is employed in an *electron microscope*, which has revealed most of what we know about the microscopic structure of living organisms and materials. Because the wavelength of an electron beam is much shorter than the wavelength of a beam of visible light, this instrument can resolve smaller details than a light microscope can (Figure 1.4.1).

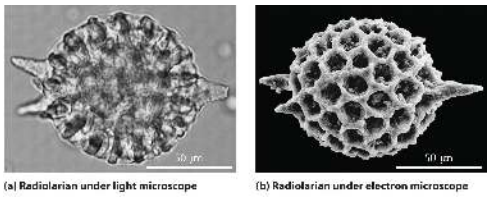


Figure 1.4.1: A Comparison of Images Obtained Using a Light Microscope and an Electron Microscope. Because of their shorter wavelength, high-energy electrons have a higher resolving power than visible light. Consequently, an electron microscope (b) is able to resolve finer details than a light microscope (a). (Radiolaria, which are shown here, are unicellular planktonic organisms.)

An Important Wave Property: Phase

A wave is a disturbance that travels in space. The magnitude of the wave at any point in space and time varies sinusoidally. While the absolute value of the magnitude of one wave at any point is not very important, the **relative** displacement of two waves called the phase difference, is vitally important because it determines whether the waves reinforce or interfere with each other. Figure 1.4.2a, on the right shows an arbitrary phase difference between two waves. Figure 1.4.2b shows what happens when the two waves are 180 degrees out of phase. The green line is their sum. Figure 1.4.2c shows what happens when the two lines are in phase, exactly superimposed on each other. Again, the green line is the sum of the intensities.

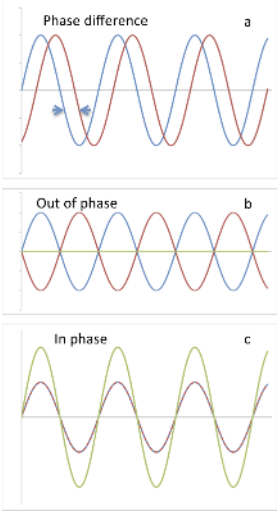


Figure 1.4.2 Phase. *Two waves traveling together are displaced by a phase difference. If the phase difference is 0 then they lay on top of each other and reinforce. If the phase difference is 180 they completely cancel each other out.*

Standing Waves

De Broglie also investigated why only certain orbits were allowed in Bohr's model of the hydrogen atom. He hypothesized that the electron behaves like a standing wave (a wave that does not travel in space). An example of a standing wave is the motion of a string of a violin or guitar. When the string is plucked, it vibrates at certain fixed frequencies because it is fastened at both ends (Figure 1.4.3). If the length of the string is L, then the lowest-energy vibration (the lowest-energy standing wave), called the fundamental, has wavelength

$$\frac{\lambda}{2} = L$$
$$\lambda = 2L \tag{1.4.4}$$

Higher-energy vibrations are called overtones (the vibration of a standing wave that is higher in energy than the fundamental vibration) and are produced when the string is plucked more strongly; they have wavelengths given by

$$\lambda = \frac{2L}{n} \tag{1.4.5}$$

where n has any integral value. Thus the resonant vibrational energies of the string are quantized. When plucked, all other frequencies die out immediately. Only the resonant frequencies survive and are heard. By analogy we can think of the resonant frequencies as being quantized. Notice in Figure 1.4.3 that all overtones have one or more nodes (the points where the amplitude of a wave is zero), points where the string does not move. The amplitude of the wave at a node is zero.

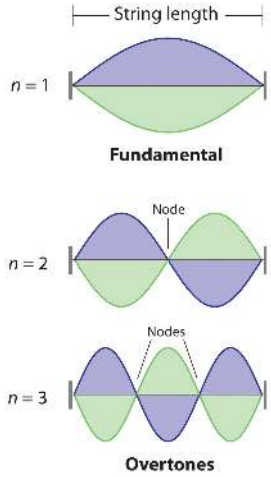


Figure 1.4.3: *Standing Waves on a Vibrating String. The vibration with n = 1 is the fundamental and contains no nodes. Vibrations with higher values of n are called overtones; they contain n − 1 nodes.*

Quantized vibrations and overtones containing nodes are not restricted to one-dimensional systems, such as strings. A two-dimensional surface, such as a drumhead, also has quantized vibrations. Similarly, when the ends of a string are joined to form a circle, the only allowed vibrations are those with wavelength

$$2\pi r = n\lambda \tag{1.4.6}$$

where *r* is the radius of the circle. De Broglie argued that Bohr's allowed orbits could be understood if the electron behaved like a *standing circular wave* (Figure 1.4.4). The standing wave could exist only if the circumference of the circle was an integral multiple of the wavelength such that the propagated waves were all in phase, thereby increasing the net amplitudes and causing *constructive interference*. Otherwise, the propagated waves would be out of phase, resulting in a net decrease in amplitude and causing *destructive interference*. The non resonant waves interfere with themselves! De Broglie's idea explained Bohr's allowed orbits and energy levels nicely: in the lowest energy level, corresponding to $n = 1$ in Equation 1.4.2, one complete wavelength would close the circle. Higher energy levels would have successively higher values of *n* with a corresponding number of nodes.

Standing waves are often observed on rivers, reservoirs, ponds, and lakes when seismic waves from an earthquake travel through the area. The waves are called *seismic seiches*, a term first used in 1955 when lake levels in England and Norway oscillated from side to side as a result of the Assam earthquake of 1950 in Tibet. They were first described in the Proceedings of the Royal Society in 1755 when they were seen in English harbors and ponds after a large earthquake in Lisbon, Portugal. Seismic seiches were also observed in many places in North America after the Alaska earthquake of March 28, 1964. Those occurring in western reservoirs lasted for two hours or longer, and amplitudes reached as high as nearly 6 ft along the Gulf Coast. The height of seiches is approximately proportional to the thickness of surface sediments; a deeper channel will produce a higher seiche.

Still, as all analogies, although the standing wave model helps us understand much about why Bohr's theory worked, it also, if pushed too far can mislead.

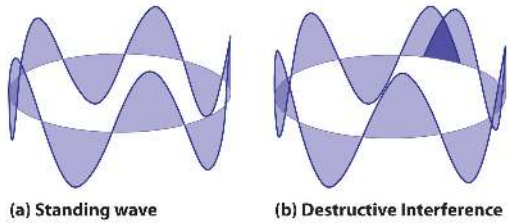


Figure 1.4.4: *Standing Circular Wave and Destructive Interference.(a) In a standing circular wave with n = 5, the circumference of the circle corresponds to exactly five wavelengths, which results in constructive interference of the wave with itself when overlapping occurs. (b) If the circumference of the circle is not equal to an integral multiple of wavelengths, then the wave does not overlap exactly with itself, and the resulting destructive interference will result in cancelation of the wave. Consequently, a standing wave cannot exist under these conditions.*

As you will see, some of de Broglie's ideas are retained in the modern theory of the electronic structure of the atom: the wave behavior of the electron and the presence of nodes that increase in number as the energy level increases. Unfortunately, his (and Bohr's) explanation also contains one major feature that we know to be incorrect: in the currently accepted model, the electron in a given orbit is *not* always at the same distance from the nucleus.

The Heisenberg Uncertainty Principle

Because a wave is a disturbance that travels in space, it has no fixed position. One might therefore expect that it would also be hard to specify the exact position of a *particle* that exhibits wavelike behavior. A characteristic of light is that is can be bent or spread out by passing through a narrow slit as shown in the video below. You can literally see this by half closing your eyes and looking through your eye lashes. This reduces the brightness of what you are seeing and somewhat fuzzes out the image, but the light bends around your lashes to provide a complete image rather than a bunch of bars across the image. This is called diffraction.

This behavior of waves is captured in Maxwell's equations (1870 or so) for electromagnetic waves and was and is well understood. Heisenberg's uncertainty principle for light is, if you will, merely a conclusion about the nature of electromagnetic waves and nothing new. DeBroglie's idea of wave particle duality means that particles such as electrons which all exhibit wave like characteristics, will also undergo diffraction from slits whose size is of the order of the electron wavelength.

This situation was described mathematically by the German physicist Werner Heisenberg (1901–1976; Nobel Prize in Physics, 1932), who related the position of a particle to its momentum. Referring to the electron, Heisenberg stated that "at every moment the electron has only an inaccurate position and an inaccurate velocity, and between these two inaccuracies there is this uncertainty

relation." Mathematically, the Heisenberg uncertainty principle is greater than or equal to Planck's constant *h* divided by 4π: states that the uncertainty in the position of a particle (Δ*x*) multiplied by the uncertainty in its momentum [Δ(*mv*)] is greater than or equal to Planck's constant divided by 4π:

$$(\Delta x)\,(\Delta\,[mv]) \geqslant \frac{h}{4\pi} \tag{1.4.7}$$

Because Planck's constant is a very small number, the Heisenberg uncertainty principle is important only for particles such as electrons that have very low masses. These are the same particles predicted by de Broglie's equation to have measurable wavelengths.

If the precise position *x* of a particle is known absolutely (Δ*x* = 0), then the uncertainty in its momentum must be infinite:

$$(\Delta\,[mv]) = \frac{h}{4\pi\,(\Delta x)} = \frac{h}{4\pi\,(0)} = \infty \tag{1.4.8}$$

Because the mass of the electron at rest (*m*) is both constant and accurately known, the uncertainty in Δ(*mv*) must be due to the Δ*v* term, which would have to be infinitely large for Δ(*mv*) to equal infinity. That is, according to Equation 1.4.8, the more accurately we know the exact position of the electron (as Δ*x* → 0), the less accurately we know the speed and the kinetic energy of the electron (1/2 mv^2) because Δ(*mv*) → ∞. Conversely, the more accurately we know the precise momentum (and the energy) of the electron [as Δ(*mv*) → 0], then Δ*x* → ∞ and we have no idea where the electron is.

Bohr's model of the hydrogen atom violated the Heisenberg uncertainty principle by trying to specify **simultaneously** both the position (an orbit of a particular radius) and the energy (a quantity related to the momentum) of the electron. Moreover, given its mass and wavelike nature, the electron in the hydrogen atom could not possibly orbit the nucleus in a well-defined circular path as predicted by Bohr. You will see, however, that the *most probable radius* of the electron in the hydrogen atom is exactly the one predicted by Bohr's model.

✔ Example 1.4.2

Calculate the minimum uncertainty in the position of the pitched baseball from Example 1.4.1 that has a mass of exactly 149 g and a speed of 100 ± 1 mi/h.

Given: mass and speed of object

Asked for: minimum uncertainty in its position

Strategy:

A. Rearrange the inequality that describes the Heisenberg uncertainty principle (Equation 1.4.7) to solve for the minimum uncertainty in the position of an object (Δ*x*).
B. Find Δ*v* by converting the velocity of the baseball to the appropriate SI units: meters per second.
C. Substitute the appropriate values into the expression for the inequality and solve for Δ*x*.

Solution:

A The Heisenberg uncertainty principle tells us that (Δ*x*)[Δ(*mv*)] = *h*/4π. Rearranging the inequality gives

$$\Delta x \geq \left(\frac{h}{4\pi}\right)\left(\frac{1}{\Delta(mv)}\right)$$

B We know that *h* = 6.626 × 10^{-34} J•s and *m* = 0.149 kg. Because there is no uncertainty in the mass of the baseball, Δ(*mv*) = *m*Δ*v* and Δ*v* = ±1 mi/h. We have

$$\Delta v = \left(\frac{1\ \cancel{mi}}{\cancel{h}}\right)\left(\frac{1\ \cancel{h}}{60\ \cancel{min}}\right)\left(\frac{1\ \cancel{min}}{60\ s}\right)\left(\frac{1.609\ \cancel{km}}{\cancel{mi}}\right)\left(\frac{1000\ m}{\cancel{km}}\right) = 0.4469\ m/s$$

C Therefore,

$$\Delta x \geqslant \left(\frac{6.626 \times 10^{-34}\ J \cdot s}{4\,(3.1416)}\right)\left(\frac{1}{(0.149\ kg)\,(0.4469\ m \cdot s^{-1})}\right)$$

Inserting the definition of a joule (1 J = 1 kg•m^2/s^2) gives

$$\Delta x \geqslant \left(\frac{6.626 \times 10^{-34} \ \cancel{kg} \cdot m^{\cancel{2}} \cdot \cancel{s}}{4\,(3.1416)\left(\cancel{s^2}\right)} \right) \left(\frac{1 \ \cancel{s}}{\left(0.149 \ \cancel{kg}\right)(0.4469 \ \cancel{m})} \right)$$

$$\Delta x \geqslant 7.92 \pm \times 10^{-34} \ m$$

This is equal to 3.12 × 10^{-32} inches. We can safely say that if a batter misjudges the speed of a fastball by 1 mi/h (about 1%), he will not be able to blame Heisenberg's uncertainty principle for striking out.

? Exercise 1.4.2

Calculate the minimum uncertainty in the position of an electron traveling at one-third the speed of light, if the uncertainty in its speed is ±0.1%. Assume its mass to be equal to its mass at rest.

Answer:

6 × 10^{-10} m, or 0.6 nm (about the diameter of a benzene molecule)

Videos and Examples

- de Broglie Waves - Sixty Symbols - a bit of history and explanation (as well as wave particle duality can be explained)
- Calculating the wavelength of a proton - Josh Samson
- Calculating the wavelength of a small car - Prof. Heath
- What is the Uncertainty Principle? - Minute Physics
- AP Chem Heisenberg Uncertainty Principle - Mind Bite
- deBroglie Example - about education
- Heisenberg uncertainty principle quiz worked out - C Craig
- Quantum Chemistry - Ohio State
- Quantum Chemistry Quizzes - mhe education
- AP Chemistry Chapter 7 Review - Science Geek

Answers for these quizzes are included.

Summary

- An electron possesses both particle and wave properties.

The modern model for the electronic structure of the atom is based on recognizing that an electron possesses particle and wave properties, the so-called **wave–particle duality**. Louis de Broglie showed that the wavelength of a particle is equal to Planck's constant divided by the mass times the velocity of the particle.

$$\lambda = \frac{h}{mv} \tag{1.4.3}$$

The electron in Bohr's circular orbits could thus be described as a **standing wave**, one that does not move through space. Standing waves are familiar from music: the lowest-energy standing wave is the **fundamental** vibration, and higher-energy vibrations are **overtones** and have successively more **nodes**, points where the amplitude of the wave is always zero. Werner Heisenberg's **uncertainty principle** states that it is impossible to precisely describe both the location and the speed of particles that exhibit wavelike behavior.

$$(\Delta x)\,(\Delta\,[mv]) \geqslant \frac{h}{4\pi} \tag{1.4.7}$$

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2.2: Electronic Structure of Atoms

Learning Objectives

- Describe how electrons are grouped within atoms into shells, subshells, and orbitals using quantum numbers.

You now know that the periodic table is arranged in groups and periods (columns and rows) based on chemical and physical properties of the different elements. The first element, hydrogen (Z=1) has one proton and one electron and as you move right across the rows, each subsequent element has one additional proton and electron. You may have asked yourself, why are periodic trends observed across the rows and down the groups? Or, why do the rows have different numbers of elements, giving the table a unique shape?

These questions can be answered by learning more about the electrons in atoms. Although we have discussed the general arrangement of subatomic particles in atoms, we have said little about how electrons occupy the space around the nucleus. Do they move around the nucleus at random, or do they exist in some ordered arrangement?

In 1913, the Danish scientist Niels Bohr suggested that the electron in a hydrogen atom could not have any random energy, having *only* certain fixed values of energy that were indexed by the number n (now called a **quantum number**). Bohr suggested that the energy of the electron in hydrogen was **quantized** because it was in a specific orbit; much like the steps on a staircase does not have half or quarter stairs or the keys on a piano don't have notes in between, there are no energy levels in between each orbit. Figure 2.2.1 shows a model of the hydrogen atom based on Bohr's ideas.

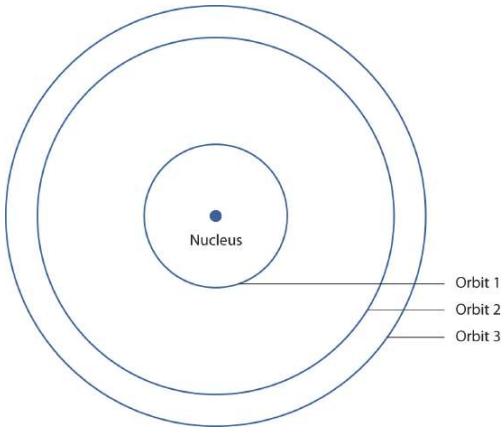


Figure 2.2.1: Bohr's Model of the Hydrogen Atom. Bohr's description of the hydrogen atom had specific orbits for the electron, which had quantized energies.

Bohr's ideas were useful, but were applicable only to the hydrogen atom. However, later researchers generalized Bohr's ideas into a new theory called **quantum mechanics**, which explains the behavior of electrons as if they were acting as a wave, not as particles. Quantum mechanics predicts two major things: quantized energies for electrons of all atoms (not just hydrogen) and an organization of electrons within atoms. Electrons are no longer thought of as being randomly distributed around a nucleus or restricted to certain orbits (in that regard, Bohr was wrong). Instead, electrons are collected into groups (*shells*) and subgroups (*subshells*) that explain much about the chemical behavior of the atom.

In the quantum-mechanical model of an atom, which is the modern and currently accepted model, the location of electrons in the atom are described by four **quantum numbers**, not just the one predicted by Bohr. Much like your home address can be used to locate you in a specific state, city, street, and house number, the first three quantum numbers identify approximately where electrons are in an atom. The fourth quantum number describes the electron and whether it is spin up or down (clockwise or counterclockwise). The theory and mathematics behind these four quantum numbers are well beyond the scope of this textbook, however, it is useful to learn some of the basics in order to understand how atoms behave and interact with (react) with other atoms.

Electron Arrangements: Shells, Subshells, and Orbitals

Electrons are organized according to their energies into sets called **shells** (labeled by the principle quantum number, ***n***). Generally the higher the energy of a shell, the farther it is (on average) from the nucleus. Shells do not have specific, fixed distances from the

nucleus, but an electron in a higher-energy shell will spend more time farther from the nucleus than does an electron in a lower-energy shell.

Shells are further divided into subsets of electrons called **subshells**, labeled by type as *s*, *p*, *d*, or *f*. The first shell has only one subshell, *s*. The second shell has two subshells, *s* and *p;* the third shell has three subshells, *s*, *p*, and *d*, and the fourth shell has four subshells, *s*, *p*, *d*, and *f*. Within each subshell, electrons are arranged into different numbers of **orbitals**, an *s* subshell is made up of one *s* orbital, a *p* subshell has three *p* orbitals, a *d* subshell, five *d* orbitals, and an *f* subshell, seven *f* orbitals. Each orbital has a different shape and orientation around the nucleus (Figure 2.2.1, however, rather than representing an orbit, as the name suggests, orbitals define a boundary for the region of space where a given electron is most likely to be found. Lastly, a single orbital can hold up to two electrons each with a different **spin**.

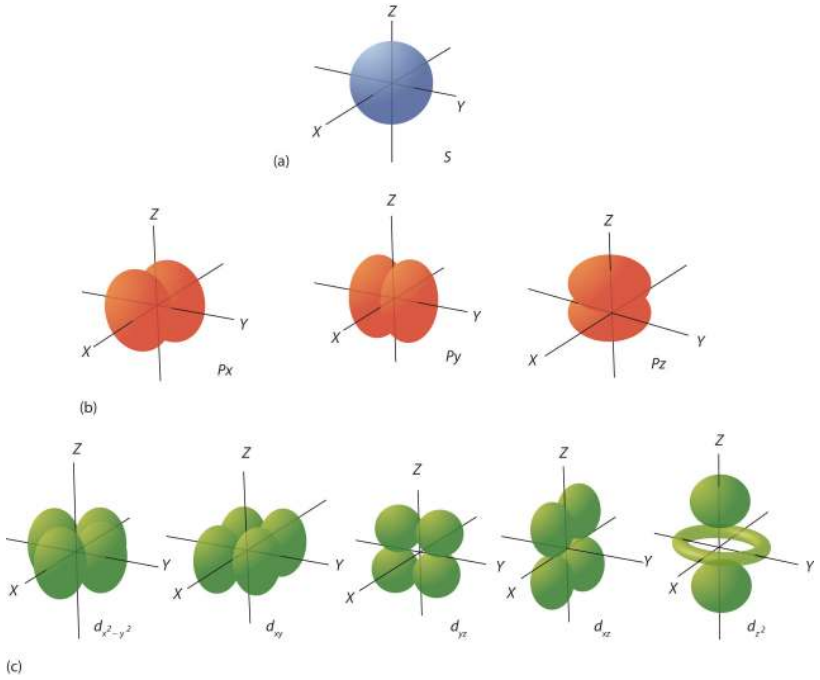


Figure 2.2.1: Electron Orbitals. (a) The lone *s* orbital in an *s* subshell is spherical in distribution. (b) The three *p* orbitals have two lobes, shaped kind of like dumbbells, each is oriented around the nucleus along a different axis. (c) The five *d* orbitals have four lobes, except for the d_{z^2} orbital, which is a "dumbbell + torus" combination. They are all oriented in different directions.

It is important to note that according to quantum theory, there are specific *allowed* combinations of quantum numbers and others that are not allowed. For example, shell two can only have two subshells, *s* with one orbital and *p* with 3 orbitals, therefore, this shell can hold a maximum of eight electrons (four orbitals times two electrons each). It takes practice to learn the allowed combinations as shown in Table \(\PageIndex{1}\ but it is helpful to visualize the atom as a sphere with the nucleus in the center. Close to the nucleus, there is a smaller amount of space for electrons – a smaller shell. As the number of electrons increases, the shells that hold the electrons get larger and thus further away from the nucleus.

Table 2.2.1: Shells and Subshells

Shell	Number of Subshells	Names of Subshells	Number of Orbitals (*per Subshell*)	Number of Electrons (*per Subshell*)	Total Electrons (*per Shell*)
1	1	*1s*	1	2	2
2	2	*2s* and *2p*	1, 3	2, 6	8
3	3	*3s*, *3p*, and *3d*	1, 3, 5	2, 6, 10	18
4	4	*4s*, *4p*, *4d*, and *4f*	1, 3, 5, 7	2, 6, 10, 14	32

All of this information about the shell, subshell, and orbital is put together to make up the "address" for an electron and all of the addresses for all the electrons in an atom make up the **electron configuration**, which is described more later.

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2.3: Electron Configurations

Learning Objectives

- Describe how electrons are arranged in an atom using electron configurations.

Previously we discussed the concept of electron *shells*, *subshells*, *orbitals*, and electron *spin*. It is the arrangement of electrons into shells and subshells that most concerns us here, so we will focus on that.

We use numbers to indicate which shell an electron is in. The first shell, closest to the nucleus and with the lowest-energy electrons, is shell 1. This first shell has only one subshell, which is labeled 1*s* and can hold a maximum of 2 electrons. We combine the shell and subshell labels when referring to the organization of electrons about a nucleus and use a superscript to indicate how many electrons are in a subshell. Thus, because a hydrogen atom has its single electron in the *s* subshell of the first shell, we use $\mathbf{1}\boldsymbol{s}^{\mathbf{1}}$ (spoken as “one-ess-one”) to describe the electron arrangement or distribution of electrons in hydrogen. This structure is called an **electron configuration** and is unique to hydrogen.

Helium atoms have 2 electrons. Both electrons fit into the 1*s* subshell because *s* subshells contain one *s* orbital which can hold up to 2 electrons; therefore, the electron configuration for helium atoms is $\mathbf{1}\boldsymbol{s}^{\mathbf{2}}$ (spoken as “one-ess-two”).

The 1*s* subshell can hold a maximum of 2 electrons, so the electron configuration for a lithium atom, which has three electrons, cannot be $1s^3$. Two of the lithium electrons can fit into the 1*s* subshell, but the third electron must go into the second shell and the lower energy orbital, which is the 2*s* orbital. Therefore, we write the electron configuration of a lithium atom as $\mathbf{1}\boldsymbol{s}^{\mathbf{2}}\mathbf{2}\boldsymbol{s}^{\mathbf{1}}$ (spoken as “one-ess-two two-ess-one”).

The shell diagram for a lithium atom (Figure 2.3.1). The shell closest to the nucleus (first shell) has 2 dots representing the 2 electrons in **1*s***, while the outermost shell (**2*s***) has 1 electron.

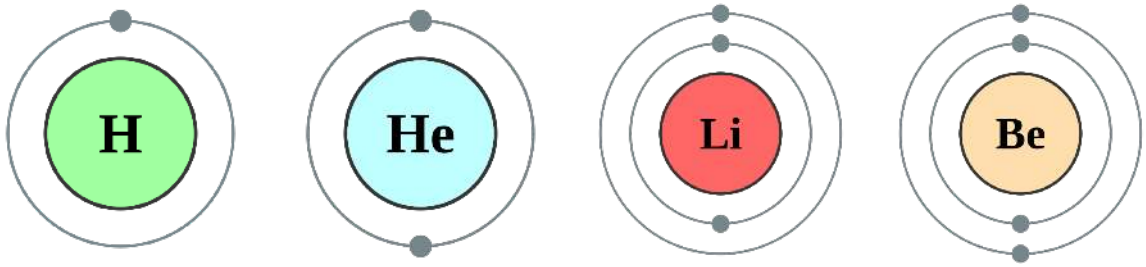


Figure 2.3.1: Shell diagrams of hydrogen (H), helium (He), lithium (Li), and Berryellium (Be) atoms. (CC BY-SA 2.0 UK; Greg Robson modified by Pumbaa via Wikipedia)

There are a set of general rules that are used to figure out the electron configuration of an atomic species: **Aufbau Principle**, **Hund's Rule** and the **Pauli-Exclusion Principle**.

- **Rule 1 (Aufbau Principle):** Electrons occupy the lowest-energy orbitals (closest to the nucleus) possible, starting with 1*s*, then 2*s*, 2*p*, and continuing on to higher energy (further away from the nucleus). Shells increase in energy in order from 1 to 2 to 3, and so on. Within these shells, an *s* subshell is the lowest energy followed by *p*, then *d*, then *f*.
- **Rule 2 (Hund's Rule):** When electrons occupy degenerate orbitals (i.e. same shell and subshell), they must first singly occupy (half-fill) each empty orbital in a subshell before double occupying (completely filling) them. Furthermore, the most stable configuration results when the spins are parallel (i.e. all spin up or all spin down). For example, all three *p* orbitals in a *p* subshell will have one electron before a single *p* orbital contains two electrons.
- **Rule 3 (Pauli-Exclusion Principle):** Each electron is described with a unique set of four quantum numbers (a unique address). Therefore, if two electrons occupy the same orbital, they must have different spins. This is the reason all orbitals can hold a maximum of two electrons.

Continuing on the periodic table to the next largest atom, beryllium, with 4 electrons, the electron configuration is $1s^2 2s^2$. Now that the 2*s* subshell is filled, electrons in larger atoms, starting with boron, begin filling the 2*p* subshell, which can hold a maximum of six electrons. The next six elements progressively fill up the 2p subshell:

- B: $1s^2 2s^2 2p^1$

- C: $1s^2 2s^2 2p^2$
- N: $1s^2 2s^2 2p^3$
- O: $1s^2 2s^2 2p^4$
- F: $1s^2 2s^2 2p^5$
- Ne: $1s^2 2s^2 2p^6$

At the end of the period the element neon, has filled the 2*s*, and 2*p* subshells, which completes the second shell. Now atoms with more electrons now must begin the third shell starting with the 3*s* subshell. The first two subshells of the third shell are filled in order—for example, the electron configuration of aluminum, with 13 electrons, is $1s^2 2s^2 2p^6 3s^2 3p^1$. However, a curious thing happens after the 3*p* subshell is filled: the 4*s* subshell begins to fill before the 3*d* subshell does. In fact, the exact ordering of subshells becomes more complicated at this point (after argon, with its 18 electrons), so we will not consider the electron configurations of larger atoms.

Table 2.3.1: Electron Configurations of the First 20 Elements

Atomic Number	Element Symbol	Outermost Shell	Electron Configuration	Noble Gas Configuration
1	H	1	$1s^1$	$1s^1$
2	He	1	$1s^2$	$1s^2$
3	Li	2	$1s^2 2s^1$	[He] $2s^1$
4	Be	2	$1s^2 2s^2$	[He] $2s^2$
5	B	2	$1s^2 2s^2 2p^1$	[He] $2s^2 2p^1$
6	C	2	$1s^2 2s^2 2p^2$	[He] $2s^2 2p^2$
7	N	2	$1s^2 2s^2 2p^3$	[He] $2s^2 2p^3$
8	O	2	$1s^2 2s^2 2p^4$	[He] $2s^2 2p^4$
9	F	2	$1s^2 2s^2 2p^5$	[He] $2s^2 2p^5$
10	Ne	2	$1s^2 2s^2 2p^6$	[He] $2s^2 2p^6$
11	Na	3	$1s^2 2s^2 2p^6 3s^1$	[Ne] $3s^1$
12	Mg	3	$1s^2 2s^2 2p^6 3s^2$	[Ne] $3s^2$
13	Al	3	$1s^2 2s^2 2p^6 3s^2 3p^1$	[Ne] $3s^2 3p^1$
14	Si	3	$1s^2 2s^2 2p^6 3s^2 3p^2$	[Ne]$3s^2 3p^2$
15	P	3	$1s^2 2s^2 2p^6 3s^2 3p^3$	[Ne] $3s^2 3p^3$
16	S	3	$1s^2 2s^2 2p^6 3s^2 3p^4$	[Ne] $3s^2 3p^4$
17	Cl	3	$1s^2 2s^2 2p^6 3s^2 3p^5$	[Ne] $3s^2 3p^5$
18	Ar	3	$1s^2 2s^2 2p^6 3s^2 3p^6$	[Ne] $3s^2 3p^6$
19	K	4	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$	[Ar] $4s^1$
20	Ca	4	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$	[Ar] $4s^2$

Noble Gas Configuration

The electron configuration of sodium is $1s^2 2s^2 2p^6 3s^1$ (Table 2.3.1). The first ten electrons of the sodium atom are the inner-shell electrons and the configuration of just those ten electrons is exactly the same as the configuration of the element neon $(Z = 10)$. This provides the basis for a shorthand notation for electron configurations called the **noble gas configuration**, which atom consists of the elemental symbol of the last noble gas prior to that atom, followed by the configuration of the remaining electrons. So for sodium, we make the substitution of $[\text{Ne}]$ for the $1s^2 2s^2 2p^6$ part of the configuration. Sodium's noble gas configuration becomes $[\text{Ne}]\, 3s^1$.

The electron filling diagram shown below in Figure 2.3.2 is useful in remembering the order for electrons to occupy shells and subshells. Although it is much easier to use the periodic table as a guide for electron filling as you will see in the next section.

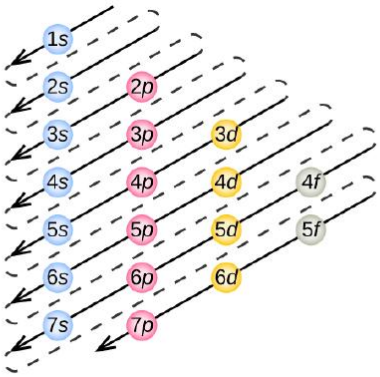


Figure 2.3.2: The order of electron filling in an atom. Follow each arrow in order **from top to bottom**. The subshells you reach along each arrow give the ordering of filling of subshells in larger atoms.

Example 2.3.1: Electronic Configuration of Phosphorus Atoms

Using Figure 2.3.2 as your guide, write the electron configuration of a neutral phosphorus atom. The atomic number of P is 15.

Solution

A neutral phosphorus atom has 15 electrons. Two electrons can go into the 1*s* subshell, 2 can go into the 2*s* subshell, and 6 can go into the 2*p* subshell. That leaves 5 electrons. Of those 5 electrons, 2 can go into the 3*s* subshell, and the remaining 3 electrons can go into the 3*p* subshell. Thus, the electron configuration of neutral phosphorus atoms is $1s^2 2s^2 2p^6 3s^2 3p^3$.

Exercise 2.3.1: Electronic Configuration of Chlorine Atoms

Using Figure 2.3.2 as your guide, write the electron configuration of a neutral chlorine atom. The atomic number of Cl is 17.

Answer

A neutral chlorine atom has 17 electrons. Two electrons can go into the 1*s* subshell, 2 can go into the 2*s* subshell, and 6 can go into the 2*p* subshell. That leaves 7 electrons. Of those 7 electrons, 2 can go into the 3*s* subshell, and the remaining 5 electrons can go into the 3*p* subshell. Thus, the electron configuration of neutral chlorine atoms is $1s^2 2s^2 2p^6 3s^2 3p^5$.

Orbital Diagrams

An **orbital diagram** is the more visual way to represent the arrangement of all the electrons in a particular atom. In an orbital diagram, the individual orbitals are shown as squares and orbitals within a sublevel are drawn next to each other horizontally. Each sublevel is labeled by its shell and sublevel. Electrons are indicated by arrows inside of the squares. An arrow pointing upwards indicates one spin direction, while a downward pointing arrow indicates the other direction. The orbital filling diagrams for hydrogen, helium, and lithium are shown in the figure below.

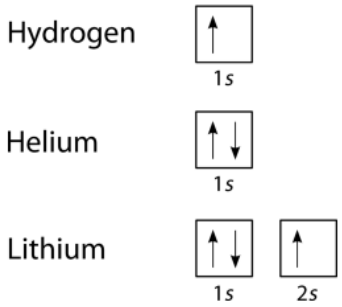


Figure 2.3.3: Orbital diagrams for hydrogen, helium, and lithium.

According to the Aufbau Principle, sublevels and orbitals are filled with electrons in order of increasing energy. Since the s sublevel consists of just one orbital, the second electron simply pairs up with the first electron as in helium. The next element is lithium and necessitates the use of the next available sublevel, the $2s$.

The orbital diagram for carbon is shown in Figure 2.3.10. There are two $2p$ electrons for carbon and each occupies its own $2p$ orbital (Hund's Rule).

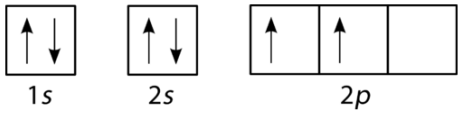


Figure 2.3.4: Orbital diagram for carbon.

Oxygen has four $2p$ electrons. After each $2p$ orbital has one electron in it, the fourth electron can be placed in the first $2p$ orbital with a spin opposite that of the other electron in that orbital.

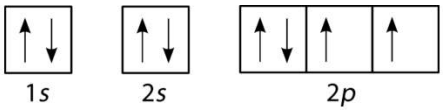


Figure 2.3.5: Orbital diagram for oxygen.

If you keep your papers in manila folders, you can pick up a folder and see how much it weighs. If you want to know how many different papers (articles, bank records, or whatever else you keep in a folder), you have to take everything out and count. A computer directory, on the other hand, tells you exactly how much you have in each file. We can get the same information on atoms. If we use an orbital filling diagram, we have to count arrows. When we look at electron configuration data, we simply add up the numbers.

Example 2.3.3: Carbon Atoms

Draw the orbital filling diagram for carbon and write its electron configuration.

Solution

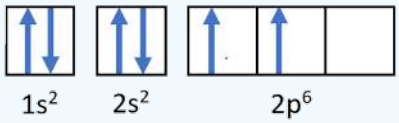
Step 1: List the known quantities and plan the problem.

Known

- Atomic number of carbon, Z=6

Use the order of fill diagram to draw an orbital filling diagram with a total of six electrons. Follow Hund's rule. Write the electron configuration.

Step 2: Construct the diagram.



Orbital filling diagram for carbon.

Electron configuration $1s^2 2s^2 2p^2$

Step 3: Think about your result.

Following the 2s sublevel is the 2p, and p sublevels always consist of three orbitals. All three orbitals need to be drawn even if one or more is unoccupied. According to Hund's rule, the sixth electron enters the second of those p orbitals and has the same spin as the fifth electron.

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2.4: Electron Configurations and the Periodic Table

Learning Objectives

- Relate the electron configurations of the elements to the shape of the periodic table.
- Determine the expected electron configuration of an element by its place on the periodic table.

Remember, that the periodic table as a tool for organizing the known chemical elements(Figure 2.4.1). The elements are listed by atomic number (the number of protons in the nucleus), and elements with similar chemical properties are grouped together in columns. Why does the periodic table have the structure it does? The answer is rather simple, if you understand electron configurations: the shape of the periodic table mimics the filling of the subshells with electrons.

> *The shape of the periodic table mimics the filling of the subshells with electrons.*

Let us start with H and He. Their electron configurations are $1s^1$ and $1s^2$, respectively; with He, the $n = 1$ shell is filled. These two elements make up the first row of the periodic table (Figure 2.4.1)

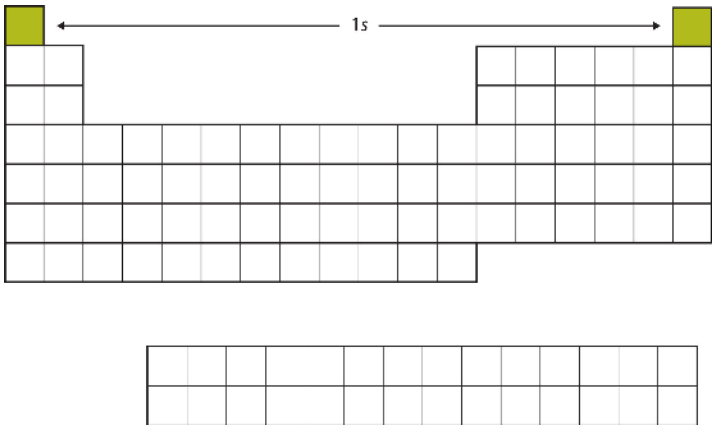


Figure 2.4.1: The 1*s* Subshell. H and He represent the filling of the 1*s* subshell.

The next two electrons, for Li and Be, would go into the 2*s* subshell. Figure 2.4.2 shows that these two elements are adjacent on the periodic table.

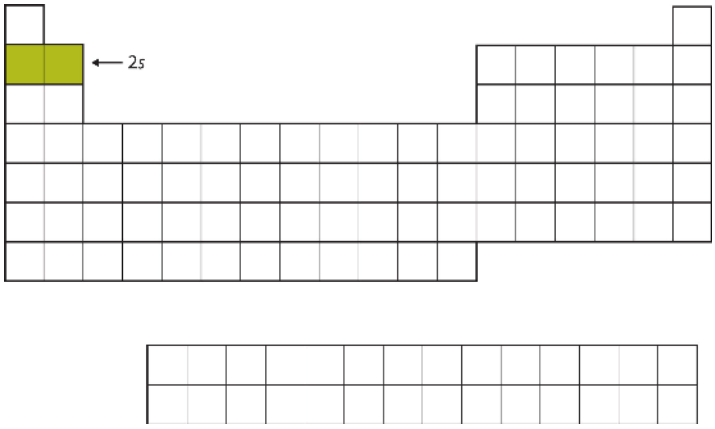


Figure 2.4.2: The 2*s* Subshell. In Li and Be, the 2*s* subshell is being filled.

For the next six elements, the 2*p* subshell is being occupied with electrons. On the right side of the periodic table, these six elements (B through Ne) are grouped together (Figure 2.4.3).

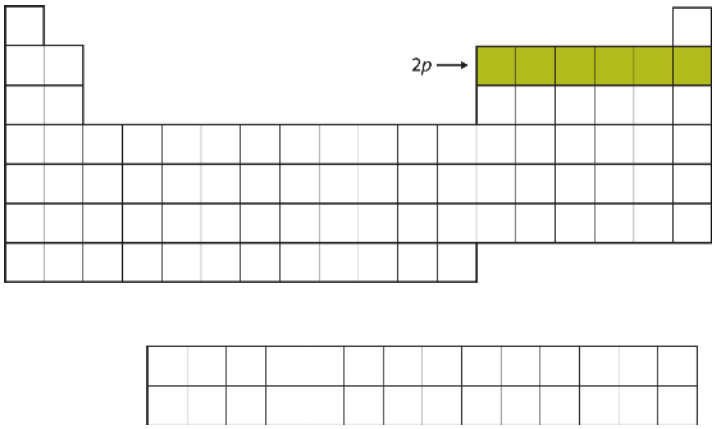


Figure 2.4.3: The 2*p* Subshell. For B through Ne, the 2*p* subshell is being occupied.

The next subshell to be filled is the 3*s* subshell. The elements when this subshell is being filled, Na and Mg, are back on the left side of the periodic table (Figure 2.4.4).

