

SPECTROSCOPY: BACKGROUND INFORMATION ON ELECTRONIC STRUCTURE OF ATOMS AND MOLECULES



Unknown

GalwayMayo_Institute_of_Technology

Spectroscopy: Background Information on Electronic Structure of Atoms and Molecules

This text is disseminated via the Open Education Resource (OER) LibreTexts Project (<https://LibreTexts.org>) and like the thousands of other texts available within this powerful platform, it is freely available for reading, printing, and "consuming."

The LibreTexts mission is to bring together students, faculty, and scholars in a collaborative effort to provide an accessible, and comprehensive platform that empowers our community to develop, curate, adapt, and adopt openly licensed resources and technologies; through these efforts we can reduce the financial burden borne from traditional educational resource costs, ensuring education is more accessible for students and communities worldwide.

Most, but not all, pages in the library have licenses that may allow individuals to make changes, save, and print this book. Carefully consult the applicable license(s) before pursuing such effects. Instructors can adopt existing LibreTexts texts or Remix them to quickly build course-specific resources to meet the needs of their students. Unlike traditional textbooks, LibreTexts' web based origins allow powerful integration of advanced features and new technologies to support learning.



LibreTexts is the adaptable, user-friendly non-profit open education resource platform that educators trust for creating, customizing, and sharing accessible, interactive textbooks, adaptive homework, and ancillary materials. We collaborate with individuals and organizations to champion open education initiatives, support institutional publishing programs, drive curriculum development projects, and more.

The LibreTexts libraries are Powered by [NICE CXone Expert](#) and were supported by the Department of Education Open Textbook Pilot Project, the California Education Learning Lab, the UC Davis Office of the Provost, the UC Davis Library, the California State University Affordable Learning Solutions Program, and Merlot. This material is based upon work supported by the National Science Foundation under Grant No. 1246120, 1525057, and 1413739.

Any opinions, findings, and conclusions or recommendations expressed in this material are those of the author(s) and do not necessarily reflect the views of the National Science Foundation nor the US Department of Education.

Have questions or comments? For information about adoptions or adaptations contact info@LibreTexts.org or visit our main website at <https://LibreTexts.org>.

The LibreTexts name, logo, and book covers are trademarked by LibreTexts, Inc. (a 501(c)(3) not-for-profit organization) and protected against unauthorized use.

This text was compiled on 10/25/2026

TABLE OF CONTENTS

Licensing

1: Chapter 1 - Electronic Structure of Atoms

1.1: Electronic Structure of Atoms

- 1.1.1: The Wave Nature of Light
- 1.1.2: Quantized Energy and Photons
- 1.1.3: Line Spectra and the Bohr Model
- 1.1.4: The Wave Behavior of Matter
- 1.1.5: Quantum Mechanics and Atomic Orbitals
- 1.1.6: 3D Representation of Orbitals
- 1.1.7: Many-Electron Atoms
- 1.1.8: Electron Configurations
- 1.1.9: Electron Configurations and the Periodic Table
- 1.1.E: Electronic Structure of Atoms (Exercises)
- 1.1.S: Electronic Structure of Atoms (Summary)

2: Chapter 2 - Basics of Chemical Bonding

2.1: Basic Concepts of Chemical Bonding

- 2.1.1: Chemical Bonds, Lewis Symbols, and the Octet Rule
- 2.1.2: Ionic Bonding
- 2.1.3: Covalent Bonding
- 2.1.4: Bond Polarity and Electronegativity
- 2.1.5: Drawing Lewis Structures
- 2.1.6: Resonance Structures
- 2.1.7: Exceptions to the Octet Rule
- 2.1.8: Strength of Covalent Bonds
- 2.1.E: Basic Concepts of Chemical Bonding (Exercises)
- 2.1.S: Basic Concepts of Chemical Bonding (Summary)

3: Chapter 3 - Molecular Shapes and Bonding Theories

3.1: Molecular Geometry and Bonding Theories

- 3.1.1: Molecular Shapes
- 3.1.2: The VSEPR Model
- 3.1.3: Molecular Shape and Molecular Polarity
- 3.1.4: Covalent Bonding and Orbital Overlap
- 3.1.5: Hybrid Orbitals
- 3.1.6: Multiple Bonds
- 3.1.7: Molecular Orbitals
- 3.1.8: Second-Row Diatomic Molecules

[3.1.E: Exercises](#)

[3.1.S: Molecular Geometry and Bonding Theories \(Summary\)](#)

[Index](#)

[Glossary](#)

[Glossary](#)

[Detailed Licensing](#)

Licensing

A detailed breakdown of this resource's licensing can be found in **Back Matter/Detailed Licensing**.

1: CHAPTER 1 - ELECTRONIC STRUCTURE OF ATOMS

1.1: Electronic Structure of Atoms

- 1.1.1: The Wave Nature of Light
- 1.1.2: Quantized Energy and Photons
- 1.1.3: Line Spectra and the Bohr Model
- 1.1.4: The Wave Behavior of Matter
- 1.1.5: Quantum Mechanics and Atomic Orbitals
- 1.1.6: 3D Representation of Orbitals
- 1.1.7: Many-Electron Atoms
- 1.1.8: Electron Configurations
- 1.1.9: Electron Configurations and the Periodic Table
- 1.1.E: Electronic Structure of Atoms (Exercises)
- 1.1.S: Electronic Structure of Atoms (Summary)

1.1: ELECTRONIC STRUCTURE OF ATOMS

A general chemistry Libretexts Textmap organized around the textbook

Chemistry: The Central Science

by Brown, LeMay, Bursten, Murphy, and Woodward

Template:HideTOC

In this chapter, we describe how electrons are arranged in atoms and how the spatial arrangements of electrons are related to their energies. We also explain how knowing the arrangement of electrons in an atom enables chemists to predict and explain the chemistry of an element. As you study the material presented in this chapter, you will discover how the shape of the periodic table reflects the electronic arrangements of elements. In this and subsequent chapters, we build on this information to explain why certain chemical changes occur and others do not. After reading this chapter, you will know enough about the theory of the electronic structure of atoms to explain what causes the characteristic colors of neon signs, how laser beams are created, and why gemstones and fireworks have such brilliant colors. In later chapters, we will develop the concepts introduced here to explain why the only compound formed by sodium and chlorine is NaCl, an ionic compound, whereas neon and argon do not form any stable compounds, and why carbon and hydrogen combine to form an almost endless array of covalent compounds, such as CH₄, C₂H₂, C₂H₄, and C₂H₆. You will discover that knowing how to use the periodic table is the single most important skill you can acquire to understand the incredible chemical diversity of the elements.

1.1.1: The Wave Nature of Light

1.1.2: Quantized Energy and Photons

1.1.3: Line Spectra and the Bohr Model

1.1.4: The Wave Behavior of Matter

1.1.5: Quantum Mechanics and Atomic Orbitals

1.1.6: 3D Representation of Orbitals

1.1.7: Many-Electron Atoms

1.1.8: Electron Configurations

1.1.9: Electron Configurations and the Periodic Table

1.1.E: Electronic Structure of Atoms (Exercises)

1.1.S: Electronic Structure of Atoms (Summary)

This page titled [1.1: Electronic Structure of Atoms](#) is shared under a [CC BY-NC-SA 4.0](#) license and was authored, remixed, and/or curated by LibreTexts.

1.1.1: The Wave Nature of Light

Learning Objectives

- To learn about the characteristics of electromagnetic waves. Light, X-Rays, infrared and microwaves are among the types of electromagnetic waves.

Scientists discovered much of what we know about the structure of the atom by observing the interaction of atoms with various forms of radiant, or transmitted, energy, such as the energy associated with the visible light we detect with our eyes, the infrared radiation we feel as heat, the ultraviolet light that causes sunburn, and the x-rays that produce images of our teeth or bones. All these forms of radiant energy should be familiar to you. We begin our discussion of the development of our current atomic model by describing the properties of waves and the various forms of electromagnetic radiation.



Figure 1.1.1.1: A Wave in Water. When a drop of water falls onto a smooth water surface, it generates a set of waves that travel outward in a circular direction.

Properties of Waves

A wave is a periodic oscillation that transmits energy through space. Anyone who has visited a beach or dropped a stone into a puddle has observed waves traveling through water (Figure 1.1.1.1). These waves are produced when wind, a stone, or some other disturbance, such as a passing boat, transfers energy to the water, causing the surface to oscillate up and down as the energy travels outward from its point of origin. As a wave passes a particular point on the surface of the water, anything floating there moves up and down.

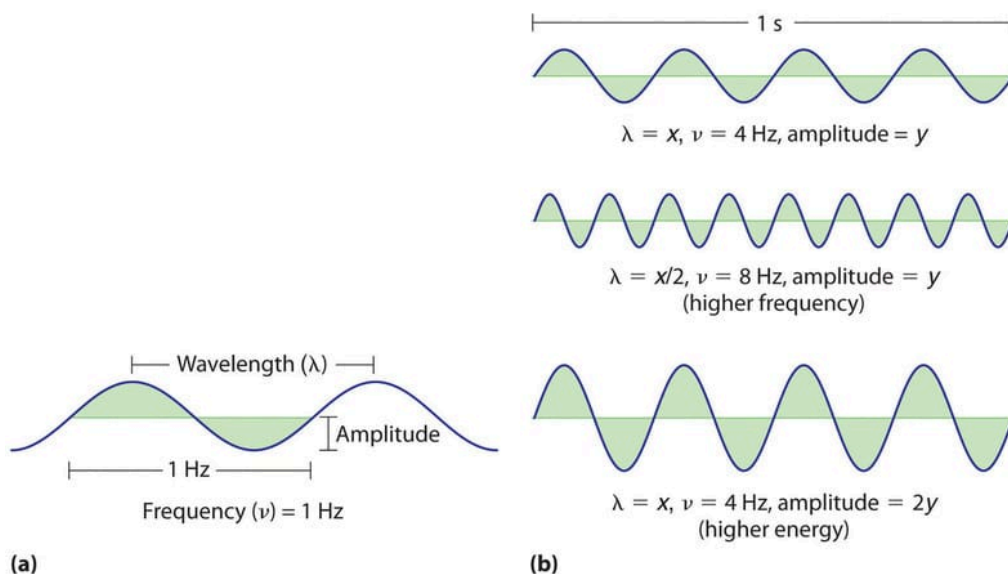


Figure 1.1.1.2: Important Properties of Waves (a) Wavelength (λ in meters), frequency (ν , in Hz), and amplitude are indicated on this drawing of a wave. (b) The wave with the shortest wavelength has the greatest number of wavelengths per unit time (i.e., the highest frequency). If two waves have the same frequency and speed, the one with the greater amplitude has the higher energy.

Waves have characteristic properties (Figure 1.1.1.2). As you may have noticed in Figure 1.1.1.1, waves are periodic, that is, they repeat regularly in both space and time. The distance between two corresponding points in a wave—between the midpoints of two peaks, for example, or two troughs—is the **wavelength** (λ , lowercase Greek lambda). Wavelengths are described by a unit of distance, typically meters. The **frequency** (ν , lowercase Greek nu) of a wave is the number of oscillations that pass a particular point in a given period of time. The usual units are oscillations per second ($1/\text{s} = \text{s}^{-1}$), which in the SI system is called the hertz (Hz). It is named after German physicist Heinrich Hertz (1857–1894), a pioneer in the field of electromagnetic radiation.

The **amplitude**, or vertical height, of a wave is defined as half the peak-to-trough height; as the amplitude of a wave with a given frequency increases, so does its energy. As you can see in Figure 1.1.1.2, two waves can have the same amplitude but different wavelengths and vice versa. The distance traveled by a wave per unit time is its speed (v), which is typically measured in meters per second (m/s). The speed of a wave is equal to the product of its wavelength and frequency:

$$(\text{wavelength})(\text{frequency}) = \text{speed} \quad (1.1.1.1)$$

$$\lambda \nu = v$$

$$\left(\frac{\text{meters}}{\text{wave}} \right) \left(\frac{\text{wave}}{\text{second}} \right) = \frac{\text{meters}}{\text{second}} \quad (1.1.1.2)$$

Be careful not to confuse the symbols for the speed, v , with the frequency, ν .

Different types of waves may have vastly different possible speeds and frequencies. Water waves are slow compared to sound waves, which can travel through solids, liquids, and gases. Whereas water waves may travel a few meters per second, the speed of sound in dry air at 20°C is 343.5 m/s. Ultrasonic waves, which travel at an even higher speed (>1500 m/s) and have a greater frequency, are used in such diverse applications as locating underwater objects and the medical imaging of internal organs.

Electromagnetic Radiation

Water waves transmit energy through space by the periodic oscillation of matter (the water). In contrast, energy that is transmitted, or radiated, through space in the form of periodic oscillations of electric and magnetic fields is known as **electromagnetic radiation**. (Figure 1.1.1.3). Some forms of electromagnetic radiation are shown in Figure 1.1.1.4. In a vacuum, all forms of electromagnetic radiation—whether microwaves, visible light, or gamma rays—travel at the speed of light (c), which turns out to be a fundamental physical constant with a value of 2.99792458×10^8 m/s (about 3.00×10^8 m/s or 1.86×10^5 mi/s). This is about a million times faster than the speed of sound.

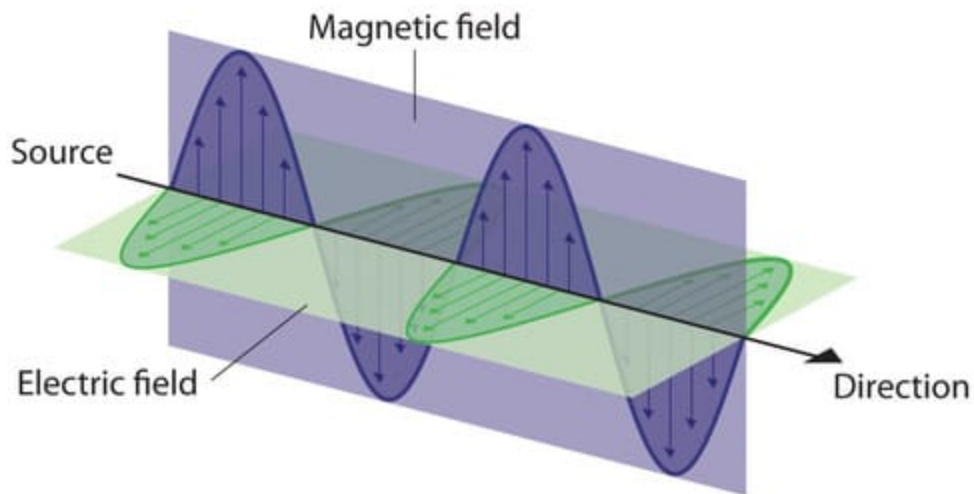


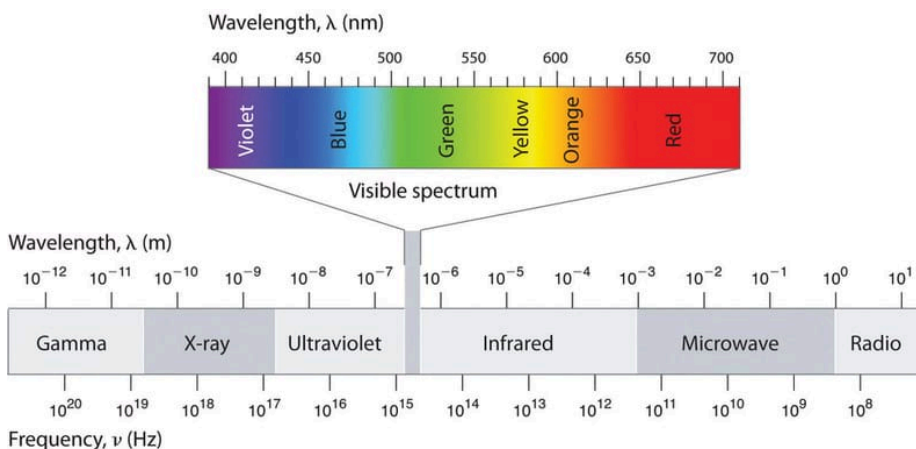
Figure 1.1.1.3: The Nature of Electromagnetic Radiation. All forms of electromagnetic radiation consist of perpendicular oscillating electric and magnetic fields.

Because the various kinds of electromagnetic radiation all have the same speed (c), they differ in only wavelength and frequency. As shown in Figure 1.1.1.4 and Table 1.1.1.1, the wavelengths of familiar electromagnetic radiation range from 10^1 m for radio waves to 10^{-12} m for gamma rays, which are emitted by nuclear reactions. By replacing v with (c/λ) in Equation 1.1.1.1, we can show that the frequency of electromagnetic radiation is inversely proportional to its wavelength:

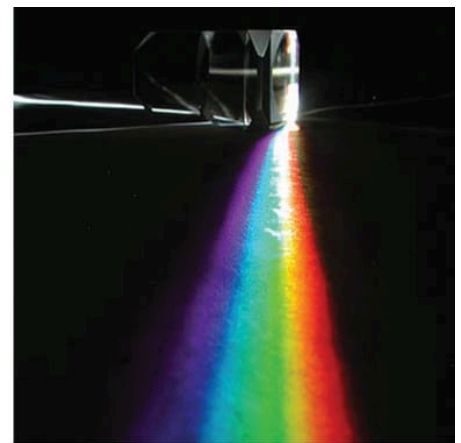
$$c = \lambda u \quad (1.1.1.3)$$

$$u = \frac{c}{\lambda} \quad (1.1.1.4)$$

For example, the frequency of radio waves is about 10^8 Hz, whereas the frequency of gamma rays is about 10^{20} Hz. Visible light, which is electromagnetic radiation that can be detected by the human eye, has wavelengths between about 7×10^{-7} m (700 nm, or 4.3×10^{14} Hz) and 4×10^{-7} m (400 nm, or 7.5×10^{14} Hz). Note that when frequency increases, wavelength decreases; c being a constant stays the same. Similarly, when frequency decreases, the wavelength increases.



(a)



(b)

Figure 1.1.1.4: The Electromagnetic Spectrum. (a) This diagram shows the wavelength and frequency ranges of electromagnetic radiation. The visible portion of the electromagnetic spectrum is the narrow region with wavelengths between about 400 and 700 nm. (b) When white light is passed through a prism, it is split into light of different wavelengths, whose colors correspond to the visible spectrum.

Within the visible range our eyes perceive radiation of different wavelengths (or frequencies) as light of different colors, ranging from red to violet in order of decreasing wavelength. The components of white light—a mixture of all the frequencies of visible light—can be separated by a prism, as shown in part (b) in Figure 1.1.1.4. A similar phenomenon creates a rainbow, where water droplets suspended in the air act as tiny prisms.

Table 1.1.1.1: Common Wavelength Units for Electromagnetic Radiation

Unit	Symbol	Wavelength (m)	Type of Radiation
picometer	pm	10^{-12}	gamma ray
angstrom	Å	10^{-10}	x-ray
nanometer	nm	10^{-9}	UV, visible
micrometer	µm	10^{-6}	infrared
millimeter	mm	10^{-3}	infrared
centimeter	cm	10^{-2}	microwave
meter	m	10^0	radio

As you will soon see, the energy of electromagnetic radiation is directly proportional to its frequency and inversely proportional to its wavelength:

$$E \propto \nu \quad (1.1.1.5)$$

$$\propto \frac{1}{\lambda} \quad (1.1.1.6)$$

Whereas visible light is essentially harmless to our skin, ultraviolet light, with wavelengths of ≤ 400 nm, has enough energy to cause severe damage to our skin in the form of sunburn. Because the ozone layer of the atmosphere absorbs sunlight with wavelengths less than 350 nm, it protects us from the damaging effects of highly energetic ultraviolet radiation.

The energy of electromagnetic radiation increases with increasing frequency and decreasing wavelength.

YouTube Video

This interactive element is not available in this format. Visit the link or scan the QR code to access it online.

[View this YouTube Video online](#)



Electromagnetic Radiation: <https://youtu.be/TZy7a69pP-w>

Example 1.1.1.1: Wavelength of Radiowaves

Your favorite FM radio station, WXYZ, broadcasts at a frequency of 101.1 MHz. What is the wavelength of this radiation?

Given: frequency

Asked for: wavelength

Strategy:

Substitute the value for the speed of light in meters per second into Equation 1.1.1.4 to calculate the wavelength in meters.

Solution:

From Equation 1.1.1.4, we know that the product of the wavelength and the frequency is the speed of the wave, which for electromagnetic radiation is 2.998×10^8 m/s:

$$\begin{aligned}\lambda\nu &= c \\ &= 2.998 \times 10^8 \text{ m/s}\end{aligned}$$

Thus the wavelength λ is given by

$$\begin{aligned}\lambda &= \frac{c}{\nu} \\ &= \left(\frac{2.988 \times 10^8 \text{ m/s}}{101.1 \text{ MHz}} \right) \left(\frac{1 \text{ MHz}}{10^6} \right) \\ &= 2.965 \text{ m}\end{aligned}$$

Exercise 1.1.1.1

As the police officer was writing up your speeding ticket, she mentioned that she was using a state-of-the-art radar gun operating at 35.5 GHz. What is the wavelength of the radiation emitted by the radar gun?

Answer available at the end of this section.

Summary

Understanding the electronic structure of atoms requires an understanding of the properties of waves and electromagnetic radiation. A **wave** is a periodic oscillation by which energy is transmitted through space. All waves are **periodic**, repeating regularly in both space and time. Waves are characterized by several interrelated properties: **wavelength** (λ), the distance between successive waves; **frequency** (ν), the number of waves that pass a fixed point per unit time; **speed** (v), the rate at which the wave propagates through space; and **amplitude**, the magnitude of the oscillation about the mean position. The speed of a wave is equal to the product of its wavelength and frequency. **Electromagnetic radiation** consists of two perpendicular waves, one electric and one magnetic, propagating at the **speed of light** (c). Electromagnetic radiation is radiant energy that includes radio waves, microwaves, visible light, x-rays, and gamma rays, which differ in their frequencies and wavelengths.

Contributors and Attributions

- Modified by Joshua Halpern (Howard University)

Answers

Exercise 1.1.1.1

8.45 mm

This page titled 1.1.1: The Wave Nature of Light is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by LibreTexts.

- 6.1: The Wave Nature of Light is licensed CC BY-NC-SA 3.0.

1.1.2: Quantized Energy and Photons

Learning Objectives

- To understand how energy is quantized.

By the late 19th century, many physicists thought their discipline was well on the way to explaining most natural phenomena. They could calculate the motions of material objects using Newton's laws of classical mechanics, and they could describe the properties of radiant energy using mathematical relationships known as Maxwell's equations, developed in 1873 by James Clerk Maxwell, a Scottish physicist. The universe appeared to be a simple and orderly place, containing matter, which consisted of particles that had mass and whose location and motion could be accurately described, and electromagnetic radiation, which was viewed as having no mass and whose exact position in space could not be fixed. Thus matter and energy were considered distinct and unrelated phenomena. Soon, however, scientists began to look more closely at a few inconvenient phenomena that could *not* be explained by the theories available at the time.

Blackbody Radiation

One phenomenon that seemed to contradict the theories of classical physics was blackbody radiation, which is electromagnetic radiation given off by a hot object. The wavelength (i.e. color) of radiant energy emitted by a blackbody depends on only its temperature, not its surface or composition. Hence an electric stove burner or the filament of a space heater glows dull red or orange when heated, whereas the much hotter tungsten wire in an incandescent light bulb gives off a yellowish light.



Figure 1.1.2.1: Blackbody Radiation. When heated, all objects emit electromagnetic radiation whose wavelength (and color) depends on the temperature of the object. A relatively low-temperature object, such as a horseshoe forged by a blacksmith, appears red, whereas a higher-temperature object, such as the surface of the sun, appears yellow or white. Images used with permission from Wikipedia.

The *intensity* of radiation is a measure of the energy emitted per unit area. A plot of the intensity of blackbody radiation as a function of wavelength for an object at various temperatures is shown in Figure 1.1.2.2. One of the major assumptions of classical physics was that energy increased or decreased in a smooth, continuous manner. For example, classical physics predicted that as wavelength decreased, the intensity of the radiation an object emits should increase in a smooth curve without limit at *all* temperatures, as shown by the broken line for 6000 K in Figure 1.1.2.2. Thus classical physics could not explain the sharp decrease in the intensity of radiation emitted at shorter wavelengths (primarily in the ultraviolet region of the spectrum), which was referred to as the "ultraviolet catastrophe." In 1900, however, the German physicist Max Planck (1858–1947) explained the ultraviolet catastrophe by proposing (in what he called "an act of despair") that the energy of electromagnetic waves is *quantized* rather than continuous. This means that for each temperature, there is a maximum intensity of radiation that is emitted in a blackbody object, corresponding to the peaks in Figure 1.1.2.2, so the intensity does not follow a smooth curve as the temperature increases, as predicted by classical physics. Thus energy could be gained or lost only in integral multiples of some smallest unit

of energy, a **quantum**.

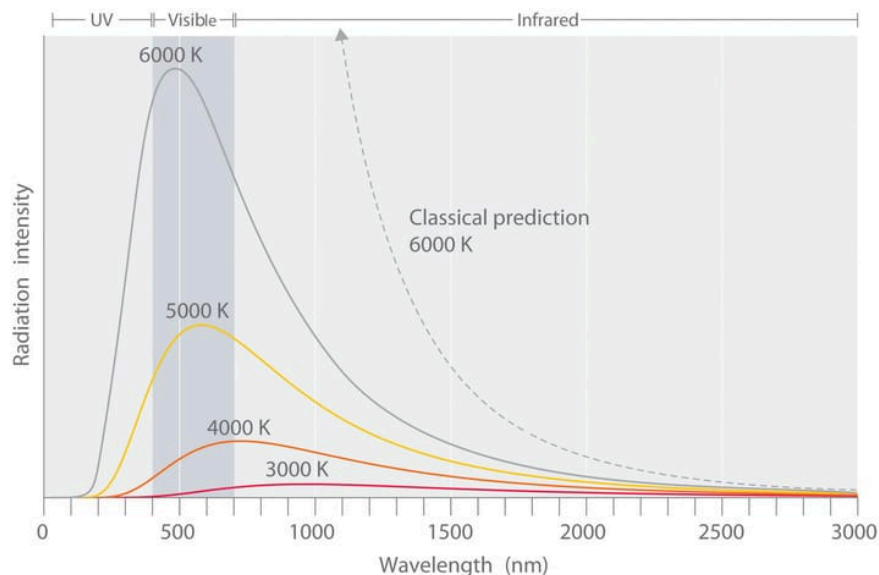
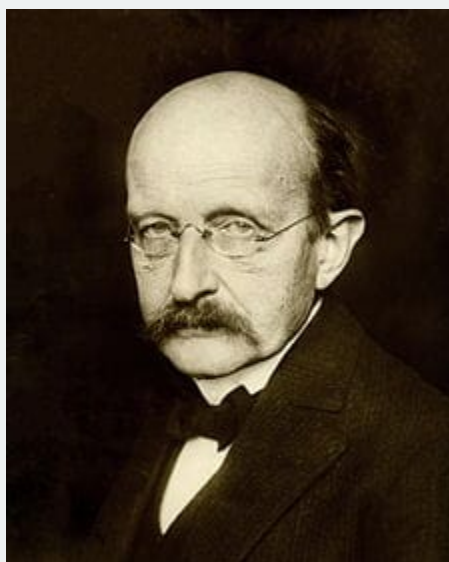


Figure 1.1.2.2: Relationship between the Temperature of an Object and the Spectrum of Blackbody Radiation it Emits. At relatively low temperatures, most radiation is emitted at wavelengths longer than 700 nm, which is in the infrared portion of the spectrum. The dull red glow of the electric stove element in Figure 1.1.2.1 is due to the small amount of radiation emitted at wavelengths less than 700 nm, which the eye can detect. As the temperature of the object increases, the maximum intensity shifts to shorter wavelengths, successively resulting in orange, yellow, and finally white light. At high temperatures, all wavelengths of visible light are emitted with approximately equal intensities. The white light spectrum shown for an object at 6000 K closely approximates the spectrum of light emitted by the sun (Figure 1.1.2.1). Note the sharp decrease in the intensity of radiation emitted at wavelengths below 400 nm, which constituted the ultraviolet catastrophe. The classical prediction fails to fit the experimental curves entirely and does not have a maximum intensity.

Max Planck (1858–1947)

In addition to being a physicist, Planck was a gifted pianist, who at one time considered music as a career. During the 1930s, Planck felt it was his duty to remain in Germany, despite his open opposition to the policies of the Nazi government.



One of his sons was executed in 1944 for his part in an unsuccessful attempt to assassinate Hitler, and bombing during the last weeks of World War II destroyed Planck's home. After WWII, the major German scientific research organization was renamed the [Max Planck Society](#).

Although quantization may seem to be an unfamiliar concept, we encounter it frequently. For example, US money is integral multiples of pennies. Similarly, musical instruments like a piano or a trumpet can produce only certain musical notes, such as C or F sharp. Because these instruments cannot produce a continuous range of frequencies, their frequencies are quantized. Even electrical charge is quantized: an ion may have a charge of -1 or -2 but *not* -1.33 electron charges.

Planck postulated that the energy of a particular quantum of radiant energy could be described by the equation

$$E = hu \quad (1.1.2.1)$$

where the proportionality constant h is called Planck's constant, one of the most accurately known fundamental constants in science. For our purposes, its value to four significant figures is generally sufficient:

$$h = 6.626 \times 10^{-34} \text{ J} \cdot \text{s (joule-segundos)}$$

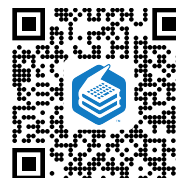
As the frequency of electromagnetic radiation increases, the magnitude of the associated quantum of radiant energy increases. By assuming that energy can be emitted by an object only in integral multiples of $h\nu$, Planck devised an equation that fit the experimental data shown in Figure 1.1.2.2. We can understand Planck's explanation of the ultraviolet catastrophe qualitatively as follows: At low temperatures, radiation with only relatively low frequencies is emitted, corresponding to low-energy quanta. As the temperature of an object increases, there is an increased probability of emitting radiation with higher frequencies, corresponding to higher-energy quanta. At any temperature, however, it is simply more probable for an object to lose energy by emitting a large number of lower-energy quanta than a single very high-energy quantum that corresponds to ultraviolet radiation. The result is a maximum in the plot of intensity of emitted radiation versus wavelength, as shown in Figure 1.1.2.2, and a shift in the position of the maximum to lower wavelength (higher frequency) with increasing temperature.

At the time he proposed his radical hypothesis, Planck could not explain *why* energies should be quantized. Initially, his hypothesis explained only one set of experimental data—blackbody radiation. If quantization were observed for a large number of different phenomena, then quantization would become a law. In time, a theory might be developed to explain that law. As things turned out, Planck's hypothesis was the seed from which modern physics grew.

YouTube Video

This interactive element is not available in this format. Visit the link or scan the QR code to access it online.

[View this YouTube Video online](#)



Energy of a Photon: [Energy of a Photon, YouTube\(opens in new window\)](#) [youtu.be]

The Photoelectric Effect

Only five years after he proposed it, Planck's quantization hypothesis was used to explain a second phenomenon that conflicted with the accepted laws of classical physics. When certain metals are exposed to light, electrons are ejected from their surface (Figure 1.1.2.3). Classical physics predicted that the number of electrons emitted and their kinetic energy should depend on only the intensity of the light, not its frequency. In fact, however, each metal was found to have a characteristic threshold frequency of light; below that frequency, no electrons are emitted regardless of the light's intensity. Above the threshold frequency, the number of electrons emitted was found to be proportional to the intensity of the light, and their kinetic energy was proportional to the frequency. This phenomenon was called the photoelectric effect (A phenomenon in which electrons are ejected from the surface of a metal that has been exposed to light).

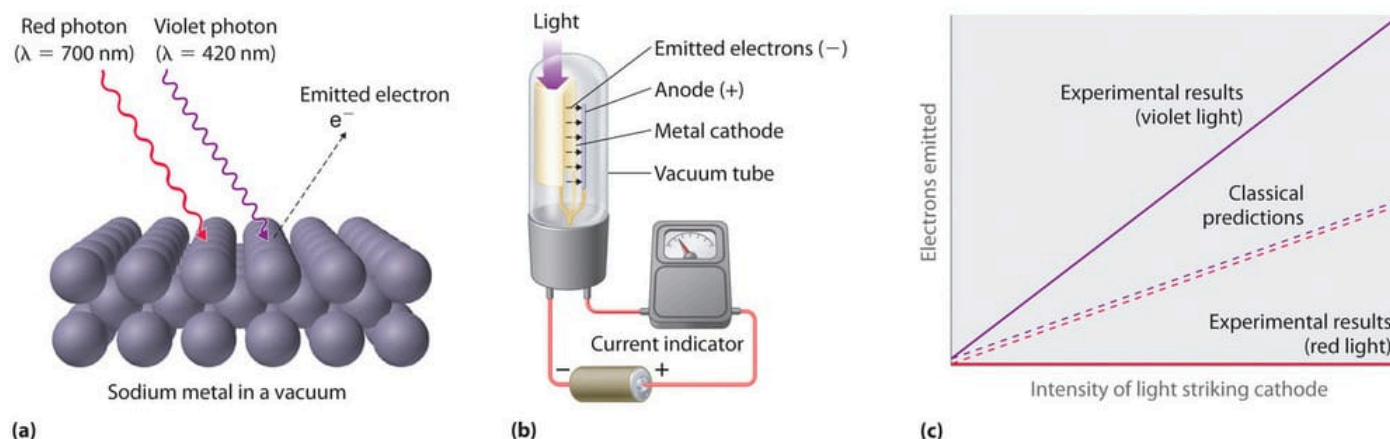


Figure 1.1.2.3: The Photoelectric Effect (a) Irradiating a metal surface with photons of sufficiently high energy causes electrons to be ejected from the metal. (b) A photocell that uses the photoelectric effect, similar to those found in automatic door openers. When light strikes the metal cathode, electrons are emitted and attracted to the anode, resulting in a flow of electrical current. If the incoming light is interrupted by, for example, a passing person, the current drops to zero. (c) In contrast to predictions using classical physics, no electrons are emitted when photons of light with energy less than E_o , such as red light, strike the cathode. The energy of violet light is above the threshold frequency, so the number of emitted photons is proportional to the light's intensity.

Albert Einstein (1879–1955; Nobel Prize in Physics, 1921) quickly realized that Planck's hypothesis about the quantization of radiant energy could also explain the photoelectric effect. The key feature of Einstein's hypothesis was the assumption that radiant energy arrives at the metal surface in particles that we now call **photons** (a quantum of radiant energy, each of which possesses a particular energy E given by Equation 1.1.2.1 Einstein postulated that each metal has a particular electrostatic attraction for its electrons that must be overcome before an electron can be emitted from its surface ($E_o = u_o$). If photons of light with energy less than E_o strike a metal surface, no single photon has enough energy to eject an electron, so no electrons are emitted regardless of the intensity of the light. If a photon with energy greater than E_o strikes the metal, then part of its energy is used to overcome the forces that hold the electron to the metal surface, and the excess energy appears as the kinetic energy of the ejected electron:

$$\begin{aligned} \text{kinetic energy of ejected electron} &= E - E_o \\ &= hu - hu_o \\ &= h(u - u_o) \end{aligned} \quad (1.1.2.2)$$

When a metal is struck by light with energy above the threshold energy E_o , the *number* of emitted electrons is proportional to the *intensity* of the light beam, which corresponds to the *number* of photons per square centimeter, but the *kinetic energy* of the emitted electrons is proportional to the *frequency* of the light. Thus Einstein showed that the energy of the emitted electrons depended on the frequency of the light, contrary to the prediction of classical physics. Moreover, the idea that light could behave not only as a wave but as a particle in the form of photons suggested that matter and energy might not be such unrelated phenomena after all.

YouTube Video

This interactive element is not available in this format. Visit the link or scan the QR code to access it online.

[View this YouTube Video online](#)



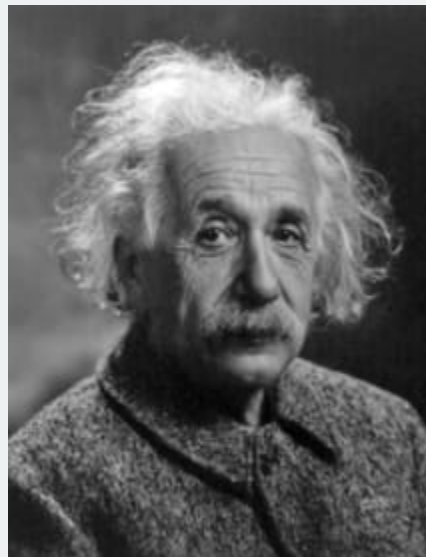
The Photoelectric Effect: [The Photoelectric Effect, YouTube\(opens in new window\)](#) [youtu.be]



Figure 1.1.2.4: A Beam of Red Light Emitted by a Helium Neon laser reads a bar code. Originally Helium neon lasers, which emit red light at a wavelength of 632.8 nm, were used to read bar codes. Today, smaller, inexpensive diode lasers are used.

Albert Einstein (1879–1955)

In 1900, Einstein was working in the Swiss patent office in Bern. He was born in Germany and throughout his childhood his parents and teachers had worried that he might be developmentally disabled. The patent office job was a low-level civil service position that was not very demanding, but it did allow Einstein to spend a great deal of time reading and thinking about physics.



In 1905, his "miracle year" he published four papers that revolutionized physics. One was on the special theory of relativity, a second on the equivalence of mass and energy, a third on Brownian motion, and the fourth on the photoelectric effect, for which he received the Nobel Prize in 1921, the theory of relativity and energy-matter equivalence being still controversial at the time

Planck's and Einstein's postulate that energy is quantized is in many ways similar to Dalton's description of atoms. Both theories are based on the existence of simple building blocks, atoms in one case and quanta of energy in the other. The work of Planck

and Einstein thus suggested a connection between the quantized nature of energy and the properties of individual atoms.

Example 1.1.2.1

A ruby laser, a device that produces light in a narrow range of wavelengths emits red light at a wavelength of 694.3 nm (Figure 1.1.2.4). What is the energy in joules of a single photon?

Given: wavelength

Asked for: energy of single photon.

Strategy:

Use Equation 1.1.2.1 and the relationship between wavelength and frequency to calculate the energy in joules.

Solution:

The energy of a single photon is given by Equation 1.1.2.1

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

Exercise 1.1.2.1

An x-ray generator, such as those used in hospitals, emits radiation with a wavelength of 1.544 Å.

- What is the energy in joules of a single photon?
- How many times more energetic is a single x-ray photon of this wavelength than a photon emitted by a ruby laser?

Answer a available at the end of this section.

External Videos and Examples

- Calculating Energy of a Mole of Photons_- Johnny Cantrell
- .Photons - ViaScience, an advanced explanation of the Planck radiation law and the photoelectric effect (below) as well as biological interactions with UV light.and the nature of light and quantum weirdness. Probably the first 6 minutes and the last 3 (from 12:00 on) as an introduction to wave particle duality.are useful to a beginning student.
- [Quantum Chemistry](#) - Ohio State
- [Quantum Chemistry Quizzes](#) - mhe education
- [AP Chemistry Chapter 7 Review](#) - Science Geek
- Quantum Theory of the Atom Practice Quiz - Northrup

Summary

The fundamental building blocks of energy are quanta and of matter are atoms. The properties of **blackbody radiation**, the radiation emitted by hot objects, could not be explained with classical physics. Max Planck postulated that energy was quantized and could be emitted or absorbed only in integral multiples of a small unit of energy, known as a **quantum**. The energy of a quantum is proportional to the frequency of the radiation; the proportionality constant h is a fundamental constant (Planck's constant). Albert Einstein used Planck's concept of the quantization of energy to explain the **photoelectric effect**, the ejection of electrons from certain metals when exposed to light. Einstein postulated the existence of what today we call **photons**, particles of light with a particular energy, $E = hu$. Both energy and matter have fundamental building blocks: quanta and atoms, respectively.

Contributors and Attributions

- Modified by [Joshua Halpern \(Howard University\)](#)
-

Answers

Exercise 1.1.2.1

$$1.287 \times 10^{-15} \text{ J/photon}$$

4497 times

This page titled [1.1.2: Quantized Energy and Photons](#) is shared under a [CC BY-NC-SA 4.0](#) license and was authored, remixed, and/or curated by LibreTexts.

- [6.2: Quantized Energy and Photons](#) is licensed [CC BY-NC-SA 3.0](#).

1.1.3: Line Spectra and the Bohr Model

Learning Objectives

- To know the relationship between atomic spectra and the electronic structure of atoms.

The concept of the photon emerged from experimentation with *thermal radiation*, electromagnetic radiation emitted as the result of a source's temperature, which produces a continuous spectrum of energies. The photoelectric effect provided indisputable evidence for the existence of the photon and thus the particle-like behavior of electromagnetic radiation. However, more direct evidence was needed to verify the quantized nature of energy in all matter. In this section, we describe how observation of the interaction of atoms with visible light provided this evidence.

Line Spectra

Although objects at high temperature emit a continuous spectrum of electromagnetic radiation, a different kind of spectrum is observed when pure samples of individual elements are heated. For example, when a high-voltage electrical discharge is passed through a sample of hydrogen gas at low pressure, the resulting individual isolated hydrogen atoms caused by the dissociation of H_2 emit a red light. Unlike blackbody radiation, the color of the light emitted by the hydrogen atoms does not depend greatly on the temperature of the gas in the tube. When the emitted light is passed through a prism, only a few narrow lines of particular wavelengths, called a **line spectrum**, are observed rather than a continuous range of wavelengths (Figure 1.1.3.1). The light emitted by hydrogen atoms is red because, of its four characteristic lines, the most intense line in its spectrum is in the red portion of the visible spectrum, at 656 nm. With sodium, however, we observe a yellow color because the most intense lines in its spectrum are in the yellow portion of the spectrum, at about 589 nm.

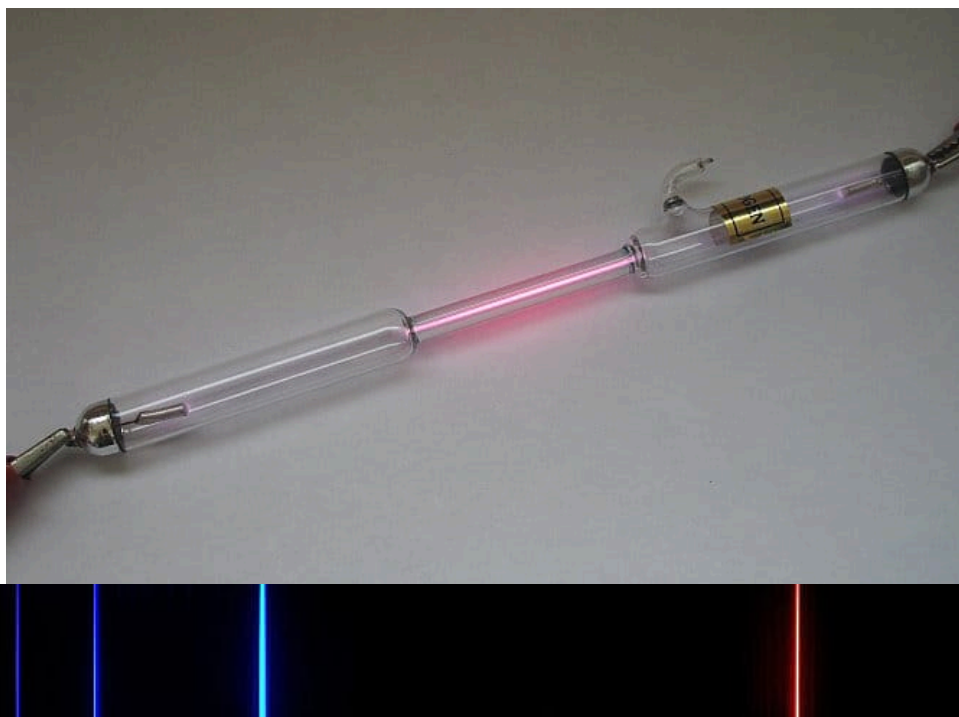


Figure 1.1.3.1: The Emission of Light by Hydrogen Atoms. (a) A sample of excited hydrogen atoms emits a characteristic red light. (CC BY-SA 3.0 Unported; [Science Made Alive](#) via [Wikipedia](#)) (b) When the light emitted by a sample of excited hydrogen atoms is split into its component wavelengths by a prism, four characteristic violet, blue, green, and red emission lines can be observed, the most intense of which is at 656 nm. (CC BY-SA 3.0; [Jan Homann](#) via [Wikipedia](#))

Such *emission spectra* were observed for many other elements in the late 19th century, which presented a major challenge

because classical physics was unable to explain them. Part of the explanation is provided by Planck's equation: the observation of only a few values of λ (or u) in the line spectrum meant that only a few values of E were possible. Thus *the energy levels of a hydrogen atom had to be quantized*; in other words, only states that had certain values of energy were possible, or *allowed*. If a hydrogen atom could have *any* value of energy, then a continuous spectrum would have been observed, similar to blackbody radiation.

In 1885, a Swiss mathematics teacher, Johann Balmer (1825–1898), showed that the frequencies of the lines observed in the visible region of the spectrum of hydrogen fit a simple equation that can be expressed as follows:

$$u = \text{constant} \left(\frac{1}{2^2} - \frac{1}{n^2} \right) \quad (1.1.3.1)$$

where $n = 3, 4, 5, 6$. As a result, these lines are known as the *Balmer series*. The Swedish physicist Johannes Rydberg (1854–1919) subsequently restated and expanded Balmer's result in the *Rydberg equation*:

$$\frac{1}{\lambda} = \mathfrak{R} \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \quad (1.1.3.2)$$

where n_1 and n_2 are positive integers, $n_2 > n_1$, and $\mathfrak{R}$ the *Rydberg constant*, has a value of $1.09737 \times 10^7 \text{ m}^{-1}$.

Johann Balmer (1825–1898)

A mathematics teacher at a secondary school for girls in Switzerland, Balmer was 60 years old when he wrote the paper on the spectral lines of hydrogen that made him famous.



Balmer published only one other paper on the topic, which appeared when he was 72 years old.

Like Balmer's equation, Rydberg's simple equation described the wavelengths of the visible lines in the emission spectrum of hydrogen (with $n_1 = 2$, $n_2 = 3, 4, 5, \dots$). More important, Rydberg's equation also predicted the wavelengths of other series of lines that would be observed in the emission spectrum of hydrogen: one in the ultraviolet ($n_1 = 1$, $n_2 = 2, 3, 4, \dots$) and one in the infrared ($n_1 = 3$, $n_2 = 4, 5, 6$). Unfortunately, scientists had not yet developed any theoretical justification for an equation of this form.

Bohr's Model

In 1913, a Danish physicist, Niels Bohr (1885–1962; Nobel Prize in Physics, 1922), proposed a theoretical model for the hydrogen atom that explained its emission spectrum. Bohr's model required only one assumption: *The electron moves around the nucleus in circular orbits that can have only certain allowed radii*. Rutherford's earlier model of the atom had also assumed that electrons moved in circular orbits around the nucleus and that the atom was held together by the electrostatic attraction between the positively charged nucleus and the negatively charged electron. Although we now know that the assumption of circular orbits was incorrect, Bohr's insight was to propose that *the electron could occupy only certain regions of space*.

Using classical physics, Niels Bohr showed that the energy of an electron in a particular orbit is given by

$$E_n = \frac{-\mathfrak{R}hc}{n^2} \quad (1.1.3.3)$$

where $\mathfrak{R}$ is the Rydberg constant, h is Planck's constant, c is the speed of light, and n is a positive integer corresponding to the number assigned to the orbit, with $n = 1$ corresponding to the orbit closest to the nucleus. In this model $n = \infty$ corresponds to the level where the energy holding the electron and the nucleus together is zero. In that level, the electron is unbound from the nucleus and the atom has been separated into a negatively charged (the electron) and a positively charged (the nucleus) ion. In this state the radius of the orbit is also infinite. The atom has been ionized.

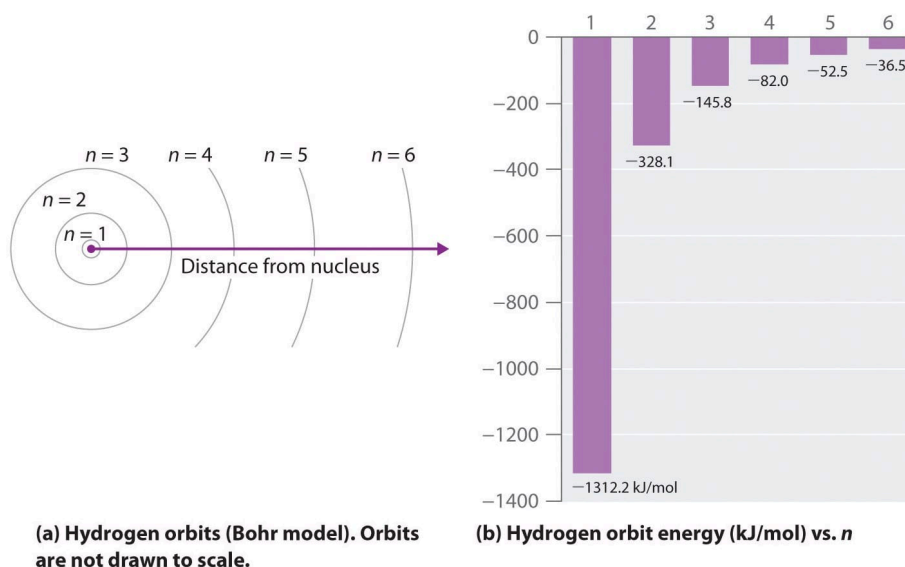
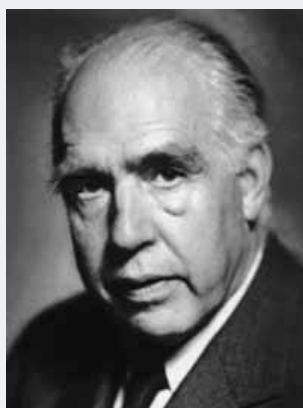


Figure 1.1.3.2: The Bohr Model of the Hydrogen Atom (a) The distance of the orbit from the nucleus increases with increasing n . (b) The energy of the orbit becomes increasingly less negative with increasing n .

Niels Bohr (1885–1962)

During the Nazi occupation of Denmark in World War II, Bohr escaped to the United States, where he became associated with the Atomic Energy Project.



In his final years, he devoted himself to the peaceful application of atomic physics and to resolving political problems arising from the development of atomic weapons.

As n decreases, the energy holding the electron and the nucleus together becomes increasingly negative, the radius of the orbit shrinks and more energy is needed to ionize the atom. The orbit with $n = 1$ is the lowest lying and most tightly bound. The negative sign in Equation 1.1.3.3 indicates that the electron-nucleus pair is more tightly bound (i.e. at a lower potential energy) when they are near each other than when they are far apart. Because a hydrogen atom with its one electron in this orbit has the lowest possible energy, this is the **ground state** (the most stable arrangement of electrons for an element or a compound) for a hydrogen

atom. As n increases, the radius of the orbit increases; the electron is farther from the proton, which results in a less stable arrangement with higher potential energy (Figure 1.1.3.2a). A hydrogen atom with an electron in an orbit with $n > 1$ is therefore in an **excited state**, defined as any arrangement of electrons that is higher in energy than the ground state. When an atom in an excited state undergoes a transition to the ground state in a process called decay, it loses energy by emitting a photon whose energy corresponds to the *difference* in energy between the two states (Figure 1.1.3.1).

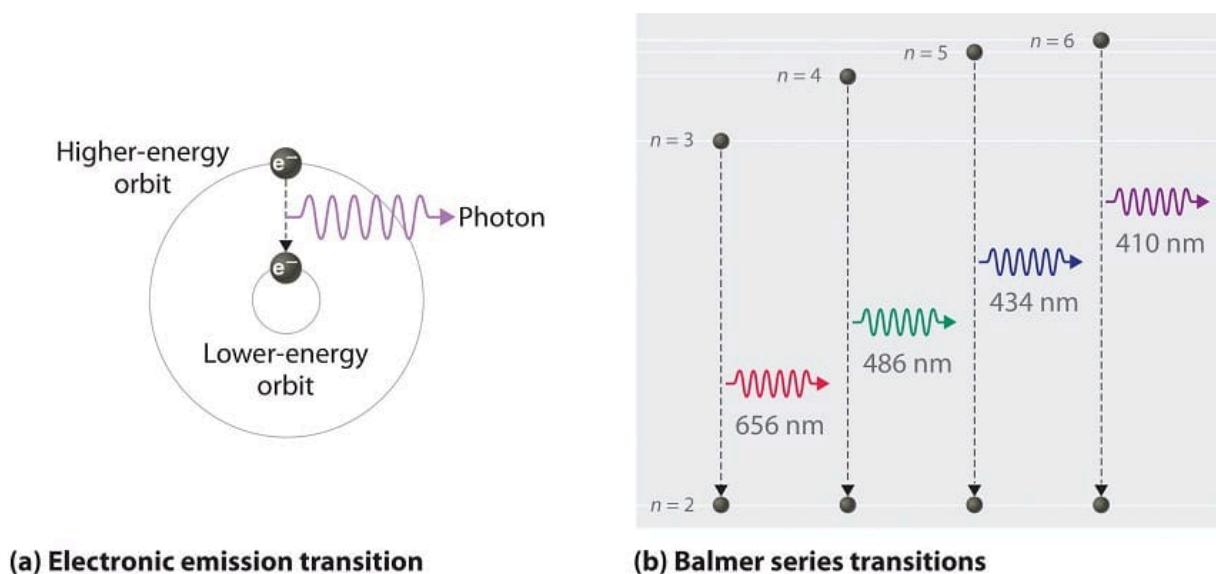


Figure 1.1.3.3: The Emission of Light by a Hydrogen Atom in an Excited State. (a) Light is emitted when the electron undergoes a transition from an orbit with a higher value of n (at a higher energy) to an orbit with a lower value of n (at lower energy). (b) The Balmer series of emission lines is due to transitions from orbits with $n \geq 3$ to the orbit with $n = 2$. The differences in energy between these levels corresponds to light in the visible portion of the electromagnetic spectrum.

So the difference in energy (ΔE) between any two orbits or energy levels is given by $\Delta E = E_{n_1} - E_{n_2}$ where n_1 is the final orbit and n_2 the initial orbit. Substituting from Bohr's equation (Equation 1.1.3.3) for each energy value gives

$$\begin{aligned}\Delta E &= E_{final} - E_{initial} \\ &= -\frac{\mathfrak{R}hc}{n_2^2} - \left(-\frac{\mathfrak{R}hc}{n_1^2}\right) \\ &= -\mathfrak{R}hc \left(\frac{1}{n_2^2} - \frac{1}{n_1^2}\right)\end{aligned}$$

If $n_2 > n_1$, the transition is from a higher energy state (larger-radius orbit) to a lower energy state (smaller-radius orbit), as shown by the dashed arrow in part (a) in Figure 1.1.3.3. Substituting hc/λ for ΔE gives

$$\Delta E = \frac{hc}{\lambda} = -\mathfrak{R}hc \left(\frac{1}{n_2^2} - \frac{1}{n_1^2}\right) \quad (1.1.3.4)$$

Canceling hc on both sides gives

$$\frac{1}{\lambda} = -\mathfrak{R} \left(\frac{1}{n_2^2} - \frac{1}{n_1^2}\right) \quad (1.1.3.5)$$

Except for the negative sign, this is the same equation that Rydberg obtained experimentally. The negative sign in Equations 1.1.3.4 and 1.1.3.5 indicates that energy is released as the electron moves from orbit n_2 to orbit n_1 because orbit n_2 is at a higher energy than orbit n_1 . Bohr calculated the value of $\mathfrak{R}$ from fundamental constants such as the charge and mass of the electron and Planck's constant and obtained a value of $1.0974 \times 10^7 \text{ m}^{-1}$, the same number Rydberg had obtained by analyzing the emission spectra.

We can now understand the physical basis for the Balmer series of lines in the emission spectrum of hydrogen (1.1.3.3b); the lines

in this series correspond to transitions from higher-energy orbits ($n > 2$) to the second orbit ($n = 2$). Thus the hydrogen atoms in the sample have absorbed energy from the electrical discharge and decayed from a higher-energy excited state ($n > 2$) to a lower-energy state ($n = 2$) by emitting a photon of electromagnetic radiation whose energy corresponds exactly to the difference in energy between the two states (Figure 1.1.3.3a). The $n = 3$ to $n = 2$ transition gives rise to the line at 656 nm (red), the $n = 4$ to $n = 2$ transition to the line at 486 nm (green), the $n = 5$ to $n = 2$ transition to the line at 434 nm (blue), and the $n = 6$ to $n = 2$ transition to the line at 410 nm (violet). Because a sample of hydrogen contains a large number of atoms, the intensity of the various lines in a line spectrum depends on the number of atoms in each excited state. At the temperature in the gas discharge tube, more atoms are in the $n = 3$ than the $n \geq 4$ levels. Consequently, the $n = 3$ to $n = 2$ transition is the most intense line, producing the characteristic red color of a hydrogen discharge (Figure 1.1.3.1a). Other families of lines are produced by transitions from excited states with $n > 1$ to the orbit with $n = 1$ or to orbits with $n \geq 3$. These transitions are shown schematically in Figure 1.1.3.4

YouTube Video

This interactive element is not available in this format. Visit the link or scan the QR code to access it online.

[View this YouTube Video online](#)



The Bohr Atom: [The Bohr Atom, YouTube\(opens in new window\) \[youtu.be\]](#)

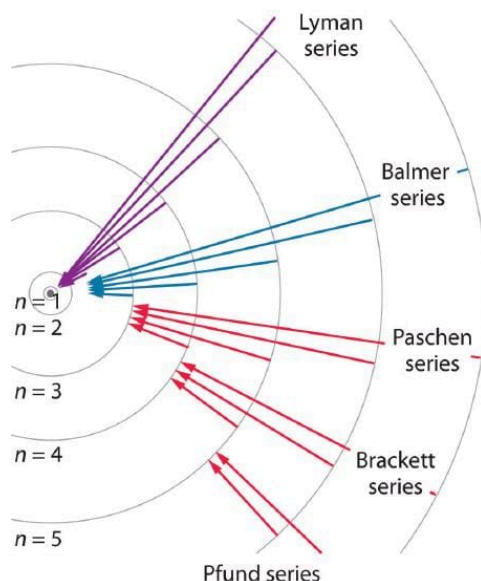


Figure 1.1.3.4: Electron Transitions Responsible for the Various Series of Lines Observed in the Emission Spectrum of Hydrogen. The Lyman series of lines is due to transitions from higher-energy orbits to the lowest-energy orbit ($n = 1$); these transitions release a great deal of energy, corresponding to radiation in the ultraviolet portion of the electromagnetic spectrum. The Paschen, Brackett, and Pfund series of lines are due to transitions from higher-energy orbits to orbits with $n = 3, 4$, and 5 , respectively; these transitions release substantially less energy, corresponding to infrared radiation. (Orbits are not drawn to scale.)

Using Atoms to Time

In contemporary applications, electron transitions are used in timekeeping that needs to be exact. Telecommunications systems, such as cell phones, depend on timing signals that are accurate to within a millionth of a second per day, as are the devices that control the US power grid. Global positioning system (GPS) signals must be accurate to within a billionth of a second per day, which is equivalent to gaining or losing no more than one second in 1,400,000 years. Quantifying time requires finding an event with an interval that repeats on a regular basis.

To achieve the accuracy required for modern purposes, physicists have turned to the atom. The current standard used to calibrate clocks is the cesium atom. Supercooled cesium atoms are placed in a vacuum chamber and bombarded with microwaves whose frequencies are carefully controlled. When the frequency is exactly right, the atoms absorb enough energy to undergo an electronic transition to a higher-energy state. Decay to a lower-energy state emits radiation. The microwave frequency is continually adjusted, serving as the clock's pendulum.

In 1967, the second was defined as the duration of 9,192,631,770 oscillations of the resonant frequency of a cesium atom, called the *cesium clock*. Research is currently under way to develop the next generation of atomic clocks that promise to be even more accurate. Such devices would allow scientists to monitor vanishingly faint electromagnetic signals produced by nerve pathways in the brain and geologists to measure variations in gravitational fields, which cause fluctuations in time, that would aid in the discovery of oil or minerals.

Example 1.1.3.1: The Lyman Series

The so-called Lyman series of lines in the emission spectrum of hydrogen corresponds to transitions from various excited states to the $n = 1$ orbit. Calculate the wavelength of the lowest-energy line in the Lyman series to three significant figures. In what region of the electromagnetic spectrum does it occur?

Given: lowest-energy orbit in the Lyman series

Asked for: wavelength of the lowest-energy Lyman line and corresponding region of the spectrum

Strategy:

- Substitute the appropriate values into Equation 1.1.3.2 (the Rydberg equation) and solve for λ .
- Use Figure 2.2.1 to locate the region of the electromagnetic spectrum corresponding to the calculated wavelength.

Solution:

We can use the Rydberg equation to calculate the wavelength:

$$\frac{1}{\lambda} = -R \left(\frac{1}{n_2^2} - \frac{1}{n_1^2} \right)$$

A For the Lyman series, $n_1 = 1$. The lowest-energy line is due to a transition from the $n = 2$ to $n = 1$ orbit because they are the closest in energy.

$$\frac{1}{\lambda} = -R \left(\frac{1}{n_2^2} - \frac{1}{n_1^2} \right) = 1.097 \times m^{-1} \left(\frac{1}{1} - \frac{1}{4} \right) = 8.228 \times 10^6 m^{-1}$$

It turns out that spectroscopists (the people who study spectroscopy) use cm^{-1} rather than m^{-1} as a common unit. Wavelength is inversely proportional to energy but frequency is directly proportional as shown by Planck's formula, $E = h\nu$.

Spectroscopists often talk about energy and frequency as equivalent. The cm^{-1} unit is particularly convenient. The infrared range is roughly 200 - 5,000 cm^{-1} , the visible from 11,000 to 25,000 cm^{-1} and the UV between 25,000 and 100,000 cm^{-1} . The units of cm^{-1} are called wavenumbers, although people often verbalize it as inverse centimeters. We can convert the answer in part A to cm^{-1} .

$$\tilde{\nu} = \frac{1}{\lambda} = 8.228 \times 10^6 m^{-1} \left(\frac{m}{100 cm} \right) = 82,280 cm^{-1}$$

and

$$\lambda = 1.215 \times 10^{-7} m = 122 nm$$

This emission line is called Lyman alpha. It is the strongest atomic emission line from the sun and drives the chemistry of the upper atmosphere of all the planets, producing ions by stripping electrons from atoms and molecules. It is completely absorbed by oxygen in the upper stratosphere, dissociating O_2 molecules to O atoms which react with other O_2 molecules to form stratospheric ozone.

B This wavelength is in the ultraviolet region of the spectrum.

Exercise 1.1.3.1: The Pfund Series

The Pfund series of lines in the emission spectrum of hydrogen corresponds to transitions from higher excited states to the $n = 5$ orbit. Calculate the wavelength of the *second* line in the Pfund series to three significant figures. In which region of the spectrum does it lie?

Answer available at the end of this section.

Bohr's model of the hydrogen atom gave an exact explanation for its observed emission spectrum. The following are his key contributions to our understanding of atomic structure:

Unfortunately, Bohr could not explain *why* the electron should be restricted to particular orbits. Also, despite a great deal of tinkering, such as assuming that orbits could be ellipses rather than circles, his model could not quantitatively explain the emission spectra of any element other than hydrogen (Figure 1.1.3.5). In fact, Bohr's model worked only for species that contained just one electron: H, He^+ , Li^{2+} , and so forth. Scientists needed a fundamental change in their way of thinking about the electronic structure of atoms to advance beyond the Bohr model.

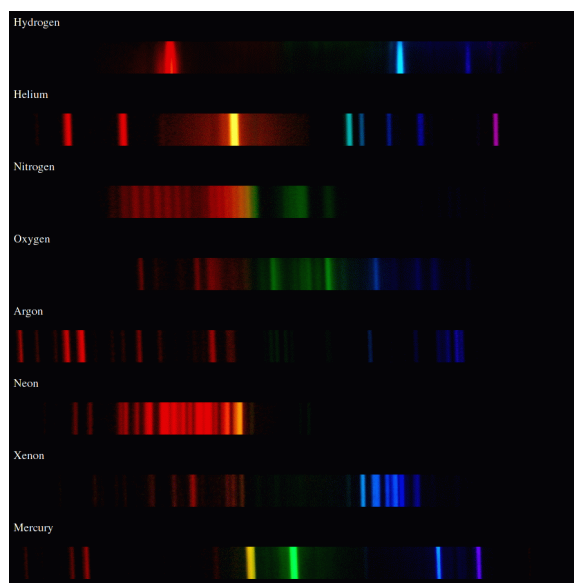


Figure 1.1.3.5: The atomic emission spectra for various elements. Each thin band in each spectrum corresponds to a single, unique transition between energy levels in an atom. [Astronomical spectra image](#)(opens in new window) from the Rochester Institute of Technology, [CC BY-NC-SA 2.0](#)(opens in new window).

The Energy States of the Hydrogen Atom

Thus far we have explicitly considered only the emission of light by atoms in excited states, which produces an emission spectrum (a spectrum produced by the emission of light by atoms in excited states). The converse, absorption of light by ground-state atoms to produce an excited state, can also occur, producing an absorption spectrum (a spectrum produced by the absorption of light by ground-state atoms).

When an atom emits light, it decays to a lower energy state; when an atom absorbs light, it is excited to a higher energy state.

If white light is passed through a sample of hydrogen, hydrogen atoms absorb energy as an electron is excited to higher energy levels (orbits with $n \geq 2$). If the light that emerges is passed through a prism, it forms a continuous spectrum with *black* lines (corresponding to no light passing through the sample) at 656, 468, 434, and 410 nm. These wavelengths correspond to the $n = 2$ to $n = 3$, $n = 2$ to $n = 4$, $n = 2$ to $n = 5$, and $n = 2$ to $n = 6$ transitions. Any given element therefore has both a characteristic emission spectrum and a characteristic absorption spectrum, which are essentially complementary images.