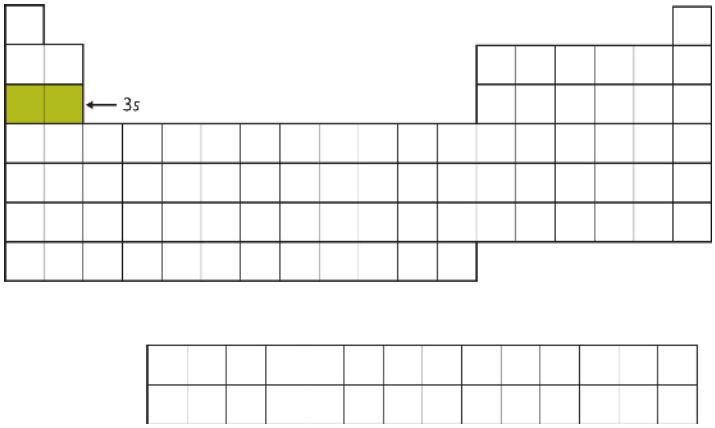


Figure 2.4.4: The 3*s* Subshell. Now the 3*s* subshell is being occupied.

Next, the 3*p* subshell is filled with the next six elements (Figure 2.4.5).

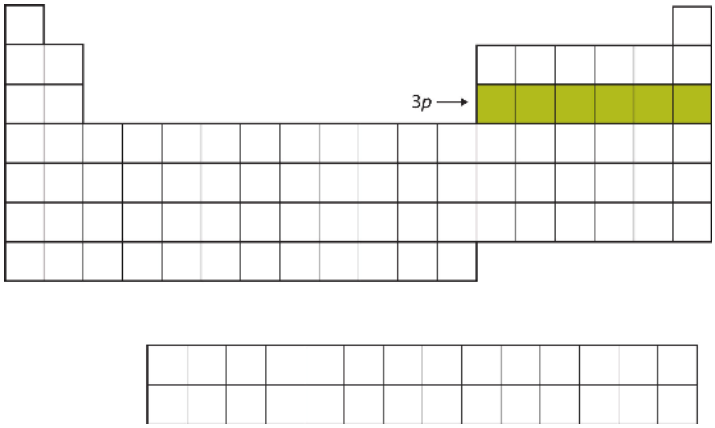


Figure 2.4.5: The 3*p* Subshell. Next, the 3*p* subshell is filled with electrons.

Instead of filling the 3*d* subshell next, electrons go into the 4*s* subshell (Figure 2.4.6).

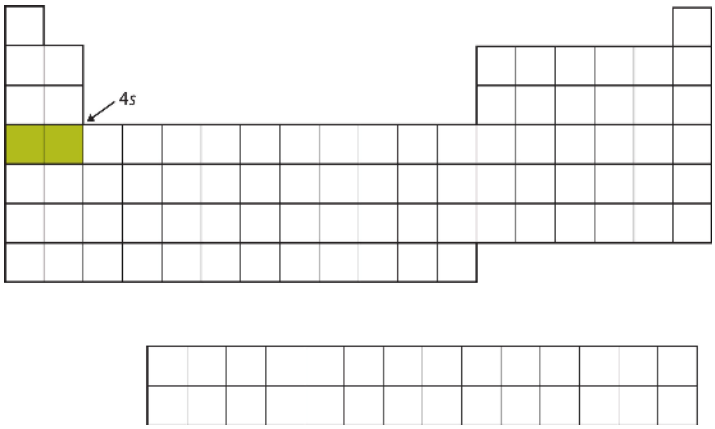


Figure 2.4.6: The 4*s* Subshell. The 4*s* subshell is filled before the 3*d* subshell. This is reflected in the structure of the periodic table.

After the 4*s* subshell is filled, the 3*d* subshell is filled with up to 10 electrons. This explains the section of 10 elements in the middle of the periodic table (Figure 2.4.7).

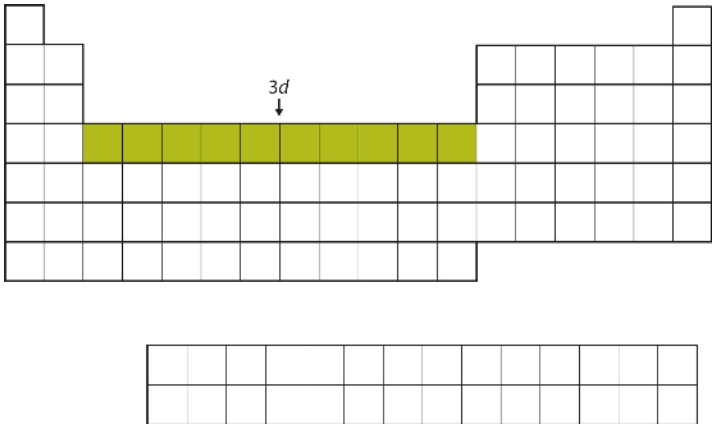


Figure 2.4.7: The 3*d* Subshell. The 3*d* subshell is filled in the middle section of the periodic table.

And so forth. As we go across the columns of the periodic table, the overall shape of the table outlines how the electrons are occupying the shells and subshells.

The first two columns on the left side of the periodic table are where the *s* subshells are being occupied. Because of this, the first two rows of the periodic table are labeled the **s block**. Similarly, the **p block** are the right-most six columns of the periodic table, the **d block** is the middle 10 columns of the periodic table, while the **f block** is the 14-column section that is normally depicted as detached from the main body of the periodic table. It could be part of the main body, but then the periodic table would be rather long and cumbersome. Figure 2.4.8 shows the blocks of the periodic table.

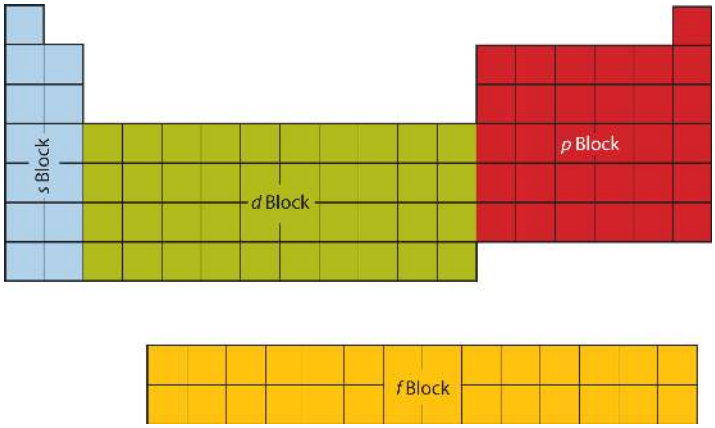


Figure 2.4.8: Blocks on the Periodic Table. The periodic table is separated into blocks depending on which subshell is being filled for the atoms that belong in that section.

The electrons in the highest-numbered shell, plus any electrons in the last unfilled subshell, are called **valence electrons**; the highest-numbered shell is called the **valence shell**. (The inner electrons are called *core electrons*.) The valence electrons largely control the chemistry of an atom. If we look at just the valence shell's electron configuration, we find that in each column, the valence shell's electron configuration is the same. For example, take the elements in the first column of the periodic table: H, Li, Na, K, Rb, and Cs. Their electron configurations (abbreviated for the larger atoms) are as follows, with the valence shell electron configuration highlighted:

Table shows first column of the periodic table and their electron configurations.

H:	$1s^{\mathbf{1}}$
Li:	$1s^2 2s^{\mathbf{1}}$
Na:	$[Ne]3s^{\mathbf{1}}$
K:	$[Ar]4s^{\mathbf{1}}$
Rb:	$[Kr]5s^{\mathbf{1}}$
Cs:	$[Xe]6s^{\mathbf{1}}$

They all have a similar electron configuration in their valence shells: a single *s* electron. Because much of the chemistry of an element is influenced by valence electrons, we would expect that these elements would have similar chemistry-*and they do*. The organization of electrons in atoms explains not only the shape of the periodic table but also the fact that elements in the same column of the periodic table have similar chemistry.

The same concept applies to the other columns of the periodic table. Elements in each column have the same valence shell electron configurations, and the elements have some similar chemical properties. This is strictly true for all elements in the *s* and *p* blocks. In the *d* and *f* blocks, because there are exceptions to the order of filling of subshells with electrons, similar valence shells are not absolute in these blocks. However, many similarities do exist in these blocks, so a similarity in chemical properties is expected.

Similarity of valence shell electron configuration implies that we can determine the electron configuration of an atom solely by its position on the periodic table. Consider Se, as shown in Figure 2.4.9. It is in the fourth column of the *p* block. This means that its electron configuration should end in a p^4 electron configuration. Indeed, the electron configuration of Se is $[Ar]4s^2 3d^{10} 4p^4$, as expected.

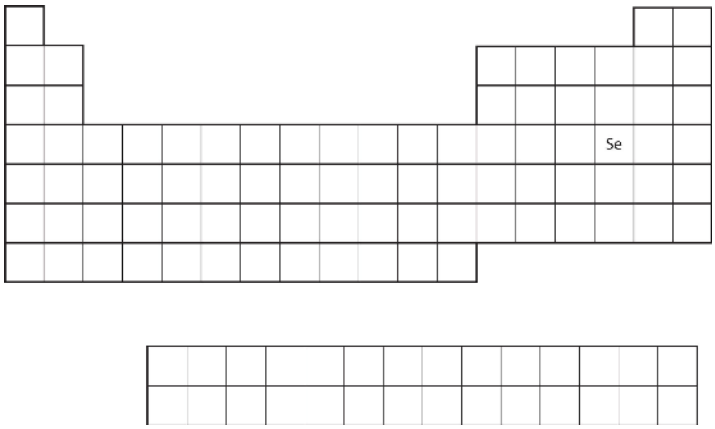


Figure 2.4.9: Selenium on the Periodic Table

Example 2.4.1

From the element's position on the periodic table, predict the valence shell electron configuration for each atom (Figure 2.4.10).

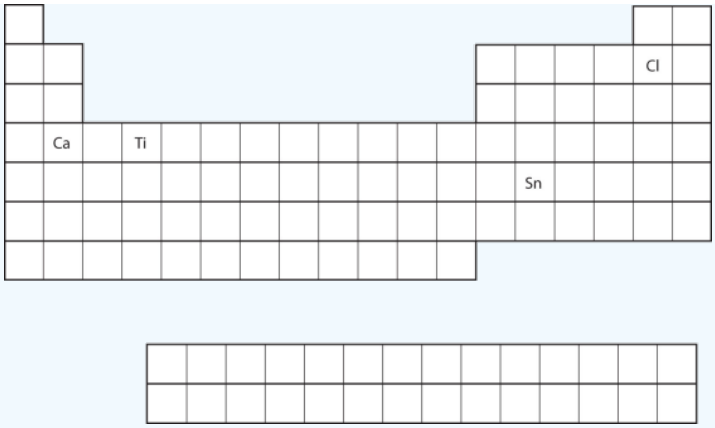


Figure 2.4.10: Various Elements on the Periodic Table

1. Ca
2. Sn

Solution

1. Ca is located in the second column of the *s* block. We would expect that its electron configuration should end with s^2. Calcium's electron configuration is [Ar]$4s^2$.
2. Sn is located in the second column of the *p* block, so we expect that its electron configuration would end in p^2. Tin's electron configuration is [Kr]$5s^2 4d^{10} 5p^2$.

? Exercise 2.4.1

From the element's position on the periodic table, predict the valence shell electron configuration for each atom. Figure 2.4.10

a. Ti
b. Cl

Answer a

[Ar]$4s^2 3d^2$

Answer b

[Ne]$3s^2 3p^5$

✔ Example 2.4.2: Aluminum

Write the electron configuration of neutral aluminum atom. The atomic number of Al is 13.

Solution

Aluminum has 13 electrons.

Start at Period 1 of the periodic table, Figure 2.4.2. Place two electrons in the 1s subshell (**$1s^2$**).

Proceed to Period 2 (left to right direction). Place the next two electrons in the 2s subshell (**$2s^2$**) and the next six electrons in the 2p subshell (**$2p^6$**).

Proceed to Period 3 (left to right direction). Place the next two electrons in the 3s subshell (**$3s^2$**) and the last one electron in the 3p subshell (**$3p^1$**).

The electron configuration of Aluminum is **$1s^2 2s^2 2p^6 3s^2 3p^1$**

? Exercise 2.4.2

Using Figure 2.4.2 as your guide, write the electron configuration of the atom that has 20 electrons

Answer

Start at Period 1 of Figure 2.4.2 Place two electrons in the 1s subshell (**$1s^2$**).

Proceed to Period 2 (left to right direction). Place the next two electrons in the 2s subshell (**$2s^2$**) and the next six electrons in the 2p subshell (**$2p^6$**).

Proceed to Period 3 (left to right direction). Place the next two electrons in the 3s subshell (**$3s^2$**) and the next six electron in the 3p subshell (**$3p^6$**).

Proceed to Period 4. Place the remaining two electrons in the 4s subshell (**$4s^2$).**

The electron configuration is **$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$**

Summary

The arrangement of electrons in atoms is responsible for the shape of the periodic table. Electron configurations can be predicted by the position of an atom on the periodic table

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2.5: Effective Nuclear Charge

Learning Objectives

- To understand the basics of electron shielding and penetration

For an atom or an ion with only a single electron, we can calculate the potential energy by considering only the electrostatic attraction between the positively charged nucleus and the negatively charged electron. When more than one electron is present, however, the total energy of the atom or the ion depends not only on attractive electron-nucleus interactions but also on repulsive electron-electron interactions. When there are two electrons, the repulsive interactions depend on the positions of *both* electrons at a given instant, but because we cannot specify the exact positions of the electrons, it is impossible to exactly calculate the repulsive interactions. Consequently, we must use approximate methods to deal with the effect of electron-electron repulsions on orbital energies.

If an electron is far from the nucleus (i.e., if the distance r between the nucleus and the electron is large), then at any given moment, most of the other electrons will be *between* that electron and the nucleus. Hence the electrons will cancel a portion of the positive charge of the nucleus and thereby decrease the attractive interaction between it and the electron farther away. As a result, the electron farther away experiences an effective nuclear charge (Z_{eff}) that is *less* than the actual nuclear charge Z. This effect is called electron shielding.

As the distance between an electron and the nucleus approaches infinity, Z_{eff} approaches a value of 1 because all the other $(Z - 1)$ electrons in the neutral atom are, on the average, between it and the nucleus. If, on the other hand, an electron is very close to the nucleus, then at any given moment most of the other electrons are farther from the nucleus and do not shield the nuclear charge. At $r \approx 0$, the positive charge experienced by an electron is approximately the full nuclear charge, or $Z_{\text{eff}} \approx Z$. At intermediate values of r, the effective nuclear charge is somewhere between 1 and Z: $1 \le Z_{\text{eff}} \le Z$. Thus the actual Z_{eff} experienced by an electron in a given orbital depends not only on the spatial distribution of the electron in that orbital but also on the distribution of all the other electrons present. This leads to large differences in Z_{eff} for different elements, as shown in Figure 2.5.1 for the elements of the first three rows of the periodic table. Notice that only for hydrogen does $Z_{\text{eff}} = Z$, and only for helium are Z_{eff} and Z comparable in magnitude.

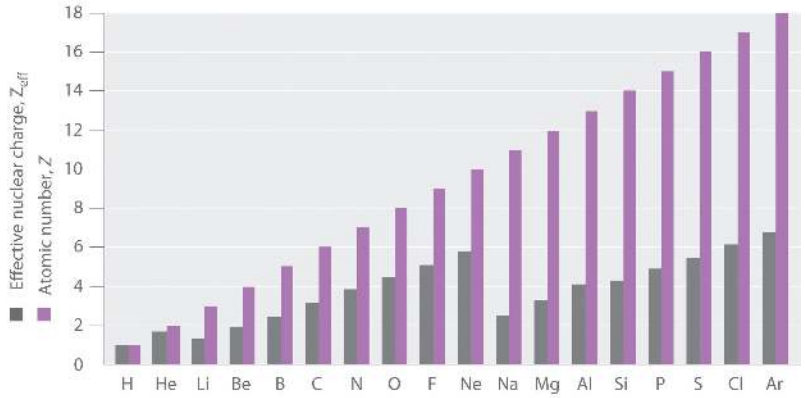


Figure 2.5.1: Relationship between the Effective Nuclear Charge Z_{eff} and the Atomic Number Z for the Outer Electrons of the Elements of the First Three Rows of the Periodic Table. Except for hydrogen, Z_{eff} is *always* less than Z, and Z_{eff} increases from left to right as you go across a row.

Because of the effects of shielding and the different radial distributions of orbitals with the same value of n but different values of l, the different subshells are not degenerate in a multielectron atom (compare with Figure 1.6.6). For a given value of n, the ns orbital is always lower in energy than the np orbitals, which are lower in energy than the nd orbitals, and so forth. As a result, some subshells with higher principal quantum numbers are actually lower in energy than subshells with a lower value of n; for example, the 4s orbital is lower in energy than the 3d orbitals for most atoms.

> *Except for the single electron containing hydrogen atom, in every other element Z_{eff} is always less than Z.*

In the next section we will consider a model for estimating the electron shielding, S. Once we have that estimate, we can calculate an estimate of Z_{eff} as follows:

$$Z_{eff} = Z - S \tag{2.5.1}$$

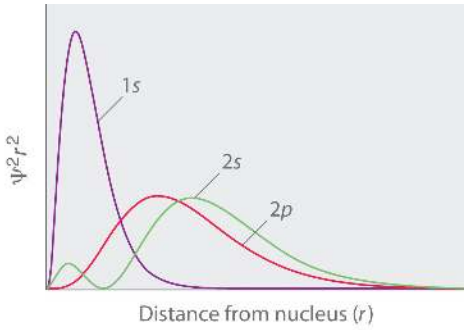


Figure 2.5.3: Orbital Penetration. A comparison of the radial probability distribution of the 2*s* and 2*p* orbitals for various states of the hydrogen atom shows that the 2*s* orbital penetrates inside the 1*s* orbital more than the 2*p* orbital does. Consequently, when an electron is in the small inner lobe of the 2*s* orbital, it experiences a relatively large value of Z_{eff}, which causes the energy of the 2*s* orbital to be lower than the energy of the 2*p* orbital.

Summary

The calculation of orbital energies in atoms or ions with more than one electron (multielectron atoms or ions) is complicated by repulsive interactions between the electrons. The concept of **electron shielding**, in which intervening electrons act to reduce the positive nuclear charge experienced by an electron, allows the use of hydrogen-like orbitals and an **effective nuclear charge** (Z_{eff}) to describe electron distributions in more complex atoms or ions. The degree to which orbitals with different values of *l* and the same value of *n* overlap or penetrate filled inner shells results in slightly different energies for different subshells in the same principal shell in most atoms.

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2.6: Slater's Rules

Learning Objective

- To quantify the shielding effect experienced by atomic electrons.

We have previously described the concepts of electron shielding, orbital penetration and effective nuclear charge, but we did so in a qualitative manner. In this section, we explore one model for quantitatively estimating the impact of electron shielding, and then use that to calculate the effective nuclear charge experienced by an electron in an atom. The model we will use is known as Slater's Rules (J.C. Slater, *Phys Rev* **1930**, *36*, 57).

Slater's Rules

The general principle behind Slater's Rule is that the actual charge felt by an electron is equal to what you'd expect the charge to be from a certain number of protons, but minus a certain amount of charge from other electrons. Slater's rules allow you to estimate the effective nuclear charge Z_{eff} from the real number of protons in the nucleus and the effective shielding of electrons in each orbital "shell" (e.g., to compare the effective nuclear charge and shielding 3d and 4s in transition metals). Slater's rules are fairly simple and produce fairly accurate predictions of things like the electron configurations and ionization energies.

Slater's Rules

- **Step 1**: Write the electron configuration of the atom in the following form:

  (1s) (2s, 2p) (3s, 3p) (3d) (4s, 4p) (4d) (4f) (5s, 5p) . . .

- **Step 2**: Identify the electron of interest, and ignore all electrons in higher groups (to the right in the list from Step 1). These do not shield electrons in lower groups
- **Step 3**: Slater's Rules is now broken into two cases:
  - the shielding experienced by an s- or p- electron,
    - electrons within same group shield **0.35**, except the 1*s* which shield **0.30**
    - electrons within the n-1 group shield **0.85**
    - electrons within the n-2 or lower groups shield **1.00**
  - the shielding experienced by n*d* or n*f* valence electrons
    - electrons within same group shield **0.35**
    - electrons within the lower groups shield **1.00**

These rules are summarized in Figure 2.6.1 and Table 2.6.1.

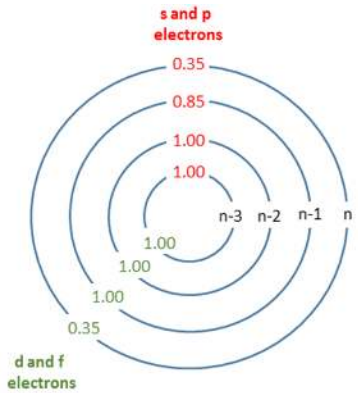


Figure 2.6.1: Graphical depiction of Slater's rules with shielding constants indicated.

Shielding happens when electrons in lower valence shells (or the same valence shell) provide a repulsive force to valence electrons, thereby "negating" some of the attractive force from the positive nucleus. Electrons really close to the atom (n-2 or lower) pretty much just look like protons, so they completely negate. As electrons get closer to the electron of interest, some more complex interactions happen that reduce this shielding.

Table 2.6.1: Slater's Rules for calculating shieldings

Group	Other electrons in the same group	Electrons in group(s) with principal quantum number n and azimuthal quantum number < l	Electrons in group(s) with principal quantum number n-1	Electrons in all group(s) with principal quantum number < n-1
[1s]	0.30	-	-	-
[*n*s,*n*p]	0.35	-	0.85	1
[*n*d] or [*n*f]	0.35	1	1	1

The shielding numbers in Table 2.6.1 were derived semi-empirically (i.e., derived from experiments) as opposed to theoretical calculations. This is because quantum mechanics makes calculating shielding effects quite difficult, which is outside the scope of this Module.

Calculating *S*

Sum together the contributions as described in the appropriate rule above to obtain an estimate of the shielding constant, S, which is found by totaling the screening by **all electrons** except the one in question.

$$S = \sum n_i S_i \tag{2.6.1}$$

where

- n_i is the number of electrons in a specific shell and subshell and
- S_i is the shielding of the electrons subject to Slater's rules (Table 2.6.1)

Example 2.6.1: The Shielding of 3*p* Electrons of Nitrogen Atoms

What is the shielding constant experienced by a 2*p* electron in the nitrogen atom?

Given: Nitrogen (N)

Asked for: S, the shielding constant, for a 2*p* electron (Equation 2.6.1)

Strategy:

A. Determine the electron configuration of nitrogen, then write it in the appropriate form.
B. Use the appropriate Slater Rule to calculate the shielding constant for the electron.

Solution A N: $1s^2\ 2s^2\ 2p^3$

N: $(1s^2)(2s^2,2p^3)$

Solution B

$$S[2p] = \underbrace{0.85(2)}_{\text{the 1s electrons}} + \underbrace{0.35(4)}_{\text{the 2s and 2p electrons}} = 3.10$$

As Table 2.6.1 indicates,

- the 1s electrons shield the other 2p electron to 0.85 "charges".
- the 2s and 2p electrons shield the other 2p electron equally at 0.35 "charges".

Exercise 2.6.1: The Shielding of valence *p* Electrons of Bromine Atoms

What is the shielding constant experienced by a valence *p*-electron in the bromine atom?

Answer

$$S = 2 + 8 + 8 \times 0.85 + 10 + 4 \times 0.35 = 28.20$$

Example 2.6.2: The Shielding of 3*d* Electrons of Bromine Atoms

What is the shielding constant experienced by a 3*d* electron in the bromine atom?

Given: Bromine (Br)

Asked for: *S*, the shielding constant, for a 3*d* electron

Strategy:

A. Determine the electron configuration of bromine, then write it in the appropriate form.
B. Use the appropriate Slater Rule to calculate the shielding constant for the electron.

Solution A Br: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^{10}\ 4p^5$

Br: $(1s^2)(2s^2,2p^6)(3s^2,3p^6)(3d^{10})(4s^2,4p^5)$

Ignore the group to the right of the 3d electrons. These do not contribute to the shielding constant.

Solution B *S*[3d] = 1.00(18) + 0.35(9) = 21.15

Exercise 2.6.2: The Shielding of 3*d* Electrons of Copper Atoms

What is the shielding constant experienced by a valence *d*-electron in the copper atom?

Answer

S = 21.15

Calculating Z_{eff}

One set of estimates for the effective nuclear charge (Z_{eff}) was presented in Figure 2.5.1. Previously, we described Z_{eff} as being less than the actual nuclear charge (Z) because of the repulsive interaction between core and valence electrons. We can quantitatively represent this difference between Z and Z_{eff} as follows:

$$S = Z - Z_{eff} \tag{2.6.2}$$

Rearranging this formula to solve for Z_{eff} we obtain:

$$Z_{eff} = Z - S \tag{2.6.3}$$

We can then substitute the shielding constant obtained using Equation 2.6.3 to calculate an estimate of Z_{eff} for the corresponding atomic electron.

Example 2.6.3: The Effective Charge of p Electrons of Boron Atoms

What is the effective nuclear charge experienced by a valence *p*- electron in boron?

Given: Boron (B)

Asked for: Z_{eff} for a valence *p*- electron

Strategy:

A. Determine the electron configuration of boron and identify the electron of interest.
B. Use the appropriate Slater Rule to calculate the shielding constant for the electron.
C. Use the Periodic Table to determine the actual nuclear charge for boron.
D. Determine the effective nuclear constant.

Solution:

A B: $1s^2\ 2s^2\ 2p^1$. The valence p- electron in boron resides in the 2*p* subshell.

B: $(1s^2)(2s^2,2p^1)$

B *S*[2*p*] = 1.00(0) + 0.85(2) + 0.35(2) = 2.40

C $Z = 5$

D Using Equation 2.6.3, $Z_{eff} = 2.60$

Exercise 2.6.3

What is the effective nuclear charge experienced by a valence d-electron in copper?

Answer

$Z_{eff} = 7.85$

Summary

Slater's Rules can be used as a model of shielding. This permits us to quantify both the amount of shielding experienced by an electron and the resulting effective nuclear charge. Others performed better optimizations of Z_{eff} using variational Hartree-Fock methods. For example, Clementi and Raimondi published "Atomic Screening Constants from SCF Functions." J Chem Phys (1963) 38, 2686–2689.

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- Kimberley A. Waldron, Erin M. Fehringer, Amy E. Streeb, Jennifer E. Trosky and Joshua J. Pearson, "Screening Percentages Based on Slater Effective Nuclear Charge as a Versatile Tool for Teaching Periodic Trends", J. Chem. Educ., 2001, 78 (5), p 635

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2.7: Magnetic Properties of Atoms and Ions

Learning Objectives

- To understand the difference between paramagnetism and diamagnetism

The magnetic moment of a system measures the strength and the direction of its magnetism. The term itself usually refers to the magnetic dipole moment. Anything that is magnetic, like a bar magnet or a loop of electric current, has a magnetic moment. A magnetic moment is a vector quantity, with a magnitude and a direction. An electron has an electron magnetic dipole moment, generated by the electron's intrinsic spin property, making it an electric charge in motion. There are many different magnetic forms: including paramagnetism, and diamagnetism, ferromagnetism, and anti-ferromagnetism.

Paramagnetism

Paramagnetism refers to the magnetic state of an atom with one or more unpaired electrons. The unpaired electrons are attracted by a magnetic field due to the electrons' magnetic dipole moments. Hund's Rule states that electrons must occupy every orbital singly before any orbital is doubly occupied. This may leave the atom with many unpaired electrons. Because unpaired electrons can spin in either direction, they display magnetic moments in any direction. This capability allows paramagnetic atoms to be attracted to magnetic fields. Diatomic oxygen, O_2 is a good example of paramagnetism (described via molecular orbital theory). The following video shows liquid oxygen attracted into a magnetic field created by a strong magnet:



Figure 2.7.1*: As shown in the video, molecular oxygen (O_2 is paramagnetic and is attracted to the magnet. Incontrast, Molecular nitrogen, N_2, however, has no unpaired electrons and it is diamagnetic (this concept is discussed below); it is therefore unaffected by the magnet.*

There are some exceptions to the paramagnetism rule; these concern some transition metals, in which the unpaired electron is not in a d-orbital. Examples of these metals include Sc^{3+}, Ti^{4+}, Zn^{2+}, and Cu^{+}. These metals are the not defined as paramagnetic: they are considered diamagnetic because all d-electrons are paired. Paramagnetic compounds sometimes display bulk magnetic properties due to the clustering of the metal atoms. This phenomenon is known as ferromagnetism, but this property is not discussed here.

Diamagnetism

Diamagnetic substances are characterized by paired electrons—except in the previously-discussed case of transition metals, there are no unpaired electrons. According to the Pauli Exclusion Principle which states that no two identical electrons may take up the same quantum state at the same time, the electron spins are oriented in opposite directions. This causes the magnetic fields of the electrons to cancel out; thus there is no net magnetic moment, and the atom cannot be attracted into a magnetic field. In fact, diamagnetic substances are weakly ***repelled*** by a magnetic field as demonstrated with the pyrolytic carbon sheet in Figure 2.7.2.

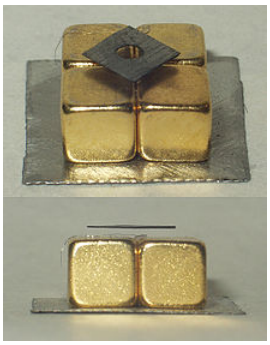


Figure 2.7.2: *Levitating pyrolytic carbon: A small (~6mm) piece of pyrolytic graphite levitating over a permanent neodymium magnet array (5mm cubes on a piece of steel). Note that the poles of the magnets are aligned vertically and alternate (two with north facing up, and two with south facing up, diagonally). from Wikipedia.*

How to tell if a substance is paramagnetic or diamagnetic

The magnetic form of a substance can be determined by examining its electron configuration: if it shows unpaired electrons, then the substance is paramagnetic; if all electrons are paired, the substance is diamagnetic. This process can be broken into four steps:

1. Find the electron configuration
2. Draw the valence orbitals
3. Look for unpaired electrons
4. Determine whether the substance is paramagnetic or diamagnetic

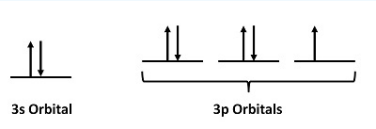
Example 2.7.1: Chlorine Atoms

Step 1: Find the electron configuration

For Cl atoms, the electron configuration is $3s^2 3p^5$

Step 2: Draw the valence orbitals

Ignore the core electrons and focus on the valence electrons only.



Step 3: Look for unpaired electrons

There is one unpaired electron.

Step 4: Determine whether the substance is paramagnetic or diamagnetic

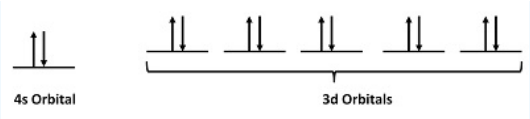
Since there is an unpaired electron, Cl atoms are paramagnetic (albeit, weakly).

Example 2.7.2: Zinc Atoms

Step 1: Find the electron configuration

For Zn atoms, the electron configuration is $4s^2 3d^{10}$

Step 2: Draw the valence orbitals



Step 3: Look for unpaired electrons

There are no unpaired electrons.

Step 4: Determine whether the substance is paramagnetic or diamagnetic

Because there are no unpaired electrons, Zn atoms are diamagnetic.

Exercise 2.7.1

a. How many unpaired electrons are found in oxygen atoms ?
b. How many unpaired electrons are found in bromine atoms?
c. Indicate whether boron atoms are paramagnetic or diamagnetic.
d. Indicate whether F^- ions are paramagnetic or diamagnetic.
e. Indicate whether Fe^{2+} ions are paramagnetic or diamagnetic.

Answer (a):

The O atom has $2s^2 2p^4$ as the electron configuration. Therefore, O has 2 unpaired electrons.

Answer (b):

The Br atom has $4s^2 3d^{10} 4p^5$ as the electron configuration. Therefore, Br has 1 unpaired electron.

Answer (c):

The B atom has $2s^2 2p^1$ as the electron configuration. Because it has one unpaired electron, it is paramagnetic.

Answer (d):

The F^- ion has $2s^2 2p^6$ has the electron configuration. Because it has no unpaired electrons, it is diamagnetic.

Answer (e):

The Fe^{2+} ion has $3d^6$ has the electron configuration. Because it has 4 unpaired electrons, it is paramagnetic.

References

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- superphysics.netfirms.com/ pp_magnetism.html
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2.8: Sizes of Atoms and Ions

Learning Objectives

- To understand periodic trends in atomic radii.
- To predict relative ionic sizes within an isoelectronic series.

Although some people fall into the trap of visualizing atoms and ions as small, hard spheres similar to miniature table-tennis balls or marbles, the quantum mechanical model tells us that their shapes and boundaries are much less definite than those images suggest. As a result, atoms and ions cannot be said to have exact sizes. In this section, we discuss how atomic and ion "sizes" are defined and obtained.

Atomic Radii

Recall that the probability of finding an electron in the various available orbitals falls off slowly as the distance from the nucleus increases. This point is illustrated in Figure 2.8.1 which shows a plot of total electron density for all occupied orbitals for three noble gases as a function of their distance from the nucleus. Electron density diminishes gradually with increasing distance, which makes it impossible to draw a sharp line marking the boundary of an atom.

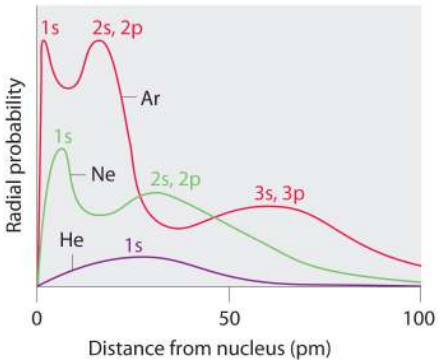


Figure 2.8.1: Plots of Radial Probability as a Function of Distance from the Nucleus for He, Ne, and Ar. In He, the 1*s* electrons have a maximum radial probability at ≈30 pm from the nucleus. In Ne, the 1*s* electrons have a maximum at ≈8 pm, and the 2*s* and 2*p* electrons combine to form another maximum at ≈35 pm (the $n = 2$ shell). In Ar, the 1*s* electrons have a maximum at ≈2 pm, the 2*s* and 2*p* electrons combine to form a maximum at ≈18 pm, and the 3*s* and 3*p* electrons combine to form a maximum at ≈70 pm.

Figure 2.8.1 also shows that there are distinct peaks in the total electron density at particular distances and that these peaks occur at different distances from the nucleus for each element. Each peak in a given plot corresponds to the electron density in a given principal shell. Because helium has only one filled shell ($n = 1$), it shows only a single peak. In contrast, neon, with filled $n = 1$ and 2 principal shells, has two peaks. Argon, with filled $n = 1$, 2, and 3 principal shells, has three peaks. The peak for the filled $n = 1$ shell occurs at successively shorter distances for neon ($Z = 10$) and argon ($Z = 18$) because, with a greater number of protons, their nuclei are more positively charged than that of helium. Because the $1s^2$ shell is closest to the nucleus, its electrons are very poorly shielded by electrons in filled shells with larger values of n. Consequently, the two electrons in the $n = 1$ shell experience nearly the full nuclear charge, resulting in a strong electrostatic interaction between the electrons and the nucleus. The energy of the $n = 1$ shell also decreases tremendously (the filled 1*s* orbital becomes more stable) as the nuclear charge increases. For similar reasons, the filled $n = 2$ shell in argon is located closer to the nucleus and has a lower energy than the $n = 2$ shell in neon.

Figure 2.8.1 illustrates the difficulty of measuring the dimensions of an individual atom. Because distances between the nuclei in pairs of covalently bonded atoms can be measured quite precisely, however, chemists use these distances as a basis for describing the approximate sizes of atoms. For example, the internuclear distance in the diatomic Cl_2 molecule is known to be 198 pm. We assign half of this distance to each chlorine atom, giving chlorine a covalent atomic radius (r_{cov}), which is half the distance between the nuclei of two like atoms joined by a covalent bond in the same molecule, of 99 pm or 0.99 Å (part (a) in Figure 2.8.2). Atomic radii are often measured in angstroms (Å), a non-SI unit: $1\ Å = 1 \times 10^{-10}$ m = 100 pm.

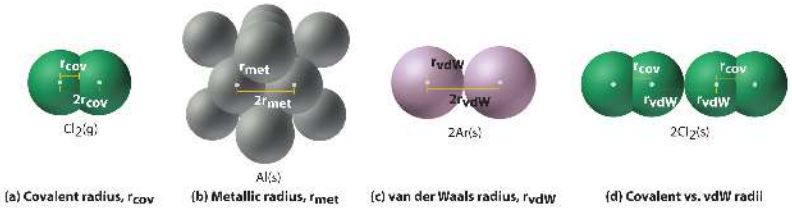


Figure 2.8.2: Definitions of the Atomic Radius. (a) The covalent atomic radius, r_{cov}, is half the distance between the nuclei of two like atoms joined by a covalent bond in the same molecule, such as Cl_2. (b) The metallic atomic radius, r_{met}, is half the distance between the nuclei of two adjacent atoms in a pure solid metal, such as aluminum. (c) The van der Waals atomic radius, r_{vdW}, is half the distance between the nuclei of two like atoms, such as argon, that are closely packed but not bonded. (d) This is a depiction of covalent versus van der Waals radii of chlorine. The covalent radius of Cl_2 is the distance between the two chlorine atoms in a single molecule of Cl_2. The van der Waals radius is the distance between chlorine nuclei in two different but touching Cl_2 molecules. Which do you think is larger? Why?

In a similar approach, we can use the lengths of carbon–carbon single bonds in organic compounds, which are remarkably uniform at 154 pm, to assign a value of 77 pm as the covalent atomic radius for carbon. If these values do indeed reflect the actual sizes of the atoms, then we should be able to predict the lengths of covalent bonds formed between different elements by adding them. For example, we would predict a carbon–chlorine distance of 77 pm + 99 pm = 176 pm for a C–Cl bond, which is very close to the average value observed in many organochlorine compounds.A similar approach for measuring the size of ions is discussed later in this section.

Covalent atomic radii can be determined for most of the nonmetals, but how do chemists obtain atomic radii for elements that do not form covalent bonds? For these elements, a variety of other methods have been developed. With a metal, for example, the metallic atomic radius (r_{met}) is defined as half the distance between the nuclei of two adjacent metal atoms (part (b) in Figure 2.8.2). For elements such as the noble gases, most of which form no stable compounds, we can use what is called the van der Waals atomic radius (r_{vdW}), which is half the internuclear distance between two nonbonded atoms in the solid (part (c) in Figure 2.8.2). This is somewhat difficult for helium which does not form a solid at any temperature. An atom such as chlorine has both a covalent radius (the distance between the two atoms in a Cl_2 molecule) and a van der Waals radius (the distance between two Cl atoms in different molecules in, for example, $Cl_{2(s)}$ at low temperatures). These radii are generally not the same (part (d) in Figure 2.8.2).

Periodic Trends in Atomic Radii

Because it is impossible to measure the sizes of both metallic and nonmetallic elements using any one method, chemists have developed a self-consistent way of calculating atomic radii using the quantum mechanical functions. Although the radii values obtained by such calculations are not identical to any of the experimentally measured sets of values, they do provide a way to compare the intrinsic sizes of all the elements and clearly show that atomic size varies in a periodic fashion (Figure 2.8.3).

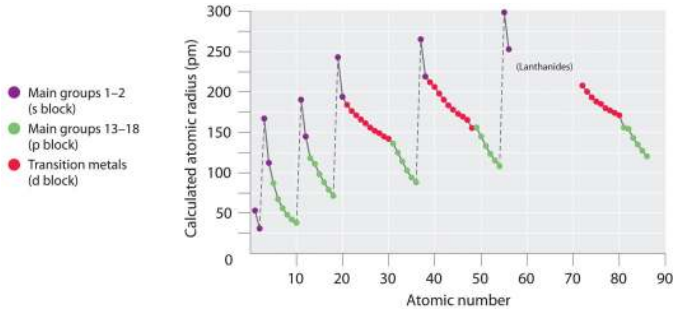


Figure 2.8.3: A Plot of Periodic Variation of Atomic Radius with Atomic Number for the First Six Rows of the Periodic Table.

In the periodic table, atomic radii decrease from left to right across a row and increase from top to bottom down a column. Because of these two trends, the largest atoms are found in the lower left corner of the periodic table, and the smallest are found in the upper right corner (Figure 2.8.4).

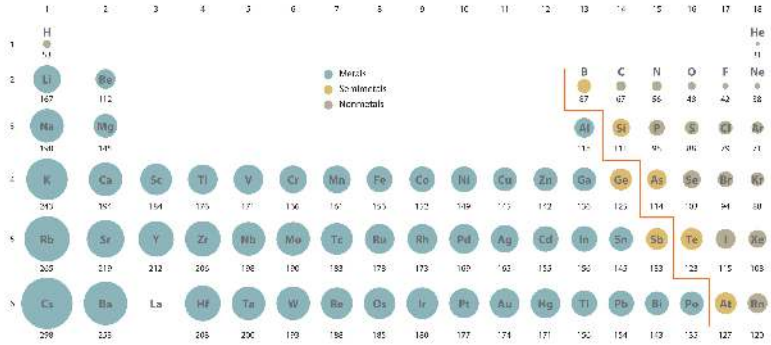


Figure 2.8.4 *Calculated Atomic Radii (in Picometers) of the s-, p-, and d-Block Elements. The sizes of the circles illustrate the relative sizes of the atoms. The calculated values are based on quantum mechanical wave functions. Source: http://www.webelements.com. Web Elements is an excellent on line source for looking up atomic properties.*

Note

Atomic radii decrease from left to right across a row (a period) and increase from top to bottom down a column (a group or family).

Trends in atomic size result from differences in the **effective nuclear charges (Z_{eff})** experienced by electrons in the outermost orbitals of the elements. For all elements except H, the effective nuclear charge is always *less* than the actual nuclear charge because of shielding effects. The greater the effective nuclear charge, the more strongly the outermost electrons are attracted to the nucleus and the smaller the atomic radius.

The atoms in the second row of the periodic table (Li through Ne) illustrate the effect of electron shielding. All have a filled $1s^2$ inner shell, but as we go from left to right across the row, the nuclear charge increases from +3 to +10. Although electrons are being added to the 2*s* and 2*p* orbitals, *electrons in the same principal shell are not very effective at shielding one another from the nuclear charge*. Thus the single 2*s* electron in lithium experiences an effective nuclear charge of approximately +1 because the electrons in the filled $1s^2$ shell effectively neutralize two of the three positive charges in the nucleus. (More detailed calculations give a value of Z_{eff} = +1.26 for Li.) In contrast, the two 2*s* electrons in beryllium do not shield each other very well, although the filled $1s^2$ shell effectively neutralizes two of the four positive charges in the nucleus. This means that the effective nuclear charge experienced by the 2*s* electrons in beryllium is between +1 and +2 (the calculated value is +1.66). Consequently, beryllium is significantly smaller than lithium. Similarly, as we proceed across the row, the increasing nuclear charge is not effectively neutralized by the electrons being added to the 2*s* and 2*p* orbitals. The result is a steady increase in the effective nuclear charge and a steady decrease in atomic size.

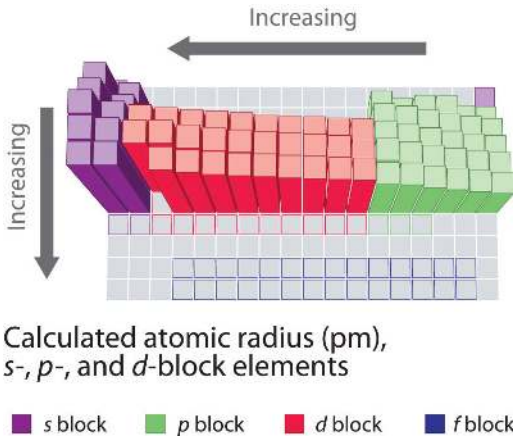


Figure 2.8.5 *The Atomic Radius of the Elements. The atomic radius of the elements increases as we go from right to left across a period and as we go down the periods in a group.*

The increase in atomic size going down a column is also due to electron shielding, but the situation is more complex because the principal quantum number *n* is not constant. As we saw in Chapter 2, the size of the orbitals increases as *n* increases, *provided the nuclear charge remains the same*. In group 1, for example, the size of the atoms increases substantially going down the column. It may at first seem reasonable to attribute this effect to the successive addition of electrons to *ns* orbitals with increasing values of *n*.

However, it is important to remember that the radius of an orbital depends dramatically on the nuclear charge. As we go down the column of the group 1 elements, the principal quantum number *n* increases from 2 to 6, but the nuclear charge increases from +3 to +55!

As a consequence the radii of the **lower electron orbitals** in Cesium are much smaller than those in lithium and the electrons in those orbitals experience a much larger force of attraction to the nucleus. That force depends on the effective nuclear charge experienced by the the inner electrons. If the outermost electrons in cesium experienced the full nuclear charge of +55, a cesium atom would be very small indeed. In fact, the effective nuclear charge felt by the outermost electrons in cesium is much less than expected (6 rather than 55). This means that cesium, with a $6s^1$ valence electron configuration, is much larger than lithium, with a $2s^1$ valence electron configuration. The effective nuclear charge changes relatively little for electrons in the outermost, or valence shell, from lithium to cesium because *electrons in filled inner shells are highly effective at shielding electrons in outer shells from the nuclear charge*. Even though cesium has a nuclear charge of +55, it has 54 electrons in its filled $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6$ shells, abbreviated as $[Xe]5s^2 4d^{10} 5p^6$, which effectively neutralize most of the 55 positive charges in the nucleus. The same dynamic is responsible for the steady increase in size observed as we go down the other columns of the periodic table. Irregularities can usually be explained by variations in effective nuclear charge.

Note

Electrons in the same principal shell are not very effective at shielding one another from the nuclear charge, whereas electrons in filled inner shells are highly effective at shielding electrons in outer shells from the nuclear charge.

Example 2.8.1

On the basis of their positions in the periodic table, arrange these elements in order of increasing atomic radius: aluminum, carbon, and silicon.

Given: three elements

Asked for: arrange in order of increasing atomic radius

Strategy:

A. Identify the location of the elements in the periodic table. Determine the relative sizes of elements located in the same column from their principal quantum number *n*. Then determine the order of elements in the same row from their effective nuclear charges. If the elements are not in the same column or row, use pairwise comparisons.
B. List the elements in order of increasing atomic radius.

Solution:

A These elements are not all in the same column or row, so we must use pairwise comparisons. Carbon and silicon are both in group 14 with carbon lying above, so carbon is smaller than silicon (C < Si). Aluminum and silicon are both in the third row with aluminum lying to the left, so silicon is smaller than aluminum (Si < Al) because its effective nuclear charge is greater. **B** Combining the two inequalities gives the overall order: C < Si < Al.

Exercise 2.8.1

On the basis of their positions in the periodic table, arrange these elements in order of increasing size: oxygen, phosphorus, potassium, and sulfur.

Answer:

O < S < P < K

Ionic Radii and Isoelectronic Series

An ion is formed when either one or more electrons are removed from a neutral atom (cations) to form a positive ion or when additional electrons attach themselves to neutral atoms (anions) to form a negative one. The designations cation or anion come from the early experiments with electricity which found that positively charged particles were attracted to the negative pole of a battery, the cathode, while negatively charged ones were attracted to the positive pole, the anode.

Ionic compounds consist of regular repeating arrays of alternating positively charged cations and negatively charges anions. Although it is not possible to measure an ionic radius directly for the same reason it is not possible to directly measure an atom's radius, it *is* possible to measure the distance between the nuclei of a cation and an adjacent anion in an ionic compound to determine the ionic radius (the radius of a cation or anion) of one or both. As illustrated in Figure 2.8.6 , the internuclear distance corresponds to the *sum* of the radii of the cation and anion. A variety of methods have been developed to divide the experimentally measured distance proportionally between the smaller cation and larger anion. These methods produce sets of ionic radii that are internally consistent from one ionic compound to another, although each method gives slightly different values. For example, the radius of the Na^+ ion is essentially the same in NaCl and Na_2S, as long as the same method is used to measure it. Thus despite minor differences due to methodology, certain trends can be observed.

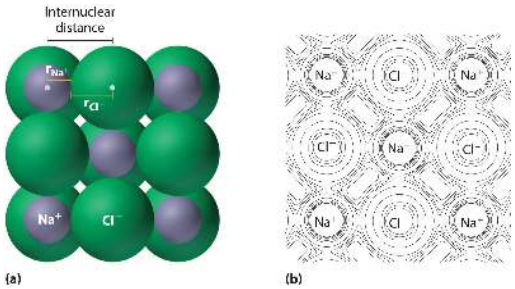


Figure 2.8.6: Definition of Ionic Radius. (a) The internuclear distance is apportioned between adjacent cations (positively charged ions) and anions (negatively charged ions) in the ionic structure, as shown here for Na^+ and Cl^- in sodium chloride. (b) This depiction of electron density contours for a single plane of atoms in the NaCl structure shows how the lines connect points of equal electron density. Note the relative sizes of the electron density contour lines around Cl^- and Na^+.

A comparison of ionic radii with atomic radii (Figure 2.8.7) *cation, having lost an electron, is always smaller than its parent neutral atom, and an anion, having gained an electron, is always larger than the parent neutral atom*. When one or more electrons is removed from a neutral atom, two things happen: (1) repulsions between electrons in the same principal shell decrease because fewer electrons are present, and (2) the effective nuclear charge felt by the remaining electrons increases because there are fewer electrons to shield one another from the nucleus. Consequently, the size of the region of space occupied by electrons decreases (compare Li at 167 pm with Li^+ at 76 pm). If different numbers of electrons can be removed to produce ions with different charges, the ion with the greatest positive charge is the smallest (compare Fe^{2+} at 78 pm with Fe^{3+} at 64.5 pm). Conversely, adding one or more electrons to a neutral atom causes electron–electron repulsions to increase and the effective nuclear charge to decrease, so the size of the probability region increases (compare F at 42 pm with F^- at 133 pm).

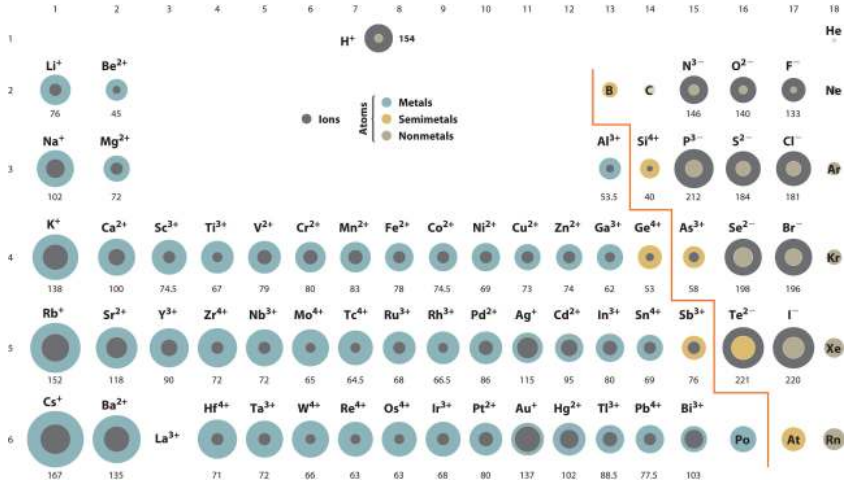


Figure 3.7. Source: Ionic radius data from R. D. Shannon, "Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides," *Acta Crystallographica* 32, no. 5 (1976): 751–767.

Note

Cations are **always** smaller than the neutral atom, and anions are **always** larger.

Because most elements form either a cation or an anion but not both, there are few opportunities to compare the sizes of a cation and an anion derived from the same neutral atom. A few compounds of sodium, however, contain the Na^- ion, allowing

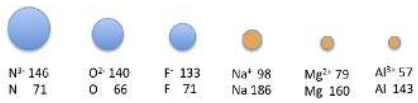
comparison of its size with that of the far more familiar Na^+ ion, which is found in *many* compounds. The radius of sodium in each of its three known oxidation states is given in Table 2.8.1. All three species have a nuclear charge of +11, but they contain 10 (Na^+), 11 (Na^0), and 12 (Na^-) electrons. The Na^+ ion is significantly smaller than the neutral Na atom because the $3s^1$ electron has been removed to give a closed shell with $n = 2$. The Na^- ion is larger than the parent Na atom because the additional electron produces a $3s^2$ valence electron configuration, while the nuclear charge remains the same.

Table 2.8.1: Experimentally Measured Values for the Radius of Sodium in Its Three Known Oxidation States

	Na^+	Na^0	Na^-
Electron Configuration	$1s^22s^22p^6$	$1s^22s^22p^63s^1$	$1s^22s^22p^63s^2$
Radius (pm)	102	154*	202†
*The metallic radius measured for Na(s).			
†Source: M. J. Wagner and J. L. Dye, "Alkalides, Electrides, and Expanded Metals," Annual Review of Materials Science 23 (1993): 225–253.			

Ionic radii follow the same vertical trend as atomic radii; that is, for ions with the same charge, the ionic radius increases going down a column. The reason is the same as for atomic radii: shielding by filled inner shells produces little change in the effective nuclear charge felt by the outermost electrons. Again, principal shells with larger values of n lie at successively greater distances from the nucleus.

Because elements in different columns tend to form ions with different charges, it is not possible to compare ions of the same charge across a row of the periodic table. Instead, elements that are next to each other tend to form ions with the same number of electrons but with different overall charges because of their different atomic numbers. Such a set of species is known as an isoelectronic series. For example, the isoelectronic series of species with the neon closed-shell configuration ($1s^22s^22p^6$) is shown in Table 7.3



The sizes of the ions in this series decrease smoothly from N^{3-} to Al^{3+}. All six of the ions contain 10 electrons in the 1*s*, 2*s*, and 2*p* orbitals, but the nuclear charge varies from +7 (N) to +13 (Al). As the positive charge of the nucleus increases while the number of electrons remains the same, there is a greater electrostatic attraction between the electrons and the nucleus, which causes a decrease in radius. Consequently, the ion with the greatest nuclear charge (Al^{3+}) is the smallest, and the ion with the smallest nuclear charge (N^{3-}) is the largest. The neon atom in this isoelectronic series is not listed in Table 2.8.3, because neon forms no covalent or ionic compounds and hence its radius is difficult to measure.

Table **2.8.3** Radius of Ions with the Neon Closed-Shell Electron Configuration. Source: R. D. Shannon, "Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides," Acta Crystallographica 32, no. 5 (1976): 751–767.

Ion	Radius (pm)	Atomic Number
N^{3-}	146	7
O^{2-}	140	8
F^-	133	9
Na^+	98	11
Mg^{2+}	79	12
Al^{3+}	57	13

Example 2.8.2

Based on their positions in the periodic table, arrange these ions in order of increasing radius: Cl^-, K^+, S^{2-}, and Se^{2-}.

Given: four ions

Asked for: order by increasing radius

Strategy:

A. Determine which ions form an isoelectronic series. Of those ions, predict their relative sizes based on their nuclear charges. For ions that do not form an isoelectronic series, locate their positions in the periodic table.
B. Determine the relative sizes of the ions based on their principal quantum numbers *n* and their locations within a row.

Solution:

A We see that S and Cl are at the right of the third row, while K and Se are at the far left and right ends of the fourth row, respectively. K^+, Cl^-, and S^{2-} form an isoelectronic series with the [Ar] closed-shell electron configuration; that is, all three ions contain 18 electrons but have different nuclear charges. Because K^+ has the greatest nuclear charge (Z = 19), its radius is smallest, and S^{2-} with Z = 16 has the largest radius. Because selenium is directly below sulfur, we expect the Se^{2-} ion to be even larger than S^{2-}. **B** The order must therefore be $K^+ < Cl^- < S^{2-} < Se^{2-}$.

Exercise 2.8.2

Based on their positions in the periodic table, arrange these ions in order of increasing size: Br^-, Ca^{2+}, Rb^+, and Sr^{2+}.

Answer:

$Ca^{2+} < Sr^{2+} < Rb^+ < Br^-$

Summary

Ionic radii share the same vertical trend as atomic radii, but the horizontal trends differ due to differences in ionic charges.

A variety of methods have been established to measure the size of a single atom or ion. The **covalent atomic radius (r_{cov})** is half the internuclear distance in a molecule with two identical atoms bonded to each other, whereas the **metallic atomic radius (r_{met})** is defined as half the distance between the nuclei of two adjacent atoms in a metallic element. The **van der Waals radius (r_{vdW})** of an element is half the internuclear distance between two nonbonded atoms in a solid. Atomic radii decrease from left to right across a row because of the increase in effective nuclear charge due to poor electron screening by other electrons in the same principal shell. Moreover, atomic radii increase from top to bottom down a column because the effective nuclear charge remains relatively constant as the principal quantum number increases. The **ionic radii** of cations and anions are always smaller or larger, respectively, than the parent atom due to changes in electron–electron repulsions, and the trends in ionic radius parallel those in atomic size. A comparison of the dimensions of atoms or ions that have the same number of electrons but different nuclear charges, called an **isoelectronic series**, shows a clear correlation between increasing nuclear charge and decreasing size.

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2.9: Ionization Energy

Learning Objectives

- To correlate ionization energies with the chemistry of the elements

We have seen that when elements react, they often gain or lose enough electrons to achieve the valence electron configuration of the nearest noble gas. In this section, we develop a more quantitative approach to predicting such reactions by examining periodic trends in the energy changes that accompany ion formation.

Ionization Energies

Because atoms do not spontaneously lose electrons, energy is required to remove an electron from an atom to form a cation. Chemists define the ionization energy (I) of an element as the amount of energy needed to remove an electron from the gaseous atom E in its ground state. I is therefore the energy required for the reaction

$$E_{(g)} \rightarrow E^{+}_{(g)} + e^{-} \qquad \text{energy required=I} \tag{2.9.1}$$

Because an input of energy is required, the ionization energy is always positive ($I > 0$) for the reaction as written in Equation 2.9.1. Larger values of *I* mean that the electron is more tightly bound to the atom and harder to remove. Typical units for ionization energies are kilojoules/mole (kJ/mol) or electron volts (eV):

$$1\ eV/atom = 96.49\ kJ/mol \tag{2.9.1}$$

If an atom possesses more than one electron, the amount of energy needed to remove successive electrons increases steadily (a simple arguement is that there exist fewer electrons to shield the valence electrons, see Slater's rules). We can define a first ionization energy (I_1), a second ionization energy (I_2), and in general an *n*th ionization energy (I_n) according to the following reactions:

$$E_{(g)} \rightarrow E^{+}_{(g)} + e^{-} \qquad I_1 = \text{1st ionization energy} \tag{2.9.2}$$

$$E_{(g)} \rightarrow E^{+}_{(g)} + e^{-} \qquad I_2 = \text{2nd ionization energy} \tag{2.9.3}$$

$$E^{+}_{(g)} \rightarrow E^{2+}_{(g)} + e^{-} \qquad I_3 = \text{3rd ionization energy} \tag{2.9.4}$$

Values for the ionization energies of Li and Be listed in Table 2.9.1 show that successive ionization energies for an element increase steadily; that is, it takes more energy to remove the second electron from an atom than the first, and so forth. There are two reasons for this trend. First, the second electron is being removed from a positively charged species rather than a neutral one, so in accordance with Coulomb's law, more energy is required. Second, removing the first electron reduces the repulsive forces among the remaining electrons, so the attraction of the remaining electrons to the nucleus is stronger.

Note

Successive ionization energies for an element **increase** steadily.

Table 2.9.1: *Ionization Energies (in kJ/mol) for Removing Successive Electrons from Li and Be. Source: Data from CRC Handbook of Chemistry and Physics (2004).*

Reaction	Electronic Transition	I (2.9.2)	Reaction	Electronic Transition	I (2.9.3)
$Li_{(g)} \rightarrow Li^{+}_{(g)} + e^{-}$	$1s^2 2s^1 \rightarrow 1s^2$	I_1 = 520.2	$Be_{(g)} \rightarrow Be^{+}_{(g)} + e^{-}$	$1s^2 2s^2 \rightarrow 1s^2 2s^1$	I_1 = 899.5
$Li^{+}_{(g)} \rightarrow Li^{2+}_{(g)} + e^{-}$	$1s^2 \rightarrow 1s^1$	I_2 = 7298.2	$Be^{+}_{(g)} \rightarrow Be^{2+}_{(g)} + e^{-}$	$1s^2 2s^1 \rightarrow 1s^2$	I_2 = 1757.1
$Li^{2+}_{(g)} \rightarrow Li^{3+}_{(g)} + e^{-}$	$1s^1 \rightarrow 1s^0$	I_3 = 11,815.0	$Be^{2+}_{(g)} \rightarrow Be^{3+}_{(g)} + e^{-}$	$1s^2 \rightarrow 1s^1$	I_3 = 14,848.8
			$Be^{3+}_{(g)} \rightarrow Be^{4+}_{(g)} + e^{-}$	$1s^1 \rightarrow 1s^0$	I_4 = 21,006.6

The most important consequence of the values listed in Table 2.9.1 is that the chemistry of Li is dominated by the Li^+ ion, while the chemistry of Be is dominated by the +2 oxidation state. The energy required to remove the *second* electron from Li

$$Li^+_{(g)} \rightarrow Li^{2+}_{(g)} + e^- \tag{2.9.5}$$

is more than 10 times greater than the energy needed to remove the first electron. Similarly, the energy required to remove the *third* electron from Be

$$Be^{2+}_{(g)} \rightarrow Be^{3+}_{(g)} + e^- \tag{2.9.6}$$

is about 15 times greater than the energy needed to remove the first electron and around 8 times greater than the energy required to remove the second electron. Both Li^+ and Be^{2+} have $1s^2$ closed-shell configurations, and much more energy is required to remove an electron from the $1s^2$ core than from the 2*s* valence orbital of the same element. The chemical consequences are enormous: lithium (and all the alkali metals) forms compounds with the 1+ ion but not the 2+ or 3+ ions. Similarly, beryllium (and all the alkaline earth metals) forms compounds with the 2+ ion but not the 3+ or 4+ ions. *The energy required to remove electrons from a filled core is prohibitively large and simply cannot be achieved in normal chemical reactions.*

Note

The energy required to remove electrons from a filled core is prohibitively large under normal reaction conditions.

Ionization Energies of *s*- and *p*-Block Elements

Ionization energies of the elements in the third row of the periodic table exhibit the same pattern as those of Li and Be (Table 2.9.2): successive ionization energies increase steadily as electrons are removed from the valence orbitals (3*s* or 3*p*, in this case), followed by an especially large increase in ionization energy when electrons are removed from filled core levels as indicated by the bold diagonal line in Table 2.9.2. Thus in the third row of the periodic table, the largest increase in ionization energy corresponds to removing the fourth electron from Al, the fifth electron from Si, and so forth—that is, removing an electron from an ion that has the valence electron configuration of the preceding noble gas. This pattern explains why the chemistry of the elements normally involves only valence electrons. Too much energy is required to either remove or share the inner electrons.

Table 2.9.2: Successive Ionization Energies (in kJ/mol) for the Elements in the Third Row of the Periodic Table.Source: Data from CRC Handbook of Chemistry and Physics (2004).

Element	I_1	I_2	I_3	I_4	I_5	I_6	I_7
Na	495.8	**4562.4***	—	—	—	—	—
Mg	737.7	1450.7	**7732.7**	—	—	—	—
Al	572.9.4	1816.7	2744.8	**11,572.9.4**	—	—	—
Si	786.5	1577.1	3231.6	4355.5	**16,090.6**	—	—
P	1011.8	1902.9.4	2914.1	4963.6	6274.0	**21,262.9.3**	—
S	999.6	2251.8	3357	4556.2	7004.3	8495.8	**27,102.9.3**
Cl	1251.2	2297.7	3822	5158.6	6540	9362	11,018.2
Ar	1520.6	2665.9	3931	5771	7238	8781.0	11,995.3

*Inner-shell electron

Example 2.9.1: Highest Fourth Ionization Energy

From their locations in the periodic table, predict which of these elements has the highest fourth ionization energy: B, C, or N.

Given: three elements

Asked for: element with highest fourth ionization energy

Strategy:

a. List the electron configuration of each element.
b. Determine whether electrons are being removed from a filled or partially filled valence shell. Predict which element has the highest fourth ionization energy, recognizing that the highest energy corresponds to the removal of electrons from a filled electron core.

Solution:

A These elements all lie in the second row of the periodic table and have the following electron configurations:

- B: [He]$2s^2 2p^1$
- C: [He]$2s^2 2p^2$
- N: [He]$2s^2 2p^3$

B The fourth ionization energy of an element (I_4) is defined as the energy required to remove the fourth electron:

$$E^{3+}_{(g)} \rightarrow E^{4+}_{(g)} + e^- \tag{2.9.4}$$

Because carbon and nitrogen have four and five valence electrons, respectively, their fourth ionization energies correspond to removing an electron from a partially filled valence shell. The fourth ionization energy for boron, however, corresponds to removing an electron from the filled $1s^2$ subshell. This should require much more energy. The actual values are as follows: B, 25,026 kJ/mol; C, 6223 kJ/mol; and N, 7475 kJ/mol.

Exercise 2.9.1: Lowest Second Ionization Energy

From their locations in the periodic table, predict which of these elements has the lowest second ionization energy: Sr, Rb, or Ar.

Answer:

Sr

The first column of data in Table 2.9.2 shows that first ionization energies tend to increase across the third row of the periodic table. This is because the valence electrons do not screen each other very well, allowing the effective nuclear charge to increase steadily across the row. The valence electrons are therefore attracted more strongly to the nucleus, so atomic sizes decrease and ionization energies increase. These effects represent two sides of the same coin: stronger electrostatic interactions between the electrons and the nucleus further increase the energy required to remove the electrons.

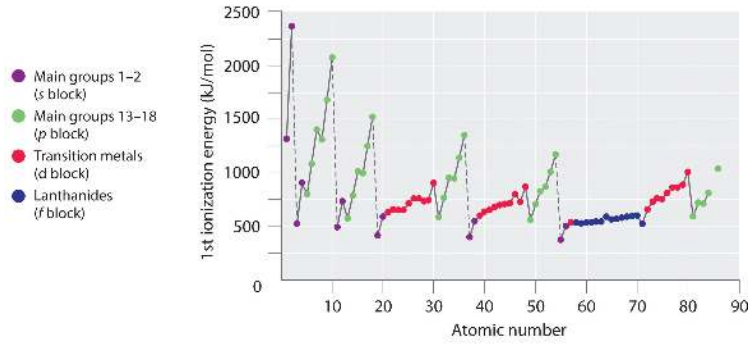


Figure 2.9.1 A Plot of Periodic Variation of First Ionization Energy with Atomic Number for the First Six Rows of the Periodic Table. There is a decrease in ionization energy within a group (most easily seen here for groups 1 and 18).

However, the first ionization energy decreases at Al ([Ne]$3s^2 3p^1$) and at S ([Ne]$3s^2 3p^4$). The electrons in aluminum's filled $3s^2$ subshell are better at screening the $3p^1$ electron than they are at screening each other from the nuclear charge, so the *s* electrons penetrate closer to the nucleus than the *p* electron does. The decrease at S occurs because the two electrons in the same *p* orbital repel each other. This makes the S atom slightly less stable than would otherwise be expected, as is true of all the group 16 elements.

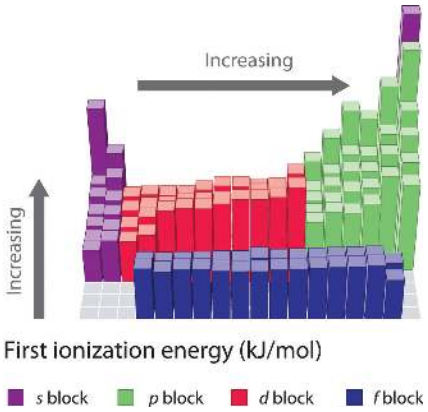


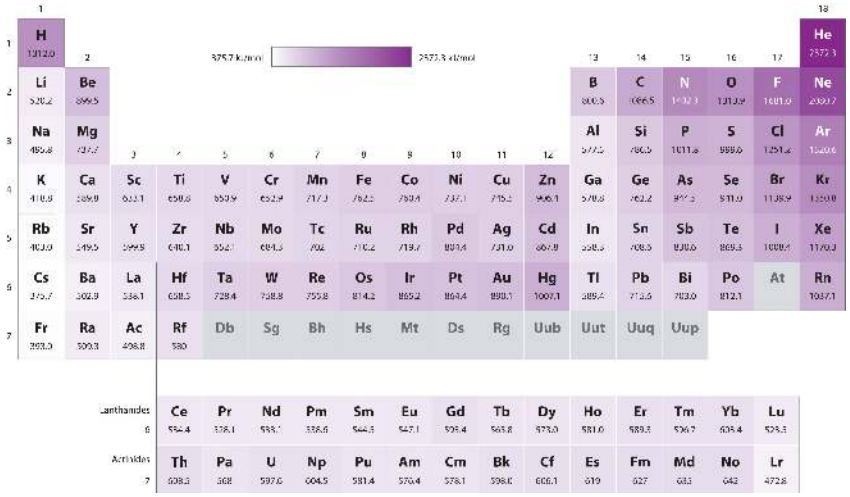
Figure 2.9.2 *First Ionization Energies of the s-, p-, d-, and f-Block Elements*

The first ionization energies of the elements in the first six rows of the periodic table are plotted in Figure 2.9.1 and are presented numerically and graphically in Figure 2.9.2. These figures illustrate three important trends:

1. The changes seen in the second (Li to Ne), fourth (K to Kr), fifth (Rb to Xe), and sixth (Cs to Rn) rows of the *s* and *p* blocks follow a pattern similar to the pattern described for the third row of the periodic table. The transition metals are included in the fourth, fifth, and sixth rows, however, and the lanthanides are included in the sixth row. The first ionization energies of the transition metals are somewhat similar to one another, as are those of the lanthanides. Ionization energies increase from left to right across each row, with discrepancies occurring at ns^2np^1 (group 13), ns^2np^4 (group 16), and $ns^2(n-1)d^{10}$ (group 12) electron configurations.
2. First ionization energies generally decrease down a column. Although the principal quantum number *n* increases down a column, filled inner shells are effective at screening the valence electrons, so there is a relatively small increase in the effective nuclear charge. Consequently, the atoms become larger as they acquire electrons. Valence electrons that are farther from the nucleus are less tightly bound, making them easier to remove, which causes ionization energies to decrease. *A larger radius corresponds to a lower ionization energy*.
3. Because of the first two trends, the elements that form positive ions most easily (have the lowest ionization energies) lie in the lower left corner of the periodic table, whereas those that are hardest to ionize lie in the upper right corner of the periodic table. Consequently, ionization energies generally increase diagonally from lower left (Cs) to upper right (He).

Note

Generally, I_1 increases diagonally from the lower left of the periodic table to the upper right.



The darkness of the shading inside the cells of the table indicates the relative magnitudes of the ionization energies. Elements in gray have undetermined first ionization energies. Source: Data from CRC Handbook of Chemistry and Physics (2004).

Gallium (Ga), which is the first element following the first row of transition metals, has the following electron configuration: $[Ar]4s^2 3d^{10} 4p^1$. Its first ionization energy is significantly lower than that of the immediately preceding element, zinc, because the filled $3d^{10}$ subshell of gallium lies inside the 4*p* subshell, screening the single 4*p* electron from the nucleus. Experiments have revealed something of even greater interest: the second and third electrons that are removed when gallium is ionized come from the $4s^2$ orbital, *not* the $3d^{10}$ subshell. The chemistry of gallium is dominated by the resulting Ga^{3+} ion, with its $[Ar]3d^{10}$ electron configuration. This and similar electron configurations are particularly stable and are often encountered in the heavier *p*-block elements. They are sometimes referred to as pseudo noble gas configurations. In fact, for elements that exhibit these configurations, *no chemical compounds are known in which electrons are removed from the* $(n - 1)d^{10}$ *filled subshell*.

Ionization Energies of Transition Metals & Lanthanides

As we noted, the first ionization energies of the transition metals and the lanthanides change very little across each row. Differences in their second and third ionization energies are also rather small, in sharp contrast to the pattern seen with the *s*- and *p*-block elements. The reason for these similarities is that the transition metals and the lanthanides form cations by losing the *ns* electrons before the $(n - 1)d$ or $(n - 2)f$ electrons, respectively. This means that transition metal cations have $(n - 1)d^n$ valence electron configurations, and lanthanide cations have $(n - 2)f^n$ valence electron configurations. Because the $(n - 1)d$ and $(n - 2)f$ shells are closer to the nucleus than the *ns* shell, the $(n - 1)d$ and $(n - 2)f$ electrons screen the *ns* electrons quite effectively, reducing the effective nuclear charge felt by the *ns* electrons. As *Z* increases, the increasing positive charge is largely canceled by the electrons added to the $(n - 1)d$ or $(n - 2)f$ orbitals.

That the *ns* electrons are removed before the $(n - 1)d$ or $(n - 2)f$ electrons may surprise you because the orbitals were filled in the reverse order. In fact, the *ns*, the $(n - 1)d$, and the $(n - 2)f$ orbitals are so close to one another in energy, and interpenetrate one another so extensively, that very small changes in the effective nuclear charge can change the order of their energy levels. As the *d* orbitals are filled, the effective nuclear charge causes the 3*d* orbitals to be slightly lower in energy than the 4*s* orbitals. The $[Ar]3d^2$ electron configuration of Ti^{2+} tells us that the 4*s* electrons of titanium are lost before the 3*d* electrons; this is confirmed by experiment. A similar pattern is seen with the lanthanides, producing cations with an $(n - 2)f^n$ valence electron configuration.

Because their first, second, and third ionization energies change so little across a row, these elements have important *horizontal* similarities in chemical properties in addition to the expected vertical similarities. For example, all the first-row transition metals except scandium form stable compounds as M^{2+} ions, whereas the lanthanides primarily form compounds in which they exist as M^{3+} ions.

Example 2.9.2: Lowest First Ionization Energy

Use their locations in the periodic table to predict which element has the lowest first ionization energy: Ca, K, Mg, Na, Rb, or Sr.

Given: six elements

Asked for: element with lowest first ionization energy

Strategy:

Locate the elements in the periodic table. Based on trends in ionization energies across a row and down a column, identify the element with the lowest first ionization energy.

Solution:

These six elements form a rectangle in the two far-left columns of the periodic table. Because we know that ionization energies increase from left to right in a row and from bottom to top of a column, we can predict that the element at the bottom left of the rectangle will have the lowest first ionization energy: Rb.

Exercise 2.9.2: Highest First Ionization Energy

Use their locations in the periodic table to predict which element has the highest first ionization energy: As, Bi, Ge, Pb, Sb, or Sn.

Answer:

As

Summary

- Generally, the first ionization energy and electronegativity values increase diagonally from the lower left of the periodic table to the upper right, and electron affinities become more negative across a row.

The tendency of an element to lose is one of the most important factors in determining the kind of compounds it forms. Periodic behavior is most evident for **ionization energy (*I*)**, the energy required to remove an electron from a gaseous atom. The energy required to remove successive electrons from an atom increases steadily, with a substantial increase occurring with the removal of an electron from a filled inner shell. Consequently, only valence electrons can be removed in chemical reactions, leaving the filled inner shell intact. Ionization energies explain the common oxidation states observed for the elements. Ionization energies increase diagonally from the lower left of the periodic table to the upper right. Minor deviations from this trend can be explained in terms of particularly stable electronic configurations, called **pseudo noble gas configurations**, in either the parent atom or the resulting ion.

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2.10: Electron Affinities

The electron affinity (EA) of an element E is defined as the energy change that occurs when an electron is added to a gaseous atom:

$$E_{(g)} + e^- \rightarrow E^-_{(g)} \qquad \text{energy change} = EA \tag{2.10.1}$$

Unlike ionization energies, which are always positive for a neutral atom because energy is required to remove an electron, electron affinities can be negative (energy is released when an electron is added), positive (energy must be added to the system to produce an anion), or zero (the process is energetically neutral). This sign convention is consistent with a negative value corresponded to the energy change for an exothermic process, which is one in which heat is released.

The chlorine atom has the most negative electron affinity of any element, which means that more energy is released when an electron is added to a gaseous chlorine atom than to an atom of any other element:

$$Cl_{(g)} + e^- \rightarrow Cl^-_{(g)} \qquad EA = -346\ kJ/mol \tag{2.10.2}$$

In contrast, beryllium does not form a stable anion, so its effective electron affinity is

$$Be_{(g)} + e^- \rightarrow Be^-_{(g)} \qquad EA \geq 0 \tag{2.10.3}$$

Nitrogen is unique in that it has an electron affinity of approximately zero. Adding an electron neither releases nor requires a significant amount of energy:

$$N_{(g)} + e^- \rightarrow N^-_{(g)} \qquad EA \approx 0 \tag{2.10.4}$$

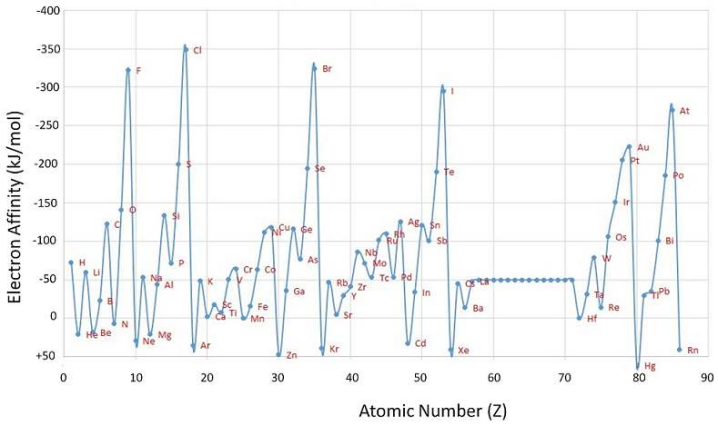


Figure 2.10.1: A Plot of Periodic Variation of Electron Affinity with Atomic Number for the First Six Rows of the Periodic Table. Notice that electron affinities can be both negative and positive. from Robert J. Lancashire (University of the West Indies)

Note

Generally, electron affinities become more negative across a row of the periodic table.

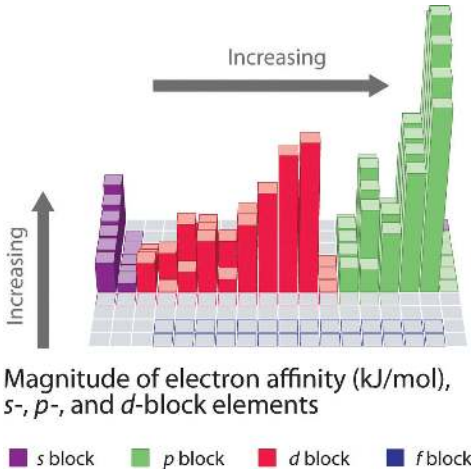
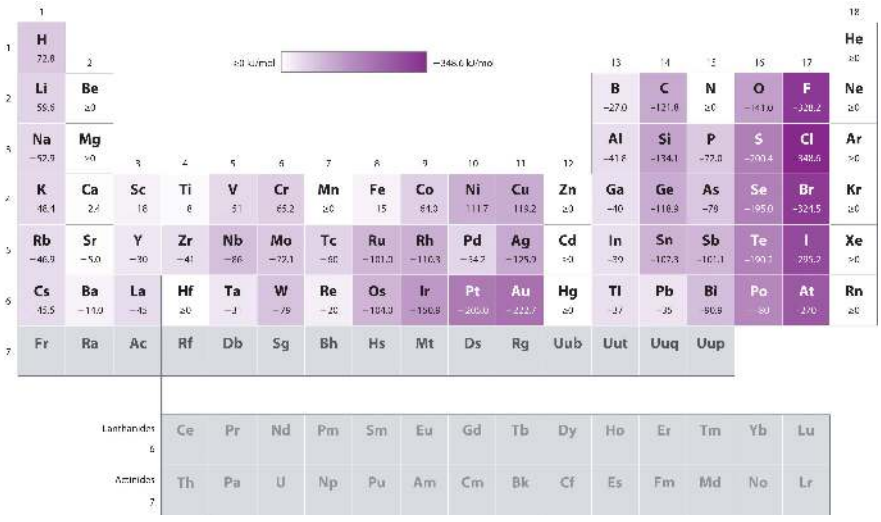


Figure 2.10.2 Electron Affinities (in kJ/mol) of the *s*-, *p*-, and *d*-Block Elements.

In general, electron affinities of the main-group elements become less negative as we proceed down a column. This is because as *n* increases, the extra electrons enter orbitals that are increasingly far from the nucleus. Atoms with the largest radii, which have the lowest ionization energies (affinity for their own valence electrons), also have the lowest affinity for an added electron. There are, however, two major exceptions to this trend:

1. The electron affinities of elements B through F in the second row of the periodic table are *less* negative than those of the elements immediately below them in the third row. Apparently, the increased electron–electron repulsions experienced by electrons confined to the relatively small 2*p* orbitals overcome the increased electron–nucleus attraction at short nuclear distances. Fluorine, therefore, has a lower affinity for an added electron than does chlorine. Consequently, the elements of the *third* row ($n = 3$) have the most negative electron affinities. Farther down a column, the attraction for an added electron decreases because the electron is entering an orbital more distant from the nucleus. Electron–electron repulsions also decrease because the valence electrons occupy a greater volume of space. These effects tend to cancel one another, so the changes in electron affinity within a family are much smaller than the changes in ionization energy.
2. The electron affinities of the alkaline earth metals become more negative from Be to Ba. The energy separation between the filled ns^2 and the empty *np* subshells decreases with increasing *n*, so that formation of an anion from the heavier elements becomes energetically more favorable.