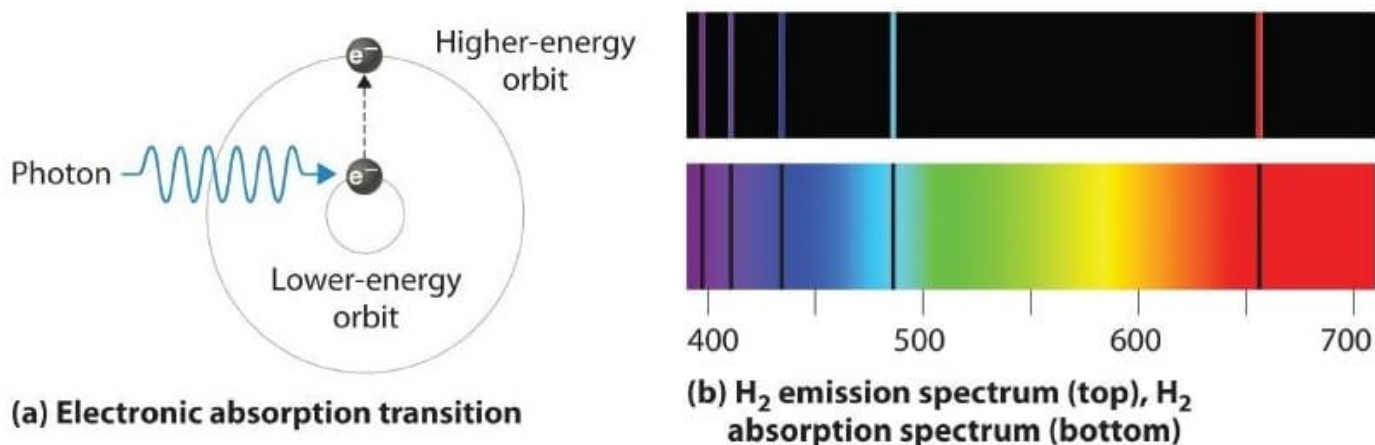


Figure 1.1.3.6: Absorption and Emission Spectra. Absorption of light by a hydrogen atom. (a) When a hydrogen atom absorbs a photon of light, an electron is excited to an orbit that has a higher energy and larger value of n . (b) Images of the emission and absorption spectra of hydrogen are shown here. (CC BY-NC-SA 3.0; anonymous)

Emission and absorption spectra form the basis of *spectroscopy*, which uses spectra to provide information about the structure and the composition of a substance or an object. In particular, astronomers use emission and absorption spectra to determine the composition of stars and interstellar matter. As an example, consider the spectrum of sunlight shown in Figure 1.1.3.7. Because the sun is very hot, the light it emits is in the form of a continuous emission spectrum. Superimposed on it, however, is a series of dark lines due primarily to the absorption of specific frequencies of light by cooler atoms in the outer atmosphere of the sun. By comparing these lines with the spectra of elements measured on Earth, we now know that the sun contains large amounts of hydrogen, iron, and carbon, along with smaller amounts of other elements. During the solar eclipse of 1868, the French astronomer Pierre Janssen (1824–1907) observed a set of lines that did not match those of any known element. He suggested that they were due to the presence of a new element, which he named *helium*, from the Greek *helios*, meaning “sun.” Helium was finally discovered in uranium ores on Earth in 1895. Alpha particles are helium nuclei. Alpha particles emitted by the radioactive uranium pick up electrons from the rocks to form helium atoms.

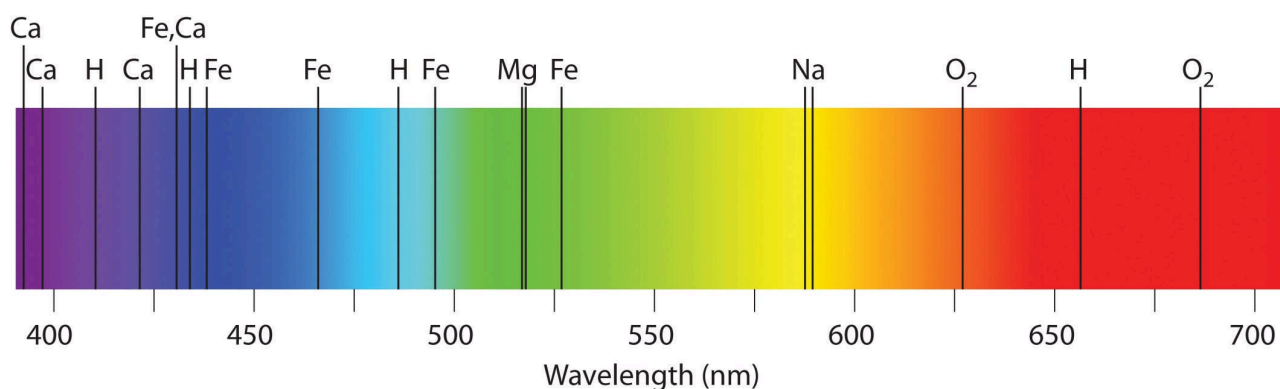


Figure 1.1.3.7: The Visible Spectrum of Sunlight. The characteristic dark lines are mostly due to the absorption of light by elements that are present in the cooler outer part of the sun's atmosphere; specific elements are indicated by the labels. The lines at 628 and 687 nm, however, are due to the absorption of light by oxygen molecules in Earth's atmosphere. (CC BY-NC-SA 3.0; anonymous)

The familiar red color of neon signs used in advertising is due to the emission spectrum of neon shown in part (b) in Figure 1.1.3.5. Similarly, the blue and yellow colors of certain street lights are caused, respectively, by mercury and sodium discharges. In all these cases, an electrical discharge excites neutral atoms to a higher energy state, and light is emitted when the atoms decay to the ground state. In the case of mercury, most of the emission lines are below 450 nm, which produces a blue light (part (c) in

Figure 1.1.3.5). In the case of sodium, the most intense emission lines are at 589 nm, which produces an intense yellow light.

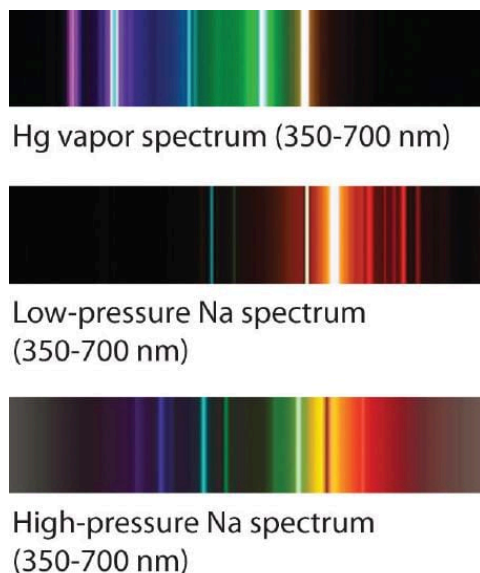


Figure 1.1.3.8: The emission spectra of sodium and mercury. Sodium and mercury spectra. Many street lights use bulbs that contain sodium or mercury vapor. Due to the very different emission spectra of these elements, they emit light of different colors. The lines in the sodium lamp are broadened by collisions. The dark line in the center of the high pressure sodium lamp where the low pressure lamp is strongest is caused by absorption of light in the cooler outer part of the lamp.

Summary

There is an intimate connection between the atomic structure of an atom and its spectral characteristics. Atoms of individual elements emit light at only specific wavelengths, producing a **line spectrum** rather than the continuous spectrum of all wavelengths produced by a hot object. Niels Bohr explained the line spectrum of the hydrogen atom by assuming that the electron moved in circular orbits and that orbits with only certain radii were allowed. Lines in the spectrum were due to transitions in which an electron moved from a higher-energy orbit with a larger radius to a lower-energy orbit with smaller radius. The orbit closest to the nucleus represented the **ground state** of the atom and was most stable; orbits farther away were higher-energy **excited states**. Transitions from an excited state to a lower-energy state resulted in the emission of light with only a limited number of wavelengths. Atoms can also absorb light of certain energies, resulting in a transition from the ground state or a lower-energy excited state to a higher-energy excited state. This produces an **absorption spectrum**, which has dark lines in the same position as the bright lines in the **emission spectrum** of an element. Bohr's model revolutionized the understanding of the atom but could not explain the spectra of atoms heavier than hydrogen.

Key Concepts

- Electrons can occupy only certain regions of space, called *orbits*.
- Orbits closer to the nucleus are lower in energy.
- Electrons can move from one orbit to another by absorbing or emitting energy, giving rise to characteristic spectra.

Contributors and Attributions

- Modified by [Joshua Halpern \(Howard University\)](#)

Answers

Exercise 1.1.3.1: The Pfund Series

4.65×10^3 nm; infrared

This page titled [1.1.3: Line Spectra and the Bohr Model](#) is shared under a [CC BY-NC-SA 4.0](#) license and was authored, remixed, and/or curated by LibreTexts.

- [6.3: Line Spectra and the Bohr Model](#) is licensed [CC BY-NC-SA 3.0](#).

1.1.4: The Wave Behavior of Matter

Learning Objectives

- To understand the wave-particle duality of matter.

Einstein's photons of light were individual packets of energy having many of the characteristics of particles. Recall that the collision of an electron (a particle) with a sufficiently energetic photon can eject a *photoelectron* from the surface of a metal. Any excess energy is transferred to the electron and is converted to the kinetic energy of the ejected electron. Einstein's hypothesis that energy is concentrated in localized bundles, however, was in sharp contrast to the classical notion that energy is spread out uniformly in a wave. We now describe Einstein's theory of the relationship between energy and mass, a theory that others built on to develop our current model of the atom.

The Wave Character of Matter

Einstein 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 famous equation:

$$E = hu = h \frac{c}{\lambda} = mc^2 \quad (1.1.4.1)$$

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

$$m = \frac{E}{c^2} = \frac{hu}{c^2} = \frac{h}{\lambda c} \quad (1.1.4.2)$$

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

$$\lambda = \frac{h}{mv} \quad (1.1.4.3)$$

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 1.1.4.1, 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.

YouTube Video

This interactive element is not available in this format. Visit the link or scan the QR code to access it online.

[View this YouTube Video online](#)



The de Broglie Equation: [The de Broglie Equation, YouTube\(opens in new window\) \[youtu.be\]](#)

Example 1.1.4.1: Wavelength of a Baseball in Motion

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:

- Convert the speed of the baseball to the appropriate SI units: meters per second.
- Substitute values into Equation 1.1.4.3 and solve for the wavelength.

Solution:

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

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

B Recall that the joule is a derived unit, whose units are $(\text{kg} \cdot \text{m}^2)/\text{s}^2$. Thus the wavelength of the baseball is

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

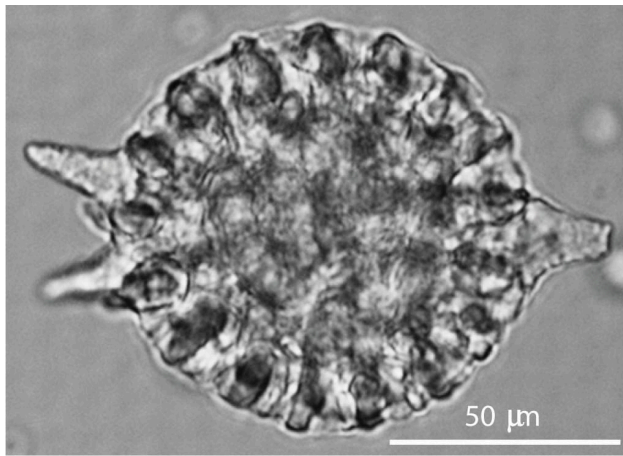
(You should verify that the units cancel to give the wavelength in meters.) Given that the diameter of the nucleus of an atom is approximately 10^{-14} m, the wavelength of the baseball is almost unimaginably small.

Exercise 1.1.4.1: Wavelength of a Neutron in Motion

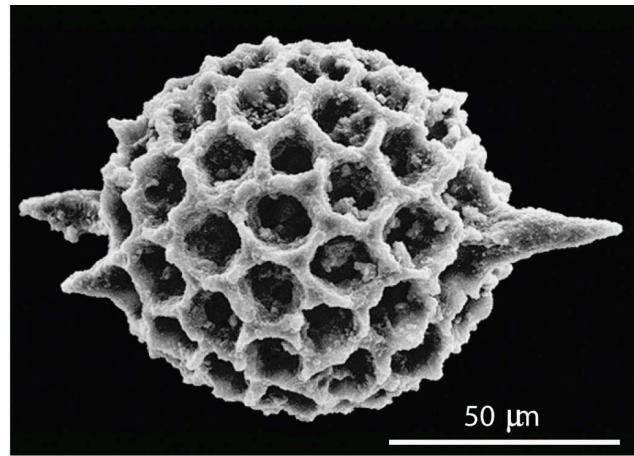
Calculate the wavelength of a neutron that is moving at 3.00×10^3 m/s.

Answer available at the end of this section.

As you calculated in Example 1.1.4.1, 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, however, 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 1.1.4.1).



(a) Radiolarian under light microscope



(b) Radiolarian under electron microscope

Figure 1.1.4.1: 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 And Interference

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 1.1.4.2A shows an arbitrary phase difference between two wave and Figure 1.1.4.2B shows what happens when the two waves are 180 degrees out of phase. The green line is their sum. Figure 1.1.4.2C 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. A pattern of constructive and destructive interference is obtained when two (or more) diffracting waves interact with each other. This principle of diffraction and interference was used to prove the wave properties of electrons and is the basis for how electron microscopes work.

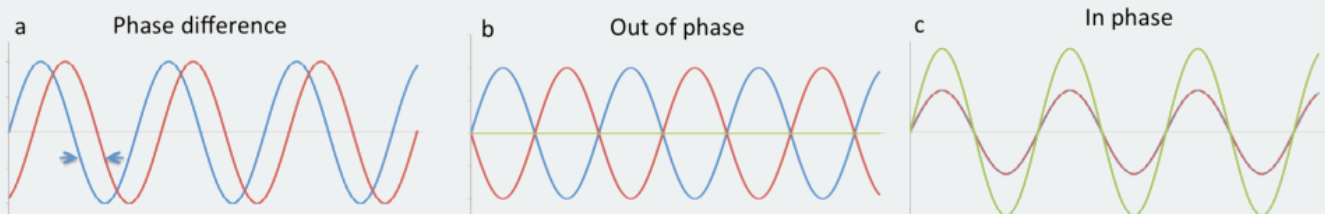
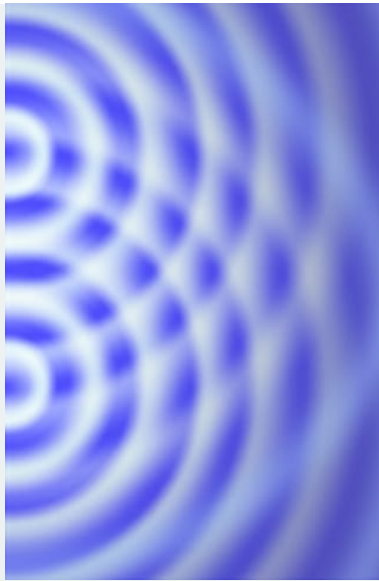


Figure 1.1.4.2: Phase. Two waves traveling together are displaced by a phase difference. If the phase difference is 0° then they lay on top of each other and reinforce. If the phase difference is 180° they completely cancel each other out.

A shows two waves with a phase difference where the peaks are slightly misaligned. B shows two waves out of phase, the two waves are opposite of each other. C shows two waves in phase, the two waves peak at the same time.



The waves are the white circles that start from the left side. The waves intersect at multiple points.

Photograph of an interference pattern produced by circular water waves in a ripple tank.

For a mathematical analysis of phase aspects in sinusoids, check the math Libretexts library.

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 1.1.4.3). If the length of the string is L , then the lowest-energy vibration (the fundamental) has wavelength

$$\begin{aligned}\frac{\lambda}{2} &= L \\ \lambda &= 2L\end{aligned}$$

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

$$\lambda = \frac{2L}{n} \quad (1.1.4.4)$$

where n has any integral value. When plucked, all other frequencies die out immediately. Only the resonant frequencies survive and are heard. Thus, we can think of the resonant frequencies of the string as being quantized. Notice in Figure 1.1.4.3 that all overtones have one or more nodes, points where the string does not move. The amplitude of the wave at a node is zero.

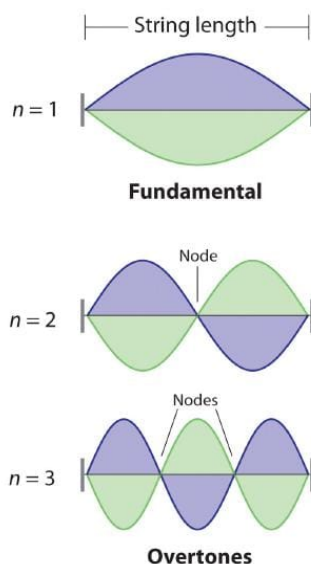


Figure 1.1.4.3: Standing Waves on a Vibrating String. The vibration with $(n = 1)$ is the fundamental and contains no nodes. Vibrations with higher values of n are called overtones; they contain $(n - 1)$ nodes.

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

$$2\pi r = n\lambda \quad (1.1.4.5)$$

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 1.1.4.4). 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 nonresonant 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 1.1.4.5, one complete wavelength would close the circle. Higher energy levels would have successively higher values of n with a corresponding number of nodes.

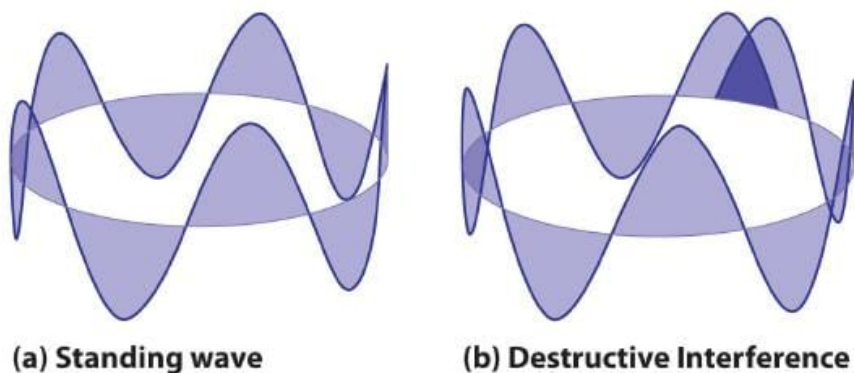


Figure 1.1.4.4: Standing Circular Wave and Destructive Interference. (a) In a standing circular wave with $(n = 5)$, the circumference of the circle corresponds to exactly five wavelengths, which results in constructive interference of the wave with itself when overlapping occurs. (b) If the circumference 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 cancellation of the wave. Consequently, a standing wave cannot exist under these conditions.

Like 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. 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 now 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 it can be bent or spread out by passing through a narrow slit. 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. An "uncertainty principle" for light is, if you will, merely a conclusion about the nature of electromagnetic waves and nothing new. De Broglie's idea of wave-particle duality means that particles such as electrons which exhibit wavelike characteristics will also undergo diffraction from slits whose size is on 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** states that the uncertainty in the position of a particle (Δx) multiplied by the uncertainty in its momentum [$\Delta(mv)$] is greater than or equal to Planck's constant divided by 4π :

$$(\Delta x)(\Delta[mv]) \geq \frac{h}{4\pi} \quad (1.1.4.6)$$

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 ($\Delta x = 0$), then the uncertainty in its momentum must be infinite:

$$(\Delta[mv]) = \frac{h}{4\pi(\Delta x)} = \frac{h}{4\pi(0)} = \infty \quad (1.1.4.7)$$

Because the mass of the electron at rest (m) is both constant and accurately known, the uncertainty in $\Delta(mv)$ must be due to the Δv term, which would have to be infinitely large for $\Delta(mv)$ to equal infinity. That is, according to Equation 1.1.4.7, the more accurately we know the exact position of the electron (as $\Delta x \rightarrow 0$), the less accurately we know the speed and the kinetic energy of the electron ($1/2 mv^2$) because $\Delta(mv) \rightarrow \infty$. Conversely, the more accurately we know the precise momentum (and the energy) of the electron [as $\Delta(mv) \rightarrow 0$], then $\Delta x \rightarrow \infty$ 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 1.1.4.1: Quantum Nature of Baseballs

Calculate the minimum uncertainty in the position of the pitched baseball from Example 1.1.4.1 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:

- Rearrange the inequality that describes the Heisenberg uncertainty principle (Equation 1.1.4.6) to solve for the minimum uncertainty in the position of an object (Δx).
- Find Δv by converting the velocity of the baseball to the appropriate SI units: meters per second.
- Substitute the appropriate values into the expression for the inequality and solve for Δx .

Solution:

A The Heisenberg uncertainty principle (Equation 1.1.4.6) tells us that

$$(\Delta x)(\Delta(mv)) = h/4\pi$$

. Rearranging the inequality gives

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

B We know that $h = 6.626 \times 10^{-34} \text{ J}\cdot\text{s}$ and $m = 0.149 \text{ kg}$. Because there is no uncertainty in the mass of the baseball, $\Delta(mv) = m\Delta v$ and $\Delta v = \pm 1 \text{ mi/h}$. We have

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

C Therefore,

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

Inserting the definition of a joule ($1 \text{ J} = 1 \text{ kg}\cdot\text{m}^2/\text{s}^2$) gives

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

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

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 1.1.4.2

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 $\pm 0.1\%$. Assume its mass to be equal to its mass at rest.

Answer available at the end of this section.

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.

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

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.

$$(\Delta x) (\Delta [mv]) \geq \frac{h}{4\pi}$$

Contributors and Attributions

- Modified by [Joshua Halpern \(Howard University\)](#)
-

Answers

Exercise 1.1.4.1: Wavelength of a Neutron in Motion

1.32 Å, or 132 pm

Exercise 1.1.4.2

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

This page titled [1.1.4: The Wave Behavior of Matter](#) is shared under a [CC BY-NC-SA 4.0](#) license and was authored, remixed, and/or curated by LibreTexts.

- [6.4: The Wave Behavior of Matter](#) is licensed [CC BY-NC-SA 3.0](#).

1.1.5: Quantum Mechanics and Atomic Orbitals

Learning Objectives

- To apply the results of quantum mechanics to chemistry.

The paradox described by Heisenberg's uncertainty principle and the wavelike nature of subatomic particles such as the electron made it impossible to use the equations of classical physics to describe the motion of electrons in atoms. Scientists needed a new approach that took the wave behavior of the electron into account. In 1926, an Austrian physicist, Erwin Schrödinger (1887–1961; Nobel Prize in Physics, 1933), developed *wave mechanics*, a mathematical technique that describes the relationship between the motion of a particle that exhibits wavelike properties (such as an electron) and its allowed energies.

Erwin Schrödinger (1887–1961)

Schrödinger's unconventional approach to atomic theory was typical of his unconventional approach to life. He was notorious for his intense dislike of memorizing data and learning from books. When Hitler came to power in Germany, Schrödinger escaped to Italy. He then worked at Princeton University in the United States but eventually moved to the Institute for Advanced Studies in Dublin, Ireland, where he remained until his retirement in 1955.

Although quantum mechanics uses sophisticated mathematics, you do not need to understand the mathematical details to follow our discussion of its general conclusions. We focus on the properties of the *wavefunctions* that are the solutions of Schrödinger's equations.

Wavefunctions

A wavefunction (Ψ) is a mathematical function that relates the location of an electron at a given point in space (identified by x , y , and z coordinates) to the amplitude of its wave, which corresponds to its energy. Thus each wavefunction is associated with a particular energy E . The properties of wavefunctions derived from quantum mechanics are summarized here:

- **A wavefunction uses three variables to describe the position of an electron.** A fourth variable is usually required to fully describe the location of objects in motion. Three specify the position in space (as with the Cartesian coordinates x , y , and z), and one specifies the time at which the object is at the specified location. For example, if you were the captain of a ship trying to intercept an enemy submarine, you would need to know its latitude, longitude, and depth, as well as the time at which it was going to be at this position (Figure 1.1.5.1). For electrons, we can ignore the time dependence because we will be using standing waves, which by definition do not change with time, to describe the position of an electron.

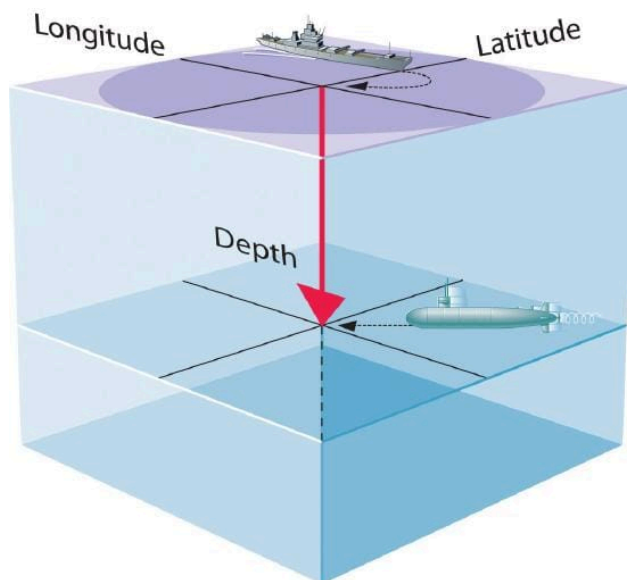


Figure 1.1.5.1: The Four Variables (Latitude, Longitude, Depth, and Time) required to precisely locate an object

- **The magnitude of the wavefunction at a particular point in space is proportional to the amplitude of the wave at that point.** Many wavefunctions are complex functions, which is a mathematical term indicating that they contain $\sqrt{-1}$, represented as i . Hence the amplitude of the wave has no real physical significance. In contrast, the sign of the wavefunction (either positive or negative) corresponds to the phase of the wave, which will be important in our discussion of chemical bonding. The sign of the wavefunction should *not* be confused with a positive or negative electrical charge.
- **The square of the wavefunction at a given point is proportional to the probability of finding an electron at that point, which leads to a distribution of probabilities in space.** The square of the wavefunction (Ψ^2) is always a real quantity [recall that that $\sqrt{-1}^2 = -1$] and is proportional to the probability of finding an electron at a given point. More accurately, the probability is given by the product of the wavefunction Ψ and its complex conjugate Ψ^* , in which all terms that contain i are replaced by $-i$. We use probabilities because, according to Heisenberg's uncertainty principle, we cannot precisely specify the position of an electron. The probability of finding an electron at any point in space depends on several factors, including the distance from the nucleus and, in many cases, the atomic equivalent of latitude and longitude. As one way of graphically representing the probability distribution, the probability of finding an electron is indicated by the density of colored dots, as shown for the ground state of the hydrogen atom in Figure 1.1.5.2.
- **Describing the electron distribution as a standing wave leads to sets of quantum numbers that are characteristic of each wavefunction.** From the patterns of one- and two-dimensional standing waves shown [previously](#), you might expect (correctly) that the patterns of three-dimensional standing waves would be complex. Fortunately, however, in the 18th century, a French mathematician, Adrien Legendre (1752–1783), developed a set of equations to describe the motion of tidal waves on the surface of a flooded planet. Schrödinger incorporated [Legendre's equations](#) into his wavefunctions. The requirement that the waves must be in phase with one another to avoid cancellation and produce a standing wave results in a limited number of solutions (wavefunctions), each of which is specified by a set of numbers called quantum numbers.
- **Each wavefunction is associated with a particular energy.** As in Bohr's model, the energy of an electron in an atom is quantized; it can have only certain allowed values. The major difference between Bohr's model and Schrödinger's approach is that Bohr had to impose the idea of quantization arbitrarily, whereas in Schrödinger's approach, quantization is a natural consequence of describing an electron as a standing wave.

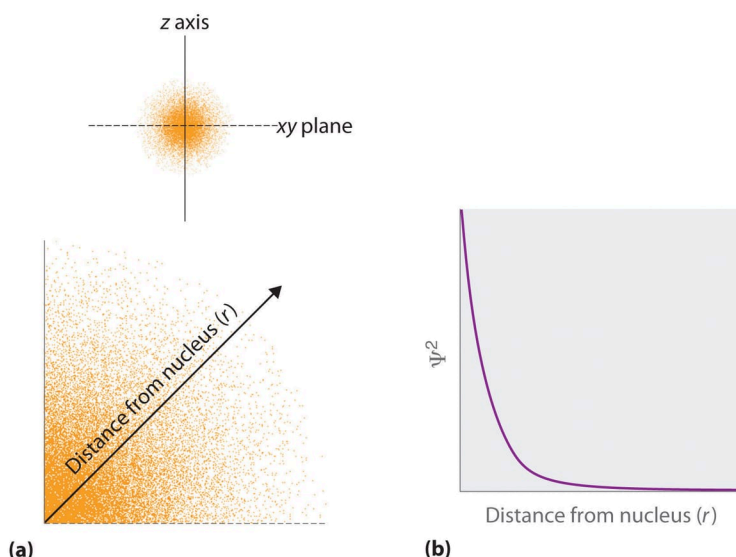


Figure 1.1.5.2: Probability of Finding the Electron in the Ground State of the Hydrogen Atom at Different Points in Space. (a) The density of the dots shows electron probability. (b) In this plot of Ψ^2 versus r for the ground state of the hydrogen atom, the electron probability density is greatest at $r = 0$ (the nucleus) and falls off with increasing r . Because the line never actually reaches the horizontal axis, the probability of finding the electron at very large values of r is very small but *not* zero.

Quantum Numbers

Schrödinger's approach uses three quantum numbers (n , l , and m_l) to specify any wavefunction. The quantum numbers provide information about the spatial distribution of an electron. Although n can be any positive integer, only certain values of l and m_l are allowed for a given value of n .

The Principal Quantum Number

The **principal quantum number** (n) tells the average relative distance of an electron from the nucleus:

$$n = 1, 2, 3, 4, \dots \quad (1.1.5.1)$$

As n increases for a given atom, so does the average distance of an electron from the nucleus. A negatively charged electron that is, on average, closer to the positively charged nucleus is attracted to the nucleus more strongly than an electron that is farther out in space. This means that electrons with higher values of n are easier to remove from an atom. All wavefunctions that have the same value of n are said to constitute a principal shell because those electrons have similar average distances from the nucleus. As you will see, the principal quantum number n corresponds to the n used by Bohr to describe electron orbits and by Rydberg to describe atomic energy levels.

The Azimuthal Quantum Number

The second quantum number is often called the **azimuthal quantum number** (l). The value of l describes the *shape* of the region of space occupied by the electron. The allowed values of l depend on the value of n and can range from 0 to $n - 1$:

$$l = 0, 1, 2, \dots, n - 1 \quad (1.1.5.2)$$

For example, if $n = 1$, l can be only 0; if $n = 2$, l can be 0 or 1; and so forth. For a given atom, all wavefunctions that have the same values of both n and l form a subshell. The regions of space occupied by electrons in the same subshell usually have the same shape, but they are oriented differently in space.

YouTube Video

This interactive element is not available in this format. Visit the link or scan the QR code to access it online.

[View this YouTube Video online](#)



Principal quantum number (n) & Orbital angular momentum (l): The Orbital Subshell:
 Principal quantum number (n) & Orbital angular momentum (l): The Orbital Subshell, YouTube(opens in new window) [youtu.be]

The Magnetic Quantum Number

The third quantum number is the magnetic quantum number (m_l). The value of m_l describes the *orientation* of the region in space occupied by an electron with respect to an applied magnetic field. The allowed values of m_l depend on the value of l : m_l can range from $-l$ to l in integral steps:

$$m_l = -l, -l + 1, \dots, 0, \dots, l - 1, l \quad (1.1.5.3)$$

For example, if $l = 0$, m_l can be only 0; if $l = 1$, m_l can be -1 , 0, or $+1$; and if $l = 2$, m_l can be -2 , -1 , 0, $+1$, or $+2$.

Each wavefunction with an allowed combination of n , l , and m_l values describes an atomic **orbital**, a particular spatial distribution for an electron. For a given set of quantum numbers, each principal shell has a fixed number of subshells, and each subshell has a fixed number of orbitals.

Example 1.1.5.1: $n=4$ Shell Structure

How many subshells and orbitals are contained within the principal shell with $n = 4$?

Given: value of n

Asked for: number of subshells and orbitals in the principal shell

Strategy:

- Given $n = 4$, calculate the allowed values of l . From these allowed values, count the number of subshells.
- For each allowed value of l , calculate the allowed values of m_l . The sum of the number of orbitals in each subshell is the number of orbitals in the principal shell.

Solution:

A We know that l can have all integral values from 0 to $n - 1$. If $n = 4$, then l can equal 0, 1, 2, or 3. Because the shell has four values of l , it has four subshells, each of which will contain a different number of orbitals, depending on the allowed values of m_l .

B For $l = 0$, m_l can be only 0, and thus the $l = 0$ subshell has only one orbital. For $l = 1$, m_l can be 0 or ± 1 ; thus the $l = 1$ subshell has three orbitals. For $l = 2$, m_l can be 0, ± 1 , or ± 2 , so there are five orbitals in the $l = 2$ subshell. The last allowed value of l is $l = 3$, for which m_l can be 0, ± 1 , ± 2 , or ± 3 , resulting in seven orbitals in the $l = 3$ subshell. The total number of orbitals in the $n = 4$ principal shell is the sum of the number of orbitals in each subshell and is equal to $n^2 = 16$

Exercise 1.1.5.1: $n=3$ Shell Structure

How many subshells and orbitals are in the principal shell with $n = 3$?

Answer available at the end of this section.

Rather than specifying all the values of n and l every time we refer to a subshell or an orbital, chemists use an abbreviated system with lowercase letters to denote the value of l for a particular subshell or orbital:

abbreviated system with lowercase letters to denote the value of l for a particular subshell or orbital

$l =$	0	1	2	3
Designation	s	p	d	f

The principal quantum number is named first, followed by the letter s, p, d, or f as appropriate. (These orbital designations are derived from historical terms for corresponding spectroscopic characteristics: sharp, principle, diffuse, and fundamental.) A 1s orbital has $n = 1$ and $l = 0$; a 2p subshell has $n = 2$ and $l = 1$ (and has three 2p orbitals, corresponding to $m_l = -1, 0$, and $+1$); a 3d subshell has $n = 3$ and $l = 2$ (and has five 3d orbitals, corresponding to $m_l = -2, -1, 0, +1$, and $+2$); and so forth.

We can summarize the relationships between the quantum numbers and the number of subshells and orbitals as follows (Table 6.5.1):

- Each principal shell has n subshells. For $n = 1$, only a single subshell is possible (1s); for $n = 2$, there are two subshells (2s and 2p); for $n = 3$, there are three subshells (3s, 3p, and 3d); and so forth. Every shell has an ns subshell, any shell with $n \geq 2$ also has an np subshell, and any shell with $n \geq 3$ also has an nd subshell. Because a 2d subshell would require both $n = 2$ and $l = 2$, which is not an allowed value of l for $n = 2$, a 2d subshell does not exist.
- Each subshell has $2l + 1$ orbitals. This means that all ns subshells contain a single s orbital, all np subshells contain three p orbitals, all nd subshells contain five d orbitals, and all nf subshells contain seven f orbitals.

Each principal shell has n subshells, and each subshell has $2l + 1$ orbitals.

Table 1.1.5.1: Values of n , l , and m_l through $n = 4$

n	l	Subshell Designation	m_l	Number of Orbitals in Subshell	Number of Orbitals in Shell
1	0	1s	0	1	1
2	0	2s	0	1	4
	1	2p	-1, 0, 1	3	
3	0	3s	0	1	9
	1	3p	-1, 0, 1	3	
	2	3d	-2, -1, 0, 1, 2	5	
4	0	4s	0	1	16
	1	4p	-1, 0, 1	3	
	2	4d	-2, -1, 0, 1, 2	5	
	3	4f	-3, -2, -1, 0, 1, 2, 3	7	

YouTube Video

This interactive element is not available in this format. Visit the link or scan the QR code to access it online.

[View this YouTube Video online](#)



Magnetic Quantum Number (m_l) & Spin Quantum Number (m_s): [Magnetic Quantum Number \(\$m_l\$ \) & Spin Quantum Number \(\$m_s\$ \)](#)
[YouTube\(opens in new window\)](#) [[youtu.be](#)] ([opens in new window](#))

Summary

There is a relationship between the motions of electrons in atoms and molecules and their energies that is described by quantum mechanics. Because of wave-particle duality, scientists must deal with the probability of an electron being at a particular point in space. To do so required the development of **quantum mechanics**, which uses **wavefunctions (Ψ)** to describe the mathematical relationship between the motion of electrons in atoms and molecules and their energies. Wavefunctions have five important properties:

1. the wavefunction uses three variables (Cartesian axes x , y , and z) to describe the position of an electron;
2. the magnitude of the wavefunction is proportional to the intensity of the wave;
3. the probability of finding an electron at a given point is proportional to the square of the wavefunction at that point, leading to a distribution of probabilities in space that is often portrayed as an **electron density** plot;
4. describing electron distributions as standing waves leads naturally to the existence of sets of **quantum numbers** characteristic of each wavefunction; and
5. each spatial distribution of the electron described by a wavefunction with a given set of quantum numbers has a particular energy.

Quantum numbers provide important information about the energy and spatial distribution of an electron. The **principal quantum number** n can be any positive integer; as n increases for an atom, the average distance of the electron from the nucleus also increases. All wavefunctions with the same value of n constitute a **principal shell** in which the electrons have similar average distances from the nucleus. The **azimuthal quantum number** l can have integral values between 0 and $n - 1$; it describes the shape of the electron distribution. Wavefunctions that have the same values of both n and l constitute a **subshell**, corresponding to electron distributions that usually differ in orientation rather than in shape or average distance from the nucleus. The **magnetic quantum number** m_l can have $2l + 1$ integral values, ranging from $-l$ to $+l$, and describes the orientation of the electron distribution. Each wavefunction with a given set of values of n , l , and m_l describes a particular spatial distribution of an electron in an atom, an **atomic orbital**.

Answers

Exercise 1.1.5.1: $n=3$ Shell Structure

three subshells; nine orbitals

This page titled [1.1.5: Quantum Mechanics and Atomic Orbitals](#) is shared under a [CC BY-NC-SA 4.0](#) license and was authored, remixed, and/or curated by LibreTexts.

- [6.5: Quantum Mechanics and Atomic Orbitals](#) is licensed [CC BY-NC-SA 3.0](#).

1.1.6: 3D Representation of Orbitals

Learning Objectives

- To understand the 3D representation of electronic orbitals

An orbital is the quantum mechanical refinement of Bohr's orbit. In contrast to his concept of a simple circular orbit with a fixed radius, orbitals are mathematically derived regions of space with different **probabilities** of containing an electron.

One way of representing electron probability distributions was illustrated [previously](#) for the **1s** orbital of hydrogen. Because Ψ^2 gives the probability of finding an electron in a given volume of space (such as a cubic picometer), a plot of Ψ^2 versus distance from the nucleus (r) is a plot of the **probability density**. The **1s** orbital is spherically symmetrical, so the probability of finding a **1s** electron at any given point depends **only** on its distance from the nucleus. The probability density is greatest at $r = 0$ (at the nucleus) and decreases steadily with increasing distance. At very large values of r , the electron probability density is very small but **not** zero.

In contrast, we can calculate the **radial probability** (the probability of finding a **1s** electron at a distance r from the nucleus) by adding together the probabilities of an electron being at all points on a series of **x** spherical shells of radius $r_1, r_2, r_3, \dots, r_x - 1, r_x$. In effect, we are dividing the atom into very thin concentric shells, much like the layers of an onion (Figure 1.1.6.1a), and calculating the probability of finding an electron on each spherical shell. Recall that the electron probability density is greatest at $r = 0$ (Figure 1.1.6.1b), so the density of dots is greatest for the smallest spherical shells in part (a) in Figure 1.1.6.1. In contrast, the surface area of each spherical shell is equal to $4\pi r^2$, which increases very rapidly with increasing r (Figure 1.1.6.1c). Because the surface area of the spherical shells increases more rapidly with increasing r than the electron probability density decreases, the plot of radial probability has a maximum at a particular distance (Figure 1.1.6.1d). Most important, when r is very small, the surface area of a spherical shell is so small that the **total** probability of finding an electron close to the nucleus is very low; at the nucleus, the electron probability vanishes (Figure 1.1.6.1d).

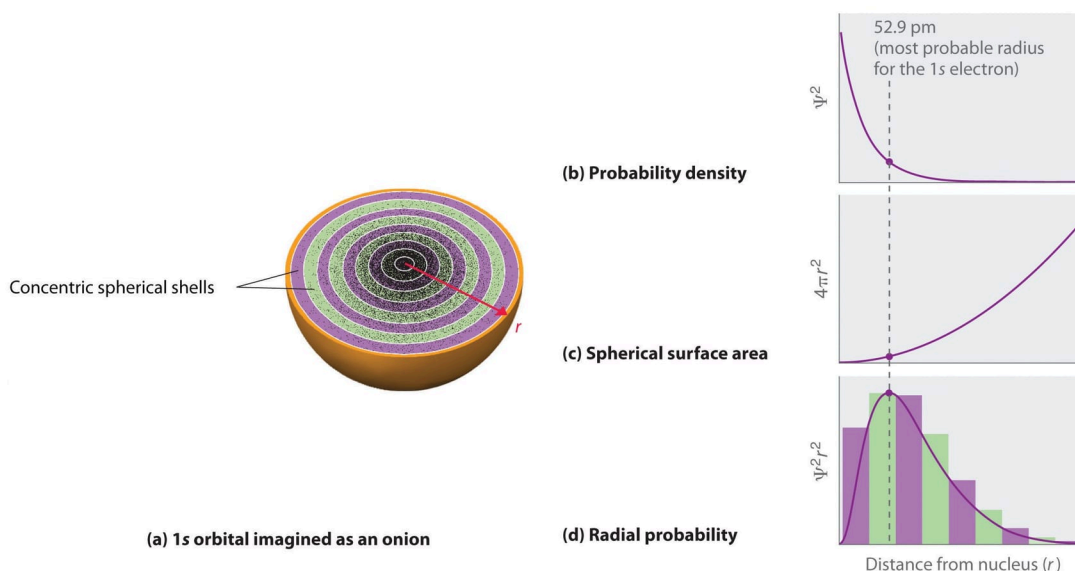


Figure 1.1.6.1: Most Probable Radius for the Electron in the Ground State of the Hydrogen Atom. (a) Imagine dividing the atom's total volume into very thin concentric shells as shown in the onion drawing. (b) A plot of electron probability density Ψ^2 versus r shows that the electron probability density is greatest at $r = 0$ and falls off smoothly with increasing r . The density of the dots is therefore greatest in the innermost shells of the onion. (c) The surface area of each shell, given by $4\pi r^2$, increases rapidly with increasing r . (d) If we count the number of dots in each spherical shell, we obtain the total probability of finding the electron at a given value of r . Because the surface area of each shell increases more rapidly with increasing r than the electron probability density decreases, a plot of electron probability versus r (the **radial probability**) shows a peak. This peak corresponds to the most probable radius for the electron, 52.9 pm, which is exactly the radius predicted by Bohr's model of the hydrogen atom.

For the hydrogen atom, the peak in the radial probability plot occurs at $r = 0.529 \text{ \AA}$ (52.9 pm), which is exactly the radius calculated by Bohr for the $n = 1$ orbit. Thus the **most probable radius** obtained from quantum mechanics is identical to the radius calculated by classical mechanics. In Bohr's model, however, the electron was assumed to be at this distance 100% of the time, whereas in the Schrödinger model, it is at this distance only some of the time. The difference between the two models is attributable to the wavelike behavior of the electron and the Heisenberg uncertainty principle.

Figure 1.1.6.2 compares the electron probability densities for the hydrogen **1s**, **2s**, and **3s** orbitals. Note that all three are spherically symmetrical. For the **2s** and **3s** orbitals, however (and for all other **s** orbitals as well), the electron probability density does not fall off smoothly with increasing r . Instead, a series of minima and maxima are observed in the radial probability plots (Figure 1.1.6.2c). The minima correspond to spherical **nodes** (regions of zero electron probability), which alternate with spherical regions of nonzero electron probability. The existence of these nodes is a consequence of changes of wave **phase** in the wavefunction Ψ .

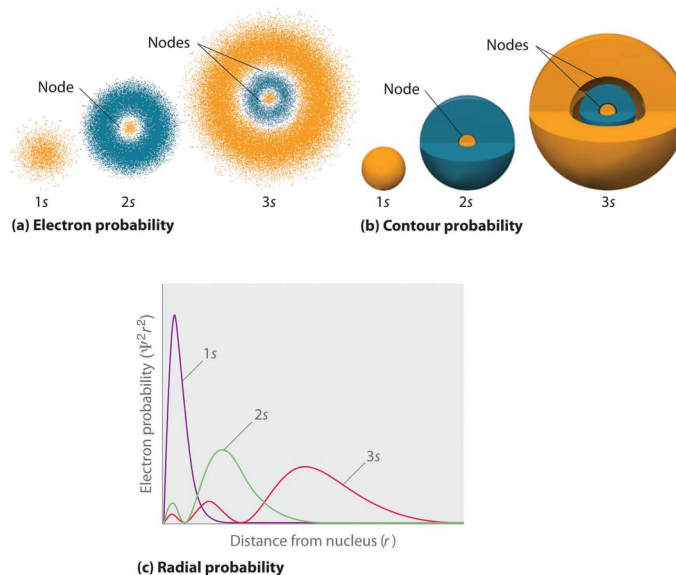


Figure 1.1.6.2: Probability Densities for the **1s**, **2s**, and **3s** Orbitals of the Hydrogen Atom. (a) The electron probability density in any plane that contains the nucleus is shown. Note the presence of circular regions, or nodes, where the probability density is zero. (b) Contour surfaces enclose 90% of the electron probability, which illustrates the different sizes of the **1s**, **2s**, and **3s** orbitals. The cutaway drawings give partial views of the internal spherical nodes. The orange color corresponds to regions of space where the phase of the wave function is positive, and the blue color corresponds to regions of space where the phase of the wave function is negative. (c) In these plots of electron probability as a function of distance from the nucleus (r) in all directions (radial probability), the most probable radius increases as n increases, but the **2s** and **3s** orbitals have regions of significant electron probability at small values of r .

s Orbitals ($l=0$)

Three things happen to **s** orbitals as n increases (Figure 1.1.6.2):

1. They become larger, extending farther from the nucleus.
2. They contain more nodes. This is similar to a standing wave that has regions of significant amplitude separated by nodes, points with zero amplitude.
3. For a given atom, the **s** orbitals also become higher in energy as n increases because of their increased distance from the nucleus.

Orbitals are generally drawn as three-dimensional surfaces that enclose 90% of the electron density, as was shown for the hydrogen **1s**, **2s**, and **3s** orbitals in part (b) in Figure 1.1.6.2. Although such drawings show the relative sizes of the orbitals, they do not normally show the spherical nodes in the **2s** and **3s** orbitals because the spherical nodes lie inside the 90% surface. Fortunately, the positions of the spherical nodes are not important for chemical bonding.

p Orbitals ($l=1$)

Only **s** orbitals are spherically symmetrical. As the value of l increases, the number of orbitals in a given subshell increases, and

the shapes of the orbitals become more complex. Because the $2p$ subshell has $l = 1$, with three values of m_l (-1 , 0 , and $+1$), there are three $2p$ orbitals.

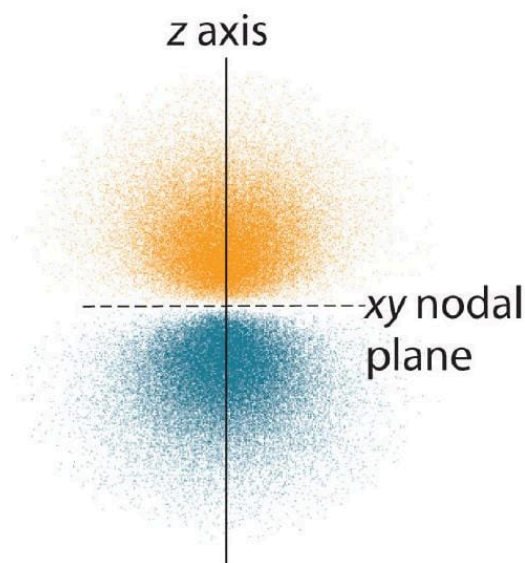


Figure 1.1.6.3: Electron Probability Distribution for a Hydrogen $2p$ Orbital. The nodal plane of zero electron density separates the two lobes of the $2p$ orbital. As in Figure 1.1.6.2, the colors correspond to regions of space where the phase of the wave function is positive (orange) and negative (blue).

The electron probability distribution for one of the hydrogen $2p$ orbitals is shown in Figure 1.1.6.3. Because this orbital has two lobes of electron density arranged along the z axis, with an electron density of zero in the xy plane (i.e., the xy plane is a nodal plane), it is a $2p_z$ orbital. As shown in Figure 1.1.6.4, the other two $2p$ orbitals have identical shapes, but they lie along the x axis ($2p_x$) and y axis ($2p_y$), respectively. Note that each p orbital has just one **nodal plane**. In each case, the phase of the wave function for each of the $2p$ orbitals is positive for the lobe that points along the positive axis and negative for the lobe that points along the negative axis. It is important to emphasize that these signs correspond to the **phase** of the wave that describes the electron motion, **not** to positive or negative charges.

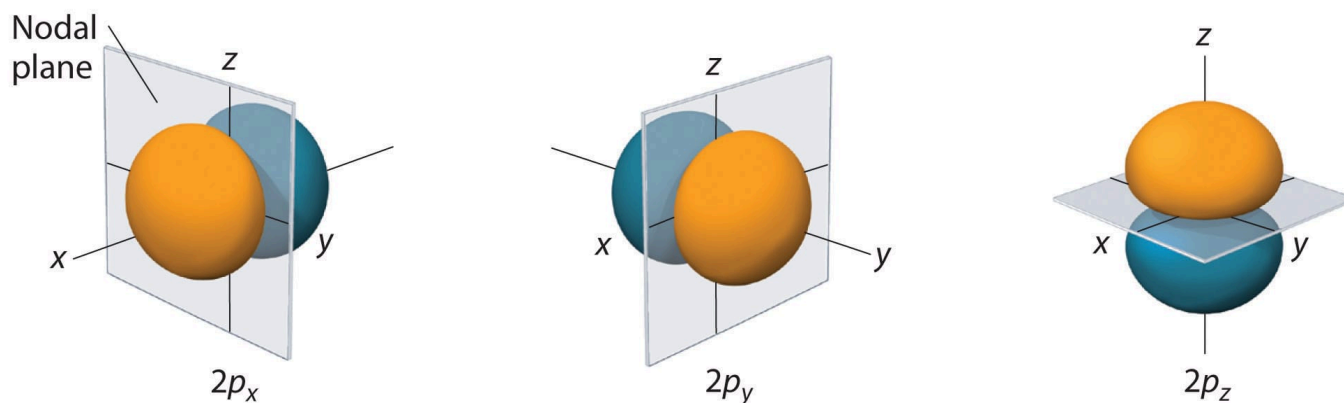


Figure 1.1.6.4 The Three Equivalent $2p$ Orbitals of the Hydrogen Atom

The surfaces shown enclose 90% of the total electron probability for the $2p_x$, $2p_y$, and $2p_z$ orbitals. Each orbital is oriented along the axis indicated by the subscript and a nodal plane that is perpendicular to that axis bisects each $2p$ orbital. The phase of the wave function is positive (orange) in the region of space where x , y , or z is positive and negative (blue) where x , y , or z is negative. Just as with the s orbitals, the size and complexity of the p orbitals for any atom increase as the principal quantum number n increases. The shapes of the 90% probability surfaces of the $3p$, $4p$, and higher-energy p orbitals are, however, essentially the same as those shown in Figure 1.1.6.4.

d Orbitals ($l=2$)

Subshells with $l = 2$ have five **d** orbitals; the first principal shell to have a **d** subshell corresponds to $n = 3$. The five **d** orbitals have m_l values of $-2, -1, 0, +1$, and $+2$.

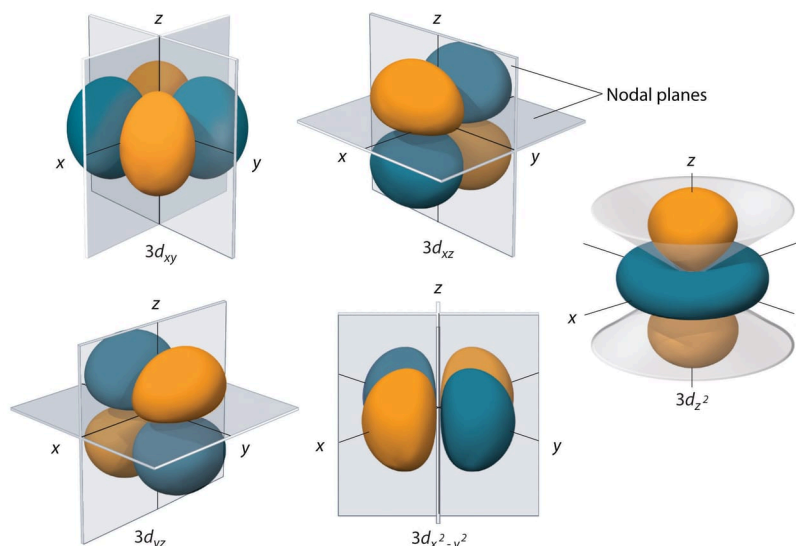


Figure 1.1.6.5: The Five Equivalent 3d Orbitals of the Hydrogen Atom. The surfaces shown enclose 90% of the total electron probability for the five hydrogen 3d orbitals. Four of the five 3d orbitals consist of four lobes arranged in a plane that is intersected by two perpendicular nodal planes. These four orbitals have the same shape but different orientations. The fifth 3d orbital, $3d_{z^2}$, has a distinct shape even though it is mathematically equivalent to the others. The phase of the wave function for the different lobes is indicated by color: orange for positive and blue for negative.

The 3 d orbitals can be broken down into $3d_{xy}$, $3d_{xz}$, $3d_{yz}$, $3d_{x^2-y^2}$, $3d_{z^2}$.

The hydrogen 3d orbitals, shown in Figure 1.1.6.5, have more complex shapes than the 2p orbitals. All five 3d orbitals contain two nodal surfaces, as compared to one for each p orbital and zero for each s orbital. In three of the d orbitals, the lobes of electron density are oriented between the x and y, x and z, and y and z planes; these orbitals are referred to as the $3d_{xy}$, $3d_{xz}$, and $3d_{yz}$ orbitals, respectively. A fourth d orbital has lobes lying along the x and y axes; this is the $3d_{x^2-y^2}$ orbital. The fifth 3d orbital, called the $3d_{z^2}$ orbital, has a unique shape: it looks like a $2p_z$ orbital combined with an additional doughnut of electron probability lying in the xy plane. Despite its peculiar shape, the $3d_{z^2}$ orbital is mathematically equivalent to the other four and has the same energy. In contrast to p orbitals, the phase of the wave function for d orbitals is the same for opposite pairs of lobes. As shown in Figure 1.1.6.5, the phase of the wave function is positive for the two lobes of the dz^2 orbital that lie along the z axis, whereas the phase of the wave function is negative for the doughnut of electron density in the xy plane. Like the s and p orbitals, as n increases, the size of the d orbitals increases, but the overall shapes remain similar to those depicted in Figure 1.1.6.5.

f Orbitals ($l=3$)

Principal shells with $n = 4$ can have subshells with $l = 3$ and m_l values of $-3, -2, -1, 0, +1, +2$, and $+3$. These subshells consist of seven **f** orbitals. Each **f** orbital has three nodal surfaces, so their shapes are complex. Because **f** orbitals are not particularly important for our purposes, we do not discuss them further, and orbitals with higher values of l are not discussed at all.

Orbital Energies

Although we have discussed the shapes of orbitals, we have said little about their comparative energies. We begin our discussion of orbital energies by considering atoms or ions with only a single electron (such as H or He^+).

The relative energies of the atomic orbitals with $n \leq 4$ for a hydrogen atom are plotted in Figure 1.1.6.6; note that the orbital energies depend on **only** the principal quantum number n . Consequently, the energies of the **2s** and **2p** orbitals of hydrogen are the same; the energies of the **3s**, **3p**, and **3d** orbitals are the same; and so forth. Quantum mechanics predicts that in the hydrogen

atom, all orbitals with the same value of n (e.g., the three $2p$ orbitals) are **degenerate**, meaning that they have the same energy. The orbital energies obtained for hydrogen using quantum mechanics are exactly the same as the allowed energies calculated by Bohr. In contrast to Bohr's model, however, which allowed only one orbit for each energy level, quantum mechanics predicts that there are **4** orbitals with different electron density distributions in the $n = 2$ principal shell (one $2s$ and three $2p$ orbitals), **9** in the $n = 3$ principal shell, and **16** in the $n = 4$ principal shell. The different values of l and m_l for the individual orbitals within a given principal shell are not important for understanding the emission or absorption spectra of the hydrogen atom under most conditions, but they do explain the splittings of the main lines that are observed when hydrogen atoms are placed in a magnetic field. Figure 1.1.6.6 shows that the energy levels become closer and closer together as the value of n increases, as expected because of the $1/n^2$ dependence of orbital energies.



Figure 1.1.6.6: Orbital Energy Level Diagram for the Hydrogen Atom with a single electron. Each box corresponds to one orbital. Note that the difference in energy between orbitals decreases rapidly with increasing values of n .

The energies of the orbitals in any species with only one electron can be calculated by a minor variation of [Bohr's equation](#), which can be extended to other single-electron species by incorporating the nuclear charge Z (the number of protons in the nucleus):

$$E = -\frac{Z^2}{n^2} R h c \quad (1.1.6.1)$$

In general, both energy and radius decrease as the nuclear charge increases. Thus the most stable orbitals (those with the lowest energy) are those closest to the nucleus. For example, in the ground state of the hydrogen atom, the single electron is in the $1s$ orbital, whereas in the first excited state, the atom has absorbed energy and the electron has been promoted to one of the $n = 2$ orbitals. In ions with only a single electron, the energy of a given orbital depends on only n , and all subshells within a principal shell, such as the p_x , p_y , and p_z orbitals, are degenerate.

Summary

The four chemically important types of atomic orbital correspond to values of $\ell = 0, 1, 2$, and 3 . Orbitals with $\ell = 0$ are s orbitals and are spherically symmetrical, with the greatest probability of finding the electron occurring at the nucleus. All orbitals with values of $n > 1$ and $\ell = 0$ contain one or more nodes. Orbitals with $\ell = 1$ are p orbitals and contain a nodal plane that includes the nucleus, giving rise to a dumbbell shape. Orbitals with $\ell = 2$ are d orbitals and have more complex shapes with at least two nodal surfaces. Orbitals with $\ell = 3$ are f orbitals, which are still more complex.

Because its average distance from the nucleus determines the energy of an electron, each atomic orbital with a given set of quantum numbers has a particular energy associated with it, the **orbital energy**.

$$E = -\frac{Z^2}{n^2} R h c$$

In atoms or ions with only a single electron, all orbitals with the same value of n have the same energy (they are degenerate), and the energies of the principal shells increase smoothly as n increases. An atom or ion with the electron(s) in the lowest-energy orbital(s) is said to be in its ground state, whereas an atom or ion in which one or more electrons occupy higher-energy orbitals is said to be in an excited state.

Contributors and Attributions

- Modified by [Joshua Halpern \(Howard University\)](#)

This page titled [1.1.6: 3D Representation of Orbitals](#) is shared under a [CC BY-NC-SA 4.0](#) license and was authored, remixed, and/or curated by LibreTexts.

- [6.6: 3D Representation of Orbitals](#) is licensed [CC BY-NC-SA 3.0](#).

1.1.7: Many-Electron Atoms

Learning Objectives

- To write the electron configuration of any element and relate its electron configuration to its position in the periodic table.

The quantum mechanical model allowed us to determine the energies of the hydrogen atomic orbitals; now we would like to extend this to describe the electronic structure of every element in the Periodic Table. The process of describing each atom's electronic structure consists, essentially, of beginning with hydrogen and adding one proton and one electron at a time to create the next heavier element in the table; however, interactions between electrons make this process a bit more complicated than it sounds. All stable nuclei other than hydrogen also contain one or more neutrons. Because neutrons have no electrical charge, however, they can be ignored in the following discussion. Before demonstrating how to do this, however, we must introduce the concept of electron spin and the Pauli principle.

Orbitals and their Energies

Unlike in hydrogen-like atoms with only one electron, in multielectron atoms the values of quantum numbers n and l determine the energies of an orbital. The energies of the different orbitals for a typical multielectron atom are shown in Figure 1.1.7.1. Within a given principal shell of a multielectron atom, the orbital energies increase with increasing l . An ns orbital always lies below the corresponding np orbital, which in turn lies below the nd orbital.

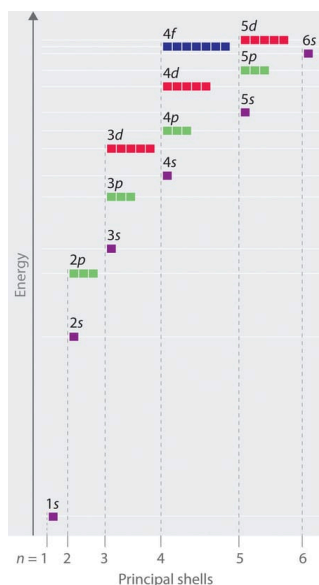


Figure 1.1.7.1: Orbital Energy Level Diagram for a Typical Multielectron Atom

These energy differences are caused by the effects of *shielding* and *penetration*, the extent to which a given orbital lies inside other filled orbitals. For example, an electron in the 2s orbital penetrates inside a filled 1s orbital more than an electron in a 2p orbital does. Since electrons, all being negatively charged, repel each other, an electron closer to the nucleus partially *shields* an electron farther from the nucleus from the attractive effect of the positively charged nucleus. Hence in an atom with a filled 1s orbital, the **effective nuclear charge** (Z_{eff}) experienced by a 2s electron is greater than the Z_{eff} experienced by a 2p electron. Consequently, the 2s electron is more tightly bound to the nucleus and has a lower energy, consistent with the order of energies shown in Figure 1.1.7.1.

Due to electron shielding, Z_{eff} increases more rapidly going across a row of the periodic table than going down a column.

Notice in Figure 1.1.7.1 that the difference in energies between subshells can be so large that the energies of orbitals from different principal shells can become approximately equal. For example, the energy of the 3d orbitals in most atoms is actually *between* the energies of the 4s and the 4p orbitals.

Electron Spin: The Fourth Quantum Number

When scientists analyzed the emission and absorption spectra of the elements more closely, they saw that for elements having more than one electron, nearly all the lines in the spectra were actually *pairs* of very closely spaced lines. Because each line represents an energy level available to electrons in the atom, there are twice as many energy levels available as would be predicted solely based on the quantum numbers n , l , and m_l . Scientists also discovered that applying a magnetic field caused the lines in the pairs to split farther apart. In 1925, two graduate students in physics in the Netherlands, George Uhlenbeck (1900–1988) and Samuel Goudsmit (1902–1978), proposed that the splittings were caused by an electron spinning about its axis, much as Earth spins about its axis. When an electrically charged object spins, it produces a magnetic moment parallel to the axis of rotation, making it behave like a magnet. Although the electron cannot be viewed solely as a particle, spinning or otherwise, it is indisputable that it does have a magnetic moment. This magnetic moment is called **electron spin**.

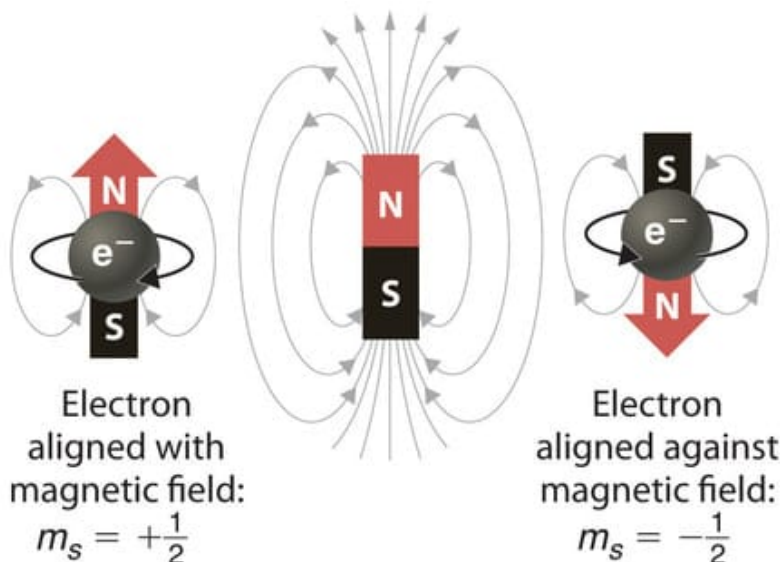


Figure 1.1.7.2: Electron Spin. In a magnetic field, an electron has two possible orientations with different energies, one with spin up, aligned with the magnetic field, and one with spin down, aligned against it. All other orientations are forbidden.

In an external magnetic field, the electron has two possible orientations (Figure 1.1.7.2). These are described by a fourth quantum number (m_s), which for any electron can have only two possible values, designated $+\frac{1}{2}$ (up) and $-\frac{1}{2}$ (down) to indicate that the two orientations are opposites; the subscript s is for spin. An electron behaves like a magnet that has one of two possible orientations, aligned either with the magnetic field or against it.

The Pauli Exclusion Principle

The implications of electron spin for chemistry were recognized almost immediately by an Austrian physicist, Wolfgang Pauli (1900–1958; Nobel Prize in Physics, 1945), who determined that each orbital can contain no more than two electrons. He developed the Pauli exclusion principle: *No two electrons in an atom can have the same values of all four quantum numbers (n , l , m_l , m_s).*

By giving the values of n , l , and m_l , we also specify a particular orbital (e.g., 1s with $n = 1$, $l = 0$, $m_l = 0$). Because m_s has only two possible values ($+\frac{1}{2}$ or $-\frac{1}{2}$), two electrons, *and only two electrons*, can occupy any given orbital, one with spin up and one with spin down. With this information, we can proceed to construct the entire periodic table, which was originally based on the

physical and chemical properties of the known elements.

Example 1.1.7.1

List all the allowed combinations of the four quantum numbers (n , l , m_l , m_s) for electrons in a $2p$ orbital and predict the maximum number of electrons the $2p$ subshell can accommodate.

Given: orbital

Asked for: allowed quantum numbers and maximum number of electrons in orbital

Strategy:

- List the quantum numbers (n , l , m_l) that correspond to an $n = 2p$ orbital. List all allowed combinations of (n , l , m_l).
- Build on these combinations to list all the allowed combinations of (n , l , m_l , m_s).
- Add together the number of combinations to predict the maximum number of electrons the $2p$ subshell can accommodate.

Solution:

A For a $2p$ orbital, we know that $n = 2$, $l = n - 1 = 1$, and $m_l = -l, (-l + 1), \dots, (l - 1), l$. There are only three possible combinations of (n , l , m_l): ($2, 1, 1$), ($2, 1, 0$), and ($2, 1, -1$).

B Because m_s is independent of the other quantum numbers and can have values of only $+\frac{1}{2}$ and $-\frac{1}{2}$, there are six possible combinations of (n , l , m_l , m_s): ($2, 1, 1, +\frac{1}{2}$), ($2, 1, 1, -\frac{1}{2}$), ($2, 1, 0, +\frac{1}{2}$), ($2, 1, 0, -\frac{1}{2}$), ($2, 1, -1, +\frac{1}{2}$), and ($2, 1, -1, -\frac{1}{2}$).

C Hence the $2p$ subshell, which consists of three $2p$ orbitals ($2p_x$, $2p_y$, and $2p_z$), can contain a total of six electrons, two in each orbital.

Exercise 1.1.7.1

List all the allowed combinations of the four quantum numbers (n , l , m_l , m_s) for a $6s$ orbital, and predict the total number of electrons it can contain.

Answer available at the end of this section.

YouTube Video

This interactive element is not available in this format. Visit the link or scan the QR code to access it online.

[View this YouTube Video online](#)



Magnetic Quantum Number (m_l) & Spin Quantum Number (m_s): [Magnetic Quantum Number \(\$m_l\$ \) & Spin Quantum Number \(\$m_s\$ \), YouTube](#)[\(opens in new window\)](#) [[youtu.be](#)] [\(opens in new window\)](#)

Summary

The arrangement of atoms in the periodic table arises from the lowest energy arrangement of electrons in the valence shell. In addition to the three quantum numbers (n , l , m_l) dictated by quantum mechanics, a fourth quantum number is required to explain certain properties of atoms. This is the **electron spin** quantum number (m_s), which can have values of $+\frac{1}{2}$ or $-\frac{1}{2}$ for any electron,

corresponding to the two possible orientations of an electron in a magnetic field. The concept of electron spin has important consequences for chemistry because the **Pauli exclusion principle** implies that no orbital can contain more than two electrons (with opposite spin).

Answers

Exercise 1.1.7.1

$(6, 0, 0, +\frac{1}{2}), (6, 0, 0, -\frac{1}{2})$; two electrons

This page titled [1.1.7: Many-Electron Atoms](#) is shared under a [CC BY-NC-SA 4.0](#) license and was authored, remixed, and/or curated by LibreTexts.

- [6.7: Many-Electron Atoms](#) is licensed [CC BY-NC-SA 3.0](#).

1.1.8: Electron Configurations

Learning Objectives

- To understand the basics of adding electrons to atomic orbitals
- To understand the basics of the Aufbau principle

The **electron configuration** of an element is the arrangement of its electrons in its atomic orbitals. By knowing the electron configuration of an element, we can predict and explain a great deal of its chemistry.

The Aufbau Principle

We construct the periodic table by following the **aufbau principle** (from German, meaning “building up”). First we determine the number of electrons in the atom; then we add electrons one at a time to the lowest-energy orbital available *without violating the Pauli principle*. We use the orbital energy diagram of Figure 1.1.8.1, recognizing that each orbital can hold two electrons, one with spin up $\uparrow$, corresponding to $m_s = +\frac{1}{2}$, which is arbitrarily written first, and one with spin down $\downarrow$, corresponding to $m_s = -\frac{1}{2}$. A filled orbital is indicated by $\uparrow\downarrow$, in which the electron spins are said to be *paired*. Here is a schematic orbital diagram for a hydrogen atom in its ground state:

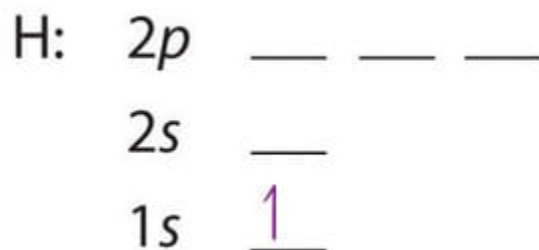
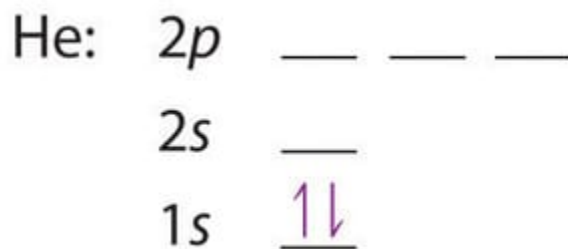


Figure 1.1.8.1: One electron in.

From the orbital diagram, we can write the electron configuration in an abbreviated form in which the occupied orbitals are identified by their principal quantum number n and their value of l (s , p , d , or f), with the number of electrons in the subshell indicated by a superscript. For hydrogen, therefore, the single electron is placed in the $1s$ orbital, which is the orbital lowest in energy (Figure 1.1.8.1), and the electron configuration is written as $1s^1$ and read as “one-s-one.”

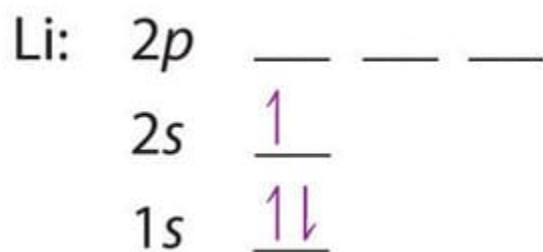
A neutral helium atom, with an atomic number of 2 ($Z = 2$), has two electrons. We place one electron in the orbital that is lowest in energy, the $1s$ orbital. From the **Pauli exclusion principle**, we know that an orbital can contain two electrons with opposite spin, so we place the second electron in the same orbital as the first but pointing down, so that the electrons are paired. The orbital diagram for the helium atom is therefore



written as $1s^2$, where the superscript 2 implies the pairing of spins. Otherwise, our configuration would violate the Pauli principle.

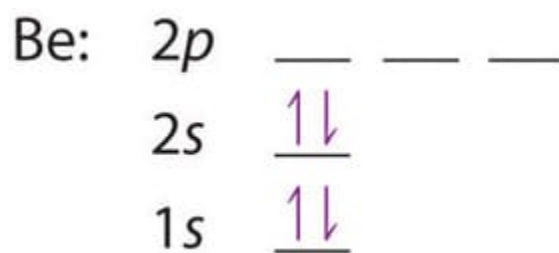
The next element is lithium, with $Z = 3$ and three electrons in the neutral atom. We know that the $1s$ orbital can hold two of the

electrons with their spins paired; the third electron must enter a higher energy orbital. Figure 6.29 tells us that the next lowest energy orbital is 2s, so the orbital diagram for lithium is

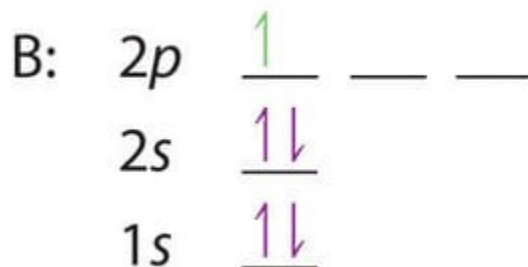


This electron configuration is written as $1s^2 2s^1$.

The next element is beryllium, with $Z = 4$ and four electrons. We fill both the 1s and 2s orbitals to achieve a $1s^2 2s^2$ electron configuration:

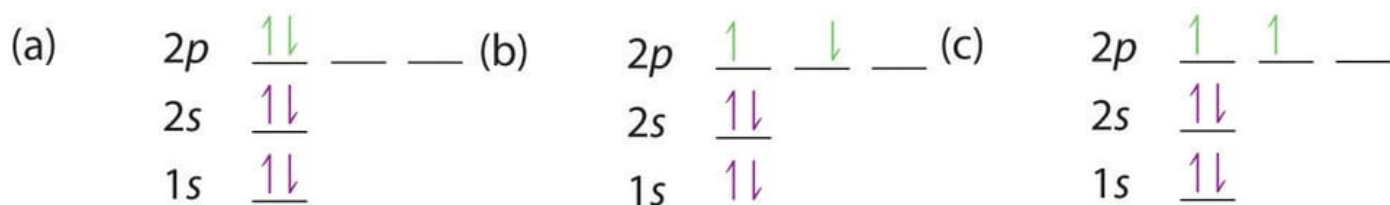


When we reach boron, with $Z = 5$ and five electrons, we must place the fifth electron in one of the 2p orbitals. Because all three 2p orbitals are degenerate, it doesn't matter which one we select. The electron configuration of boron is $1s^2 2s^2 2p^1$:



Boron has one electron pair in the 1 s orbital, one electron pair in the 2 s orbital, and one electron in the 2 p orbital.

At carbon, with $Z = 6$ and six electrons, we are faced with a choice. Should the sixth electron be placed in the same 2p orbital that already has an electron, or should it go in one of the empty 2p orbitals? If it goes in an empty 2p orbital, will the sixth electron have its spin aligned with or be opposite to the spin of the fifth? In short, which of the following three orbital diagrams is correct for carbon, remembering that the 2p orbitals are degenerate?



Three diagrams on where the sixth electron should go, a) paired with the lone electron in the 2 p orbital, b) unpaired with the lone electron and pointing downward, and c) unpaired with the lone electron

Because of electron-electron interactions, it is more favorable energetically for an electron to be in an unoccupied orbital than in one that is already occupied; hence we can eliminate choice a. Similarly, experiments have shown that choice b is slightly higher in energy (less stable) than choice c because electrons in degenerate orbitals prefer to line up with their spins parallel; thus, we can eliminate choice b. Choice c illustrates **Hund's rule** (named after the German physicist Friedrich H. Hund, 1896–1997), which today says that the lowest-energy electron configuration for an atom is the one that has the maximum number of electrons with parallel spins in degenerate orbitals. By Hund's rule, the electron configuration of carbon, which is $1s^2 2s^2 2p^2$, is understood to correspond to the orbital diagram shown in c. Experimentally, it is found that the ground state of a neutral carbon atom does indeed contain two unpaired electrons.

When we get to nitrogen ($Z = 7$, with seven electrons), Hund's rule tells us that the lowest-energy arrangement is

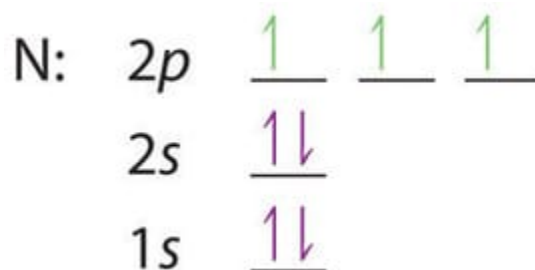
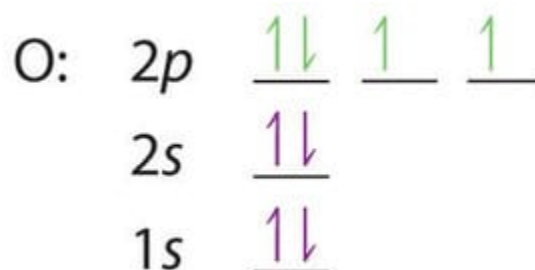


Figure 1.1.8.1: Copy and Paste Caption here. (Copyright; author via source)

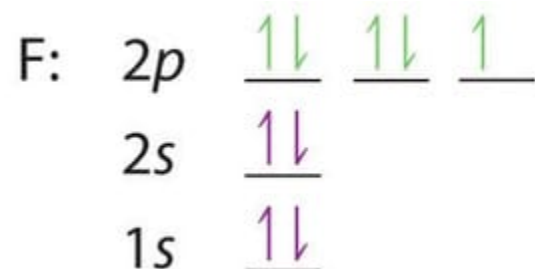
with three unpaired electrons. The electron configuration of nitrogen is thus $1s^2 2s^2 2p^3$.

At oxygen, with $Z = 8$ and eight electrons, we have no choice. One electron must be paired with another in one of the $2p$ orbitals, which gives us two unpaired electrons and a $1s^2 2s^2 2p^4$ electron configuration. Because all the $2p$ orbitals are degenerate, it doesn't matter which one has the pair of electrons.



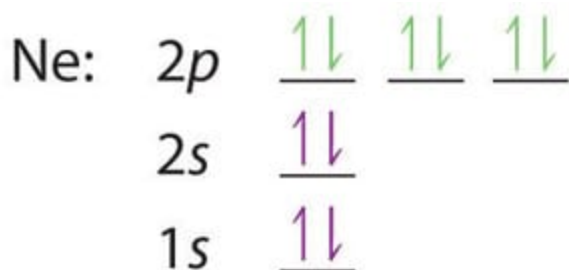
Oxygen has one electron pair in the $1s$ orbital, one electron pair in the $2s$ orbital, and one electron pair, and 2 unpaired electrons in the $2p$ orbitals.

Similarly, fluorine has the electron configuration $1s^2 2s^2 2p^5$:



Fluorine has one electron pair in the $1s$ orbital, one electron pair in the $2s$ orbital, and 2 electrons pairs with one unpaired electron in the $2p$ orbital.

When we reach neon, with $Z = 10$, we have filled the $2p$ subshell, giving a $1s^2 2s^2 2p^6$ electron configuration:



Neon has one electron pair in the 1 s orbital, one electron pair in the 2 s orbital, and 3 electron pairs in the 2 p orbital.

Notice that for neon, as for helium, all the orbitals through the 2p level are completely filled. This fact is very important in dictating both the chemical reactivity and the bonding of helium and neon, as you will see.

YouTube Video

This interactive element is not available in this format. Visit the link or scan the QR code to access it online.

[View this YouTube Video online](#)



Electron Configuration of Atoms: [Electron Configuration of Atoms, YouTube\(opens in new window\)](#)
[youtu.be]

Valence Electrons

As we continue through the periodic table in this way, writing the electron configurations of larger and larger atoms, it becomes tedious to keep copying the configurations of the filled inner subshells. In practice, chemists simplify the notation by using a bracketed noble gas symbol to represent the configuration of the noble gas from the preceding row because all the orbitals in a noble gas are filled. For example, [Ne] represents the $1s^2 2s^2 2p^6$ electron configuration of neon ($Z = 10$), so the electron configuration of sodium, with $Z = 11$, which is $1s^2 2s^2 2p^6 3s^1$, is written as $[\text{Ne}]3s^1$:

Electron Configuration of Neon and Sodium

Neon	$Z = 10$	$1s^2 2s^2 2p^6$
Sodium	$Z = 11$	$1s^2 2s^2 2p^6 3s^1 = [\text{Ne}]3s^1$

Because electrons in filled inner orbitals are closer to the nucleus and more tightly bound to it, they are rarely involved in chemical reactions. This means that the chemistry of an atom depends mostly on the electrons in its outermost shell, which are called the **valence electrons**. The simplified notation allows us to see the valence-electron configuration more easily. Using this notation to compare the electron configurations of sodium and lithium, we have:

Electron Configuration of Sodium and Lithium

Sodium	$1s^2 2s^2 2p^6 3s^1 = [\text{Ne}]3s^1$
Lithium	$1s^2 2s^1 = [\text{He}]2s^1$

It is readily apparent that both sodium and lithium have one s electron in their valence shell. We would therefore predict that sodium and lithium have very similar chemistry, which is indeed the case.

As we continue to build the eight elements of period 3, the 3s and 3p orbitals are filled, one electron at a time. This row concludes

with the noble gas argon, which has the electron configuration $[\text{Ne}]3s^23p^6$, corresponding to a filled valence shell.

Example 1.1.8.1: Electronic Configuration of Phosphorus

Draw an orbital diagram and use it to derive the electron configuration of phosphorus, $Z = 15$. What is its valence electron configuration?

Given: atomic number

Asked for: orbital diagram and valence electron configuration for phosphorus

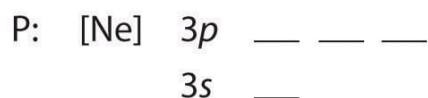
Strategy:

- Locate the nearest noble gas preceding phosphorus in the periodic table. Then subtract its number of electrons from those in phosphorus to obtain the number of valence electrons in phosphorus.
- Referring to Figure 1.1.8.1, draw an orbital diagram to represent those valence orbitals. Following Hund's rule, place the valence electrons in the available orbitals, beginning with the orbital that is lowest in energy. Write the electron configuration from your orbital diagram.
- Ignore the inner orbitals (those that correspond to the electron configuration of the nearest noble gas) and write the valence electron configuration for phosphorus.

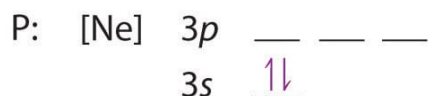
Solution:

A Because phosphorus is in the third row of the periodic table, we know that it has a $[\text{Ne}]$ closed shell with 10 electrons. We begin by subtracting 10 electrons from the 15 in phosphorus.

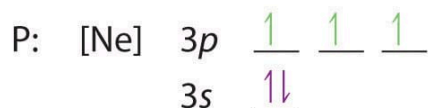
B The additional five electrons are placed in the next available orbitals, which Figure 1.1.8.1 tells us are the 3s and 3p orbitals:



Because the 3s orbital is lower in energy than the 3p orbitals, we fill it first:



Hund's rule tells us that the remaining three electrons will occupy the degenerate 3p orbitals separately but with their spins aligned:



The electron configuration is $[\text{Ne}]3s^23p^3$.

C We obtain the valence electron configuration by ignoring the inner orbitals, which for phosphorus means that we ignore the [Ne] closed shell. This gives a valence-electron configuration of $3s^2 3p^3$.

Exercise 1.1.8.1

Draw an orbital diagram and use it to derive the electron configuration of chlorine, $Z = 17$. What is its valence electron configuration?

Answer available at the end of this section.

YouTube Video

This interactive element is not available in this format. Visit the link or scan the QR code to access it online.

[View this YouTube Video online](#)



Definition of Valence Electrons: [Definition of Valence Electrons, YouTube\(opens in new window\)](#) [youtu.be]

The general order in which orbitals are filled is depicted in Figure 1.1.8.2. Subshells corresponding to each value of n are written from left to right on successive horizontal lines, where each row represents a row in the periodic table. The order in which the orbitals are filled is indicated by the diagonal lines running from the upper right to the lower left. Accordingly, the $4s$ orbital is filled prior to the $3d$ orbital because of shielding and penetration effects. Consequently, the electron configuration of potassium, which begins the fourth period, is $[\text{Ar}]4s^1$, and the configuration of calcium is $[\text{Ar}]4s^2$. Five $3d$ orbitals are filled by the next 10 elements, the transition metals, followed by three $4p$ orbitals. Notice that the last member of this row is the noble gas krypton ($Z = 36$), $[\text{Ar}]4s^2 3d^{10} 4p^6 = [\text{Kr}]$, which has filled $4s$, $3d$, and $4p$ orbitals. The fifth row of the periodic table is essentially the same as the fourth, except that the $5s$, $4d$, and $5p$ orbitals are filled sequentially.

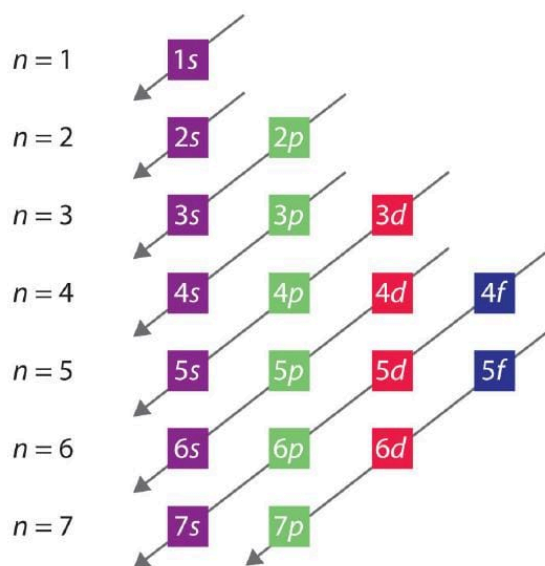


Figure 1.1.8.2: Predicting the Order in Which Orbitals Are Filled in Multielectron Atoms. If you write the subshells for each value of the principal quantum number on successive lines, the observed order in which they are filled is indicated by a series of diagonal lines running from the upper right to the lower left.

The sixth row of the periodic table will be different from the preceding two because the $4f$ orbitals, which can hold 14 electrons, are filled between the $6s$ and the $5d$ orbitals. The elements that contain $4f$ orbitals in their valence shell are the lanthanides. When the $6p$ orbitals are finally filled, we have reached the next noble gas, radon ($Z = 86$), $[\text{Xe}]6s^2 4f^{14} 5d^{10} 6p^6 = [\text{Rn}]$. In the last row, the $5f$ orbitals are filled between the $7s$ and the $6d$ orbitals, which gives the 14 actinide elements. Because the large number of protons makes their nuclei unstable, all the actinides are radioactive.

Example 1.1.8.2: Electron Configuration of Mercury

Write the electron configuration of mercury ($Z = 80$), showing all the inner orbitals.

Given: atomic number

Asked for: complete electron configuration

Strategy:

Using the orbital diagram in Figure 1.1.8.1 and the periodic table as a guide, fill the orbitals until all 80 electrons have been placed.

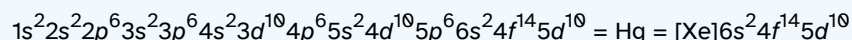
Solution:

By placing the electrons in orbitals following the order shown in Figure 1.1.8.2 and using the periodic table as a guide, we obtain

Solution to Example 6.8.2

$1s^2$	row 1	2 electrons
$2s^2 2p^6$	row 2	8 electrons
$3s^2 3p^6$	row 3	8 electrons
$4s^2 3d^{10} 4p^6$	row 4	18 electrons
$5s^2 4d^{10} 5p^6$	row 5	18 electrons
	row 1–5	54 electrons

After filling the first five rows, we still have $80 - 54 = 26$ more electrons to accommodate. According to Figure 1.1.8.2, we need to fill the $6s$ (2 electrons), $4f$ (14 electrons), and $5d$ (10 electrons) orbitals. The result is mercury's electron configuration:



with a filled $5d$ subshell, a $6s^2 4f^{14} 5d^{10}$ valence shell configuration, and a total of 80 electrons. (You should always check to be sure that the total number of electrons equals the atomic number.)

Exercise 1.1.8.2: Electron Configuration of Flerovium

Although element 114 is not stable enough to occur in nature, atoms of element 114 were created for the first time in a nuclear reactor in 1998 by a team of Russian and American scientists. The element is named after the Flerov Laboratory of Nuclear Reactions of the Joint Institute for Nuclear Research in Dubna, Russia, where the element was discovered. The name of the laboratory, in turn, honors the Russian physicist Georgy Flyorov. Write the complete electron configuration for element 114.

Answer available at the end of this section.

The electron configurations of the elements are presented in Figure 1.1.8.2, which lists the orbitals in the order in which they are filled. In several cases, the ground state electron configurations are different from those predicted by Figure 1.1.8.1. Some of

these anomalies occur as the $3d$ orbitals are filled. For example, the observed ground state electron configuration of chromium is $[\text{Ar}]4s^13d^5$ rather than the predicted $[\text{Ar}]4s^23d^4$. Similarly, the observed electron configuration of copper is $[\text{Ar}]4s^13d^{10}$ instead of $[\text{Ar}]s^23d^9$. The actual electron configuration may be rationalized in terms of an added stability associated with a half-filled (ns^1, np^3, nd^5, nf^7) or filled ($ns^2, np^6, nd^{10}, nf^{14}$) subshell. (In fact, this "special stability" is really another consequence of the *instability* caused by pairing an electron with another in the same orbital, as illustrated by Hund's rule.) Given the small differences between higher energy levels, this added stability is enough to shift an electron from one orbital to another. In heavier elements, other more complex effects can also be important, leading to many additional anomalies. For example, cerium has an electron configuration of $[\text{Xe}]6s^24f^15d^1$, which is impossible to rationalize in simple terms. In most cases, however, these apparent anomalies do not have important chemical consequences.

Additional stability is associated with half-filled or filled subshells.

YouTube Video

This interactive element is not available in this format. Visit the link or scan the QR code to access it online.

[View this YouTube Video online](#)



Electron Configuration of Transition Metals: [Electron Configuration of Transition Metals, YouTube\(opens in new window\)](#)
[youtu.be]

Summary

Based on the Pauli principle and a knowledge of orbital energies obtained using hydrogen-like orbitals, it is possible to construct the periodic table by filling up the available orbitals beginning with the lowest-energy orbitals (the **aufbau principle**), which gives rise to a particular arrangement of electrons for each element (its **electron configuration**). **Hund's rule** says that the lowest-energy arrangement of electrons is the one that places them in degenerate orbitals with their spins parallel. For chemical purposes, the most important electrons are those in the outermost principal shell, the **valence electrons**.

Answers

Exercise 1.1.8.1

$[\text{Ne}]3s^23p^5; 3s^23p^5$

Exercise 1.1.8.2: Electron Configuration of Flerovium

$s^22s^22p^63s^23p^64s^23d^{10}4p^65s^24d^{10}5p^66s^24f^{14}5d^{10}6p^67s^25f^{14}6d^{10}7p^2$

This page titled [1.1.8: Electron Configurations](#) is shared under a [CC BY-NC-SA 4.0](#) license and was authored, remixed, and/or curated by LibreTexts.

- [6.8: Electron Configurations](#) is licensed [CC BY-NC-SA 3.0](#).

1.1.9: Electron Configurations and the Periodic Table

Learning Objectives

- To correlate the arrangement of atoms in the periodic table results in blocks corresponding to filling of the ns , np , nd , and nf orbitals

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

Figure 1.1.9.2: Electron Configurations of the Elements. The electron configurations of elements indicated in red are exceptions due to the added stability associated with half-filled and filled subshells. The electron configurations of the elements indicated in blue are also anomalous, but the reasons for the observed configurations are more complex. For elements after No, the electron configurations are tentative.

Example 1.1.9.1

Use the periodic table to predict the valence electron configuration of all the elements of group 2 (beryllium, magnesium, calcium, strontium, barium, and radium).

Given: series of elements

Asked for: valence electron configurations

Strategy:

- Identify the block in the periodic table to which the group 2 elements belong. Locate the nearest noble gas preceding each element and identify the principal quantum number of the valence shell of each element.
- Write the valence electron configuration of each element by first indicating the filled inner shells using the symbol for the nearest preceding noble gas and then listing the principal quantum number of its valence shell, its valence orbitals, and the number of valence electrons in each orbital as superscripts.

Solution:

A The group 2 elements are in the s block of the periodic table, and as group 2 elements, they all have two valence electrons. Beginning with beryllium, we see that its nearest preceding noble gas is helium and that the principal quantum number of its valence shell is $n = 2$.

B Thus beryllium has an $[\text{He}]s^2$ electron configuration. The next element down, magnesium, is expected to have exactly the same arrangement of electrons in the $n = 3$ principal shell: $[\text{Ne}]s^2$. By extrapolation, we expect all the group 2 elements to have an ns^2 electron configuration.

Exercise 1.1.9.1

Use the periodic table to predict the characteristic valence electron configuration of the halogens in group 17.

Answer available at the end of this section.

Summary

The arrangement of atoms in the periodic table results in blocks corresponding to filling of the ns , np , nd , and nf orbitals to produce the distinctive chemical properties of the elements in the **s block**, **p block**, **d block**, and **f block**, respectively.

Answers

Exercise 1.1.9.1

All have an ns^2np^5 electron configuration, one electron short of a noble gas electron configuration. (Note that the heavier halogens also have filled $(n-1)d^{10}$ subshells, as well as an $(n-2)f^{14}$ subshell for Rn; these do not, however, affect their chemistry in any significant way.

This page titled [1.1.9: Electron Configurations and the Periodic Table](#) is shared under a [CC BY-NC-SA 4.0](#) license and was authored, remixed, and/or curated by LibreTexts.

- [6.9: Electron Configurations and the Periodic Table](#) is licensed [CC BY-NC-SA 3.0](#).

1.1.E: Electronic Structure of Atoms (Exercises)

6.1: The Wave Nature of Light

Conceptual Problems

1. What are the characteristics of a wave? What is the relationship between electromagnetic radiation and wave energy?
2. At constant wavelength, what effect does increasing the frequency of a wave have on its speed? its amplitude?
3. List the following forms of electromagnetic radiation in order of increasing wavelength: x-rays, radio waves, infrared waves, microwaves, ultraviolet waves, visible waves, and gamma rays. List them in order of increasing frequency. Which has the highest energy?
4. A large industry is centered on developing skin-care products, such as suntan lotions and cosmetics, that cannot be penetrated by ultraviolet radiation. How does the wavelength of visible light compare with the wavelength of ultraviolet light? How does the energy of visible light compare with the energy of ultraviolet light? Why is this industry focused on blocking ultraviolet light rather than visible light?

Numerical Problems

1. The human eye is sensitive to what fraction of the electromagnetic spectrum, assuming a typical spectral range of 10^4 to 10^{20} Hz? If we came from the planet Krypton and had x-ray vision (i.e., if our eyes were sensitive to x-rays in addition to visible light), how would this fraction be changed?
2. What is the frequency in megahertz corresponding to each wavelength?
 1. 755 m
 2. 6.73 nm
 3. 1.77×10^3 km
 4. 9.88 Å
 5. 3.7×10^{-10} m
3. What is the frequency in megahertz corresponding to each wavelength?
 1. 5.8×10^{-7} m
 2. 2.3 Å
 3. 8.6×10^7 m
 4. 6.2 mm
 5. 3.7 nm
4. Line spectra are also observed for molecular species. Given the following characteristic wavelengths for each species, identify the spectral region (ultraviolet, visible, etc.) in which the following line spectra will occur. Given 1.00 mol of each compound and the wavelength of absorbed or emitted light, how much energy does this correspond to?
 1. NH_3 , 1.0×10^{-2} m
 2. $\text{CH}_3\text{CH}_2\text{OH}$, 9.0 μm
 3. Mo atom, 7.1 Å
5. What is the speed of a wave in meters per second that has a wavelength of 1250 m and a frequency of $2.36 \times 10^5 \text{ s}^{-1}$?
6. A wave travels at 3.70 m/s with a frequency of 4.599×10^7 Hz and an amplitude of 1.0 m. What is its wavelength in nanometers?
7. An AM radio station broadcasts with a wavelength of 248.0 m. What is the broadcast frequency of the station in kilohertz?

An AM station has a broadcast range of 92.6 MHz. What is the corresponding wavelength range in meters for this reception?

8. An FM radio station broadcasts with a wavelength of 3.21 m. What is the broadcast frequency of the station in megahertz? An FM radio typically has a broadcast range of 82–112 MHz. What is the corresponding wavelength range in meters for this reception?
9. A microwave oven operates at a frequency of approximately 2450 MHz. What is the corresponding wavelength? Water, with its polar molecules, absorbs electromagnetic radiation primarily in the infrared portion of the spectrum. Given this fact, why are microwave ovens used for cooking food?

6.2: Quantized Energy and Photons

Conceptual Problems

1. Describe the relationship between the energy of a photon and its frequency.
2. How was the ultraviolet catastrophe explained?
3. If electromagnetic radiation with a continuous range of frequencies above the threshold frequency of a metal is allowed to strike a metal surface, is the kinetic energy of the ejected electrons continuous or quantized? Explain your answer.
4. The vibrational energy of a plucked guitar string is said to be quantized. What do we mean by this? Are the sounds emitted from the 88 keys on a piano also quantized?
5. Which of the following exhibit quantized behavior: a human voice, the speed of a car, a harp, the colors of light, automobile tire sizes, waves from a speedboat?

Conceptual Answers

1. The energy of a photon is directly proportional to the frequency of the electromagnetic radiation.
- 2.
- 3.
- 4.
5. Quantized: harp, tire size, speedboat waves; continuous: human voice, colors of light, car speed.

Numerical Problems

1. What is the energy of a photon of light with each wavelength? To which region of the electromagnetic spectrum does each wavelength belong?
 1. 4.33×10^5 m
 2. 0.065 nm
 3. 786 μ m
2. How much energy is contained in each of the following? To which region of the electromagnetic spectrum does each wavelength belong?
 1. 250 photons with a wavelength of 3.0 m
 2. 4.2×10^6 photons with a wavelength of 92 μ m
 3. 1.78×10^{22} photons with a wavelength of 2.1 Å
3. A 6.023×10^{23} photons are found to have an energy of 225 kJ. What is the wavelength of the radiation?
4. Use the data in Table 2.1.1 to calculate how much more energetic a single gamma-ray photon is than a radio-wave photon. How many photons from a radio source operating at a frequency of 8×10^5 Hz would be required to provide the same amount of energy as a single gamma-ray photon with a frequency of 3×10^{19} Hz?

5. Use the data in Table 2.1.1 to calculate how much more energetic a single x-ray photon is than a photon of ultraviolet light.
6. A radio station has a transmitter that broadcasts at a frequency of 100.7 MHz with a power output of 50 kW. Given that $1 \text{ W} = 1 \text{ J/s}$, how many photons are emitted by the transmitter each second?

Numerical Answers

1. $4.59 \times 10^{-31} \text{ J/photon, radio}$
2. $3.1 \times 10^{-15} \text{ J/photon, gamma ray}$
3. $2.53 \times 10^{-16} \text{ J/photon, gamma ray}$
- 2.
3. 532 nm

6.3: Line Spectra and the Bohr Model

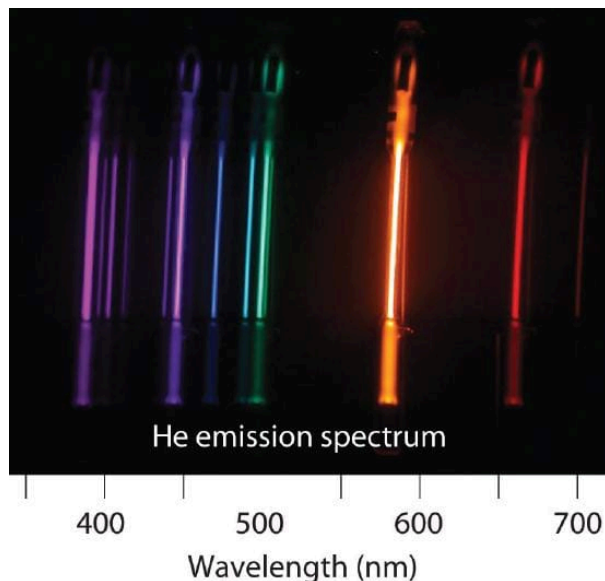
Conceptual Problems

1. Is the spectrum of the light emitted by isolated atoms of an element discrete or continuous? How do these spectra differ from those obtained by heating a bulk sample of a solid element? Explain your answers.
2. Explain why each element has a characteristic emission and absorption spectra. If spectral emissions had been found to be continuous rather than discrete, what would have been the implications for Bohr's model of the atom?
3. Explain the differences between a ground state and an excited state. Describe what happens in the spectrum of a species when an electron moves from a ground state to an excited state. What happens in the spectrum when the electron falls from an excited state to a ground state?
4. What phenomenon causes a neon sign to have a characteristic color? If the emission spectrum of an element is constant, why do some neon signs have more than one color?
5. How is light from a laser different from the light emitted by a light source such as a light bulb? Describe how a laser produces light.

Numerical Problems

1. Using a Bohr model and the transition from $n = 2$ to $n = 3$ in an atom with a single electron, describe the mathematical relationship between an emission spectrum and an absorption spectrum. What is the energy of this transition? What does the sign of the energy value represent in this case? What range of light is associated with this transition?
2. If a hydrogen atom is excited from an $n = 1$ state to an $n = 3$ state, how much energy does this correspond to? Is this an absorption or an emission? What is the wavelength of the photon involved in this process? To what region of the electromagnetic spectrum does this correspond?
3. The hydrogen atom emits a photon with a 486 nm wavelength, corresponding to an electron decaying from the $n = 4$ level to which level? What is the color of the emission?
4. An electron in a hydrogen atom can decay from the $n = 3$ level to $n = 2$ level. What is the color of the emitted light? What is the energy of this transition?
5. Calculate the wavelength and energy of the photon that gives rise to the third line in order of increasing energy in the Lyman series in the emission spectrum of hydrogen. In what region of the spectrum does this wavelength occur? Describe qualitatively what the absorption spectrum looks like.
6. The wavelength of one of the lines in the Lyman series of hydrogen is 121 nm. In what region of the spectrum does this occur? To which electronic transition does this correspond?

7. The emission spectrum of helium is shown. Estimate what change in energy (ΔE) gives rise to each line?



8. Removing an electron from solid potassium requires 222 kJ/mol. Would you expect to observe a photoelectric effect for potassium using a photon of blue light ($\lambda = 485$ nm)? What is the longest wavelength of energy capable of ejecting an electron from potassium? What is the corresponding color of light of this wavelength?
9. The binding energy of an electron is the energy needed to remove an electron from its lowest energy state. According to Bohr's postulates, calculate the binding energy of an electron in a hydrogen atom. There are 6.02×10^{23} atoms in 1g of hydrogen atoms. What wavelength in nanometers is required to remove such an electron from one hydrogen atom?
10. As a radio astronomer, you have observed spectral lines for hydrogen corresponding to a state with $n = 320$, and you would like to produce these lines in the laboratory. Is this feasible? Why or why not?

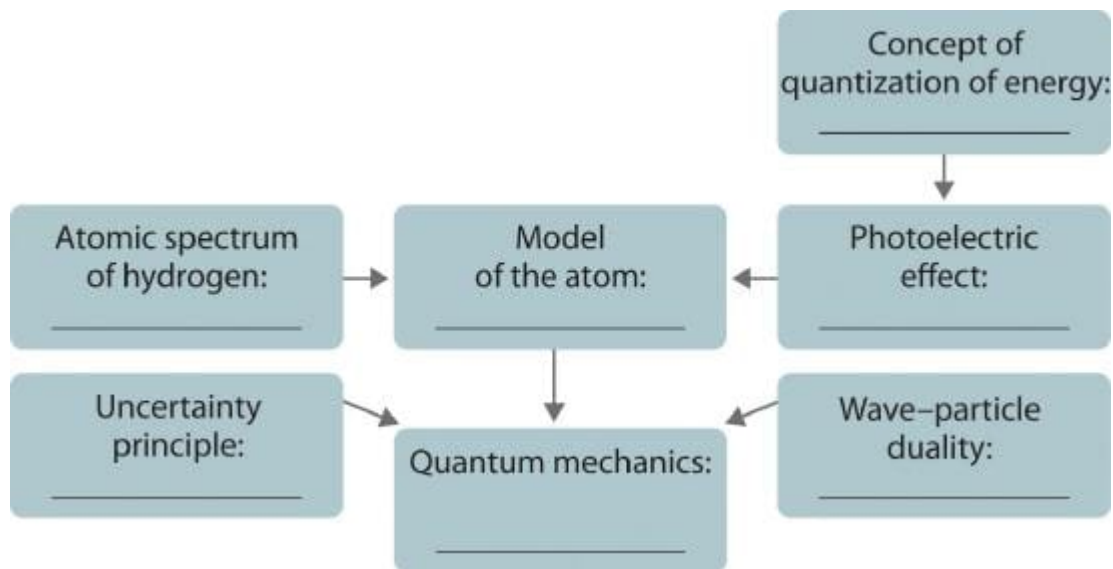
Numerical Answers

- 656 nm; red light
-
- $n = 2$, blue-green light
-
- 97.2 nm, 2.04×10^{-18} J/photon, ultraviolet light, absorption spectrum is a single dark line at a wavelength of 97.2 nm
-
- Violet: 390 nm, 307 kJ/mol photons; Blue-purple: 440 nm, 272 kJ/mol photons; Blue-green: 500 nm, 239 kJ/mol photons; Orange: 580 nm, 206 kJ/mol photons; Red: 650 nm, 184 kJ/mol photons
-
- 1313 kJ/mol, $\lambda \leq 91.1$ nm

6.4: The Wave Behavior of Matter

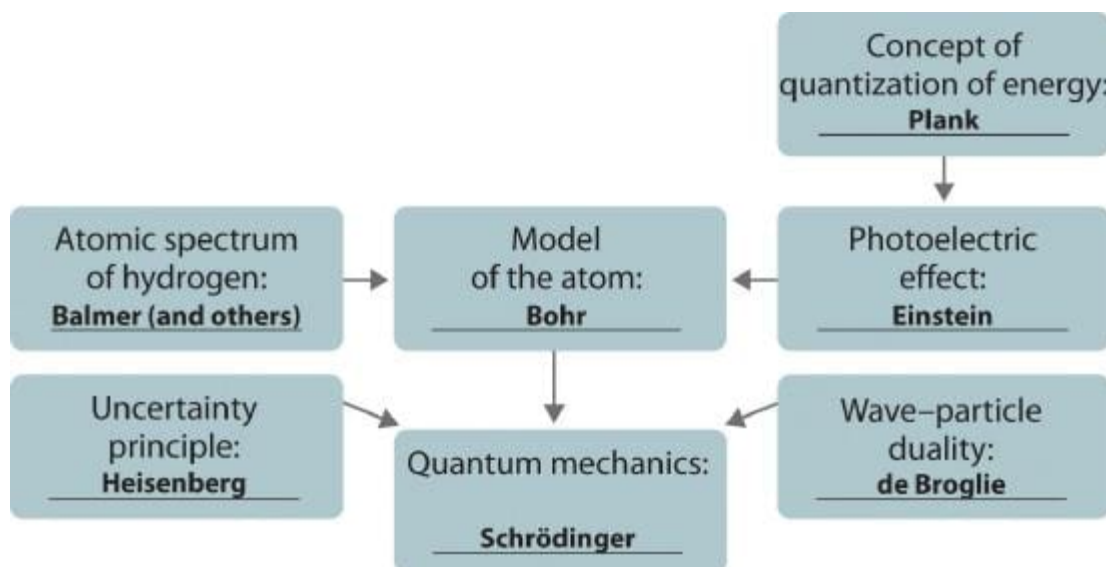
Conceptual Problems

- Explain what is meant by each term and illustrate with a sketch:
 - standing wave
 - fundamental
 - overtone
 - node
- How does Einstein's theory of relativity illustrate the wave-particle duality of light? What properties of light can be explained by a wave model? What properties can be explained by a particle model?
- In the modern theory of the electronic structure of the atom, which of de Broglie's ideas have been retained? Which proved to be incorrect?
- According to Bohr, what is the relationship between an atomic orbit and the energy of an electron in that orbit? Is Bohr's model of the atom consistent with Heisenberg's uncertainty principle? Explain your answer.
- The development of ideas frequently builds on the work of predecessors. Complete the following chart by filling in the names of those responsible for each theory shown.



Conceptual Answer

-
-
-
-



5.

Numerical Problems

- How much heat is generated by shining a carbon dioxide laser with a wavelength of $1.065 \mu\text{m}$ on a 68.95 kg sample of water if 1.000 mol of photons is absorbed and converted to heat? Is this enough heat to raise the temperature of the water by 4°C ?
- Show the mathematical relationship between energy and mass and between wavelength and mass. What is the effect of doubling the
 - mass of an object on its energy?
 - mass of an object on its wavelength?
 - frequency on its mass?
- What is the de Broglie wavelength of a 39 g bullet traveling at $1020 \text{ m/s} \pm 10 \text{ m/s}$? What is the minimum uncertainty in the bullet's position?
- What is the de Broglie wavelength of a 6800 tn aircraft carrier traveling at $18 \pm 0.1 \text{ knots}$ ($1 \text{ knot} = 1.15 \text{ mi/h}$)? What is the minimum uncertainty in its position?
- Calculate the mass of a particle if it is traveling at $2.2 \times 10^6 \text{ m/s}$ and has a frequency of $6.67 \times 10^7 \text{ Hz}$. If the uncertainty in the velocity is known to be 0.1% , what is the minimum uncertainty in the position of the particle?
- Determine the wavelength of a 2800 lb automobile traveling at $80 \text{ mi/h} \pm 3\%$. How does this compare with the diameter of the nucleus of an atom? You are standing 3 in. from the edge of the highway. What is the minimum uncertainty in the position of the automobile in inches?

Numerical Answers

- $E = 112.3 \text{ kJ}$, $\Delta T = 0.3893^\circ\text{C}$, over ten times more light is needed for a 4.0°C increase in temperature
-
- $1.7 \times 10^{-35} \text{ m}$, uncertainty in position is $\geq 1.4 \times 10^{-34} \text{ m}$
-
- $9.1 \times 10^{-39} \text{ kg}$, uncertainty in position $\geq 2.6 \text{ m}$

6.5: Quantum Mechanics and Atomic Orbitals

Conceptual Problems

- Why does an electron in an orbital with $n = 1$ in a hydrogen atom have lower energy than a free electron ($n = \infty$)?
- What four variables are required to fully describe the position of any object in space? In quantum mechanics, one of these variables is not explicitly considered. Which one and why?
- Chemists generally refer to the square of the wave function rather than to the wave function itself. Why?
- Orbital energies of species with only one electron are defined by only one quantum number. Which one? In such a species, is the energy of an orbital with $n = 2$ greater than, less than, or equal to the energy of an orbital with $n = 4$? Justify your answer.
- In each pair of subshells for a hydrogen atom, which has the higher energy? Give the principal and the azimuthal quantum number for each pair.
 - 1s, 2p
 - 2p, 2s
 - 2s, 3s
 - 3d, 4s
- What is the relationship between the energy of an orbital and its average radius? If an electron made a transition from an orbital with an average radius of 846.4 pm to an orbital with an average radius of 476.1 pm, would an emission spectrum or an absorption spectrum be produced? Why?
- In making a transition from an orbital with a principal quantum number of 4 to an orbital with a principal quantum number of 7, does the electron of a hydrogen atom emit or absorb a photon of energy? What would be the energy of the photon? To what region of the electromagnetic spectrum does this energy correspond?
- What quantum number defines each of the following?
 - the overall shape of an orbital
 - the orientation of an electron with respect to a magnetic field
 - the orientation of an orbital in space
 - the average energy and distance of an electron from the nucleus
- In an attempt to explain the properties of the elements, Niels Bohr initially proposed electronic structures for several elements with orbits holding a certain number of electrons, some of which are in the following table:

Element	Number of Electrons	Electrons in orbits with $n =$			
		4	3	2	1
H	1				1
He	2				2
Ne	10			8	2
Ar	18		8	8	2
Li	3			1	2
Na	11		1	8	2
K	19	1	8	8	2
Be	4			2	2

- Draw the electron configuration of each atom based only on the information given in the table. What are the differences between Bohr's initially proposed structures and those accepted today?

- b. Using Bohr's model, what are the implications for the reactivity of each element?
- c. Give the actual electron configuration of each element in the table.

Numerical Problems

1. How many subshells are possible for $n = 3$? What are they?
2. How many subshells are possible for $n = 5$? What are they?
3. What value of l corresponds to a d subshell? How many orbitals are in this subshell?
4. What value of l corresponds to an f subshell? How many orbitals are in this subshell?
5. State the number of orbitals and electrons that can occupy each subshell.
 1. $2s$
 2. $3p$
 3. $4d$
 4. $6f$
6. State the number of orbitals and electrons that can occupy each subshell.
 1. $1s$
 2. $4p$
 3. $5d$
 4. $4f$
7. How many orbitals and subshells are found within the principal shell $n = 6$? How do these orbital energies compare with those for $n = 4$?
8. How many nodes would you expect a $4p$ orbital to have? A $5s$ orbital?
9. A p orbital is found to have one node in addition to the nodal plane that bisects the lobes. What would you predict to be the value of n ? If an s orbital has two nodes, what is the value of n ?

Numerical Answers

1. Three subshells, with $l = 0$ (s), $l = 1$ (p), and $l = 2$ (d).
- 2.
3. A d subshell has $l = 2$ and contains 5 orbitals.
- 4.
5.
 1. 2 electrons; 1 orbital
 2. 6 electrons; 3 orbitals
 3. 10 electrons; 5 orbitals
 4. 14 electrons; 7 orbitals
- 6.
7. A principal shell with $n = 6$ contains six subshells, with $l = 0, 1, 2, 3, 4$, and 5 , respectively. These subshells contain 1, 3, 5, 7, 9, and 11 orbitals, respectively, for a total of 36 orbitals. The energies of the orbitals with $n = 6$ are higher than those of the corresponding orbitals with the same value of l for $n = 4$.

6.6: Representation of Orbitals

6.7: Many-Electron Atoms

Conceptual Problems

1. A set of four quantum numbers specifies each wave function. What information is given by each quantum number? What does the specified wave function describe?
2. List two pieces of evidence to support the statement that electrons have a spin.
3. The periodic table is divided into blocks. Identify each block and explain the principle behind the divisions. Which quantum number distinguishes the horizontal rows?
4. Identify the element with each ground state electron configuration.
 1. $[\text{He}]2s^2 2p^3$
 2. $[\text{Ar}]4s^2 3d^1$
 3. $[\text{Kr}]5s^2 4d^{10} 5p^3$
 4. $[\text{Xe}]6s^2 4f^6$
5. Identify the element with each ground state electron configuration.
 1. $[\text{He}]2s^2 2p^1$
 2. $[\text{Ar}]4s^2 3d^8$
 3. $[\text{Kr}]5s^2 4d^{10} 5p^4$
 4. $[\text{Xe}]6s^2$
6. Propose an explanation as to why the noble gases are inert.

Numerical Problems

1. How many magnetic quantum numbers are possible for a $4p$ subshell? A $3d$ subshell? How many orbitals are in these subshells?
2. How many magnetic quantum numbers are possible for a $6s$ subshell? A $4f$ subshell? How many orbitals does each subshell contain?
3. If $l = 2$ and $m_l = 2$, give all the allowed combinations of the four quantum numbers (n, l, m_l, m_s) for electrons in the corresponding $3d$ subshell.
4. Give all the allowed combinations of the four quantum numbers (n, l, m_l, m_s) for electrons in a $4d$ subshell. How many electrons can the $4d$ orbital accommodate? How would this differ from a situation in which there were only three quantum numbers (n, l, m)?
5. Given the following sets of quantum numbers (n, l, m_l, m_s), identify each principal shell and subshell.
 1. $1, 0, 0, \frac{1}{2}$
 2. $2, 1, 0, \frac{1}{2}$
 3. $3, 2, 0, \frac{1}{2}$
 4. $4, 3, 3, \frac{1}{2}$
6. Is each set of quantum numbers allowed? Explain your answers.
 1. $n = 2; l = 1; m_l = 2; m_s = +\frac{1}{2}$
 2. $n = 3, l = 0; m_l = -1; m_s = -\frac{1}{2}$
 3. $n = 2; l = 2; m_l = 1; m_s = +\frac{1}{2}$

4. $n = 3; l = 2; m_l = 2; m_s = +\frac{1}{2}$
7. List the set of quantum numbers for each electron in the valence shell of each element.
1. beryllium
 2. xenon
 3. lithium
 4. fluorine
8. List the set of quantum numbers for each electron in the valence shell of each element.
1. carbon
 2. magnesium
 3. bromine
 4. sulfur
9. Sketch the shape of the periodic table if there were three possible values of m_s for each electron ($+\frac{1}{2}$, $-\frac{1}{2}$, and 0); assume that the Pauli principle is still valid.
10. Predict the shape of the periodic table if eight electrons could occupy the p subshell.
11. If the electron could only have spin $+\frac{1}{2}$, what would the periodic table look like?
12. If three electrons could occupy each s orbital, what would be the electron configuration of each species?
1. sodium
 2. titanium
 3. fluorine
 4. calcium
13. If Hund's rule were not followed and maximum pairing occurred, how many unpaired electrons would each species have? How do these numbers compare with the number found using Hund's rule?
1. phosphorus
 2. iodine
 3. manganese
14. Write the electron configuration for each element in the ground state.
1. aluminum
 2. calcium
 3. sulfur
 4. tin
 5. nickel
 6. tungsten
 7. neodymium
 8. americium
15. Write the electron configuration for each element in the ground state.
1. boron
 2. rubidium
 3. bromine
 4. germanium
 5. vanadium
 6. palladium
 7. bismuth
 8. europium
16. Give the complete electron configuration for each element.

1. magnesium
 2. potassium
 3. titanium
 4. selenium
 5. iodine
 6. uranium
 7. germanium
17. Give the complete electron configuration for each element.
1. tin
 2. copper
 3. fluorine
 4. hydrogen
 5. thorium
 6. yttrium
 7. bismuth
18. Write the valence electron configuration for each element:
1. samarium
 2. praseodymium
 3. boron
 4. cobalt
19. Using the Pauli exclusion principle and Hund's rule, draw valence orbital diagrams for each element.
1. barium
 2. neodymium
 3. iodine
20. Using the Pauli exclusion principle and Hund's rule, draw valence orbital diagrams for each element.
1. chlorine
 2. silicon
 3. scandium
21. How many unpaired electrons does each species contain?
1. lead
 2. cesium
 3. copper
 4. silicon
 5. selenium
22. How many unpaired electrons does each species contain?
1. helium
 2. oxygen
 3. bismuth
 4. silver
 5. boron
23. For each element, give the complete electron configuration, draw the valence electron configuration, and give the number of unpaired electrons present.
1. lithium
 2. magnesium
 3. silicon
 4. cesium

5. lead
24. Use an orbital diagram to illustrate the aufbau principle, the Pauli exclusion principle, and Hund's rule for each element.
 1. carbon
 2. sulfur

Numerical Answers

1. For a $4p$ subshell, $n = 4$ and $l = 1$. The allowed values of the magnetic quantum number, m_l , are therefore $+1$, 0 , -1 , corresponding to three $4p$ orbitals. For a $3d$ subshell, $n = 3$ and $l = 2$. The allowed values of the magnetic quantum number, m_l , are therefore $+2$, $+1$, 0 , -1 , -2 , corresponding to five $3d$ orbitals.

6.8: Electron Configurations

6.9: Electron Configurations and the Periodic Table

1.1.S: Electronic Structure of Atoms (Summary)

Understanding the electronic structure of atoms requires an understanding of the properties of waves and electromagnetic radiation. A basic knowledge of the electronic structure of atoms requires an understanding of the properties of waves and electromagnetic radiation. A wave is a periodic oscillation by which energy is transmitted through space. All waves are periodic, repeating regularly in both space and time. Waves are characterized by several interrelated properties.

- **Electronic structure:** arrangement of electrons in atoms
- **Electromagnetic radiation:** aka **radiant energy**; form of energy that has wave characteristics and carries energy through space. *All types of electromagnetic radiation move through a vacuum at a speed of 3.00×10^8 m/s (speed of light).*
- **Wavelength:** the distance between identical points on successive waves
- **Frequency:** the number of complete wavelengths that pass a given point in 1s

$$\nu\lambda = c$$

where ν = frequency, λ = wavelength, and c = speed of light

Wavelength is expressed in units of length.

- **Electromagnetic spectrum:** various types of electromagnetic radiations arranged in order of increasing wavelength.

Frequency is expressed in Hertz (Hz), also denoted by s^{-1} or /s

Quantum Effects and Photons

- **Quantum:** smallest quantity of energy that can be emitted or absorbed as electromagnetic radiation

$$E = h\nu$$

where E = energy, h = Planck's constant, ν = frequency

Planck's constant = 6.63×10^{-34} J•s

According to Planck's theory, energy is always emitted or absorbed in whole-number multiples of $h\nu$, for example, $h\nu$, $2h\nu$, $3h\nu$, and so forth. We say that the allowed energies are *quantized* (that is, their values are restricted to certain quantities).

6.2: Quantized Energy and Photons

Blackbody radiation is the radiation emitted by hot objects and could not be explained with classical physics. Max Planck postulated that energy was quantized and may be emitted or absorbed only in integral multiples of a small unit of energy, known as a quantum. The energy of a quantum is proportional to the frequency of the radiation; the proportionality constant h is a fundamental constant (Planck's constant). Albert Einstein used the quantization of energy to explain the photoelectric effect

- The photoelectric effect: when photons of sufficiently high energy strike a metal surface, electrons are emitted from the metal. The emitted electrons are drawn toward the other electrode, which is a positive terminal. As a result, current flows in a circuit.
- **Photon:** smallest increment (a *quantum*) of radiant energy; a photon of light with frequency ν has an energy equal to $h\nu$.
- When a photon strikes the metal, its energy is transferred to an electron in the metal. A certain amount of energy is required for the electron to overcome the attractive forces that hold it within the metal. If the photons have less energy than this energy threshold, the electrons cannot escape from the metal surface. If a photon has sufficient energy, an electron is emitted. If the photon has more energy than necessary, the excess appears as kinetic energy of the emitted electron.

6.3: Line Spectra and the Bohr Model

There is an intimate connection between the atomic structure of an atom and its spectral characteristics. Most light is

polychromatic and contains light of many wavelengths. Light that has only a single wavelength is monochromatic and is produced by devices called lasers, which use transitions between two atomic energy levels to produce light in a very narrow range of wavelengths. Atoms can also absorb light of certain energies, resulting in a transition from the ground state or a lower-energy e

Line Spectra

Radiation composed of a single wavelength is said to be *monochromatic*.

- **Spectrum:** distribution among various wavelengths of the radiant energy emitted or absorbed by an object
- **Continuous spectrum:** rainbow of colors, containing light of all wavelengths. *Not all radiation sources produce a continuous spectrum*
- **Line spectrum:** spectrum containing radiation of only specific wavelengths

Bohr's Model

Electrons in a permitted orbit have a specific energy and are said to be in an "allowed" energy state. An electron in an allowed energy state will not radiate energy and therefore will not spiral into the nucleus.

$$E_n = -R_H \frac{1}{n^2}$$

- R_H = Rydberg constant: $2.18 \times 10^{-18} \text{ J}$
- n = principal quantum number, corresponds to the different allowed orbits for the electron

All energies given by this equation will be negative. The lower (more negative) the energy is, the more stable the atom is. The lowest energy state is that for which $n=1$.

- **Ground state:** lowest energy state of an atom, $n=1$
- **Excited state:** when the electron is in higher energy orbit (less negative), $n=2$ or higher

If n becomes infinitely large (∞), the electron is completely separated from the nucleus:

$$E_{\infty} = (-2.18 \times 10^{-18} \text{ J}) \left(\frac{1}{\infty^2} \right) = 0$$

Thus, the state in which the electron is removed from the nucleus is the reference, or zero-energy, state of the hydrogen atom. It is important to remember that this zero-energy state is higher in energy than the states with negative energies

Electrons can change from one energy state to another by absorbing or emitting radiant energy. Radiant energy must be absorbed for an electron to move to a higher energy state, but is emitted when the electron moves to a lower energy state. .

$$\Delta E = E_f - E_i$$

- If $n_f > n_i$, then ΔE is positive, radiant energy is absorbed
- If $n_f < n_i$, then ΔE is negative, radiant energy is emitted

6.4: The Wave Behavior of Matter

An electron possesses both particle and wave properties. 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. The electron in Bohr's circular orbits could thus be described as a standing wave, one that does not move through space. 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.

- **Momentum:** the product of the mass, m , and the velocity, v , of a particle
- **Matter waves:** term used to describe the wave characteristics of a particle

$$\lambda = h/mv$$

λ = wavelength, h = Planck's constant, m = mass, v = velocity

The Uncertainty Principle

- **Uncertainty principle:** theory first put forth by Heisenberg, states that it is impossible to determine both the exact momentum of the electron and its exact location.

6.5: Quantum Mechanics and Atomic Orbitals

There is a relationship between the motions of electrons in atoms and molecules and their energies that is described by quantum mechanics. Because of wave-particle duality, scientists must deal with the probability of an electron being at a particular point in space. To do so required the development of quantum mechanics, which uses wavefunctions to describe the mathematical relationship between the motion of electrons in atoms and molecules and their energies.

- **Wave functions:** represented by ψ , square of wave function, ψ^2 , provides information about an electron's location when it is in an allowed energy state.
- **Probability density:** represented by ψ^2 , value that represents the probability that an electron will be found at a given point in space
- **Electron density:** the probability of finding an electron at any particular point in an atom. Equals ψ^2 .

Orbitals and Quantum Numbers

-**Orbital:** allowed energy state of an electron in the quantum-mechanical model of the atom; also used to describe the spatial distribution of an electron. Defined by the value of 3 quantum numbers; n , l , and m_l .

value of 3 quantum numbers; n , l , and m_l .

Value of l	0	1	2	3
Letter used	s	p	d	f

1. The principal quantum number, n , can have integral values of 1, 2, 3 and so forth. As n increases, the orbital becomes larger; the electron has a higher energy and is farther away from the nucleus.
2. The second quantum number, l , can have integral values from 0 to $n - 1$ for each value of n . This quantum number defines the shape of the orbital. Generally designated by the letters s, p, d, and f. These correspond to values ranging from 0 to 3.
3. The magnetic quantum number, m_l , can have integral values between l and $-l$, including zero. This quantum number describes the orientation of the orbital in space.

Electron shell: collection of orbitals with the same value of n

Subshell: one or more orbitals with the same set of n and l values

1. Each shell is divided into the number of subshells equal to the principal quantum number, n , for that shell. The first shell consists of only the 1s subshell; the second shell consists of two subshells, 2s and 2p; the third of three subshells, 3s, 3p and 3d, and so forth.
2. Each subshell is divided into orbitals. Each s subshell consists of one orbital; each p subshell of three orbitals, each d subshell of five, and each f subshell of seven orbitals.

6.6: 3D Representation of Orbitals

Orbitals with $l = 0$ are s orbitals and are spherically symmetrical, with the greatest probability of finding the electron occurring at the nucleus. Orbitals with values of $n > 1$ and $l = 0$ contain one or more nodes. Orbitals with $l = 1$ are p orbitals and contain a nodal plane that includes the nucleus, giving rise to a dumbbell shape. Orbitals with $l = 2$ are d orbitals and have more complex shapes with at least two nodal surfaces. $l = 3$ orbitals are f orbitals, which are still more complex.

The s Orbitals: 1s orbital: most stable, spherically symmetric, figure indicates that the probability decreases as we move away from the nucleus. ALL s ORBITALS ARE SPHERICALLY SYMMETRIC.

- **Nodal surfaces (nodes):** intermediate regions where ψ^2 goes to zero. The number of nodes increases with increasing value

for the principal quantum number, n .

The p Orbitals: Electron density is concentrated on two sides of the nucleus, separated by a node at the nucleus. The orbitals of a given subshell have the same size and shape but differ from each other in orientation. The axis along which the orbital is oriented is not related to m_l .

6.7: Many-Electron Atoms

In addition to the three quantum numbers (n , l , m_l) dictated by quantum mechanics, a fourth quantum number is required to explain certain properties of atoms. This is the electron spin quantum number (m_s), which can have values of $+\frac{1}{2}$ or $-\frac{1}{2}$ for any electron, corresponding to the two possible orientations of an electron in a magnetic field. This is important for chemistry because the Pauli exclusion principle implies that no orbital can contain more than two electrons (with opposite spin).

Although the shapes of the orbitals for many-electron atoms are the same as those for hydrogen, the presence of more than one electron greatly changes the energies of the orbitals. In hydrogen, the energy of an orbital depends only on its principal quantum number, however, in many-electron atoms, electron-electron repulsions cause different subshells to be at different energies

Effective Nuclear Charge

- *Effective nuclear charge:* net positive charge attracting electrons

$$Z_{eff} = Z - S$$

- Z_{eff} = effective nuclear charge
- Z = number of protons in the nucleus
- S = average number of electrons between the nucleus and electron in question
- *Screening effect:* effect of inner electrons in decreasing the nuclear charge experienced by outer electrons

Energies of Orbitals

The extent to which an electron will be screened by the other electrons depends on its electron distribution as we move outward from the nucleus.

- *In a many-electron atom, for a given value of n , Z_{eff} decreases with increasing value of l .*
- *In a many-electron atom, for a given value of n , the energy of an orbital increases with increasing value of l .*

Degenerate: orbitals that have the same energy

Electron Spin and the Pauli Exclusion Principle

- **Electron spin:** property of the electron that makes it behave as though it were a tiny magnet. The electron behaves as if it were spinning on its axis; electron spin is quantized.
- **Electron spin quantum number:** denoted as m_s . It can only have two possible values, $+\frac{1}{2}$ and $-\frac{1}{2}$, which we can interpret as indicating the two opposite directions in which the electron can spin.
- **Pauli exclusion principle:** states that no two electrons in an atom can have the same set of four quantum numbers n , l , m_l , m_s . This means that if we wish to put two electrons in an orbital and satisfy Pauli's exclusion principle, our only choice is to assign different m_s values to the electrons. Because there are only two values, *we can conclude that an electron can hold a maximum of two electrons and they must have opposite spins.*

6.8: Electron Configurations

Based on the Pauli principle and a knowledge of orbital energies obtained using hydrogen-like orbitals, it is possible to construct the periodic table by filling up the available orbitals beginning with the lowest-energy orbitals (the aufbau principle), which gives rise to a particular arrangement of electrons for each element (its electron configuration). Hund's rule says that the lowest-energy arrangement of electrons is the one that places them in degenerate orbitals with parallel spins.