There are many more exceptions to the trends across rows and down columns than with first ionization energies. Elements that do not form stable ions, such as the noble gases, are assigned an effective electron affinity that is greater than or equal to zero. Elements for which no data are available are shown in gray. Source: Data from Journal of Physical and Chemical Reference Data 28, no. 6 (1999).

Note

In general, electron affinities become more negative across a row and less negative down a column.

The equations for second and higher electron affinities are analogous to those for second and higher ionization energies:

$$E_{(g)} + e^- \rightarrow E^-_{(g)} \qquad \text{energy change} = EA_1 \tag{2.10.5}$$

$$E^-_{(g)} + e^- \rightarrow E^{2-}_{(g)} \qquad \text{energy change} = EA_2 \tag{2.10.6}$$

As we have seen, the first electron affinity can be greater than or equal to zero or negative, depending on the electron configuration of the atom. In contrast, the second electron affinity is *always* positive because the increased electron–electron repulsions in a dianion are far greater than the attraction of the nucleus for the extra electrons. For example, the first electron affinity of oxygen is −141 kJ/mol, but the second electron affinity is +744 kJ/mol:

$$O_{(g)} + e^- \rightarrow O^-_{(g)} \qquad EA_1 = -141\ kJ/mol \tag{2.10.7}$$

$$O^-_{(g)} + e^- \rightarrow O^{2-}_{(g)} \qquad EA_2 = +744\ kJ/mol \tag{2.10.8}$$

Thus the formation of a gaseous oxide (O^{2-}) ion is energetically quite *unfavorable* (estimated by adding both steps):

$$O_{(g)} + 2e^- \rightarrow O^{2-}_{(g)} \qquad EA = +603\ kJ/mol \tag{2.10.9}$$

Similarly, the formation of all common dianions (such as S^{2-}) or trianions (such as P^{3-}) is energetically unfavorable in the gas phase.

Note

While first electron affinities can be negative, positive, or zero, second electron affinities are always positive.

If energy is required to form both positively charged ions and monatomic polyanions, why do ionic compounds such as MgO, Na_2S, and Na_3P form at all? The key factor in the formation of stable ionic compounds is the favorable electrostatic interactions between the cations and the anions *in the crystalline salt*.

Example 2.10.1: Contrasting Electron Affinities of Sb, Se, and Te

Based on their positions in the periodic table, which of Sb, Se, or Te would you predict to have the most negative electron affinity?

Given: three elements

Asked for: element with most negative electron affinity

Strategy:

A. Locate the elements in the periodic table. Use the trends in electron affinities going down a column for elements in the same group. Similarly, use the trends in electron affinities from left to right for elements in the same row.
B. Place the elements in order, listing the element with the most negative electron affinity first.

Solution:

A We know that electron affinities become less negative going down a column (except for the anomalously low electron affinities of the elements of the second row), so we can predict that the electron affinity of Se is more negative than that of Te. We also know that electron affinities become more negative from left to right across a row, and that the group 15 elements tend to have values that are less negative than expected. Because Sb is located to the left of Te and belongs to group 15, we predict that the electron affinity of Te is more negative than that of Sb. The overall order is Se < Te < Sb, so Se has the most negative electron affinity among the three elements.

Exercise 2.10.1: Contrasting Electron Affinities of Rb, Sr, and Xe

Based on their positions in the periodic table, which of Rb, Sr, or Xe would you predict to most likely form a gaseous anion?

Answer:

Rb

Summary

The **electron affinity** (*EA*) of an element is the energy change that occurs when an electron is added to a gaseous atom to give an anion. In general, elements with the most negative electron affinities (the highest affinity for an added electron) are those with the smallest size and highest ionization energies and are located in the upper right corner of the periodic table.

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2.11: Electronegativity

Learning Objectives

- To define eletronegativity

The electron pairs shared between two atoms ***are not necessarily shared equally.*** For example, while the shared electron pairs is shared equally in the covalent bond in Cl_2, in $NaCl$ the 3s electron is stripped from the Na atom and is incorporated into the electronic structure of the Cl atom - and the compound is most accurately described as consisting of individual Na^+ and Cl^- ions (ionic bonding). For most covalent substances, their bond character falls **between** these two extremes. We demonstrated below, the **bond polarity** is a useful concept for describing the sharing of electrons between atoms within a covalent bond:

- A ***nonpolar covalent bond*** is one in which the electrons are shared *equally* between two atoms.
- A ***polar covalent bond*** is one in which ***one atom has a greater attraction for the electrons than the other atom***. If this relative attraction is great enough, then the bond is an ***ionic bond.***

Electronegativity

The elements with the highest ionization energies are generally those with the most negative electron affinities, which are located toward the upper right corner of the periodic table (compare Figure 2.9.2 and Figure 2.10.2). Conversely, the elements with the lowest ionization energies are generally those with the least negative electron affinities and are located in the lower left corner of the periodic table.

Because the tendency of an element to gain or lose electrons is so important in determining its chemistry, various methods have been developed to quantitatively describe this tendency. The most important method uses a measurement called electronegativity (represented by the Greek letter *chi*, χ, pronounced “ky” as in “sky”), defined as the *relative* ability of an atom to attract electrons to itself *in a chemical compound*. Elements with high electronegativities tend to acquire electrons in chemical reactions and are found in the upper right corner of the periodic table. Elements with low electronegativities tend to lose electrons in chemical reactions and are found in the lower left corner of the periodic table.

Unlike ionization energy or electron affinity, the electronegativity of an atom is not a simple, fixed property that can be directly measured in a single experiment. In fact, an atom’s electronegativity should depend to some extent on its chemical environment because the properties of an atom are influenced by its neighbors in a chemical compound. Nevertheless, when different methods for measuring the electronegativity of an atom are compared, they all tend to assign similar relative values to a given element. For example, all scales predict that fluorine has the highest electronegativity and cesium the lowest of the stable elements, which suggests that all the methods are measuring the same fundamental property.

Note

Electronegativity is defined as the ability of an atom in a particular molecule to attract electrons to itself. The **greater** the value, the **greater** the attractiveness for electrons.

Electronegativity is a function of: (1) the atom's ***ionization energy*** (how strongly the atom holds on to its own electrons) and (2) the atom's ***electron affinity*** (how strongly the atom attracts other electrons). Both of these are properties of the *isolated* atom. An element that is will be *highly electronegative* has:

- a large (negative) electron affinity
- a high ionization energy (always endothermic, or positive for neutral atoms)

and will

- attract electrons from other atoms
- resist having its own electrons attracted away.

The Pauling Electronegativity Scale

The original electronegativity scale, developed in the 1930s by Linus Pauling (1901– 1994) was based on measurements of the strengths of covalent bonds between different elements. Pauling arbitrarily set the electronegativity of fluorine at 4.0 (although today it has been refined to 3.98), thereby creating a scale in which all elements have values between 0 and 4.0.

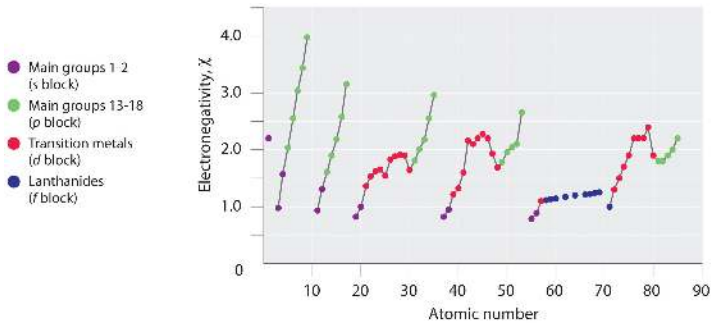


Figure 2.12.1 A Plot of Periodic Variation of Electronegativity with Atomic Number for the First Six Rows of the Periodic Table

Periodic variations in Pauling's electronegativity values are illustrated in Figure 2.12.1 and Figure 2.12.2. If we ignore the inert gases and elements for which no stable isotopes are known, we see that fluorine ($\chi = 3.98$) is the most electronegative element and cesium is the least electronegative nonradioactive element ($\chi = 0.79$). Because electronegativities generally increase diagonally from the lower left to the upper right of the periodic table, elements lying on diagonal lines running from upper left to lower right tend to have comparable values (e.g., O and Cl and N, S, and Br).

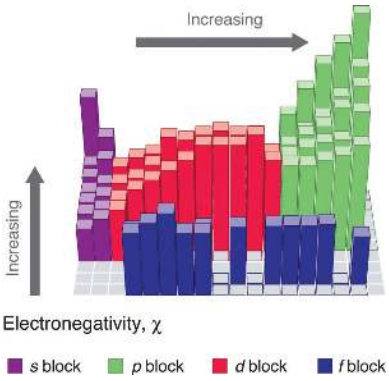
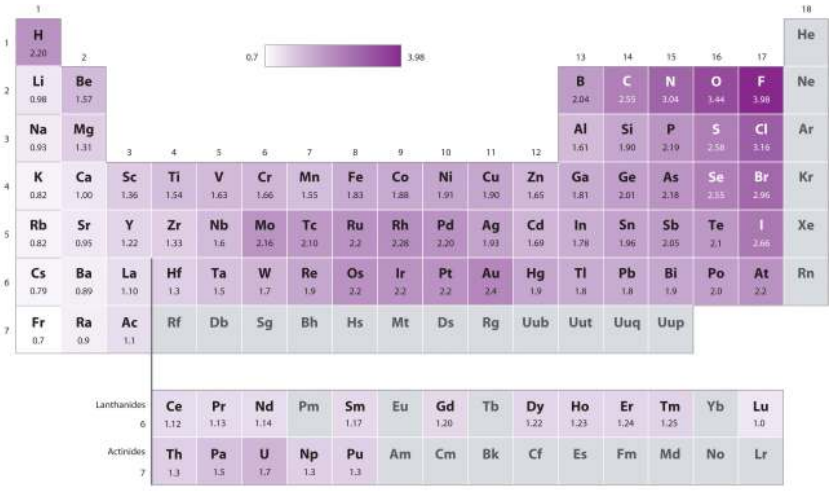


Figure 2.12.2: *Pauling Electronegativity Values of the s-, p-, d-, and f-Block Elements. Values for most of the actinides are approximate. Elements for which no data are available are shown in gray. Source: Data from L. Pauling, The Nature of the Chemical Bond, 3rd ed. (1960).*

Linus Pauling (1901-1994)

Pauling won two Nobel Prizes, one for chemistry in 1954 and one for peace in 1962. When he was nine, Pauling's father died, and his mother tried to convince him to quit school to support the family. He did not quit school but was denied a high school degree because of his refusal to take a civics class.



Pauling's method is limited by the fact that many elements do not form stable covalent compounds with other elements; hence their electronegativities cannot be measured by his method. Other definitions have since been developed that address this problem (e.g., the Mulliken electronegativity scale).

Electronegativity Differences between Metals and Nonmetals

An element's electronegativity provides us with a single value that we can use to characterize the chemistry of an element. Elements with a high electronegativity ($\chi \geq 2.2$ in Figure 2.12.2) have very negative affinities and large ionization potentials, so they are generally nonmetals and electrical insulators that tend to gain electrons in chemical reactions (i.e., they are *oxidants*). In contrast, elements with a low electronegativity ($\chi \leq 1.8$) have electron affinities that have either positive or small negative values and small ionization potentials, so they are generally metals and good electrical conductors that tend to lose their valence electrons in chemical reactions (i.e., they are *reductants*). In between the metals and nonmetals, along the heavy diagonal line running from B to At is a group of elements with intermediate electronegativities ($\chi \sim 2.0$). These are the **semimetals** (or metalloids), elements that have some of the chemical properties of both nonmetals and metals. The distinction between metals and nonmetals is one of the most fundamental we can make in categorizing the elements and predicting their chemical behavior. Figure 2.12.3 shows the strong correlation between electronegativity values, metallic versus nonmetallic character, and location in the periodic table.

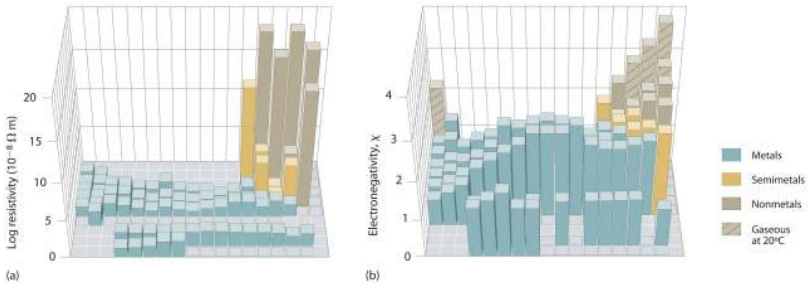


Figure 2.12.3: Three-Dimensional Plots Demonstrating the Relationship between Electronegativity and the Metallic/Nonmetallic Character of the Elements. (a) A plot of electrical resistivity (measured resistivity to electron flow) at or near room temperature shows that substances with high resistivity (little to no measured electron flow) are electrical insulators, whereas substances with low resistivity (high measured electron flow) are metals. (b) A plot of Pauling electronegativities for a like set of elements shows that high electronegativity values (≥ about 2.2) correlate with high electrical resistivities (insulators). Low electronegativity values (≤ about 2.2) correlate with low resistivities (metals). Because electrical resistivity is typically measured only for solids and liquids, the gaseous elements do not appear in part (a).

Note

Electronegativity values *increase* from lower left to upper right in the periodic table.

The rules for assigning oxidation states are based on the relative electronegativities of the elements; the more electronegative element in a binary compound is assigned a negative oxidation state. As we shall see, electronegativity values are also used to predict bond energies, bond polarities, and the kinds of reactions that compounds undergo.

Example 2.12.1

On the basis of their positions in the periodic table, arrange Cl, Se, Si, and Sr in order of increasing electronegativity and classify each as a metal, a nonmetal, or a semimetal.

Given: four elements

Asked for: order by increasing electronegativity and classification

Strategy:

A. Locate the elements in the periodic table. From their diagonal positions from lower left to upper right, predict their relative electronegativities.
B. Arrange the elements in order of increasing electronegativity.
C. Classify each element as a metal, a nonmetal, or a semimetal according to its location about the diagonal belt of semimetals running from B to At.

Solution:

A Electronegativity increases from lower left to upper right in the periodic table (Figure 2.12.2). Because Sr lies far to the left of the other elements given, we can predict that it will have the lowest electronegativity. Because Cl lies above and to the right of Se, we can predict that $\chi_{Cl} > \chi_{Se}$. Because Si is located farther from the upper right corner than Se or Cl, its electronegativity should be lower than those of Se and Cl but greater than that of Sr. **B** The overall order is therefore $\chi_{Sr} < \chi_{Si} < \chi_{Se} < \chi_{Cl}$.

C To classify the elements, we note that Sr lies well to the left of the diagonal belt of semimetals running from B to At; while Se and Cl lie to the right and Si lies in the middle. We can predict that Sr is a metal, Si is a semimetal, and Se and Cl are nonmetals.

Exercise 2.12.1

On the basis of their positions in the periodic table, arrange Ge, N, O, Rb, and Zr in order of increasing electronegativity and classify each as a metal, a nonmetal, or a semimetal.

Answer:

- Rb < Zr < Ge < N < O;
- metals (Rb, Zr); semimetal (Ge); nonmetal (N, O)

Summary

The **electronegativity (χ)** of an element is the relative ability of an atom to attract electrons to itself in a chemical compound and increases diagonally from the lower left of the periodic table to the upper right. The Pauling electronegativity scale is based on measurements of the strengths of covalent bonds between different atoms, whereas the Mulliken electronegativity of an element is the average of its first ionization energy and the absolute value of its electron affinity. Elements with a high electronegativity are generally nonmetals and electrical insulators and tend to behave as oxidants in chemical reactions. Conversely, elements with a low electronegativity are generally metals and good electrical conductors and tend to behave as reductants in chemical reactions.

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CHAPTER OVERVIEW

3: Molecular Orbital Theory

3.1: Molecular Orbital Theory
3.2: MO Diagrams for Linear Triatomic Molecules
3.3: Frontier MOs- An Acid-Base Theory
3.4: Bonding in Metals

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3.1: Molecular Orbital Theory

Previously, we described the electrons in isolated atoms as having certain spatial distributions, called *orbitals*, each with a particular *orbital energy*. Just as the positions and energies of electrons in *atoms* can be described in terms of *atomic orbitals* (AOs), the positions and energies of electrons in *molecules* can be described in terms of molecular orbitals (MOs) A particular spatial distribution of electrons in a molecule that is associated with a particular orbital energy.—a spatial distribution of electrons *in a molecule* that is associated with a particular orbital energy. As the name suggests, molecular orbitals are not localized on a single atom but extend over the entire molecule. Consequently, the molecular orbital approach, called molecular orbital theory is a *delocalized* approach to bonding.

Although the molecular orbital theory is computationally demanding, the principles on which it is based are similar to those we used to determine electron configurations for atoms. The key difference is that in molecular orbitals, the electrons are allowed to interact with more than one atomic nucleus at a time. Just as with atomic orbitals, we create an energy-level diagram by listing the molecular orbitals in order of increasing energy. We then fill the orbitals with the required number of valence electrons according to the Pauli principle. This means that each molecular orbital can accommodate a maximum of two electrons with opposite spins.

Molecular Orbitals Involving Only *ns* Atomic Orbitals

We begin our discussion of molecular orbitals with the simplest molecule, H_2, formed from two isolated hydrogen atoms, each with a $1s^1$ electron configuration. As discussed previously, electrons can behave like waves. In the molecular orbital approach, the overlapping atomic orbitals are described by mathematical equations called *wave functions*. The 1*s* atomic orbitals on the two hydrogen atoms interact to form two new molecular orbitals, one produced by taking the *sum* of the two H 1*s* wave functions, and the other produced by taking their *difference*:

$$\begin{aligned} MO(1) = &\quad AO(atom\ A) &+ &\quad AO(atom B) \\ MO(1) = &\quad AO(atom\ A) &- &\quad AO(atom B) \end{aligned} \tag{3.1.1}$$

The molecular orbitals created from Equation 3.1.1 are called linear combinations of atomic orbitals (LCAOs) Molecular orbitals created from the sum and the difference of two wave functions (atomic orbitals). A molecule must have as many molecular orbitals as there are atomic orbitals.

Adding two atomic orbitals corresponds to *constructive* interference between two waves, thus reinforcing their intensity; the internuclear electron probability density is *increased*. The molecular orbital corresponding to the sum of the two H 1*s* orbitals is called a σ_{1s} combination (pronounced “sigma one ess”) (part (a) and part (b) in Figure 3.1.1). In a sigma (σ) orbital, A bonding molecular orbital in which the electron density along the internuclear axis and between the nuclei has cylindrical symmetry, the electron density along the internuclear axis and between the nuclei has cylindrical symmetry; that is, all cross-sections perpendicular to the internuclear axis are circles. The subscript 1*s* denotes the atomic orbitals from which the molecular orbital was derived: The ≈ sign is used rather than an = sign because we are ignoring certain constants that are not important to our argument.

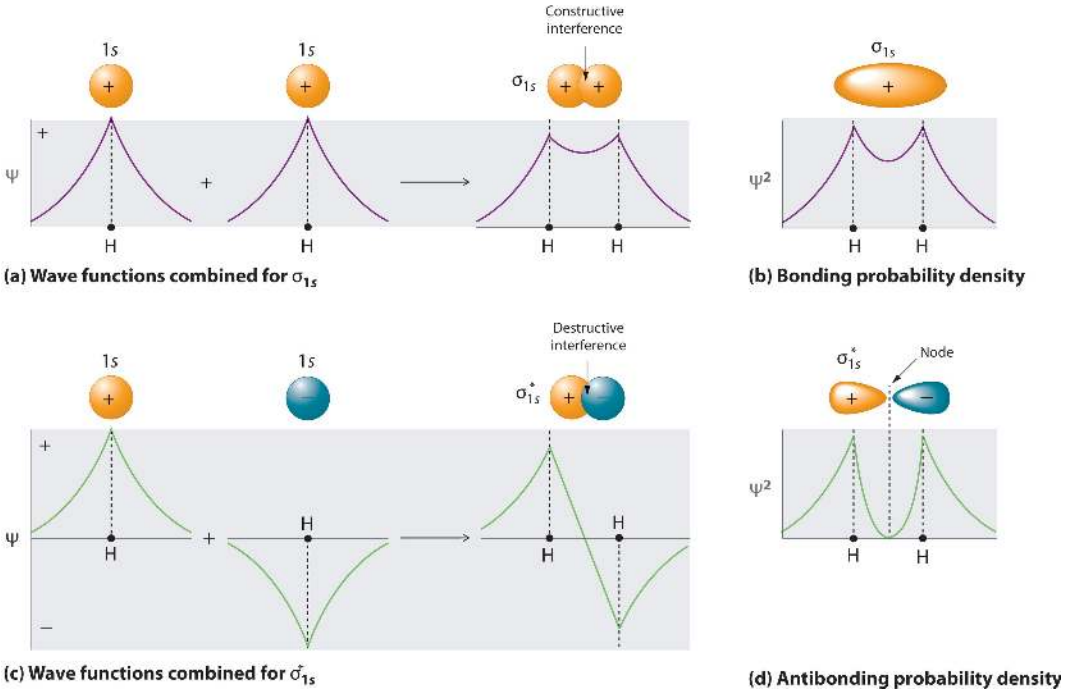


Figure 3.1.1: Molecular Orbitals for the H_2 Molecule**.** (a) This diagram shows the formation of a bonding σ_{1s} molecular orbital for H_2 as the sum of the wave functions (Ψ) of two H 1s atomic orbitals. (b) This plot of the square of the wave function (Ψ^2) for the bonding σ_{1s} molecular orbital illustrates the increased electron probability density between the two hydrogen nuclei. (Recall that the probability density is proportional to the square of the wave function.) (c) This diagram shows the formation of an antibonding σ^*_{1s} molecular orbital for H_2 as the difference of the wave functions (Ψ) of two H 1s atomic orbitals. (d) This plot of the square of the wave function (Ψ^2) for the σ^*_{1s} antibonding molecular orbital illustrates the node corresponding to zero electron probability density between the two hydrogen nuclei.

$$\sigma_{1s} \approx 1s\,(A) + 1s\,(B) \tag{3.1.2}$$

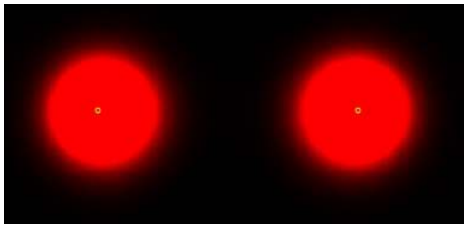


Figure 3.1.2: Bonding molecular orbital of the 2s orbitals of two hydrogen atoms (Attribution: www.falstad.com/qmmo/)

Conversely, subtracting one atomic orbital from another corresponds to *destructive* interference between two waves, which reduces their intensity and causes a *decrease* in the internuclear electron probability density (part (c) and part (d) in Figure 3.1.1). The resulting pattern contains a *node* where the electron density is zero. The molecular orbital corresponding to the difference is called σ^*_{1s} (“sigma one ess star”). In a sigma star (σ*) orbital An antibonding molecular orbital in which there is a region of zero electron probability (a nodal plane) perpendicular to the internuclear axis., there is a region of zero electron probability, a nodal plane, perpendicular to the internuclear axis:

$$\sigma^\star_{1s} \approx 1s\,(A) - 1s\,(B) \tag{3.1.3}$$

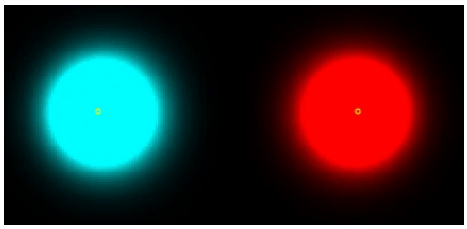


Figure 3.1.3: Anti-bonding molecular orbital of the 2s orbitals of two hydrogen atoms (Attribution: www.falstad.com/qmmo/)

> *A molecule must have as many molecular orbitals as there are atomic orbitals.*

The electron density in the σ_{1s} molecular orbital is greatest between the two positively charged nuclei, and the resulting electron–nucleus electrostatic attractions reduce repulsions between the nuclei. Thus the σ_{1s} orbital represents a bonding molecular orbital. A molecular orbital that forms when atomic orbitals or orbital lobes with the same sign interact to give increased electron probability between the nuclei due to constructive reinforcement of the wave functions. In contrast, electrons in the $\sigma^{\star}_{1s}$ orbital are generally found in the space outside the internuclear region. Because this allows the positively charged nuclei to repel one another, the $\sigma^{\star}_{1s}$ orbital is an antibonding molecular orbital (a molecular orbital that forms when atomic orbitals or orbital lobes of opposite sign interact to give decreased electron probability between the nuclei due to destructive reinforcement of the wave functions).

> *Antibonding orbitals contain a node perpendicular to the internuclear axis; bonding orbitals do not.*

Energy-Level Diagrams

Because electrons in the σ_{1s} orbital interact simultaneously with both nuclei, they have a lower energy than electrons that interact with only one nucleus. This means that the σ_{1s} molecular orbital has a *lower* energy than either of the hydrogen 1*s* atomic orbitals. Conversely, electrons in the $\sigma^{\star}_{1s}$ orbital interact with only one hydrogen nucleus at a time. In addition, they are farther away from the nucleus than they were in the parent hydrogen 1*s* atomic orbitals. Consequently, the $\sigma^{\star}_{1s}$ molecular orbital has a *higher* energy than either of the hydrogen 1*s* atomic orbitals. The σ_{1s} (bonding) molecular orbital is *stabilized* relative to the 1*s* atomic orbitals, and the $\sigma^{\star}_{1s}$ (antibonding) molecular orbital is *destabilized*. The relative energy levels of these orbitals are shown in the energy-level diagram (a schematic drawing that compares the energies of the molecular orbitals (bonding, antibonding, and nonbonding) with the energies of the parent atomic orbitals) in Figure 3.1.2

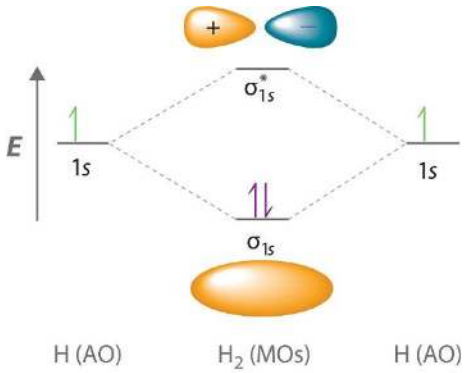


Figure 3.1.4: Molecular Orbital Energy-Level Diagram for H_2. The two available electrons (one from each H atom) in this diagram fill the bonding σ_{1s} molecular orbital. Because the energy of the σ_{1s} molecular orbital is lower than that of the two H 1*s* atomic orbitals, the H_2 molecule is more stable (at a lower energy) than the two isolated H atoms.

> *A bonding molecular orbital is always lower in energy (more stable) than the component atomic orbitals, whereas an antibonding molecular orbital is always higher in energy (less stable).*

To describe the bonding in a homonuclear diatomic molecule (a molecule that consists of two atoms of the same element) such as H_2, we use molecular orbitals; that is, for a molecule in which two identical atoms interact, we insert the total number of valence electrons into the energy-level diagram (Figure 3.1.4). We fill the orbitals according to the Pauli principle and Hund's rule: each orbital can accommodate a maximum of two electrons with opposite spins, and the orbitals are filled in order of increasing energy.

Because each H atom contributes one valence electron, the resulting two electrons are exactly enough to fill the σ_{1s} bonding molecular orbital. The two electrons enter an orbital whose energy is lower than that of the parent atomic orbitals, so the H_2 molecule is more stable than the two isolated hydrogen atoms. Thus molecular orbital theory correctly predicts that H_2 is a stable molecule. Because bonds form when electrons are concentrated in the space between nuclei, this approach is also consistent with our earlier discussion of electron-pair bonds.

Bond Order in Molecular Orbital Theory

In the Lewis electron structures, the number of electron pairs holding two atoms together was called the *bond order*. In the molecular orbital approach, bond order One-half the net number of bonding electrons in a molecule. is defined as one-half the *net* number of bonding electrons:

$$bond\ order = \frac{number\ of\ bonding\ electrons - number\ of\ antibonding\ electrons}{2} \tag{3.1.4}$$

To calculate the bond order of H_2, we see from Figure 3.1.4 that the σ_{1s} (bonding) molecular orbital contains two electrons, while the $\sigma^{\star}_{1s}$ (antibonding) molecular orbital is empty. The bond order of H_2 is therefore

$$\frac{2-0}{2} = 1 \tag{3.1.5}$$

This result corresponds to the single covalent bond predicted by Lewis dot symbols. Thus molecular orbital theory and the Lewis electron-pair approach agree that a single bond containing two electrons has a bond order of 1. Double and triple bonds contain four or six electrons, respectively, and correspond to bond orders of 2 and 3.

We can use energy-level diagrams such as the one in Figure 3.1.4 to describe the bonding in other pairs of atoms and ions where *n* = 1, such as the H_2^+ ion, the He_2^+ ion, and the He_2 molecule. Again, we fill the lowest-energy molecular orbitals first while being sure not to violate the Pauli principle or Hund's rule.

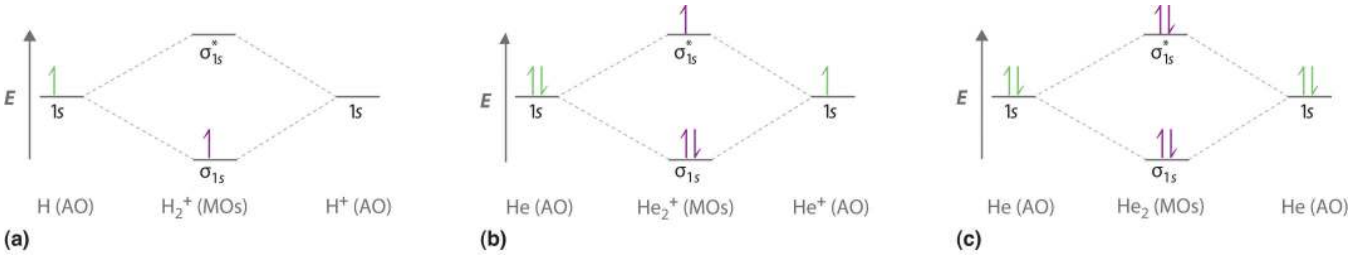


Figure 3.1.5: Molecular Orbital Energy-Level Diagrams for Diatomic Molecules with Only 1*s* Atomic Orbitals. (a) The H_2^+ ion, (b) the He_2^+ ion, and (c) the He_2 molecule are shown here.

Part (a) in Figure 3.1.5 shows the energy-level diagram for the H_2^+ ion, which contains two protons and only one electron. The single electron occupies the σ_{1s} bonding molecular orbital, giving a $(\sigma_{1s})^1$ electron configuration. The number of electrons in an orbital is indicated by a superscript. In this case, the bond order is (1-0)/2=1/2 Because the bond order is greater than zero, the H_2^+ ion should be more stable than an isolated H atom and a proton. We can therefore use a molecular orbital energy-level diagram and the calculated bond order to predict the relative stability of species such as H_2^+. With a bond order of only 1/2 the bond in H_2^+ should be weaker than in the H_2 molecule, and the H–H bond should be longer. As shown in Table 3.1.1, these predictions agree with the experimental data.

Part (b) in Figure 3.1.5 is the molecular orbital energy-level diagram for He_2^+. This ion has a total of three valence electrons. Because the first two electrons completely fill the σ_{1s} molecular orbital, the Pauli principle states that the third electron must be in the $\sigma^{\star}_{1s}$ antibonding orbital, giving a $(\sigma_{1s})^2(\sigma^{\star}_{1s})^1$ electron configuration. This electron configuration gives a bond order of (2-1)/2=1/2. As with H_2^+, the He_2^+ ion should be stable, but the He–He bond should be weaker and longer than in H_2. In fact, the He_2^+ ion can be prepared, and its properties are consistent with our predictions (Table 3.1.1).

Table 3.1.1: Molecular Orbital Electron Configurations, Bond Orders, Bond Lengths, and Bond Energies for some Simple Homonuclear Diatomic Molecules and Ions

Molecule or Ion	Electron Configuration	Bond Order	Bond Length (pm)	Bond Energy (kJ/mol)
H_2^+	$(\sigma_{1s})^1$	1/2	106	269

Molecule or Ion	Electron Configuration	Bond Order	Bond Length (pm)	Bond Energy (kJ/mol)
H_2	$(\sigma_{1s})^2$	1	74	436
He_2^+	$(\sigma_{1s})^2(\sigma_{1s}^\star)^1$	1/2	108	251
He_2	$(\sigma_{1s})^2(\sigma_{1s}^\star)^2$	0	not observed	not observed

Finally, we examine the He_2 molecule, formed from two He atoms with $1s^2$ electron configurations. Part (c) in Figure 3.1.5 is the molecular orbital energy-level diagram for He_2. With a total of four valence electrons, both the σ_{1s} bonding and $\sigma_{1s}^\star$ antibonding orbitals must contain two electrons. This gives a $(\sigma_{1s})^2(\sigma_{1s}^\star)^1$ electron configuration, with a predicted bond order of $(2 - 2) \div 2 = 0$, which indicates that the He_2 molecule has no net bond and is not a stable species. Experiments show that the He_2 molecule is actually *less* stable than two isolated He atoms due to unfavorable electron–electron and nucleus–nucleus interactions.

In molecular orbital theory, *electrons in antibonding orbitals effectively cancel the stabilization resulting from electrons in bonding orbitals*. Consequently, any system that has equal numbers of bonding and antibonding electrons will have a bond order of 0, and it is predicted to be unstable and therefore not to exist in nature. In contrast to Lewis electron structures and the valence bond approach, molecular orbital theory is able to accommodate systems with an odd number of electrons, such as the H_2^+ ion.



Molecular Orbital Theory: https://youtu.be/XgtOG0ezw78

> In contrast to Lewis electron structures and the valence bond approach, molecular orbital theory can accommodate systems with an odd number of electrons.

Example 3.1.1

Use a molecular orbital energy-level diagram, such as those in Figure 3.1.3, to predict the bond order in the He_2^{2+} ion. Is this a stable species?

Given: chemical species

Asked for: molecular orbital energy-level diagram, bond order, and stability

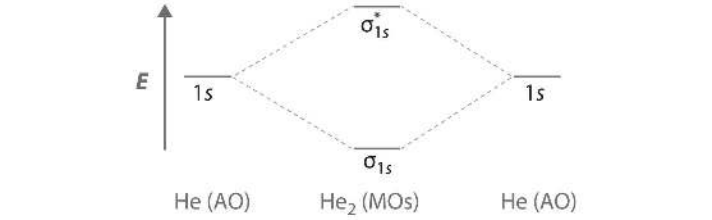
Strategy:

A. Combine the two He valence atomic orbitals to produce bonding and antibonding molecular orbitals. Draw the molecular orbital energy-level diagram for the system.
B. Determine the total number of valence electrons in the He_2^{2+} ion. Fill the molecular orbitals in the energy-level diagram beginning with the orbital with the lowest energy. Be sure to obey the Pauli principle and Hund's rule while doing so.
C. Calculate the bond order and predict whether the species is stable.

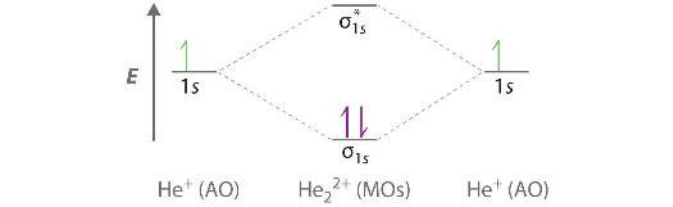
Solution:

A Two He 1*s* atomic orbitals combine to give two molecular orbitals: a σ_{1s} bonding orbital at lower energy than the atomic orbitals and a $\sigma_{1s}^\star$ antibonding orbital at higher energy. The bonding in any diatomic molecule with two He atoms can be

described using the following molecular orbital diagram:



B The He_2^{2+} ion has only two valence electrons (two from each He atom minus two for the +2 charge). We can also view He_2^{2+} as being formed from two He^+ ions, each of which has a single valence electron in the 1*s* atomic orbital. We can now fill the molecular orbital diagram:



The two electrons occupy the lowest-energy molecular orbital, which is the bonding (σ_{1s}) orbital, giving a $(\sigma_{1s})^2$ electron configuration. To avoid violating the Pauli principle, the electron spins must be paired. **C** So the bond order is

$$\frac{2-0}{2}=1$$

He_2^{2+} is therefore predicted to contain a single He–He bond. Thus it should be a stable species.

Exercise 3.1.1

Use a molecular orbital energy-level diagram to predict the valence-electron configuration and bond order of the H_2^{2-} ion. Is this a stable species?

Answer

H_2^{2-} has a valence electron configuration of $(\sigma_{1s})^2(\sigma_{1s}^\star)^2$ with a bond order of 0. It is therefore predicted to be unstable.

So far, our discussion of molecular orbitals has been confined to the interaction of valence orbitals, which tend to lie farthest from the nucleus. When two atoms are close enough for their valence orbitals to overlap significantly, the filled inner electron shells are largely unperturbed; hence they do not need to be considered in a molecular orbital scheme. Also, when the inner orbitals are completely filled, they contain exactly enough electrons to completely fill both the bonding and antibonding molecular orbitals that arise from their interaction. Thus the interaction of filled shells always gives a bond order of 0, so filled shells are not a factor when predicting the stability of a species. This means that we can focus our attention on the molecular orbitals derived from valence atomic orbitals.

A molecular orbital diagram that can be applied to any **homonuclear diatomic molecule** with two identical alkali metal atoms (Li_2 and Cs_2, for example) is shown in part (a) in Figure 3.1.4, where M represents the metal atom. Only two energy levels are important for describing the valence electron molecular orbitals of these species: a σ_{ns} bonding molecular orbital and a σ^*_{ns} antibonding molecular orbital. Because each alkali metal (M) has an ns^1 valence electron configuration, the M_2 molecule has two valence electrons that fill the σ_{ns} bonding orbital. As a result, a bond order of 1 is predicted for all homonuclear diatomic species formed from the alkali metals (Li_2, Na_2, K_2, Rb_2, and Cs_2). The general features of these M_2 diagrams are identical to the diagram for the H_2 molecule in Figure 3.1.2. Experimentally, all are found to be stable in the gas phase, and some are even stable in solution.

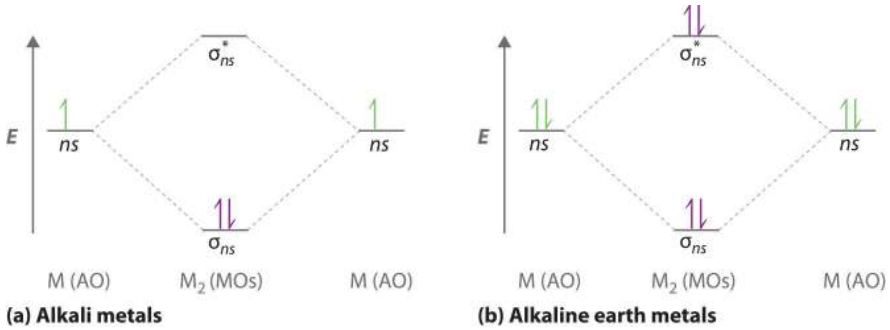


Figure 3.1.6: Molecular Orbital Energy-Level Diagrams for Alkali Metal and Alkaline Earth Metal Diatomic (M_2) Molecules. *(a) For alkali metal diatomic molecules, the two valence electrons are enough to fill the σ_{ns} (bonding) level, giving a bond order of 1. (b) For alkaline earth metal diatomic molecules, the four valence electrons fill both the σ_{ns} (bonding) and the σ_{ns}* (nonbonding) levels, leading to a predicted bond order of 0.*

Similarly, the molecular orbital diagrams for homonuclear diatomic compounds of the alkaline earth metals (such as Be_2), in which each metal atom has an ns^2 valence electron configuration, resemble the diagram for the He_2 molecule in part (c) in Figure 3.1.5 As shown in part (b) in Figure 3.1.6, this is indeed the case. All the homonuclear alkaline earth diatomic molecules have four valence electrons, which fill both the σ_{ns} bonding orbital and the σ_{ns}* antibonding orbital and give a bond order of 0. Thus Be_2, Mg_2, Ca_2, Sr_2, and Ba_2 are all expected to be unstable, in agreement with experimental data.In the solid state, however, all the alkali metals and the alkaline earth metals exist as extended lattices held together by metallic bonding. At low temperatures, Be_2 is stable.