- **Electron configuration:** the way in which the electrons are distributed among the various orbitals. The most stable, or

ground, electron configuration of an atom is that in which the electrons are in the lowest possible energy level

- **Orbital diagram:** representation of electron configuration in which each orbital is represented by a box and each electron by a half-arrow. A half-arrow pointing upward represents an electron with positive spin; one pointing downward represents an electron with a negative spin.

Writing Electron Configurations

- **Hund's rule:** rule stating that electrons occupy degenerate orbitals in such a way as to maximize the number of electrons with the same spin. In other words, each orbital has one electron placed in it before pairing of electron in orbitals occurs. Note that this rule applies to orbitals that are *degenerate*, which means that they have the same energy.
- **Valence electrons:** electrons in the outer shells
- **Core electrons:** electrons in the inner shells
- **Transition elements:** aka **Transition metals**; elements of the *d* orbitals
- **Lanthanide elements:** aka **Rare-earth elements**; 14 elements of the 4f orbitals, # 58-71
- **Actinide elements:** 14 elements of 5f orbitals, # 90-103. Most are not found in nature.

6.9: Electron Configurations and the Periodic Table

The arrangement of atoms in the periodic table results in blocks corresponding to filling of the ns, np, nd, and nf orbitals to produce the distinctive chemical properties of the elements in the s block, p block, d block, and f block, respectively.

- **Main group elements:** aka **Representatives**; s and p block elements
- **F-block metals:** 28 elements located below the table, f block elements

This page titled [1.1.S: Electronic Structure of Atoms \(Summary\)](#) is shared under a [CC BY-NC-SA 4.0](#) license and was authored, remixed, and/or curated by LibreTexts.

- [6.S: Electronic Structure of Atoms \(Summary\)](#) is licensed [CC BY-NC-SA 3.0](#).

2: CHAPTER 2 - BASICS OF CHEMICAL BONDING

2.1: Basic Concepts of Chemical Bonding

2.1.1: Chemical Bonds, Lewis Symbols, and the Octet Rule

2.1.2: Ionic Bonding

2.1.3: Covalent Bonding

2.1.4: Bond Polarity and Electronegativity

2.1.5: Drawing Lewis Structures

2.1.6: Resonance Structures

2.1.7: Exceptions to the Octet Rule

2.1.8: Strength of Covalent Bonds

2.1.E: Basic Concepts of Chemical Bonding (Exercises)

2.1.S: Basic Concepts of Chemical Bonding (Summary)

2.1: BASIC CONCEPTS OF CHEMICAL BONDING

A general chemistry Libretexts Textmap organized around the textbook

Chemistry: The Central Science

by Brown, LeMay, Bursten, Murphy, and Woodward

[Template:HideTOC](#)

We described the relationship between the chemical properties and reactivity of an element and its position in the periodic table. In this chapter and the following chapter, we describe the interactions that hold atoms together in chemical substances, and we examine the factors that determine how the atoms of a substance are arranged in space. Our goal is to understand how the properties of the component atoms in a chemical compound determine the structure and reactivity of the compound. The properties described previously were properties of isolated atoms, yet most of the substances in our world consist of atoms held together in molecules, ionic compounds, or metallic solids. The properties of these substances depend on not only the characteristics of the component atoms but also how those atoms are bonded to one another.

What you learn in this chapter about chemical bonding and molecular structure will help you understand how different substances with the same atoms can have vastly different physical and chemical properties. For example, oxygen gas (O_2) is essential for life, yet ozone (O_3) is toxic to cells, although as you learned previously, ozone in the upper atmosphere shields us from harmful ultraviolet light. Moreover, you saw that diamond is a hard, transparent solid that is a gemstone; graphite is a soft, black solid that is a lubricant; and fullerenes are molecular species with carbon cage structures—yet all of these are composed of carbon. As you learn about bonding, you will also discover why, although carbon and silicon both have ns^2np^2 valence electron configurations and form dioxides, CO_2 is normally a gas that condenses into the volatile molecular solid known as dry ice, whereas SiO_2 is a nonvolatile solid with a network structure that can take several forms, including beach sand and quartz crystals.

2.1.1: Chemical Bonds, Lewis Symbols, and the Octet Rule

2.1.2: Ionic Bonding

2.1.3: Covalent Bonding

2.1.4: Bond Polarity and Electronegativity

2.1.5: Drawing Lewis Structures

2.1.6: Resonance Structures

2.1.7: Exceptions to the Octet Rule

2.1.8: Strength of Covalent Bonds

2.1.E: Basic Concepts of Chemical Bonding (Exercises)

2.1.S: Basic Concepts of Chemical Bonding (Summary)

This page titled [2.1: Basic Concepts of Chemical Bonding](#) is shared under a [CC BY-NC-SA 4.0](#) license and was authored, remixed, and/or curated by LibreTexts.

2.1.1: Chemical Bonds, Lewis Symbols, and the Octet Rule

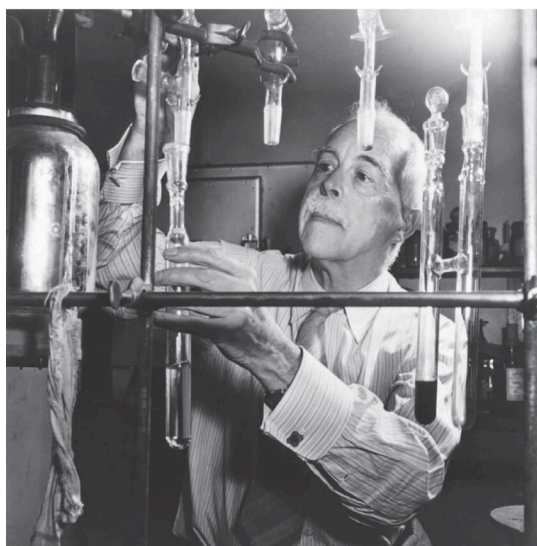
Learning Objectives

- To use Lewis electron dot symbols to predict the number of bonds an element will form.

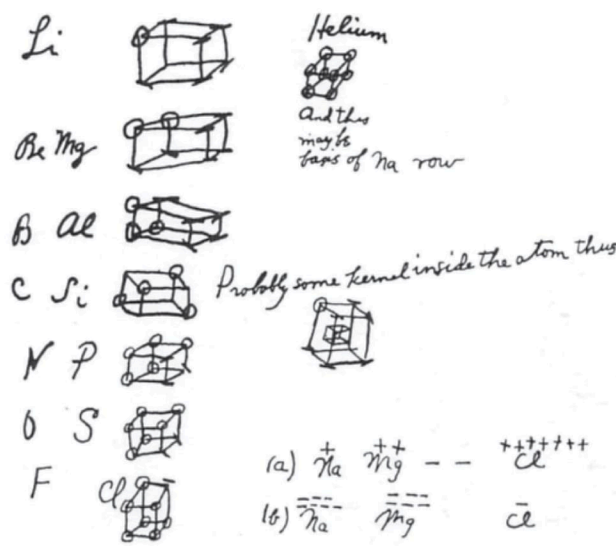
Why are some substances chemically bonded molecules and others are an association of ions? The answer to this question depends upon the electronic structures of the atoms and nature of the chemical forces within the compounds. Although there are no sharply defined boundaries, chemical bonds are typically classified into three main types: ionic bonds, covalent bonds, and metallic bonds. In this chapter, each type of bond will be discussed and the general properties found in typical substances in which the bond type occurs

1. Ionic bonds results from **electrostatic forces that exist between ions of opposite charge**. These bonds typically involves a metal with a nonmetal
2. Covalent bonds **result from the sharing of electrons between two atoms**. The bonds typically involves one nonmetallic element with another
3. Metallic bonds These bonds are found in solid metals (copper, iron, aluminum) with each metal bonded to several neighboring groups and bonding electrons free to move throughout the 3-dimensional structure.

Each bond classification is discussed in detail in subsequent sections of the chapter. Let's look at the preferred arrangements of electrons in atoms when they form chemical compounds.



(a)



(b)

Figure 2.1.1.1: G. N. Lewis and the Octet Rule. (a) Lewis is working in the laboratory. (b) In Lewis's original sketch for the octet rule, he initially placed the electrons at the corners of a cube rather than placing them as we do now.

Lewis Symbols

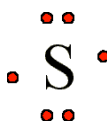
At the beginning of the 20th century, the American chemist G. N. Lewis (1875–1946) devised a system of symbols—now called *Lewis electron dot symbols* (often shortened to *Lewis dot symbols*) that can be used for predicting the number of bonds formed by most elements in their compounds. Each Lewis dot symbol consists of the chemical symbol for an element surrounded by dots

that represent its valence electrons.

Lewis Dot symbols:

- convenient representation of valence electrons
- allows you to keep track of valence electrons during bond formation
- consists of the chemical symbol for the element plus a dot for each valence electron

To write an element's Lewis dot symbol, we place dots representing its valence electrons, one at a time, around the element's chemical symbol. Up to four dots are placed above, below, to the left, and to the right of the symbol (in any order, as long as elements with four or fewer valence electrons have no more than one dot in each position). The next dots, for elements with more than four valence electrons, are again distributed one at a time, each paired with one of the first four. For example, the electron configuration for atomic sulfur is $[\text{Ne}]3s^23p^4$, thus there are **six** valence electrons. Its Lewis symbol would therefore be:



Fluorine, for example, with the electron configuration $[\text{He}]2s^22p^5$, has seven valence electrons, so its Lewis dot symbol is constructed as follows:



Figure 8.1.2.

Lewis used the unpaired dots to predict the number of bonds that an element will form in a compound. Consider the symbol for nitrogen in Figure 8.1.2. The Lewis dot symbol explains why nitrogen, with three unpaired valence electrons, tends to form compounds in which it shares the unpaired electrons to form three bonds. Boron, which also has three unpaired valence electrons in its Lewis dot symbol, also tends to form compounds with three bonds, whereas carbon, with four unpaired valence electrons in its Lewis dot symbol, tends to share all of its unpaired valence electrons by forming compounds in which it has four bonds.

Element	Electron config.	Electron dot symbol
Li	$[\text{He}]2s^1$	Li •
Be	$[\text{He}]2s^2$	•Be•
B	$[\text{He}]2s^22p^1$	•B• •
C	$[\text{He}]2s^22p^2$	•C• • •
N	$[\text{He}]2s^22p^3$	•N: • •
O	$[\text{He}]2s^22p^4$	•O: • •
F	$[\text{He}]2s^22p^5$	•F: • •
Ne	$[\text{He}]2s^22p^6$	•Ne: • •

Figure 2.1.1.2: Lewis Dot Symbols for the Elements in Period 2

Li has one dot on the right, Be has one dot on the left and right, B has one dot on the left, right, and above. C has one dot above, below, on the left and on the right. N has one dot above, below, on the left and two dots on the right. O has two dots on the left and right and one dot above and below. F has two dots above, on the left, on the right and on dot below. Ne has two dots above, below, on the right, and on the left.

YouTube Video

This interactive element is not available in this format. Visit the link or scan the QR code to access it online.

[View this YouTube Video online](#)



The Octet Rule

In 1904, Richard Abegg formulated what is now known as *Abegg's rule*, which states that the difference between the maximum positive and negative valences of an element is frequently eight. This rule was used later in 1916 when Gilbert N. Lewis formulated the "octet rule" in his cubical atom theory. The **octet rule** refers to the tendency of atoms to prefer to have eight electrons in the *valence shell*. When atoms have fewer than eight electrons, they tend to react and form more stable compounds. Atoms will react to get in the most stable state possible. A complete octet is very stable because all orbitals will be full. Atoms with greater stability have less energy, so a reaction that increases the stability of the atoms will release energy in the form of heat or light; reactions that decrease stability must absorb energy, getting colder.

When discussing the octet rule, we do not consider *d* or *f* electrons. Only the *s* and *p* electrons are involved in the octet rule, making it a useful rule for the *main group elements* (elements not in the transition metal or inner-transition metal blocks); an octet in these atoms corresponds to an electron configurations ending with s^2p^6 .

Definition: Octet Rule

A stable arrangement is attained when the atom is surrounded by eight electrons. This octet can be made up by own electrons and some electrons which are shared. Thus, an atom continues to form bonds until an octet of electrons is made. This is known as octet rule by Lewis.

1. Normally two electrons pairs up and forms a bond, e.g., H_2
2. For most atoms there will be a maximum of eight electrons in the valence shell (octet structure), e.g., CH_4

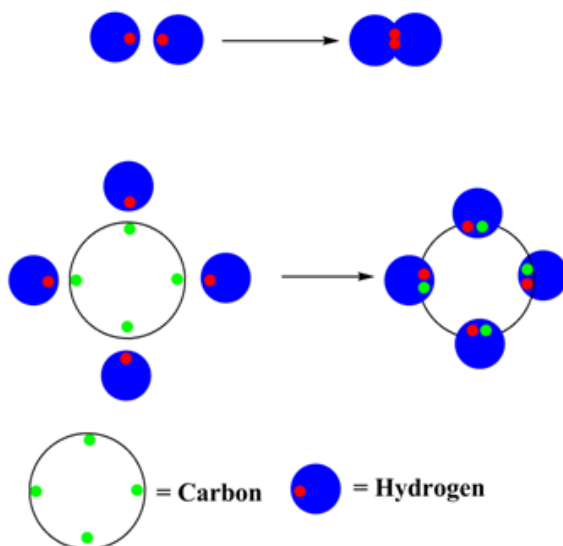


Figure 1: Bonding in H_2 and methane (CH_4)

A hydrogen bonds with each of the four valence electrons of a carbon meaning that four hydrogens can bond with one carbon.

The other tendency of atoms is to maintain a neutral charge. Only the noble gases (the elements on the right-most column of

the periodic table) have zero charge with filled valence octets. All of the other elements have a charge when they have eight electrons all to themselves. The result of these two guiding principles is the explanation for much of the reactivity and bonding that is observed within atoms: atoms seek to share electrons in a way that minimizes charge while fulfilling an octet in the valence shell.

The noble gases rarely form compounds. They have the most stable configuration (full octet, no charge), so they have no reason to react and change their configuration. All other elements attempt to gain, lose, or share electrons to achieve a noble gas configuration.

Example 2.1.1.1: Salt

The formula for table salt is NaCl. It is the result of Na^+ ions and Cl^- ions bonding together. If sodium metal and chlorine gas mix under the right conditions, they will form salt. The sodium loses an electron, and the chlorine gains that electron. In the process, a great amount of light and heat is released. The resulting salt is mostly unreactive — it is stable. It will not undergo any explosive reactions, unlike the sodium and chlorine that it is made of. Why?

Solution

Referring to the octet rule, atoms attempt to get a noble gas electron configuration, which is eight valence electrons. Sodium has one valence electron, so giving it up would result in the same electron configuration as neon. Chlorine has seven valence electrons, so if it takes one it will have eight (an octet). Chlorine has the electron configuration of argon when it gains an electron.

The octet rule could have been satisfied if chlorine gave up all seven of its valence electrons and sodium took them. In that case, both would have the electron configurations of noble gases, with a full valence shell. However, their charges would be much higher. It would be Na^{7-} and Cl^{7+} , which is much less stable than Na^+ and Cl^- . Atoms are more stable when they have no charge, or a small charge.

Lewis dot symbols can also be used to represent the ions in ionic compounds. The reaction of cesium with fluorine, for example, to produce the ionic compound CsF can be written as follows:



No dots are shown on Cs^+ in the product because cesium has lost its single valence electron to fluorine. The transfer of this electron produces the Cs^+ ion, which has the valence electron configuration of Xe, and the F^- ion, which has a total of eight valence electrons (an octet) and the Ne electron configuration. This description is consistent with the statement that among the main group elements, ions in simple binary ionic compounds generally have the electron configurations of the nearest noble gas. The charge of each ion is written in the product, and the anion and its electrons are enclosed in brackets. This notation emphasizes that the ions are associated electrostatically; no electrons are shared between the two elements.

Atoms often gain, lose, or share electrons to achieve the same number of electrons as the noble gas closest to them in the periodic table.

As you might expect for such a qualitative approach to bonding, there are exceptions to the octet rule, which we describe elsewhere. These include molecules in which one or more atoms contain fewer or more than eight electrons.

Summary

Lewis dot symbols can be used to predict the number of bonds formed by most elements in their compounds. One convenient way to predict the number and basic arrangement of bonds in compounds is by using **Lewis electron dot symbols**, which consist of the chemical symbol for an element surrounded by dots that represent its valence electrons, grouped into pairs often placed above, below, and to the left and right of the symbol. The structures reflect the fact that the elements in period 2 and beyond tend

to gain, lose, or share electrons to reach a total of eight valence electrons in their compounds, the so-called **octet rule**. Hydrogen, with only two valence electrons, does not obey the octet rule.

Contributors and Attributions

- [Mike Blaber](#) ([Florida State University](#))
- [Wikipedia](#)
- National Programme on Technology Enhanced Learning (India)

This page titled [2.1.1: Chemical Bonds, Lewis Symbols, and the Octet Rule](#) is shared under a [CC BY-NC-SA 4.0](#) license and was authored, remixed, and/or curated by LibreTexts.

- [8.1: Chemical Bonds, Lewis Symbols, and the Octet Rule](#) is licensed [CC BY-NC-SA 3.0](#).

2.1.2: Ionic Bonding

Learning Objectives

- To describe the characteristics of ionic bonding.
- To quantitatively describe the energetic factors involved in the formation of an ionic bond.

Ions are atoms or molecules which are electrically charged. **Cations** are positively charged and **anions** carry a negative charge. Ions form when atoms gain or lose electrons. Since electrons are negatively charged, an atom that loses one or more electrons will become positively charged; an atom that gains one or more electrons becomes negatively charged. **Ionic bonding** is the attraction between positively- and negatively-charged ions. These oppositely charged ions attract each other to form ionic networks (or **lattices**). Electrostatics explains why this happens: opposite charges attract and like charges repel. When many ions attract each other, they form large, ordered, crystal lattices in which each ion is surrounded by ions of the opposite charge. Generally, when metals react with non-metals, electrons are transferred from the metals to the non-metals. The metals form positively-charged ions and the non-metals form negatively-charged ions.

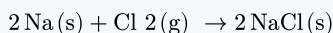
Generating Ionic Bonds

Ionic bonds form when metals and non-metals chemically react. By definition, a metal is relatively stable if it loses electrons to form a complete valence shell and becomes positively charged. Likewise, a non-metal becomes stable by gaining electrons to complete its valence shell and become negatively charged. When metals and non-metals react, the metals lose electrons by transferring them to the non-metals, which gain them. Consequently, ions are formed, which instantly attract each other—ionic bonding.

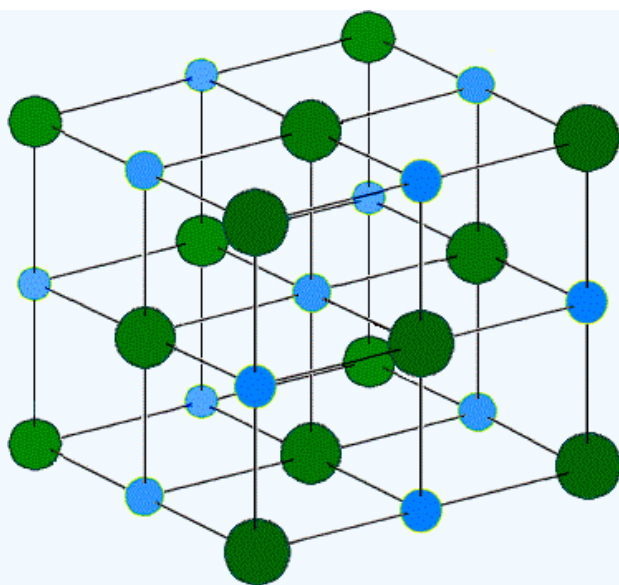
In the overall ionic compound, positive and negative charges must be balanced, because electrons cannot be created or destroyed, only transferred. Thus, the total number of electrons lost by the cationic species must equal the total number of electrons gained by the anionic species.

Example 2.1.2.1: Sodium Chloride

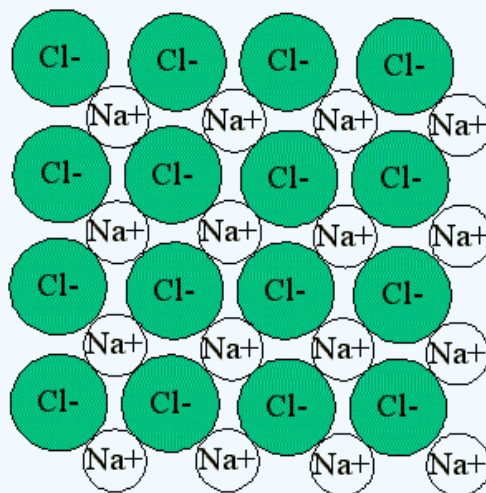
For example, in the reaction of Na (sodium) and Cl (chlorine), each Cl atom takes one electron from a Na atom. Therefore each Na becomes a Na^+ cation and each Cl atom becomes a Cl^- anion. Due to their opposite charges, they attract each other to form an ionic lattice. The formula (ratio of positive to negative ions) in the lattice is NaCl .



These ions are arranged in solid NaCl in a regular three-dimensional arrangement (or lattice):

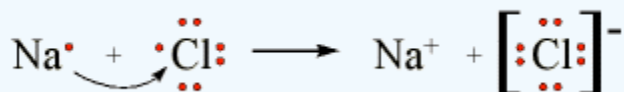


Slice through a NaCl crystal



NaCl lattice. (left) 3-D structure and (right) simple 2D slice through lattice. Images used with permission from Wikipedia and Mike Blaber.

The chlorine has a high affinity for electrons, and the sodium has a low ionization energy. Thus the chlorine gains an electron from the sodium atom. This can be represented using [Lewis dot symbols](#) (here we will consider one chlorine atom, rather than Cl_2):



Chlorine becomes more negative when it takes the one valence electron from sodium when it makes an octet.

The arrow indicates the transfer of the electron from sodium to chlorine to form the Na^+ metal ion and the Cl^- chloride ion. Each ion now has an **octet** of electrons in its **valence** shell:

- $\text{Na}^+ : 2s^2 2p^6$
- $\text{Cl}^- : 3s^2 3p^6$

Energetics of Ionic Bond Formation

Ionic bonds are formed when positively and negatively charged ions are held together by electrostatic forces. Consider a single pair of ions, one cation and one anion. How strong will the force of their attraction be? According to **Coulomb's Law**, the energy of the electrostatic attraction (E) between two charged particles is proportional to the magnitude of the charges and inversely proportional to the internuclear distance between the particles (r):

$$E \propto \frac{Q_1 Q_2}{r} \quad (2.1.2.1)$$

$$E = k \frac{Q_1 Q_2}{r} \quad (2.1.2.2)$$

where each ion's charge is represented by the symbol Q . The proportionality constant k is equal to $2.31 \times 10^{-28} \text{ J}\cdot\text{m}$. This value of k includes the charge of a single electron ($1.6022 \times 10^{-19} \text{ C}$) for each ion. The equation can also be written using the charge of each ion, expressed in coulombs (C), incorporated in the constant. In this case, the proportionality constant, k , equals $8.999 \times 10^9 \text{ J}\cdot\text{m}/\text{C}^2$. In the example given, $Q_1 = +1(1.6022 \times 10^{-19} \text{ C})$ and $Q_2 = -1(1.6022 \times 10^{-19} \text{ C})$. If Q_1 and Q_2 have opposite signs (as

in NaCl, for example, where Q_1 is +1 for Na^+ and Q_2 is -1 for Cl^- , then E is negative, which means that energy is *released* when oppositely charged ions are brought together from an infinite distance to form an isolated ion pair.

Energy is always released when a bond is formed and correspondingly, it always requires energy to break a bond.

As shown by the green curve in the lower half of Figure 2.1.2.1, the maximum energy would be released when the ions are infinitely close to each other, at $r = 0$. Because ions occupy space and have a structure with the positive nucleus being surrounded by electrons, however, they cannot be infinitely close together. At very short distances, repulsive electron-electron interactions between electrons on adjacent ions become stronger than the attractive interactions between ions with opposite charges, as shown by the red curve in the upper half of Figure 2.1.2.1. The total energy of the system is a balance between the attractive and repulsive interactions. The purple curve in Figure 2.1.2.1 shows that the total energy of the system reaches a minimum at r_0 , the point where the electrostatic repulsions and attractions are exactly balanced. This distance is the same as the experimentally measured **bond distance**.

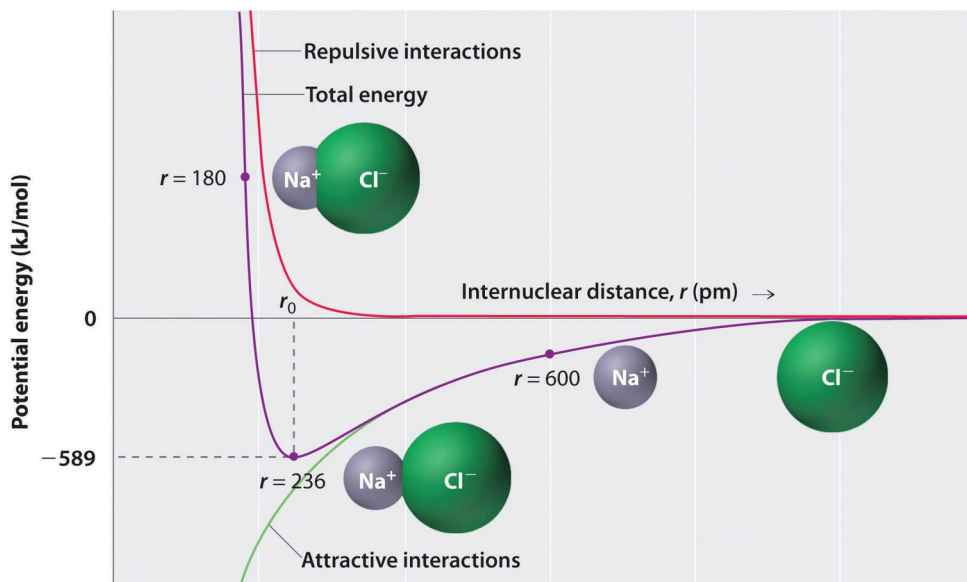


Figure 2.1.2.1: A Plot of Potential Energy versus Internuclear Distance for the Interaction between a Gaseous Na^+ Ion and a Gaseous Cl^- Ion. The energy of the system reaches a minimum at a particular distance (r_0) when the attractive and repulsive interactions are balanced.

Consider the energy released when a gaseous Na^+ ion and a gaseous Cl^- ion are brought together from $r = \infty$ to $r = r_0$. Given that the observed gas-phase internuclear distance is 236 pm, the energy change associated with the formation of an ion pair from an $\text{Na}_{(g)}^+$ ion and a $\text{Cl}_{(g)}^-$ ion is as follows:

$$\begin{aligned} E &= k \frac{Q_1 Q_2}{r_0} \\ &= (2.31 \times 10^{-28} \text{ J} \cdot \text{m}) \left(\frac{(+1)(-1)}{236 \text{ pm} \times 10^{-12} \text{ m/pm}} \right) \\ &= -9.79 \times 10^{-19} \text{ J/ion pair} \end{aligned}$$

The negative value indicates that energy is released. Our convention is that if a chemical process provides energy to the outside world, the energy change is negative. If it requires energy, the energy change is positive. To calculate the energy change in the formation of a mole of NaCl pairs, we need to multiply the energy per ion pair by Avogadro's number:

$$E = (-9.79 \times 10^{-19} \text{ J/ion pair}) (6.022 \times 10^{23} \text{ ion pair/mol}) = -589 \text{ kJ/mol} \quad (2.1.2.3)$$

This is the energy released when 1 mol of gaseous ion pairs is formed, *not* when 1 mol of positive and negative ions condenses to form a crystalline lattice. Because of long-range interactions in the lattice structure, this energy does not correspond directly to the **lattice energy** of the crystalline solid. However, the large negative value indicates that bringing positive and negative ions together is energetically very favorable, whether an ion pair or a crystalline lattice is formed.

We summarize the important points about ionic bonding:

- At r_0 , the ions are more stable (have a lower potential energy) than they are at an infinite internuclear distance. When oppositely charged ions are brought together from $r = \infty$ to $r = r_0$, the energy of the system is lowered (energy is released).
- Because of the low potential energy at r_0 , energy must be added to the system to separate the ions. The amount of energy needed is the bond energy.
- The energy of the system reaches a minimum at a particular internuclear distance (the bond distance).

Example 2.1.2.2: LiF

Calculate the amount of energy released when 1 mol of gaseous Li^+F^- ion pairs is formed from the separated ions. The observed internuclear distance in the gas phase is 156 pm.

Given: cation and anion, amount, and internuclear distance

Asked for: energy released from formation of gaseous ion pairs

Strategy:

Substitute the appropriate values into Equation 2.1.2.2 to obtain the energy released in the formation of a single ion pair and then multiply this value by Avogadro's number to obtain the energy released per mole.

Solution:

Inserting the values for Li^+F^- into Equation 2.1.2.2 (where $Q_1 = +1$, $Q_2 = -1$, and $r = 156$ pm), we find that the energy associated with the formation of a single pair of Li^+F^- ions is

$$\begin{aligned} E &= k \frac{Q_1 Q_2}{r_0} \\ &= (2.31 \times 10^{-28} \text{ J} \cdot \cancel{\text{m}}) \left(\frac{(+1)(-1)}{156 \text{ pm} \times 10^{-12} \cancel{\text{m/pm}}} \right) \\ &= -1.48 \times 10^{-18} \end{aligned}$$

Then the energy released per mole of Li^+F^- ion pairs is

$$\begin{aligned} E &= (-1.48 \times 10^{-18} \text{ J} / \cancel{\text{ion pair}}) (6.022 \times 10^{23} \cancel{\text{ion pair}} / \text{mol}) \\ &= -891 \text{ kJ/mol} \end{aligned}$$

Because Li^+ and F^- are smaller than Na^+ and Cl^- (see Section 7.3), the internuclear distance in LiF is shorter than in NaCl. Consequently, in accordance with Equation 2.1.2.2, much more energy is released when 1 mol of gaseous Li^+F^- ion pairs is formed (-891 kJ/mol) than when 1 mol of gaseous Na^+Cl^- ion pairs is formed (-589 kJ/mol).

Exercise 2.1.2.2: Magnesium oxide

Calculate the amount of energy released when 1 mol of gaseous MgO ion pairs is formed from the separated ions. The internuclear distance in the gas phase is 175 pm.

Answer available at the end of this section.

Electron Configuration of Ions

How does the energy released in lattice formation compare to the energy required to strip away a second electron from the Na^+ ion? Since the Na^+ ion has a noble gas electron configuration, stripping away the next electron from this stable arrangement would require more energy than what is released during lattice formation (Sodium $I_2 = 4,560 \text{ kJ/mol}$). Thus, sodium is present in ionic compounds as Na^+ and not Na^{2+} . Likewise, adding an electron to fill a valence shell (and achieve noble gas electron configuration) is exothermic or only slightly endothermic. To add an additional electron into a **new** subshell requires tremendous energy - more than the lattice energy. Thus, we find Cl^- in ionic compounds, but not Cl^{2-} .

Table 2.1.2.1: Lattice energies range from around 700 kJ/mol to 4000 kJ/mol:

Compound	Lattice Energy (kJ/mol)
LiF	1024
LiI	744
NaF	911
NaCl	788
NaI	693
KF	815
KBr	682
KI	641
MgF_2	2910
SrCl_2	2130
MgO	3938

This amount of energy can compensate for values as large as I_3 for valence electrons (i.e. can strip away up to 3 valence electrons). Because most transition metals would require the removal of more than 3 electrons to attain a noble gas core, they are not found in ionic compounds with a noble gas core. A transition metal always loses electrons first from the higher 's' subshell, before losing from the underlying 'd' subshell. (The remaining electrons in the unfilled d subshell are the reason for the bright colors observed in many transition metal compounds!) For example, iron ions will **not** form a noble gas core:

- Fe: $[\text{Ar}]4s^23d^6$
- Fe^{2+} : $[\text{Ar}] 3d^6$
- Fe^{3+} : $[\text{Ar}] 3d^5$

Some metal ions can form a pseudo noble gas core (and be colorless), for example:

- Ag: $[\text{Kr}]5s^14d^{10}$ Ag^+ $[\text{Kr}]4d^{10}$ Compound: AgCl
- Cd: $[\text{Kr}]5s^24d^{10}$ Cd^{2+} $[\text{Kr}]4d^{10}$ Compound: CdS

The valence electrons do not adhere to the "octet rule" in this case (a limitation of the usefulness of this rule). Note: The silver and cadmium atoms lost the 5s electrons in achieving the ionic state.

When a positive ion is formed from an atom, electrons are **always** lost first from the subshell with the largest principle quantum number

Polyatomic Ions

Not all ionic compounds are formed from only two elements. Many **polyatomic ions** exist, in which two or more atoms are bound together by covalent bonds. They form a stable grouping which carries a charge (positive or negative). The group of atoms as a

whole acts as a charged species in forming an ionic compound with an oppositely charged ion. Polyatomic ions may be either positive or negative, for example:

- NH_4^+ (ammonium) = cation
- SO_4^{2-} (sulfate) = anion

The principles of ionic bonding with polyatomic ions are the same as those with monatomic ions. Oppositely charged ions come together to form a crystalline lattice, releasing a lattice energy. Based on the shapes and charges of the polyatomic ions, these compounds may form crystalline lattices with interesting and complex structures.

Summary

The amount of energy needed to separate a gaseous ion pair is its bond energy. The formation of ionic compounds are usually **extremely exothermic**. The strength of the electrostatic attraction between ions with opposite charges is directly proportional to the magnitude of the charges on the ions and inversely proportional to the internuclear distance. The total energy of the system is a balance between the repulsive interactions between electrons on adjacent ions and the attractive interactions between ions with opposite charges.

Contributors and Attributions

- [Wikibooks](https://en.wikibooks.org) [en.wikibooks.org]
 - [Mike Blaber](#) (Florida State University)
 - Modified by [Joshua Halpern](#) (Howard University)
-

Answers

Exercise 2.1.2.2: Magnesium oxide

$$-3180 \text{ kJ/mol} = -3.18 \times 10^3 \text{ kJ/mol}$$

This page titled [2.1.2: Ionic Bonding](#) is shared under a [CC BY-NC-SA 4.0](#) license and was authored, remixed, and/or curated by LibreTexts.

- [8.2: Ionic Bonding](#) is licensed [CC BY-NC-SA 3.0](#).

2.1.3: Covalent Bonding

Learning Objectives

- To understand the relationship between bond order, bond length, and bond energy.

In proposing his theory that octets can be completed by two atoms sharing electron pairs, Lewis provided scientists with the first description of covalent bonding. In this section, we expand on this and describe some of the properties of covalent bonds. The general properties of Ionic substances are:

- usually brittle
- high melting point
- organized into an ordered lattice of atoms, which can be cleaved along a smooth line

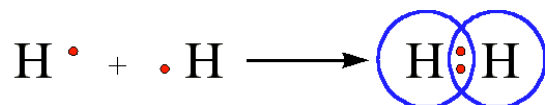
However, the vast majority of chemical substances are **not ionic** in nature. G.N. Lewis reasoned that an atom might attain a noble gas electron configuration by **sharing** electrons.

A chemical bond formed by sharing a pair of electrons is called a covalent bond

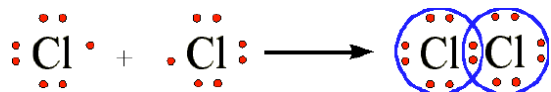
Lewis Structures

Lewis structures (also known as Lewis dot diagrams, electron dot diagrams, Lewis dot formulas, Lewis dot structures, and electron dot structures) are diagrams that show the bonding between atoms of a molecule and the lone pairs of electrons that may exist in the molecule. Lewis structures show each atom and its position in the structure of the molecule using its chemical symbol. Lines are drawn between atoms that are bonded to one another (pairs of dots can be used instead of lines). Excess electrons that form lone pairs are represented as pairs of dots, and are placed next to the atoms.

The diatomic hydrogen molecule (H_2) is the simplest model of a covalent bond, and is represented in Lewis structures as:



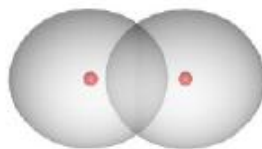
The **shared pair** of electrons provides **each** hydrogen atom with two electrons in its valence shell (the 1s) orbital. In a sense, each hydrogen atom has the electron configuration of the noble gas helium. When two chlorine atoms covalently bond to form Cl_2 , the following sharing of electrons occurs:



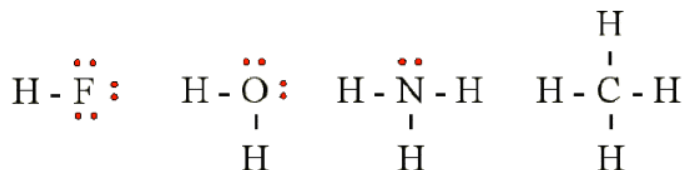
Each chlorine atom shared the bonding pair of electrons and achieves the electron configuration of the noble gas argon. In Lewis structures the bonding pair of electrons is usually displayed as a line, and the unshared electrons as dots:



The shared electrons are not located in a fixed position between the nuclei. In the case of the H_2 compound, the electron density is concentrated between the two nuclei:



The two atoms are bound into the H_2 molecule mainly due to the attraction of the positively charged nuclei for the negatively charged electron cloud located between them. Examples of hydride compounds of the above elements (covalent bonds with hydrogen):



Multiple bonds

The sharing of a pair of electrons represents a single covalent bond, usually just referred to as a **single bond**. However, in many molecules atoms attain complete octets by sharing more than one pair of electrons between them:

- Two electron pairs shared a **double bond**
- Three electron pairs shared a **triple bond**



If two electron pairs are shared then two lines are drawn. If three electron pairs are shared then three lines are drawn

Because each nitrogen contains 5 valence electrons, they need to share 3 pairs to each achieve a valence octet. N_2 is fairly inert, due to the strong triple bond between the two nitrogen atoms and the N - N bond distance in N_2 is $1.10 \text{ \AA}$ (fairly short). From a study of various Nitrogen containing compounds bond distance as a function of bond type can be summarized as follows:

- N-N: $1.47 \text{ \AA}$
- N=N: $1.24 \text{ \AA}$
- N : =N: $1.10 \text{ \AA}$

For the nonmetals (and the 's' block metals) the number of valence electrons is equal to the group number:

nonmetals (and the 's' block metals) the number of valence electrons is equal to the group number

Element	Group	Valence electrons	Bonds needed to form valence octet
aF	17	7	1
O	16	6	2
N	15	5	3
C	14	4	4

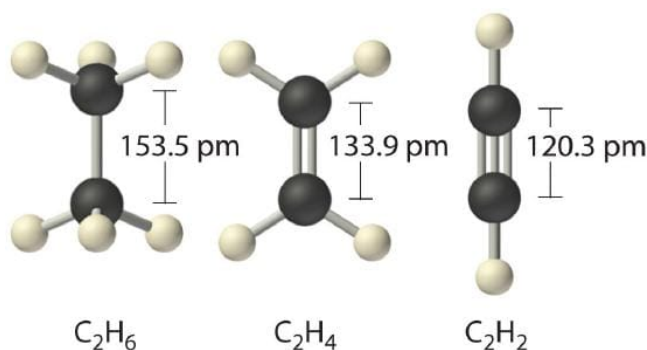
YouTube Video

This interactive element is not available in this format. Visit the link or scan the QR code to access it online.

[View this YouTube Video online](#)



Thus, the Lewis bonds successfully describe the covalent interactions between various nonmetal elements. When we draw Lewis structures, we place one, two, or three pairs of electrons between adjacent atoms. In the Lewis bonding model, the number of electron pairs that hold two atoms together is called the bond order. For a single bond, such as the C–C bond in $\text{H}_3\text{C}-\text{CH}_3$, the bond order is one. For a double bond (such as $\text{H}_2\text{C}=\text{CH}_2$), the bond order is two. For a triple bond, such as $\text{HC}\equiv\text{CH}$, the bond order is three.



When analogous bonds in similar compounds are compared, bond length decreases as bond order increases. The bond length data in Table 2.1.3.1, for example, show that the C–C distance in $\text{H}_3\text{C}-\text{CH}_3$ (153.5 pm) is longer than the distance in $\text{H}_2\text{C}=\text{CH}_2$ (133.9 pm), which in turn is longer than that in $\text{HC}\equiv\text{CH}$ (120.3 pm). Additionally, as noted in Section 8.5, molecules or ions whose bonding must be described using resonance structures usually have bond distances that are intermediate between those of single and double bonds, as we demonstrated with the C–C distances in benzene. The relationship between bond length and bond order is not linear, however. A double bond is not half as long as a single bond, and the length of a C=C bond is not the average of the lengths of C≡C and C–C bonds. Nevertheless, as bond orders increase, bond lengths generally decrease.

Table 2.1.3.1: Bond Lengths and Bond Dissociation Energies for Bonds with Different Bond Orders in Selected Gas-Phase Molecules at 298 K

Compound	Bond Order	Bond Length (pm)	Bond Dissociation Energy (kJ/mol)	Compound	Bond Order	Bond Length (pm)	Bond Dissociation Energy (kJ/mol)
$\text{H}_3\text{C}-\text{CH}_3$	1	153.5	376	$\text{H}_3\text{C}-\text{NH}_2$	1	147.1	331
$\text{H}_2\text{C}=\text{CH}_2$	2	133.9	728	$\text{H}_2\text{C}=\text{NH}$	2	127.3	644
$\text{HC}\equiv\text{CH}$	3	120.3	965	$\text{HC}\equiv\text{N}$	3	115.3	937
$\text{H}_2\text{N}-\text{NH}_2$	1	144.9	275.3	$\text{H}_3\text{C}-\text{OH}$	1	142.5	377
$\text{HN}=\text{NH}$	2	125.2	456	$\text{H}_2\text{C}=\text{O}$	2	120.8	732
$\text{N}\equiv\text{N}$	3	109.8	945.3	$\text{O}=\text{C}=\text{O}$	2	116.0	799
$\text{HO}-\text{OH}$	1	147.5	213	$\text{C}\equiv\text{O}$	3	112.8	1076.5
$\text{O}=\text{O}$	2	120.7	498.4				

Sources: Data from *CRC Handbook of Chemistry and Physics* (2004); *Lange's Handbook of Chemistry* (2005); CCCBDB [cccbdb.nist.gov].

As a general rule, the distance between bonded atoms decreases as the number of shared electron pairs increases

YouTube Video

This interactive element is not available in this format. Visit the link or scan the QR code to access it online.

[View this YouTube Video online](#)



The Relationship between Bond Order & Bond Energy

As shown in Table 2.1.3.1, triple bonds between like atoms are shorter than double bonds, and because more energy is required to completely break all three bonds than to completely break two, a triple bond is also stronger than a double bond. Similarly, double bonds between like atoms are stronger and shorter than single bonds. Bonds of the same order between *different* atoms show a wide range of bond energies, however.

Table 2.1.3.1: Average Bond Energies (kJ/mol) for Commonly Encountered Bonds at 273 K

Single Bonds										Multiple Bonds	
H-H	432	C-C	346	N-N	≈167	O-O	≈142	F-F	155	C=C	602
H-C	411	C-Si	318	N-O	201	O-F	190	F-Cl	249	C≡C	835
H-Si	318	C-N	305	N-F	283	O-Cl	218	F-Br	249	C=N	615
H-N	386	C-O	358	N-Cl	313	O-Br	201	F-I	278	C≡N	887
H-P	≈322	C-S	272	N-Br	243	O-I	201	Cl-Cl	240	C=O	749
H-O	459	C-F	485	P-P	201	S-S	226	Cl-Br	216	C≡O	1072
H-S	363	C-Cl	327			S-F	284	Cl-I	208	N=N	418
H-F	565	C-Br	285			S-Cl	255	Br-Br	190	N≡N	942
H-Cl	428	C-I	213			S-Br	218	Br-I	175	N=O	607
H-Br	362	Si-Si	222					I-I	149	O=O	494
H-I	295	Si-O	452							S=O	532

Source: Data from J. E. Huheey, E. A. Keiter, and R. L. Keiter, *Inorganic Chemistry*, 4th ed. (1993).

Table 2.1.3.2 lists the average values for some commonly encountered bonds. Although the values shown vary widely, we can observe four trends:

1. Bonds between hydrogen and atoms in the same column of the periodic table decrease in strength as we go down the column. Thus an H-F bond is stronger than an H-I bond, H-C is stronger than H-Si, H-N is stronger than H-P, H-O is stronger than H-S, and so forth. The reason for this is that the region of space in which electrons are shared between two atoms becomes proportionally smaller as one of the atoms becomes larger (part (a) in Figure 8.3.1).
2. Bonds between like atoms usually become *weaker* as we go down a column (important exceptions are noted later). For example, the C-C single bond is stronger than the Si-Si single bond, which is stronger than the Ge-Ge bond, and so forth. As two bonded atoms become larger, the region between them occupied by bonding electrons becomes *proportionally* smaller, as illustrated in part (b) in Figure 8.3.1. Noteworthy exceptions are single bonds between the period 2 atoms of groups 15, 16, and 17 (i.e., N, O, F), which are unusually weak compared with single bonds between their larger congeners. It is likely that the N-N, O-O, and F-F single bonds are weaker than might be expected due to strong repulsive interactions between lone pairs of electrons on *adjacent* atoms. The trend in bond energies for the halogens is therefore $\text{Cl-Cl} > \text{Br-Br} > \text{F-F} > \text{I-I}$. Similar effects are also seen for the O-O versus S-S and for N-N versus P-P single bonds.

Bonds between hydrogen and atoms in a given column in the periodic table are weaker down the column; bonds between like atoms usually become weaker down a column.

- Because elements in periods 3 and 4 rarely form multiple bonds with themselves, their multiple bond energies are not accurately known. Nonetheless, they are presumed to be significantly weaker than multiple bonds between lighter atoms of the same families. Compounds containing an Si=Si double bond, for example, have only recently been prepared, whereas compounds containing C=C double bonds are one of the best-studied and most important classes of organic compounds.
- Multiple bonds between carbon, oxygen, or nitrogen and a period 3 element such as phosphorus or sulfur tend to be unusually strong. In fact, multiple bonds of this type dominate the chemistry of the period 3 elements of groups 15 and 16. Multiple bonds to phosphorus or sulfur occur as a result of *d*-orbital interactions, e.g., for the SO_4^{2-} ion. In contrast, silicon in group 14 has little tendency to form discrete silicon-oxygen double bonds. Consequently, SiO_2 has a three-dimensional network structure in which each silicon atom forms four Si-O single bonds, which makes the physical and chemical properties of SiO_2 very different from those of CO_2 .

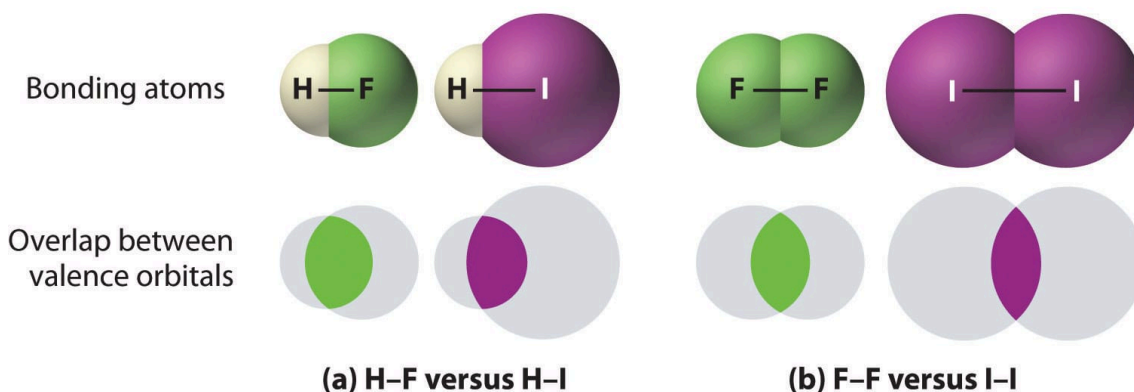


Figure 2.1.3.1: The Strength of Covalent Bonds Depends on the Overlap between the Valence Orbitals of the Bonded Atoms. The relative sizes of the region of space in which electrons are shared between (a) a hydrogen atom and lighter (smaller) vs. heavier (larger) atoms in the same periodic group; and (b) two lighter versus two heavier atoms in the same group. Although the absolute amount of shared space increases in both cases on going from a light to a heavy atom, the amount of space *relative to the size of the bonded atom* decreases; that is, the *percentage* of total orbital volume decreases with increasing size. Hence the strength of the bond decreases.

Bond strengths increase as bond order **increases**, while bond distances **decrease**.

The Relationship between Molecular Structure and Bond Energy

Bond energy is defined as the energy required to break a particular bond in a molecule in the gas phase. Its value depends on not only the identity of the bonded atoms but also their environment. Thus the bond energy of a C-H single bond is *not* the same in all organic compounds. For example, the energy required to break a C-H bond in methane varies by as much as 25% depending on how many other bonds in the molecule have already been broken (Table 2.1.3.2); that is, the C-H bond energy depends on its molecular environment. Except for diatomic molecules, the bond energies listed in Table 2.1.3.2 are *average* values for all bonds of a given type in a range of molecules. Even so, they are not likely to differ from the actual value of a given bond by more than about 10%.

Table 2.1.3.3: *Energies for the Dissociation of Successive C-H Bonds in Methane*

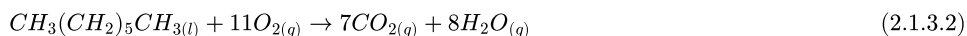
Reaction	D (kJ/mol)
$\text{CH}_4(\text{g}) \rightarrow \text{CH}_3(\text{g}) + \text{H}(\text{g})$	439
$\text{CH}_3(\text{g}) \rightarrow \text{CH}_2(\text{g}) + \text{H}(\text{g})$	462
$\text{CH}_2(\text{g}) \rightarrow \text{CH}(\text{g}) + \text{H}(\text{g})$	424
$\text{CH}(\text{g}) \rightarrow \text{C}(\text{g}) + \text{H}(\text{g})$	338
Source: Data from <i>CRC Handbook of Chemistry and Physics</i> (2004).	

We can estimate the enthalpy change for a chemical reaction by adding together the average energies of the bonds broken in the reactants and the average energies of the bonds formed in the products and then calculating the difference between the two. If the bonds formed in the products are stronger than those broken in the reactants, then energy will be released in the reaction ($\Delta H_{\text{rxn}} < 0$):

$$\Delta H_{\text{rxn}} \approx \sum (\text{bond energies of bonds broken}) - \sum (\text{bond energies of bonds formed}) \quad (2.1.3.1)$$

The $\approx$ sign is used because we are adding together *average* bond energies; hence this approach does not give exact values for ΔH_{rxn} .

Let's consider the reaction of 1 mol of *n*-heptane (C_7H_{16}) with oxygen gas to give carbon dioxide and water. This is one reaction that occurs during the combustion of gasoline:



In this reaction, 6 C-C bonds, 16 C-H bonds, and 11 O=O bonds are broken per mole of *n*-heptane, while 14 C=O bonds (two for each CO_2) and 16 O-H bonds (two for each H_2O) are formed. The energy changes can be tabulated as follows:

Bonds Broken (kJ/mol) and Bonds Formed (kJ/mol)

Bonds Broken (kJ/mol)		Bonds Formed (kJ/mol)	
6 C-C	$346 \times 6 = 2076$	14 C=O	$799 \times 14 = 11,186$
16 C-H	$411 \times 16 = 6576$	16 O-H	$459 \times 16 = 7344$
11 O=O	$494 \times 11 = 5434$		Total = 18,530
	Total = 14,086		

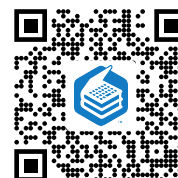
The bonds in the products are stronger than the bonds in the reactants by about 4444 kJ/mol. This means that ΔH_{rxn} is approximately -4444 kJ/mol, and the reaction is highly exothermic (which is not too surprising for a combustion reaction).

If we compare this approximation with the value obtained from measured ΔH_f° values ($\Delta H_{\text{rxn}} = -4817 \text{ kJ/mol}$), we find a discrepancy of only about 8%, less than the 10% typically encountered. Chemists find this method useful for calculating approximate enthalpies of reaction for molecules whose actual ΔH_f° values are unknown. These approximations can be important for predicting whether a reaction is **exothermic** or **endothermic**—and to what degree.

YouTube Video

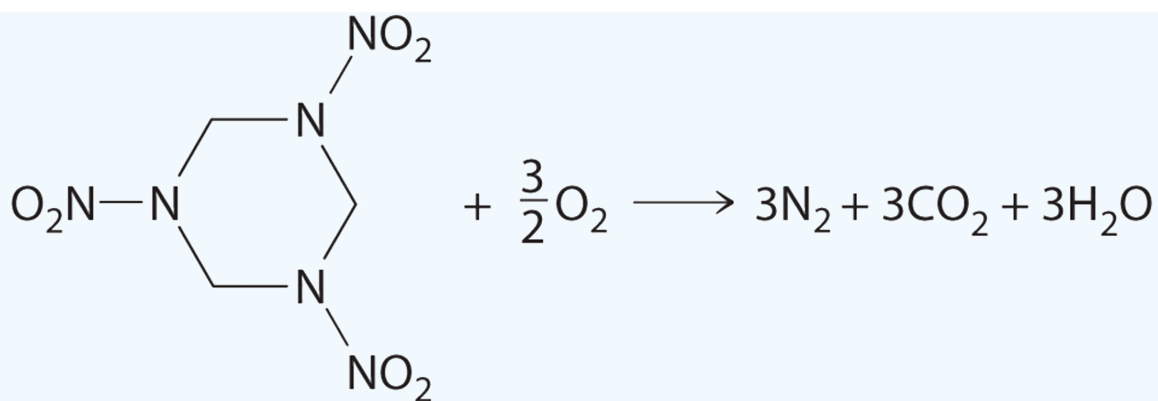
This interactive element is not available in this format. Visit the link or scan the QR code to access it online.

[View this YouTube Video online](#)

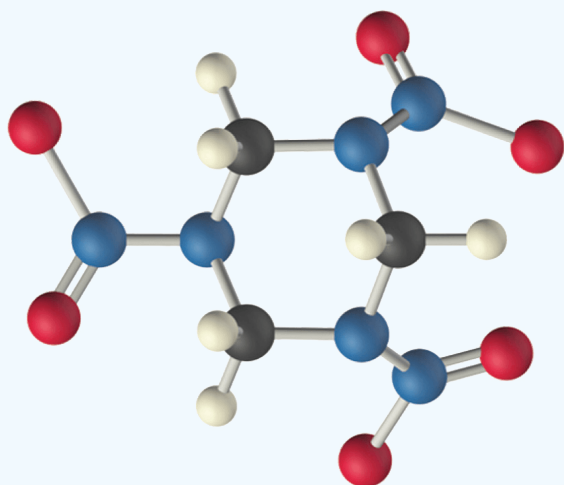


Example 2.1.3.1

The compound **RDX** (Research Development Explosive) is a more powerful explosive than dynamite and is used by the military. When detonated, it produces gaseous products and heat according to the following reaction. Use the approximate bond energies in Table 8.3.2 to estimate the ΔH_{rxn} per mole of RDX.



RDX



RDX

Given: chemical reaction, structure of reactant, and Table 8.3.2.

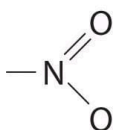
Asked for: ΔH_{rxn} per mole

Strategy:

- List the types of bonds broken in RDX, along with the bond energy required to break each type. Multiply the number of each type by the energy required to break one bond of that type and then add together the energies. Repeat this procedure for the bonds formed in the reaction.
- Use Equation 8.3.1 to calculate the amount of energy consumed or released in the reaction (ΔH_{rxn}).

Solution:

We must add together the energies of the bonds in the reactants and compare that quantity with the sum of the energies of the bonds in the products. A nitro group ($-\text{NO}_2$) can be viewed as having one N-O single bond and one N=O double bond, as follows:



In fact, however, both N–O distances are usually the same because of the presence of two equivalent resonance structures.

A We can organize our data by constructing a table:

Bonds Broken (kJ/mol)

Bonds Broken (kJ/mol)		Bonds Broken (kJ/mol)	
6 C–H	$411 \times 6 = 2466$	6 C=O	$799 \times 6 = 4794$
3 N–N	$167 \times 3 = 501$	6 O–H	$459 \times 6 = 2754$
3 N–O	$201 \times 3 = 603$		Total = 10,374
3 N=O	$607 \times 3 = 1821$		
1.5 O=O	$494 \times 1.5 = 741$		
	Total = 7962		

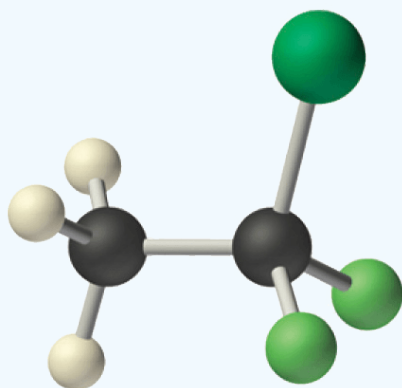
B From Equation 8.3.1, we have

$$\begin{aligned}
 \Delta H_{rxn} &\approx \sum (\text{bond energies of bonds broken}) - \sum (\text{bond energies of bonds formed}) \\
 &= 7962 \text{ kJ/mol} - 10,374 \text{ kJ/mol} \\
 &= [-2412 \text{ kJ/mol}]
 \end{aligned}$$

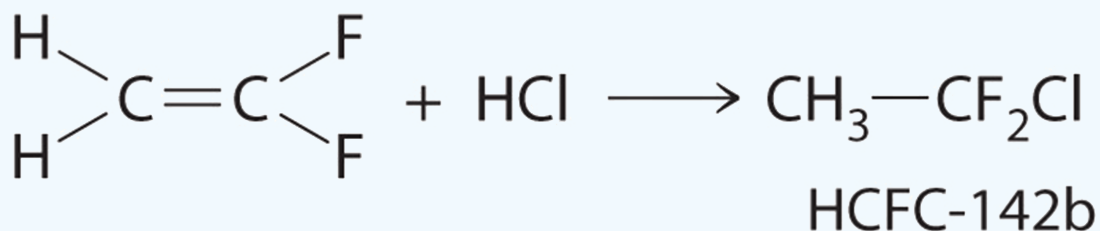
Thus this reaction is also highly exothermic.

Exercise 2.1.3.1

The molecule HCFC-142b, a hydrochlorofluorocarbon used in place of chlorofluorocarbons (CFCs) such as the Freons, can be prepared by adding HCl to 1,1-difluoroethylene:



HCFC-142b



Use tabulated bond energies to calculate ΔH_{rxn} .

Answer available at the end of this section.

Summary

The strength of a covalent bond depends on the overlap between the valence orbitals of the bonded atoms. **Bond order** is the number of electron pairs that hold two atoms together. Single bonds have a bond order of one, and multiple bonds with bond orders of two (a double bond) and three (a triple bond) are quite common. In closely related compounds with bonds between the same kinds of atoms, the bond with the highest bond order is both the shortest and the strongest. In bonds with the same bond order between different atoms, trends are observed that, with few exceptions, result in the strongest single bonds being formed between the smallest atoms. Tabulated values of average bond energies can be used to calculate the enthalpy change of many chemical reactions. If the bonds in the products are stronger than those in the reactants, the reaction is exothermic and vice versa.

Contributors and Attributions

- [Mike Blaber \(Florida State University\)](#)
- [Wikipedia](#)

Answers

Exercise 2.1.3.1

–54 kJ/mol

This page titled [2.1.3: Covalent Bonding](#) is shared under a [CC BY-NC-SA 4.0](#) license and was authored, remixed, and/or curated by LibreTexts.

- [8.3: Covalent Bonding](#) is licensed [CC BY-NC-SA 3.0](#).

2.1.4: Bond Polarity and Electronegativity

Learning Objectives

- To define electronegativity and bond polarity
- To calculate the percent ionic character of a covalent polar bond

The electron pairs shared between two atoms **are not necessarily shared equally**. For example, while the bonding electron pair 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. As 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. 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.

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 will be *highly electronegative* if it has a large (negative) electron affinity and a high ionization energy (always endothermic, or positive for neutral atoms). Thus, it will attract electrons from other atoms and 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.

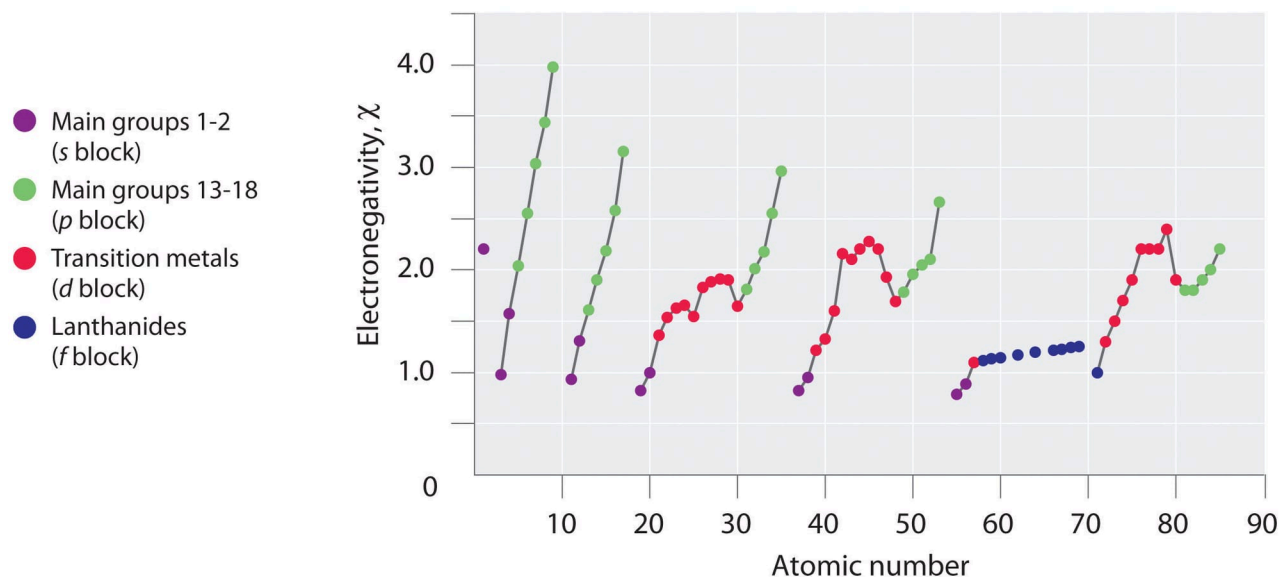
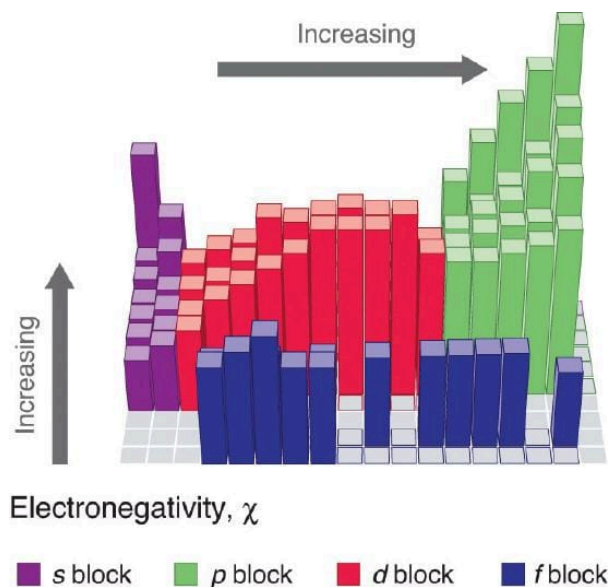


Figure 2.1.4.1: A Plot of Periodic Variation of Electronegativity with Atomic Number for the First Six Rows of the Periodic Table

The main groups 1 and 2 are purple, the main groups 13 through 18 are green, the transition metals are red, and the lanthanides are blue.

Periodic variations in Pauling's electronegativity values are illustrated in Figures 2.1.4.1 and 2.1.4.2. 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).

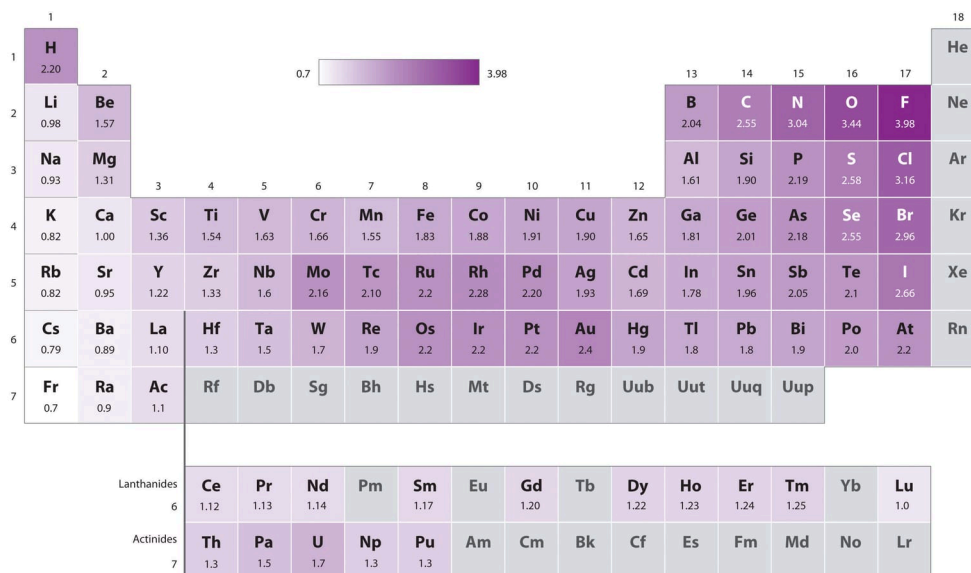


The s blocks are purple, the p blocks are green, the d blocks are red, and the f blocks are blue. Electronegativity increase from bottom to top and left to right.