Example 3.1.2

Use a qualitative molecular orbital energy-level diagram to predict the valence electron configuration, bond order, and likely existence of the Na_2^- ion.

Given: chemical species

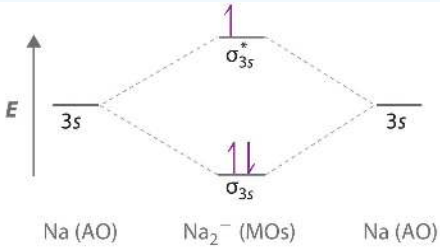
Asked for: molecular orbital energy-level diagram, valence electron configuration, bond order, and stability

Strategy:

A. Combine the two sodium valence atomic orbitals to produce bonding and antibonding molecular orbitals. Draw the molecular orbital energy-level diagram for this system.
B. Determine the total number of valence electrons in the Na_2^- ion. Fill the molecular orbitals in the energy-level diagram beginning with the orbital with the lowest energy. Be sure to obey the Pauli principle and Hund's rule while doing so.
C. Calculate the bond order and predict whether the species is stable.

Solution:

A Because sodium has a [Ne]$3s^1$ electron configuration, the molecular orbital energy-level diagram is qualitatively identical to the diagram for the interaction of two 1*s* atomic orbitals. **B** The Na_2^- ion has a total of three valence electrons (one from each Na atom and one for the negative charge), resulting in a filled σ_{3s} molecular orbital, a half-filled σ_{3s*} and a $(\sigma_{3s})^2(\sigma^\star_{3s})^1$ electron configuration.



C The bond order is (2-1)÷2=1/2 With a fractional bond order, we predict that the Na_2^- ion exists but is highly reactive.

? Exercise 3.1.2

Use a qualitative molecular orbital energy-level diagram to predict the valence electron configuration, bond order, and likely existence of the Ca_2^+ ion.

Answer

Ca_2^+ has a $(\sigma_{4s})^2(\sigma^\star_{4s})^1$ electron configurations and a bond order of 1/2 and should exist.

Molecular Orbitals Formed from *ns* and *np* Atomic Orbitals

Atomic orbitals other than *ns* orbitals can also interact to form molecular orbitals. Because individual *p*, *d*, and *f* orbitals are not spherically symmetrical, however, we need to define a coordinate system so we know which lobes are interacting in three-dimensional space. Recall that for each *np* subshell, for example, there are np_x, np_y, and np_z orbitals. All have the same energy and are therefore degenerate, but they have different spatial orientations.

$$\sigma_{np_z} = np_z\,(A) - np_z\,(B) \tag{3.1.6}$$

Just as with *ns* orbitals, we can form molecular orbitals from *np* orbitals by taking their mathematical sum and difference. When two positive lobes with the appropriate spatial orientation overlap, as illustrated for two np_z atomic orbitals in part (a) in Figure 3.1.5, it is the mathematical *difference* of their wave functions that results in *constructive* interference, which in turn increases the electron probability density between the two atoms. The difference therefore corresponds to a molecular orbital called a σ_{np_z} *bonding molecular orbital* because, just as with the σ orbitals discussed previously, it is symmetrical about the internuclear axis (in this case, the *z*-axis):

$$\sigma_{np_z} = np_z\,(A) - np_z\,(B) \tag{3.1.7}$$

The other possible combination of the two np_z orbitals is the mathematical sum:

$$\sigma_{np_z} = np_z\,(A) + np_z\,(B) \tag{3.1.8}$$

In this combination, shown in part (b) in Figure 3.1.7, the positive lobe of one np_z atomic orbital overlaps the negative lobe of the other, leading to *destructive* interference of the two waves and creating a node between the two atoms. Hence this is an antibonding molecular orbital. Because it, too, is symmetrical about the internuclear axis, this molecular orbital is called a $\sigma_{np_z} = np_z\,(A) - np_z\,(B)$ *antibonding molecular orbital*. Whenever orbitals combine, *the bonding combination is always lower in energy* (more stable) than the atomic orbitals from which it was derived, and *the antibonding combination is higher in energy* (less stable).

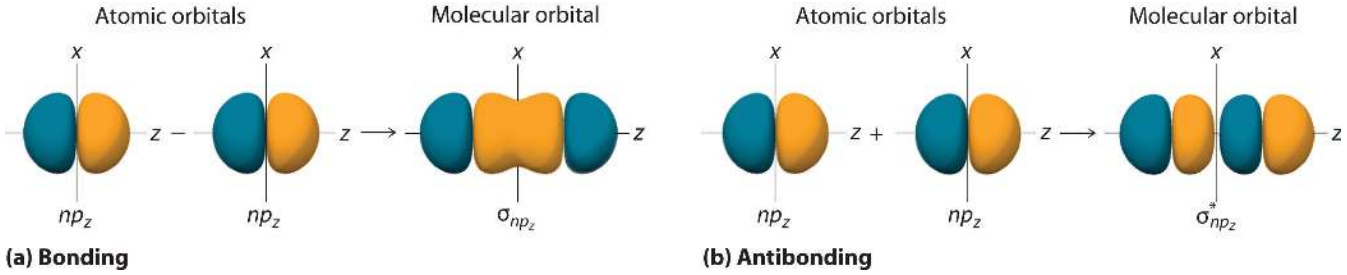


Figure 3.1.7: Formation of Molecular Orbitals from np_z Atomic Orbitals on Adjacent Atoms.(a) By convention, in a linear molecule or ion, the *z*-axis always corresponds to the internuclear axis, with +*z* to the right. As a result, the signs of the lobes of the np_z atomic orbitals on the two atoms alternate − + − +, from left to right. In this case, the σ (bonding) molecular orbital corresponds to the mathematical *difference*, in which the overlap of lobes with the same sign results in increased probability density between the nuclei. (b) In contrast, the σ* (antibonding) molecular orbital corresponds to the mathematical *sum*, in which the overlap of lobes with opposite signs results in a nodal plane of zero probability density perpendicular to the internuclear axis.

Overlap of atomic orbital lobes with the *same sign* produces a bonding molecular orbital, regardless of whether it corresponds to the sum or the difference of the atomic orbitals.

The remaining *p* orbitals on each of the two atoms, np_x and np_y, do not point directly toward each other. Instead, they are perpendicular to the internuclear axis. If we arbitrarily label the axes as shown in Figure 3.1.8, we see that we have two pairs of *np* orbitals: the two np_x orbitals lying in the plane of the page, and two np_y orbitals perpendicular to the plane. Although these two pairs are equivalent in energy, the np_x orbital on one atom can interact with only the np_x orbital on the other, and the np_y orbital on one atom can interact with only the np_y on the other. These interactions are side-to-side rather than the head-to-head interactions characteristic of σ orbitals. Each pair of overlapping atomic orbitals again forms two molecular orbitals: one corresponds to the arithmetic sum of the two atomic orbitals and one to the difference. The sum of these side-to-side interactions increases the electron probability in the region above and below a line connecting the nuclei, so it is a bonding molecular orbital that is called a pi (π) orbital (a bonding molecular orbital formed from the side-to-side interactions of two or more parallel np atomic orbitals). The difference results in the overlap of orbital lobes with opposite signs, which produces a nodal plane perpendicular to the internuclear axis; hence it is an antibonding molecular orbital, called a pi star (π*) orbital An antibonding molecular orbital formed from the difference of the side-to-side interactions of two or more parallel *np* atomic orbitals, creating a nodal plane perpendicular to the internuclear axis..

$$\pi_{np_x} = np_x\,(A) + np_x\,(B) \tag{3.1.9}$$

$$\pi^{\star}_{np_x} = np_x\,(A) - np_x\,(B) \tag{3.1.10}$$

The two np_y orbitals can also combine using side-to-side interactions to produce a bonding π_{np_y} molecular orbital and an antibonding $\pi^{\star}_{np_y}$ molecular orbital. Because the np_x and np_y atomic orbitals interact in the same way (side-to-side) and have the same energy, the π_{np_x} and π_{np_y} molecular orbitals are a degenerate pair, as are the $\pi^{\star}_{np_x}$ and $\pi^{\star}_{np_y}$ molecular orbitals.

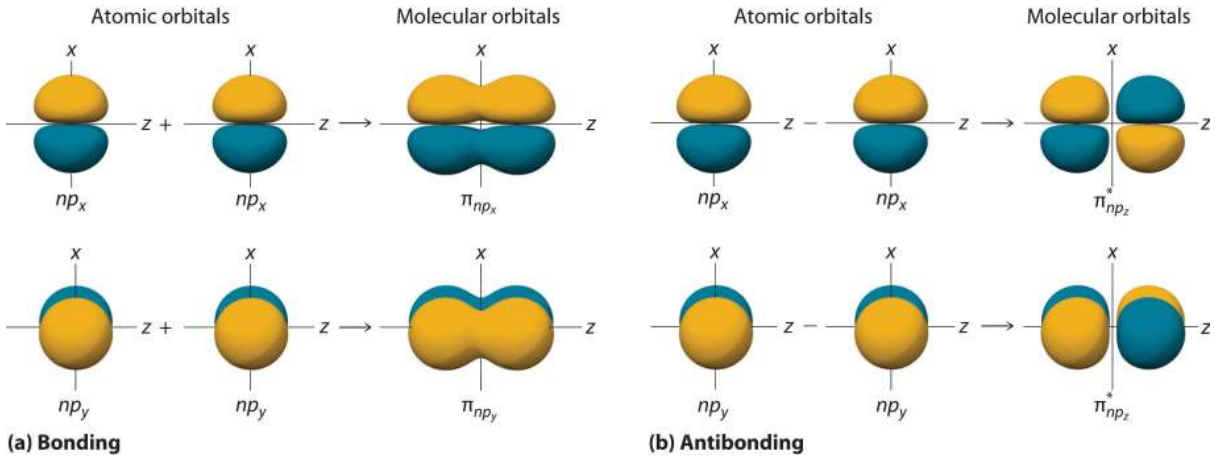


Figure 3.1.8: Formation of π Molecular Orbitals from np_x and np_y Atomic Orbitals on Adjacent Atoms.(a) Because the signs of the lobes of both the np_x and the np_y atomic orbitals on adjacent atoms are the same, in both cases the mathematical sum corresponds to a π (bonding) molecular orbital. (b) In contrast, in both cases, the mathematical difference corresponds to a π* (antibonding) molecular orbital, with a nodal plane of zero probability density perpendicular to the internuclear axis.

Figure 3.1.9 is an energy-level diagram that can be applied to two identical interacting atoms that have three *np* atomic orbitals each. There are six degenerate *p* atomic orbitals (three from each atom) that combine to form six molecular orbitals, three bonding and three antibonding. The bonding molecular orbitals are lower in energy than the atomic orbitals because of the increased stability associated with the formation of a bond. Conversely, the antibonding molecular orbitals are higher in energy, as shown. The energy difference between the σ and σ* molecular orbitals is significantly greater than the difference between the two π and π* sets. The reason for this is that the atomic orbital overlap and thus the strength of the interaction are greater for a σ bond than a π bond, which means that the σ molecular orbital is more stable (lower in energy) than the π molecular orbitals.

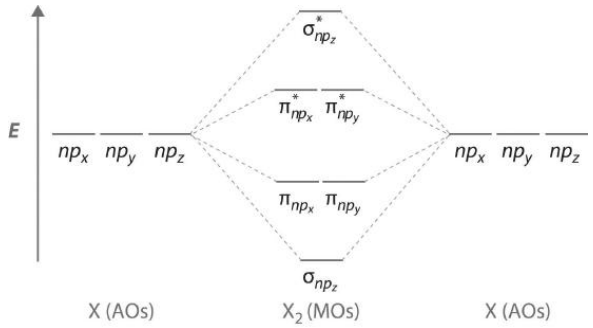


Figure 3.1.9: The Relative Energies of the σ and π Molecular Orbitals Derived from np_x, np_y, and np_z Orbitals on Identical Adjacent Atoms. Because the two np_z orbitals point directly at each other, their orbital overlap is greater, so the difference in energy between the σ and σ* molecular orbitals is greater than the energy difference between the π and π* orbitals.

Although many combinations of atomic orbitals form molecular orbitals, we will discuss only one other interaction: an *ns* atomic orbital on one atom with an np_z atomic orbital on another. As shown in Figure 3.1.10, the sum of the two atomic wave functions ($ns + np_z$) produces a σ bonding molecular orbital. Their difference ($ns - np_z$) produces a σ* antibonding molecular orbital, which has a nodal plane of zero probability density perpendicular to the internuclear axis.

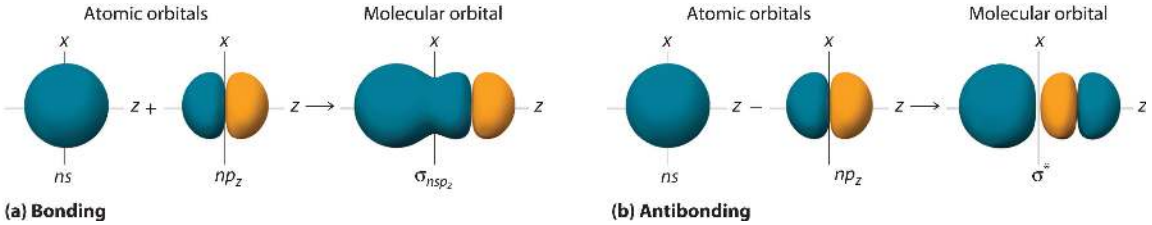


Figure 3.1.10: Formation of Molecular Orbitals from an ns Atomic Orbital on One Atom and an np_z Atomic Orbital on an Adjacent Atom.(a) The mathematical sum results in a σ (bonding) molecular orbital, with increased probability density between the nuclei. (b) The mathematical difference results in a σ* (antibonding) molecular orbital, with a nodal plane of zero probability density perpendicular to the internuclear axis.

Second Row Diatomic Molecules

If we combine the splitting schemes for the 2s and 2p orbitals, we can predict bond order in all of the diatomic molecules and ions composed of elements in the first complete row of the periodic table. Remember that only the valence orbitals of the atoms need be considered; as we saw in the cases of lithium hydride and dilithium, the inner orbitals remain tightly bound and retain their localized atomic character.

We now describe examples of systems involving period 2 homonuclear diatomic molecules, such as N_2, O_2, and F_2. When we draw a molecular orbital diagram for a molecule, there are four key points to remember:

1. The number of molecular orbitals produced is the same as the number of atomic orbitals used to create them (the law of conservation of orbitals).
2. As the overlap between two atomic orbitals increases, the difference in energy between the resulting bonding and antibonding molecular orbitals increases.
3. When two atomic orbitals combine to form a pair of molecular orbitals, the bonding molecular orbital is stabilized about as much as the antibonding molecular orbital is destabilized.
4. The interaction between atomic orbitals is greatest when they have the same energy.

> The number of molecular orbitals is **always** equal to the total number of atomic orbitals we started with.

We illustrate how to use these points by constructing a molecular orbital energy-level diagram for F_2. We use the diagram in part (a) in Figure 3.1.11; the $n = 1$ orbitals (σ_{1s} and σ_{1s}*) are located well below those of the $n = 2$ level and are not shown. As illustrated in the diagram, the σ_{2s} and σ_{2s}* molecular orbitals are much lower in energy than the molecular orbitals derived from the 2*p* atomic orbitals because of the large difference in energy between the 2*s* and 2*p* atomic orbitals of fluorine. The lowest-energy molecular orbital derived from the three 2*p* orbitals on each F is σ_{2p_z} and the next most stable are the two degenerate orbitals, π_{2p_x} and π_{2p_y}. For each bonding orbital in the diagram, there is an antibonding orbital, and the antibonding orbital is destabilized by

about as much as the corresponding bonding orbital is stabilized. As a result, the $\sigma^{\star}_{2p_z}$ orbital is higher in energy than either of the degenerate $\pi^{\star}_{2p_x}$ and $\pi^{\star}_{2p_y}$ orbitals. We can now fill the orbitals, beginning with the one that is lowest in energy.

Each fluorine has 7 valence electrons, so there are a total of 14 valence electrons in the F_2 molecule. Starting at the lowest energy level, the electrons are placed in the orbitals according to the Pauli principle and Hund's rule. Two electrons each fill the σ_{2s} and σ_{2s}* orbitals, 2 fill the σ_{2p_z} orbital, 4 fill the two degenerate π orbitals, and 4 fill the two degenerate π^* orbitals, for a total of 14 electrons. To determine what type of bonding the molecular orbital approach predicts F_2 to have, we must calculate the bond order. According to our diagram, there are 8 bonding electrons and 6 antibonding electrons, giving a bond order of $(8 - 6) \div 2 = 1$. Thus F_2 is predicted to have a stable F–F single bond, in agreement with experimental data.

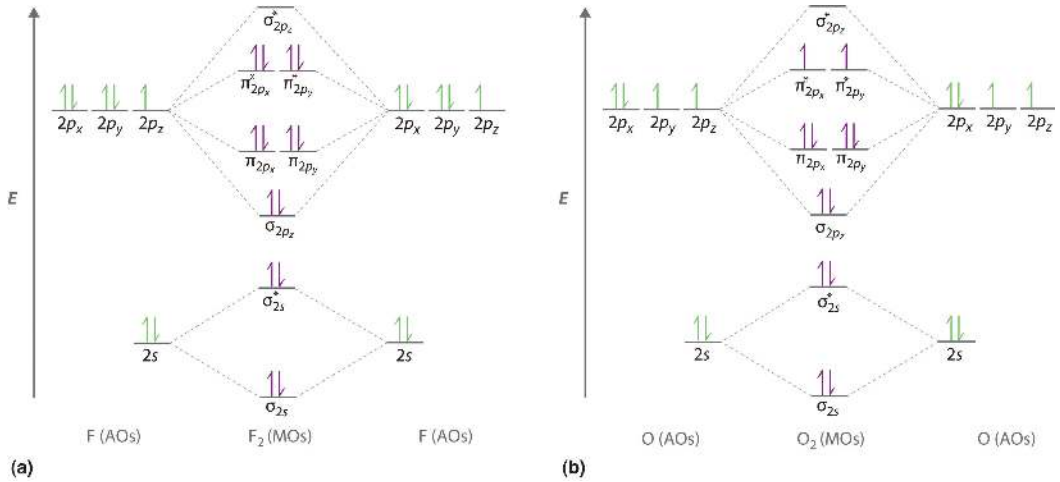


Figure 3.1.11: Molecular Orbital Energy-Level Diagrams for Homonuclear Diatomic Molecules.(a) For F_2, with 14 valence electrons (7 from each F atom), all of the energy levels except the highest, $\sigma^{\star}_{2p_z}$ are filled. This diagram shows 8 electrons in bonding orbitals and 6 in antibonding orbitals, resulting in a bond order of 1. (b) For O_2, with 12 valence electrons (6 from each O atom), there are only 2 electrons to place in the $\left(\pi^{\star}_{np_x}, \pi^{\star}_{np_y}\right)$ pair of orbitals. Hund's rule dictates that one electron occupies each orbital, and their spins are parallel, giving the O_2 molecule two unpaired electrons. This diagram shows 8 electrons in bonding orbitals and 4 in antibonding orbitals, resulting in a predicted bond order of 2.

We now turn to a molecular orbital description of the bonding in O_2. It so happens that the molecular orbital description of this molecule provided an explanation for a long-standing puzzle that could not be explained using other bonding models. To obtain the molecular orbital energy-level diagram for O_2, we need to place 12 valence electrons (6 from each O atom) in the energy-level diagram shown in part (b) in Figure 3.1.11. We again fill the orbitals according to Hund's rule and the Pauli principle, beginning with the orbital that is lowest in energy. Two electrons each are needed to fill the σ_{2s} and σ_{2s}* orbitals, 2 more to fill the σ_{2p_z} orbital, and 4 to fill the degenerate $\pi^{\star}_{2p_x}$ and $\pi^{\star}_{2p_y}$ orbitals. According to Hund's rule, the last 2 electrons must be placed in separate π^* orbitals with their spins parallel, giving two unpaired electrons. This leads to a predicted bond order of $(8 - 4) \div 2 = 2$, which corresponds to a double bond, in agreement with experimental data (Table 4.5): the O–O bond length is 120.7 pm, and the bond energy is 498.4 kJ/mol at 298 K.

None of the other bonding models can predict the presence of two unpaired electrons in O_2. Chemists had long wondered why, unlike most other substances, liquid O_2 is attracted into a magnetic field. As shown in Figure 3.1.12, it actually remains suspended between the poles of a magnet until the liquid boils away. The only way to explain this behavior was for O_2 to have unpaired electrons, making it paramagnetic, exactly as predicted by molecular orbital theory. This result was one of the earliest triumphs of molecular orbital theory over the other bonding approaches we have discussed.



Figure 3.1.12: Liquid O_2 Suspended between the Poles of a Magnet.Because the O_2 molecule has two unpaired electrons, it is paramagnetic. Consequently, it is attracted into a magnetic field, which allows it to remain suspended between the poles of a powerful magnet until it evaporates. Full video can be found at https://www.youtube.com/watch?featur...&v=Lt4P6ctf06Q.

The magnetic properties of O_2 are not just a laboratory curiosity; they are absolutely crucial to the existence of life. Because Earth's atmosphere contains 20% oxygen, all organic compounds, including those that compose our body tissues, should react rapidly with air to form H_2O, CO_2, and N_2 in an exothermic reaction. Fortunately for us, however, this reaction is very, very slow. The reason for the unexpected stability of organic compounds in an oxygen atmosphere is that virtually all organic compounds, as well as H_2O, CO_2, and N_2, have only paired electrons, whereas oxygen has two unpaired electrons. Thus the reaction of O_2 with organic compounds to give H_2O, CO_2, and N_2 would require that at least one of the electrons on O_2 change its spin during the reaction. This would require a large input of energy, an obstacle that chemists call a *spin barrier*. Consequently, reactions of this type are usually exceedingly slow. If they were not so slow, all organic substances, including this book and you, would disappear in a puff of smoke!

For period 2 diatomic molecules to the left of N_2 in the periodic table, a slightly different molecular orbital energy-level diagram is needed because the σ_{2p_z} molecular orbital is slightly *higher* in energy than the degenerate $\pi^*_{np_x}$ and $\pi^*_{np_y}$ orbitals. The difference in energy between the 2*s* and 2*p* atomic orbitals increases from Li_2 to F_2 due to increasing nuclear charge and poor screening of the 2*s* electrons by electrons in the 2*p* subshell. The bonding interaction between the 2*s* orbital on one atom and the 2*pz* orbital on the other is most important when the two orbitals have similar energies. This interaction decreases the energy of the σ_{2s} orbital and increases the energy of the σ_{2p_z} orbital. Thus for Li_2, Be_2, B_2, C_2, and N_2, the σ_{2p_z} orbital is higher in energy than the σ_{3p_z} orbitals, as shown in Figure 3.1.11 Experimentally, it is found that the energy gap between the *ns* and *np* atomic orbitals *increases* as the nuclear charge increases (Figure 3.1.13). Thus for example, the σ_{2p_z} molecular orbital is at a lower energy than the $\pi_{2p_{x,y}}$ pair.

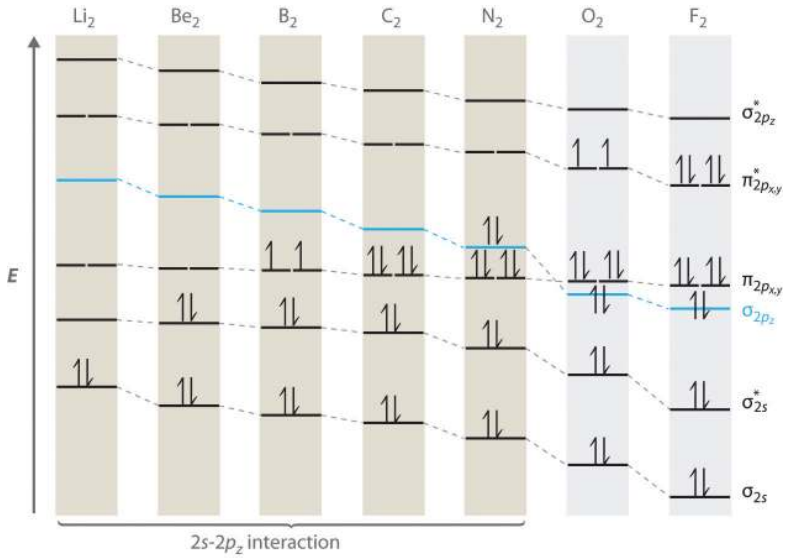


Figure 3.1.13: Molecular Orbital Energy-Level Diagrams for the Diatomic Molecules of the Period 2 Elements. Unlike earlier diagrams, only the molecular orbital energy levels for the molecules are shown here. For simplicity, the atomic orbital energy levels for the component *atoms* have been omitted. For Li_2 through N_2, the σ_{2p_z} orbital is higher in energy than the $\pi_{2p_{x,y}}$ orbitals. In contrast, the σ_{2p_z} orbital is *lower* in energy than the $\pi_{2p_{x,y}}$ orbitals for O_2 and F_2 due to the increase in the energy difference between the 2*s* and 2*p* atomic orbitals as the nuclear charge increases across the row.

Completing the diagram for N_2 in the same manner as demonstrated previously, we find that the 10 valence electrons result in 8 bonding electrons and 2 antibonding electrons, for a predicted bond order of 3, a triple bond. Experimental data show that the N–N bond is significantly shorter than the F–F bond (109.8 pm in N_2 versus 141.2 pm in F_2), and the bond energy is much greater for N_2 than for F_2 (945.3 kJ/mol versus 158.8 kJ/mol, respectively). Thus the N_2 bond is much shorter and stronger than the F_2 bond, consistent with what we would expect when comparing a triple bond with a single bond.

✔ Example 3.1.3

Use a qualitative molecular orbital energy-level diagram to predict the electron configuration, the bond order, and the number of unpaired electrons in S_2, a bright blue gas at high temperatures.

Given: chemical species

Asked for: molecular orbital energy-level diagram, bond order, and number of unpaired electrons

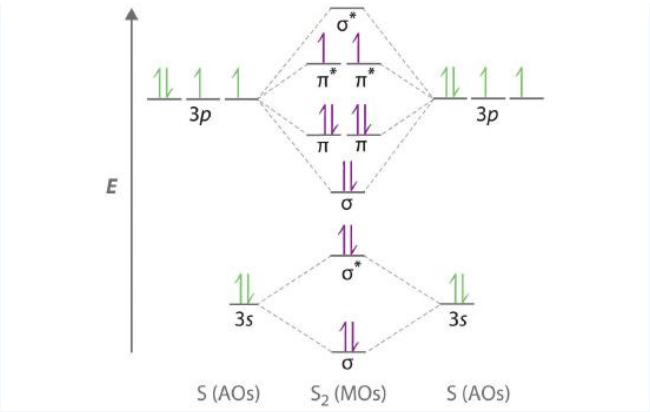
Strategy:

A. Write the valence electron configuration of sulfur and determine the type of molecular orbitals formed in S_2. Predict the relative energies of the molecular orbitals based on how close in energy the valence atomic orbitals are to one another.
B. Draw the molecular orbital energy-level diagram for this system and determine the total number of valence electrons in S_2.
C. Fill the molecular orbitals in order of increasing energy, being sure to obey the Pauli principle and Hund's rule.
D. Calculate the bond order and describe the bonding.

Solution:

A Sulfur has a $[Ne]3s^23p^4$ valence electron configuration. To create a molecular orbital energy-level diagram similar to those in Figure 3.1.11 and Figure 3.1.13, we need to know how close in energy the 3*s* and 3*p* atomic orbitals are because their energy separation will determine whether the $\pi_{3p_{x,y}}$ or the σ_{3p_z}> molecular orbital is higher in energy. Because the *ns*–*np* energy gap *increases* as the nuclear charge increases (Figure 3.1.13), the σ_{3p_z} molecular orbital will be lower in energy than the $\pi_{3p_{x,y}}$ pair.

B The molecular orbital energy-level diagram is as follows:



Each sulfur atom contributes 6 valence electrons, for a total of 12 valence electrons.

C Ten valence electrons are used to fill the orbitals through π_{3p_x} and π_{3p_y}, leaving 2 electrons to occupy the degenerate $\pi^{\star}_{3p_x}$ and $\pi^{\star}_{3p_y}$ pair. From Hund's rule, the remaining 2 electrons must occupy these orbitals separately with their spins aligned. With the numbers of electrons written as superscripts, the electron configuration of S_2 is $(\sigma_{3s})^2(\sigma^{\star}_{3s})^2(\sigma_{3p_z})^2(\pi_{3p_{x,y}})^4(\pi_{3p^{\star}_{x,y}})^2$ with 2 unpaired electrons. The bond order is (8 − 4) ÷ 2 = 2, so we predict an S=S double bond.

? Exercise 3.1.3

Use a qualitative molecular orbital energy-level diagram to predict the electron configuration, the bond order, and the number of unpaired electrons in the peroxide ion (O_2^{2-}).

Answer

$(\sigma_{2s})^2(\sigma^{\star}_{2s})^2(\sigma_{2p_z})^2\left(\pi_{2p_{x,y}}\right)^4(\pi_{2p^{\star}_{x,y}})^4$

bond order of 1;

no unpaired electrons

Molecular Orbitals for Heteronuclear Diatomic Molecules

Diatomic molecules with two different atoms are called heteronuclear diatomic molecules. When two nonidentical atoms interact to form a chemical bond, the interacting atomic orbitals do not have the same energy. If, for example, element B is more electronegative than element A ($\chi_B > \chi_A$), the net result is a "skewed" molecular orbital energy-level diagram, such as the one shown for a hypothetical A–B molecule in Figure 3.1.14 The atomic orbitals of element B are uniformly lower in energy than the corresponding atomic orbitals of element A because of the enhanced stability of the electrons in element B. The molecular orbitals are no longer symmetrical, and the energies of the bonding molecular orbitals are more similar to those of the atomic orbitals of B. Hence the electron density of bonding electrons is likely to be closer to the more electronegative atom. In this way, molecular orbital theory can describe a polar covalent bond.

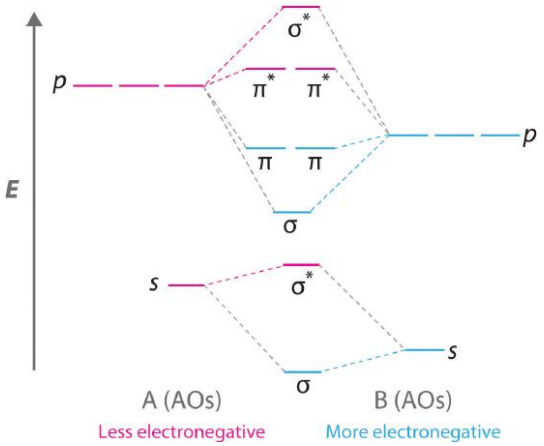


Figure 3.1.14: Molecular Orbital Energy-Level Diagram for a Heteronuclear Diatomic Molecule AB, Where $\chi_B > \chi_A$. The bonding molecular orbitals are closer in energy to the atomic orbitals of the more electronegative B atom. Consequently, the electrons in the bonding orbitals are not shared equally between the two atoms. On average, they are closer to the B atom, resulting in a polar covalent bond.

> *A molecular orbital energy-level diagram is always skewed toward the more electronegative atom.*

An Odd Number of Valence Electrons: NO

Nitric oxide (NO) is an example of a heteronuclear diatomic molecule. The reaction of O_2 with N_2 at high temperatures in internal combustion engines forms nitric oxide, which undergoes a complex reaction with O_2 to produce NO_2, which in turn is responsible for the brown color we associate with air pollution. Recently, however, nitric oxide has also been recognized to be a vital biological messenger involved in regulating blood pressure and long-term memory in mammals.

Because NO has an odd number of valence electrons (5 from nitrogen and 6 from oxygen, for a total of 11), its bonding and properties cannot be successfully explained by either the Lewis electron-pair approach or valence bond theory. The molecular orbital energy-level diagram for NO (Figure 3.1.15) shows that the general pattern is similar to that for the O_2 molecule (Figure 3.1.13). Because 10 electrons are sufficient to fill all the bonding molecular orbitals derived from 2*p* atomic orbitals, the 11th electron must occupy one of the degenerate π^* orbitals. The predicted bond order for NO is therefore (8-3) ÷ 2 = 2 1/2 . Experimental data, showing an N–O bond length of 115 pm and N–O bond energy of 631 kJ/mol, are consistent with this description. These values lie between those of the N_2 and O_2 molecules, which have triple and double bonds, respectively. As we stated earlier, molecular orbital theory can therefore explain the bonding in molecules with an odd number of electrons, such as NO, whereas Lewis electron structures cannot.

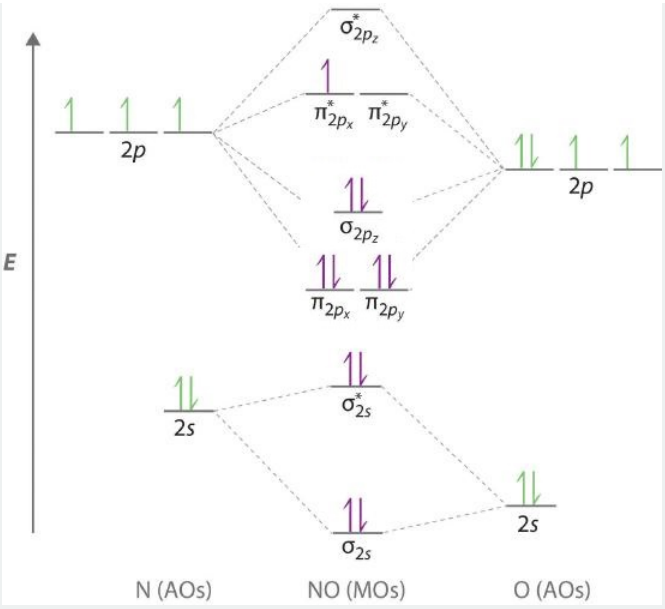


Figure 3.1.15: Molecular Orbital Energy-Level Diagram for NO. Because NO has 11 valence electrons, it is paramagnetic, with a single electron occupying the $\left(\pi^{\star}_{2p_x},\ \pi^{\star}_{2p_y}\right)$ pair of orbitals.

Note that electronic structure studies show the ground state configuration of NO to be $(\sigma_{2s})^2\left(\sigma^{\star}_{2s}\right)^2\left(\pi_{2p_{x,y}}\right)^4\left(\sigma_{2p_z}\right)^2\left(\pi_{2p^{\star}_{x,y}}\right)^2$ in order of increasing energy. Hence, the $\pi_{2p_{x,y}}$ orbitals are lower in energy than the σ_{2p_z} orbital. This is because the NO molecule is near the transition of flipping energies levels observed in homonuclear diatomics where the sigma bond drops below the pi bond (Figure 3.1.13).

Molecular orbital theory can also tell us something about the *chemistry* of NO. As indicated in the energy-level diagram in Figure 3.1.15, NO has a single electron in a relatively high-energy molecular orbital. We might therefore expect it to have similar reactivity as alkali metals such as Li and Na with their single valence electrons. In fact, NO is easily oxidized to the NO^+ cation, which is isoelectronic with N_2 and has a bond order of 3, corresponding to an N≡O triple bond.



Molecular Orbital Bonding for Second Row Elements: https://youtu.be/A_5Xa3sK_YE

Nonbonding Molecular Orbitals

Molecular orbital theory is also able to explain the presence of lone pairs of electrons. Consider, for example, the HCl molecule, whose Lewis electron structure has three lone pairs of electrons on the chlorine atom. Using the molecular orbital approach to describe the bonding in HCl, we can see from Figure 3.1.16 that the 1*s* orbital of atomic hydrogen is closest in energy to the 3*p* orbitals of chlorine. Consequently, the filled Cl 3*s* atomic orbital is not involved in bonding to any appreciable extent, and the only important interactions are those between the H 1*s* and Cl 3*p* orbitals. Of the three *p* orbitals, only one, designated as $3p_z$, can

interact with the H 1*s* orbital. The $3p_x$ and $3p_y$ atomic orbitals have no net overlap with the 1*s* orbital on hydrogen, so they are not involved in bonding. Because the energies of the Cl 3*s*, $3p_x$, and $3p_y$ orbitals do not change when HCl forms, they are called **nonbonding molecular orbitals**. A nonbonding molecular orbital occupied by a pair of electrons is the molecular orbital equivalent of a lone pair of electrons. By definition, electrons in nonbonding orbitals have no effect on bond order, so they are not counted in the calculation of bond order. Thus the predicted bond order of HCl is (2 − 0) ÷ 2 = 1. Because the σ bonding molecular orbital is closer in energy to the Cl $3p_z$ than to the H 1*s* atomic orbital, the electrons in the σ orbital are concentrated closer to the chlorine atom than to hydrogen. A molecular orbital approach to bonding can therefore be used to describe the polarization of the H–Cl bond to give $H^{\delta+}--Cl^{\delta-}$.

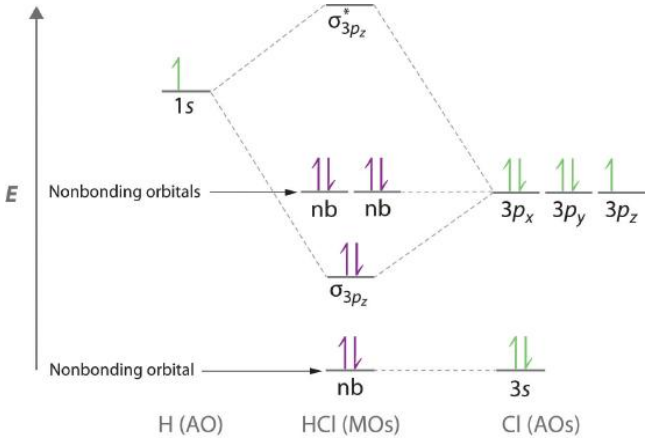


Figure 3.1.16: Molecular Orbital Energy-Level Diagram for HCl. The hydrogen 1*s* atomic orbital interacts most strongly with the $3p_z$ orbital on chlorine, producing a bonding/antibonding pair of molecular orbitals. The other electrons on Cl are best viewed as nonbonding. As a result, only the bonding σ orbital is occupied by electrons, giving a bond order of 1.

> *Electrons in nonbonding molecular orbitals have **no effect** on bond order.*

Example 3.1.4

Use a "skewed" molecular orbital energy-level diagram like the one in Figure 3.1.14 to describe the bonding in the cyanide ion (CN^-). What is the bond order?

Given: chemical species

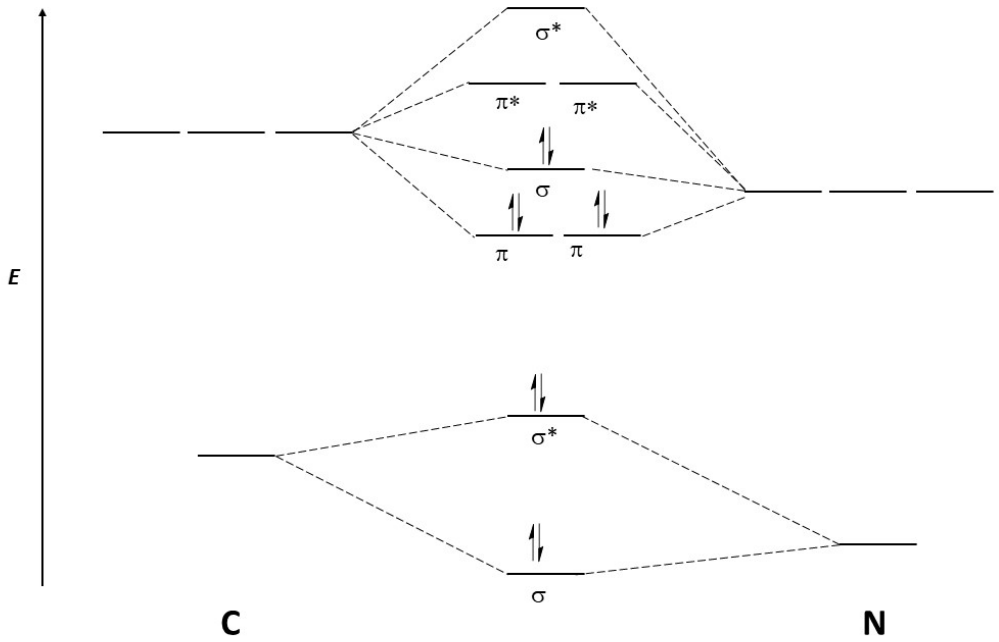
Asked for: "skewed" molecular orbital energy-level diagram, bonding description, and bond order

Strategy:

A. Calculate the total number of valence electrons in CN^-. Then place these electrons in a molecular orbital energy-level diagram like Figure 3.1.14 in order of increasing energy. Be sure to obey the Pauli principle and Hund's rule while doing so.
B. Calculate the bond order and describe the bonding in CN^-.

Solution:

A The CN^- ion has a total of 10 valence electrons: 4 from C, 5 from N, and 1 for the −1 charge. Placing these electrons in an energy-level diagram like Figure 3.1.14 fills the five lowest-energy orbitals, as shown here:



Because $\chi_N > \chi_C$, the atomic orbitals of N (on the right) are lower in energy than those of C. **B** The resulting valence electron configuration gives a predicted bond order of $(8 - 2) \div 2 = 3$, indicating that the CN^- ion has a triple bond, analogous to that in N_2. Note however, that because orbital mixing occurs between the 2s orbital on carbon and the 2p orbital on nitrogen, the sigma orbital arising from the overlap of p orbitals is raised in energy to above the level of the pi orbital formed from the overlap of p orbitals.

? Exercise 3.1.4

Use a qualitative molecular orbital energy-level diagram to describe the bonding in the hypochlorite ion (OCl^-). What is the bond order?

Answer: All molecular orbitals except the highest-energy σ* are filled, giving a bond order of 1.

Although the molecular orbital approach reveals a great deal about the bonding in a given molecule, the procedure quickly becomes computationally intensive for molecules of even moderate complexity. Furthermore, because the computed molecular orbitals extend over the entire molecule, they are often difficult to represent in a way that is easy to visualize. Therefore we do not use a pure molecular orbital approach to describe the bonding in molecules or ions with more than two atoms. Instead, we use a valence bond approach and a molecular orbital approach to explain, among other things, the concept of resonance, which cannot adequately be explained using other methods.

Summary

- Molecular orbital theory, a delocalized approach to bonding, can often explain a compound's color, why a compound with unpaired electrons is stable, semiconductor behavior, and resonance, none of which can be explained using a localized approach.

A **molecular orbital (MO)** is an allowed spatial distribution of electrons in a molecule that is associated with a particular orbital energy. Unlike an atomic orbital (AO), which is centered on a single atom, a molecular orbital extends over all the atoms in a molecule or ion. Hence the **molecular orbital theory** of bonding is a *delocalized* approach. Molecular orbitals are constructed using **linear combinations of atomic orbitals (LCAOs)**, which are usually the mathematical sums and differences of wave functions that describe overlapping atomic orbitals. Atomic orbitals interact to form three types of molecular orbitals.

1. Orbitals or orbital lobes with the same sign interact to give increased electron probability along the plane of the internuclear axis because of *constructive* reinforcement of the wave functions. Consequently, electrons in such molecular orbitals help to hold the positively charged nuclei together. Such orbitals are **bonding molecular orbitals**, and they are always lower in energy than the parent atomic orbitals.
2. Orbitals or orbital lobes with opposite signs interact to give decreased electron probability density between the nuclei because of *destructive* interference of the wave functions. Consequently, electrons in such molecular orbitals are primarily located outside the internuclear region, leading to increased repulsions between the positively charged nuclei. These orbitals are called **antibonding molecular orbitals**, and they are always higher in energy than the parent atomic orbitals.
3. Some atomic orbitals interact only very weakly, and the resulting molecular orbitals give essentially no change in the electron probability density between the nuclei. Hence electrons in such orbitals have no effect on the bonding in a molecule or ion. These orbitals are **nonbonding molecular orbitals**, and they have approximately the same energy as the parent atomic orbitals.

A completely bonding molecular orbital contains no nodes (regions of zero electron probability) perpendicular to the internuclear axis, whereas a completely **antibonding molecular orbital** contains at least one node perpendicular to the internuclear axis. A **sigma (σ) orbital** (bonding) or a **sigma star (σ*) orbital** (antibonding) is symmetrical about the internuclear axis. Hence all cross-sections perpendicular to that axis are circular. Both a **pi (π) orbital** (bonding) and a **pi star (π*) orbital** (antibonding) possess a nodal plane that contains the nuclei, with electron density localized on both sides of the plane.

The energies of the molecular orbitals versus those of the parent atomic orbitals can be shown schematically in an **energy-level diagram**. The electron configuration of a molecule is shown by placing the correct number of electrons in the appropriate energy-level diagram, starting with the lowest-energy orbital and obeying the Pauli principle; that is, placing only two electrons with opposite spin in each orbital. From the completed energy-level diagram, we can calculate the **bond order**, defined as one-half the net number of bonding electrons. In bond orders, electrons in antibonding molecular orbitals cancel electrons in bonding molecular orbitals, while electrons in nonbonding orbitals have no effect and are not counted. Bond orders of 1, 2, and 3 correspond to single, double, and triple bonds, respectively. Molecules with predicted bond orders of 0 are generally less stable than the isolated atoms and do not normally exist.

Molecular orbital energy-level diagrams for diatomic molecules can be created if the electron configuration of the parent atoms is known, following a few simple rules. Most important, the number of molecular orbitals in a molecule is the same as the number of atomic orbitals that interact. The difference between bonding and antibonding molecular orbital combinations is proportional to the overlap of the parent orbitals and decreases as the energy difference between the parent atomic orbitals increases. With such an approach, the electronic structures of virtually all commonly encountered **homonuclear diatomic molecules**, molecules with two identical atoms, can be understood. The molecular orbital approach correctly predicts that the O_2 molecule has two unpaired electrons and hence is attracted into a magnetic field. In contrast, most substances have only paired electrons. A similar procedure can be applied to molecules with two dissimilar atoms, called **heteronuclear diatomic molecules**, using a molecular orbital energy-level diagram that is skewed or tilted toward the more electronegative element. Molecular orbital theory is able to describe the bonding in a molecule with an odd number of electrons such as NO and even to predict something about its chemistry.

Contributors and Attributions

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3.2: MO Diagrams for Linear Triatomic Molecules

Skills to Develop

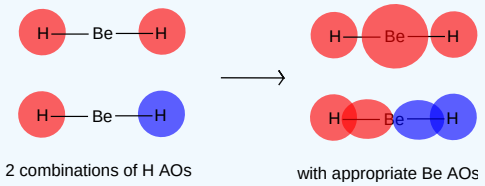
- Construct MO diagrams for simple linear triatomic molecules and/or compounds

What's Different if we have 3 Atoms?

We won't go into the details of MO theory for complex molecules, because that's a topic for more advanced classes, like Inorganic Chemistry. However, we'll show a couple examples of simple molecules so you can get the idea. We'll focus on molecules with 1 central atom and some others around it. In this case, first we combine the AOs of the outer atoms into sensible combinations, then we see how these combinations interact with the AOs on the central atom. Don't forget about **net overlap**, which is important for deciding how the orbitals interact. If they don't have net overlap, they can't interact.

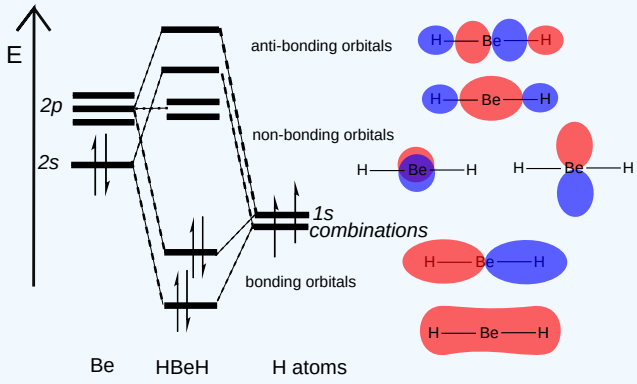
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BeH_2 might be hard to make, but it's very nice and simple as an example! Using the electron domain model we predict that it will be linear. Be has 2s and 2p orbitals, and it is in the middle. H has 1s orbitals; there are 2 H atoms on the outside. We need to make combinations of the H AOs, and we'll use the same combinations we used to make H_2, except now they aren't touching. These combinations will match the 2s and $2p_z$ on Be, as shown in the figure.



Forming MOs for BeH_2.

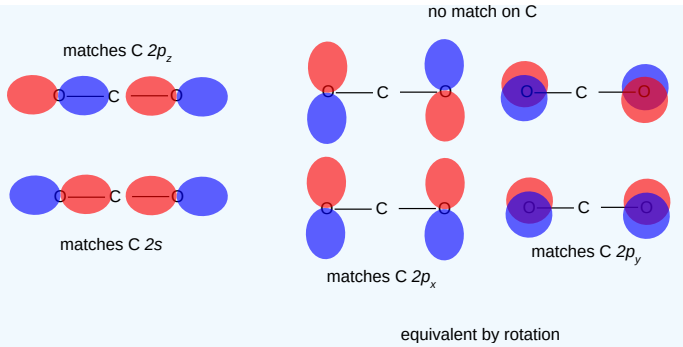
Then we can put the MO diagram together just the way we usually do, starting with the outside, drawing in bonding, non-bonding and anti-bonding MOs, and filling the electrons. The bond order is 2.



MO diagram for BeH_2.

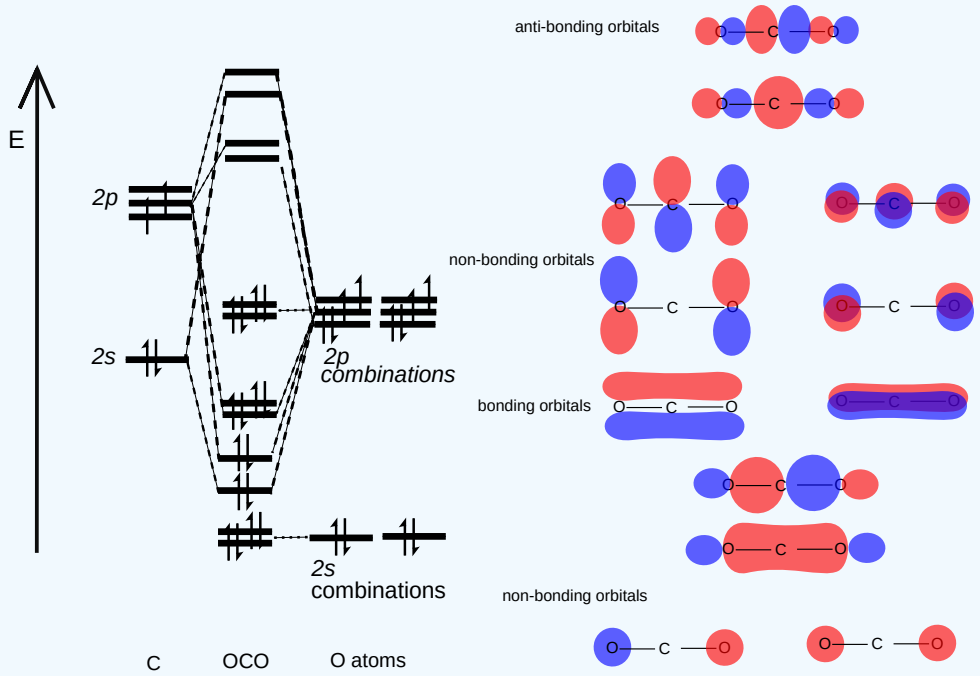
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This is a little more complicated example. Now we have to make combinations of 4 different AOs from oxygen. We can combine 2s orbitals, $2p_x$ orbitals, $2p_y$ orbitals and $2p_z$ orbitals. Each pair will make the same add/subtract combinations we've seen before. However, for a basic diagram, we will include only the O 2p orbitals, because the O 2s orbitals are much lower in energy; they have a bad energy match so they won't interact very much. The O 2p combinations that we will use are shown in the figure, and labeled with which carbon AO they match.



Oxygen AO combinations for CO_2.

Then we combine these oxygen AO combinations with the AOs on C. We still make bonding and anti-bonding combinations just like before. And there are some non-bonding orbitals too. Just as we expect from Lewis structures, there are 2 σ bonds and 2 π bonds. However, each of these is **delocalized** over the whole molecule. The bonds aren't just between 2 atoms at a time, they connect all 3 atoms.



MO diagram for CO_2.

Contributors and Attributions

- Emily V Eames (City College of San Francisco)

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3.3: Frontier MOs- An Acid-Base Theory

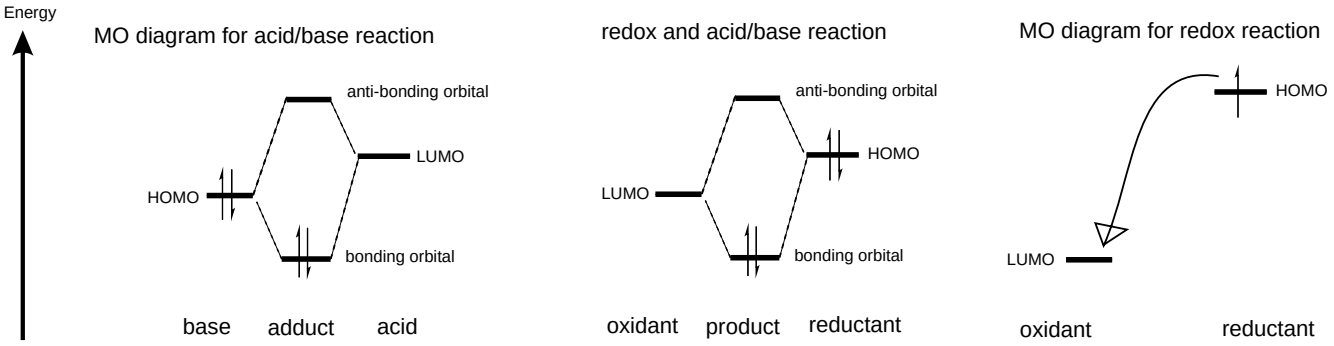
Skills to Develop

- Distinguish and describe the significance of frontier MOs

Frontier means a border area, between two things (often, between 2 countries). In this case, we are interested in the MOs at the border between occupied and empty. The **frontier MOs** are called the HOMO and the LUMO. HOMO is Highest Occupied MO, the highest-energy MO that has electrons in it. LUMO is Lowest Unoccupied MO, the lowest-energy MO that doesn't have any electrons in it.

Frontier MOs are very important for reactivity. Earlier, we said that most reactions can be called either Lewis acid/base or redox. In a Lewis acid/base reaction, an electron pair from the base is shared with the acid. What this really means is that the base has a HOMO that is pretty high-energy (a lone pair), and the acid has a LUMO that is pretty low energy. (A lone pair in MO theory is an electron pair in a non-bonding MO. A low LUMO usually means an empty valence orbital, like on B or on a cation.) We can make a bonding and anti-bonding combination of the base HOMO and acid LUMO, and that will stabilize the electrons from the base's HOMO, lowering the total energy. This creates a bond between the acid and base.

In a redox reaction, the oxidant has a low LUMO, and the reductant has a high HOMO, but this time the oxidant LUMO is lower than the reductant HOMO, so that the electrons in the reductant HOMO move completely to the oxidant LUMO. Often the energy match is bad, so that no covalent bond forms, just the electron moves. Sometimes a covalent bond forms also. This depends on the AO energies, which depends on the electronegativity, just like you would expect. You can still predict covalent/ionic bonding based on electronegativity.

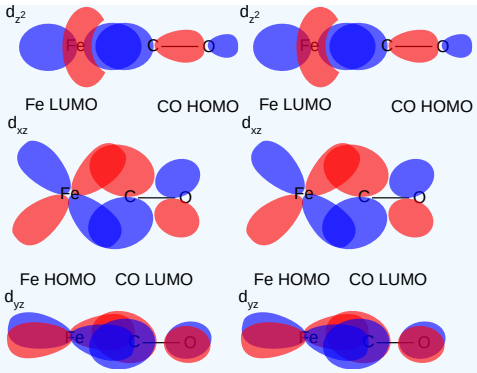


Diagrams of acid/base, redox, and both reactions.

Molecules with low HOMO and high LUMO, a big HOMO-LUMO gap, are not very reactive! Hydrocarbons are a good example (like oil, etc). They do burn easily, but you have to get them hot first. At room temperature, they don't react. This is why if you want to store something reactive like K metal, you probably keep it in a bottle of oil.

Example 3.3.1: CO Toxicity

You probably know that CO is toxic (which is why you shouldn't stay in a garage with a car running, because the CO from incomplete combustion can kill you). The reason CO is toxic is because it binds metal ions really tightly. You use Fe(II) ions in your blood to bind O_2 and carry it to your cells. CO binds to the Fe(II) more tightly than O_2, so if you breathe too much CO, your cells won't get any oxygen, because all the Fe(II) in your blood bound CO instead. We can understand how and why CO binds Fe(II) using MO theory. Go back and look at the MO diagram for CO. The HOMO is a slightly-bonding orbital that is mostly on carbon. It is pretty high-energy. The LUMO is a π* orbital that is also mostly on carbon, and it is kind of low-energy because the splitting of π MOs is smaller than σ MOs (because of less overlap). CO has a small gap between the HOMO and LUMO. Fe(II) also has a small gap between HOMO and LUMO, because it has 6 electrons in 3d orbitals. The HOMO is high, because 3d is not so stable, and the LUMO is low, because it is also 3d and not much higher than the HOMO (there is a gap because the other atoms around the Fe(II) in hemoglobin make the d orbitals different energies). So what can happen is that the HOMO on CO makes a σ bond with the LUMO on Fe(II), and the HOMO on Fe(II) makes a π bond with the LUMO on CO. This "multiple bond" between CO and Fe(II) makes CO toxic. And because the HOMO and LUMO of CO are big on carbon, you won't be surprised that the bond is Fe-C=O, not Fe-O=C.



MO interactions between Fe and CO frontier MOs. Top: σ interaction. Bottom: π interactions (2 CO LUMOs, 2 Fe HOMOs, related by 90° rotation)

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3.4: Bonding in Metals

Bonding in metals and semiconductors can be described using band theory, in which a set of molecular orbitals is generated that extends throughout the solid. The primary learning objective of this Module is to describe the electrical properties of solid using band theory.

Band Theory

To explain the observed properties of metals, a more sophisticated approach is needed than the electron-sea model commonly described. The molecular orbital theory used to explain the delocalized π bonding in polyatomic ions and molecules such as NO_2^-, ozone, and 1,3-butadiene can be adapted to accommodate the much higher number of atomic orbitals that interact with one another simultaneously in metals.

In a 1 mol sample of a metal, there can be more than 10^{24} orbital interactions to consider. In our molecular orbital description of metals, however, we begin by considering a simple one-dimensional example: a linear arrangement of n metal atoms, each containing a single electron in an s orbital. We use this example to describe an approach to metallic bonding called band theory, which assumes that the valence orbitals of the atoms in a solid interact, generating a set of molecular orbitals that extend throughout the solid.

One-Dimensional Systems

If the distance between the metal atoms is short enough for the orbitals to interact, they produce bonding, antibonding, and nonbonding molecular orbitals. The left portion of Figure 3.4.1 shows the pattern of molecular orbitals that results from the interaction of ns orbitals as n increases from 2 to 5.

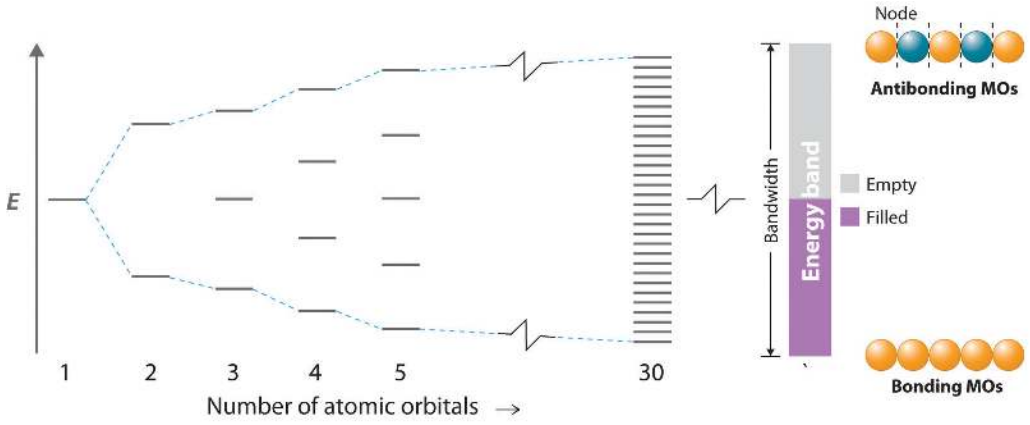


Figure 3.4.1: The Molecular Orbital Energy-Level Diagram for a Linear Arrangement of n Atoms, Each of Which Contains a Singly Occupied s Orbital. As n becomes very large, the energy separation between adjacent levels becomes so small that a single continuous band of allowed energy levels results. The lowest-energy molecular orbital corresponds to positive overlap between all the atomic orbitals to give a totally bonding combination, whereas the highest-energy molecular orbital contains a node between each pair of atoms and is thus totally antibonding.

As we saw previously, the lowest-energy orbital is the completely bonding molecular orbital, whereas the highest-energy orbital is the completely antibonding molecular orbital. Molecular orbitals of intermediate energy have fewer nodes than the totally antibonding molecular orbital. The energy separation between adjacent orbitals decreases as the number of interacting orbitals increases. For n = 30, there are still discrete, well-resolved energy levels, but as n increases from 30 to a number close to Avogadro's number, the spacing between adjacent energy levels becomes almost infinitely small. The result is essentially a continuum of energy levels, as shown on the right in Figure 3.4.1, each of which corresponds to a particular molecular orbital extending throughout the linear array of metal atoms. The levels that are lowest in energy correspond to mostly bonding combinations of atomic orbitals, those highest in energy correspond to mostly antibonding combinations, and those in the middle correspond to essentially nonbonding combinations.

The continuous set of allowed energy levels shown on the right in Figure 3.4.1 is called an energy band. The difference in energy between the highest and lowest energy levels is the bandwidth and is proportional to the strength of the interaction between orbitals on adjacent atoms: the stronger the interaction, the larger the bandwidth. Because the band contains as many energy levels as molecular orbitals, and the number of molecular orbitals is the same as the number of interacting atomic orbitals, the band in Figure

3.4.1 contains n energy levels corresponding to the combining of s orbitals from n metal atoms. Each of the original s orbitals could contain a maximum of two electrons, so the band can accommodate a total of 2n electrons. Recall, however, that each of the metal atoms we started with contained only a single electron in each s orbital, so there are only n electrons to place in the band. Just as with atomic orbitals or molecular orbitals, the electrons occupy the lowest energy levels available. Consequently, only the lower half of the band is filled. This corresponds to filling all of the bonding molecular orbitals in the linear array of metal atoms and results in the strongest possible bonding.

Multidimensional Systems

The previous example was a one-dimensional array of atoms that had only s orbitals. To extrapolate to two- or three-dimensional systems and atoms with electrons in p and d orbitals is straightforward in principle, even though in practice the mathematics becomes more complex, and the resulting molecular orbitals are more difficult to visualize. The resulting energy-level diagrams are essentially the same as the diagram of the one-dimensional example in Figure 3.4.1, with the following exception: they contain as many bands as there are different types of interacting orbitals. Because different atomic orbitals interact differently, each band will have a different bandwidth and will be centered at a different energy, corresponding to the energy of the parent atomic orbital of an isolated atom.

Band Gap

Because the 1s, 2s, and 2p orbitals of a period 3 atom are filled core levels, they do not interact strongly with the corresponding orbitals on adjacent atoms. Hence they form rather narrow bands that are well separated in energy (Figure 3.4.2). These bands are completely filled (both the bonding and antibonding levels are completely populated), so they do not make a net contribution to bonding in the solid. The energy difference between the highest level of one band and the lowest level of the next is the band gap. It represents a set of forbidden energies that do not correspond to any allowed combinations of atomic orbitals.

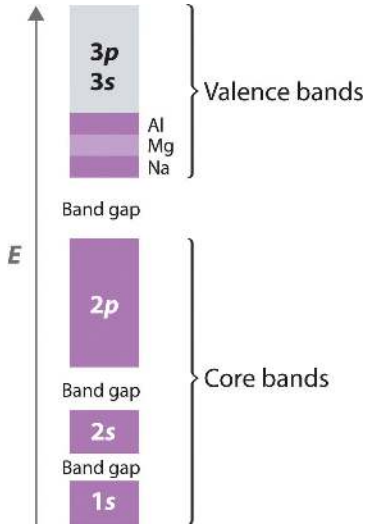


Figure 3.4.2: The Band Structures of the Period 3 Metals Na, Mg, and Al. The 3s and 3p valence bands overlap in energy to form a continuous set of energy levels that can hold a maximum of eight electrons per atom.

Because they extend farther from the nucleus, the valence orbitals of adjacent atoms (3s and 3p in Figure 3.4.2) interact much more strongly with one another than do the filled core levels; as a result, the valence bands have a larger bandwidth. In fact, the bands derived from the 3s and 3p atomic orbitals are wider than the energy gap between them, so the result is overlapping bands. These have molecular orbitals derived from two or more valence orbitals with similar energies. As the valence band is filled with one, two, or three electrons per atom for Na, Mg, and Al, respectively, the combined band that arises from the overlap of the 3s and 3p bands is also filling up; it has a total capacity of eight electrons per atom (two electrons for each 3s orbital and six electrons for each set of 3p orbitals). With Na, therefore, which has one valence electron, the combined valence band is one-eighth filled; with Mg (two valence electrons), it is one-fourth filled; and with Al, it is three-eighths filled, as indicated in Figure 3.4.2. The partially filled valence band is absolutely crucial for explaining metallic behavior because it guarantees that there are unoccupied energy levels at an infinitesimally small energy above the highest occupied level.

Band theory can explain virtually all the properties of metals. Metals conduct electricity, for example, because only a very small amount of energy is required to excite an electron from a filled level to an empty one, where it is free to migrate rapidly throughout

the crystal in response to an applied electric field. Similarly, metals have high heat capacities (as you no doubt remember from the last time a doctor or a nurse placed a stethoscope on your skin) because the electrons in the valence band can absorb thermal energy by being excited to the low-lying empty energy levels. Finally, metals are lustrous because light of various wavelengths can be absorbed, causing the valence electrons to be excited into any of the empty energy levels above the highest occupied level. When the electrons decay back to low-lying empty levels, they emit light of different wavelengths. Because electrons can be excited from many different filled levels in a metallic solid and can then decay back to any of many empty levels, light of varying wavelengths is absorbed and reemitted, which results in the characteristic shiny appearance that we associate with metals.

Requirements for Metallic Behavior

For a solid to exhibit metallic behavior,

- it must have a set of delocalized orbitals forming a band of allowed energy levels, and
- the resulting band must be partially filled (10%–90%) with electrons.

Without a set of delocalized orbitals, there is no pathway by which electrons can move through the solid.

Band theory explains the correlation between the valence electron configuration of a metal and the strength of metallic bonding. The valence electrons of transition metals occupy either their valence ns, (n − 1)d, and np orbitals (with a total capacity of 18 electrons per metal atom) or their ns and (n − 1)d orbitals (a total capacity of 12 electrons per metal atom). These atomic orbitals are close enough in energy that the derived bands overlap, so the valence electrons are not confined to a specific orbital. Metals with 6 to 9 valence electrons (which correspond to groups 6–9) are those most likely to fill the valence bands approximately halfway. Those electrons therefore occupy the highest possible number of bonding levels, while the number of antibonding levels occupied is minimal. Not coincidentally, the elements of these groups exhibit physical properties consistent with the presence of the strongest metallic bonding, such as very high melting points.

Insulators

In contrast to metals, electrical insulators are materials that conduct electricity poorly because their valence bands are full. The energy gap between the highest filled levels and the lowest empty levels is so large that the empty levels are inaccessible: thermal energy cannot excite an electron from a filled level to an empty one. The valence-band structure of diamond, for example, is shown in Figure 3.4.3*a*. Because diamond has only 4 bonded neighbors rather than the 6 to 12 typical of metals, the carbon 2s and 2p orbitals combine to form two bands in the solid, with the one at lower energy representing bonding molecular orbitals and the one at higher energy representing antibonding molecular orbitals. Each band can accommodate four electrons per atom, so only the lower band is occupied. Because the energy gap between the filled band and the empty band is very large (530 kJ/mol), at normal temperatures thermal energy cannot excite electrons from the filled level into the empty band. Thus there is no pathway by which electrons can move through the solid, so diamond has one of the lowest electrical conductivities known.

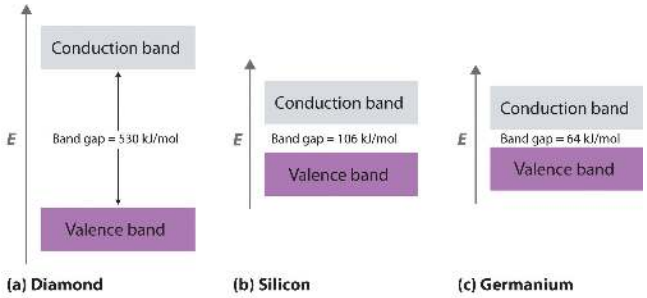


Figure 3.4.2: Energy-Band Diagrams for Diamond, Silicon, and Germanium. The band gap gets smaller from C to Ge.

Semiconductors

What if the difference in energy between the highest occupied level and the lowest empty level is intermediate between those of electrical conductors and insulators? This is the case for silicon and germanium, which have the same structure as diamond. Because Si–Si and Ge–Ge bonds are substantially weaker than C–C bonds, the energy gap between the filled and empty bands becomes much smaller as we go down group 14 (part (b) and part (c) of Figure 3.4.2). Consequently, thermal energy is able to excite a small number of electrons from the filled valence band of Si and Ge into the empty band above it, which is called the conduction band.

Exciting electrons from the filled valence band to the empty conduction band causes an increase in electrical conductivity for two reasons:

1. The electrons in the previously vacant conduction band are free to migrate through the crystal in response to an applied electric field.
2. Excitation of an electron from the valence band produces a “hole” in the valence band that is equivalent to a positive charge. The hole in the valence band can migrate through the crystal in the direction opposite that of the electron in the conduction band by means of a “bucket brigade” mechanism in which an adjacent electron fills the hole, thus generating a hole where the second electron had been, and so forth.

Consequently, Si is a much better electrical conductor than diamond, and Ge is even better, although both are still much poorer conductors than a typical metal (Figure 3.4.4).

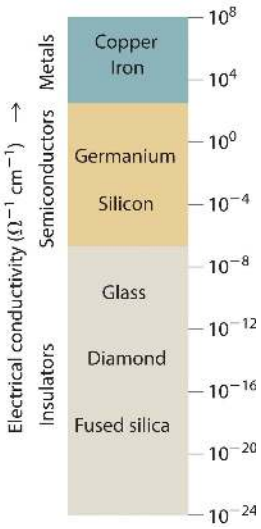


Figure 3.4.4: A Logarithmic Scale Illustrating the Enormous Range of Electrical Conductivities of Solids

Substances such as Si and Ge that have conductivities between those of metals and insulators are called semiconductors. Many binary compounds of the main group elements exhibit semiconducting behavior similar to that of Si and Ge. For example, gallium arsenide (GaAs) is isoelectronic with Ge and has the same crystalline structure, with alternating Ga and As atoms; not surprisingly, it is also a semiconductor. The electronic structure of semiconductors is compared with the structures of metals and insulators in Figure 3.4.5.

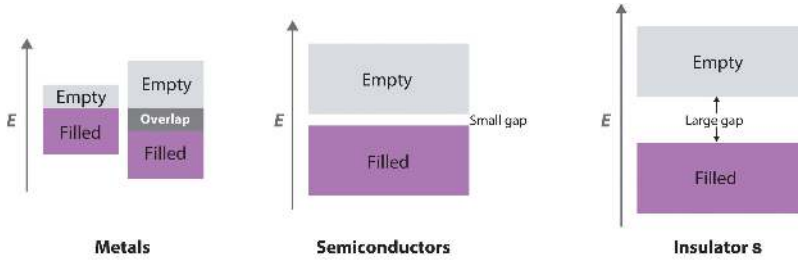


Figure 3.4.5: A Comparison of the Key Features of the Band Structures of Metals, Semiconductors, and Insulators. Metallic behavior can arise either from the presence of a single partially filled band or from two overlapping bands (one full and one empty).

Temperature and Conductivity

Because thermal energy can excite electrons across the band gap in a semiconductor, increasing the temperature increases the number of electrons that have sufficient kinetic energy to be promoted into the conduction band. The electrical conductivity of a semiconductor therefore increases rapidly with increasing temperature, in contrast to the behavior of a purely metallic crystal. In a metal, as an electron travels through the crystal in response to an applied electrical potential, it cannot travel very far before it encounters and collides with a metal nucleus. The more often such encounters occur, the slower the net motion of the electron through the crystal, and the lower the conductivity. As the temperature of the solid increases, the metal atoms in the lattice acquire more and more kinetic energy. Because their positions are fixed in the lattice, however, the increased kinetic energy increases only

the extent to which they vibrate about their fixed positions. At higher temperatures, therefore, the metal nuclei collide with the mobile electrons more frequently and with greater energy, thus decreasing the conductivity. This effect is, however, substantially smaller than the increase in conductivity with temperature exhibited by semiconductors. For example, the conductivity of a tungsten wire decreases by a factor of only about two over the temperature range 750–1500 K, whereas the conductivity of silicon increases approximately 100-fold over the same temperature range. These trends are illustrated in Figure 3.4.6.

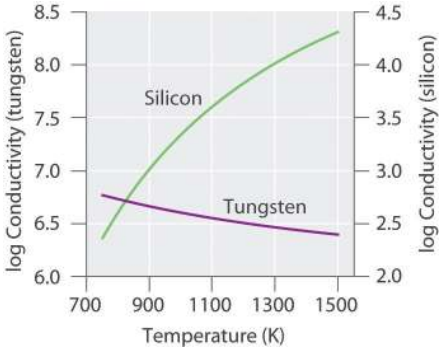


Figure 3.4.6: The Temperature Dependence of the Electrical Conductivity of a Metal versus a Semiconductor. The conductivity of the metal (tungsten) decreases relatively slowly with increasing temperature, whereas the conductivity of the semiconductor (silicon) increases much more rapidly.

n- and p-Type Semiconductors

Doping is a process used to tune the electrical properties of commercial semiconductors by deliberately introducing small amounts of impurities. If an impurity contains more valence electrons than the atoms of the host lattice (e.g., when small amounts of a group 15 atom are introduced into a crystal of a group 14 element), then the doped solid has more electrons available to conduct current than the pure host has. As shown in Figure 3.4.7*a*, adding an impurity such as phosphorus to a silicon crystal creates occasional electron-rich sites in the lattice. The electronic energy of these sites lies between those of the filled valence band and the empty conduction band but closer to the conduction band. Because the atoms that were introduced are surrounded by host atoms, and the electrons associated with the impurity are close in energy to the conduction band, those extra electrons are relatively easily excited into the empty conduction band of the host. Such a substance is called an n-type semiconductor, with the n indicating that the added charge carriers are negative (they are electrons).

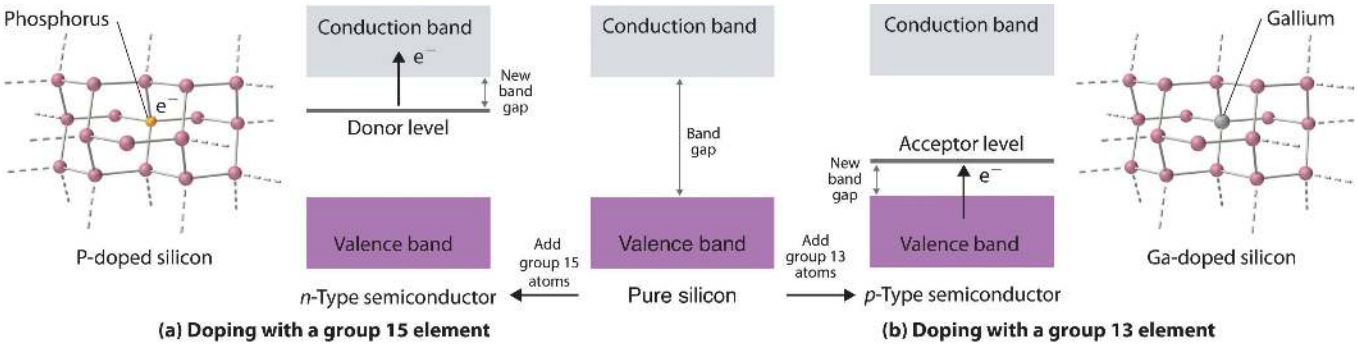


Figure 3.4.7: Structures and Band Diagrams of n-Type and p-Type Semiconductors. (a) Doping silicon with a group 15 element results in a new filled level between the valence and conduction bands of the host. (b) Doping silicon with a group 13 element results in a new empty level between the valence and conduction bands of the host. In both cases, the effective band gap is substantially decreased, and the electrical conductivity at a given temperature increases dramatically.

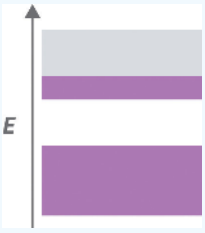
If the impurity atoms contain fewer valence electrons than the atoms of the host (e.g., when small amounts of a group 13 atom are introduced into a crystal of a group 14 element), then the doped solid has fewer electrons than the pure host. Perhaps unexpectedly, this also results in increased conductivity because the impurity atoms generate holes in the valence band. As shown in Figure 3.4.7*b*, adding an impurity such as gallium to a silicon crystal creates isolated electron-deficient sites in the host lattice. The electronic energy of these empty sites also lies between those of the filled valence band and the empty conduction band of the host but much closer to the filled valence band. It is therefore relatively easy to excite electrons from the valence band of the host to the isolated impurity atoms, thus forming holes in the valence band. This kind of substance is called a *p-type semiconductor*, with the p standing for positive charge carrier (i.e., a hole). Holes in what was a filled band are just as effective as electrons in an empty band at conducting electricity.

The electrical conductivity of a semiconductor is roughly proportional to the number of charge carriers, so doping is a precise way to adjust the conductivity of a semiconductor over a wide range. The entire semiconductor industry is built on methods for preparing samples of Si, Ge, or GaAs doped with precise amounts of desired impurities and assembling silicon chips and other complex devices with junctions between n- and p-type semiconductors in varying numbers and arrangements.

Because silicon does not stand up well to temperatures above approximately 100°C, scientists have been interested in developing semiconductors made from diamonds, a more thermally stable material. A new method has been developed based on vapor deposition, in which a gaseous mixture is heated to a high temperature to produce carbon that then condenses on a diamond kernel. This is the same method now used to create cultured diamonds, which are indistinguishable from natural diamonds. The diamonds are heated to more than 2000°C under high pressure to harden them even further. Doping the diamonds with boron has produced p-type semiconductors, whereas doping them with boron and deuterium achieves n-type behavior. Because of their thermal stability, diamond semiconductors have potential uses as microprocessors in high-voltage applications.

Example 3.4.1

A crystalline solid has the following band structure, with the purple areas representing regions occupied by electrons. The lower band is completely occupied by electrons, and the upper level is about one-third filled with electrons.



a. Predict the electrical properties of this solid.
b. What would happen to the electrical properties if all of the electrons were removed from the upper band? Would you use a chemical oxidant or reductant to effect this change?
c. What would happen to the electrical properties if enough electrons were added to completely fill the upper band? Would you use a chemical oxidant or reductant to effect this change?

Given: band structure

Asked for: variations in electrical properties with conditions

Strategy:

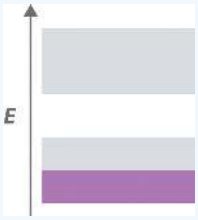
A. **B**ased on the occupancy of the lower and upper bands, predict whether the substance will be an electrical conductor. Then predict how its conductivity will change with temperature.
B. After all the electrons are removed from the upper band, predict how the band gap would affect the electrical properties of the material. Determine whether you would use a chemical oxidant or reductant to remove electrons from the upper band.
C. Predict the effect of a filled upper band on the electrical properties of the solid. Then decide whether you would use an oxidant or a reductant to fill the upper band.

Solution:

A. The material has a partially filled band, which is critical for metallic behavior. The solid will therefore behave like a metal, with high electrical conductivity that decreases slightly with increasing temperature.
B. Removing all of the electrons from the partially filled upper band would create a solid with a filled lower band and an empty upper band, separated by an energy gap. If the band gap is large, the material will be an electrical insulator. If the gap is relatively small, the substance will be a semiconductor whose electrical conductivity increases rapidly with increasing temperature. Removing the electrons would require an oxidant because oxidants accept electrons.
C. Adding enough electrons to completely fill the upper band would produce an electrical insulator. Without another empty band relatively close in energy above the filled band, semiconductor behavior would be impossible. Adding electrons to the solid would require a reductant because reductants are electron donors.

Exercise 3.4.1

A substance has the following band structure, in which the lower band is half-filled with electrons (purple area) and the upper band is empty.



a. Predict the electrical properties of the solid.
b. What would happen to the electrical properties if all of the electrons were removed from the lower band? Would you use a chemical oxidant or reductant to effect this change?
c. What would happen to the electrical properties if enough electrons were added to completely fill the lower band? Would you use a chemical oxidant or reductant to effect this change?