Figure 2.1.4.2: 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*

Linus Pauling (1901-1994)

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 later denied a high school degree, and had to work several jobs to put himself through college. Pauling would go on to become one of the most influential chemists of the century if not all time. He won two Nobel Prizes, one for chemistry in 1954 and one for peace in 1962.



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](#), [Allred-Rochow](#), and Allen electronegativity scales. The Mulliken electronegativity of an element is the average of its first ionization energy and the absolute value of its electron affinity, showing the relationship between electronegativity and these other periodic properties.

YouTube Video

This interactive element is not available in this format. Visit the link or scan the QR code to access it online.

[View this YouTube Video online](#)



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 2.1.4.2) 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 **metalloids** (or semimetals), 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 2.1.4.3 shows the strong correlation between electronegativity values, metallic versus nonmetallic character, and location in the periodic table.

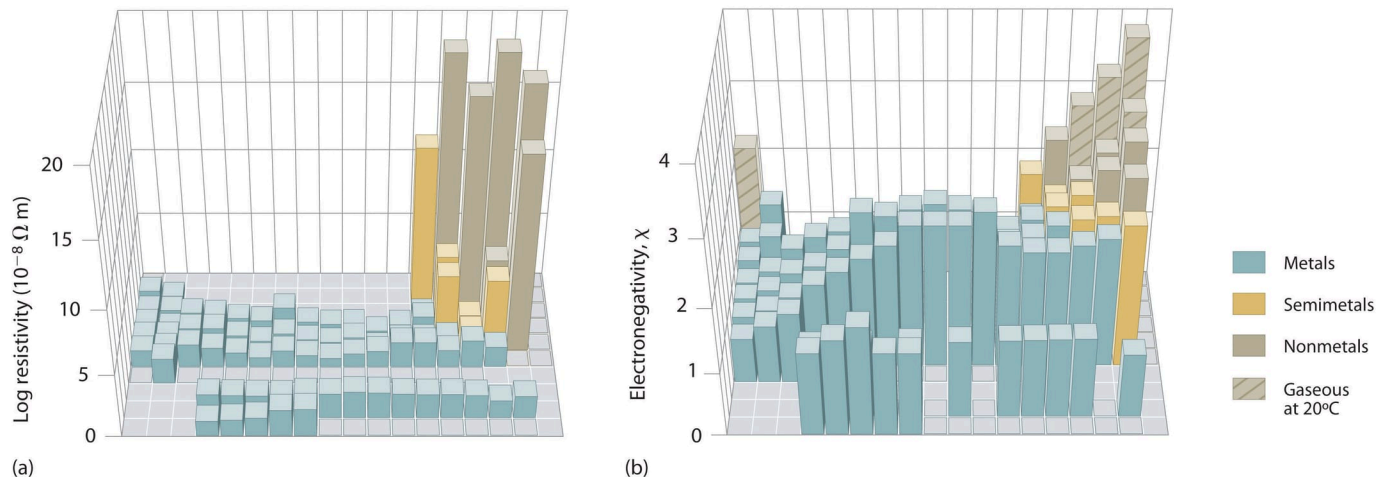


Figure 2.1.4.3: Three-Dimensional Plots Demonstrating the Relationship between Electronegativity and the Metallic/Nonmetallic Character of the Elements. (a) A plot of electrical resistivity (measured resistivity to electron flow) at or near room temperature shows that substances with high resistivity (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 ($\geq$ about 2.2) correlate with high electrical resistivities (insulators). Low electronegativity values ($\leq$ 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). Metals are blue, semimetals are yellow, nonmetals are gray, gaseous at 20 degrees C are gray with dashed lines.

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

The [rules for assigning oxidation states](#)(opens in new window) 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 2.1.4.1: Increasing Electronegativity

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 metalloid.

Given: four elements

Asked for: order by increasing electronegativity and classification

Strategy:

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

Solution:

A Electronegativity increases from lower left to upper right in the periodic table (Figure 8.4.2). 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 $\chi_{\text{Cl}} > \chi_{\text{Se}}$. 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 $\chi_{\text{Sr}} < \chi_{\text{Si}} < \chi_{\text{Se}} < \chi_{\text{Cl}}$.

C To classify the elements, we note that Sr lies well to the left of the diagonal belt of metalloids 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 metalloid, and Se and Cl are nonmetals.

Exercise 2.1.4.1

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 metalloid.

Answer available at the end of this section.

Percent Ionic Character of a Covalent polar bond

The two idealized extremes of chemical bonding: (1) ionic bonding—in which one or more electrons are transferred completely from one atom to another, and the resulting ions are held together by purely electrostatic forces—and (2) covalent bonding, in which electrons are shared equally between two atoms. Most compounds, however, have polar covalent bonds, which means that electrons are shared unequally between the bonded atoms. Figure 2.1.4.4 compares the electron distribution in a polar covalent bond with those in an ideally covalent and an ideally ionic bond. Recall that a lowercase Greek delta (δ) is used to indicate that a bonded atom possesses a partial positive charge, indicated by δ^+ , or a partial negative charge, indicated by δ^- , and a bond between two atoms that possess partial charges is a polar bond.

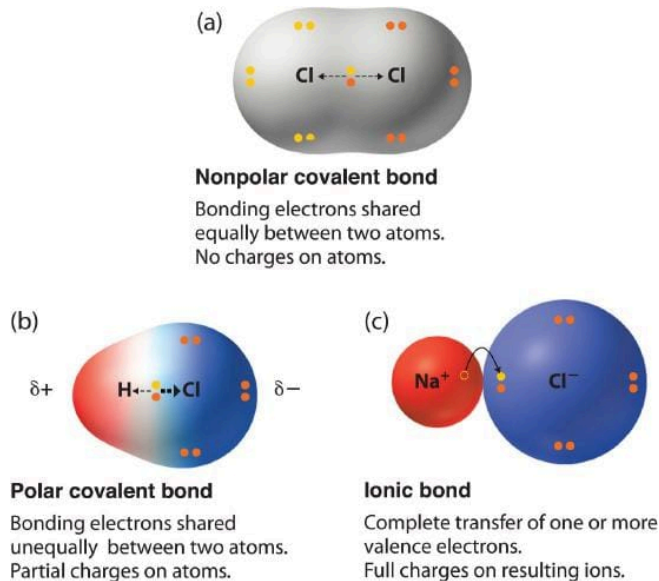


Figure 2.1.4.4: The Electron Distribution in a Nonpolar Covalent Bond, a Polar Covalent Bond, and an Ionic Bond Using Lewis Electron Structures. In a purely covalent bond (a), the bonding electrons are shared equally between the atoms. In a purely ionic bond (c), an electron has been transferred completely from one atom to the other. A polar covalent bond (b) is intermediate between the two extremes: the bonding electrons are shared unequally between the two atoms, and the electron distribution is asymmetrical with the electron density being greater around the more electronegative atom. Electron-rich (negatively charged) regions are shown in blue; electron-poor (positively charged) regions are shown in red.

Bond Polarity

The polarity of a bond—the extent to which it is polar—is determined largely by the relative electronegativities of the bonded atoms. Electronegativity (χ) was defined as the ability of an atom in a molecule or an ion to attract electrons to itself. Thus there is a direct correlation between electronegativity and bond polarity. A bond is *nonpolar* if the bonded atoms have equal electronegativities. If the electronegativities of the bonded atoms are not equal, however, the bond is *polarized* toward the more electronegative atom. A bond in which the electronegativity of B (χ_B) is greater than the electronegativity of A (χ_A), for example, is indicated with the partial negative charge on the more electronegative atom:



One way of estimating the ionic character of a bond—that is, the magnitude of the charge separation in a polar covalent bond—is to calculate the difference in electronegativity between the two atoms: $\Delta\chi = \chi_B - \chi_A$.

To predict the polarity of the bonds in Cl_2 , HCl , and NaCl , for example, we look at the electronegativities of the relevant atoms: $\chi_{\text{Cl}} = 3.16$, $\chi_{\text{H}} = 2.20$, and $\chi_{\text{Na}} = 0.93$. Cl_2 must be nonpolar because the electronegativity difference ($\Delta\chi$) is zero; hence the two chlorine atoms share the bonding electrons equally. In NaCl , $\Delta\chi$ is 2.23. This high value is typical of an ionic compound ($\Delta\chi \geq \approx 1.5$) and means that the valence electron of sodium has been completely transferred to chlorine to form Na^+ and Cl^- ions. In HCl , however, $\Delta\chi$ is only 0.96. The bonding electrons are more strongly attracted to the more electronegative chlorine atom, and so the charge distribution is



Remember that electronegativities are difficult to measure precisely and different definitions produce slightly different numbers. In practice, the polarity of a bond is usually estimated rather than calculated.

Bond polarity and ionic character **increase** with an increasing difference in electronegativity.

As with bond energies, the electronegativity of an atom depends to some extent on its chemical environment. It is therefore unlikely that the reported electronegativities of a chlorine atom in NaCl , Cl_2 , ClF_5 , and HClO_4 would be exactly the same.

Dipole Moments

The asymmetrical charge distribution in a polar substance such as HCl produces a **dipole moment** where Qr in meters (m), is abbreviated by the Greek letter mu (μ). The dipole moment is defined as the product of the partial charge Q on the bonded atoms and the distance r between the partial charges:

$$\mu = Qr \quad (2.1.4.2)$$

where Q is measured in coulombs (C) and r in meters. The unit for dipole moments is the debye (D):

$$1 \text{ D} = 3.3356 \times 10^{-30} \text{ C} \cdot \text{m} \quad (2.1.4.3)$$

When a molecule with a dipole moment is placed in an electric field, it tends to orient itself with the electric field because of its asymmetrical charge distribution (Figure 2.1.4.4).

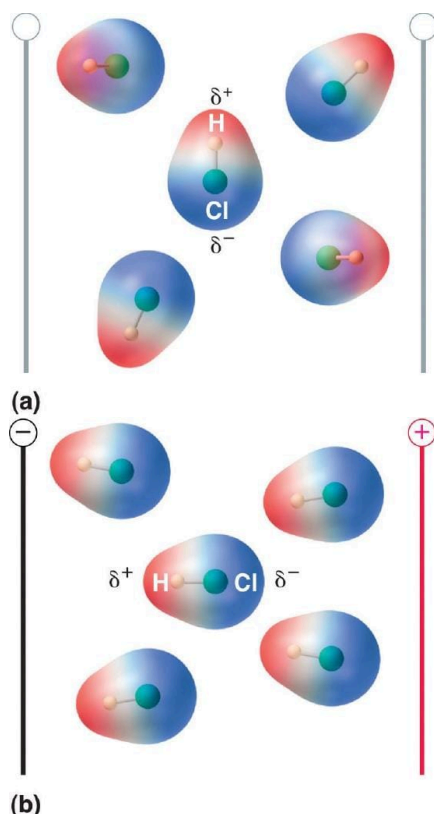


Figure 2.1.4.5: Molecules That Possess a Dipole Moment Partially Align Themselves with an Applied Electric Field. In the absence of a field (a), the HCl molecules are randomly oriented. When an electric field is applied (b), the molecules tend to align themselves with the field, such that the positive end of the molecular dipole points toward the negative terminal and vice versa.

We can measure the partial charges on the atoms in a molecule such as HCl using Equation 2.1.4.2. If the bonding in HCl were purely ionic, an electron would be transferred from H to Cl, so there would be a full +1 charge on the H atom and a full –1 charge on the Cl atom. The dipole moment of HCl is 1.109 D, as determined by measuring the extent of its alignment in an electric field, and the reported gas-phase H–Cl distance is 127.5 pm. Hence the charge on each atom is

$$Q = \frac{\mu}{r} = 1.109 \text{ D} \left(\frac{3.3356 \times 10^{-30} \text{ C} \cdot \text{m}}{1 \text{ D}} \right) \left(\frac{1}{127.8 \text{ pm}} \right) \left(\frac{1 \text{ pm}}{10^{-12} \text{ m}} \right) = 2.901 \times 10^{-20} \text{ C} \quad (2.1.4.4)$$

By dividing this calculated value by the charge on a single electron ($1.6022 \times 10^{-19} \text{ C}$), we find that the electron distribution in HCl is asymmetric and that effectively it appears that there is a net negative charge on the Cl of about –0.18, effectively corresponding to about 0.18 e^- . This certainly does not mean that there is a fraction of an electron on the Cl atom, but that the distribution of electron probability favors the Cl atom side of the molecule by about this amount.

$$\frac{2.901 \times 10^{-20} \text{ C}}{1.6022 \times 10^{-19} \text{ C}} = 0.1811 e^- \quad (2.1.4.5)$$

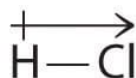
To form a neutral compound, the charge on the H atom must be equal but opposite. Thus the measured dipole moment of HCl indicates that the H–Cl bond has approximately 18% ionic character (0.1811×100), or 82% covalent character. Instead of writing HCl as



we can therefore indicate the charge separation quantitatively as



Our calculated results are in agreement with the electronegativity difference between hydrogen and chlorine ($\chi_{\text{H}} = 2.20$; $\chi_{\text{Cl}} = 3.16$, $\chi_{\text{Cl}} - \chi_{\text{H}} = 0.96$), a value well within the range for polar covalent bonds. We indicate the dipole moment by writing an arrow above the molecule. Mathematically, dipole moments are vectors, and they possess both a magnitude and a direction. The dipole moment of a molecule is the vector sum of the dipoles of the individual bonds. In HCl, for example, the dipole moment is indicated as follows:



The arrow shows the direction of electron flow by pointing toward the more electronegative atom.

The charge on the atoms of many substances in the gas phase can be calculated using measured dipole moments and bond distances. Figure 2.1.4.6 shows a plot of the percent ionic character versus the difference in electronegativity of the bonded atoms for several substances. According to the graph, the bonding in species such as NaCl(g) and CsF(g) is substantially less than 100% ionic in character. As the gas condenses into a solid, however, dipole-dipole interactions between polarized species increase the charge separations. In the crystal, therefore, an electron is transferred from the metal to the nonmetal, and these substances behave like classic ionic compounds. The data in Figure 2.1.4.6 show that diatomic species with an electronegativity difference of less than 1.5 are less than 50% ionic in character, which is consistent with our earlier description of these species as containing polar covalent bonds. The use of dipole moments to determine the ionic character of a polar bond is illustrated in Example 2.1.4.2.

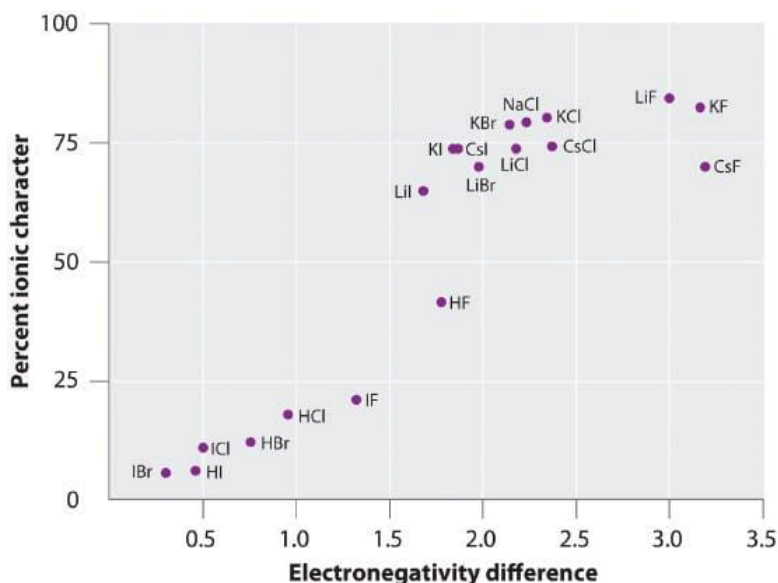


Figure 2.1.4.6: A Plot of the Percent Ionic Character of a Bond as Determined from Measured Dipole Moments versus the Difference in Electronegativity of the Bonded Atoms. In the gas phase, even CsF, which has the largest possible difference in electronegativity between atoms, is not 100% ionic. Solid CsF, however, is best viewed as 100% ionic because of the additional electrostatic interactions in the lattice.

Example 2.1.4.2

In the gas phase, NaCl has a dipole moment of 9.001 D and an Na–Cl distance of 236.1 pm. Calculate the percent ionic character in NaCl.

Given: chemical species, dipole moment, and internuclear distance

Asked for: percent ionic character

Strategy:

A Compute the charge on each atom using the information given and Equation 2.1.4.2.

B Find the percent ionic character from the ratio of the actual charge to the charge of a single electron.

Solution:

A The charge on each atom is given by

$$Q = \frac{\mu}{r} = 9.001 \cancel{\text{D}} \left(\frac{3.3356 \times 10^{-30} \text{ C} \cdot \cancel{\text{m}}}{1 \cancel{\text{D}}} \right) \left(\frac{1}{236.1 \cancel{\text{pm}}} \right) \left(\frac{1 \cancel{\text{pm}}}{10^{-12} \cancel{\text{m}}} \right) = 1.272 \times 10^{-19} \text{ C}$$

Thus NaCl behaves as if it had charges of $1.272 \times 10^{-19} \text{ C}$ on each atom separated by 236.1 pm.

B The percent ionic character is given by the ratio of the actual charge to the charge of a single electron (the charge expected for the complete transfer of one electron):

$$\% \text{ ionic character} = \left(\frac{1.272 \times 10^{-19} \cancel{\text{C}}}{1.6022 \times 10^{-19} \cancel{\text{C}}} \right) (100) = 79.39\% \approx 79\%$$

Exercise 2.1.4.2

In the gas phase, silver chloride (AgCl) has a dipole moment of 6.08 D and an Ag-Cl distance of 228.1 pm. What is the percent ionic character in silver chloride?

Answer available at the end of this section.

Summary

Bond polarity and ionic character increase with an increasing difference in electronegativity. 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.

Compounds with **polar covalent bonds** have electrons that are shared unequally between the bonded atoms. The polarity of such a bond is determined largely by the relative electronegativities of the bonded atoms. The asymmetrical charge distribution in a polar substance produces a **dipole moment**, which is the product of the partial charges on the bonded atoms and the distance between them.

Answers

Exercise 2.1.4.1

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

Exercise 2.1.4.2

55.5%

This page titled [2.1.4: Bond Polarity and Electronegativity](#) is shared under a [CC BY-NC-SA 4.0](#) license and was authored, remixed, and/or curated by LibreTexts.

- [8.4: Bond Polarity and Electronegativity](#) is licensed [CC BY-NC-SA 3.0](#).

2.1.5: Drawing Lewis Structures

Learning Objectives

- To use Lewis dot symbols to explain the stoichiometry of a compound

We begin our discussion of the relationship between structure and bonding in covalent compounds by describing the interaction between two identical neutral atoms—for example, the H_2 molecule, which contains a purely covalent bond. Each hydrogen atom in H_2 contains one electron and one proton, with the electron attracted to the proton by electrostatic forces. As the two hydrogen atoms are brought together, additional interactions must be considered (Figure 2.1.5.1):

- The electrons in the two atoms repel each other because they have the same charge (
- The electrons in the two atoms repel each other because they have the same charge ($E > 0$).*
- Similarly, the protons in adjacent atoms repel each other ($E > 0$).*
- The electron in one atom is attracted to the oppositely charged proton in the other atom and vice versa ($E < 0$). Recall that it is impossible to specify precisely the position of the electron in either hydrogen atom. Hence the quantum mechanical probability distributions must be used.*

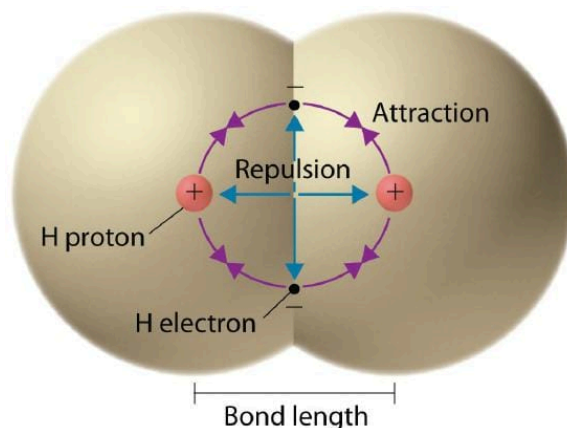


Figure 2.1.5.1: Attractive and Repulsive Interactions between Electrons and Nuclei in the Hydrogen Molecule. Electron–electron and proton–proton interactions are repulsive; electron–proton interactions are attractive. At the observed bond distance, the repulsive and attractive interactions are balanced.

A plot of the potential energy of the system as a function of the internuclear distance (Figure 2.1.5.2) shows that the system becomes more stable (the energy of the system decreases) as two hydrogen atoms move toward each other from $r = \infty$, until the energy reaches a minimum at $r = r_0$ (the observed internuclear distance in H_2 is 74 pm). Thus at intermediate distances, proton–electron attractive interactions dominate, but as the distance becomes very short, electron–electron and proton–proton repulsive interactions cause the energy of the system to increase rapidly. Notice the similarity between Figures 2.1.5.1 and 2.1.5.2, which described a system containing two oppositely charged *ions*. The shapes of the energy versus distance curves in the two figures are similar because they both result from attractive and repulsive forces between charged entities.

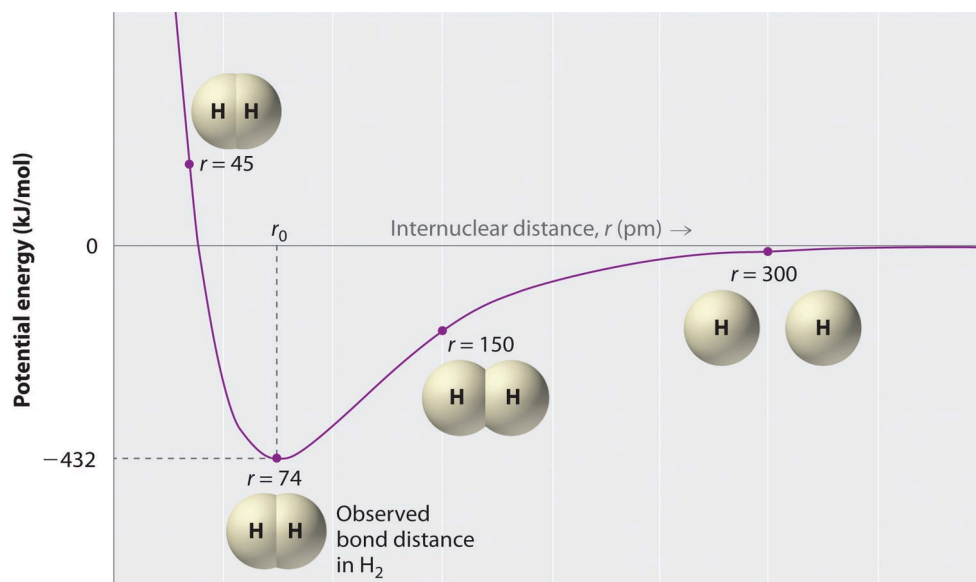
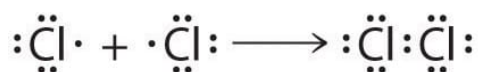


Figure 2.1.5.2: A Plot of Potential Energy versus Internuclear Distance for the Interaction between Two Gaseous Hydrogen Atoms.

At long distances, both attractive and repulsive interactions are small. As the distance between the atoms decreases, the attractive electron–proton interactions dominate, and the energy of the system decreases. At the observed bond distance, the repulsive electron–electron and proton–proton interactions just balance the attractive interactions, preventing a further decrease in the internuclear distance. At very short internuclear distances, the repulsive interactions dominate, making the system less stable than the isolated atoms.

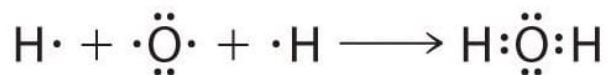
Using Lewis Dot Symbols to Describe Covalent Bonding

The valence electron configurations of the constituent atoms of a covalent compound are important factors in determining its structure, stoichiometry, and properties. For example, chlorine, with seven valence electrons, is one electron short of an octet. If two chlorine atoms share their unpaired electrons by making a covalent bond and forming Cl_2 , they can each complete their valence shell:



Each chlorine atom now has an octet. The electron pair being shared by the atoms is called a bonding pair; the other three pairs of electrons on each chlorine atom are called lone pairs. Lone pairs are not involved in covalent bonding. If both electrons in a covalent bond come from the same atom, the bond is called a coordinate covalent bond. Examples of this type of bonding are presented in Section 8.6 when we discuss atoms with less than an octet of electrons.

We can illustrate the formation of a water molecule from two hydrogen atoms and an oxygen atom using Lewis dot symbols:



The structure on the right is the *Lewis electron structure*, or *Lewis structure*, for H_2O . With two bonding pairs and two lone pairs, the oxygen atom has now completed its octet. Moreover, by sharing a bonding pair with oxygen, each hydrogen atom now has a full valence shell of two electrons. Chemists usually indicate a bonding pair by a single line, as shown here for our two examples:



The following procedure can be used to construct Lewis electron structures for more complex molecules and ions:

1. **Arrange the atoms to show specific connections.** When there is a central atom, it is usually the least electronegative element in the compound. Chemists usually list this central atom first in the chemical formula (as in CCl_4 and CO_3^{2-} , which both have C as the central atom), which is another clue to the compound's structure. Hydrogen and the halogens are almost always connected to only one other atom, so they are usually *terminal* rather than central.
2. **Determine the total number of valence electrons in the molecule or ion.** Add together the valence electrons from each atom. (Recall that the number of valence electrons is indicated by the position of the element in the periodic table.) If the species is a polyatomic ion, remember to add or subtract the number of electrons necessary to give the total charge on the ion. For CO_3^{2-} , for example, we add two electrons to the total because of the -2 charge.
3. **Place a bonding pair of electrons between each pair of adjacent atoms to give a single bond.** In H_2O , for example, there is a bonding pair of electrons between oxygen and each hydrogen.
4. **Beginning with the terminal atoms, add enough electrons to each atom to give each atom an octet (two for hydrogen).** These electrons will usually be lone pairs.
5. **If any electrons are left over, place them on the central atom.** We will explain later that some atoms are able to accommodate more than eight electrons.
6. **If the central atom has fewer electrons than an octet, use lone pairs from terminal atoms to form multiple (double or triple) bonds to the central atom to achieve an octet.** This will not change the number of electrons on the terminal atoms.

Now let's apply this procedure to some particular compounds, beginning with one we have already discussed.

The central atom is usually the least electronegative element in the molecule or ion; hydrogen and the halogens are usually terminal.

The H_2O Molecule

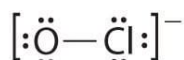
1. Because H atoms are almost always terminal, the arrangement within the molecule must be HOH.
2. Each H atom (group 1) has 1 valence electron, and the O atom (group 16) has 6 valence electrons, for a total of 8 valence electrons.
3. Placing one bonding pair of electrons between the O atom and each H atom gives $\text{H}:\text{O}:\text{H}$, with 4 electrons left over.
4. Each H atom has a full valence shell of 2 electrons.
5. Adding the remaining 4 electrons to the oxygen (as two lone pairs) gives the following structure:



This is the Lewis structure we drew earlier. Because it gives oxygen an octet and each hydrogen two electrons, we do not need to use step 6.

The OCl^- Ion

1. With only two atoms in the molecule, there is no central atom.
2. Oxygen (group 16) has 6 valence electrons, and chlorine (group 17) has 7 valence electrons; we must add one more for the negative charge on the ion, giving a total of 14 valence electrons.
3. Placing a bonding pair of electrons between O and Cl gives $\text{O}:\text{Cl}$, with 12 electrons left over.
4. If we place six electrons (as three lone pairs) on each atom, we obtain the following structure:



Both the oxygen and chlorine have 3 electron pairs drawn around them with a bond drawn between them. The molecule has square brackets placed around it and has a negative charge.

Each atom now has an octet of electrons, so steps 5 and 6 are not needed. The Lewis electron structure is drawn within brackets as is customary for an ion, with the overall charge indicated outside the brackets, and the bonding pair of electrons is indicated by a solid line. OCl^- is the hypochlorite ion, the active ingredient in chlorine laundry bleach and swimming pool disinfectant.

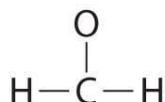
The CH_2O Molecule

1. Because carbon is less electronegative than oxygen and hydrogen is normally terminal, C must be the central atom. One possible arrangement is as follows:



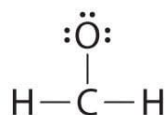
2. Each hydrogen atom (group 1) has one valence electron, carbon (group 14) has 4 valence electrons, and oxygen (group 16) has 6 valence electrons, for a total of $[(2)(1) + 4 + 6] = 12$ valence electrons.

3. Placing a bonding pair of electrons between each pair of bonded atoms gives the following:



Six electrons are used, and 6 are left over.

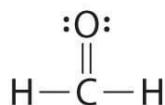
4. Adding all 6 remaining electrons to oxygen (as three lone pairs) gives the following:



Although oxygen now has an octet and each hydrogen has 2 electrons, carbon has only 6 electrons.

5. There are no electrons left to place on the central atom.

6. To give carbon an octet of electrons, we use one of the lone pairs of electrons on oxygen to form a carbon-oxygen double bond:



The bond between the oxygen and carbon is replaced with a double bond. The oxygen also has two lone pairs drawn.

Both the oxygen and the carbon now have an octet of electrons, so this is an acceptable Lewis electron structure. The O has two bonding pairs and two lone pairs, and C has four bonding pairs. This is the structure of formaldehyde, which is used in embalming fluid.

An alternative structure can be drawn with one H bonded to O. *Formal charges*, discussed later in this section, suggest that such a structure is less stable than that shown previously.

Example 2.1.5.1

Write the Lewis electron structure for each species.

- NCl_3
- S_2^{2-}
- NOCl

Given: chemical species

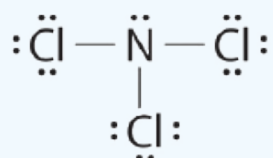
Asked for: Lewis electron structures

Strategy:

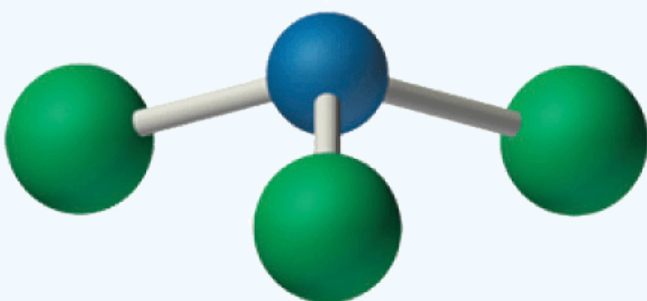
Use the six-step procedure to write the Lewis electron structure for each species.

Solution:

- a. Nitrogen is less electronegative than chlorine, and halogen atoms are usually terminal, so nitrogen is the central atom. The nitrogen atom (group 15) has 5 valence electrons and each chlorine atom (group 17) has 7 valence electrons, for a total of 26 valence electrons. Using 2 electrons for each N-Cl bond and adding three lone pairs to each Cl account for $(3 \times 2) + (3 \times 2 \times 3) = 24$ electrons. Rule 5 leads us to place the remaining 2 electrons on the central N:

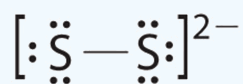


Nitrogen trichloride is an unstable oily liquid once used to bleach flour; this use is now prohibited in the United States.



Nitrogen trichloride

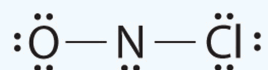
- b. In a diatomic molecule or ion, we do not need to worry about a central atom. Each sulfur atom (group 16) contains 6 valence electrons, and we need to add 2 electrons for the -2 charge, giving a total of 14 valence electrons. Using 2 electrons for the S-S bond, we arrange the remaining 12 electrons as three lone pairs on each sulfur, giving each S atom an octet of electrons:



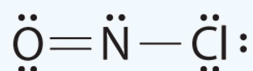
- c. Because nitrogen is less electronegative than oxygen or chlorine, it is the central atom. The N atom (group 15) has 5 valence electrons, the O atom (group 16) has 6 valence electrons, and the Cl atom (group 17) has 7 valence electrons, giving a total of 18 valence electrons. Placing one bonding pair of electrons between each pair of bonded atoms uses 4 electrons and gives the following:



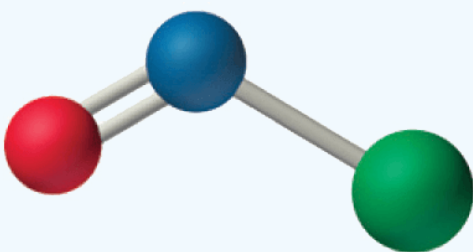
Adding three lone pairs each to oxygen and to chlorine uses 12 more electrons, leaving 2 electrons to place as a lone pair on nitrogen:



Because this Lewis structure has only 6 electrons around the central nitrogen, a lone pair of electrons on a terminal atom must be used to form a bonding pair. We could use a lone pair on either O or Cl. Because we have seen many structures in which O forms a double bond but none with a double bond to Cl, it is reasonable to select a lone pair from O to give the following:



All atoms now have octet configurations. This is the Lewis electron structure of nitrosyl chloride, a highly corrosive, reddish-orange gas.

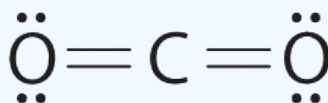


Nitrosyl chloride

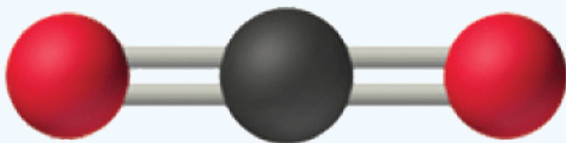
Exercise 2.1.5.1

Write Lewis electron structures for CO_2 and SCl_2 , a vile-smelling, unstable red liquid that is used in the manufacture of rubber.

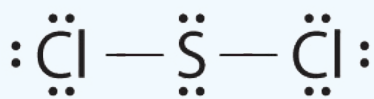
Answer



1.

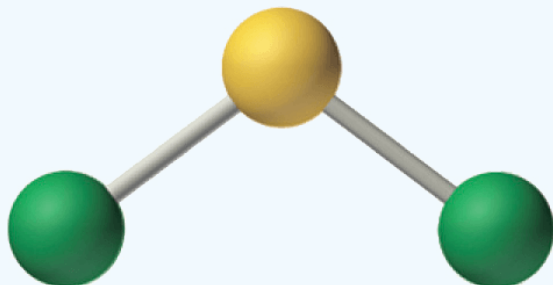


Carbon dioxide



2.

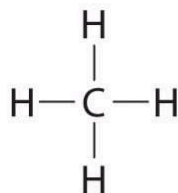
Two chlorines are bonded to a sulfur. The sulfur has 2 lone pairs while the chlorines have 3 lone pairs each.



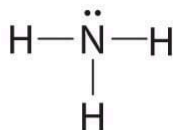
Sulfur dichloride

Using Lewis Electron Structures to Explain Stoichiometry

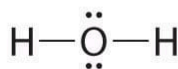
Lewis dot symbols provide a simple rationalization of why elements form compounds with the observed stoichiometries. In the Lewis model, the number of bonds formed by an element in a neutral compound is the same as the number of unpaired electrons it must share with other atoms to complete its octet of electrons. For the elements of [Group 17 \(the halogens\)](#), this number is one; for the elements of [Group 16 \(the chalcogens\)](#), it is two; for [Group 15 elements](#), three; and for [Group 14 elements](#) four. These requirements are illustrated by the following Lewis structures for the hydrides of the lightest members of each group:



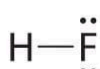
Group 14



Group 15

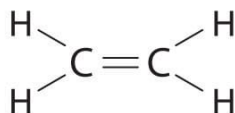


Group 16



Group 17

Elements may form multiple bonds to complete an octet. In ethylene, for example, each carbon contributes two electrons to the double bond, giving each carbon an octet (two electrons/bond $\times$ four bonds = eight electrons). Neutral structures with fewer or more bonds exist, but they are unusual and violate the octet rule.



Ethylene

Allotropes of an element can have very different physical and chemical properties because of different three-dimensional arrangements of the atoms; the number of bonds formed by the component atoms, however, is always the same. As noted at the beginning of the chapter, diamond is a hard, transparent solid; graphite is a soft, black solid; and the fullerenes have open cage structures. Despite these differences, the carbon atoms in all three allotropes form four bonds, in accordance with the octet rule.

Lewis structures explain why the elements of groups 14–17 form neutral compounds with four, three, two, and one bonded atom(s), respectively.

Elemental phosphorus also exists in three forms: white phosphorus, a toxic, waxy substance that initially glows and then spontaneously ignites on contact with air; red phosphorus, an amorphous substance that is used commercially in safety matches, fireworks, and smoke bombs; and black phosphorus, an unreactive crystalline solid with a texture similar to graphite (Figure 2.1.5.3). Nonetheless, the phosphorus atoms in all three forms obey the octet rule and form three bonds per phosphorus atom.

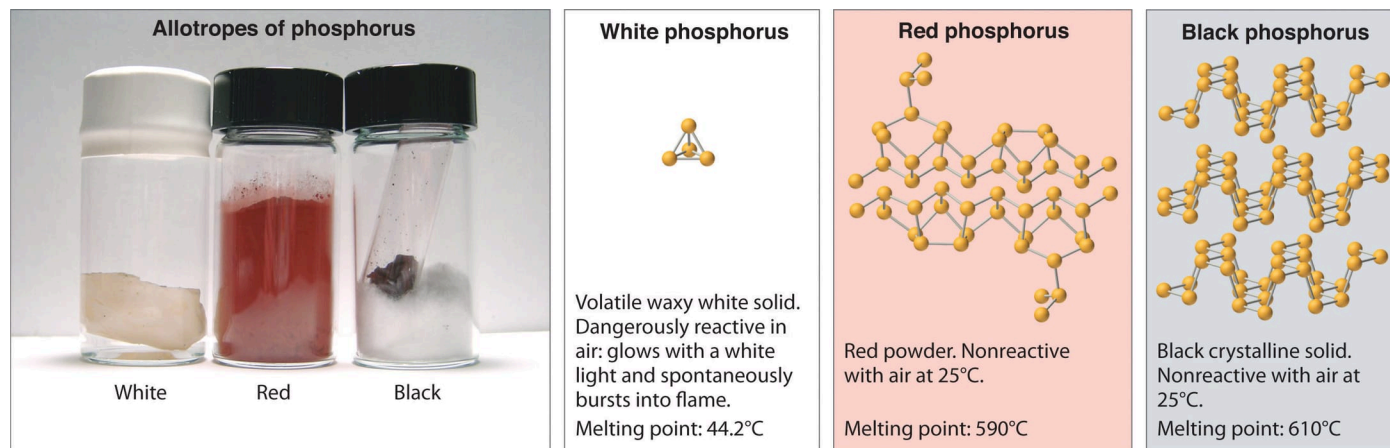


Figure 2.1.5.3: The Three Allotropes of Phosphorus: White, Red, and Black. All three forms contain only phosphorus atoms, but they differ in the arrangement and connectivity of their atoms. White phosphorus contains P₄ tetrahedra, red phosphorus is a network of linked P₈ and P₉ units, and black phosphorus forms sheets of six-membered rings. As a result, their physical and chemical properties differ dramatically.

Formal Charges

It is sometimes possible to write more than one Lewis structure for a substance that does not violate the octet rule, as we saw for CH₂O, but not every Lewis structure may be equally reasonable. In these situations, we can choose the most stable Lewis structure by considering the formal charge on the atoms, which is the difference between the number of valence electrons in the free atom and the number assigned to it in the Lewis electron structure. The formal charge is a way of computing the charge distribution within a Lewis structure; the sum of the formal charges on the atoms within a molecule or an ion must equal the overall charge on the molecule or ion. A formal charge does *not* represent a true charge on an atom in a covalent bond but is simply used to predict the most likely structure when a compound has more than one valid Lewis structure.

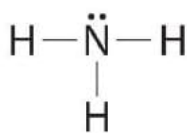
To calculate formal charges, we assign electrons in the molecule to individual atoms according to these rules:

- Nonbonding electrons are assigned to the atom on which they are located.
- Bonding electrons are divided equally between the bonded atoms.

For each atom, we then compute a formal charge:

$$\text{formal charge} = \underset{\text{(free atom)}}{\text{valence } e^-} - \left(\underset{\text{(atom in Lewis structure)}}{\text{non-bonding } e^-} + \frac{\text{bonding } e^-}{2} \right) \text{ (atom in Lewis structure)}$$

To illustrate this method, let's calculate the formal charge on the atoms in ammonia (NH₃) whose Lewis electron structure is as follows:



Ammonia

A neutral nitrogen atom has five valence electrons (it is in group 15). From its Lewis electron structure, the nitrogen atom in ammonia has one lone pair and shares three bonding pairs with hydrogen atoms, so nitrogen itself is assigned a total of five electrons [2 nonbonding e^- + (6 bonding e^- /2)]. Substituting into Equation 2.1.5.1, we obtain

$$\text{formal charge}(N) = 5 \text{ valence } e^- - \left(2 \text{ non-bonding } e^- + \frac{6 \text{ bonding } e^-}{2} \right) = 0 \quad (2.1.5.1)$$

A neutral hydrogen atom has one valence electron. Each hydrogen atom in the molecule shares one pair of bonding electrons and is therefore assigned one electron [0 nonbonding e^- + (2 bonding e^- /2)]. Using Equation 2.1.5.1 to calculate the formal charge on hydrogen, we obtain

$$\text{formal charge}(H) = 1 \text{ valence } e^- - \left(0 \text{ non-bonding } e^- + \frac{2 \text{ bonding } e^-}{2} \right) = 0 \quad (2.1.5.2)$$

The hydrogen atoms in ammonia have the same number of electrons as neutral hydrogen atoms, and so their formal charge is also zero. Adding together the formal charges should give us the overall charge on the molecule or ion. In this example, the nitrogen and each hydrogen has a formal charge of zero. When summed the overall charge is zero, which is consistent with the overall charge on the NH_3 molecule.

An atom, molecule, or ion has a formal charge of zero if it has the number of bonds that is typical for that species.

Typically, the structure with the most charges on the atoms closest to zero is the more stable Lewis structure. In cases where there are positive or negative formal charges on various atoms, stable structures generally have negative formal charges on the more electronegative atoms and positive formal charges on the less electronegative atoms. The next example further demonstrates how to calculate formal charges.

YouTube Video

This interactive element is not available in this format. Visit the link or scan the QR code to access it online.

[View this YouTube Video online](#)



Example 2.1.5.2: The Ammonium Ion

Calculate the formal charges on each atom in the NH_4^+ ion.

Given: chemical species

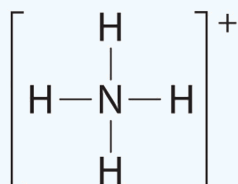
Asked for: formal charges

Strategy:

Identify the number of valence electrons in each atom in the NH_4^+ ion. Use the Lewis electron structure of NH_4^+ to identify the number of bonding and nonbonding electrons associated with each atom and then use Equation 2.1.5.1 to calculate the formal charge on each atom.

Solution:

The Lewis electron structure for the NH_4^+ ion is as follows:



The central nitrogen is bonded to four hydrogens. The molecule is surrounded by square brackets. Outside the bracket is where the positive charge is placed.

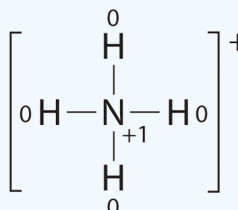
The nitrogen atom shares four bonding pairs of electrons, and a neutral nitrogen atom has five valence electrons. Using Equation ??, the formal charge on the nitrogen atom is therefore

$$\text{formal charge}(N) = 5 - \left(0 + \frac{8}{2} \right) = 0$$

Each hydrogen atom in has one bonding pair. The formal charge on each hydrogen atom is therefore

$$\text{formal charge}(H) = 1 - \left(0 + \frac{2}{2} \right) = 0$$

The formal charges on the atoms in the NH_4^+ ion are thus



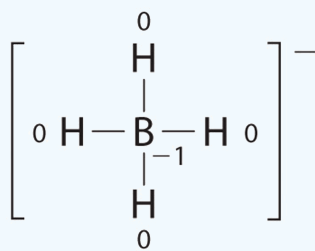
In the Lewis structure, each hydrogen has a zero placed nearby while the nitrogen has a +1 placed nearby.

Adding together the formal charges on the atoms should give us the total charge on the molecule or ion. In this case, the sum of the formal charges is $0 + 1 + 0 + 0 + 0 = +1$.

Exercise 2.1.5.2

Write the formal charges on all atoms in BH_4^- .

Answer



Four hydrogens are bonded to a central boron. Each hydrogen has a zero placed nearby while the boron has a -1. The molecule is surrounded by square brackets. Outside of the brackets is a negative charge.

If an atom in a molecule or ion has the number of bonds that is typical for that atom (e.g., four bonds for carbon), its formal charge is zero.

Using Formal Charges to Distinguish Viable Lewis Structures

This page titled [2.1.5: Drawing Lewis Structures](#) is shared under a [CC BY-NC-SA 4.0](#) license and was authored, remixed, and/or curated by LibreTexts.

- [8.5: Drawing Lewis Structures](#) is licensed [CC BY-NC-SA 3.0](#).

2.1.6: Resonance Structures

Learning Objectives

- To understand the concept of resonance.

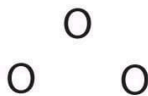
Resonance structures are a set of two or more Lewis Structures that collectively describe the electronic bonding of a single polyatomic species including fractional bonds and fractional charges. Resonance structures are capable of describing delocalized electrons that cannot be expressed by a single Lewis formula with an integral number of covalent bonds.

Sometimes one Lewis Structure is not Enough

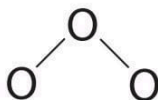
Sometimes, even when [formal charges](#) are considered, the bonding in some molecules or ions cannot be described by a single Lewis structure. Resonance is a way of describing delocalized electrons within certain molecules or polyatomic ions where the bonding cannot be expressed by a single Lewis formula. A molecule or ion with such delocalized electrons is represented by several contributing structures (also called resonance structures or canonical forms). Such is the case for [ozone](#) (O_3), an allotrope of oxygen with a V-shaped structure and an O–O–O angle of 117.5° .

Ozone (O_3)

1. We know that ozone has a V-shaped structure, so one O atom is central:

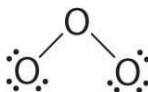


2. Each O atom has 6 valence electrons, for a total of 18 valence electrons.
3. Assigning one bonding pair of electrons to each oxygen–oxygen bond gives



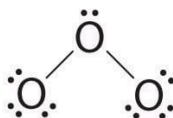
with 14 electrons left over.

4. If we place three lone pairs of electrons on each terminal oxygen, we obtain

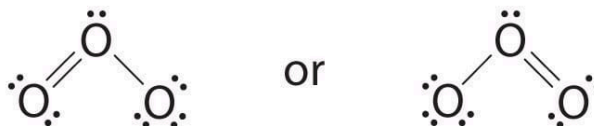


and have 2 electrons left over.

5. At this point, both terminal oxygen atoms have octets of electrons. We therefore place the last 2 electrons on the central atom:

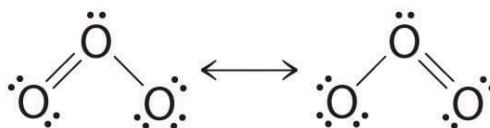


6. The central oxygen has only 6 electrons. We must convert one lone pair on a terminal oxygen atom to a bonding pair of electrons—but which one? Depending on which one we choose, we obtain either



Which is correct? In fact, neither is correct. Both predict one O–O single bond and one O=O double bond. As you will learn, if the bonds were of different types (one single and one double, for example), they would have different lengths. It turns out, however, that both O–O bond distances are identical, 127.2 pm, which is shorter than a typical O–O single bond (148 pm) and longer than the O=O double bond in O₂ (120.7 pm).

Equivalent Lewis dot structures, such as those of ozone, are called **resonance structures**. The position of the *atoms* is the same in the various resonance structures of a compound, but the position of the *electrons* is different. Double-headed arrows link the different resonance structures of a compound:



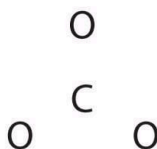
The double-headed arrow indicates that the actual electronic structure is an *average* of those shown, not that the molecule oscillates between the two structures.

When it is possible to write more than one equivalent resonance structure for a molecule or ion, the actual structure is the average of the resonance structures.

The Carbonate (CO_3^{2-}) Ion

Like ozone, the electronic structure of the carbonate ion cannot be described by a single Lewis electron structure. Unlike O₃, though, the actual structure of CO_3^{2-} is an average of *three* resonance structures.

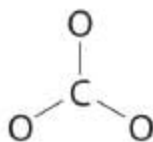
1. Because carbon is the least electronegative element, we place it in the central position:



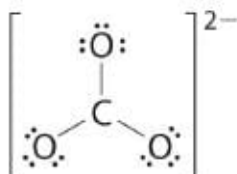
The three oxygens are drawn in the shape of a triangle with the carbon at the center of the triangle.

2. Carbon has 4 valence electrons, each oxygen has 6 valence electrons, and there are 2 more for the -2 charge. This gives $4 + (3 \times 6) + 2 = 24$ valence electrons.

3. Six electrons are used to form three bonding pairs between the oxygen atoms and the carbon:



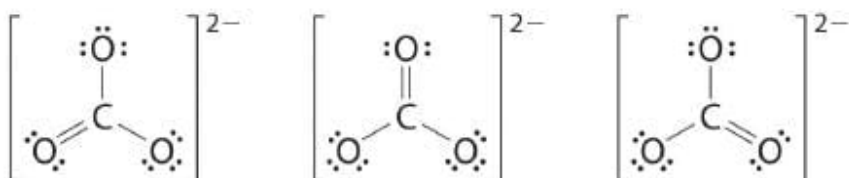
4. We divide the remaining 18 electrons equally among the three oxygen atoms by placing three lone pairs on each and indicating the -2 charge:



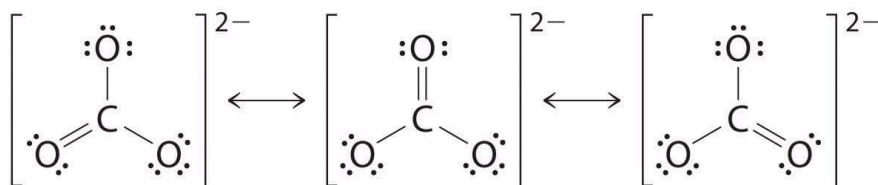
The Lewis dot structure has a central carbon that is bonded to 3 oxygens. Each oxygen has 3 lone pairs. The molecule is inside square brackets and has a charge of minus 2.

5. No electrons are left for the central atom.

6. At this point, the carbon atom has only 6 valence electrons, so we must take one lone pair from an oxygen and use it to form a carbon-oxygen double bond. In this case, however, there are *three* possible choices:



As with ozone, none of these structures describes the bonding exactly. Each predicts one carbon-oxygen double bond and two carbon-oxygen single bonds, but experimentally all C-O bond lengths are identical. We can write resonance structures (in this case, three of them) for the carbonate ion:



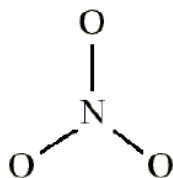
The resonance structure includes all three Lewis dot structures with double headed arrows between them.

The actual structure is an average of these three resonance structures.

The Nitrate (NO_3^-) ion

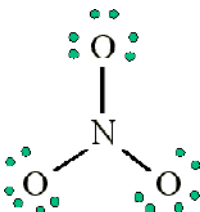
1. Count up the valence electrons: $(1 \times 5) + (3 \times 6) + 1(\text{ion}) = \mathbf{24}$ electrons

2. Draw the bond connectivities:

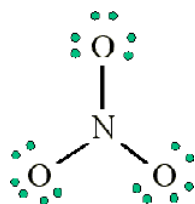


The three oxygens are drawn in the shape of a triangle with the nitrogen at the center of the triangle.

3. Add octet electrons to the atoms bonded to the center atom:

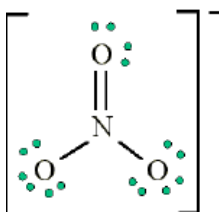


4. Place any leftover electrons (24-24 = 0) on the center atom:



5. Does the central atom have an octet?

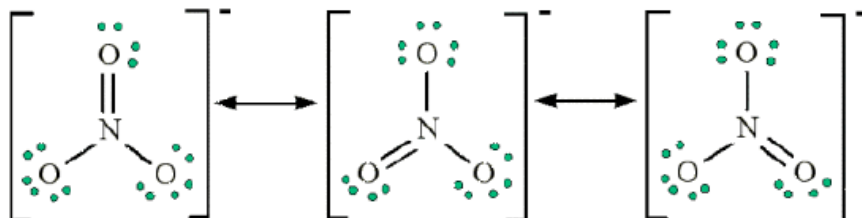
- **NO**, it has 6 electrons
- Add a multiple bond (first try a double bond) to see if the central atom can achieve an octet:



A double bond is added between one oxygen and the central nitrogen. The molecule has a negative charge.

6. Does the central atom have an octet?

- YES
- Are there possible resonance structures? YES



Note: We would expect that the bond lengths in the NO_3^- ion to be somewhat shorter than a single bond.

YouTube Video

This interactive element is not available in this format. Visit the link or scan the QR code to access it online.

[View this YouTube Video online](#)



Example 2.1.6.1: Benzene

Benzene is a common organic solvent that was previously used in gasoline; it is no longer used for this purpose, however, because it is now known to be a carcinogen. The benzene molecule (C_6H_6) consists of a regular hexagon of carbon atoms, each of which is also bonded to a hydrogen atom. Use resonance structures to describe the bonding in benzene.

Given: molecular formula and molecular geometry

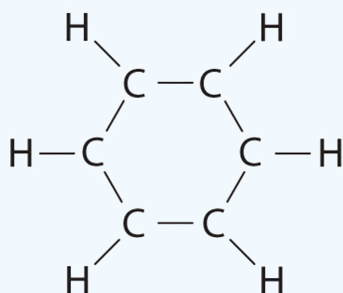
Asked for: resonance structures

Strategy:

- Draw a structure for benzene illustrating the bonded atoms. Then calculate the number of valence electrons used in this drawing.
- Subtract this number from the total number of valence electrons in benzene and then locate the remaining electrons such that each atom in the structure reaches an octet.
- Draw the resonance structures for benzene.

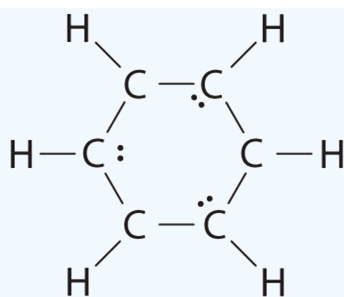
Solution:

A Each hydrogen atom contributes 1 valence electron, and each carbon atom contributes 4 valence electrons, for a total of $(6 \times 1) + (6 \times 4) = 30$ valence electrons. If we place a single bonding electron pair between each pair of carbon atoms and between each carbon and a hydrogen atom, we obtain the following:



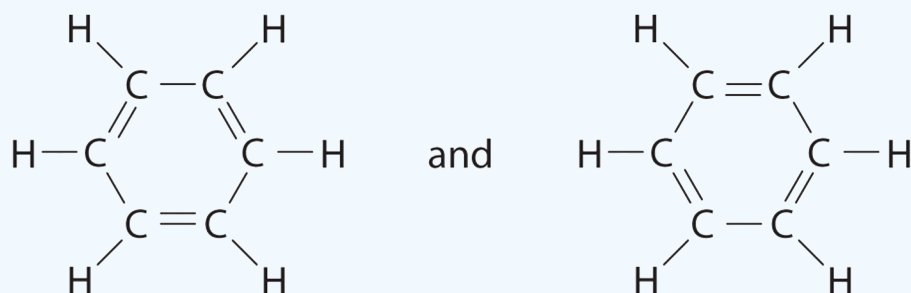
Each carbon atom in this structure has only 6 electrons and has a formal charge of +1, but we have used only 24 of the 30 valence electrons.

B If the 6 remaining electrons are uniformly distributed pairwise on alternate carbon atoms, we obtain the following:

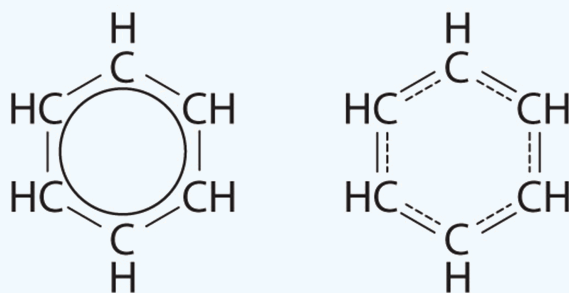


Three carbon atoms now have an octet configuration and a formal charge of -1 , while three carbon atoms have only 6 electrons and a formal charge of $+1$. We can convert each lone pair to a bonding electron pair, which gives each atom an octet of electrons and a formal charge of 0, by making three C=C double bonds.

There are, however, two ways to do this:



Each structure has alternating double and single bonds, but experimentation shows that each carbon-carbon bond in benzene is identical, with bond lengths (139.9 pm) intermediate between those typically found for a C-C single bond (154 pm) and a C=C double bond (134 pm). We can describe the bonding in benzene using the two resonance structures, but the actual electronic structure is an average of the two. The existence of multiple resonance structures for aromatic hydrocarbons like benzene is often indicated by drawing either a circle or dashed lines inside the hexagon:



Benzene

Exercise 2.1.6.1: Nitrite Ion

The sodium salt of nitrite is used to relieve muscle spasms. Draw two resonance structures for the nitrite ion (NO_2^-).

Warning

If several reasonable resonance forms for a molecule exists, the "actual electronic structure" of the molecule will probably be intermediate between all the forms that you can draw. The classic example is benzene in Example 2.1.6.1. One would expect the double bonds to be shorter than the single bonds, but if one overlays the two structures, you see that one structure has a single bond where the other structure has a double bond. The best measurements that we can make of benzene do not show two bond lengths - instead, they show that the bond length is intermediate between the two resonance structures.

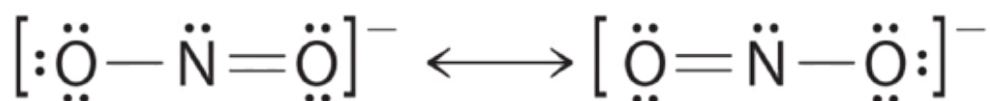
Resonance structures is a mechanism that allows us to use all of the possible resonance structures to try to predict what the actual form of the molecule would be. Single bonds, double bonds, triple bonds, +1 charges, -1 charges, these are our limitations in explaining the structures, and the true forms can be in between - a carbon-carbon bond could be mostly single bond with a little bit of double bond character and a partial negative charge, for example.

Summary

Some molecules have two or more chemically equivalent Lewis electron structures, called resonance structures. Resonance is a mental exercise and method within the [Valence Bond Theory](#) of bonding that describes the delocalization of electrons within molecules. These structures are written with a **double-headed arrow** between them, indicating that none of the Lewis structures accurately describes the bonding but that the actual structure is an average of the individual resonance structures. Resonance structures are used when one Lewis structure for a single molecule cannot fully describe the bonding that takes place between neighboring atoms relative to the empirical data for the actual bond lengths between those atoms. The net sum of valid resonance structures is defined as a resonance hybrid, which represents the overall delocalization of electrons within the molecule. A molecule that has several resonance structures is more stable than one with fewer. Some resonance structures are more favorable than others.

Answers

Exercise 2.1.6.1: Nitrite Ion



There is a double bond between one oxygen and the nitrogen, It can be found on the left oxygen or the right oxygen.

Resonance structures are particularly common in oxoanions of the *p*-block elements, such as sulfate and phosphate, and in aromatic hydrocarbons, such as benzene and naphthalene.

2.1.7: Exceptions to the Octet Rule

Learning Objectives

- To assign a Lewis dot symbol to elements not having an octet of electrons in their compounds.

Three cases can be constructed that do not follow the octet rule, and as such, they are known as the exceptions to the octet rule. Following the Octet Rule for Lewis Dot Structures leads to the most accurate depictions of stable molecular and atomic structures and because of this we always want to use the octet rule when drawing Lewis Dot Structures. However, it is hard to imagine that one rule could be followed by all molecules. There is always an exception, and in this case, three exceptions:

1. When there are an odd number of valence electrons
2. When there are too few valence electrons
3. When there are too many valence electrons

Exception 1: Species with Odd Numbers of Electrons

The first exception to the Octet Rule is when there are an odd number of valence electrons. An example of this would be Nitrogen (II) Oxide also called nitric oxide (NO). Nitrogen has 5 valence electrons while Oxygen has 6. The total would be 11 valence electrons to be used. The Octet Rule for this molecule is fulfilled in the above example, however that is with 10 valence electrons. The last one does not know where to go. The lone electron is called an unpaired electron. But where should the unpaired electron go? The unpaired electron is usually placed in the Lewis Dot Structure so that each element in the structure will have the *lowest formal charge* possible. The formal charge is *the perceived charge on an individual atom in a molecule when atoms do not contribute equal numbers of electrons to the bonds they participate in*.

No formal charge at all is the most ideal situation. An example of a stable molecule with an odd number of valence electrons would be nitric oxide. nitric oxide has 11 valence electrons. If you need more information about formal charges, see Lewis Structures. If we were to imagine nitric oxide had ten valence electrons we would come up with the Lewis Structure (Figure 2.1.7.1):

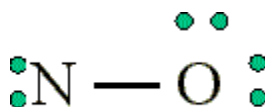


Figure 2.1.7.1: This is if nitric oxide has only ten valence electrons, which it does not.

Let's look at the formal charges of Figure 2.1.7.2 based on this Lewis structure. Nitrogen normally has five valence electrons. In Figure 2.1.7.1, it has two lone pair electrons and it participates in two bonds (a double bond) with oxygen. This results in nitrogen having a formal charge of +1. Oxygen normally has six valence electrons. In Figure 2.1.7.1, oxygen has four lone pair electrons and it participates in two bonds with nitrogen. Oxygen therefore has a formal charge of 0. The overall molecule here has a formal charge of +1 (+1 for nitrogen, 0 for oxygen. +1 + 0 = +1). However, if we add the eleventh electron to nitrogen (because we want the molecule to have the *lowest* total formal charge), it will bring both the nitrogen and the molecule's overall charges to zero, the most ideal formal charge situation. That is exactly what is done to get the correct Lewis structure for nitric oxide (Figure 2.1.7.2):

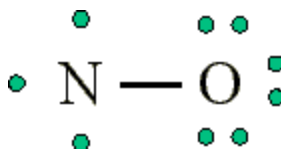


Figure 2.1.7.2: The proper Lewis structure for NO molecule

Free Radicals

There are actually very few stable molecules with odd numbers of electrons that exist, since that unpaired electron is willing to react with other unpaired electrons. Most odd electron species are highly reactive, which we call Free Radicals. Because of their instability, free radicals bond to atoms in which they can take an electron from in order to become stable, making them very chemically reactive. Radicals are found as both reactants and products, but generally react to form more stable molecules as soon as they can. In order to emphasize the existence of the unpaired electron, radicals are denoted with a dot in front of their chemical symbol as with $\cdot OH$, the hydroxyl radical. An example of a radical you may be familiar with already is the gaseous chlorine atom, denoted $\cdot Cl$. Interestingly, an odd Number of Valence Electrons will result in the molecule being paramagnetic.

Exception 2: Incomplete Octets

The second exception to the Octet Rule is when there are too few valence electrons that results in an incomplete Octet. There are even more occasions where the octet rule does not give the most correct depiction of a molecule or ion. This is also the case with incomplete octets. Species with incomplete octets are pretty rare and generally are only found in some beryllium, aluminum, and boron compounds including the boron hydrides. Let's take a look at one such hydride, BH_3 (Borane).

If one were to make a Lewis structure for BH_3 following the basic strategies for drawing Lewis structures, one would probably come up with this structure (Figure 2.1.7.2):

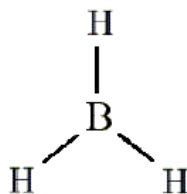


Figure 2.1.7.3: The structure of BH_3 is square planar.

The problem with this structure is that boron has an incomplete octet; it only has six electrons around it. Hydrogen atoms can naturally only have only 2 electrons in their outermost shell (their version of an octet), and as such there are no spare electrons to form a double bond with boron. One might surmise that the failure of this structure to form complete octets must mean that this bond should be ionic instead of covalent. However, boron has an electronegativity that is very similar to hydrogen, meaning there is likely very little ionic character in the hydrogen to boron bonds, and as such this Lewis structure, though it does not fulfill the octet rule, is likely the best structure possible for depicting BH_3 with Lewis theory. One of the things that may account for BH_3 's incomplete octet is that it is commonly a transitory species, formed temporarily in reactions that involve multiple steps.

Let's take a look at another incomplete octet situation dealing with boron, BF_3 (Boron trifluorine). Like with BH_3 , the initial drawing of a Lewis structure of BF_3 will form a structure where boron has only six electrons around it (Figure 2.1.7.4).