Answer:

a. The solid has a partially filled band, so it has the electrical properties of a conductor.
b. Removing all of the electrons from the lower band would produce an electrical insulator with two empty bands. An oxidant is required.
c. Adding enough electrons to completely fill the lower level would result in an electrical insulator if the energy gap between the upper and lower bands is relatively large, or a semiconductor if the band gap is relatively small. A reductant is required.

- Metallic behavior requires a set of delocalized orbitals and a band of allowed energy levels that is partially occupied.
- The electrical conductivity of a semiconductor increases with increasing temperature, whereas the electrical conductivity of a metal decreases with increasing temperature.
- n-Type semiconductors are negative charge carriers; the impurity has more valence electrons than the host. p-Type semiconductors are positive charge carriers; the impurity has fewer valence electrons than the host.

Summary

Band theory assumes that the valence orbitals of the atoms in a solid interact to generate a set of molecular orbitals that extend throughout the solid; the continuous set of allowed energy levels is an energy band. The difference in energy between the highest and lowest allowed levels within a given band is the bandwidth, and the difference in energy between the highest level of one band and the lowest level of the band above it is the band gap. If the width of adjacent bands is larger than the energy gap between them, overlapping bands result, in which molecular orbitals derived from two or more kinds of valence orbitals have similar energies. Metallic properties depend on a partially occupied band corresponding to a set of molecular orbitals that extend throughout the solid to form a band of energy levels. If a solid has a filled valence band with a relatively low-lying empty band above it (a conduction band), then electrons can be excited by thermal energy from the filled band into the vacant band where they can then migrate through the crystal, resulting in electrical conductivity. Electrical insulators are poor conductors because their valence bands are full. Semiconductors have electrical conductivities intermediate between those of insulators and metals. The electrical conductivity of semiconductors increases rapidly with increasing temperature, whereas the electrical conductivity of metals decreases slowly with increasing temperature. The properties of semiconductors can be modified by doping, or introducing impurities. Adding an element with more valence electrons than the atoms of the host populates the conduction band, resulting in an n-type semiconductor with increased electrical conductivity. Adding an element with fewer valence electrons than the atoms of the host generates holes in the valence band, resulting in a p-type semiconductor that also exhibits increased electrical conductivity.

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CHAPTER OVERVIEW

4: Acids and Bases

4.1: Lewis Acids and Bases

4.2: Molecular Orbital Theory and Lewis acid-base reactions

4.3: Hard and Soft Acids and Bases

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4.1: Lewis Acids and Bases

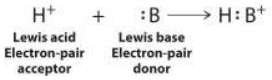
Learning Objectives

Make sure you thoroughly understand the following essential ideas which have been presented. It is especially important that you know the precise meanings of all the highlighted terms in the context of this topic.

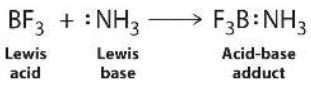
- Give an example of a **Lewis acid-base reaction** that does not involve protons.
- Write equations illustrating the behavior of a given **non-aqueous acid-base system**.

Lewis Acids and Bases

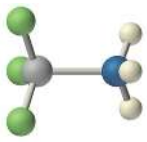
Electron-deficient molecules, such as BCl_3, contain less than an octet of electrons around one atom and have a strong tendency to gain an additional pair of electrons by reacting with substances that possess a lone pair of electrons. Lewis's definition, which is less restrictive than either the Brønsted–Lowry or the Arrhenius definition, grew out of his observation of this tendency. A general Brønsted–Lowry acid–base reaction can be depicted in Lewis electron symbols as follows:



The proton (H^+), which has no valence electrons, is a Lewis acid because it accepts a lone pair of electrons on the base to form a bond. The proton, however, is just one of many electron-deficient species that are known to react with bases. For example, neutral compounds of boron, aluminum, and the other Group 13 elements, which possess only six valence electrons, have a very strong tendency to gain an additional electron pair. Such compounds are therefore potent Lewis acids that react with an electron-pair donor such as ammonia to form an acid–base adduct, a new covalent bond, as shown here for boron trifluoride (BF_3):



The bond formed between a Lewis acid and a Lewis base is a *coordinate covalent bond* because both electrons are provided by only one of the atoms (N, in the case of $F_3B{:}NH_3$). After it is formed, however, a coordinate covalent bond behaves like any other covalent single bond.



Boron trifluoride-ammonia adduct

Species that are very weak Brønsted–Lowry bases can be relatively strong Lewis bases. For example, many of the group 13 trihalides are highly soluble in ethers (R–O–R′) because the oxygen atom in the ether contains two lone pairs of electrons, just as in H_2O. Hence the predominant species in solutions of electron-deficient trihalides in ether solvents is a Lewis acid–base adduct. A reaction of this type is shown in Figure 4.1.1 for boron trichloride and diethyl ether:

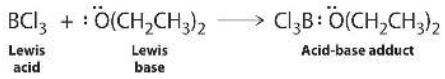


Figure 4.1.1: *Lewis Acid/Base reaction of boron trichloride and diethyl ether reaction*

Note

- Electron-deficient molecules (those with less than an octet of electrons) are Lewis acids.
- The acid-base behavior of many compounds can be explained by their Lewis electron structures.

Many molecules with multiple bonds can act as Lewis acids. In these cases, the Lewis base typically donates a pair of electrons to form a bond to the central atom of the molecule, while a pair of electrons displaced from the multiple bond becomes a lone pair on a terminal atom.

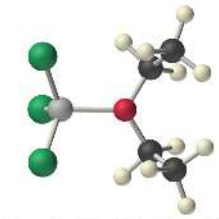


Figure 4.1.2. The highly electronegative oxygen atoms pull electron density away from carbon, so the carbon atom acts as a Lewis acid. Arrows indicate the direction of electron flow.

Example 4.1.1

Identify the acid and the base in each Lewis acid–base reaction.

a. $BH_3 + (CH_3)_2S \rightarrow H_3B{:}S(CH_3)_2$
b. $CaO + CO_2 \rightarrow CaCO_3$
c. $BeCl_2 + 2\ Cl^- \rightarrow BeCl_4^{2-}$

Given: reactants and products

Asked for: identity of Lewis acid and Lewis base

Strategy:

In each equation, identify the reactant that is electron deficient and the reactant that is an electron-pair donor. The electron-deficient compound is the Lewis acid, whereas the other is the Lewis base.

Solution:

a. In BH_3, boron has only six valence electrons. It is therefore electron deficient and can accept a lone pair. Like oxygen, the sulfur atom in $(CH_3)_2S$ has two lone pairs. Thus $(CH_3)_2S$ donates an electron pair on sulfur to the boron atom of BH_3. The Lewis base is $(CH_3)_2S$, and the Lewis acid is BH_3.
b. As in the reaction shown in Equation 8.21, CO_2 accepts a pair of electrons from the O^{2-} ion in CaO to form the carbonate ion. The oxygen in CaO is an electron-pair donor, so CaO is the Lewis base. Carbon accepts a pair of electrons, so CO_2 is the Lewis acid.
c. The chloride ion contains four lone pairs. In this reaction, each chloride ion donates one lone pair to $BeCl_2$, which has only four electrons around Be. Thus the chloride ions are Lewis bases, and $BeCl_2$ is the Lewis acid.

Exercise 4.1.1

Identify the acid and the base in each Lewis acid–base reaction.

a. $(CH_3)_2O + BF_3 \rightarrow (CH_3)_2O{:}BF_3$
b. $H_2O + SO_3 \rightarrow H_2SO_4$

Answer

a. Lewis base: $(CH_3)_2O$; Lewis acid: BF_3
b. Lewis base: H_2O; Lewis acid: SO_3

Exercise 4.1.2

Here are several more examples of Lewis acid-base reactions that **cannot** be accommodated within the Brønsted or Arrhenius models. Identify the Lewis acid and Lewis base in each reaction.

a. $Al(OH)_3 + OH^- \rightarrow Al(OH)_4^-$
b. $SnS_2 + S^{2-} \rightarrow SnS_3^{2-}$
c. $Cd(CN)_2 + 2CN^- \rightarrow Cd(CN)_4^{2+}$
d. $AgCl + 2NH_3 \rightarrow Ag(NH_3)_2^+ + Cl^-$
e. $Fe^{2+} + NO \rightarrow Fe(NO)^{2+}$

f. $[Ni^{2+} + 6NH_3 \rightarrow Ni(NH_3)_5^{2+}$

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4.2: Molecular Orbital Theory and Lewis acid-base reactions

A brief review of the Lewis acid-base theory

In this chapter we will discuss Lewis-acid base reactions from the perspective of molecular orbital theory. The Lewis acid-base concept has been developed by Gilbert Lewis (Fig. 4.1.1).



Figure 4.1.1 Gilbert Lewis (1875-1946) (Attribution: es una imagen de licencia libre, no tiene autor / CC BY-SA (https://creativecommons.org/licenses/by-sa/4.0) https://commons.wikimedia.org/wiki/F...wton-Lewis.jpg)

It is a very general acid-base concept, and includes the Broensted and Arrhenius acid-base concepts. It is very important for coordination chemistry. Let us briefly review what a Lewis acid, a Lewis base, and a Lewis acid-base reaction is.

A Lewis acid is defined as an electron pair acceptor.

Definition: Lewis Acid

A Lewis acid is an electron pair acceptor

A Lewis base is defined as an electron pair donor.

Definition: Lewis Base

A Lewis base is an electron pair donor

An example of a Lewis acid is BH_3, and an example for a Lewis base is NH_3. What happens in a Lewis-acid base reaction?

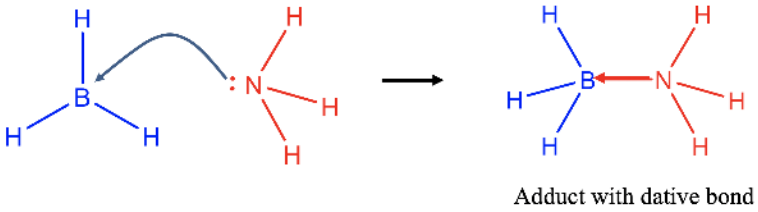


Figure 4.1.2 Acid-base reaction between NH_3 and BH_3

The Lewis base donates an electron pair to form a covalent bond with the Lewis acid (Fig. 4.1.2). A covalent bond formed in a Lewis acid-base reaction is usually called a dative bond because both electrons in the covalent bond come from a single partner. In a "conventional" covalent bond both partners contribute one electron to the covalent bond. There is however no fundamental difference between a “conventional” covalent bond and a dative covalent bond, it is just a matter of perspective. To indicate a dative bond one can draw an arrow pointing from the donor to the acceptor atom, instead of just a line. The reaction product of a Lewis acid-base reaction is called an adduct.

As mentioned previously, the Lewis acid-base concept is quite general and can explain the bonding in quite different compounds. It includes the Broensted acid-base concept, meaning that any Broensted acid is also a Lewis acid, and any Broensted base is also a Lewis base. However, the reverse is not true. Not every Lewis acid is a Broensted acid, and not every Lewis base is a Broensted base.

Here are a few examples that can illustrate the generality of the Lewis acid-base concept.

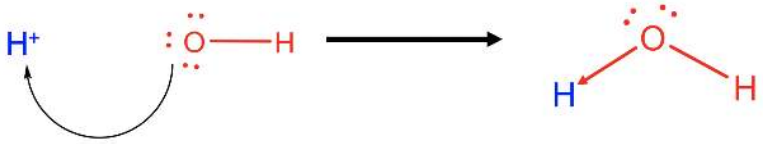


Figure 4.1.3 Acid-base reaction between H^+ and OH^-

For example, an H^+ ion is a Lewis acid and an OH^- anion is a Lewis base, and the two can react to form water as a Lewis-acid base adduct. In this case one of the O-H bonds in the water molecule would be viewed as a dative bond, while the other one would be viewed as a "regular" covalent bond. Of course, there is no actual difference between the two bonds, we just have a different perspective on them. The same reaction could also be viewed as a Broensted acid base reaction with the OH^- ion as the proton acceptor, and the H^+ ion as the proton donor.

The Lewis acid-base concept also explains bonding in coordination compounds, and the formation of coordination compounds from metal ions and ligands. The ligand is the Lewis base and the metal ion is the Lewis acid, the coordination compound is the Lewis acid-base adduct. The bond between the metal ion and ligand is a dative bond pointing from the ligand to the metal.

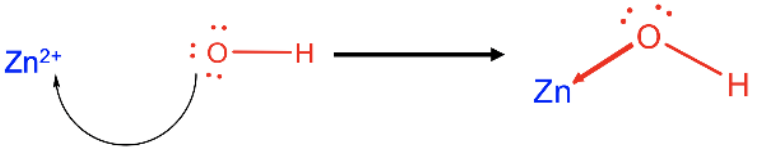


Figure 4.1.4 Acid-base reaction between Zn^{2+} and OH^-

For example, Zn^{2+} acts as a Lewis acid when reacting with 4 OH^- as a Lewis base to form tetrahydroxo zincate (2-) anions (Fig. 4.1.4). The formed Zn-O bonds are dative bonds indicated as arrows pointing from the O to the Zn.

The Lewis acid-base concept can even be used to explain bonding in ionic crystals. In this case the anion would be the donor and the cation the acceptor.

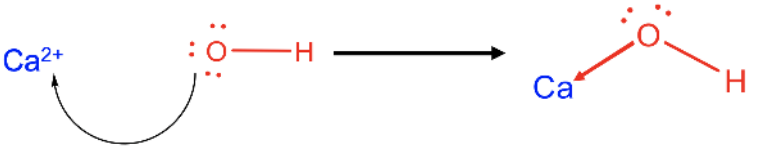


Figure 4.1.5 Acid-base reaction between Ca^{2+} and OH^-

For example Ca^{2+} can be viewed as a Lewis acid, and OH^- as a Lewis base in a reaction that forms calcium hydroxide $Ca(OH)_2$ as the Lewis acid-base adduct. The bonds between Ca^{2+} and OH^- would be viewed as a dative bonds indicated as arrows pointing from O to Ca. In this case the ionic bonds would be interpreted as highly polar dative bonds. You may want to remember in this context that completely ionic bonds are not possible in general, and there must also be some degree of covalency due to the finite electronegativity difference between two elements.

MO theory and Lewis Bases

MO theory is a theory designed to explain covalent bonding. Because dative bonds are covalent bonds, MO theory should be able to explain dative bonds. So how can Lewis acids and bases and their reactions be viewed from an MO theory perspective? MO theory states that a molecule is a Lewis base when its HOMO is approximately non-bonding (Fig. 4.1.6).

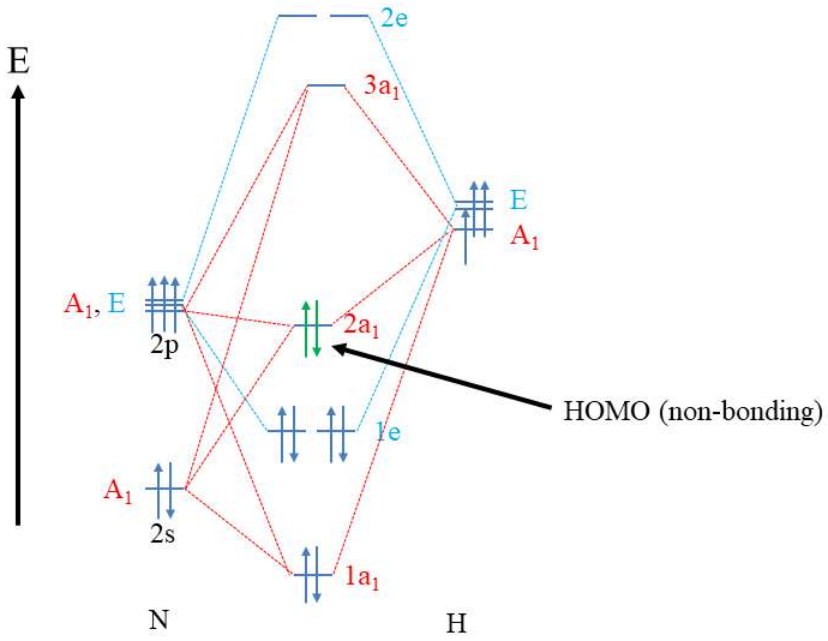


Figure 4.1.6 Molecular orbital diagram of NH_3

This explains, for example, that NH_3 is a Lewis base. Remember, its HOMO, the $2a_1$ orbital, is approximately non-bonding. Why does an approximately non-bonding HOMO make a molecule a Lewis base? Firstly, because the HOMO electrons are the highest energy electrons and thus the most reactive electrons, they get donated preferentially over all other electrons. The non-bonding nature of the HOMO is ideal, because if the HOMO was anti-bonding, the electrons would be so reactive, so that they would likely get completely transferred to the reaction partner. In this case we would not have a Lewis acid-base reaction, but a redox reaction. We would not form a covalent bond, but an ionic bond. If the HOMO was bonding, then the energy of the electrons would be too unreactive, simply no reaction would likely be observed.

MO theory and Lewis Acids

So what is then a Lewis acid according to MO theory? A Lewis acid, from the MO theory perspective, is a molecule that has an approximately non-bonding lowest unoccupied molecular orbital. The orbital needs to unoccupied, otherwise no electrons could be donated into it. For energy minimization arguments, electrons would be donated into the unoccupied orbital that has the lowest energy, which is the LUMO. So why is it ideal if the LUMO is non-bonding? If it was anti-bonding, its energy would likely be too high, and the donor would be unable to donate its electrons. There would not be a stabilization of electrons due to the high energy of the LUMO. The molecule would remain unreactive. If the LUMO was a bonding orbital, then its energy would likely be so low so that the electrons would likely be completely transferred to the Lewis acid. In this case we would not form a dative bond but an ionic bond via a redox reaction.

Bonding in Lewis Acid Base Adducts

The greatest covalent interaction between two orbitals it is achieved when both orbitals have the same energy. We learned this previously in Chapter 3 when we discussed the energy criterion. The same holds for dative bonds. The more similar the energies of the donor HOMO and the LUMO acceptor, the greater the covalent interaction. Ideally, the energies are exactly same. In this case we form a perfect covalent bond with the electrons equally shared between the donor and the acceptor. We can graphically illustrate this in an MO diagram the following way (Fig. 4.1.9).

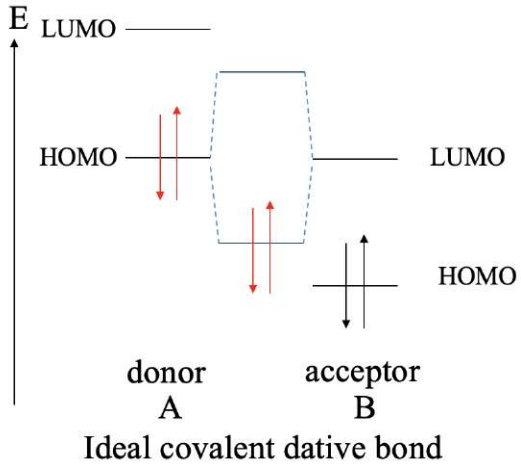


Figure 4.1.9 Covalent interaction between the HOMO of donor A and the LUMO of acceptor B with the same energy

Let us assume a molecule A that acts as a donor and a molecule B that acts as an acceptor. The donor A has a HOMO and a LUMO that have a certain energy. The acceptor molecule B also has a HOMO and a LUMO with the LUMO having the same energy as the HOMO of A. The molecule B will also have HOMO which is energetically below that LUMO. Because their identical energies the combination of the HOMO of A with the LUMO of B leads to a bonding MO and an anti-bonding MO with equally shared electron density. Both MOs have equidistant energy from the HOMO of A and the LUMO of B. The electrons coming from the HOMO of A will be in the bonding MO. They will be equally shared, and the dative bond is an ideal covalent bond.

The exact match of the HOMO and LUMO energies of the donor and acceptor is rarely achieved. Let us consider a number of scenarios in which these energies are not the same, and what consequences this has for the dative bond.

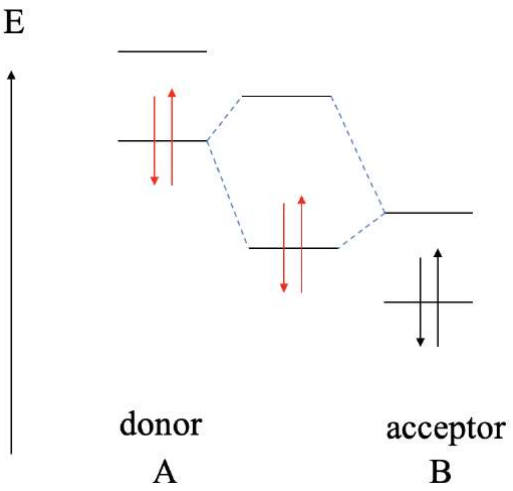


Figure 4.1.10 Covalent interaction between a LUMO of acceptor B that has somewhat lower energy than the HOMO of donor A

Let us assume next, that the LUMO of the acceptor B is somewhat lower than the HOMO of donor A. In this case, we can still form a bonding MO and an anti-bonding MO due to covalent interaction between the HOMO of A and the LUMO of B. However, now the bonding MO will be localized primarily at B, and the anti-bonding MO will be localized mostly at A. The electrons from the HOMO of A will be in the bonding MO, and thus the bonding electrons in the dative bond will be localized mostly at B. This means that the dative bond is polar, and polarized toward the acceptor.

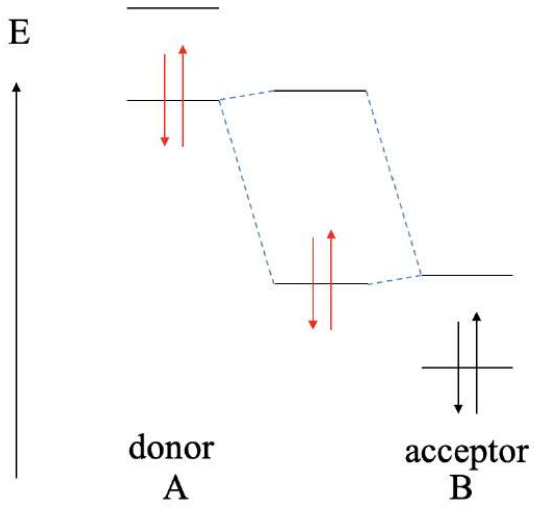


Figure 4.1.11 Covalent interaction between a LUMO of the acceptor that is much lower energy than the HOMO of the donor

Let us consider next, what the bonding will be if the LUMO of the acceptor is much lower than the HOMO of the donor (Fig. 4.1.11). In this case, there is still the possibility to form a bonding MO and an anti-bonding MO, but the bonding MO will be localized practically exclusively at the acceptor, and the anti-bonding MO will be localized practically completely ar the donor. The electrons from the donor will be in the bonding MO, but because the bonding MO is located almost entirely at the acceptor, the electrons are transferred completely from A to B in a redox reaction, and the bonding will be ionic, and we have an ionic compound AB made of A^{2+} cations and B^{2-} anions. This reaction would no longer be considered a Lewis acid-base reaction, and the reaction product will no longer be considered a Lewis acid-base adduct.

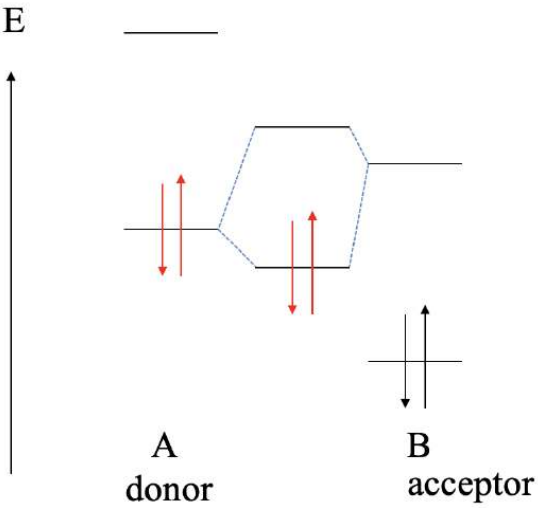


Figure 4.1.12 Covalent interaction when the LUMO of the acceptor B is higher in energy than the HOMO of donor A

The next possibility to consider is that the LUMO of B is higher in energy than the HOMO of A (Fig. 4.1.12). In this case the bonding MO will be localized primarily at the donor A and the electrons in the dative bond will be predominantly at A. We have a polar, dative bond which is polarized toward A.

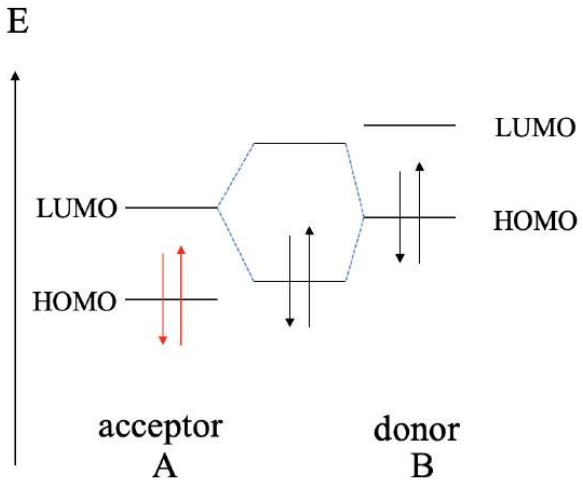


Figure 4.1.13 Covalent interaction when the LUMO of A is of similar energy compared to the HOMO of B and the LUMO of B is energetically much higher than the LUMO of A.

Next, let us raise the energy of the HOMO and the LUMO of B even higher. This leads to the fact that now the HOMO of B is energetically closer to the LUMO of A, compared to the energy difference between the HOMO of A and the LUMO of B. This results in the fact that the interaction will be mostly between the HOMO of B and and the LUMO of A. As a consequence, B will act now as the donor, and A will act as the acceptor. The dative bond may be polarized toward A or B, or not be polar at all depending on the relative energy of the HOMO of B and the LUMO of A.

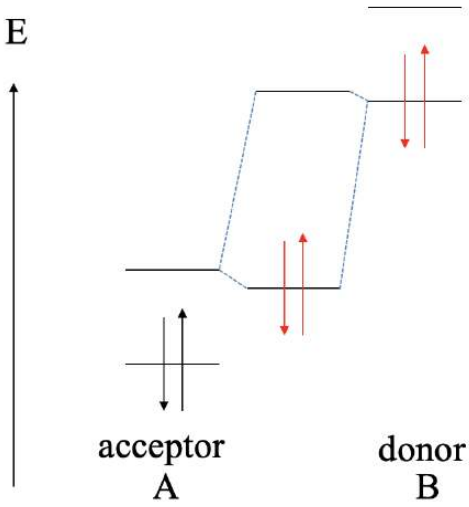


Figure 4.1.14 Covalent interaction between LUMO of acceptor A and HOMO of donor B, when the HOMO of B is much higher in energy than the HOMO of A

If we raise the orbital energies of B even further, and the HOMO of B is much higher than the HOMO of A, then we will get a redox reaction. B gets oxidized, and A gets reduced. B^{2+} cations and A^{2-} anions will form an ionic compound of the composition AB.

Examples

Generally spoken, the relative HOMO and LUMO energies of reaction partners decide if a Lewis acid-base, or a redox reaction takes place, and what the polarity of the bond is. Here are a few examples that will illustrate our general considerations (Fig. 4.1.15).

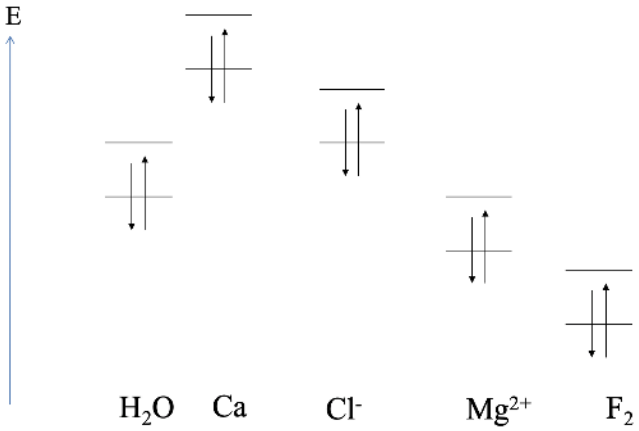


Figure 4.1.15 Practical examples of covalent Lewis acid-base reactions

The relative orbital energies of the highest occupied atomic orbitals and the lowest unoccupied atomic orbitals of calcium, and the HOMO and LUMO energies of H_2O are shown (Fig. 4.1.15). Can we predict the type of reaction? We can see that the highest occupied Ca orbital has a much higher energy than the LUMO of water. We would therefore expect that Ca gets oxidized, and water gets reduced. An ionic compound would be expected. This is what actually happens in experiment. The reaction of water and calcium yields calcium hydroxide and hydrogen gas.

Next, let us consider a possible reaction between water and chloride. We can see that the HOMO of Cl^- is similar in energy compared to the LUMO of H_2O. We would therefore expect a Lewis acid-base interaction with Cl^- as the donor and H_2O as the acceptor. Such an interaction indeed occurs in aqueous solutions containing Cl^- in the form of weak hydrogen bonding between Cl^- and H_2O.

Next, let us consider the interactions between Mg^{2+} and H_2O. In this case the LUMO of Mg^{2+} has about the energy of the HOMO of the water molecule. We would therefore expect that the water molecule acts as the donor and the Mg^{2+} acts as the acceptor. Indeed, Mg^{2+} forms a hexaaqua complex with water, which has the composition $Mg(H_2O)_6^{2+}$. The bonding should be very little polar.

Lastly, what are the interactions between F_2 and H_2O? The HOMO of H_2O is much higher than the LUMO of F_2. We would therefore expect a redox reaction in which F_2 is reduced, and H_2O is oxidized. In reality F_2 can oxidize H_2O to form OF_2 and HF.

From the above examples it becomes also clear that we cannot necessarily predict the strength of the Lewis-acid base interactions. For example, the hydrogen bonding between H_2O and Cl^- is much weaker than the dative bonds between H_2O and Mg^{2+}. Other factors such as orbital overlap also need to be taken into consideration to make statements about the strength of the interactions.

Dr. Kai Landskron (Lehigh University). If you like this textbook, please consider to make a donation to support the author's research at Lehigh University: Click Here to Donate.

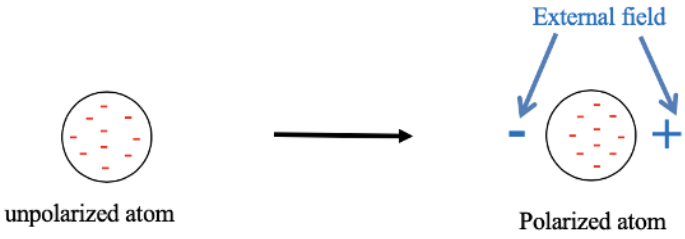
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4.3: Hard and Soft Acids and Bases

The Hard and Soft Bases Concept (HSAB)

The hard and soft acid and base concept (HSAB) can be conceived as a refinement of the Lewis-acid and base concept. Its most useful feature is that it can make predictions about the strength of the acid-base interactions. It can also estimate if the interactions are more ionic or more more covalent.



4.2.1 Visual representation of a unpolarized atom and an atom polarized in an electric field.

Let us first clarify what is meant by hard and soft, respectively. These terms refer to the polarizability of the electrons in an atom or a molecule (Fig. 4.2.1). An atom is soft when its electrons are easily polarizable. This means that the electron cloud easily deforms in an electric field. Easy deformation is consistent with the term “soft”. In an electric field the negatively charged electrons are attracted to the positive pole of the electric field. Therefore, the electron cloud distorts toward the positive end of the electric field, and the atom is polarized. Vice versa, when the electron cloud is not easily polarizable, we say the atom is hard. What is then meant by a hard and a soft acid or base? A hard or soft acid is a hard or soft Lewis acid, and a hard or soft base is a hard or soft Lewis base. As mentioned previously, the HSAB concept is useful because it make statements about the strength of the acid-base interactions, and thus the strength of the bonds. It can also make statements on whether the bonding is more covalent or more ionic (Fig. 4.2.2).

Hard-hard interactions: strong (mostly ionic)
Soft-soft interactions: strong (mostly covalent)
Hard-soft interactions: weak

Figure 4.2.2 Relationships between the hardness of acids and bases, and the strength and nature of the acid-base interactions

Generally, hard-hard interactions, meaning the interactions between a hard acid and a hard base, tend to be strong. The bonding is more likely ionic. Soft-soft interactions also tend to be strong, but they are more likely covalent. Hard-soft interactions tend to be weak.

Species with large donor/acceptor atoms: soft
Species with small donor/acceptor atoms: hard

Figure 4.2.3 Size of donor atoms affect on hard-soft behavior

Why are soft-soft and hard-hard interactions strong, while hard-soft interactions are weak? To answer this question, we must first understand what makes and acid or base hard or soft. Generally, we can say that the more delocalized the electrons are, the softer the species. For a single atom or ion this means that the larger the atom or ion is the softer the species. The larger the atom size, the more delocalized are its valence electrons. The size of a neutral atom is defined by its position in the periodic table. Generally, the higher the period, the softer the atom (Fig. 4.2.3).

For cations:
Higher positive charge → smaller radius → higher hardness

For anions:
Higher charge → larger radius → smaller hardness

Figure 4.2.4 Effect of charge on hard-soft behavior

For ions, also the charge plays a role. For cations, a higher positive charge makes a cation harder, for anions a higher negative charge makes the anion softer (Fig. 4.2.4).

If species is large, then it can nonetheless be hard if no orbitals are available for π-bonding (e.g. Cs^+ is hard acid).

If species is small, then it can be soft when orbitals for π-bonding is available (e.g. d orbitals can be used for π-bonding: Cu^+ is soft acid, or π-orbitals can be used, e.g. CN^- ,CO are soft bases).

Figure 4.2.5 π-bonding effect on hard-soft behavior

The size of the donor/acceptor atom is not the only factor that determines the hardness. Also the ability of the species to make π-bonding is important. Species that have orbitals suitable for π-bonding tend to be soft even if size arguments suggest that they are hard. This is because π-bonding increases electron delocalization (Fig. 4.2.5).

For example, transition metals have d-orbitals available which are suitable for π-bonding with ligands, while alkali metals do not. Therefore, a relatively small transition metal cation such as Cu^+ is softer than large alkali metal ions such as Cs^+. For anions π-bonding is also important. For instance, CN^- anions are soft bases even though the donor carbon atom is small because the CN^- ligand has π-orbitals available for π-bonding with Lewis acids.

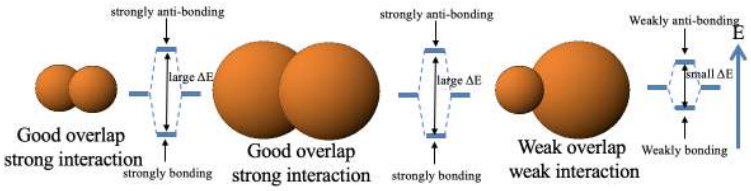


Figure 4.2.6 Orbital overlap criterion

So back to the question: Why are soft-soft and hard-hard interactions strong, but hard-soft interactions weak? This essentially boils down to rule 2 of the orbital overlap criterion (see chapter 3 on MO theory). Two small orbitals have typically good overlap, and two large orbitals also have good orbital overlap, and thus the interaction is strong. However, large and small orbitals tend to have weak orbital overlap, and thus the bonding weak.

Now to the question of why soft-soft interactions tend to be more covalent, while hard-hard interactions tend to be more ionic. The answer has to do with the fact that in smaller atoms the energy differences between atomic orbitals tends to be larger compared to large atoms. As a consequence, it is statistically more likely that the HOMO and LUMO of two soft species have more similar energies compared to two hard species. When the HOMO and LUMO of a Lewis acid and a Lewis base are similar in energy, then the bonding is more covalent. When they are significantly different, then the bonding is more ionic.

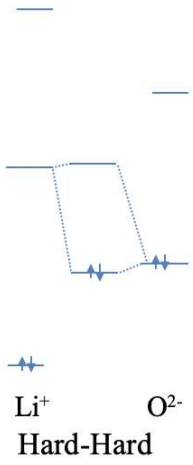


Figure 4.2.7 Hard-hard covalent interactions in lithium oxide

Let us illustrate this by two qualitiative examples. Lithium oxide is made of O^{2-} anions and Li^+ cations. If we view the ionic bonding between the O^{2-} and the Li^+ ions as an extreme case of a polar, dative bond, then oxide anion acts as a Lewis base, and the Li^+ ion acts as a Lewis acid. How can the high ionicity be explained? Both the Li^+ and the O^{2-} are small ions, thus they are both hard. The small size also implies that the energy differences between the atomic orbitals are large. Because of this, it is unlikely that the highest occupied atomic orbital of the O^{2-} ion has a similar energy than the lowest unoccupied atomic orbital of the Li^+ ion. Due to the large energy difference, the bonding MO will be localized almost completely at the O^{2-} anion, and the bonding will be ionic (Fig. 4.2.7).

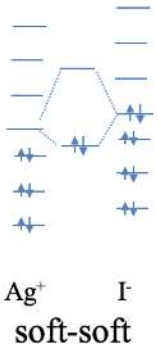


Figure 4.2.8 Soft-soft covalent interactions in silver iodide

An example of a compound with strong soft-soft-interactions is silver iodide. While AgI is considered an ionic compound, the interactions have a significantly stronger covalent character. The soft nature of Ag^+ is readily understood from the fact that Ag^+ is a period 5 transition metal ion with low positive charge, and d-orbitals available for π-bonding. Iodine is a period 6 element, thus iodide is quite soft. Because Ag and I are elements of period 5 and 6, respectively, their orbital energy differences are significantly smaller than those of O and Li which are period 2 elements. Thus, the HOMO of I^- and the LUMO of Ag^+ are naturally closer in energy resulting in a more covalent interaction (Fig. 4.2.8).

We should be aware that we need to treat these considerations with caution. For example, B-O bonds are fairly covalent bonds despite the fact that B and O are both quite hard. The HOMO of the donor and the LUMO of the acceptor of hard species are not necessarily much different. Other parameters such as electronegativity differences also weigh in and must be taken into account to correctly predict the nature of the chemical bond.

Examples - Bases

To get a feeling for correctly estimating the hardness of a species let us consider a few examples. Let us start with some bases.

F^- Cl^- Br^- I^-

Figure 4.2.9 Example of bases

What statements about hardness can you make for the series F^-, Cl^-, Br^-, I^- (Fig. 4.2.9). They are all halogenide ions with the same negative charge. The size increases from fluoride to chloride, to bromide to iodide. Thus, the softness should increase in the same order. F^- is a small ion with a small negative charge and should be be hard, I is a very heavy element therefore I^- is very soft. Cl^- and Br^- are moderately hard, and soft ions, respectively.

H_2O OH^- O^{2-} CH_3O^- PhO^-

Figure 4.2.10 Example series with O donor atoms

Next, consider the series H_2O, OH^-, O^{2-}, CH_3O^-, and PhO^-. All of the species contain small O donor atoms, so all of them should be considered hard. The OH^- ion is somewhat softer than the H_2O because of the negative charge that increases the size of the donor O atom. For the same reason O^{2-} is somewhat softer than OH^-. CH_3O^- is somewhat softer than O^{2-} because of the positive inductive effect of the methyl group. The phenolate ion is the softest because the negative charge at O can be delocalized in the aromatic ring. The delocalization of the negative charge leads to a greater polarizability, and thus softness. We could also think about if F^- would likely be harder or softer than H_2O. F is a little smaller than O, but F carries a negative charge, so the case is ambiguous.

NH_3 CH_3NH_2 $PhNH_2$

Figure 4.2.11 Example series with N donor atoms

Next, let us look at the series NH_3, CH_3NH_2, and $PhNH_2$ (Fig. 4.2.11). The N donor atom is a small, little polarizable atom, thus the species should be regarded hard. N is somewhat larger than O though, which means that NH_3 is somewhat softer than H_2O. CH_3NH_2 would be a bit softer than NH_3 because the positive inductive effect of the methyl group, and aniline would be a bit softer than methyl amine because of possibility to delocalize the lone pair at N in the aromatic ring.

H_2S RSH, RSR

Figure 4.2.12 Example series with S donor atoms

What about H_2S, alkyl thiols and di alkyl thiols (4.2.12)? The S donor atom is in the 3rd period, and large enough to be considered soft. The softness would be expected to somewhat increase from H_2S to R-SH to R-S-R because of the positive inductive effect of the alkyl group.

PR_3

Figure 4.2.13 Example of PR_3

The next example is a phospine of the general formula PR_3 (4.2.13). Like sulfur, phosphorus is a period 3 donor atom, and phosphines are generally soft.

$CO \qquad CN^-$

Figure 4.2.14 Example series with C donor atoms

Lastly, let us look at carbon monoxide and cyanide (Fig. 4.2.14). At first glance these species appear like hard bases because of the small carbon donor atoms. However, they are actually quite soft because of their ability to use their π and π* orbitals in π-bonding with Lewis acids, in particular transition metal ions. We will look closer at this issue later when we discuss the bonding in transition metal complexes in detail.