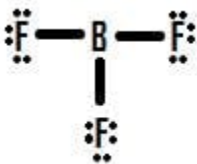


Figure 2.1.7.4

If you look Figure 2.1.7.4, you can see that the fluorine atoms possess extra lone pairs that they can use to make additional bonds with boron, and you might think that all you have to do is make one lone pair into a bond and the structure will be correct. If we add one double bond between boron and one of the fluorines we get the following Lewis Structure (Figure 2.1.7.5):

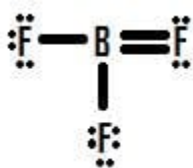


Figure 2.1.7.5

Each fluorine has eight electrons, and the boron atom has eight as well! Each atom has a perfect octet, right? Not so fast. We must examine the formal charges of this structure. The fluorine that shares a double bond with boron has six electrons around it (four from its two lone pairs of electrons and one each from its two bonds with boron). This is one less electron than the number of valence electrons it would have naturally (Group Seven elements have seven valence electrons), so it has a formal charge of +1. The two fluorines that share single bonds with boron have seven electrons around them (six from their three lone pairs and one from their single bonds with boron). This is the same amount as the number of valence electrons they would have on their own, so they both have a formal charge of zero. Finally, boron has four electrons around it (one from each of its four bonds shared with fluorine). This is one more electron than the number of valence electrons that boron would have on its own, and as such boron has a formal charge of -1.

This structure is supported by the fact that the experimentally determined bond length of the boron to fluorine bonds in BF_3 is less than what would be typical for a single bond (see [Bond Order and Lengths](#)). However, this structure contradicts one of the major rules of formal charges: Negative formal charges are supposed to be found on the more electronegative atom(s) in a bond, but in the structure depicted in Figure 2.1.7.5, a *positive* formal charge is found on fluorine, which not only is the most electronegative element in the structure, but the most electronegative element in the entire periodic table ($\chi = 4.0$). Boron on the other hand, with the much lower electronegativity of 2.0, has the negative formal charge in this structure. This formal charge-electronegativity disagreement makes this double-bonded structure impossible.

However the large electronegativity difference here, as opposed to in BH_3 , signifies significant polar bonds between boron and fluorine, which means there is a high ionic character to this molecule. This suggests the possibility of a semi-ionic structure such as seen in Figure 2.1.7.6:

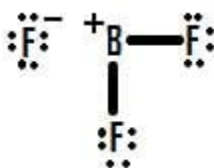


Figure 2.1.7.6

A bond is broken between one of the fluorine's and the boron making the free fluorine negatively charged and the boron positively charged.

None of these three structures is the "correct" structure in this instance. The most "correct" structure is most likely a [resonance](#) of all three structures: the one with the incomplete octet (Figure 2.1.7.4), the one with the double bond (Figure 2.1.7.5), and the one with the ionic bond (Figure 2.1.7.6). The most contributing structure is probably the incomplete octet structure (due to Figure 2.1.7.5 being basically impossible and Figure 2.1.7.6 not matching up with the behavior and properties of BF_3). As you can see even when other possibilities exist, incomplete octets may best portray a molecular structure.

As a side note, it is important to note that BF_3 frequently bonds with a F^- ion in order to form BF_4^- rather than staying as BF_3 . This structure completes boron's octet and it is more common in nature. This exemplifies the fact that incomplete octets are rare, and other configurations are typically more favorable, including bonding with additional ions as in the case of BF_3 .

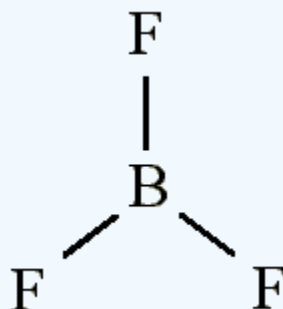
Example 2.1.7.1: NF_3

Draw the Lewis structure for boron trifluoride (BF_3).

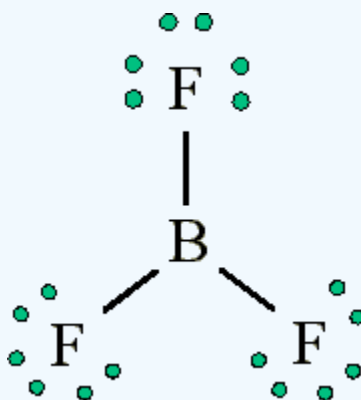
Solution

1. Add electrons $(3 \times 7) + 3 = 24$

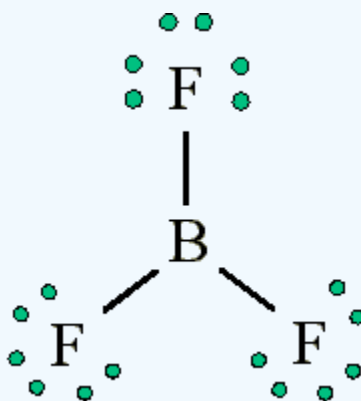
2. Draw connectivities:



3. Add octets to outer atoms:

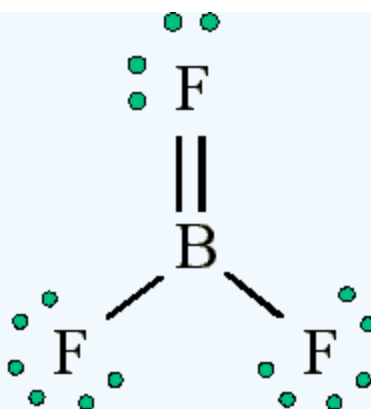


4. Add extra electrons $(24 - 24 = 0)$ to central atom:



5. Does central electron have octet?

- NO. It has 6 electrons
- Add a multiple bond (double bond) to see if central atom can achieve an octet:

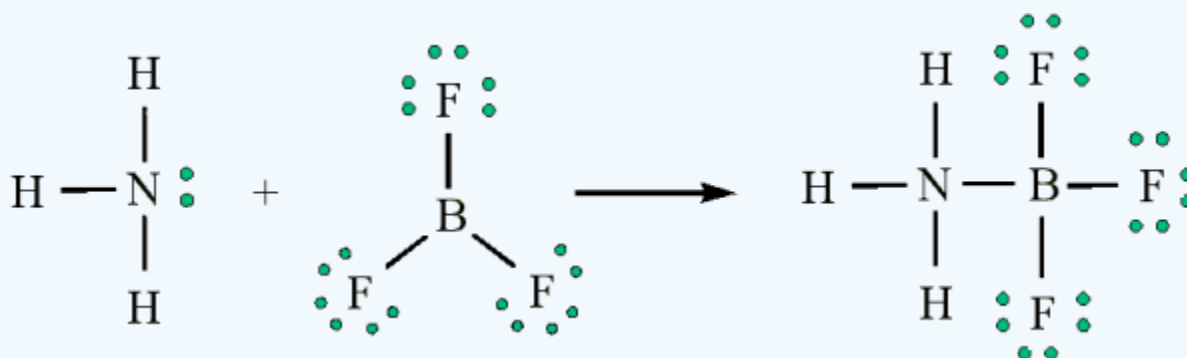


6. The central Boron now has an octet (there would be three resonance Lewis structures)

However...

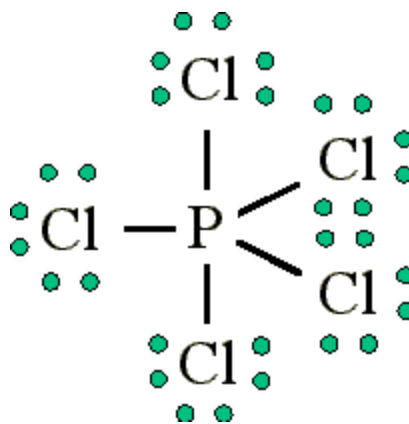
- In this structure with a double bond the fluorine atom is sharing extra electrons with the boron.
- The fluorine would have a '+' partial charge, and the boron a '-' partial charge, this is inconsistent with the electronegativities of fluorine and boron.
- Thus, **the structure of BF_3 , with single bonds, and 6 valence electrons around the central boron is the most likely structure**

BF_3 reacts strongly with compounds which have an unshared pair of electrons which can be used to form a bond with the boron:



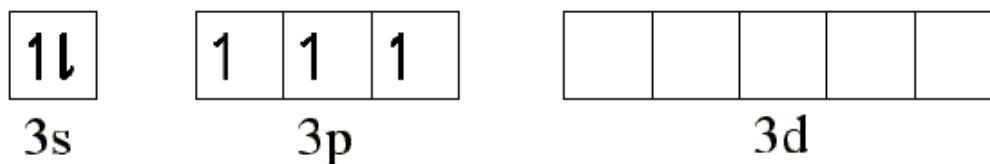
Exception 3: Expanded Valence Shells

More common than incomplete octets are expanded octets where the central atom in a Lewis structure has more than eight electrons in its valence shell. In expanded octets, the central atom can have ten electrons, or even twelve. *Molecules with expanded octets involve highly electronegative terminal atoms, and a nonmetal central atom found in the third period or below, which those terminal atoms bond to.* For example, PCl_5 is a legitimate compound (whereas NCl_5) is not:



Expanded valence shells are observed **only** for elements in period 3 (i.e. $n=3$) and beyond

The 'octet' rule is based upon available ns and np orbitals for valence electrons (2 electrons in the s orbitals, and 6 in the p orbitals). Beginning with the $n=3$ principle quantum number, the d orbitals become available ($l=2$). The orbital diagram for the valence shell of phosphorous is:



Hence, the third period elements occasionally exceed the octet rule by using their empty d orbitals to accommodate additional electrons. Size is also an important consideration:

- The larger the central atom, the larger the number of electrons which can surround it
- Expanded valence shells occur most often when the central atom is bonded to small electronegative atoms, such as F, Cl and O.

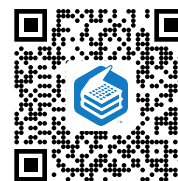
There is currently much scientific exploration and inquiry into the reason why expanded valence shells are found. The top area of interest is figuring out where the extra pair(s) of electrons are found. Many chemists think that there is not a very large energy difference between the $3p$ and $3d$ orbitals, and as such it is plausible for extra electrons to easily fill the $3d$ orbital when an expanded octet is more favorable than having a complete octet. This matter is still under hot debate, however and there is even debate as to what makes an expanded octet more favorable than a configuration that follows the octet rule.

One of the situations where expanded octet structures are treated as more favorable than Lewis structures that follow the octet rule is when the formal charges in the expanded octet structure are smaller than in a structure that adheres to the octet rule, or when there are less formal charges in the expanded octet than in the structure a structure that adheres to the octet rule.

YouTube Video

This interactive element is not available in this format. Visit the link or scan the QR code to access it online.

[View this YouTube Video online](#)



Example 2.1.7.2: The SO_4^{2-} ion

Such is the case for the sulfate ion, SO_4^{2-} . A strict adherence to the octet rule forms the following Lewis structure:

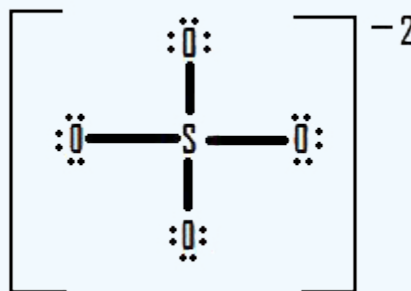


Figure 2.1.7.12

Four oxygens are bonded to a central sulfur. Each oxygen has 3 lone pairs. The molecule has a minus 2 charge.

If we look at the formal charges on this molecule, we can see that all of the oxygen atoms have seven electrons around them (six from the three lone pairs and one from the bond with sulfur). This is one more electron than the number of valence electrons then they would have normally, and as such each of the oxygens in this structure has a formal charge of -1. Sulfur has four electrons around it in this structure (one from each of its four bonds) which is two electrons more than the number of valence electrons it would have normally, and as such it carries a formal charge of +2.

If instead we made a structure for the sulfate ion with an expanded octet, it would look like this:

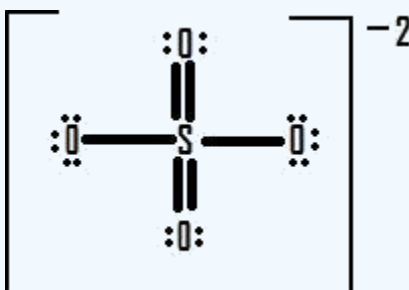


Figure 2.1.7.13

Looking at the formal charges for this structure, the sulfur ion has six electrons around it (one from each of its bonds). This is the same amount as the number of valence electrons it would have naturally. This leaves sulfur with a formal charge of zero. The two oxygens that have double bonds to sulfur have six electrons each around them (four from the two lone pairs and one each from the two bonds with sulfur). This is the same amount of electrons as the number of valence electrons that oxygen atoms have on their own, and as such both of these oxygen atoms have a formal charge of zero. The two oxygens with the single bonds to sulfur have seven electrons around them in this structure (six from the three lone pairs and one from the bond to sulfur). That is one electron more than the number of valence electrons that oxygen would have on its own, and as such those two oxygens carry a formal charge of -1. Remember that with formal charges, the goal is to keep the formal charges

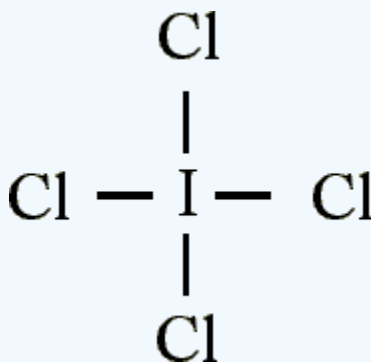
(or the difference between the formal charges of each atom) as small as possible. The number of and values of the formal charges on this structure (-1 and 0 (difference of 1) in Figure 2.1.7.12, as opposed to +2 and -1 (difference of 3) in Figure 2.1.7.12) is significantly lower than on the structure that follows the octet rule, and as such an expanded octet is plausible, and even preferred to a normal octet, in this case.

Example 2.1.7.3: The ICl_4^- Ion

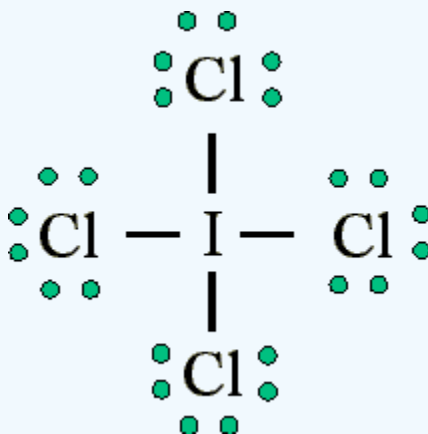
Draw the Lewis structure for ICl_4^- ion.

Solution

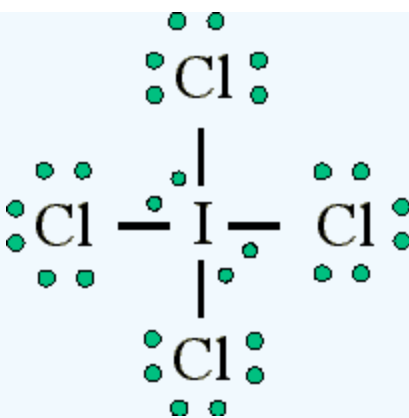
1. Count up the valence electrons: $7 + (4 \times 7) + 1 = 36$ electrons
2. Draw the connectivities:



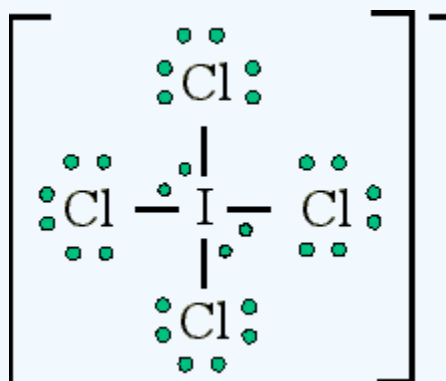
3. Add octet of electrons to outer atoms:



4. Add extra electrons ($36 - 32 = 4$) to central atom:



5. The ICl_4^- ion thus has 12 valence electrons around the central Iodine (in the $5d$ orbitals)



Expanded Lewis structures are also plausible depictions of molecules when experimentally determined bond lengths suggest partial double bond characters even when single bonds would already fully fill the octet of the central atom. Despite the cases for expanded octets, as mentioned for incomplete octets, it is important to keep in mind that, in general, the octet rule applies.

Summary

Following the Octet Rule for Lewis Dot Structures leads to the most accurate depictions of stable molecular and atomic structures and because of this we always want to use the octet rule when drawing Lewis Dot Structures. There are three exceptions: (1) When there are an odd number of valence electrons, (2) When there are too few valence electrons, and (3) when there are too many valence electrons

References

1. Petrucci, Ralph H.; Harwood, William S.; Herring, F. G.; Madura, Jeffrey D. General Chemistry: Principles & Modern Applications. 9th Ed. New Jersey. Pearson Education, Inc. 2007.
2. Moore, John W.; Stanitski, Conrad L.; Jurs, Peter C. Chemistry: The Molecular Science. 2nd Ed. 2004.

Contributors and Attributions

- Mike Blaber (Florida State University)

This page titled [2.1.7: Exceptions to the Octet Rule](#) is shared under a [CC BY-NC-SA 4.0](#) license and was authored, remixed, and/or curated by LibreTexts.

- [8.7: Exceptions to the Octet Rule](#) is licensed [CC BY-NC-SA 3.0](#).

2.1.8: Strength of Covalent Bonds

Learning Objectives

- The define Bond-dissociation energy (bond energy)
- To correlate bond strength with bond length
- To define and used *average bond energies*

In proposing his theory that octets can be completed by two atoms sharing electron pairs, Lewis provided scientists with the first description of covalent bonding. In this section, we expand on this and describe some of the properties of covalent bonds. The stability of a molecule is a function of the strength of the covalent bonds holding the atoms together.

The Relationship between Bond Order and Bond Energy

Triple bonds between like atoms are shorter than double bonds, and because more energy is required to completely break all three bonds than to completely break two, a triple bond is also stronger than a double bond. Similarly, double bonds between like atoms are stronger and shorter than single bonds. Bonds of the same order between *different* atoms show a wide range of bond energies, however. Table 2.1.8.1 lists the average values for some commonly encountered bonds. Although the values shown vary widely, we can observe four trends:

Table 2.1.8.1: Average Bond Energies (kJ/mol) for Commonly Encountered Bonds at 273 K

Single Bonds								Multiple Bonds			
H-H	432	C-C	346	N-N	≈167	O-O	≈142	F-F	155	C=C	602
H-C	411	C-Si	318	N-O	201	O-F	190	F-Cl	249	C≡C	835
H-Si	318	C-N	305	N-F	283	O-Cl	218	F-Br	249	C=N	615
H-N	386	C-O	358	N-Cl	313	O-Br	201	F-I	278	C≡N	887
H-P	≈322	C-S	272	N-Br	243	O-I	201	Cl-Cl	240	C=O	749
H-O	459	C-F	485	P-P	201	S-S	226	Cl-Br	216	C≡O	1072
H-S	363	C-Cl	327			S-F	284	Cl-I	208	N=N	418
H-F	565	C-Br	285			S-Cl	255	Br-Br	190	N≡N	942
H-Cl	428	C-I	213			S-Br	218	Br-I	175	N=O	607
H-Br	362	Si-Si	222					I-I	149	O=O	494
H-I	295	Si-O	452							S=O	532

Source: Data from J. E. Huheey, E. A. Keiter, and R. L. Keiter, *Inorganic Chemistry*, 4th ed. (1993).

1. Bonds between hydrogen and atoms in the same column of the periodic table decrease in strength as we go down the column. Thus an H-F bond is stronger than an H-I bond, H-C is stronger than H-Si, H-N is stronger than H-P, H-O is stronger than H-S, and so forth. The reason for this is that the region of space in which electrons are shared between two atoms becomes proportionally smaller as one of the atoms becomes larger (part (a) in Figure 8.11).
2. Bonds between like atoms usually become *weaker* as we go down a column (important exceptions are noted later). For example, the C-C single bond is stronger than the Si-Si single bond, which is stronger than the Ge-Ge bond, and so forth. As two bonded atoms become larger, the region between them occupied by bonding electrons becomes *proportionally* smaller, as illustrated in part (b) in Figure 8.11. Noteworthy exceptions are single bonds between the period 2 atoms of groups 15, 16, and 17 (i.e., N, O, F), which are unusually weak compared with single bonds between their larger congeners. It is likely that the N-N, O-O, and F-F single bonds are weaker than might be expected due to strong repulsive interactions between lone pairs of electrons on *adjacent* atoms. The trend in bond energies for the halogens is therefore



Similar effects are also seen for the O–O versus S–S and for N–N versus P–P single bonds.

Bonds between hydrogen and atoms in a given column in the periodic table are weaker down the column; bonds between like atoms usually become weaker down a column.

3. Because elements in periods 3 and 4 rarely form multiple bonds with themselves, their multiple bond energies are not accurately known. Nonetheless, they are presumed to be significantly weaker than multiple bonds between lighter atoms of the same families. Compounds containing an Si=Si double bond, for example, have only recently been prepared, whereas compounds containing C=C double bonds are one of the best-studied and most important classes of organic compounds.

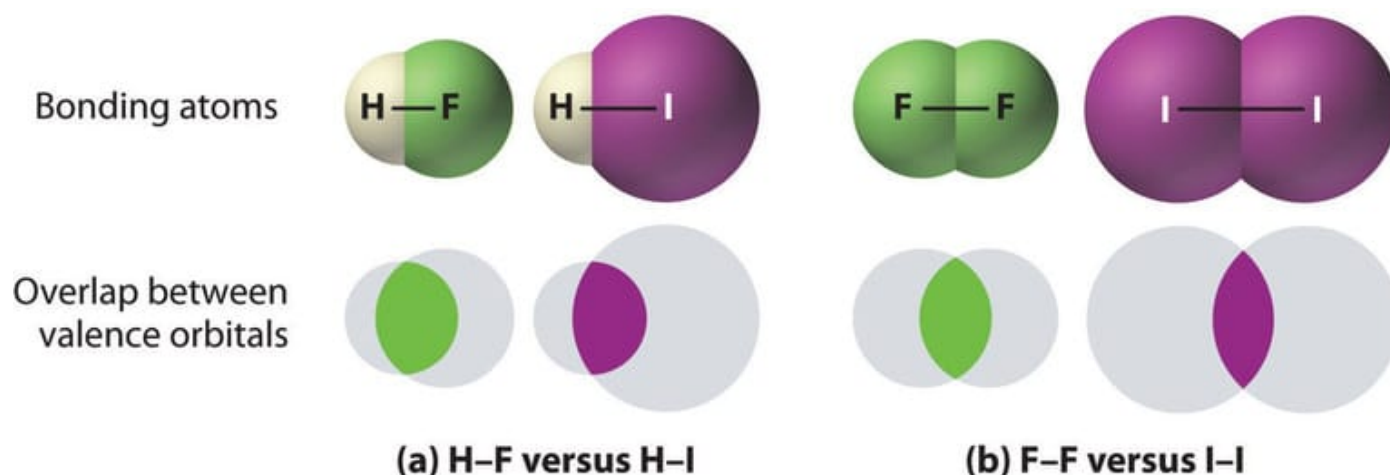


Figure 2.1.8.1: The Strength of Covalent Bonds Depends on the Overlap between the Valence Orbitals of the Bonded Atoms. The relative sizes of the region of space in which electrons are shared between (a) a hydrogen atom and lighter (smaller) vs. heavier (larger) atoms in the same periodic group; and (b) two lighter versus two heavier atoms in the same group. Although the absolute amount of shared space increases in both cases on going from a light to a heavy atom, the amount of space *relative to the size of the bonded atom* decreases; that is, the *percentage* of total orbital volume decreases with increasing size. Hence the strength of the bond decreases.

4. Multiple bonds between carbon, oxygen, or nitrogen and a period 3 element such as phosphorus or sulfur tend to be unusually strong. In fact, multiple bonds of this type dominate the chemistry of the period 3 elements of [groups 15](#) and [16](#). Multiple bonds to phosphorus or sulfur occur as a result of *d*-orbital interactions, as we discussed for the SO_4^{2-} ion in Section 8.6. In contrast, silicon in group 14 has little tendency to form discrete silicon–oxygen double bonds. Consequently, SiO_2 has a three-dimensional network structure in which each silicon atom forms four Si–O single bonds, which makes the physical and chemical properties of SiO_2 very different from those of CO_2 .

Bond strengths increase as bond order **increases**, while bond distances **decrease**.

The Relationship between Molecular Structure and Bond Energy

Bond energy is defined as the energy required to break a particular bond in a molecule in the gas phase. Its value depends on not only the identity of the bonded atoms but also their environment. Thus the bond energy of a C–H single bond is *not* the same in all organic compounds. For example, the energy required to break a C–H bond in methane varies by as much as 25% depending on how many other bonds in the molecule have already been broken (Table 2.1.8.2); that is, the C–H bond energy depends on its molecular environment. Except for diatomic molecules, the bond energies listed in Table 2.1.8.1 are *average* values for all bonds of a given type in a range of molecules. Even so, they are not likely to differ from the actual value of a given bond by more than about 10%.

Table 2.1.8.2: *Energies for the Dissociation of Successive C–H Bonds in Methane. Source: Data from [CRC Handbook of Chemistry and Physics](#) (2004).*

Reaction	D (kJ/mol)
$\text{CH}_4(\text{g}) \rightarrow \text{CH}_3(\text{g}) + \text{H}(\text{g})$	439

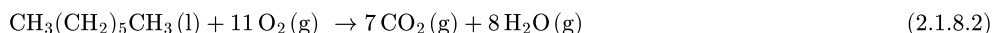
Reaction	D (kJ/mol)
$\text{CH}_3(\text{g}) \rightarrow \text{CH}_2(\text{g}) + \text{H}(\text{g})$	462
$\text{CH}_2(\text{g}) \rightarrow \text{CH}(\text{g}) + \text{H}(\text{g})$	424
$\text{CH}(\text{g}) \rightarrow \text{C}(\text{g}) + \text{H}(\text{g})$	338

We can estimate the enthalpy change for a chemical reaction by adding together the average energies of the bonds broken in the reactants and the average energies of the bonds formed in the products and then calculating the difference between the two. If the bonds formed in the products are stronger than those broken in the reactants, then energy will be released in the reaction ($\Delta H_{\text{rxn}} < 0$):

$$\Delta H_{\text{rxn}} \approx \sum (\text{bond energies of bonds broken}) - \sum (\text{bond energies of bonds formed}) \quad (2.1.8.1)$$

The $\approx$ sign is used because we are adding together *average* bond energies; hence this approach does not give exact values for ΔH_{rxn} .

Let's consider the reaction of 1 mol of *n*-heptane (C_7H_{16}) with oxygen gas to give carbon dioxide and water. This is one reaction that occurs during the combustion of gasoline:



In this reaction, 6 C–C bonds, 16 C–H bonds, and 11 O=O bonds are broken per mole of *n*-heptane, while 14 C=O bonds (two for each CO_2) and 16 O–H bonds (two for each H_2O) are formed. The energy changes can be tabulated as follows:

Bonds Broken (kJ/mol) and Bonds Formed (kJ/mol)

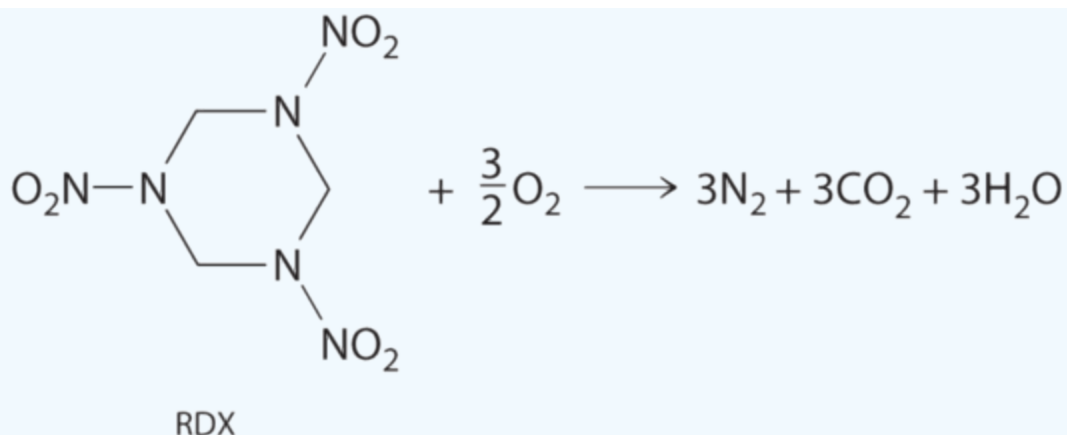
Bonds Broken (kJ/mol)		Bonds Formed (kJ/mol)	
6 C–C	$346 \times 6 = 2076$	14 C=O	$799 \times 14 = 11,186$
16 C–H	$411 \times 16 = 6576$	16 O–H	$459 \times 16 = 7344$
11 O=O	$494 \times 11 = 5434$		Total = 18,530
	Total = 14,086		

The bonds in the products are stronger than the bonds in the reactants by about 4444 kJ/mol. This means that ΔH_{rxn} is approximately –4444 kJ/mol, and the reaction is highly exothermic (which is not too surprising for a combustion reaction).

If we compare this approximation with the value obtained from measured ΔH_f° values ($\Delta H_{\text{rxn}} = -4817 \text{ kJ/mol}$), we find a discrepancy of only about 8%, less than the 10% typically encountered. Chemists find this method useful for calculating approximate enthalpies of reaction for molecules whose actual ΔH_f° values are unknown. These approximations can be important for predicting whether a reaction is **exothermic** or **endothermic**—and to what degree.

Example 2.1.8.1: Explosives

The compound **RDX** (Research Development Explosive) is a more powerful explosive than dynamite and is used by the military. When detonated, it produces gaseous products and heat according to the following reaction. Use the approximate bond energies in Table 2.1.8.1 to estimate the ΔH_{rxn} per mole of RDX.



Given: chemical reaction, structure of reactant, and Table 2.1.8.1.

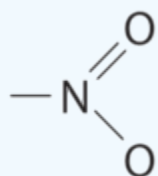
Asked for: ΔH_{rxn} per mole

Strategy:

- List the types of bonds broken in RDX, along with the bond energy required to break each type. Multiply the number of each type by the energy required to break one bond of that type and then add together the energies. Repeat this procedure for the bonds formed in the reaction.
- Use Equation 2.1.8.1 to calculate the amount of energy consumed or released in the reaction (ΔH_{rxn}).

Solution:

We must add together the energies of the bonds in the reactants and compare that quantity with the sum of the energies of the bonds in the products. A nitro group ($-\text{NO}_2$) can be viewed as having one N–O single bond and one N=O double bond, as follows:



In fact, however, both N–O distances are usually the same because of the presence of two equivalent resonance structures.

A We can organize our data by constructing a table:

Bonds Broken (kJ/mol)

Bonds Broken (kJ/mol)		Bonds Broken (kJ/mol)	
6 C–H	$411 \times 6 = 2466$	6 C=O	$799 \times 6 = 4794$
3 N–N	$167 \times 3 = 501$	6 O–H	$459 \times 6 = 2754$
3 N–O	$201 \times 3 = 603$		Total = 10,374
3 N=O	$607 \times 3 = 1821$		
1.5 O=O	$494 \times 1.5 = 741$		
	Total = 7962		

B From Equation 2.1.8.1, we have

$$\begin{aligned}\Delta H_{rxn} &\approx \sum (\text{bond energies of bonds broken}) - \sum (\text{bond energies of bonds formed}) \\ &= 7962 \text{ kJ/mol} - 10,374 \text{ kJ/mol} \\ &= -2412 \text{ kJ/mol}\end{aligned}$$

Thus this reaction is also highly exothermic

Exercise 2.1.8.1: Freon

The molecule HCFC-142b is a hydrochlorofluorocarbon that is used in place of chlorofluorocarbons (CFCs) such as the Freons and can be prepared by adding HCl to 1,1-difluoroethylene:

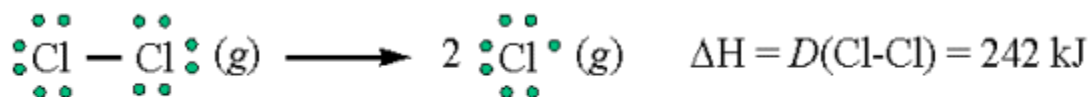
1,1-difluoroethylene reacts with HCl to produce CH₃CF₂Cl and HCFC142b.

Use tabulated bond energies to calculate ΔH_{rxn} .

Answer available at the end of this section.

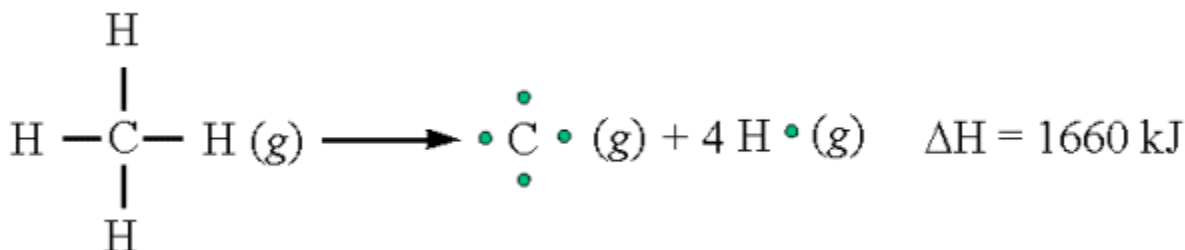
Bond Dissociation Energy

Bond Dissociation Energy (also referred to as Bond energy) is the enthalpy change (ΔH , heat input) required to break a bond (in 1 mole of a gaseous substance)



where " $D(\text{Cl-Cl})$ " represents the bond dissociation energy for the Cl-Cl bond

What about when we have a compound which is not a diatomic molecule? Consider the dissociation of **methane**:



There are four equivalent C-H bonds, thus we can that the dissociation energy for a single C-H bond would be:

$$\begin{aligned}D(\text{C-H}) &= (1660/4) \text{ kJ/mol} \\ &= 415 \text{ kJ/mol}\end{aligned}$$

The bond energy for a given bond is influenced by the rest of the molecule. However, this is a relatively small effect (suggesting that bonding electrons are localized between the bonding atoms). Thus, the bond energy for most bonds varies little from the average bonding energy for that type of bond

Bond energy is always a *positive* value - it takes energy to break a covalent bond (conversely energy is released during bond formation)

Table 2.1.8.4: Average bond energies:

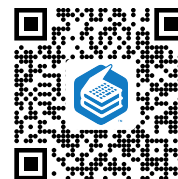
Bond	(kJ/mol)
C-F	485
C-Cl	328
C-Br	276
C-I	240
C-C	348
C-N	293
C-O	358
C-F	485
C-C	348
C=C	614
C≡C	839

The more stable a molecule (i.e. the stronger the bonds) the less likely the molecule is to undergo a chemical reaction.

YouTube Video

This interactive element is not available in this format. Visit the link or scan the QR code to access it online.

[View this YouTube Video online](#)



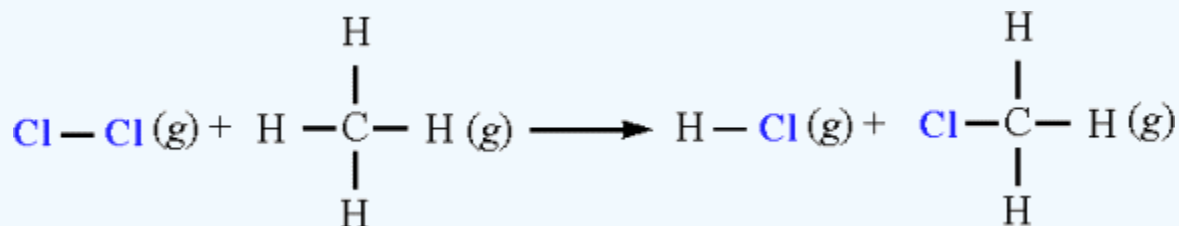
Bond Energies and the Enthalpy of Reactions

If we know which bonds are broken and which bonds are made during a chemical reaction, we can estimate the enthalpy change of the reaction (ΔH_{rxn}) even if we do not know the enthalpies of formation (ΔH_f°) for the reactants and products:

$$\Delta H = \sum \text{bond energies of broken bonds} - \sum \text{bond energies of formed bonds} \quad (2.1.8.3)$$

Example 2.1.8.2: Chlorination of Methane

What is the enthalpy of reaction between 1 mol of chlorine and 1 mol methane?



Solution

We use Equation 2.1.8.3, which requires tabulating bonds broken and formed.

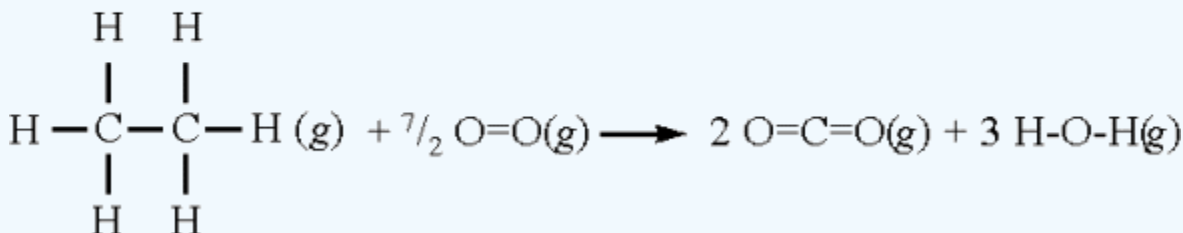
- **Bonds broken:** 1 mol of Cl-Cl bonds, 1 mol of C-H bonds
- **Bonds formed:** 1 mol of H-Cl bonds, 1 mol of C-Cl bonds

$$\begin{aligned}\Delta H &= [D(\text{Cl}-\text{Cl}) + D(\text{C}-\text{H})] - [D(\text{H}-\text{Cl}) + D(\text{C}-\text{Cl})] \\ &= [242\text{kJ} + 413\text{kJ}] - [431\text{kJ} + 328\text{kJ}] \\ &= -104\text{kJ}\end{aligned}$$

Thus, the reaction is **exothermic** (because the bonds in the products are stronger than the bonds in the reactants)

Example 2.1.8.3: Combustion of Ethane

What is the enthalpy of reaction for the combustion of 1 mol of ethane?



Solution

We use Equation 2.1.8.3, which requires tabulating bonds broken and formed.

- **bonds broken:** 6 moles C-H bonds, 1 mol C-C bonds, $\frac{7}{2}$ moles of O=O bonds
- **bonds formed:** 4 moles C=O bonds, 6 moles O-H bonds

$$\begin{aligned}\Delta H &= [(6 \times 413) + (348) + (\frac{7}{2} \times 495)] - [(4 \times 799) + (6 \times 463)] \\ &= 4558 - 5974 \\ &= -1416\text{ kJ}\end{aligned}$$

Therefore the reaction is exothermic.

Table 2.1.8.5: Bond strength and bond length

Bond	Bond Energy (kJ/mol)	Bond Length (Å)
C-C	348	1.54
C=C	614	1.34
C≡C	839	1.

As the number of bonds between two atoms increases, the bond grows shorter and stronger

SummaryEdit section

Bond order is the number of electron pairs that hold two atoms together. Single bonds have a bond order of one, and multiple bonds with bond orders of two (a double bond) and three (a triple bond) are quite common. In closely related compounds

with bonds between the same kinds of atoms, the bond with the highest bond order is both the shortest and the strongest. In bonds with the same bond order between different atoms, trends are observed that, with few exceptions, result in the strongest single bonds being formed between the smallest atoms. Tabulated values of average bond energies can be used to calculate the enthalpy change of many chemical reactions. If the bonds in the products are stronger than those in the reactants, the reaction is exothermic and vice versa.

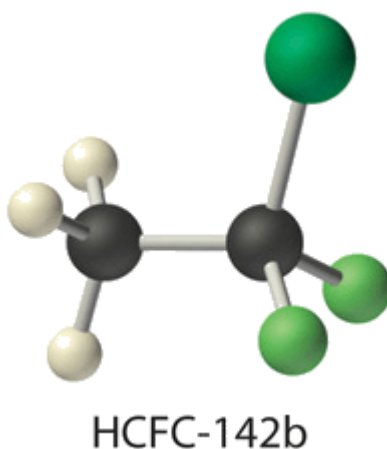
The breakage and formation of bonds is similar to a relationship: you can either get married or divorced and it is more favorable to be married.

- Energy is always **released** to make bonds, which is why the enthalpy change for breaking bonds is always **positive**.
- Energy is always **required** to break bonds. Atoms are much happier when they are "married" and release energy because it is easier and more stable to be in a relationship (e.g., to generate *octet electronic configurations*). The enthalpy change is always **negative** because the system is releasing energy when forming bond.

Answers

Exercise 2.1.8.1: Freon

-54 kJ/mol



This page titled [2.1.8: Strength of Covalent Bonds](#) is shared under a [CC BY-NC-SA 4.0](#) license and was authored, remixed, and/or curated by LibreTexts.

- [8.8: Strength of Covalent Bonds](#) is licensed [CC BY-NC-SA 3.0](#).

2.1.E: Basic Concepts of Chemical Bonding (Exercises)

8.1: CHEMICAL BONDS, LEWIS SYMBOLS AND THE OCTET RULE

Conceptual Problems

1. The Lewis electron system is a simplified approach for understanding bonding in covalent and ionic compounds. Why do chemists still find it useful?
2. Is a Lewis dot symbol an exact representation of the valence electrons in an atom or ion? Explain your answer.
3. How can the Lewis electron dot system help to predict the stoichiometry of a compound and its chemical and physical properties?
4. How is a Lewis dot symbol consistent with the quantum mechanical model of the atom? How is it different?

Conceptual Answer

3. Lewis dot symbols allow us to predict the number of bonds atoms will form, and therefore the stoichiometry of a compound. The Lewis structure of a compound also indicates the presence or absence of lone pairs of electrons, which provides information on the compound's chemical reactivity and physical properties.

8.2: IONIC BONDING

Conceptual Problems

1. Describe the differences in behavior between NaOH and CH₃OH in aqueous solution. Which solution would be a better conductor of electricity? Explain your reasoning.
2. What is the relationship between the strength of the electrostatic attraction between oppositely charged ions and the distance between the ions? How does the strength of the electrostatic interactions change as the size of the ions increases?
3. Which will result in the release of more energy: the interaction of a gaseous sodium ion with a gaseous oxide ion or the interaction of a gaseous sodium ion with a gaseous bromide ion? Why?
4. Which will result in the release of more energy: the interaction of a gaseous chloride ion with a gaseous sodium ion or a gaseous potassium ion? Explain your answer.
5. What are the predominant interactions when oppositely charged ions are
 1. far apart?
 2. at internuclear distances close to r_0 ?
 3. very close together (at a distance that is *less* than the sum of the ionic radii)?
6. Several factors contribute to the stability of ionic compounds. Describe one type of interaction that *destabilizes* ionic compounds. Describe the interactions that *stabilize* ionic compounds.
7. What is the relationship between the electrostatic attractive energy between charged particles and the distance between the particles?

Conceptual Answer

- 1.
- 2.
3. The interaction of a sodium ion and an oxide ion. The electrostatic attraction energy between ions of opposite charge is

directly proportional to the charge on each ion (Q_1 and Q_2 in Equation 9.1). Thus, more energy is released as the charge on the ions increases (assuming the internuclear distance does not increase substantially). A sodium ion has a +1 charge; an oxide ion, a -2 charge; and a bromide ion, a -1 charge. For the interaction of a sodium ion with an oxide ion, $Q_1 = +1$ and $Q_2 = -2$, whereas for the interaction of a sodium ion with a bromide ion, $Q_1 = +1$ and $Q_2 = -1$. The larger value of $Q_1 \times Q_2$ for the sodium ion-oxide ion interaction means it will release more energy.

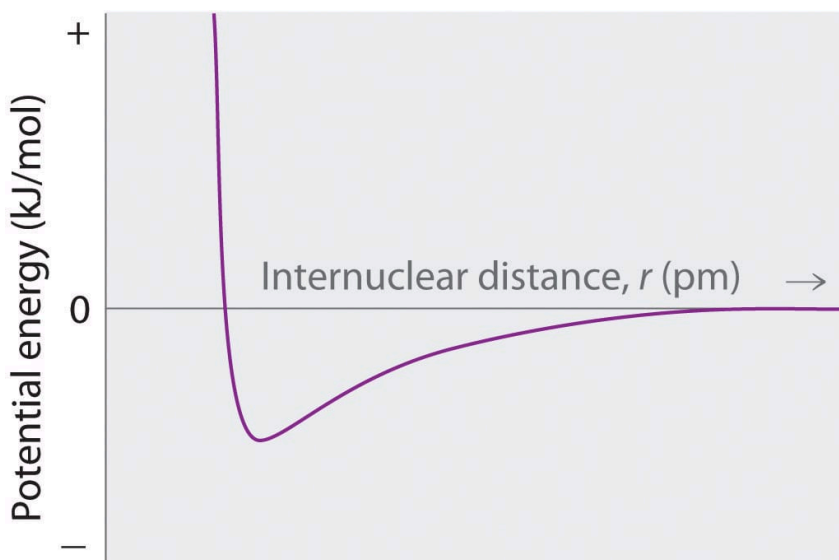
Numerical Problems

1. How does the energy of the electrostatic interaction between ions with charges +1 and -1 compare to the interaction between ions with charges +3 and -1 if the distance between the ions is the same in both cases? How does this compare with the magnitude of the interaction between ions with +3 and -3 charges?
2. How many grams of gaseous MgCl_2 are needed to give the same electrostatic attractive energy as 0.5 mol of gaseous LiCl ? The ionic radii are $\text{Li}^+ = 76 \text{ pm}$, $\text{Mg}^{+2} = 72 \text{ pm}$, and $\text{Cl}^- = 181 \text{ pm}$.
3. Sketch a diagram showing the relationship between potential energy and internuclear distance (from $r = \infty$ to $r = 0$) for the interaction of a bromide ion and a potassium ion to form gaseous KBr . Explain why the energy of the system increases as the distance between the ions decreases from $r = r_0$ to $r = 0$.
4. Calculate the magnitude of the electrostatic attractive energy (E , in kilojoules) for 85.0 g of gaseous SrS ion pairs. The observed internuclear distance in the gas phase is 244.05 pm.
5. What is the electrostatic attractive energy (E , in kilojoules) for 130 g of gaseous HgI_2 ? The internuclear distance is 255.3 pm.

Numerical Answers

1. According to Equation 9.1, in the first case $Q_1Q_2 = (+1)(-1) = -1$; in the second case, $Q_1Q_2 = (+3)(-1) = -3$. Thus, E will be three times larger for the +3/-1 ions. For +3/-3 ions, $Q_1Q_2 = (+3)(-3) = -9$, so E will be nine times larger than for the +1/-1 ions.

2.



3.

At $r < r_0$, the energy of the system increases due to electron-electron repulsions between the overlapping electron distributions on *adjacent* ions. At very short internuclear distances, electrostatic repulsions between adjacent *nuclei* also become important.

8.3: COVALENT BONDING

Conceptual Problems

1. Which would you expect to be stronger—an S–S bond or an Se–Se bond? Why?
2. Which element—nitrogen, phosphorus, or arsenic—will form the strongest multiple bond with oxygen? Why?
3. Why do multiple bonds between oxygen and period 3 elements tend to be unusually strong?
4. What can bond energies tell you about reactivity?
5. Bond energies are typically reported as average values for a range of bonds in a molecule rather than as specific values for a single bond? Why?
6. If the bonds in the products are weaker than those in the reactants, is a reaction exothermic or endothermic? Explain your answer.
7. A student presumed that because heat was required to initiate a particular reaction, the reaction product would be stable. Instead, the product exploded. What information might have allowed the student to predict this outcome?

Numerical Problems

1. What is the bond order about the central atom(s) of hydrazine (N_2H_4), nitrogen, and diimide (N_2H_2)? Draw Lewis electron structures for each compound and then arrange these compounds in order of increasing N–N bond distance. Which of these compounds would you expect to have the largest N–N bond energy? Explain your answer.
2. What is the carbon–carbon bond order in ethylene (C_2H_4), $\text{BrH}_2\text{CCH}_2\text{Br}$, and FCCH ? Arrange the compounds in order of increasing C–C bond distance. Which would you expect to have the largest C–C bond energy? Why?
3. From each pair of elements, select the one with the greater bond strength? Explain your choice in each case.
 1. P–P, Sb–Sb
 2. Cl–Cl, I–I
 3. O–O, Se–Se
 4. S–S, Cl–Cl
 5. Al–Cl, B–Cl
4. From each pair of elements, select the one with the greater bond strength? Explain your choice in each case.
 1. Te–Te, S–S
 2. C–H, Ge–H
 3. Si–Si, P–P
 4. Cl–Cl, F–F
 5. Ga–H, Al–H
5. Approximately how much energy per mole is required to completely dissociate acetone [$(\text{CH}_3)_2\text{CO}$] and urea [$(\text{NH}_2)_2\text{CO}$] into their constituent atoms?
6. Approximately how much energy per mole is required to completely dissociate ethanol, formaldehyde, and hydrazine into their constituent atoms?
7. Is the reaction of diimine (N_2H_2) with oxygen to produce nitrogen and water exothermic or endothermic? Quantify your answer.

Numerical Answer

1. N_2H_4 , bond order 1; N_2H_2 , bond order 2; N_2 , bond order 3; N–N bond distance: $\text{N}_2 < \text{N}_2\text{H}_2 < \text{N}_2\text{H}_4$; Largest bond energy: N_2 ; Highest bond order correlates with strongest and shortest bond.

8.4: BOND POLARITY AND ELECTRONEGATIVITY

Conceptual Problems

1. Why do ionic compounds such as KI exhibit substantially less than 100% ionic character in the gas phase?
2. Of the compounds LiI and LiF, which would you expect to behave more like a classical ionic compound? Which would have the greater dipole moment in the gas phase? Explain your answers.

Numerical Problems

1. Predict whether each compound is purely covalent, purely ionic, or polar covalent.
 1. RbCl
 2. S₈
 3. TiCl₂
 4. SbCl₃
 5. LiI
 6. Br₂
2. Based on relative electronegativities, classify the bonding in each compound as ionic, covalent, or polar covalent. Indicate the direction of the bond dipole for each polar covalent bond.
 1. NO
 2. HF
 3. MgO
 4. AlCl₃
 5. SiO₂
 6. the C=O bond in acetone
 7. O₃
3. Based on relative electronegativities, classify the bonding in each compound as ionic, covalent, or polar covalent. Indicate the direction of the bond dipole for each polar covalent bond.
 1. NaBr
 2. OF₂
 3. BCl₃
 4. the S-S bond in CH₃CH₂SSCH₂CH₃
 5. the C-Cl bond in CH₂Cl₂
 6. the O-H bond in CH₃OH
 7. PtCl₄²⁻
4. Classify each species as having 0%–40% ionic character, 40%–60% ionic character, or 60%–100% ionic character based on the type of bonding you would expect. Justify your reasoning.
 1. CaO
 2. S₈
 3. AlBr₃
 4. ICl
 5. Na₂S
 6. SiO₂
 7. LiBr
5. If the bond distance in HCl (dipole moment = 1.109 D) were double the actual value of 127.46 pm, what would be the effect on the charge localized on each atom? What would be the percent negative charge on Cl? At the actual bond distance, how would doubling the charge on each atom affect the dipole moment? Would this represent more ionic or covalent character?
6. Calculate the percent ionic character of HF (dipole moment = 1.826 D) if the H-F bond distance is 92 pm.

7. Calculate the percent ionic character of CO (dipole moment = 0.110 D) if the C–O distance is 113 pm .
8. Calculate the percent ionic character of PbS and PbO in the gas phase, given the following information: for PbS, $r = 228.69\text{ pm}$ and $\mu = 3.59\text{ D}$; for PbO, $r = 192.18\text{ pm}$ and $\mu = 4.64\text{ D}$. Would you classify these compounds as having covalent or polar covalent bonds in the solid state?

8.5: DRAWING LEWIS STRUCTURES

Conceptual Problems

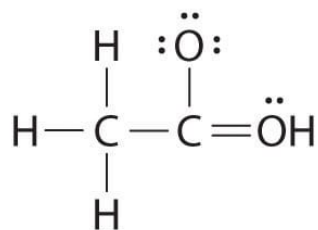
1. Compare and contrast covalent and ionic compounds with regard to
 1. volatility.
 2. melting point.
 3. electrical conductivity.
 4. physical appearance.
2. What are the similarities between plots of the overall energy versus internuclear distance for an ionic compound and a covalent compound? Why are the plots so similar?
3. Which atom do you expect to be the central atom in each of the following species?
 1. SO_4^{2-}
 2. NH_4^+
 3. BCl_3
 4. SO_2Cl_2
4. Which atom is the central atom in each of the following species?
 1. PCl_3
 2. CHCl_3
 3. SO_2
 4. IF_3
5. What is the relationship between the number of bonds typically formed by the period 2 elements in groups 14, 15, and 16 and their Lewis electron structures?
6. Although formal charges do not represent actual charges on atoms in molecules or ions, they are still useful. Why?

Numerical Problems

1. Give the electron configuration and the Lewis dot symbol for the following. How many more electrons can each atom accommodate?
 1. Se
 2. Kr
 3. Li
 4. Sr
 5. H
2. Give the electron configuration and the Lewis dot symbol for the following. How many more electrons can each atom accommodate?
 1. Na
 2. Br
 3. Ne

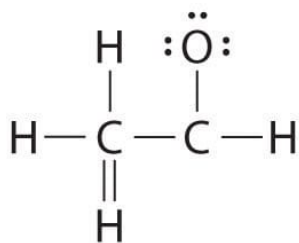
4. C
 5. Ga
3. Based on Lewis dot symbols, predict the preferred oxidation state of Be, F, B, and Cs.
 4. Based on Lewis dot symbols, predict the preferred oxidation state of Br, Rb, O, Si, and Sr.
 5. Based on Lewis dot symbols, predict how many bonds gallium, silicon, and selenium will form in their neutral compounds.
 6. Determine the total number of valence electrons in the following.
 1. Cr
 2. Cu^+
 3. NO^+
 4. XeF_2
 5. Br_2
 6. CH_2Cl_2
 7. NO_3^-
 8. H_3O^+
 7. Determine the total number of valence electrons in the following.
 1. Ag
 2. Pt^{2+}
 3. H_2S
 4. OH^-
 5. I_2
 6. CH_4
 7. SO_4^{2-}
 8. NH_4^+
 8. Draw Lewis electron structures for the following.
 1. F_2
 2. SO_2
 3. AlCl_4^-
 4. SO_3^{2-}
 5. BrCl
 6. XeF_4
 7. NO^+
 8. PCl_3
 9. Draw Lewis electron structures for the following.
 1. Br_2
 2. CH_3Br
 3. SO_4^{2-}
 4. O_2
 5. S_2^{2-}
 6. BF_3
 10. Draw Lewis electron structures for CO_2 , NO_2^- , SO_2 , and NO_2^+ . From your diagram, predict which pair(s) of compounds have similar electronic structures.

11. Write Lewis dot symbols for each pair of elements. For a reaction between each pair of elements, predict which element is the oxidant, which element is the reductant, and the final stoichiometry of the compound formed.
 1. K, S
 2. Sr, Br
 3. Al, O
 4. Mg, Cl
12. Write Lewis dot symbols for each pair of elements. For a reaction between each pair of elements, predict which element is the oxidant, which element is the reductant, and the final stoichiometry of the compound formed.
 1. Li, F
 2. Cs, Br
 3. Ca, Cl
 4. B, F
13. Use Lewis dot symbols to predict whether ICl and NO_4^- are chemically reasonable formulas.
14. Draw a plausible Lewis electron structure for a compound with the molecular formula Cl_3PO .
15. Draw a plausible Lewis electron structure for a compound with the molecular formula CH_4O .
16. While reviewing her notes, a student noticed that she had drawn the following structure in her notebook for acetic acid:



Why is this structure not feasible? Draw an acceptable Lewis structure for acetic acid. Show the formal charges of all nonhydrogen atoms in both the correct and incorrect structures.

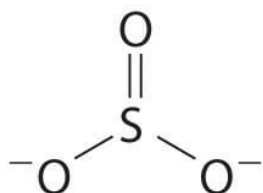
17. A student proposed the following Lewis structure shown for acetaldehyde.



Why is this structure not feasible? Draw an acceptable Lewis structure for acetaldehyde. Show the formal charges of all nonhydrogen atoms in both the correct and incorrect structures.

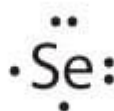
18. Draw the most likely structure for HCN based on formal charges, showing the formal charge on each atom in your structure. Does this compound have any plausible resonance structures? If so, draw one.
19. Draw the most plausible Lewis structure for NO_3^- . Does this ion have any other resonance structures? Draw at least one other Lewis structure for the nitrate ion that is not plausible based on formal charges.
20. At least two Lewis structures can be drawn for BCl_3 . Using arguments based on formal charges, explain why the most likely structure is the one with three B-Cl single bonds.

21. Using arguments based on formal charges, explain why the most feasible Lewis structure for SO_4^{2-} has two sulfur-oxygen double bonds.
22. At least two distinct Lewis structures can be drawn for N_3^- . Use arguments based on formal charges to explain why the most likely structure contains a nitrogen-nitrogen double bond.
23. Is $\text{H}-\text{O}-\text{N}=\text{O}$ a reasonable structure for the compound HNO_2 ? Justify your answer using Lewis electron dot structures.
24. Is $\text{H}-\text{O}=\text{C}-\text{H}$ a reasonable structure for a compound with the formula CH_2O ? Use Lewis electron dot structures to justify your answer.
25. Explain why the following Lewis structure for SO_3^{2-} is or is not reasonable.



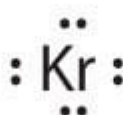
Numerical Answers

1. 1. $[\text{Ar}]4s^23d^{10}4p^4$



Selenium can accommodate two more electrons, giving the Se^{2-} ion.

2. $[\text{Ar}]4s^23d^{10}4p^6$



Krypton has a closed shell electron configuration, so it cannot accommodate any additional electrons.

3. $1s^22s^1$



Lithium can accommodate one additional electron in its 2s orbital, giving the Li^- ion.

4. $[\text{Kr}]5s^2$



Strontium has a filled 5s subshell, and additional electrons would have to be placed in an orbital with a higher energy. Thus strontium has no tendency to accept an additional electron.

5. $1s^1$



Hydrogen can accommodate one additional electron in its 1s orbital, giving the H^- ion.

2.

3. Be^{2+} , F^- , B^{3+} , Cs^+

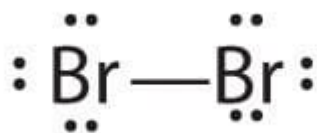
4.

5.

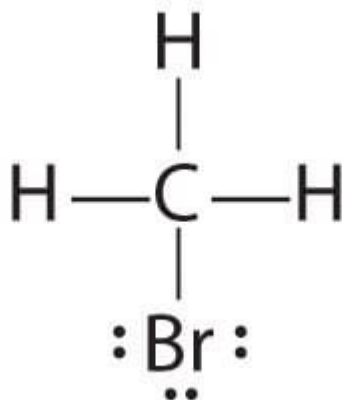
6.

- 7.
1. 11
 2. 8
 3. 8
 4. 8
 5. 14
 6. 8
 7. 32
 8. 8

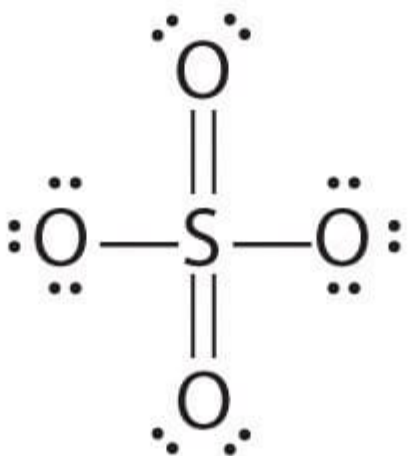
8.



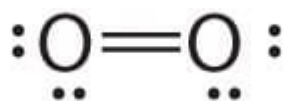
9. 1.



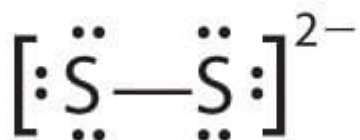
2.



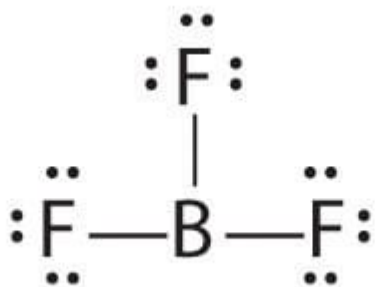
3.



4.



5.



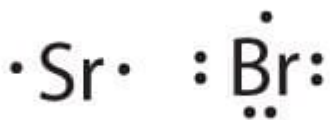
6.

10.



11. 1.

K is the reductant; S is the oxidant. The final stoichiometry is K_2S .



2.

Sr is the reductant; Br is the oxidant. The final stoichiometry is SrBr_2 .



3.

Al is the reductant; O is the oxidant. The final stoichiometry is Al_2O_3 .



4.

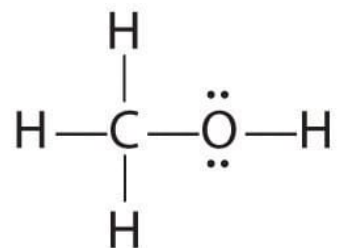
Mg is the reductant; Cl is the oxidant. The final stoichiometry is MgCl_2 .

12.

13.

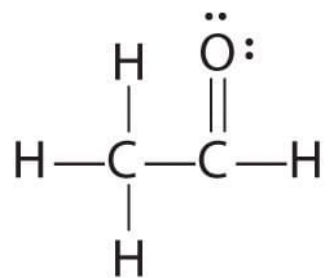
14.

15. The only structure that gives both oxygen and carbon an octet of electrons is the following:

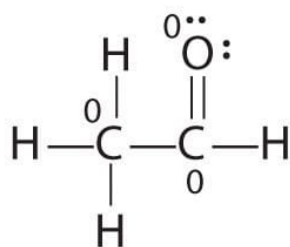


16.

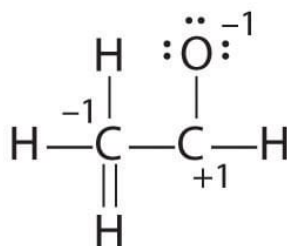
17. The student's proposed structure has two flaws: the hydrogen atom with the double bond has four valence electrons (H can only accommodate two electrons), and the carbon bound to oxygen only has six valence electrons (it should have an octet). An acceptable Lewis structure is



The formal charges on the correct and incorrect structures are as follows:



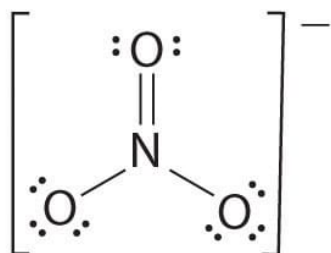
Correct



Incorrect

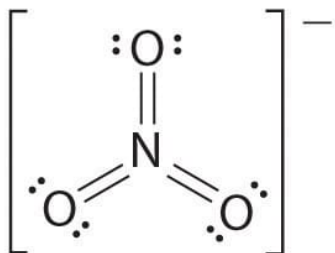
18.

19. The most plausible Lewis structure for NO_3^- is:



There are three equivalent resonance structures for nitrate (only one is shown), in which nitrogen is doubly bonded to one of the three oxygens. In each resonance structure, the formal charge of N is +1; for each singly bonded O, it is -1; and for the doubly bonded oxygen, it is 0.

The following is an example of a Lewis structure that is *not* plausible:



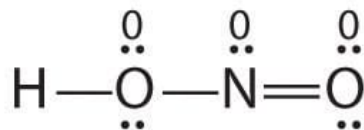
This structure nitrogen has six bonds (nitrogen can form only four bonds) and a formal charge of -1.

20.

21. With four S-O single bonds, each oxygen in SO_4^{2-} has a formal charge of -1, and the central sulfur has a formal charge of +2. With two S=O double bonds, only two oxygens have a formal charge of -1, and sulfur has a formal charge of zero. Lewis structures that minimize formal charges tend to be lowest in energy, making the Lewis structure with two S=O double bonds the most probable.

22.

23. Yes. This is a reasonable Lewis structure, because the formal charge on all atoms is zero, and each atom (except H) has an

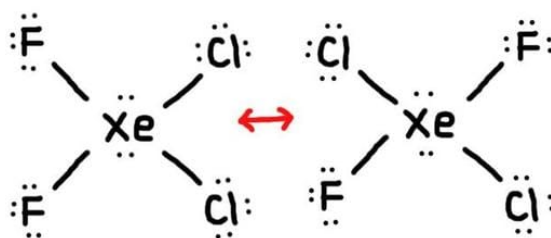


octet of electrons.

8.6: RESONANCE STRUCTURES

Conceptual Problems

1. Why are resonance structures important?
2. In what types of compounds are resonance structures particularly common?
3. True or False, The picture below is a resonance structure?

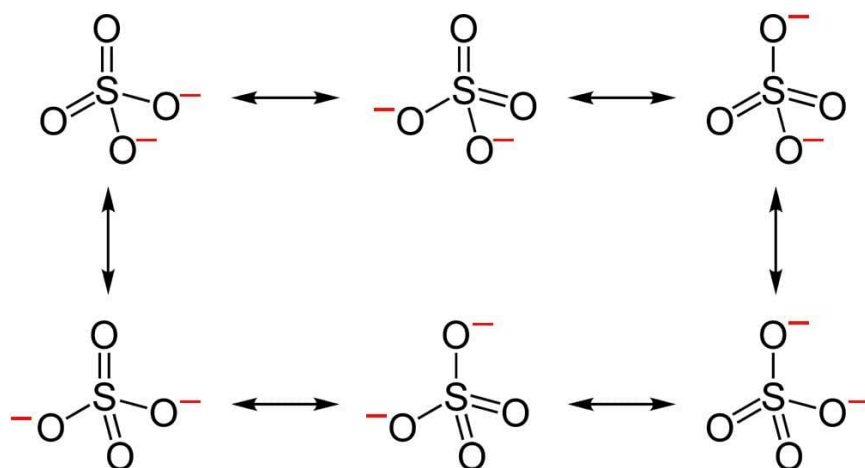


Numerical Problems

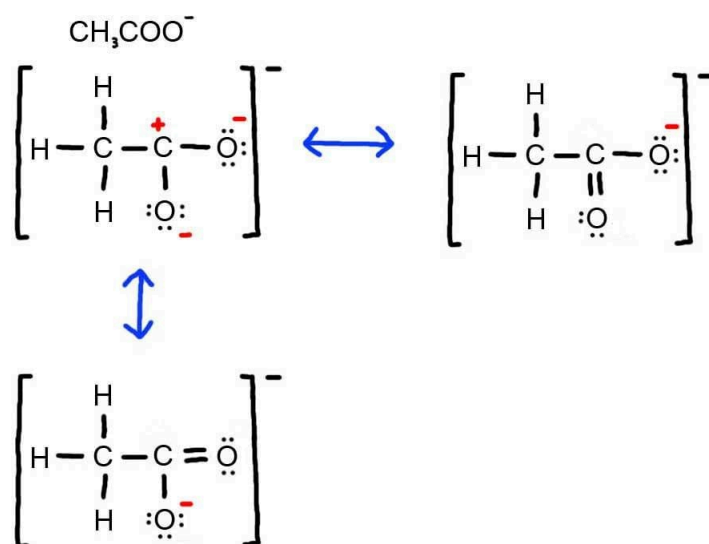
1. Draw all the resonance structures for each ion.
 - a. HSO_4^-
 - b. HSO_3^-
2. Draw the Lewis Dot Structure for SO_4^{2-} and all possible resonance structures. Which of the following resonance structure is not favored among the Lewis Structures? Explain why. Assign Formal Charges.
3. Draw the Lewis Dot Structure for CH_3COO^- and all possible resonance structures. Assign Formal Charges. Choose the most favorable Lewis Structure.
4. Draw the Lewis Dot Structure for HPO_3^{2-} and all possible resonance structures. Assign Formal Charges.
5. Draw the Lewis Dot Structure for CHO_2^{1-} and all possible resonance structures. Assign Formal Charges.
6. Draw the Resonance Hybrid Structure for PO_4^{3-} .
7. Draw the Resonance Hybrid Structure for NO_3^- .

Numerical Answers

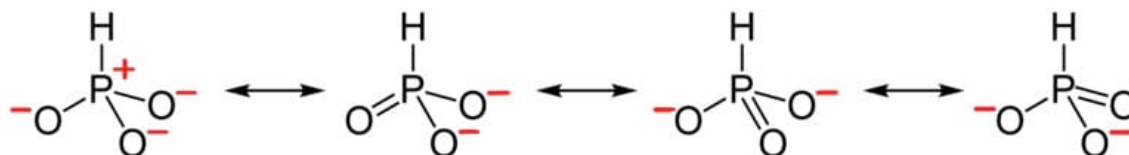
1. False, because the electrons were not moved around, only the atoms (this violates the Resonance Structure Rules).
3. Below are the all Lewis dot structure with formal charges (in red) for Sulfate (SO_4^{2-}). There isn't a most favorable resonance of the Sulfate ion because they are all identical in charge and there is no change in Electronegativity between the Oxygen atoms.



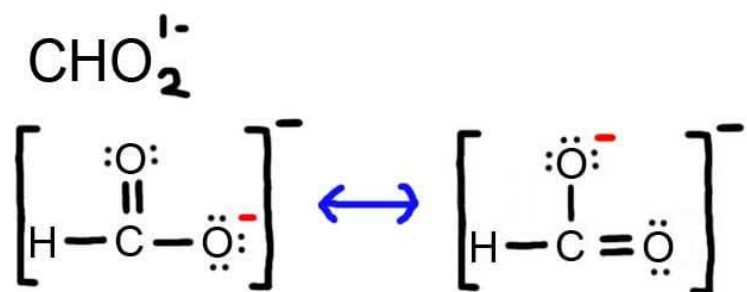
4. Below is the resonance for **CH₃COO⁻**, formal charges are displayed in red. The Lewis Structure with the most formal charges is not desirable, because we want the Lewis Structure with the least formal charge.



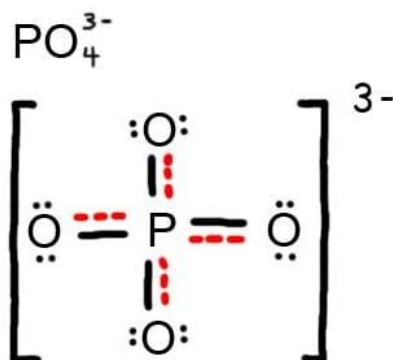
5. The resonance for **HPO₃²⁻**, and the formal charges (in red).



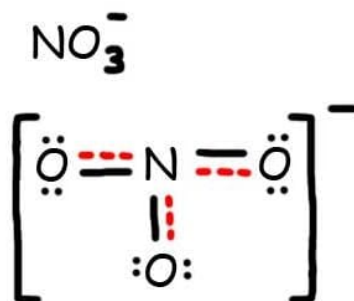
6. The resonance for **CHO₂¹⁻**, and the formal charges (in red).



7. The resonance hybrid for PO_4^{3-} , hybrid bonds are in red.



8. The resonance hybrid for NO_3^- , hybrid bonds are in red.



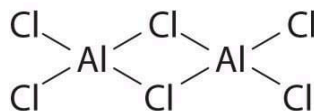
8.7: EXCEPTIONS TO THE OCTET RULE

Conceptual Problems

1. What regions of the periodic table contain elements that frequently form molecules with an odd number of electrons? Explain your answer.
2. How can atoms expand their valence shell? What is the relationship between an expanded valence shell and the stability of an ion or a molecule?
3. What elements are known to form compounds with less than an octet of electrons? Why do electron-deficient compounds form?
4. List three elements that form compounds that do not obey the octet rule. Describe the factors that are responsible for the stability of these compounds.

Numerical Problems

1. What is the major weakness of the Lewis system in predicting the electron structures of PCl_6^- and other species containing atoms from period 3 and beyond?
2. The compound aluminum trichloride consists of Al_2Cl_6 molecules with the following structure (lone pairs of electrons removed for clarity):

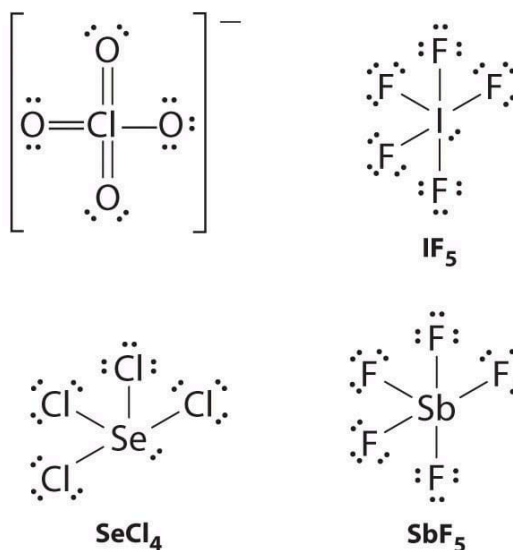


Does this structure satisfy the octet rule? What is the formal charge on each atom? Given the chemical similarity between aluminum and boron, what is a plausible explanation for the fact that aluminum trichloride forms a dimeric structure rather than the monomeric trigonal planar structure of BCl_3 ?

3. Draw Lewis electron structures for ClO_4^- , IF_5 , SeCl_4 , and SbF_5 .
4. Draw Lewis electron structures for ICl_3 , Cl_3PO , Cl_2SO , and AsF_6^- .
5. Draw plausible Lewis structures for the phosphate ion, including resonance structures. What is the formal charge on each atom in your structures?
6. Draw an acceptable Lewis structure for PCl_5 , a compound used in manufacturing a form of cellulose. What is the formal charge of the central atom? What is the oxidation number of the central atom?
7. Using Lewis structures, draw all of the resonance structures for the BrO_3^- ion.
8. Draw an acceptable Lewis structure for xenon trioxide (XeO_3), including all resonance structures.

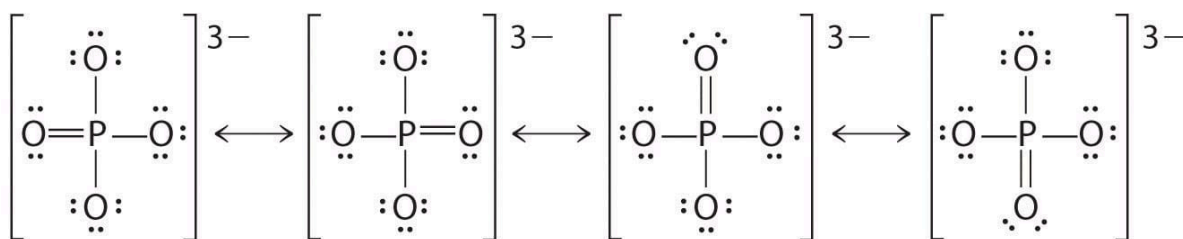
Numerical Answers

- 1.
- 2.
3. ClO_4^- (one of four equivalent resonance structures)



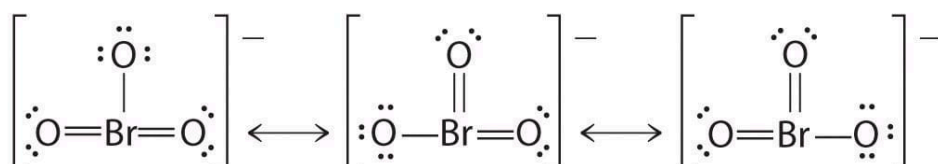
4.

5.



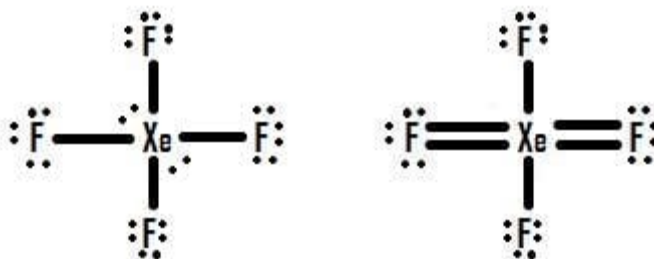
The formal charge on phosphorus is 0, while three oxygen atoms have a formal charge of -1 and one has a formal charge of zero.

6.



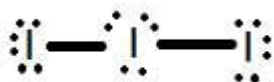
Practice Problems

1. Draw the Lewis structure for the molecule I_3^- .
2. Draw the molecule ClF_3 .
3. The central atom for an expanded octet must have an atomic number larger than what?
4. Draw the Lewis structure for the molecule NO_2 .
5. Which Lewis structure is more likely?

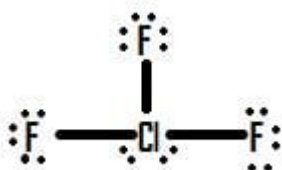


or

Practice Answers

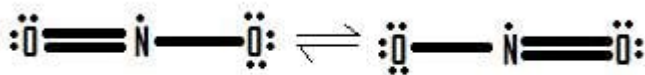


1.

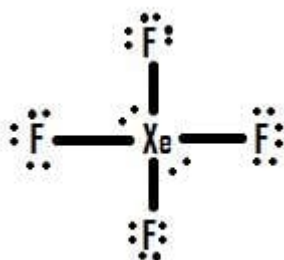


2.

3. 10 (Sodium and higher)



4.



5.

8.8: STRENGTHS OF COVALENT BONDS

This page titled [2.1.E: Basic Concepts of Chemical Bonding \(Exercises\)](#) is shared under a [CC BY-NC-SA 4.0](#) license and was authored, remixed, and/or curated by LibreTexts.

2.1.S: Basic Concepts of Chemical Bonding (Summary)

8.1: CHEMICAL BONDS, LEWIS SYMBOLS AND THE OCTET RULE

Lewis dot symbols can be used to predict the number of bonds formed by most elements in their compounds. Lewis electron dot symbols, which consist of the chemical symbol for an element surrounded by dots that represent its valence electrons, grouped into pairs often placed above, below, and to the left and right of the symbol. The structures reflect the fact that the elements in period 2 and beyond tend to gain, lose, or share electrons to reach a total of 8 valence electrons in their compounds.

- **Ionic bond:** bond formed on the basis of electrostatic forces that exist between oppositely charged ions. The ions are formed from atoms by transfer of one or more electrons
- **Covalent bond:** bond formed between two or more atoms by a sharing of electrons
- **Metallic bond:** bonding in which the bonding electrons are relatively free to move throughout the 3D structure
- **Electron dot symbols:** aka **Lewis symbols**; simple and convenient way of showing the valence electrons of atoms and keeping track of them in the course of bond formation
- The number of valence electrons of any representative element is the same as the column number of the element in the periodic table
- **Octet rule:** atoms tend to lose or gain electrons until they are surrounded by 8 valence electrons

8.2: IONIC BONDING

The amount of energy needed to separate a gaseous ion pair is its bond energy. Forming ionic compounds is usually extremely exothermic. The strength of the electrostatic attraction between ions with opposite charges is directly proportional to the magnitude of the charges on the ions and inversely proportional to the internuclear distance.

Energies of Ionic Bond Formation

The formation of ionic compounds is very exothermic

Removing an electron from an atom, such as Na, is endothermic because energy needs to be used to overcome the attractive forces within the atom. Adding an electron is the opposite process and releases lots of energy

The principal reason that ionic compounds are stable is the attraction between ions of unlike charge. This attraction draws the ions together, releasing energy and causing the ions to form a solid array (lattice)

Lattice energy: energy required to separate completely a mole of a solid ionic compounds into its gaseous ions

Large values of lattice energy mean that the ions are strongly attracted to one another

Energy released by the attraction between the ions of unlike charges more than makes up for the endothermic nature of ionization energies, making the formation of ionic compounds an exothermic process

$$E = k \frac{Q_1 Q_2}{d}$$

- E = potential energy of two interacting charged particles
- Q_1 and Q_2 = charges on the particles
- D= distance between the particles
- K = constant; $8.99 \times 10^9 \text{ Jm/C}^2$

For a given arrangement of ions, the lattice energy increases as the charges of ions increase and as their radii decrease. The magnitude of lattice energies depends primarily on the ionic charges because ionic radii do not vary over a wide range.

Electron Configurations of Ions

Many ions tend to have noble gas electron configurations. This is why Na can have a +1 charge, but not a +2 one. Once an ion has reached noble gas configuration, it wants to stay there.

- Na: $1s^2 2s^2 2p^6 3s^1 = [\text{Ne}] 3s^1$
- Na^+ : $1s^2 2s^2 2p^6 = [\text{Ne}]$
- Na^{2+} : $1s^2 2s^2 2p^5$

Similarly, addition of electrons to nonmetals is either exothermic or slightly endothermic as long as electrons are being added to the valence shell. Further addition of electrons requires tremendous amounts of energy; more than is available from the lattice energy

- Cl: $1s^2 2s^2 2p^6 3s^2 3p^5 = [\text{Ne}] 3s^2 3p^5$
- Cl^- : $1s^2 2s^2 2p^6 3s^2 3p^6 = [\text{Ar}]$
- Cl^{2-} : $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1 = [\text{Ar}]$

The lattice energies of ionic compounds are generally large enough to compensate for the loss of up to only 3 electrons from atoms. Thus we find cations only having charges of +1, +2, or +3.

Because most transition metals have more than 3 electrons beyond a noble gas core, attainment of a noble gas configuration for these ions is usually impossible.

When a positive ion is formed from an atom, electrons are always lost first from the subshell with the largest value of n . Thus, a transition metal always loses the outer s electrons before it loses electrons from the underlying d subshell.

8.3 Sizes of Ions

Sizes of ions are important in determining both the way in which the ions pack in a solid and the lattice energy of the solid. It is also a major factor governing the properties of ions in solution

The size of an atom depends on its nuclear charge, the number of electrons it possesses, and the orbitals in which the outer-shell electrons reside

Positive ions are formed by removing 1 or more electrons from the outermost region of the atom. Thus, the formation of a cation not only vacates the most spatially extended orbitals, it also decreases the total electron-electron repulsions. Hence, cations are smaller than the original atoms from which they came.

The opposite happens when speaking of negative ions. An added electron increases electron-electron repulsions and causes the electrons to spread out more in space.

For ions of the same charge, size increases as we go down a group

8.3: COVALENT BONDING

The strength of a covalent bond depends on the overlap between the valence orbitals of the bonded atoms. Bond order is the number of electron pairs that hold two atoms together. Single bonds have a bond order of one, and multiple bonds with bond orders of two (a double bond) and three (a triple bond) are quite common. In closely related compounds with bonds between the same kinds of atoms, the bond with the highest bond order is both the shortest and the strongest.

Ionic substances are usually brittle with high melting points. They are usually crystalline, meaning that they have flat surfaces that make characteristic angles with one another.

- **Covalent bond:** chemical bond formed by sharing a pair of electrons
- **Lewis structure:** structure that represents bonding using dots for unpaired electrons and lines for bonds

For nonmetals, the number of valence electrons is the same as the group number

Knowing this, we can predict that an element in Group 7A would need one covalent bond in order to get an octet, an element in Group 6A would need two, and so on.

Multiple Bonds

- **Single bond:** sharing of one pair of electrons, one covalent bond
- **Double bond:** two shared electrons

Distance between bonded atoms decreases as the number of shared electron pairs increases

8.4: BOND POLARITY AND ELECTRONEGATIVITY

Bond polarity and ionic character increase with an increasing difference in electronegativity. 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

- **Bond polarity:** measure of how equally the electrons are shared between the atoms in a chemical bond
- **Nonpolar bond:** one in which the electrons are shared equally between the two atoms
- **Polar covalent bond:** one of the atoms exerts a greater attraction for the electron than the other

Electronegativity

Used to estimate whether a bond will be nonpolar, polar covalent, or ionic

Electronegativity: ability of an atom *in a molecule* to attract electrons to itself

An atom with a very negative electron affinity and high ionization energy will both attract electrons from other atoms and resist having its electrons attracted away; it will be highly electronegative

Highest electronegativity = 4.0 (Fluorine), lowest = 0.7 (Cesium)

Electronegativity increases from left to right, and usually decreases with increasing atomic number in any one group

Electronegativity and Bond Polarity

Differences in electronegativities:

Nonpolar = 0 – 0.4

Polar covalent = 0.4 – 1.6

Ionic = > 1.6 (> 50% = ionic)

δ^+ and δ^- : "delta sign"; represent partial positive and negative charge. The atom with the δ^- is the more electronegative one

8.5: DRAWING LEWIS STRUCTURES

Lewis dot symbols provide a simple rationalization of why elements form compounds with the observed stoichiometries. A plot of the overall energy of a covalent bond as a function of internuclear distance is identical to a plot of an ionic pair because both result from attractive and repulsive forces between charged entities. Lewis structures are an attempt to rationalize why certain stoichiometries are commonly observed for the elements of particular families.

1. Sum the valence electrons from all atoms. For an anion, add an electron to the total negative charge. For a cation, subtract an electron.
2. Write the symbols for the atoms to show which atoms are attached to which, and connect them with a single bond.
3. Complete the octets of the atoms bonded to the central atom.
4. Place any leftover electrons on the central atom, even if doing so results in more than an octet

5. If there are not enough electrons to give the central atom an octet, try multiple bonds

8.6: RESONANCE STRUCTURES

Some molecules have two or more chemically equivalent Lewis electron structures, called *resonance structures*. Resonance is a mental exercise and method within the Valence Bond Theory of bonding that describes the delocalization of electrons within molecules. These structures are written with a double-headed arrow between them, indicating that none of the Lewis structures accurately describes the bonding but that the actual structure is an average of the individual resonance structures.

Resonance structures (resonance forms) are individual Lewis structures in cases where two or more Lewis structures are equally good descriptions of a single molecule. If a molecule (or ion) has two or more resonance structures, the molecule is a blend of these structures. The molecule *does not* oscillate rapidly between two or more different forms.

8.7: EXCEPTIONS TO THE OCTET RULE

Following the Octet Rule for Lewis Dot Structures leads to the most accurate depictions of stable molecular and atomic structures and because of this we always want to use the octet rule when drawing Lewis Dot Structures. There are three exceptions: (1) When there are an odd number of valence electrons, (2) When there are too few valence electrons, and (3) when there are too many valence electrons

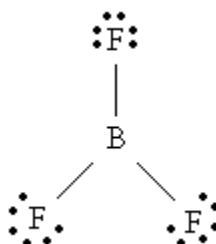
1. Molecules with an odd number of electrons
2. Molecules in which an atom has less than an octet
3. Molecules in which an atom has more than an octet

Odd Number of Electrons

In a few molecules, such as ClO_2 , NO , and NO_2 , the number of electrons is odd. In NO for example, there are $5+6 = 11$ valence electron. Hence, complete pairing of these electrons is impossible and an octet around each atom cannot be achieved.

Less Than an Octet

Second type of exception occurs when there are fewer than eight electrons around an atom in a molecule or ion. Relatively rare situation; most often encountered in compounds of Boron and Beryllium. For example, let's consider Boron Trifluoride, BF_3



There are 6 electrons around the Boron atom. We can form a double bond between Boron and any of the 3 Fluorine atoms (3 possible resonance structures)

However, by doing so, we forced a Fluorine atom to share additional electrons with Boron. This would make the F atom to have a +1 charge, and the Boron atom to have a -1 charge, which is extremely unfavorable.

We then conclude that the structures containing the double bonds are less important than the one illustrated on the right. *Since in this case Boron has only 6 valence electrons, it will react violently with molecules that have an unshared pair of electrons.*

More Than an Octet

The octet rule works as well as it does because the representative elements usually employ only an ns and three np valence shell orbitals in bonding, and these hold eight electrons.

Because elements of the second period have only 2s and 2p orbitals, they cannot have more than an octet of electrons in their valence shells. However, from the third period on, the elements have unfilled *nd* orbitals that can be used in bonding.

Size also plays an important role in determining whether an atom can accommodate more than eight electrons. The larger the central atom, the larger the number of atoms that can surround it. The size of the surrounding atoms is also important. Expanded valence shells occur most often when the central atom is bonded to the smallest and most electronegative atoms.

8.8: STRENGTHS OF COVALENT BONDS

Bond order is the number of electron pairs that hold two atoms together. Single bonds have a bond order of one, and multiple bonds with bond orders of two (a double bond) and three (a triple bond) are quite common. The bond with the highest bond order is both the shortest and the strongest. In bonds with the same bond order between different atoms, trends are observed that, with few exceptions, result in the strongest single bonds being formed between the smallest atoms.

Bond dissociation energy: aka **bond energy**; enthalpy change, ΔH , required to break a particular bond in a mole of gaseous substance.

For polyatomic molecules, we must often utilize average bond energies.

Bond energy is *always* positive, the greater the bond energy, the stronger the bond

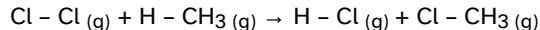
A molecule with strong bonds generally has less tendency to undergo chemical change than does one with weak bonds

Bond Energies and the Enthalpy of Reactions

$$\Delta H = \Sigma (\text{bond energies of bonds broken}) - \Sigma (\text{bond energies of bonds formed})$$

If $\Delta H > 0$, the reaction is endothermic

If $\Delta H < 0$, the reaction is exothermic



Bonds broken: 1 mol Cl – Cl, 1 mol C – H

Bonds made: 1 mol H – Cl, 1 mol C – Cl

$$\begin{aligned} \Delta H &= [D(\text{Cl}-\text{Cl}) + D(\text{C}-\text{H})] - [D(\text{H}-\text{Cl}) + D(\text{Cl}-\text{Cl})] \\ &= (242 \text{ kJ} + 413 \text{ kJ}) - (431 \text{ kJ} + 328 \text{ kJ}) \\ &= 104 \text{ kJ} \end{aligned}$$

Bond Strength and Bond Length

As the number of bonds between a given element increase, the bond energy increases and the bond length decreases. Hence, the atoms are held more tightly and closely together. In general, *as the number of bonds between two atoms increases, the bond grows shorter and stronger.*

8.10 Oxidation Numbers

Oxidation Numbers: aka **Oxidation states**; a positive or negative whole number assigned to an element in a molecule or ion on the basis of a set of normal rules; to some degree it reflects the positive or negative character of an atom

Oxidation numbers do NOT correspond to real charges on the atoms, EXCEPT in the special case of simple ionic substances

1. *The oxidation form of an element in its elemental form is zero.*
2. *The oxidation number of a monoatomic ion is the same as its charge.* For example, the oxidation number of sodium in Na^+ is +1, and that of sulfur in S^{2-} is –2

3. *In binary compounds (those with two different elements), the element with greater electronegativity is assigned a negative oxidation number equal to its charge in simple ionic compounds the element.* For example, consider the oxidation state of Cl in PCl_3 . Cl is more electronegative than P. In its simple ionic compounds, Cl appears as the ion Cl^- . Thus, in PCl_3 , Cl is assigned an oxidation number of -1 .
4. *The sum of the oxidation numbers equals zero for an electrically neutral compound and equals the overall charge of the ionic species.* For example, PCl_3 is a neutral molecule. Thus, the sum of oxidation number of the P and Cl atoms must equal zero. Because the oxidation number of each Cl in this compound is -1 (rule 3), the oxidation number of P must be $+3$.

Group 1A elements are $+1$, Group 2A elements are $+2$, and Aluminum is $+3$.

The most electronegative element, F, is always found in the -1 oxidation state. Oxygen is usually in the -2 state, however, it can be -1 in peroxides.

Hydrogen has an oxidation number of $+1$ when it is bonded to a more electronegative element (most nonmetals), and of -1 when bonded to less electronegative elements (most metals)

Oxidation Numbers and Nomenclature

Name of the less electronegative element is given first, followed by the name of the more electronegative element modified to have an *-ide* ending

Compounds of metals in higher oxidation states tend to be molecular rather than ionic

This page titled [2.1.S: Basic Concepts of Chemical Bonding \(Summary\)](#) is shared under a [CC BY-NC-SA 4.0](#) license and was authored, remixed, and/or curated by LibreTexts.

- [8.S: Basic Concepts of Chemical Bonding \(Summary\)](#) is licensed [CC BY-NC-SA 3.0](#).

3: CHAPTER 3 - MOLECULAR SHAPES AND BONDING THEORIES

3.1: Molecular Geometry and Bonding Theories

3.1.1: Molecular Shapes

3.1.2: The VSEPR Model

3.1.3: Molecular Shape and Molecular Polarity

3.1.4: Covalent Bonding and Orbital Overlap

3.1.5: Hybrid Orbitals

3.1.6: Multiple Bonds

3.1.7: Molecular Orbitals

3.1.8: Second-Row Diatomic Molecules

3.1.E: Exercises

3.1.S: Molecular Geometry and Bonding Theories (Summary)

3.1: MOLECULAR GEOMETRY AND BONDING THEORIES

A general chemistry Libretexts Textmap organized around the textbook

Chemistry: The Central Science

by Brown, LeMay, Bursten, Murphy, and Woodward

Template:HideTOC

3.1.1: Molecular Shapes

3.1.2: The VSEPR Model

3.1.3: Molecular Shape and Molecular Polarity

3.1.4: Covalent Bonding and Orbital Overlap

3.1.5: Hybrid Orbitals

3.1.6: Multiple Bonds

3.1.7: Molecular Orbitals

3.1.8: Second-Row Diatomic Molecules

3.1.E: Exercises

3.1.S: Molecular Geometry and Bonding Theories (Summary)

This page titled [3.1: Molecular Geometry and Bonding Theories](#) is shared under a [CC BY-NC-SA 4.0](#) license and was authored, remixed, and/or curated by LibreTexts.

3.1.1: Molecular Shapes

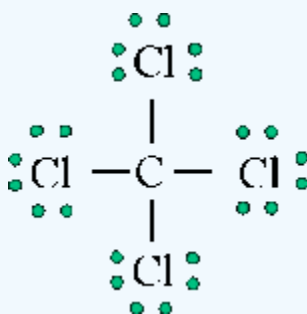
The [Lewis electron-pair approach](#) described previously can be used to predict the number and types of bonds between the atoms in a substance, and it indicates which atoms have lone pairs of electrons. This approach gives no information about the actual arrangement of atoms in space, however.

Molecular Geometry

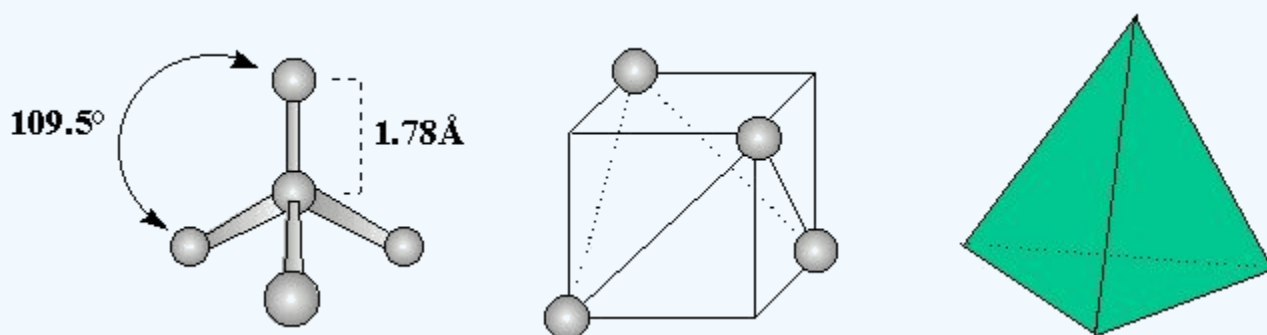
The specific three dimensional arrangement of atoms in molecules is referred to as **molecular geometry**. We also define molecular geometry as the positions of the atomic nuclei in a molecule. There are various instrumental techniques such as [X-Ray crystallography](#) and other experimental techniques which can be used to tell us where the atoms are located in a molecule. Using advanced techniques, very complicated structures for proteins, enzymes, DNA, and RNA have been determined. Molecular geometry is associated with the chemistry of vision, smell, taste, drug reactions, and enzyme controlled reactions to name a few.

Example 3.1.1.1: Carbon Tetrachloride

The Lewis structure of carbon tetrachloride provides information about connectivities, provides information about valence orbitals, and provides information about bond character.



However, the Lewis structure provides no information about the shape of the molecule, which is defined by *the bond angles and the bond lengths*. For carbon tetrachloride, each C-Cl bond length is $1.78\text{\AA}$ and each Cl-C-Cl bond angle is 109.5° . Hence, carbon tetrachloride is **tetrahedral** in structure:

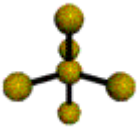
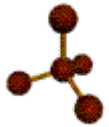
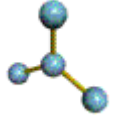
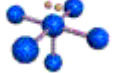
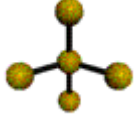
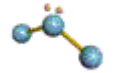
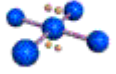
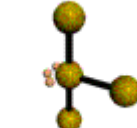


Molecular Geometries of AB_n molecules

Molecular geometry is associated with the specific orientation of bonding atoms. A careful analysis of electron distributions in orbitals will usually result in correct molecular geometry determinations. In addition, the simple writing of Lewis diagrams can also provide important clues for the determination of molecular geometry. Molecular shapes, or geometries, are critical to molecular recognition and function. Table 3.1.1.1 shows some examples of geometries where a central atom A is bonded to two

or more X atoms. As indicated in several of the geometries below, non-bonding electrons E can strongly influence the molecular geometry of the molecule.

Table 3.1.1.1:

6	5	4	3	2
AX_6  octahedral	AX_5  trigonal bipyramidal	AX_4  tetrahedral	AX_3  trigonal planar	AX_2 Linear linear
1 lone pair of electrons				
AX_5E  square pyramidal	AX_4E  distorted tetrahedron	AX_3E  pyramidal	AX_2E  nonlinear	AXE Linear linear
2 lone pairs of electrons				
AX_4E_2  square planar	AX_3E_2  T-shaped	AX_2E_2  bent	AXE_2 Linear linear	

These structures can generally be predicted, when A is a nonmetal, using the "valence-shell electron-pair repulsion model (VSEPR) discussed in the next section.

Contributors and Attributions

- Mike Blaber (Florida State University)
- Robyn Rindge (Class of '98) who now works for PDI Dreamworks (look for his name in the credits of Shrek2.). Robyn drew these rotating molecules using Infini-D (MetaCreations).
- Paul Groves, chemistry teacher at South Pasadena High School and [Chemmy Bear\(opens in new window\)](#)

This page titled 3.1.1: Molecular Shapes is shared under a CC BY-NC-SA 4.0 license and was authored, remixed, and/or curated by LibreTexts.

- 9.1: Molecular Shapes is licensed CC BY-NC-SA 3.0.

3.1.2: The VSEPR Model

Learning Objectives

- To use the **VSEPR** model to predict molecular geometries.
- To predict whether a molecule has a dipole moment.

The Lewis electron-pair approach can be used to predict the number and types of bonds between the atoms in a substance, and it indicates which atoms have lone pairs of electrons. This approach gives no information about the actual arrangement of atoms in space, however. We continue our discussion of structure and bonding by introducing the **valence-shell electron-pair repulsion** (VSEPR) model (pronounced “vesper”), which can be used to predict the shapes of many molecules and polyatomic ions. Keep in mind, however, that the VSEPR model, like any model, is a limited representation of reality; the model provides no information about bond lengths or the presence of multiple bonds.

The VSEPR Model

The VSEPR model can predict the structure of nearly any molecule or polyatomic ion in which the central atom is a nonmetal, as well as the structures of many molecules and polyatomic ions with a central metal atom. The premise of the VSEPR theory is that electron pairs located in bonds and lone pairs repel each other and will therefore adopt the geometry that places electron pairs as far apart from each other as possible. This theory is very simplistic and does not account for the subtleties of orbital interactions that influence molecular shapes; however, the simple VSEPR counting procedure accurately predicts the three-dimensional structures of a large number of compounds, which cannot be predicted using the Lewis electron-pair approach.



Figure 3.1.2.1: Common Structures for Molecules and Polyatomic Ions That Consist of a Central Atom Bonded to Two or Three Other Atoms. (CC BY-NC-SA; anonymous)

We can use the VSEPR model to predict the geometry of most polyatomic molecules and ions by focusing only on the number of electron pairs around the *central atom*, ignoring all other valence electrons present. According to this model, valence electrons in the Lewis structure form *groups*, which may consist of a single bond, a double bond, a triple bond, a lone pair of electrons, or even a single unpaired electron, which in the VSEPR model is counted as a lone pair. Because electrons repel each other electrostatically, the most stable arrangement of electron groups (i.e., the one with the lowest energy) is the one that minimizes repulsions. Groups are positioned around the central atom in a way that produces the molecular structure with the lowest energy, as illustrated in Figures 3.1.2.1 and 3.1.2.2.

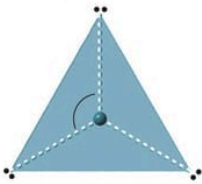
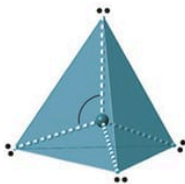
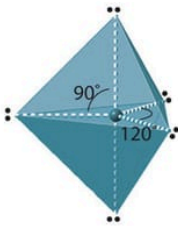
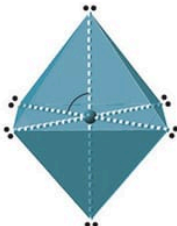
Electron Groups	2	3	4	5	6
Geometry	Linear	Trigonal planar	Tetrahedral	Trigonal bipyramidal	Octahedral
					
Predicted Bond Angles	180°	120°	109.5°	90°, 120°	90°

Figure 3.1.2.2: Electron Geometries for Species with Two to Six Electron Groups. Groups are placed around the central atom in a way that produces a molecular structure with the lowest energy, that is, the one that minimizes repulsions. (CC BY-NC-SA; anonymous)

In the VSEPR model, the molecule or polyatomic ion is given an AX_mE_n designation, where A is the central atom, X is a bonded atom, E is a nonbonding valence electron group (usually a lone pair of electrons), and m and n are integers. Each group around the central atom is designated as a bonding pair (BP) or lone (nonbonding) pair (LP). From the BP and LP interactions we can predict both the relative positions of the atoms and the angles between the bonds, called the bond angles. Using this information, we can describe the molecular geometry, the arrangement of the *bonded atoms* in a molecule or polyatomic ion.

VSEPR Procedure to predict Molecular geometry

This VSEPR procedure is summarized as follows:

1. Draw the Lewis electron structure of the molecule or polyatomic ion.
2. Determine the electron group arrangement around the central atom that minimizes repulsions.
3. Assign an AX_mE_n designation; then identify the LP-LP, LP-BP, or BP-BP interactions and predict deviations from ideal bond angles.
4. Describe the molecular geometry.

We will illustrate the use of this procedure with several examples, beginning with atoms with two electron groups. In our discussion we will refer to Figure 3.1.2.2 and Figure 3.1.2.3, which summarize the common molecular geometries and idealized bond angles of molecules and ions with two to six electron groups.

AX _m E _n Notation	AX ₂	AX ₂ E	AX ₃	AX ₃ E
Geometry	Linear 	Bent (V-shaped) 	Trigonal planar 	Trigonal pyramidal 
Idealized Bond Angles	180°	<180°	120°	<120°
AX _m E _n Notation	AX ₄ E ₂	AX ₄	AX ₅	AX ₆
Geometry	Square planar 	Tetrahedral 	Trigonal bipyramidal 	Octahedral 
Idealized Bond Angles	90°	109.5°	90°, 120°	90°

Figure 3.1.2.3: Common Molecular Geometries for Species with Two to Six Electron Groups. Lone pairs are shown using a dashed line. (CC BY-NC-SA; anonymous)

Linear, bent, trigonal planar, trigonal pyramidal, square planar, tetrahedral, trigonal bipyramidal, octahedral.

Two Electron Groups

Our first example is a molecule with two bonded atoms and no lone pairs of electrons, BeH_2 .

AX₂ Molecules: BeH_2

1. The central atom, beryllium, contributes two valence electrons, and each hydrogen atom contributes one. The Lewis electron structure is

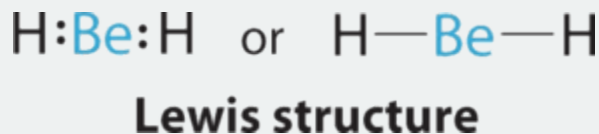
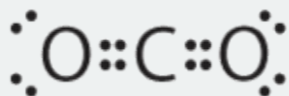


Figure 3.1.2.2 that the arrangement that minimizes repulsions places the groups 180° apart. (CC BY-NC-SA; anonymous)

3. Both groups around the central atom are bonding pairs (BP). Thus BeH_2 is designated as AX₂.
4. From Figure 3.1.2.3 we see that with two bonding pairs, the molecular geometry that minimizes repulsions in BeH_2 is *linear*.

AX₂ Molecules: CO_2

1. The central atom, carbon, contributes four valence electrons, and each oxygen atom contributes six. The Lewis electron structure is



2. The carbon atom forms two double bonds. Each double bond is a group, so there are two electron groups around the central atom. Like BeH_2 , the arrangement that minimizes repulsions places the groups 180° apart.

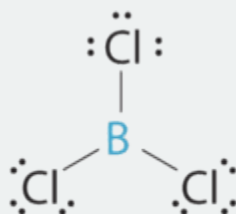
3. Once again, both groups around the central atom are bonding pairs (BP), so CO_2 is designated as AX_2 .

4. VSEPR only recognizes groups around the *central* atom. Thus the lone pairs on the oxygen atoms do not influence the molecular geometry. With two bonding pairs on the central atom and no lone pairs, the molecular geometry of CO_2 is linear (Figure 3.1.2.3). The structure of CO_2 is shown in Figure 3.1.2.1.

Three Electron Groups

AX_3 Molecules: BCl_3

1. The central atom, boron, contributes three valence electrons, and each chlorine atom contributes seven valence electrons. The Lewis electron structure is



Lewis structure

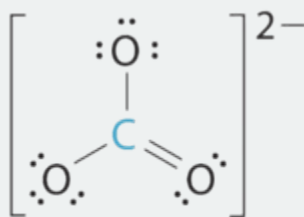
Figure 3.1.2.2): (CC BY-NC-SA; anonymous)

3. All electron groups are bonding pairs (BP), so the structure is designated as AX_3 .

4. From Figure 3.1.2.3 we see that with three bonding pairs around the central atom, the molecular geometry of BCl_3 is *trigonal planar*, as shown in Figure 3.1.2.2.

AX_3 Molecules: CO_3^{2-}

1. The central atom, carbon, has four valence electrons, and each oxygen atom has six valence electrons. As you learned previously, the Lewis electron structure of one of three resonance forms is represented as



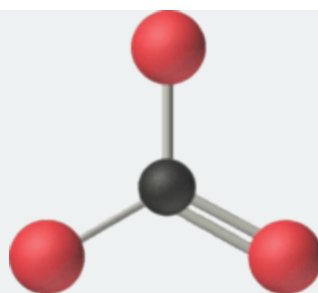
Lewis structure

Figure 3.1.2.2).

The three oxygens are arranged in a triangular shape with carbon at the center. Two of the oxygens have three lone pairs. One oxygen has 2 lone pairs and is double bonded to the carbon. The molecule has a minus 2 charge.

3. All electron groups are bonding pairs (BP). With three bonding groups around the central atom, the structure is designated as AX_3 .

4. We see from Figure 3.1.2.3 that the molecular geometry of CO_3^{2-} is trigonal planar with bond angles of 120° .



Molecular geometry
(trigonal planar)

In our next example we encounter the effects of lone pairs and multiple bonds on molecular geometry for the first time.

AX₂E Molecules: SO₂

1. The central atom, sulfur, has 6 valence electrons, as does each oxygen atom. With 18 valence electrons, the Lewis electron structure is shown below.

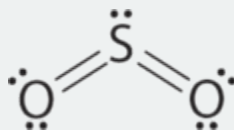


Figure 3.1.2.2): (CC BY-NC-SA; anonymous)

The two oxygens are double bonded to the sulfur. The oxygens have 2 lone pairs while sulfur had one lone pair.

3. There are two bonding pairs and one lone pair, so the structure is designated as AX₂E. This designation has a total of three electron pairs, two X and one E. Because a lone pair is not shared by two nuclei, it occupies more space near the central atom than a bonding pair (Figure 3.1.2.4). Thus bonding pairs and lone pairs repel each other electrostatically in the order BP-BP < LP-BP < LP-LP. In SO₂, we have one BP-BP interaction and two LP-BP interactions.

4. The molecular geometry is described only by the positions of the nuclei, *not* by the positions of the lone pairs. Thus with two nuclei and one lone pair the shape is *bent*, or *V shaped*, which can be viewed as a trigonal planar arrangement with a missing vertex (Figures 3.1.2.2 and 3.1.2.3). The O-S-O bond angle is expected to be *less than* 120° because of the extra space taken up by the lone pair.

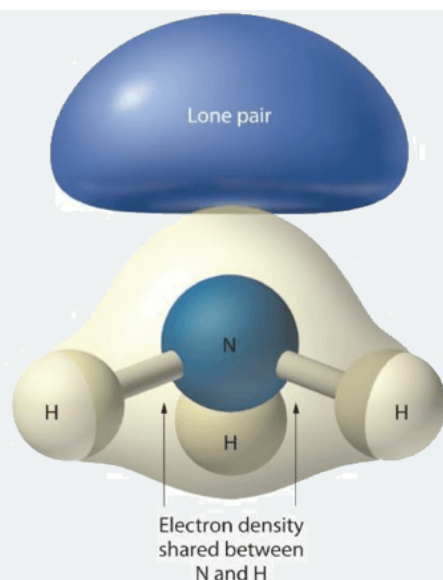
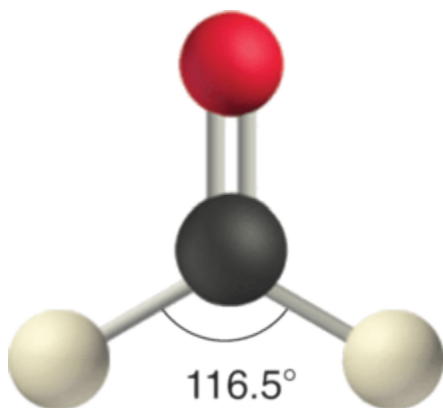


Figure 3.1.2.4: The Difference in the Space Occupied by a Lone Pair of Electrons and by a Bonding Pair. (CC BY-NC-SA; anonymous)

As with SO_2 , this composite model of electron distribution and negative electrostatic potential in ammonia shows that a lone pair of electrons occupies a larger region of space around the nitrogen atom than does a bonding pair of electrons that is shared with a hydrogen atom.

Like lone pairs of electrons, multiple bonds occupy more space around the central atom than a single bond, which can cause other bond angles to be somewhat smaller than expected. This is because a multiple bond has a higher electron density than a single bond, so its electrons occupy more space than those of a single bond. For example, in a molecule such as CH_2O (AX_3), whose structure is shown below, the double bond repels the single bonds more strongly than the single bonds repel each other. This causes a deviation from ideal geometry (an $\text{H}-\text{C}-\text{H}$ bond angle of 116.5° rather than 120°).

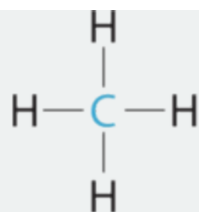


Four Electron Groups

One of the limitations of Lewis structures is that they depict molecules and ions in only two dimensions. With four electron groups, we must learn to show molecules and ions in three dimensions.

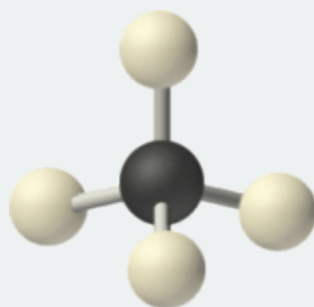
AX_4 Molecules: CH_4

1. The central atom, carbon, contributes four valence electrons, and each hydrogen atom has one valence electron, so the full Lewis electron structure is



Lewis structure

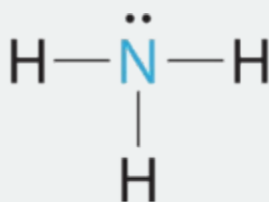
2. There are four electron groups around the central atom. As shown in Figure 3.1.2.2, repulsions are minimized by placing the groups in the corners of a tetrahedron with bond angles of 109.5° .
3. All electron groups are bonding pairs, so the structure is designated as AX_4 .
4. With four bonding pairs, the molecular geometry of methane is *tetrahedral* (Figure 3.1.2.3).



Molecular geometry
(tetrahedral)

AX_3E Molecules: NH_3

1. In ammonia, the central atom, nitrogen, has five valence electrons and each hydrogen donates one valence electron, producing the Lewis electron structure



Lewis structure

2. There are four electron groups around nitrogen, three bonding pairs and one lone pair. Repulsions are minimized by directing each hydrogen atom and the lone pair to the corners of a tetrahedron.
3. With three bonding pairs and one lone pair, the structure is designated as AX_3E . This designation has a total of four electron pairs, three X and one E. We expect the LP-BP interactions to cause the bonding pair angles to deviate significantly from the angles of a perfect tetrahedron.

4. There are three nuclei and one lone pair, so the molecular geometry is *trigonal pyramidal*. In essence, this is a tetrahedron with a vertex missing (Figure 3.1.2.3). However, the H-N-H bond angles are less than the ideal angle of 109.5° because of LP-BP repulsions (Figure 3.1.2.3 and Figure 3.1.2.4).

AX₂E₂ Molecules: H₂O

1. Oxygen has six valence electrons and each hydrogen has one valence electron, producing the Lewis electron structure

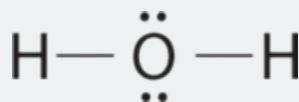
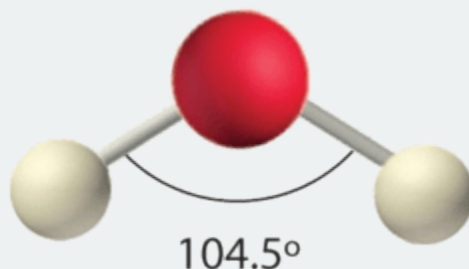


Figure 3.1.2.2: (CC BY-NC-SA; anonymous)

3. With two bonding pairs and two lone pairs, the structure is designated as AX₂E₂ with a total of four electron pairs. Due to LP-LP, LP-BP, and BP-BP interactions, we expect a significant deviation from idealized tetrahedral angles.

4. With two hydrogen atoms and two lone pairs of electrons, the structure has significant lone pair interactions. There are two nuclei about the central atom, so the molecular shape is *bent*, or *V shaped*, with an H-O-H angle that is even less than the H-N-H angles in NH₃, as we would expect because of the presence of two lone pairs of electrons on the central atom rather than one. This molecular shape is essentially a tetrahedron with two missing vertices.



Five Electron Groups

In previous examples it did not matter where we placed the electron groups because all positions were equivalent. In some cases, however, the positions are not equivalent. We encounter this situation for the first time with five electron groups.

AX₅ Molecules: PCl₅

1. Phosphorus has five valence electrons and each chlorine has seven valence electrons, so the Lewis electron structure of PCl₅ is

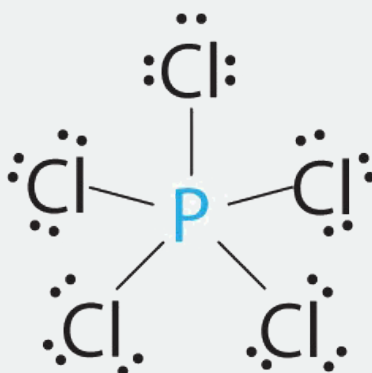
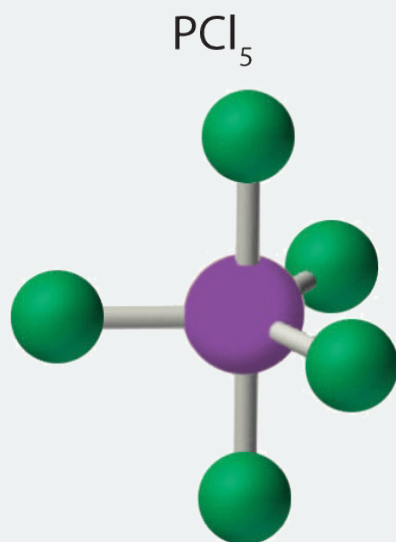


Figure 3.1.2.2): (CC BY-NC-SA; anonymous)

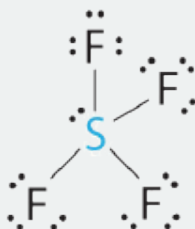
3. All electron groups are bonding pairs, so the structure is designated as AX_5 . There are no lone pair interactions.

4. The molecular geometry of PCl_5 is *trigonal bipyramidal*, as shown in Figure 3.1.2.3. The molecule has three atoms in a plane in *equatorial* positions and two atoms above and below the plane in *axial* positions. The three equatorial positions are separated by 120° from one another, and the two axial positions are at 90° to the equatorial plane. The axial and equatorial positions are not chemically equivalent, as we will see in our next example.



AX₄E Molecules: SF₄

1. The sulfur atom has six valence electrons and each fluorine has seven valence electrons, so the Lewis electron structure is



Lewis structure

Four fluorenes are bonded to a central sulfur. Each fluorine has three lone pairs. Sulfur has one lone pair.

With an expanded valence, this species is an exception to the octet rule.

2. There are five groups around sulfur, four bonding pairs and one lone pair. With five electron groups, the lowest energy arrangement is a trigonal bipyramid, as shown in Figure 3.1.2.2.

3. We designate SF_4 as AX_4E ; it has a total of five electron pairs. However, because the axial and equatorial positions are not chemically equivalent, where do we place the lone pair? If we place the lone pair in the axial position, we have three LP-BP repulsions at 90° . If we place it in the equatorial position, we have two 90° LP-BP repulsions at 90° . With fewer 90° LP-BP repulsions, we can predict that the structure with the lone pair of electrons in the *equatorial position* is *more stable than the one with the lone pair in the axial position*. We also expect a deviation from ideal geometry because a lone pair of electrons occupies more space than a bonding pair.

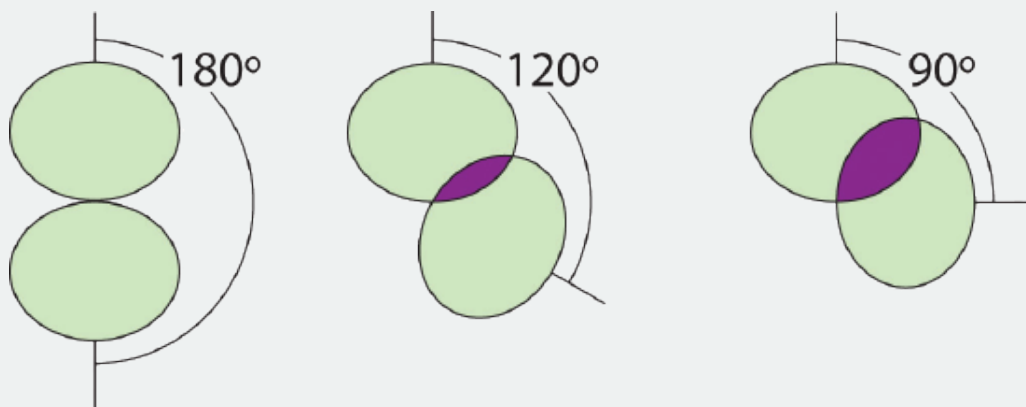
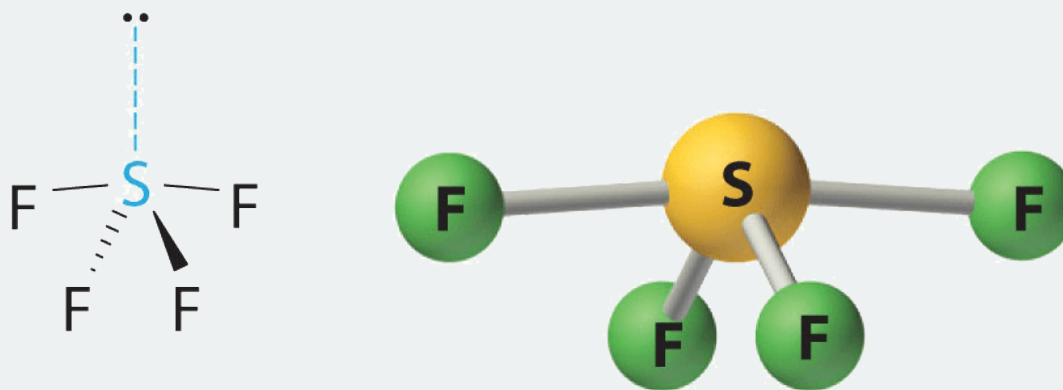


Figure 3.1.2.5: Illustration of the Area Shared by Two Electron Pairs versus the Angle between Them

180 degree angle has no shared space between two electron pairs, 120 degree angle has some shared area between two electron pairs. 90 degree angle has more shared space than 120.

At 90° , the two electron pairs share a relatively large region of space, which leads to strong repulsive electron-electron interactions.

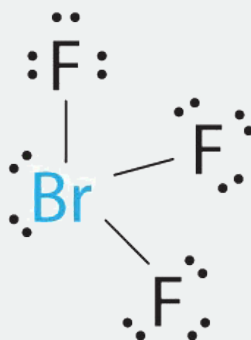
4. With four nuclei and one lone pair of electrons, the molecular structure is based on a trigonal bipyramid with a missing equatorial vertex; it is described as a *seesaw*. The $\text{F}_{\text{axial}}\text{-S-F}_{\text{axial}}$ angle is 173° rather than 180° because of the lone pair of electrons in the equatorial plane.



Molecular geometry (seesaw)

AX₃E₂ Molecules: BrF₃

1. The bromine atom has seven valence electrons, and each fluorine has seven valence electrons, so the Lewis electron structure is



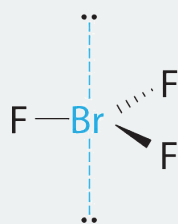
Lewis structure

Three fluorines are bonded to a central bromine. Each fluorine has three lone pairs, Bromine has two lone pairs.

Once again, we have a compound that is an exception to the octet rule.

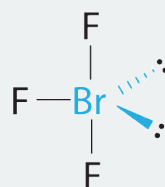
2. There are five groups around the central atom, three bonding pairs and two lone pairs. We again direct the groups toward the vertices of a trigonal bipyramid.

3. With three bonding pairs and two lone pairs, the structural designation is AX₃E₂ with a total of five electron pairs. Because the axial and equatorial positions are not equivalent, we must decide how to arrange the groups to minimize repulsions. If we place both lone pairs in the axial positions, we have six LP-BP repulsions at 90°. If both are in the equatorial positions, we have four LP-BP repulsions at 90°. If one lone pair is axial and the other equatorial, we have one LP-LP repulsion at 90° and three LP-BP repulsions at 90°:



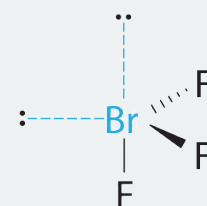
Lone pairs axial

(a)



Lone pairs equatorial

(b)



Lone pairs axial and equatorial

(c)

Interactions

90° LP-LP	0	0	1
90° LP-BP	6	4	3

If the lone pairs are axial, the 90 degree LP-LP interactions are 0 and the 90 degree LP-BP interaction is zero. If the Lone pairs are equatorial there are zero 90 degree LP-LP interactions and four 90 degree LP-BP interactions. If the lone pairs are axial and equatorial there is one 90 degree LP-LP interaction and three 90 degree LP-BP interaction.

Structure (c) can be eliminated because it has a LP-LP interaction at 90°. Structure (b), with fewer LP-BP repulsions at 90° than (a), is lower in energy. However, we predict a deviation in bond angles because of the presence of the two lone pairs of electrons.

4. The three nuclei in BrF_3 determine its molecular structure, which is described as *T shaped*. This is essentially a trigonal bipyramid that is missing two equatorial vertices. The $\text{F}_{\text{axial}}\text{-Br-F}_{\text{axial}}$ angle is 172°, less than 180° because of LP-BP repulsions (Figure 3.1.2.2.1).

Because lone pairs occupy more space around the central atom than bonding pairs, electrostatic repulsions are more important for lone pairs than for bonding pairs.

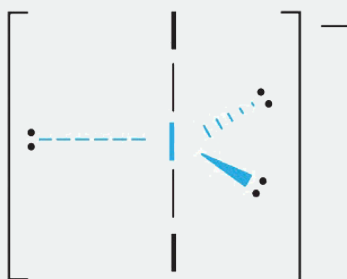
AX_2E_3 Molecules: I_3^-

1. Each iodine atom contributes seven electrons and the negative charge one, so the Lewis electron structure is



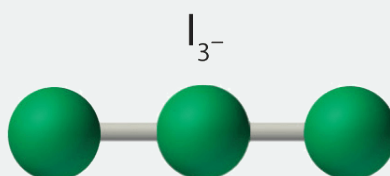
2. There are five electron groups about the central atom in I_3^- , two bonding pairs and three lone pairs. To minimize repulsions, the groups are directed to the corners of a trigonal bipyramid.

3. With two bonding pairs and three lone pairs, I_3^- has a total of five electron pairs and is designated as AX_2E_3 . We must now decide how to arrange the lone pairs of electrons in a trigonal bipyramid in a way that minimizes repulsions. Placing them in the axial positions eliminates 90° LP-LP repulsions and minimizes the number of 90° LP-BP repulsions.



The three lone pairs of electrons have equivalent interactions with the three iodine atoms, so we do not expect any deviations in bonding angles.

4. With three nuclei and three lone pairs of electrons, the molecular geometry of I_3^- is linear. This can be described as a trigonal bipyramid with three equatorial vertices missing. The ion has an I–I–I angle of 180° , as expected.

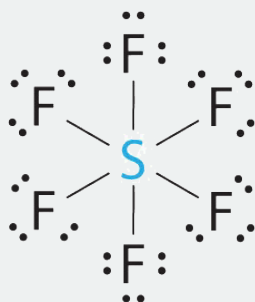


Six Electron Groups

Six electron groups form an *octahedron*, a polyhedron made of identical equilateral triangles and six identical vertices (Figure 3.1.2.2.)

AX₆ Molecules: SF₆

1. The central atom, sulfur, contributes six valence electrons, and each fluorine atom has seven valence electrons, so the Lewis electron structure is



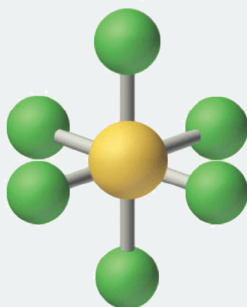
Lewis structure

With an expanded valence, this species is an exception to the octet rule.

2. There are six electron groups around the central atom, each a bonding pair. We see from Figure 3.1.2.2 that the geometry that minimizes repulsions is *octahedral*.

3. With only bonding pairs, SF₆ is designated as AX₆. All positions are chemically equivalent, so all electronic interactions are equivalent.

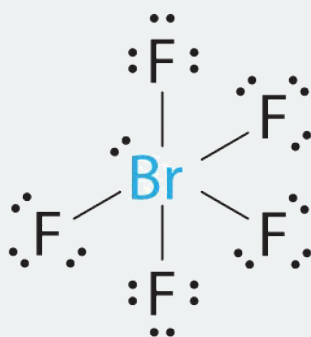
4. There are six nuclei, so the molecular geometry of SF_6 is octahedral.



Molecular geometry
(octahedral)

AX₅E Molecules: BrF_5

1. The central atom, bromine, has seven valence electrons, as does each fluorine, so the Lewis electron structure is

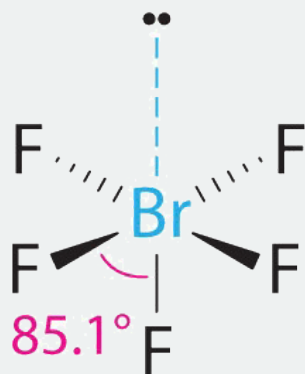


Lewis structure

Five fluorines are bonded to a central bromine. Each fluorine has three lone pairs, Bromine has one lone pair.

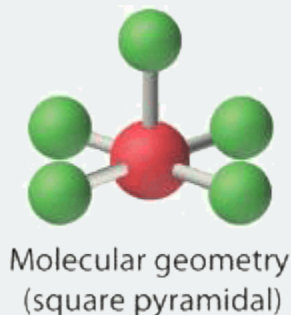
With its expanded valence, this species is an exception to the octet rule.

2. There are six electron groups around the Br, five bonding pairs and one lone pair. Placing five F atoms around Br while minimizing BP-BP and LP-BP repulsions gives the following structure:



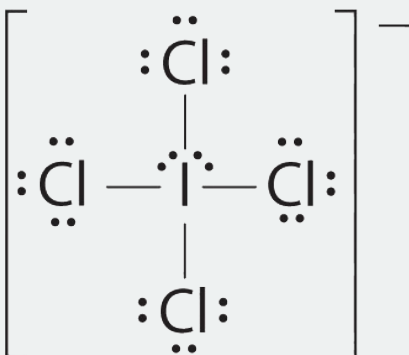
3. With five bonding pairs and one lone pair, BrF_5 is designated as AX_5E ; it has a total of six electron pairs. The BrF_5 structure has four fluorine atoms in a plane in an equatorial position and one fluorine atom and the lone pair of electrons in the axial positions. We expect all $\text{F}_{\text{axial}}\text{-Br-F}_{\text{equatorial}}$ angles to be less than 90° because of the lone pair of electrons, which occupies more space than the bonding electron pairs.

4. With five nuclei surrounding the central atom, the molecular structure is based on an octahedron with a vertex missing. This molecular structure is *square pyramidal*. The $\text{F}_{\text{axial}}\text{-Br-F}_{\text{equatorial}}$ angles are 85.1° , less than 90° because of LP-BP repulsions.



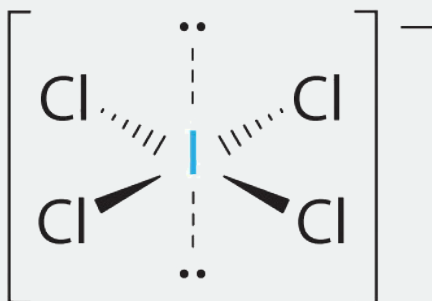
AX_4E_2 Molecules: ICl_4^-

1. The central atom, iodine, contributes seven electrons. Each chlorine contributes seven, and there is a single negative charge. The Lewis electron structure is



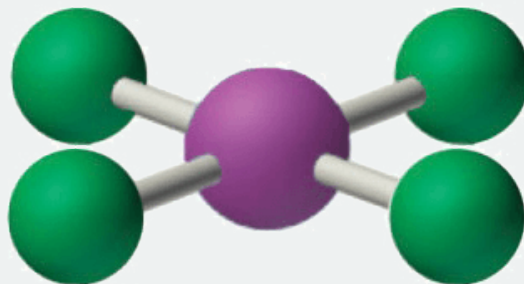
Four chlorines are bonded to a central iodine. Each chlorine has three electron pairs. The iodine has two electron pairs. The molecule is negatively charged.

2. There are six electron groups around the central atom, four bonding pairs and two lone pairs. The structure that minimizes LP-LP, LP-BP, and BP-BP repulsions is



3. ICl_4^- is designated as AX_4E_2 and has a total of six electron pairs. Although there are lone pairs of electrons, with four bonding electron pairs in the equatorial plane and the lone pairs of electrons in the axial positions, all LP-BP repulsions are the same. Therefore, we do not expect any deviation in the Cl-I-Cl bond angles.

4. With five nuclei, the ICl_4^- ion forms a molecular structure that is *square planar*, an octahedron with two opposite vertices missing.



The relationship between the number of electron groups around a central atom, the number of lone pairs of electrons, and the molecular geometry is summarized in Figure 3.1.2.6.