Example - Acids

Now let us think about the hardness of acids.

$H^+ \qquad Li^+ \qquad Na^+ \qquad K^+$

Figure 4.2.15 Example series of alkali metal cations

In the series H^+, Li^+, Na^+, K^+: Are these hard or soft acids and how does the hardness change within this series (Fig. 4.2.15)? The answer is: All alkali metal cations are considered hard acids, even the relatively large K^+ cation in the 4th period. This is because alkali metal cations have only s-valence orbitals and thus a lack of orbitals suitable for π-bonding. Within the series H^+ is the hardest and K^+ is the softest because the ionic radius increases with increasing period.

$Be^{2+} \qquad Mg^{2+} \qquad Ca^{2+}$

Figure 4.2.16 Example series of earth alkali metal cations

Similarly, the earth alkaline metals Be^{2+}, Mg^{2+}, and Ca^{2+} are hard cations with the hardness decreasing from Be^{2+} to Ca^{2+}. Due the the 2+ charge earth alkaline metal cations are expected harder than alkali metal cations of the same period, for example Be^{2+} should be estimated harder than Li^+.

$BF_3 \qquad BCl_3 \qquad B(CH_3)_3 \qquad BH_3$

Figure 4.2.17 Example series with boron

In the next series BF_3, BCl_3, $B(CH_3)$, and BH_3 the hardness declines from BF_3 to BH_3 (Fig. 4.2.17). BCl_3 is a softer than BF_3 because of the smaller electronegativity of Cl versus F. The more electronegative F withdraws more electron density from the boron making it smaller, and thus harder. Because of the positive inductive effect, the $B(CH_3)_3$ is softer than BCl_3. The BF_3 and BCl_3 molecules are considered hard acids overall, the $B(CH_3)_3$ is an intermediate case. At first glance, it would appear that BH_3 is harder than $B(CH_3)_3$, nonetheless it acts more like a soft acid, possibly because of the hydride-like character of the compound.

$Fe^{2+} \qquad Fe^{3+} \qquad Co^{2+} \qquad Co^{3+} \qquad Rh^{3+} \qquad Ir^{3+}$

Figure 4.2.18 Example series with transition metal ions

Next let us consider the transition metal ion series Fe^{2+}, Fe^{3+}, Co^{2+}, Co^{3+}, Rh^{3+}, Ir^{3+} (Fig. 4.2.18). These cations have the ability to make π-bonding, but because of the higher 2+ and 3+ charge respectively, none of them are soft. All period 4 cations with a 3+ charge, namely Fe^{3+} and Co^{3+} are hard acids, the Fe^{2+} and Co^{2+} ions are at the borderline between hard and soft due to their lower charge. Rh^{3+} and Ir^{3+} are also at the borderline. They have a higher positive charge, but are in period 5 and 6, respectively. Rh^{3+} would be expected to be harder than Ir^{3+} because it is in a lower period.

$Ti^{4+} \qquad Si^{4+}$

Figure 4.2.19 Example series of transition metals with 4+ charges

Ti^{4+} and Si^{4+} are both hard acids (Fig. 4.2.19). Generally, all ions with a charge of +4 or higher are hard acids.

Cu^{+} Cd^{2+} Hg^{2+} Pd^{2+} Pt^{2+}

Figure 4.2.20 Example series of period 4 transition metal ions

What about the last series Cu^{+}, Cd^{2+}, Hg^{2+}, Pd^{2+}, and Pt^{2+} (Fig,. 4.2.20)? Think about it. They are all considered soft acids. Cu^{+} is a relatively low period 4 element, but has only a 1+ charge, and has d-orbitals for π-bonding. Hg^{2+}, Pd^{2+}, and Pt^{2+} have a somewhat higher 2+ charge, but are period 5 and 6 elements, and also have d-orbitals for π-bonding. Pt^{2+} would be expected softer than Pd^{2+} because of its higher period.

Quantitative Measures for Hardness

Note that there is a quantitative measure for the Hardness of a Lewis acid and Lewis base. For the time being, it is enough to recognize that such a quantitative scale exists, and focus instead on the qualitative understanding of the concept and how it can be useful in explaining some observable phenomena.

The HSAB Concept and Solubilities

Because the HSAB concept can estimate the strength of the interactions between Lewis acids and Lewis bases, it can also estimate a number of other properties that derive from this strength of interactions. For example, it can be used to estimate solubilities. When the Lewis acid-base interaction between cation and anion is strong we would expect low solubility, when the interaction is weak then we would expect high solubility.

$$\text{Solubility in } H_2O : AgI < AgBr < AgCl < AgF$$

Figure 4.2.23 Solubility of silver halogenides

For example, it is know that the solubility of silver halogenides in water increases from AgI to AgBr to AgCl to AgF (Fig. 4.2.23). This is in accordance with the HSAB concept. Ag^{+} is considered soft, and thus it would make the strongest interactions with the softest anion, the iodide I^{-}. Ag^{+} would make the weakest interactions with F^{-}, because it is the hardest.

$$\text{HSAB would expect LiI} > \text{LiBr} > \text{LiCl} > \text{LiF}$$
$$\text{Found: LiBr} > \text{LiCl} > \text{LiI} > \text{LiF}$$

Figure 4.2.24 Solubility of lithium halogenides

What would be our expectations for the lithium halogenides (Fig. 4.2.24)? In this case, we would expect the solubility to decline from LiI to LiBr, to LiCl, to LiF. Why? This is because Li^{+} is a hard cation, and thus the strongest interactions should result with F^{-}. Consequently, LiF would have the lowest solubility. I^{-} is the softest anion, thus it should make the weakest interactions with Li^{+}.Consequently, the LiI would have the highest solubility. Is this what we observe experimentally? The experimentally greatest observed solubility is that of LiBr, followed by LiCl, followed by LiI. LiF has the lowest solubility. We can see that the LiI solubility is not what we expected. Instead of having the highest solubility, it has the second-lowest solubility. We can see here the limitations of the HSAB concept. There are also other factors that determine solubility, in particular solvation enthalpy. I^{-} has a very low hydration enthalpy, which explains the lower than expected LiI solubility. In a way, the HSAB concept is able to explain the low hydration enthalpy of I^{-} because it is based on the strength of interaction between I^{-} and water. The water is a hard acid and therefore interacts only weakly with a soft base like I^{-}. This can serve as an explanation for the low hydration enthalpy.

Another good example to illustrate the effects of solvation enthalpy on solubility is the solubility of the silver halogenides in liquid ammonia (not aqueous ammonia). It is actually reversed, the AgF has the smallest solubility , and the AgI has the highest solubility. The HSAB interaction between Ag^{+} and the halogenide ions are the same no matter of the solvent. Therefore, they cannot serve as an explanation. Rather, we can argue that the reverse enthalpies of solvation in liquid ammonia compared to liquid water are responsible for the inverse behavior. From the standpoint of HSAB, the ammonia molecules are already significantly softer than the water molecules, therefore interactions with the soft anions become significantly stronger.

The HSAB Concept and Stability

The HSAB concept can also be used to estimate thermodynamic stabilities of compounds, such as decomposition points, melting points etc. Generally, the greater the acid-base interactions the greater the expected thermodynamic stability. Let us do couple of exercises to practice this concept.

$$Li_2O > Na_2O > K_2O > Rb_2O > Cs_2O$$

Figure 4.2.25 Thermodynamic stability for alkali oxides

What order of thermodynamic stability would you expect for the alkali oxides (Fig. 4.2.25)? The answer is: The stability declines with increasing period of the alkali metal. Why? The oxide anion is considered a hard base due to its relatively small radius. Thus, the strongest interactions are expected with the Li^+ which is the hardest alkali metal, and the weakest interactions would be expected for the Cs^+ which is the softest alkali metal. This is in line with experimental observations. Only Li gives Li_2O when burned in O_2, Na gives sodium peroxide and the remaining alkali metals give superoxides.

$$BeO > MgO > CaO > SrO > BaO$$

Figure 4.2.26 Thermodynamic stability for earth alkali oxides

We can ask the same question for the earth alkaline oxides (Fig. 4.2.26). Similarly, the stability of BeO is the highest because Be has the highest hardness. BaO has the lowest stability because Ba^{2+} is the softest earth alkali cation. Ba gives barium peroxide instead of barium oxide when burned in O_2.

The HSAB Concept and Acidity

The HSAB concept can also explain Brønsted acidity. How?

$$\text{Acidity: } H_2O < H_2S < H_2Se$$

Figure 4.2.27 Acidity of the series of H_2O, H_2S, and H_2Se

Let us look at the series H_2O, H_2S, and H_2Se (Fig. 4.2.27). The Brønsted acidity increases from H_2O to H_2S to H_2Se. Why? H^+ is a hard acid, and therefore the strongest interactions would be expected with the hardest base, the oxide ion, and the weakest interactions would be expected with the softest base, the Se^{2-} anion. Therefore, H_2Se loses a proton most easily, making it the strongest acid. For H_2O the acidity is the smallest because the interactions between H^+ and O^{2-} are the greatest.

$$HClO_4 > HClO_3 > HClO_2 > HClO$$

Figure 4.2.28 Acidity of the series of $HClO_4$ to $HClO_3$ to $HClO_2$ to HClO

Let us go to a somewhat more complicated example (Fig. 4.2.28). The acidity of perchloric acid, chloric acid, chlorous acid, and hypochlorous acid declines from $HClO_4$ to $HClO_3$ to $HClO_2$ to HClO. In this case all protons are bound to oxygen, so we cannot argue as before. However, we can argue that the negative charge in the anions of the acids is most delocalized in the case of the perchloric acid because the greatest number of resonance structures can be drawn for perchloric acid. Because the negative charge is most delocalized, the electron is most polarizable, and thus the softest. For the hypochloric acid we have the opposite case. There is no electron delocalization possible and only one resonance structure can be drawn for the hypochlorite anion. It is therefore the hardest, interacting the strongest with the proton.

$$NH_3 < PH_3 < AsH_3$$

Figure 4.2.29 Basicity of the series of NH_3, PH_3, and AsH_3

Lastly, let us think about the relative basicity of NH_3, PH_3, and AsH_3 (Fig. 4.2.29)? The N atom is the hardest base, and the interactions with protons are the strongest. Therefore, NH_3 is the strongest base. AsH_3 is the weakest base because As is the softest atom making the weakest interactions with protons.

Dr. Kai Landskron (Lehigh University). If you like this textbook, please consider to make a donation to support the author's research at Lehigh University: Click Here to Donate.

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CHAPTER OVERVIEW

5: Transition Metal Complexes

5.1: History

5.2: Nomenclature

5.3: Isomerism

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5.1: History

Coordination Chemistry

Now let us direct our focus toward actual coordination chemistry, also often called complex chemistry. In the following, we will apply the previously learned concepts about atomic theory, symmetry, molecular orbital theory, and acid-base chemistry to coordination compounds. Let us first ask: How are coordination compounds, or complexes defined? They are typically Lewis-acid base adducts between a metal atom or a metal ion as the Lewis acid and one or more ligands as a Lewis base. These ligands can be inorganic ligands such as halogenide ions, water, and ammonia molecules, or organic ligands like amines or alcohols. Coordination compounds are known since the antique due to their often intense color, and are used as a pigment or dye, for example Prussian Blue ($KFe[Fe(CN)_6]$ or tetrammine copper, both of which are intensely blue. You can see a few examples of coordination compounds below, namely the hexahydrate of copper (II) sulfate which is blue, iron (III) chloride, which is yellow, and nickel sulfate which is greenish-blue. Because of their intense color they have also attracted the attention of modern chemists from the early on, but the chemical bonding in these compounds remained a mystery for a relatively long time. The bonding in these compounds seemed more complex, hence the name complex compounds.



Figure 5.1.1 $Cu(SO_4)$ x 5 H_2O (Attribution: No machine-readable author provided. Yuvalif assumed (based on copyright claims). / Public domain https://commons.wikimedia.org/wiki/F...er-Sulfate.JPG), $FeCl_3$ x 6 H_2O (Attribution: Benjah-bmm27 / Public domain https://commons.wikimedia.org/wiki/F...ate-sample.jpg) and $NiSO_4$ x 6 H_2O (Attribution: Benjah-bmm27 / Public domain https://commons.wikimedia.org/wiki/F...ate-sample.jpg), respectively

History on Coordination Compounds

What was the problem with the bonding in coordination compounds? Their empirical formulas could be easily determined by element analysis, but the results could not be explained with the concept of valence. In the early days of modern chemistry it was believed that the number of bonds in a compound could not exceed the valence. For example, in the compound of the formula $Co(NH_3)_6Cl_3$ the valence of Co would be +3, therefore cobalt could not make more than three bonds. Assuming that the Co^{3+} ion would make three bonds to the 3 Cl^- ions, how would one involve the six NH_3 molecules in the bonding?



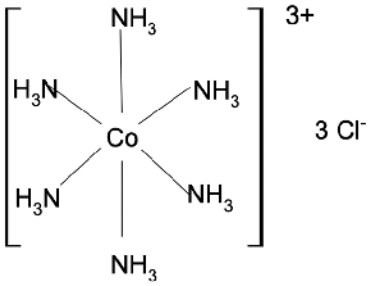
Figure 5.1.2 Alfred Werner (1866-1919) (Attribution: ETH Zürich / CC BY-SA (https://creativecommons.org/licenses/by-sa/3.0) https://commons.wikimedia.org/wiki/F...ortr_09965.jpg)

The chemist who solved this mystery was Alfred Werner. He correctly suggested that the number of bonds would not be restricted to the valence, but that more bonds would be allowed. It would be possible that the six NH_3 molecules bind directly to Co^{3+} forming a so-called complex cation. They would be in the so-called first coordination sphere around the Co. The three chloride ions

would then be bound loosely to the complex cation balancing the charge of the complex cation. They would be in the second coordination sphere.

Formula Writing in Coordination Chemistry

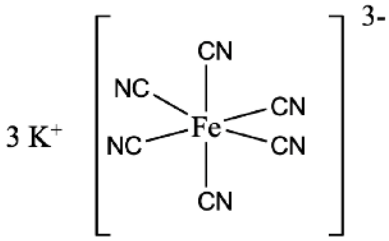
How can we write a formula of a coordination compound that contains complex ions?



$[Co(NH_3)_6]Cl_3$

Figure 5.1.3 Example of complex cation notation

For complex cations we write the element symbol for the metal ion first followed by the formula for the ligands. If there is more than one ligand, then we will place the ligands in parentheses, and indicate their number by a subscript behind the parentheses. The entire complex cation is placed in brackets. The formula for the anion in the second coordination sphere is placed behind the brackets and the number of anions is indicated by a subscript (Fig. 5.1.3).



$K_3[Fe(CN)_6]$

Figure 5.1.4 Example of a formula for a complex with a complex anion

For complex anions, we write the formula for the counter cation first, followed by the complex anion in brackets. You can see two examples above (Fig. 5.1.3 and 5.1.4). We have complex cations of Co with six NH_3 ligands coordinated to it in the first coordination sphere. Three Cl^- ions are in the second coordination sphere. Hence the formula is $[Co(NH_3)_6]Cl_3$. The second example is the coordination compound with the complex anion having a 3- charge in which six cyanide anions bind to a central Fe^{3+} ion. The K^+ ion in the second coordination sphere compensates the charge of the complex anion. Hence the formula is $K_3[Fe(CN)_6]$.

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5.2: Nomenclature

Classification of Ligands

Let us look a little closer at ligands and see how we can classify them. One way is to categorize them into monodentate and multi-dentate ligands.

Monodentate ligands have only one point of attachment to the metal ion.

Definition: Monodentate ligand

Monodentate ligands have only one point of attachment to the metal ion

Examples for such ligands are halogenide ligands, ammonia as ligand, and water as ligand. The molecules often have different names when acting as ligands, and you must know these names. For example, water as a ligand is called an aqua ligand, ammonia as a ligand is called an ammine ligand, chloride as a ligand is called a chloro ligand.

Ligands with more than one point of attachment are called multidentate ligands, or chelate ligands.

Definition: Multidentate ligands

Multi-dentate ligands have two or more points of attachment to the metal ion

Complexes with chelate ligands are called chelate complexes. Greek prefixes indicate how many points of attachment the ligand has (Fig. 5.2.1).

2: bi-dentate
3: tri-dentate
4: tetra-dentate
5: penta-dentate
6: hexa-dentate

Figure 5.2.1 Greek prefixes indicating how many points of attachment the chelating ligand has

If there are two, then we have a bidentate ligand, when there are three, we have a tridentate ligand. We use the prefixes tetra, penta, and hexa to indicate four, five, and six points of attachment, respectively. Multi-dentate ligands with more than six points of attachment are rare.

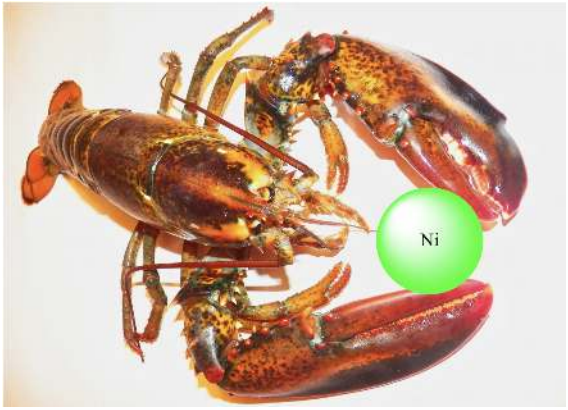
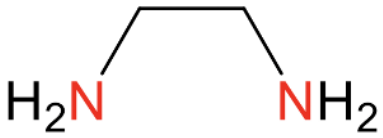


Figure 5.2.2 Visual representation of the origin of the word chelate (Attribution: Junior Libby https://www.publicdomainpictures.net...503683515x.jpg)

The name chelate ligand comes from the Greek word chela, meaning great claw of the lobster. We can see that our lobster in Figure 5.2.2 happily chelates a Ni^{2+} ion with its two great claws!

Common Bidentate Ligands

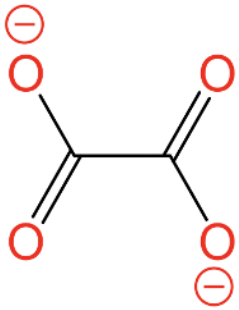
A few common bidentate ligands are shown below.



Ethylenediamine (en)

Figure 5.2.3 The ethylenediamine (en) ligand. Donor atoms are denoted red.

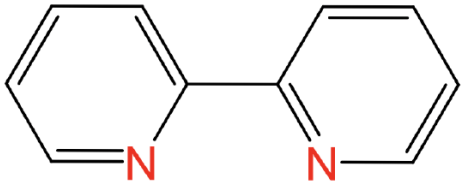
The first one is ethylene diamine. It has two nitrogen donor atoms that can bind to the metal, and they are separated by an ethylene group (Fig. 5.2.3).



Oxalate (ox)

Figure 5.2.4 The oxalate (ox) ligand. Donor atoms are denoted red.

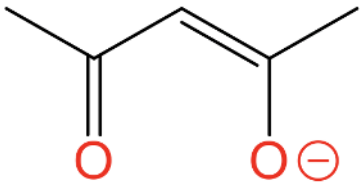
Another common ligand is the oxalate ligand. It has two O donor atoms separated by two carbon atoms. There are two negative charges that are delocalized over the four O atoms (Fig. 5.2.4).



bipyridyl (bipy)

Figure 5.2.5 The Bipyridyl (bipy) ligand. Donor atoms are denoted red.

As a third example you can see the bipyridyl ligand having two N donor atoms as part of two aromatic rings. The two N atoms are separated by two carbon atoms (Fig. 5.2.5).



acetylacetonate (acac)

Figure 5.2.6 Acetylacetonate (acac). Donor atoms are denoted red.

Lastly, there is the acetyl acetonate ligand with two O donor atoms separated by three C atoms (Fig. 5.2.6). The acetyl acetonate carries a negative charge that is delocalized between the two O atoms. In this case the donor atoms are separated by three carbons.

Common ligands often have specific abbreviations. They are often used in the formulas of coordination compounds with these ligands. For example, the ethylene diamine ligand is abbreviated *en*, the oxalate ligand is abbreviated *ox*, the bipyridyl ligand is abbreviated *bipy*, and the acetyl acetonate ligand is abbreviated *acac*. There are not only bidentate ligands with O and N donor atoms, but also with others such as P and S.

Rings in Complexes with Chelate Ligands

In most chelating ligands the donor atoms are separated by two or three other atoms, mostly carbon atoms. This is because in this case the chelate ligands can form five- and six-membered rings with the metal ion (Fig. 5.2.7).

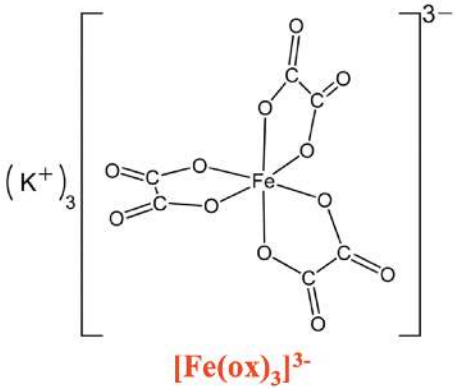


Figure 5.2.7 Trioxolato iron complex (Attribution: Benjah-bmm27 / Public domain https://commons.wikimedia.org/wiki/F...oxalate-2D.png)

You can see that the trioxolato iron complex above has three five-membered rings containing one Fe, two O, and two C atoms. These ring sizes are particularly stable because they have the least ring strain. As a consequence, the respective chelate complexes are particularly stable.

Tridentate Ligands

Here are a couple of examples for tridentate ligands.

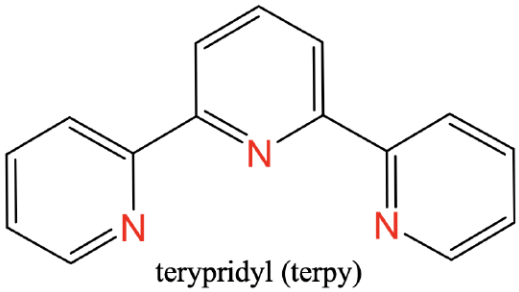


Figure 5.2.8 Terypridyl (terpy). Donor atoms are denoted red.

The first one is terpyridyl, abbreviated “Terpy”(Fig. 5.2.8), the second one is bisethylenetriamine, abbreviated “tris” (Fig. 5.2.9).

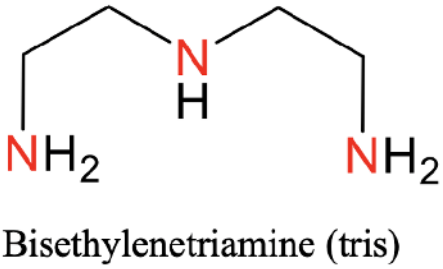


Figure 5.2.9 Bisethylenetriamine (tris). Donor atoms are denoted red.

Both of them have three N-donor atoms separated by two carbon atoms. In the “tris”-ligand there are two ethylene groups between the N atoms, in the case of the “terpy”-ligand the N-atoms are part of three aromatic rings (Fig. 5.2.8. and Fig. 5.2.9)

Tetradentate Ligands

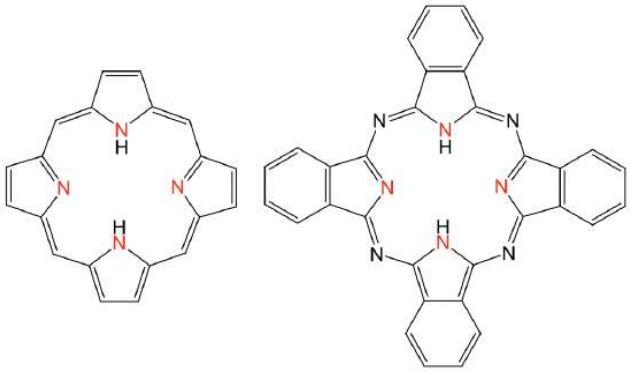


Figure 5.2.10 Porphyrine (left) and Phtalocyanine (right). Donor atoms are denoted red.

Two common tetradentate ligands are porphyrine and phtalocyanine (Fig. 5.2.9 and 5.2.10). Both are co-called macrocyclic ligands because they are large cycles. They both have four N-donor atoms pointing inside of the cycle. The phtalocyanine ligand has four additional N atoms connecting the five-membered rings via imine-linkages. Further the phtalocyanine has four benzene rings fused to the four five-membered rings. The porphyrine ligand is very important in biological systems. For example, it is part of the protein hemoglobin. In this case a an Fe^{2+} ion sits in the center of the porphyrin ring. It is also a component of chlorophyll in which case an Mg^{2+} ion sits in the center of the ring. Phtalocyanine ligands are important as components of dyes.

Hexadentate Ligand, EDTA

A very common hexadentate ligand is the ethylenediamine tetraacetic acid (EDTA) ligand. You can see its structure below (Fig. 5.2.11).

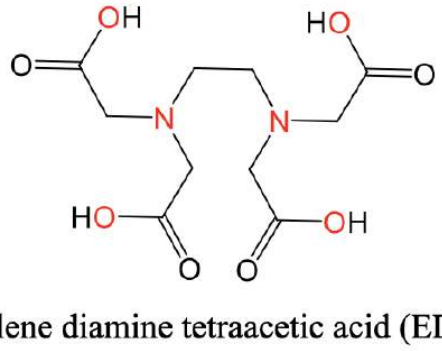


Figure 5.2.11 Structure of EDTA (donor atoms are denoted red)

It has two N-donor atoms separated by an ethylene group. Each N-atom is further connected to two acetyl groups. The overall four acetyl groups carry four O-donor atoms. Overall, there are six donor atoms. The six donor atoms can coordinate octahedrally to a metal ion such as a Ca^{2+} ion (Fig. 5.2.12).

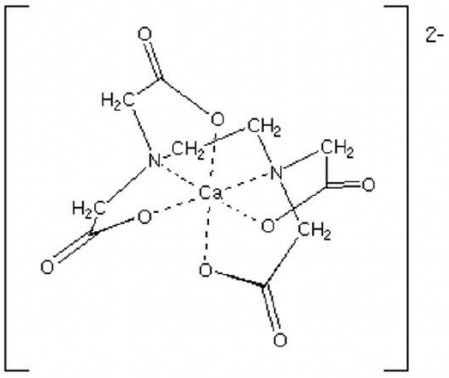


Figure 5.2.12 EDTA complex with Ca^{2+}

In coordinated form the EDTA ligand is deprotonated, and the O donor atoms carry a negative charge. Therefore an EDTA complex with a divalent cation such as Ca^{2+} has a 2- charge.

Nomenclature of Complexes

Now let us develop a nomenclature for coordination chemistry so that we can communicate them in an educated manner. One important aspect is that we name the number of ligands. To indicate the number of a particular ligand we use Greek prefixes (Fig. 5.2.13).

2	di
3	tri
4	tetra
5	penta
6	hexa
7	hepta
8	octa

Figure 5.2.13 Greek prefixes associated with the number of ligands in a coordination compound.

These are the same prefixes we got to know when we discussed multidentate ligands. If there are two ligands we use the prefix di, if there are three we use the prefix tri- and so fourth.

Note that there are a few more rules and guides for nomenclature of these types of compounds. For the time being, this level of detail should be enough to let you put together what type of compound is being discussed.

Dr. Kai Landskron (Lehigh University). If you like this textbook, please consider to make a donation to support the author's research at Lehigh University: Click Here to Donate.

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5.3: Isomerism

This section will be about isomerism in coordination compounds. First, let us first briefly review the definition of isomerism: Isomerism is when two or more compounds have identical empirical formulas but different structures.

Definition: Isomerism

When two or more compounds have identical empirical formulas but different structures they are called isomers.

We distinguish between two basic types of isomerisms: Constitutional isomerism and stereoisomerism. What is the difference? In constitutional isomerism the bonds are not between the same atoms.

Definition: Constitutional Isomers

In constitutional isomers the bonds are not between the same atoms.

In stereoisomerism, the bonds are between the same atoms, but ligands are at different coordination sites.

Definition: Stereoisomers

In stereoisomers, the bonds are between same atoms, but the ligands are at different coordination sites.

Forms of Constitutional Isomerism

Hydrate Isomerism

First, let us look more closely at hydrate isomerism. In hydrate isomerism, in one isomer a water ligand is in the first coordination sphere, and in the other isomer it is in the second coordination sphere. A water molecule in the second coordination sphere is only defined for the solid state, but not in solution. This is because in solution the water molecule would become part of the solvent. Here are a few examples for hydrate isomers.

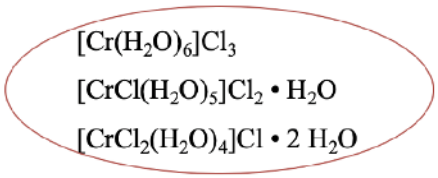


Figure 5.3.1 Two hydrate isomers of the complex $[Cr(H_2O)_6]Cl_3$

In the complex $[Cr(H_2O)_6]Cl_3$ there are six aqua ligands in the first coordination sphere (Figure 5.3.1). In one hydrate isomer, there are only five water molecules in the first coordination sphere, the sixth one is in the second coordination sphere. One chloride anion has moved from the second to the first coordination sphere. There is a third hydrate isomer which has four aqua ligands in the first coordination sphere and two water molecules in the second coordination sphere. Two chloro ligands are now in the first coordination sphere, and one in the second coordination sphere. More hydrate isomers would be possible theoretically, but for some reason nature does not make them.

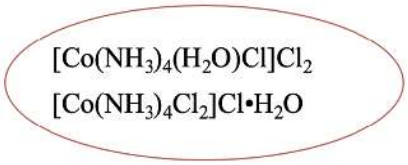


Figure 5.3.2 The hydrate isomers of the complex $[Co(NH_3)_4(H_2O)Cl]Cl_2$

Another example is $[Co(NH_3)_4(H_2O)Cl]Cl_2$. It has a hydrate isomer in which one aqua ligand has moved to the second coordination sphere, and one chloride anion has moved from the second to the first coordination sphere (Figure 5.3.2).

Ionization Isomerism

A second form of isomerism is the ionization isomerism. In this case an ion moves from the first to the second coordination sphere and/or vice versa.

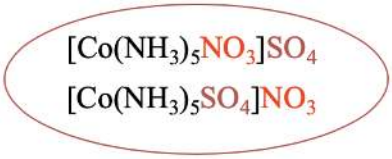


Figure 5.3.3 Two ionization isomers of the complex $[Co(NH_3)_5NO_3]SO_4$

For example, in the compound $[Co(NH_3)_5NO_3]SO_4$ there is a nitrate ion in the first coordination sphere, and a sulfate ion in the second coordination sphere (Figure 5.3.3). There is an ionization isomer to this compound, in which the sulfate ion is now in the first coordination sphere, and the nitrate is in the second coordination sphere.

Coordination Isomerism

Another form of constitutional isomerism is coordination isomerism. In this isomerism, ligands are bound to different metal ions. Naturally, this implies that this form of isomerism can only exist if at least one isomer has two distinguishable metal ions.

$$[Co(en)_3]Cr(CN)_6] \text{ and } [Cr(en)_3][Co(CN)_6]$$

Figure 5.3.4 Example of two coordination isomers with metal ions of different elements

In the example shown (Figure 5.3.4), the first isomer has ethylenediamine bound to Co and cyanide bound to Cr, whereas in the second isomer ethylenediamine is bound to Cr and the cyano ligand is bound to Co.

$$[Pt(NH_3)]_4[PtCl_6] \text{ and } [Pt(NH_3)_4Cl_2][PtCl_4]$$

$$\text{Pt(II)} \quad \text{Pt(IV)} \qquad \text{Pt(IV)} \qquad \text{Pt(IV)}$$

Figure 5.3.5 Two coordination isomers with metal ions in different oxidation states (Oxidation states noted below each coordination sphere)

Further, in coordination isomers metal ions can be in different oxidation states. We can see that in the two depicted isomers there are complex cations, and complex anions with Pt in in different oxidation states (Figure 5.3.5). In the first isomer Pt(II) makes the complex cation having four ammine ligands attached to it. Pt(IV) is part of the complex anion being surrounded by six chloro ligands. In the second isomer Pt(IV) forms the complex cation having four ammine and two chloro ligands in the first coordination sphere, and Pt(II) forms the complex anion having four chloro ligands.

Linkage isomerism

Linkage isomerism, also called ambidentate isomerism, is an isomerism that can be observed for ligands that have more than one reactive end. In two linkage isomers, the ligands will bind with different ends to the metal. Which end is reactive depends on the effective HOMO-LUMO interactions. Soft donor atoms tend to bind to soft metals, and hard donor atoms tend to bind to hard metals. Also the solvent can play a big role.

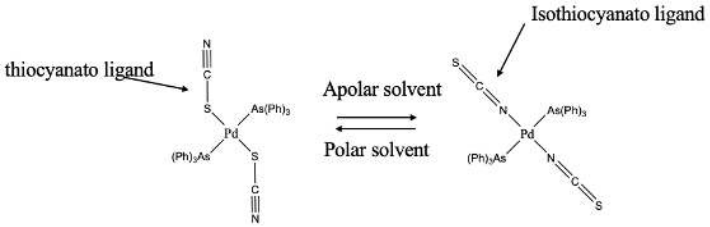


Figure 5.3.6 Two ambidentate isomers of thiocyanate

An example of an ambidentate ligand is the thiocyanate anion (Figure 5.3.6). It can bind either with the sulfur or with the nitrogen end to a metal ion. When it binds with the S-end it is called the thiocyanato-ligand, when it binds with the N-end it is called the isothiocyanato ligand. Which atom binds to the metal can depend on the solvent. In the example shown, thiocyanate binds with S to Pd in polar solvents, but with N in apolar solvents. We could try to rationalize why. A possibility is that in polar solvents the more electronegative N atom can engage in hydrogen bonding which is not possible in apolar solvents. Steric arguments could also play

a role. You can see that the triphenyl arsine ligands are fairly bulky. When the ligand binds with the nitrogen, then it binds in linear fashion avoiding steric interference with one of the arsine ligands. So it may be that in apolar solvents steric interactions dominate the behavior, while in polar solvents solvent-ligand interactions are in control.

It is even possible that two, same ambidentate ligands bind with opposite ends to the metal in one and the same molecule.

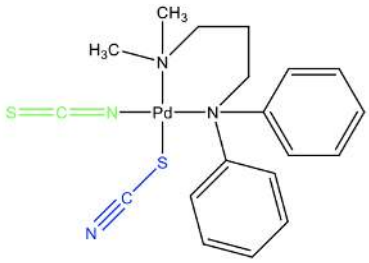


Figure 5.3.7 An example of two, same ambidentate ligands binding with opposite ends to the metal in one and the same molecule.

An example is the complex shown (Figure 5.3.7). In this molecule, there is a thiocyanato and an isocyanato ligand binding to Pd. What arguments would we have to explain this ambidentate isomerism? Think about it for a moment. We can see that the two methyl groups are far less bulky than the two phenyl groups. When thiocyanate binds with the S-atom, then it can bend away from the two bulky phenyl groups. The second thiocyanate anion binds with the N atom because there is no significant interference between the methyl groups and the linear isothiocyanate ligand. This behavior indicates that thermodynamically, the Pd-N interaction is stronger, but only a little bit stronger because other factors such as steric interference can easily reverse the behavior.

Thio- and isothiocyanato ligands are not the only examples of ambidentate ligands.

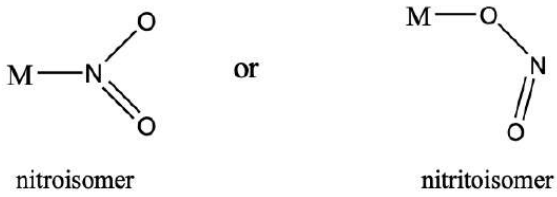


Figure 5.3.8 Two linkage isomers of the nitrite anion

Another example is the nitrite anion. It can either bind with the N- end or the O-end to a metal. In the first case it is called a nitroisomer, in the latter it is called a nitrito isomer (Figure 5.3.8). Nitritoisomers are usually more stable.

Stereoisomers (Configuration Isomers)

Now let us discuss the second major type of isomerism: Stereisomerism. As mentioned previously, in stereoisomerism the bonds are between the same atoms, but the positions at which the ligands bind, the coordination sites, are different. For the time being, we will only examine simple types of isomers, which are commonly called Geometric Isomers. Note that although the term Geometric Isomers is not IUPAC approved, it is commonly used by practicing chemists and is a handy way means of starting to learn about these concepts.

There is another class of stereoisomerism (Optical Isomerism) that we will not be studying in this course. Once you have learned about Optical Isomerism in simpler (typically carbon-based) molecules, then those same concepts can be applied to the sometimes more complicated coordination complexes in a future course.

Cis-Trans Isomerism

Let us now discuss some common forms of stereoisomerism, in this case Geometric Isomerism. The cis-trans isomerism is one very common stereoisomerism. It occurs when two, same ligands are in adjacent or opposite positions. For example, in a square planar complex two ligands can be adjacent or in opposite positions. When in adjacent position, the bond angle is 90° and we have a cis-isomer, when in opposite position, the bond angle is 180° and we have a trans-isomer.

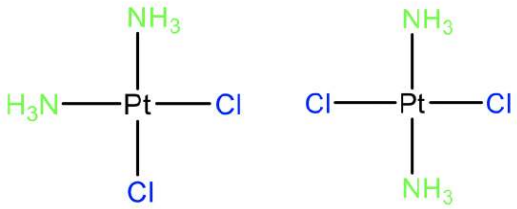


Figure 5.3.9 Cis-platinum and trans-platinum, respectively

The probably most well known example of a cis-isomer in coordination chemistry is cis-platinum which is an anti-cancer drug (Figure 5.3.9). Its trans-isomers does not have these pharmaceutical properties showing that cis-trans isomerism can have a profound impact on the properties of a molecule. Overall cis-trans isomerism in Pt(II) complexes have been most intensely studied, but cis-trans isomerism is also known for other d^8 metal ions in square planar complexes. We can also ask if cis- and trans isomers are diastereomers or enantiomers. Let us look at the example of cis- and trans-platinum to answer this question.

Cis-trans isomerism extends beyond square planar complexes, and is also known for other shapes, for example, the trigonal bipyramidal shape, and the octahedral shape. In the cis-isomer of an octahedral complex two ligands occupy positions on the same face of the octahedron, whereas in the trans-isomer they occupy opposite position of the octahedron.

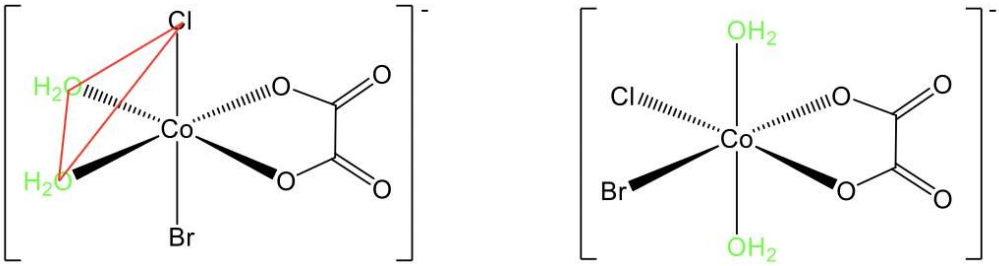


Figure 5.3.10 Cis and trans isomers of the diaquabromochlorooxalato cobalt(1-) complex, respectively

For example, in the complex diaquabromochlorooxalato cobalt(1-) there are cis and trans isomers known (Figure 5.3.10). In the trans-isomer the two aqua-ligands stand in opposite position, and there is a 180° angle between them. In the cis-isomer they are in adjacent position, and the angle is 90°. We can see that the two ligands are on the same triangular face of the octahedron, shown in red.

Are there rules that can help us to decide if a cis- or a trans- complex will form? As you might suspect, the largest ligands usually go in trans-position due to steric repulsion arguments. Bidentate ligands usually form the cis-isomer because bidentate ligands are usually designed to make five- or six-membered rings with the metal ion.

Fac-mer Isomerism

Another common type of stereoisomerism in coordination chemistry is fac-mer isomerism. Fac stands for facial and mer stands for meridional. In a fac-isomer the same ligands are on a common face of a polyhedral complex, in the mer isomer they are on a plane that bisects the polyhedron. This kind of isomerism is very common for octahedral complexes, but not restricted to those.



Figure 5.3.11 Fac- (left) and mer-isomers (right) of the triammine trichloro cobalt(III) complex.

For example the complex triammine trichloro cobalt(III) (Figure 5.3.11)has a fac- and a mer-isomer. You can see that in the fac-isomer the identical ligands are on two opposite triangular faces of the octahedron. In the mer-isomers they lie on two planes that bisect the octahedron.

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valence shell electron pair repulsion theory
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