Electron Groups	2	3	4	5	6
Molecular Geometry	 Linear	 Trigonal planar	 Tetrahedral	 Trigonal bipyramidal	 Octahedral
Zero Lone Pairs	 Linear AX_2	 Trigonal planar AX_3	 Tetrahedral AX_4	 Trigonal bipyramidal AX_5	 Octahedral AX_6
One Lone Pair		 Bent (V-shaped) AX_2E	 Trigonal pyramidal AX_3E	 Seesaw AX_4E One axial lone pair	 Square pyramidal AX_5E
Two Lone Pairs			 Bent (V-shaped) AX_2E_2	 T-shaped AX_3E_2 Two axial lone pairs	 Square planar AX_4E_2
Three Lone Pairs				 Linear AX_2E_3 Three axial lone pairs	

Figure 3.1.2.6: Overview of Molecular Geometries

YouTube Video

This interactive element is not available in this format. Visit the link or scan the QR code to access it online.

[View this YouTube Video online](#)



Example 3.1.2.1

Using the VSEPR model, predict the molecular geometry of each molecule or ion.

1. PF_5 (phosphorus pentafluoride, a catalyst used in certain organic reactions)
2. H_3O^+ (hydronium ion)

Given: two chemical species

Asked for: molecular geometry

Strategy:

- A. Draw the Lewis electron structure of the molecule or polyatomic ion.
- B. Determine the electron group arrangement around the central atom that minimizes repulsions.
- C. Assign an AX_mE_n designation; then identify the LP-LP, LP-BP, or BP-BP interactions and predict deviations in bond angles.
- D. Describe the molecular geometry.

Solution:

1. **A** The central atom, P, has five valence electrons and each fluorine has seven valence electrons, so the Lewis structure of PF_5 is

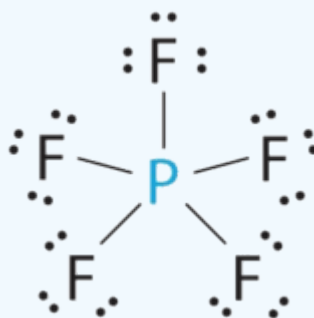
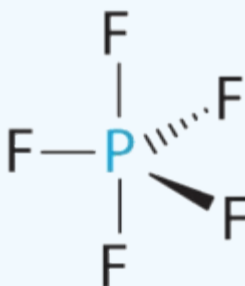


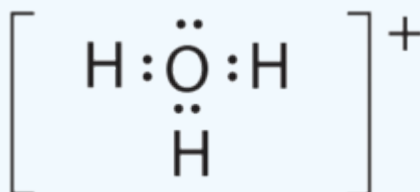
Figure 3.1.2.6): (CC BY-NC-SA; anonymous)

C All electron groups are bonding pairs, so PF_5 is designated as AX_5 . Notice that this gives a total of five electron pairs. With no lone pair repulsions, we do not expect any bond angles to deviate from the ideal.

D The PF_5 molecule has five nuclei and no lone pairs of electrons, so its molecular geometry is trigonal bipyramidal.



2. **A** The central atom, O, has six valence electrons, and each H atom contributes one valence electron. Subtracting one electron for the positive charge gives a total of eight valence electrons, so the Lewis electron structure is

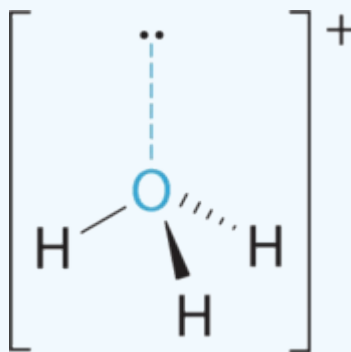


Three hydrogens are bonded to a central oxygen. The oxygen has two lone pairs. The molecule has a charge of plus one.

B There are four electron groups around oxygen, three bonding pairs and one lone pair. Like NH_3 , repulsions are minimized by directing each hydrogen atom and the lone pair to the corners of a tetrahedron.

C With three bonding pairs and one lone pair, the structure is designated as AX_3E and has a total of four electron pairs (three X and one E). We expect the LP-BP interactions to cause the bonding pair angles to deviate significantly from the angles of a perfect tetrahedron.

D There are three nuclei and one lone pair, so the molecular geometry is *trigonal pyramidal*, in essence a tetrahedron missing a vertex. However, the H-O-H bond angles are less than the ideal angle of 109.5° because of LP-BP repulsions:



Exercise 3.1.2.1

Using the VSEPR model, predict the molecular geometry of each molecule or ion.

- XeO_3
- PF_6^-
- NO_2^+

Example 3.1.2.2

Predict the molecular geometry of each molecule.

1. XeF_2
2. SnCl_2

Given: two chemical compounds

Asked for: molecular geometry

Strategy:

Use the strategy given in Example 3.1.2.1.

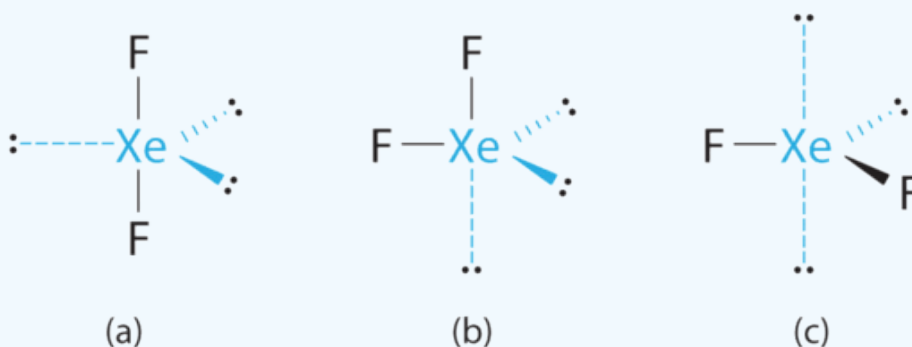
Solution:

1. **A** Xenon contributes eight electrons and each fluorine seven valence electrons, so the Lewis electron structure is



B There are five electron groups around the central atom, two bonding pairs and three lone pairs. Repulsions are minimized by placing the groups in the corners of a trigonal bipyramid.

C From B, XeF_2 is designated as AX_2E_3 and has a total of five electron pairs (two X and three E). With three lone pairs about the central atom, we can arrange the two F atoms in three possible ways: both F atoms can be axial, one can be axial and one equatorial, or both can be equatorial:



Interactions

90 LP–LP

0

2

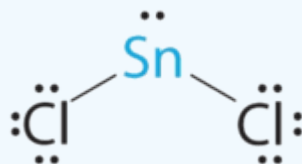
2

If the two F atoms are axial there are zero 90° LP–LP interactions. If the two F atoms are axial and equatorial or just equatorial, there are 2 90° LP–LP interactions.

The structure with the lowest energy is the one that minimizes LP–LP repulsions. Both (b) and (c) have two 90° LP–LP interactions, whereas structure (a) has none. Thus both F atoms are in the axial positions, like the two iodine atoms around the central iodine in I_3^- . All LP–BP interactions are equivalent, so we do not expect a deviation from an ideal 180° in the F–Xe–F bond angle.

D With two nuclei about the central atom, the molecular geometry of XeF_2 is linear. It is a trigonal bipyramid with three missing equatorial vertices.

2. **A** The tin atom donates 4 valence electrons and each chlorine atom donates 7 valence electrons. With 18 valence electrons, the Lewis electron structure is



Two chlorines are bonded to a central tin. Each chlorine has three lone pairs. Tin has one lone pair.

B There are three electron groups around the central atom, two bonding groups and one lone pair of electrons. To minimize repulsions the three groups are initially placed at 120° angles from each other.

C From B we designate SnCl_2 as AX_2E . It has a total of three electron pairs, two X and one E. Because the lone pair of electrons occupies more space than the bonding pairs, we expect a decrease in the Cl-Sn-Cl bond angle due to increased LP-BP repulsions.

D With two nuclei around the central atom and one lone pair of electrons, the molecular geometry of SnCl_2 is bent, like SO_2 , but with a Cl-Sn-Cl bond angle of 95° . The molecular geometry can be described as a trigonal planar arrangement with one vertex missing.

Exercise 3.1.2.2

Predict the molecular geometry of each molecule.

- SO_3
- XeF_4

Answer a available at the end of this section.

YouTube Video

This interactive element is not available in this format. Visit the link or scan the QR code to access it online.

[View this YouTube Video online](#)

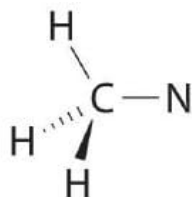


Molecules with No Single Central Atom

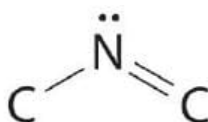
The VSEPR model can be used to predict the structure of somewhat more complex molecules with no single central atom by treating them as linked AX_mE_n fragments. We will demonstrate with methyl isocyanate ($\text{CH}_3\text{-N=C=O}$), a volatile and highly toxic molecule that is used to produce the pesticide Sevin. In 1984, large quantities of Sevin were accidentally released in Bhopal, India, when water leaked into storage tanks. The resulting highly exothermic reaction caused a rapid increase in pressure that ruptured the tanks, releasing large amounts of methyl isocyanate that killed approximately 3800 people and wholly or partially disabled about 50,000 others. In addition, there was significant damage to livestock and crops.

We can treat methyl isocyanate as linked AX_mE_n fragments beginning with the carbon atom at the left, which is connected to three H atoms and one N atom by single bonds. The four bonds around carbon mean that it must be surrounded by four bonding electron pairs in a configuration similar to AX_4 . We can therefore predict the $\text{CH}_3\text{-N}$ portion of the molecule to be roughly

tetrahedral, similar to methane:



The nitrogen atom is connected to one carbon by a single bond and to the other carbon by a double bond, producing a total of three bonds, C–N=C. For nitrogen to have an octet of electrons, it must also have a lone pair:



One carbon bonded to nitrogen and another carbon double bonded to the nitrogen. The nitrogen has one lone pair.

Because multiple bonds are not shown in the VSEPR model, the nitrogen is effectively surrounded by three electron pairs. Thus according to the VSEPR model, the C–N=C fragment should be bent with an angle less than 120° .

The carbon in the –N=C=O fragment is doubly bonded to both nitrogen and oxygen, which in the VSEPR model gives carbon a total of two electron pairs. The N=C=O angle should therefore be 180° , or linear. The three fragments combine to give the following structure:

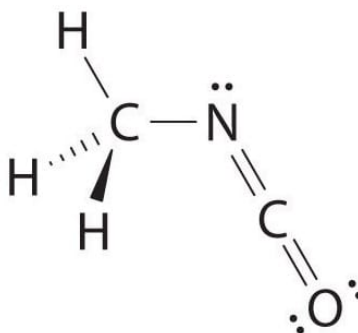


Figure 3.1.2.7).

Three hydrogens are bonded to a carbon. The carbon is also bonded to a nitrogen. The nitrogen is double bonded to another carbon. The second carbon is double bonded to an oxygen. The nitrogen has one lone pair. The oxygen has two lone pairs.

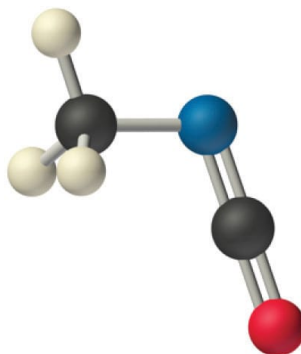


Figure 3.1.2.7: The Experimentally Determined Structure of Methyl Isocyanate

Certain patterns are seen in the structures of moderately complex molecules. For example, carbon atoms with four bonds (such as the carbon on the left in methyl isocyanate) are generally tetrahedral. Similarly, the carbon atom on the right has two double bonds that are similar to those in CO_2 , so its geometry, like that of CO_2 , is linear. Recognizing similarities to simpler molecules

will help you predict the molecular geometries of more complex molecules.

Example 3.1.2.3

Use the VSEPR model to predict the molecular geometry of propyne ($\text{H}_3\text{C}-\text{C}\equiv\text{CH}$), a gas with some anesthetic properties.

Given: chemical compound

Asked for: molecular geometry

Strategy:

Count the number of electron groups around each carbon, recognizing that in the VSEPR model, a multiple bond counts as a single group. Use Figure 3.1.2.3 to determine the molecular geometry around each carbon atom and then deduce the structure of the molecule as a whole.

Solution:

Because the carbon atom on the left is bonded to four other atoms, we know that it is approximately tetrahedral. The next two carbon atoms share a triple bond, and each has an additional single bond. Because a multiple bond is counted as a single bond in the VSEPR model, each carbon atom behaves as if it had two electron groups. This means that both of these carbons are linear, with $\text{C}-\text{C}\equiv\text{C}$ and $\text{C}\equiv\text{C}-\text{H}$ angles of 180° .

Exercise 3.1.2.3

Predict the geometry of allene ($\text{H}_2\text{C}=\text{C}=\text{CH}_2$), a compound with narcotic properties that is used to make more complex organic molecules.

Answer available at the end of this section.

Molecular Dipole Moments

You previously learned how to calculate the **dipole moments** of simple diatomic molecules. In more complex molecules with polar covalent bonds, the three-dimensional geometry and the compound's symmetry determine whether there is a net dipole moment. Mathematically, dipole moments are *vectors*; they possess both a *magnitude* and a *direction*. The dipole moment of a molecule is therefore the *vector sum* of the dipole moments of the individual bonds in the molecule. If the individual bond dipole moments cancel one another, there is no net dipole moment. Such is the case for CO_2 , a linear molecule (Figure 3.1.2.8a). Each C–O bond in CO_2 is polar, yet experiments show that the CO_2 molecule has no dipole moment. Because the two C–O bond dipoles in CO_2 are equal in magnitude and oriented at 180° to each other, they cancel. As a result, the CO_2 molecule has no *net* dipole moment even though it has a substantial separation of charge. In contrast, the H_2O molecule is not linear (Figure 3.1.2.8b); it is bent in three-dimensional space, so the dipole moments do not cancel each other. Thus a molecule such as H_2O has a net dipole moment. We expect the concentration of negative charge to be on the oxygen, the more electronegative atom, and positive charge on the two hydrogens. This charge polarization allows H_2O to hydrogen-bond to other polarized or charged species, including other water molecules.

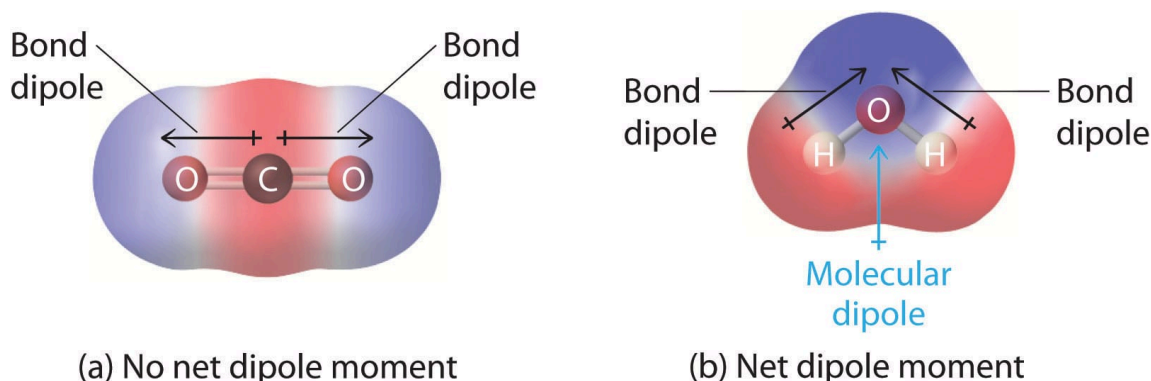


Figure 3.1.2.8: How Individual Bond Dipole Moments Are Added Together to Give an Overall Molecular Dipole Moment for Two Triatomic Molecules with Different Structures. (a) In CO_2 , the C–O bond dipoles are equal in magnitude but oriented in opposite directions (at 180°). Their vector sum is zero, so CO_2 therefore has no net dipole. (b) In H_2O , the O–H bond dipoles are also equal in magnitude, but they are oriented at 104.5° to each other. Hence the vector sum is not zero, and H_2O has a net dipole moment.

Other examples of molecules with polar bonds are shown in Figure 3.1.2.9. In molecular geometries that are highly symmetrical (most notably tetrahedral and square planar, trigonal bipyramidal, and octahedral), individual bond dipole moments completely cancel, and there is no net dipole moment. Although a molecule like CHCl_3 is best described as tetrahedral, the atoms bonded to carbon are not identical. Consequently, the bond dipole moments cannot cancel one another, and the molecule has a dipole moment. Due to the arrangement of the bonds in molecules that have V-shaped, trigonal pyramidal, seesaw, T-shaped, and square pyramidal geometries, the bond dipole moments cannot cancel one another. Consequently, molecules with these geometries always have a nonzero dipole moment. Molecules with asymmetrical charge distributions have a net dipole moment.

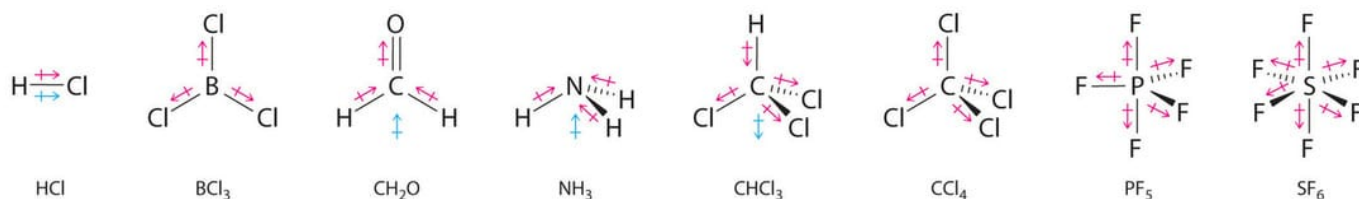


Figure 3.1.2.9: Molecules with Polar Bonds. Individual bond dipole moments are indicated in red. Due to their different three-dimensional structures, some molecules with polar bonds have a net dipole moment (HCl , CH_2O , NH_3 , and CHCl_3), indicated in blue, whereas others do not because the bond dipole moments cancel (BCl_3 , CCl_4 , PF_5 , and SF_6).

YouTube Video

This interactive element is not available in this format. Visit the link or scan the QR code to access it online.

[View this YouTube Video online](#)



Example 3.1.2.4

Which molecule(s) has a net dipole moment?

- H_2S
- NHF_2
- BF_3

Given: three chemical compounds

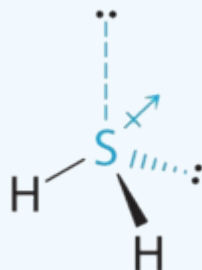
Asked for: net dipole moment

Strategy:

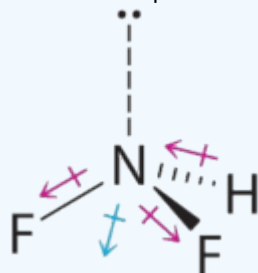
For each three-dimensional molecular geometry, predict whether the bond dipoles cancel. If they do not, then the molecule has a net dipole moment.

Solution:

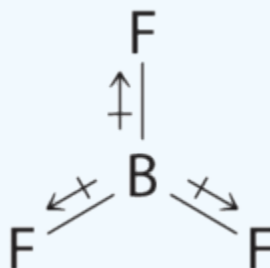
1. The total number of electrons around the central atom, S, is eight, which gives four electron pairs. Two of these electron pairs are bonding pairs and two are lone pairs, so the molecular geometry of H_2S is bent (Figure 3.1.2.6). The bond dipoles cannot cancel one another, so the molecule has a net dipole moment.



2. Difluoroamine has a trigonal pyramidal molecular geometry. Because there is one hydrogen and two fluorines, and because of the lone pair of electrons on nitrogen, the molecule is not symmetrical, and the bond dipoles of NHF_2 cannot cancel one another. This means that NHF_2 has a net dipole moment. We expect polarization from the two fluorine atoms, the most electronegative atoms in the periodic table, to have a greater affect on the net dipole moment than polarization from the lone pair of electrons on nitrogen.



3. The molecular geometry of BF_3 is trigonal planar. Because all the B-F bonds are equal and the molecule is highly symmetrical, the dipoles cancel one another in three-dimensional space. Thus BF_3 has a net dipole moment of zero:



Exercise 3.1.2.4

Which molecule(s) has a net dipole moment?

- CH_3Cl
- SO_3
- XeO_3

Answer available at the end of this section.

Summary

Lewis electron structures give no information about **molecular geometry**, the arrangement of bonded atoms in a molecule or polyatomic ion, which is crucial to understanding the chemistry of a molecule. The **valence-shell electron-pair repulsion (VSEPR) model** allows us to predict which of the possible structures is actually observed in most cases. It is based on the assumption that pairs of electrons occupy space, and the lowest-energy structure is the one that minimizes electron pair–electron pair repulsions. In the VSEPR model, the molecule or polyatomic ion is given an AX_mE_n designation, where A is the central atom, X is a bonded atom, E is a nonbonding valence electron group (usually a lone pair of electrons), and m and n are integers. Each group around the central atom is designated as a bonding pair (BP) or lone (nonbonding) pair (LP). From the BP and LP interactions we can predict both the relative positions of the atoms and the angles between the bonds, called the **bond angles**. From this we can describe the **molecular geometry**. The VSEPR model can be used to predict the shapes of many molecules and polyatomic ions, but it gives no information about bond lengths and the presence of multiple bonds. A combination of VSEPR and a bonding model, such as Lewis electron structures, is necessary to understand the presence of multiple bonds.

Molecules with polar covalent bonds can have a *dipole moment*, an asymmetrical distribution of charge that results in a tendency for molecules to align themselves in an applied electric field. Any diatomic molecule with a polar covalent bond has a dipole moment, but in polyatomic molecules, the presence or absence of a net dipole moment depends on the structure. For some highly symmetrical structures, the individual bond dipole moments cancel one another, giving a dipole moment of zero.

Answers

Exercise 3.1.2.1

trigonal pyramidal
octahedral
linear

Exercise 3.1.2.2

trigonal planar
square planar

Exercise 3.1.2.3

The terminal carbon atoms are trigonal planar, the central carbon is linear, and the C–C–C angle is 180° .

Exercise 3.1.2.4

CH_3Cl and XeO_3

- [9.2: The VSEPR Model](#) is licensed [CC BY-NC-SA 3.0](#).

3.1.3: Molecular Shape and Molecular Polarity

Learning Objectives

- To calculate the percent ionic character of a covalent polar bond

Previously, we described the two idealized extremes of chemical bonding:

- ionic bonding**—in which one or more electrons are transferred completely from one atom to another, and the resulting ions are held together by purely electrostatic forces—and
- covalent bonding**, in which electrons are shared *equally* between two atoms.

Most compounds, however, have polar covalent bonds, which means that electrons are shared *unequally* between the bonded atoms. Figure 3.1.3.1 compares the electron distribution in a polar covalent bond with those in an ideally covalent and an ideally ionic bond. Recall that a lowercase Greek delta (δ) is used to indicate that a bonded atom possesses a partial positive charge, indicated by δ^+ , or a partial negative charge, indicated by δ^- , and a bond between two atoms that possess partial charges is a *polar bond*.

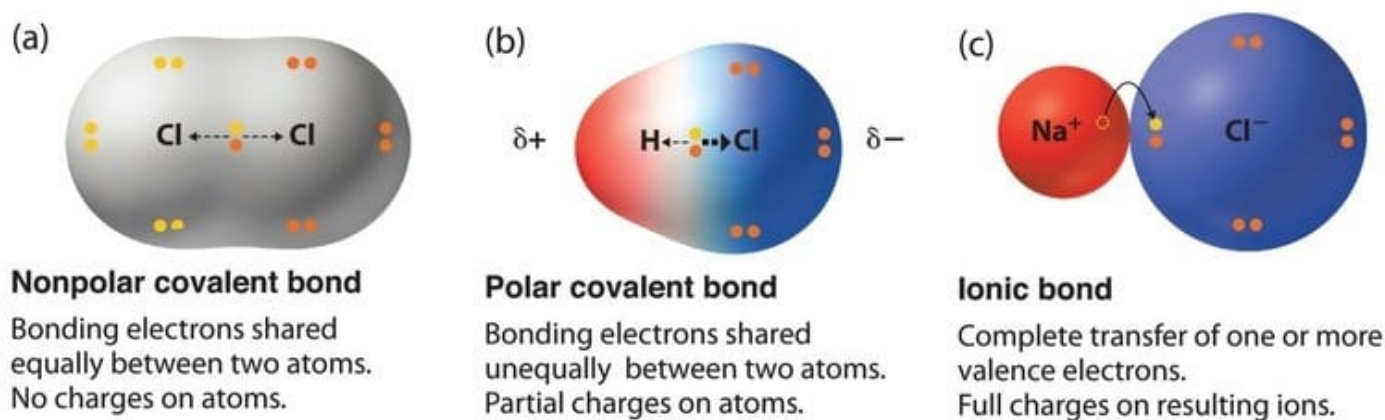


Figure 3.1.3.1: The Electron Distribution in a Nonpolar Covalent Bond, a Polar Covalent Bond, and an Ionic Bond Using Lewis Electron Structures. In a purely covalent bond (a), the bonding electrons are shared equally between the atoms. In a purely ionic bond (c), an electron has been transferred completely from one atom to the other. A polar covalent bond (b) is intermediate between the two extremes: the bonding electrons are shared unequally between the two atoms, and the electron distribution is asymmetrical with the electron density being greater around the more electronegative atom. Electron-rich (negatively charged) regions are shown in blue; electron-poor (positively charged) regions are shown in red.

Bond Polarity

The polarity of a bond—the extent to which it is polar—is determined largely by the relative electronegativities of the bonded atoms. *Electronegativity* (χ) was defined as the ability of an atom in a molecule or an ion to attract electrons to itself. Thus there is a direct correlation between electronegativity and bond polarity. A bond is *nonpolar* if the bonded atoms have equal electronegativities. If the electronegativities of the bonded atoms are not equal, however, the bond is *polarized* toward the more electronegative atom. A bond in which the electronegativity of B (χ_B) is greater than the electronegativity of A (χ_A), for example, is indicated with the partial negative charge on the more electronegative atom:



One way of estimating the ionic character of a bond—that is, the magnitude of the charge separation in a polar covalent bond—is to calculate the difference in electronegativity between the two atoms:

$$\Delta\chi = \chi_B - \chi_A.$$

To predict the polarity of the bonds in Cl_2 , HCl , and NaCl , for example, we look at the electronegativities of the relevant atoms (Table A2): $\chi_{\text{Cl}} = 3.16$, $\chi_{\text{H}} = 2.20$, and $\chi_{\text{Na}} = 0.93$. Cl_2 must be nonpolar because the electronegativity difference ($\Delta\chi$) is zero; hence the two chlorine atoms share the bonding electrons equally. In NaCl , $\Delta\chi$ is 2.23. This high value is typical of an ionic compound ($\Delta\chi \geq 1.5$) and means that the valence electron of sodium has been completely transferred to chlorine to form Na^+ and Cl^- ions. In HCl , however, $\Delta\chi$ is only 0.96. The bonding electrons are more strongly attracted to the more electronegative chlorine atom, and so the charge distribution is



Remember that electronegativities are difficult to measure precisely and different definitions produce slightly different numbers. In practice, the polarity of a bond is usually estimated rather than calculated.

Bond polarity and ionic character increase with an increasing difference in electronegativity.

As with bond energies, the electronegativity of an atom depends to some extent on its chemical environment. It is therefore unlikely that the reported electronegativities of a chlorine atom in NaCl , Cl_2 , ClF_5 , and HClO_4 would be exactly the same.

Dipole Moments

The asymmetrical charge distribution in a polar substance such as HCl produces a dipole moment where Qr in meters (m), is abbreviated by the Greek letter mu (μ). The dipole moment is defined as the product of the partial charge Q on the bonded atoms and the distance r between the partial charges:

$$\mu = Qr \quad (3.1.3.2)$$

where Q is measured in coulombs (C) and r in meters. The unit for dipole moments is the debye (D):

$$1 D = 3.3356 \times 10^{-30} C \cdot m \quad (3.1.3.3)$$

When a molecule with a dipole moment is placed in an electric field, it tends to orient itself with the electric field because of its asymmetrical charge distribution (Figure 3.1.3.2).

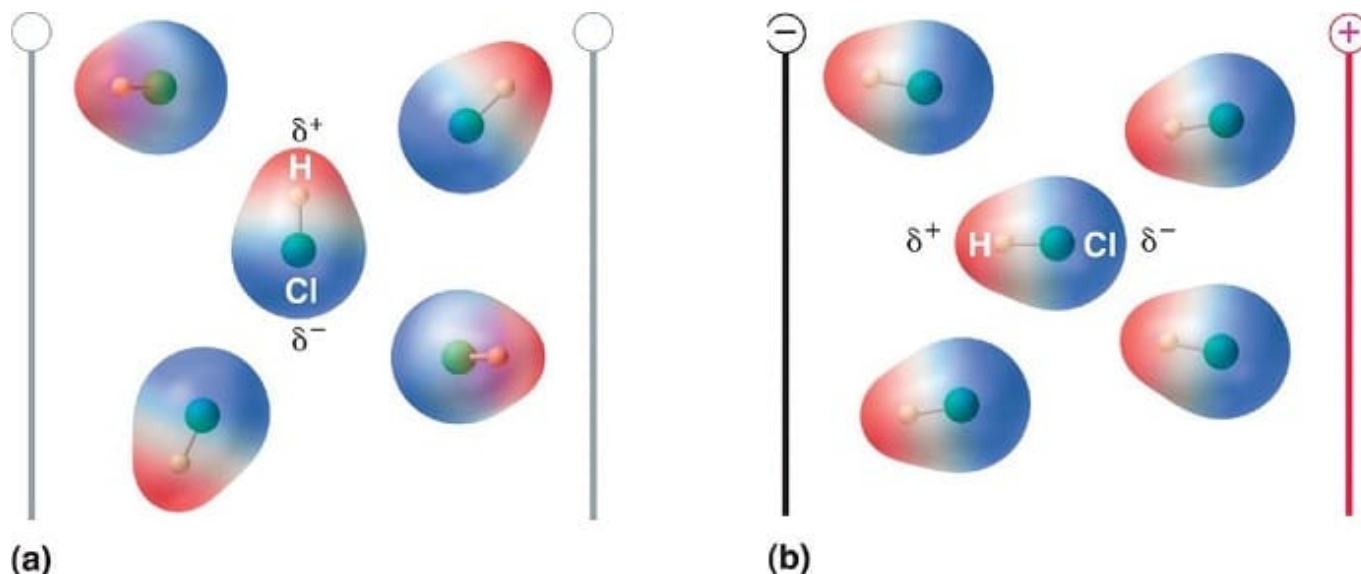


Figure 3.1.3.2: Molecules That Possess a Dipole Moment Partially Align Themselves with an Applied Electric Field In the absence of a field (a), the HCl molecules are randomly oriented. When an electric field is applied (b), the molecules tend to align themselves with the field, such that the positive end of the molecular dipole points toward the negative terminal and vice versa.

We can measure the partial charges on the atoms in a molecule such as HCl using Equation 3.1.3.2. If the bonding in HCl were purely ionic, an electron would be transferred from H to Cl, so there would be a full +1 charge on the H atom and a full -1 charge on the Cl atom. The dipole moment of HCl is 1.109 D, as determined by measuring the extent of its alignment in an electric field, and the reported gas-phase H-Cl distance is 127.5 pm. Hence the charge on each atom is

$$\begin{aligned} Q &= \frac{\mu}{r} \\ &= 1.109 \text{ D} \left(\frac{3.3356 \times 10^{-30} \text{ C} \cdot \text{m}}{1 \text{ D}} \right) \left(\frac{1}{127.5 \text{ pm}} \right) \left(\frac{1 \text{ pm}}{10^{-12} \text{ m}} \right) \\ &= 2.901 \times 10^{-20} \text{ C} \end{aligned}$$

By dividing this calculated value by the charge on a single electron ($1.6022 \times 10^{-19} \text{ C}$), we find that the electron distribution in HCl is asymmetric and that effectively it appears that there is a net negative charge on the Cl of about -0.18, effectively corresponding to about 0.18 e^- . This certainly does not mean that there is a fraction of an electron on the Cl atom, but that the distribution of electron probability favors the Cl atom side of the molecule by about this amount.

$$\frac{2.901 \times 10^{-20} \text{ C}}{1.6022 \times 10^{-19} \text{ C}} = 0.1811 e^- \quad (3.1.3.4)$$

To form a neutral compound, the charge on the H atom must be equal but opposite. Thus the measured dipole moment of HCl indicates that the H-Cl bond has approximately 18% ionic character (0.1811×100), or 82% covalent character. Instead of writing HCl as



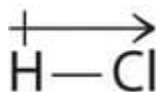
we can therefore indicate the charge separation quantitatively as



Our calculated results are in agreement with the electronegativity difference between hydrogen and chlorine ($\chi_{\text{H}} = 2.20$ and $\chi_{\text{Cl}} = 3.16$) so

$$\chi_{\text{Cl}} - \chi_{\text{H}} = 0.96$$

This is a value well within the range for polar covalent bonds. We indicate the dipole moment by writing an arrow above the molecule. Mathematically, dipole moments are vectors, and they possess both a magnitude and a direction. The dipole moment of a molecule is the vector sum of the dipoles of the individual bonds. In HCl, for example, the dipole moment is indicated as follows:



The arrow shows the direction of electron flow by pointing toward the more electronegative atom.

YouTube Video

This interactive element is not available in this format. Visit the link or scan the QR code to access it online.

[View this YouTube Video online](#)



A warning about Dipole Moment arrows

As the figure above shows, we represent dipole moments by an arrow with a length proportional to μ and pointing from the positive charge to the negative charge. However, the **opposite** convention is still widely used especially among physicists.

The charge on the atoms of many substances in the gas phase can be calculated using measured dipole moments and bond distances. Figure 3.1.3.2 shows a plot of the percent ionic character versus the difference in electronegativity of the bonded atoms for several substances. According to the graph, the bonding in species such as $\text{NaCl}_{(g)}$ and $\text{CsF}_{(g)}$ is substantially less than 100% ionic in character. As the gas condenses into a solid, however, dipole-dipole interactions between polarized species increase the charge separations. In the crystal, therefore, an electron is transferred from the metal to the nonmetal, and these substances behave like classic ionic compounds. The data in Figure 3.1.3.2 show that diatomic species with an electronegativity difference of less than 1.5 are less than 50% ionic in character, which is consistent with our earlier description of these species as containing polar covalent bonds. The use of dipole moments to determine the ionic character of a polar bond is illustrated in Example 3.1.3.1.

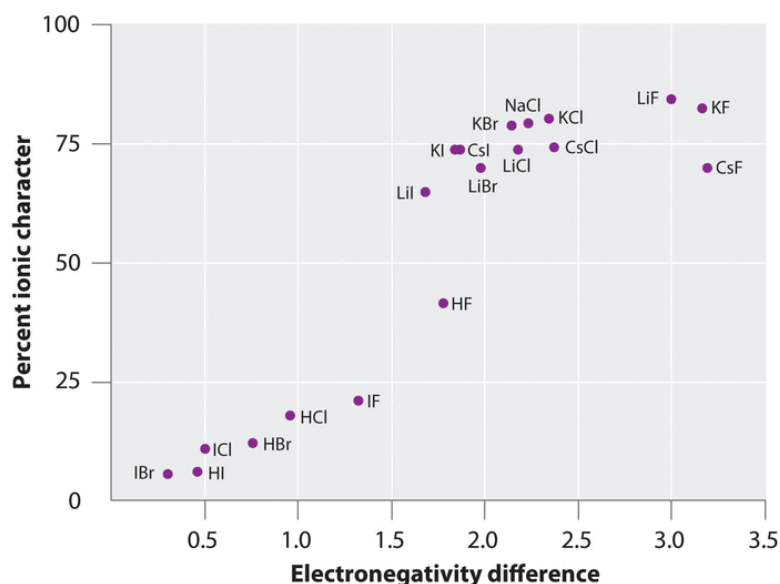


Figure 3.1.3.2: A Plot of the Percent Ionic Character of a Bond as Determined from Measured Dipole Moments versus the Difference in Electronegativity of the Bonded Atoms. In the gas phase, even CsF, which has the largest possible difference in electronegativity between atoms, is not 100% ionic. Solid CsF, however, is best viewed as 100% ionic because of the additional electrostatic interactions in the lattice.

Example 3.1.3.1: percent ionic character

In the gas phase, NaCl has a dipole moment of 9.001 D and an Na–Cl distance of 236.1 pm. Calculate the percent ionic character in NaCl.

Given: chemical species, dipole moment, and internuclear distance

Asked for: percent ionic character

Strategy:

- Compute the charge on each atom using the information given and Equation 3.1.3.2
- Find the percent ionic character from the ratio of the actual charge to the charge of a single electron.

Solution:

A The charge on each atom is given by

$$\begin{aligned}
 Q &= \frac{\mu}{r} \\
 &= 9.001 \cancel{\text{D}} \left(\frac{3.3356 \times 10^{-30} \text{ C} \cdot \cancel{\text{m}}}{1 \cancel{\text{D}}} \right) \left(\frac{1}{236.1 \cancel{\text{pm}}} \right) \left(\frac{1 \cancel{\text{pm}}}{10^{-12} \cancel{\text{m}}} \right) \\
 &= 1.272 \times 10^{-19} \text{ C}
 \end{aligned}$$

Thus NaCl behaves as if it had charges of $1.272 \times 10^{-19} \text{ C}$ on each atom separated by 236.1 pm.

B The percent ionic character is given by the ratio of the actual charge to the charge of a single electron (the charge expected for the complete transfer of one electron):

$$\begin{aligned}
 \text{ionic character} &= \left(\frac{1.272 \times 10^{-19} \cancel{\text{C}}}{1.6022 \times 10^{-19} \cancel{\text{C}}} \right) (100) \\
 &= 79.39\% \approx 79\%
 \end{aligned}$$

Exercise 3.1.3.1

In the gas phase, silver chloride (AgCl) has a dipole moment of 6.08 D and an Ag-Cl distance of 228.1 pm. What is the percent ionic character in silver chloride?

Answer available at the end of this section.

Summary

Bond polarity and ionic character increase with an increasing difference in electronegativity.

$$\mu = Qr$$

Compounds with **polar covalent bonds** have electrons that are shared unequally between the bonded atoms. The polarity of such a bond is determined largely by the relative electronegativities of the bonded atoms. The asymmetrical charge distribution in a polar substance produces a **dipole moment**, which is the product of the partial charges on the bonded atoms and the distance between them.

Contributors and Attributions

- Modified by Joshua Halpern (Howard University)

Answers

Exercise 3.1.3.1

55.5%

This page titled [3.1.3: Molecular Shape and Molecular Polarity](#) is shared under a [CC BY-NC-SA 4.0](#) license and was authored, remixed, and/or curated by LibreTexts.

- [9.3: Molecular Shape and Molecular Polarity](#) is licensed [CC BY-NC-SA 3.0](#).

3.1.4: Covalent Bonding and Orbital Overlap

Learning Objectives

- To describe the bonding in simple compounds using valence bond theory.

Although the VSEPR model is a simple and useful method for qualitatively predicting the structures of a wide range of compounds, it is *not* infallible. It predicts, for example, that H_2S and PH_3 should have structures similar to those of H_2O and NH_3 , respectively. In fact, structural studies have shown that the H-S-H and H-P-H angles are more than 12° smaller than the corresponding bond angles in H_2O and NH_3 . More disturbing, the VSEPR model predicts that the simple group 2 halides (MX_2), which have four valence electrons, should all have linear X-M-X geometries. Instead, many of these species, including SrF_2 and BaF_2 , are significantly bent. A more sophisticated treatment of bonding is needed for systems such as these. In this section, we present a quantum mechanical description of bonding, in which bonding electrons are viewed as being localized between the nuclei of the bonded atoms. The overlap of bonding orbitals is substantially increased through a process called *hybridization*, which results in the formation of stronger bonds.

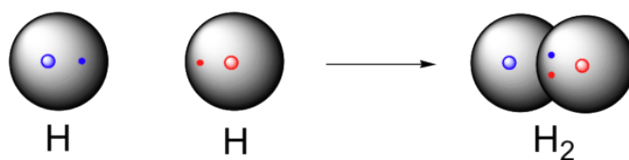
Introduction

As we have talked about using Lewis structures to depict the bonding in covalent compounds, we have been very vague in our language about the actual nature of the chemical bonds themselves. We know that a covalent bond involves the ‘sharing’ of a pair of electrons between two atoms - but how does this happen, and how does it lead to the formation of a bond holding the two atoms together?

The **valence bond theory** is introduced to describe bonding in covalent molecules. In this model, bonds are considered to form from the overlapping of two atomic orbitals on different atoms, each orbital containing a single electron. In looking at simple inorganic molecules such as H_2 or HF , our present understanding of s and p atomic orbitals will suffice. To explain the bonding in organic molecules, however, we will need to introduce the concept of **hybrid orbitals**.

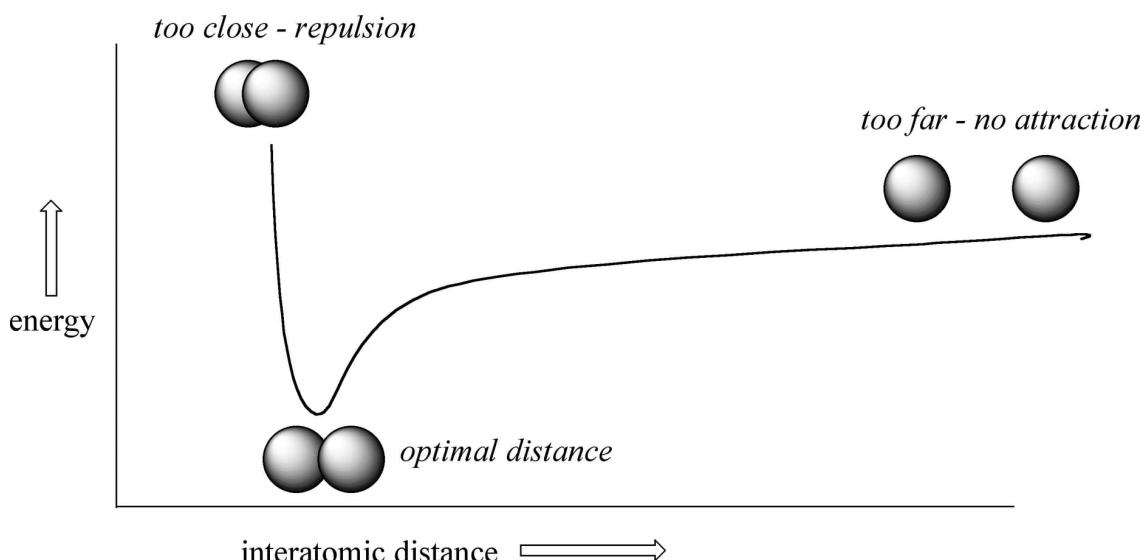
Example: The H_2 molecule

The simplest case to consider is the hydrogen molecule, H_2 . When we say that the two electrons from each of the hydrogen atoms are shared to form a covalent bond between the two atoms, what we mean in valence bond theory terms is that the two spherical 1s orbitals overlap, allowing the two electrons to form a pair within the two overlapping orbitals. In simple terms, we can say that both electrons now spend more time *between* the two nuclei and thus hold the atoms together. As we will see, the situation is not quite so simple as that, because the electron pair must still obey quantum mechanics - that is, the two electrons must now occupy a *shared orbital space*. This will be the essential principle of valence bond theory.



These two electrons are now attracted to the positive charge of both of the hydrogen nuclei, with the result that they serve as a sort of ‘chemical glue’ holding the two nuclei together.

How far apart are the two nuclei? That is a very important issue to consider. If they are too far apart, their respective 1s orbitals cannot overlap, and thus no covalent bond can form - they are still just two separate hydrogen atoms. As they move closer and closer together, orbital overlap begins to occur, and a bond begins to form. This lowers the potential energy of the system, as new, *attractive* positive-negative electrostatic interactions become possible between the nucleus of one atom and the electron of the second. However, something else is happening at the same time: as the atoms get closer, the *repulsive* positive-positive interaction between the two nuclei also begins to increase.



Graph of increasing energy against increasing interatomic distance. If the two are too close there is repulsion, if the two are too far there is no attraction. There is an optimal distance.

At first this repulsion is more than offset by the attraction between nuclei and electrons, but at a certain point, as the nuclei get even closer, the repulsive forces begin to overcome the attractive forces, and the potential energy of the system rises quickly. When the two nuclei are 'too close', we have a very unstable, high-energy situation. There is a defined optimal distance between the nuclei in which the potential energy is at a minimum, meaning that the combined attractive and repulsive forces add up to the greatest overall attractive force. This optimal internuclear distance is the **bond length**. For the H_2 molecule, this distance is 74×10^{-12} meters, or $0.74 \text{ \AA}$ ($\text{\AA}$ means angstrom, or 10^{-10} meters). Likewise, the difference in potential energy between the lowest state (at the optimal internuclear distance) and the state where the two atoms are completely separated is called the **bond energy**. For the hydrogen molecule, this energy is equal to about 104 kcal/mol .

Every covalent bond in a given molecule has a characteristic length and strength. In general, carbon-carbon single bonds are about $1.5 \text{ \AA}$ long ($\text{\AA}$ means angstrom, or 10^{-10} meters) while carbon-carbon double bonds are about $1.3 \text{ \AA}$, carbon-oxygen double bonds are about $1.2 \text{ \AA}$, and carbon-hydrogen bonds are in the range of $1.0 - 1.1 \text{ \AA}$. Most covalent bonds in organic molecules range in strength from just under 100 kcal/mole (for a carbon-hydrogen bond in ethane, for example) up to nearly 200 kcal/mole . You can refer to tables in reference books such as the CRC Handbook of Chemistry and Physics for extensive lists of bond lengths, strengths, and many other data for specific organic compounds.

Balls and Springs

Although we tend to talk about "bond length" as a specific distance, it is not accurate to picture covalent bonds as rigid sticks of unchanging length - rather, it is better to picture them as *springs* which have a defined length when relaxed, but which can be compressed, extended, and bent. This 'springy' picture of covalent bonds will become very important, when we study the analytical technique known as infrared (IR) spectroscopy.

Valence Bond Theory: A Localized Bonding Approach

You learned that as two hydrogen atoms approach each other from an infinite distance, the energy of the system reaches a minimum. This region of minimum energy in the energy diagram corresponds to the formation of a covalent bond between the two atoms at an H-H distance of 74 pm (Figure 3.1.4.1). According to quantum mechanics, bonds form between atoms because their atomic orbitals overlap, with each region of overlap accommodating a *maximum of two electrons with opposite spin*, in accordance with the Pauli principle. In this case, a bond forms between the two hydrogen atoms when the singly occupied $1s$ atomic orbital of one hydrogen atom overlaps with the singly occupied $1s$ atomic orbital of a second hydrogen atom. Electron density between the nuclei is increased because of this orbital overlap and results in a *localized electron-pair bond* (Figure 3.1.4.1).

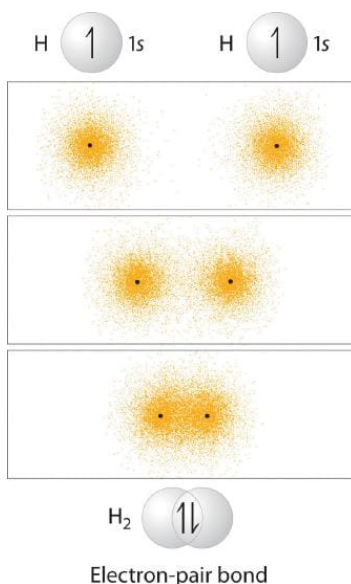


Figure 3.1.4.1: Overlap of Two Singly Occupied Hydrogen 1s Atomic Orbitals Produces an H-H Bond in H_2 . The formation of H_2 from two hydrogen atoms, each with a single electron in a 1s orbital, occurs as the electrons are shared to form an electron-pair bond, as indicated schematically by the gray spheres and black arrows. The orange electron density distributions show that the formation of an H_2 molecule increases the electron density in the region between the two positively charged nuclei.

Although Lewis and VSEPR structures also contain localized electron-pair bonds, neither description uses an atomic orbital approach to predict the stability of the bond. Doing so forms the basis for a description of chemical bonding known as valence bond theory, which is built on two assumptions:

1. The strength of a covalent bond is proportional to the amount of overlap between atomic orbitals; that is, the greater the overlap, the more stable the bond.
2. An atom can use different combinations of atomic orbitals to maximize the overlap of orbitals used by bonded atoms.

Figure 3.1.4.2 shows an electron-pair bond formed by the overlap of two ns atomic orbitals, two np atomic orbitals, and an ns and an np orbital where $n = 2$. Notice that bonding overlap occurs when the interacting atomic orbitals have the correct orientation (are "pointing at" each other) and are *in phase* (represented by colors in Figure 3.1.4.2).

Maximum overlap occurs between orbitals with the same spatial orientation and similar energies.

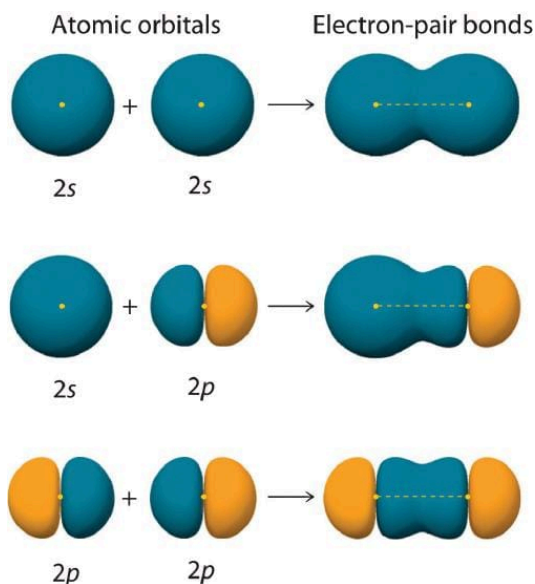


Figure 3.1.4.2 : Three Different Ways to Form an Electron-Pair Bond. An electron-pair bond can be formed by the overlap of any of the following combinations of two singly occupied atomic orbitals: two ns atomic orbitals (a), an ns and an np atomic orbital (b), and two np atomic orbitals (c) where $n = 2$. The positive lobe is indicated in yellow, and the negative lobe is in blue.

Let's examine the bonds in BeH_2 , for example. According to the VSEPR model, BeH_2 is a linear compound with four valence electrons and two Be–H bonds. Its bonding can also be described using an atomic orbital approach. Beryllium has a $1s^2 2s^2$ electron configuration, and each H atom has a $1s^1$ electron configuration. Because the Be atom has a filled $2s$ subshell, however, it has no singly occupied orbitals available to overlap with the singly occupied $1s$ orbitals on the H atoms. If a singly occupied $1s$ orbital on hydrogen were to overlap with a filled $2s$ orbital on beryllium, the resulting bonding orbital would contain *three* electrons, but the maximum allowed by quantum mechanics is *two*. How then is beryllium able to bond to two hydrogen atoms? One way would be to add enough energy to excite one of its $2s$ electrons into an empty $2p$ orbital and reverse its spin, in a process called promotion:



The ground state of beryllium has one electron pair in the $2s$ orbital. The excited state of beryllium takes one of the electrons from the $2s$ orbital and moves it to the $2p$ orbital.

In this excited state, the Be atom would have two singly occupied atomic orbitals (the $2s$ and one of the $2p$ orbitals), each of which could overlap with a singly occupied $1s$ orbital of an H atom to form an electron-pair bond. Although this would produce BeH_2 , the two Be–H bonds would not be equivalent: the $1s$ orbital of one hydrogen atom would overlap with a Be $2s$ orbital, and the $1s$ orbital of the other hydrogen atom would overlap with an orbital of a different energy, a Be $2p$ orbital. Experimental evidence indicates, however, that the two Be–H bonds have identical energies. To resolve this discrepancy and explain how molecules such as BeH_2 form, scientists developed the concept of hybridization.

Contributors and Attributions

- [Organic Chemistry With a Biological Emphasis](#) by Tim Soderberg (University of Minnesota, Morris)

This page titled [3.1.4: Covalent Bonding and Orbital Overlap](#) is shared under a [CC BY-NC-SA 4.0](#) license and was authored, remixed, and/or curated by LibreTexts.

- [9.4: Covalent Bonding and Orbital Overlap](#) is licensed [CC BY-NC-SA 3.0](#).

3.1.5: Hybrid Orbitals

The localized **valence bond theory** uses a process called **hybridization**, in which atomic orbitals that are similar in energy but not equivalent are combined mathematically to produce sets of equivalent orbitals that are properly oriented to form bonds. These new combinations are called hybrid atomic orbitals because they are produced by combining (*hybridizing*) two or more atomic orbitals from the same atom.

Hybridization of *s* and *p* Orbitals

In BeH₂, we can generate two equivalent orbitals by combining the 2*s* orbital of beryllium and any one of the three degenerate 2*p* orbitals. By taking the sum and the difference of Be 2*s* and 2*p_z* atomic orbitals, for example, we produce two new orbitals with major and minor lobes oriented along the *z*-axes, as shown in Figure 3.1.5.1.

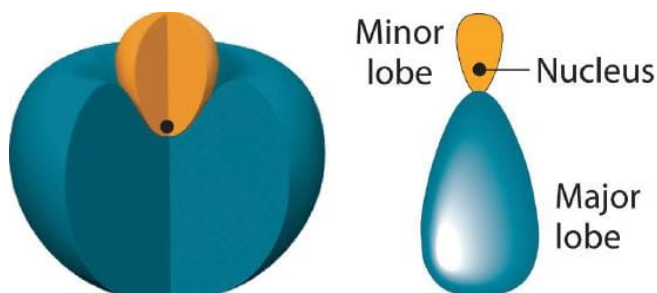


Figure 3.1.5.1: The position of the atomic nucleus with respect to an *sp* hybrid orbital. The nucleus is actually located slightly inside the minor lobe, not at the node separating the major and minor lobes.

Because the difference $A - B$ can also be written as $A + (-B)$, in Figure 3.1.5.2 and subsequent figures we have reversed the phase(s) of the orbital being subtracted, which is the same as multiplying it by -1 and adding. This gives us Equation 3.1.5.2, where the value $\frac{1}{\sqrt{2}}$ is needed mathematically to indicate that the 2*s* and 2*p* orbitals contribute equally to each hybrid orbital.

$$sp = \frac{1}{\sqrt{2}}(2s + 2p_z) \quad (3.1.5.1)$$

and

$$sp = \frac{1}{\sqrt{2}}(2s - 2p_z) \quad (3.1.5.2)$$

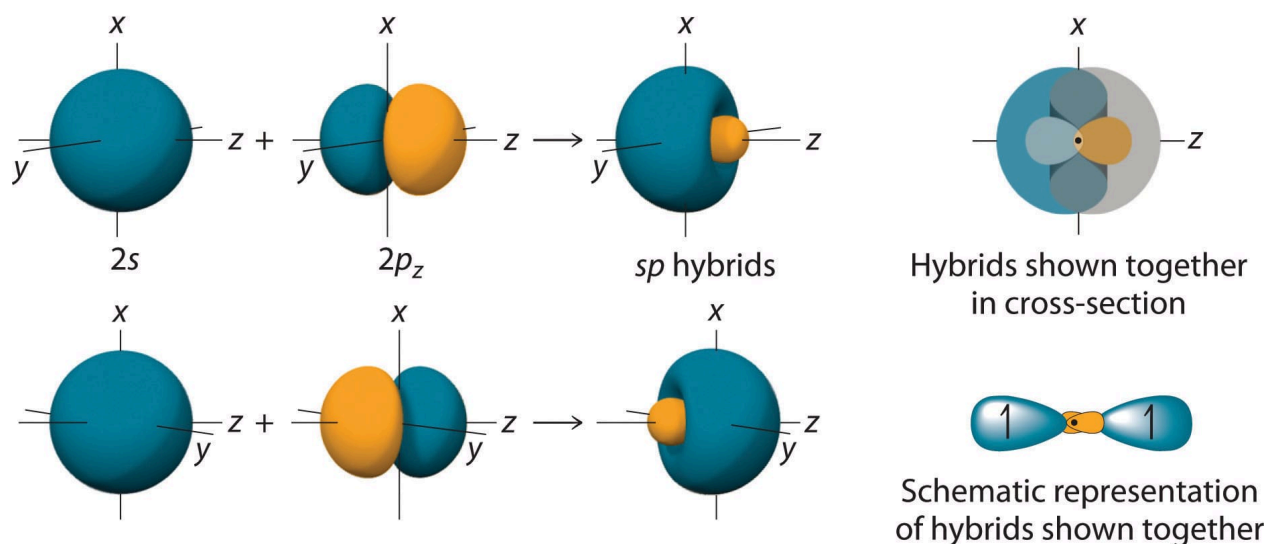


Figure 3.1.5.2: The Formation of sp Hybrid Orbitals. Taking the sum and difference of an ns and an np atomic orbital where $n = 2$ gives two equivalent sp hybrid orbitals oriented at 180° to each other.

The nucleus resides just inside the minor lobe of each orbital. In this case, the new orbitals are called sp hybrids because they are formed from one s and one p orbital. The two new orbitals are equivalent in energy, and their energy is between the energy values associated with pure s and p orbitals, as illustrated in this diagram:

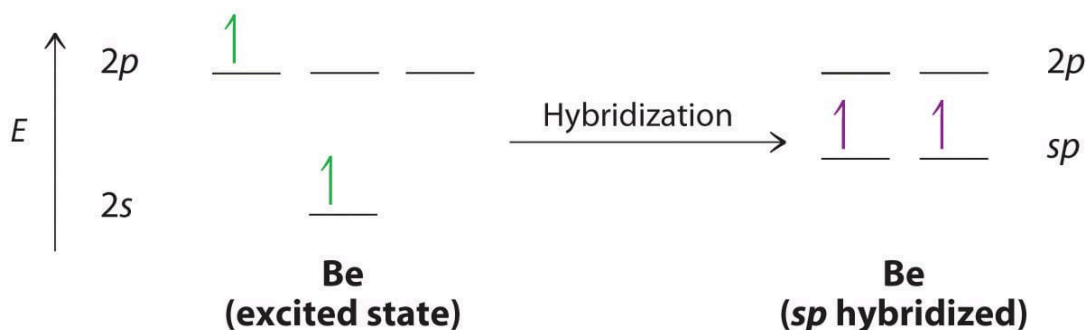


Figure 3.1.5.3. each sp orbital on Be has the correct orientation for the major lobes to overlap with the $1s$ atomic orbital of an H atom. The formation of two energetically equivalent Be-H bonds produces a linear BeH_2 molecule. Thus valence bond theory does what neither the Lewis electron structure nor the VSEPR model is able to do; it explains why the bonds in BeH_2 are equivalent in energy and why BeH_2 has a linear geometry.

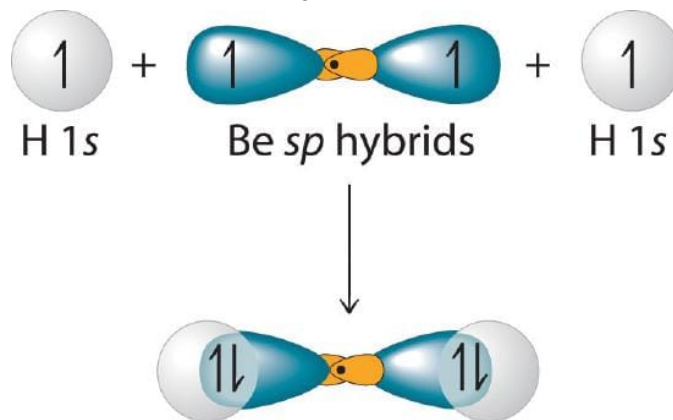


Figure 3.1.5.3: Explanation of the Bonding in BeH_2 Using sp Hybrid Orbitals. Each singly occupied sp hybrid orbital on beryllium can form an electron-pair bond with the singly occupied $1s$ orbital of a hydrogen atom. Because the two sp hybrid orbitals are oriented at a 180° angle, the BeH_2 molecule is linear.

Because both promotion and hybridization require an input of energy, the formation of a set of singly occupied hybrid atomic

orbitals is energetically uphill. The overall process of forming a compound with hybrid orbitals will be energetically favorable *only* if the amount of energy released by the formation of covalent bonds is greater than the amount of energy used to form the hybrid orbitals (Figure 3.1.5.4). As we will see, some compounds are highly unstable or do not exist because the amount of energy required to form hybrid orbitals is greater than the amount of energy that would be released by the formation of additional bonds.

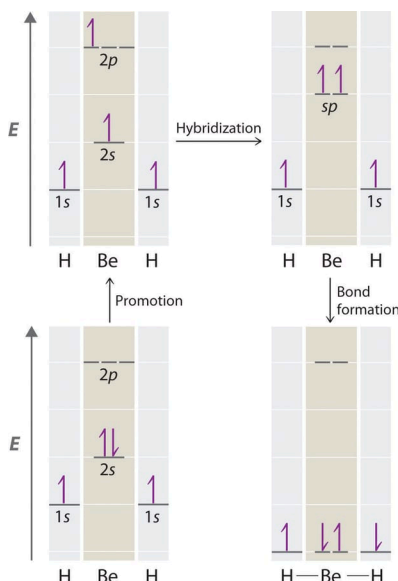


Figure 3.1.5.4: A Hypothetical Stepwise Process for the Formation of BeH_2 from a Gaseous Be Atom and Two Gaseous H Atoms. The promotion of an electron from the $2s$ orbital of beryllium to one of the $2p$ orbitals is energetically uphill. The overall process of forming a BeH_2 molecule from a Be atom and two H atoms will therefore be energetically favorable *only* if the amount of energy released by the formation of the two Be–H bonds is greater than the amount of energy required for promotion and hybridization.

YouTube Video

This interactive element is not available in this format. Visit the link or scan the QR code to access it online.

[View this YouTube Video online](#)



The concept of hybridization also explains why boron, with a $2s^2 2p^1$ valence electron configuration, forms three bonds with fluorine to produce BF_3 , as predicted by the Lewis and VSEPR approaches. With only a single unpaired electron in its ground state, boron should form only a single covalent bond. By the promotion of one of its $2s$ electrons to an unoccupied $2p$ orbital, however, followed by the hybridization of the three singly occupied orbitals (the $2s$ and two $2p$ orbitals), boron acquires a set of three equivalent hybrid orbitals with one electron each, as shown here:

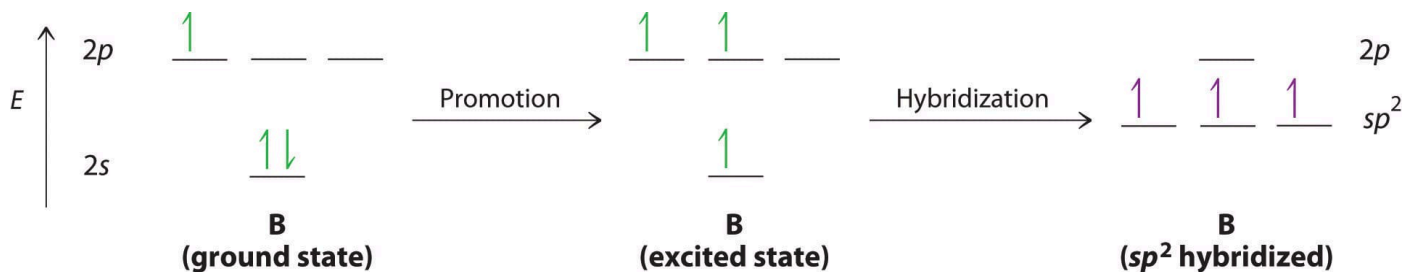


Figure 3.1.5.5). Because the hybrid atomic orbitals are formed from one s and two p orbitals, boron is said to be sp^2 hybridized (pronounced “s-p-two” or “s-p-squared”). The singly occupied sp^2 hybrid atomic orbitals can overlap with the singly occupied orbitals on each of the three F atoms to form a trigonal planar structure with three energetically equivalent B–F bonds.

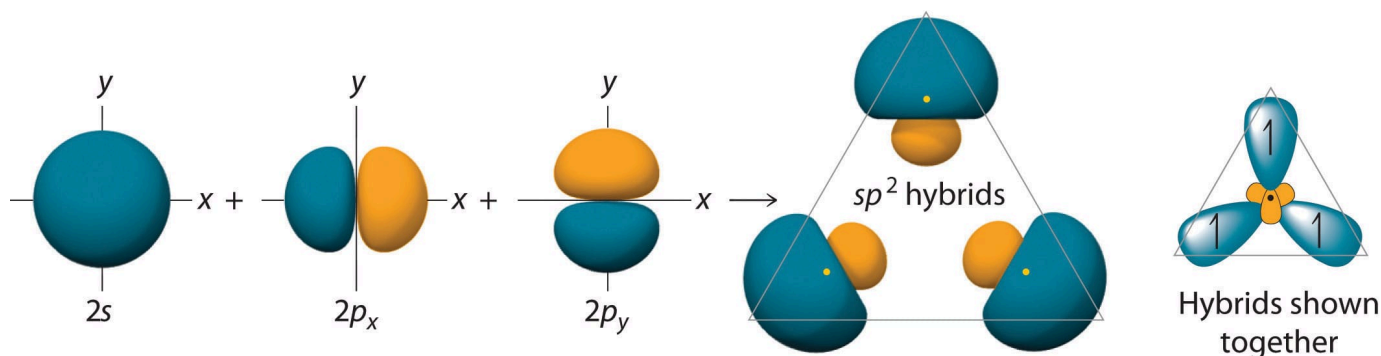


Figure 3.1.5.5: Formation of sp^2 Hybrid Orbitals. Combining one ns and two np atomic orbitals gives three equivalent sp^2 hybrid orbitals in a trigonal planar arrangement; that is, oriented at 120° to one another.

YouTube Video

This interactive element is not available in this format. Visit the link or scan the QR code to access it online.

[View this YouTube Video online](#)



Looking at the $2s^2 2p^2$ valence electron configuration of carbon, we might expect carbon to use its two unpaired $2p$ electrons to form compounds with only two covalent bonds. We know, however, that carbon typically forms compounds with four covalent bonds. We can explain this apparent discrepancy by the hybridization of the $2s$ orbital and the three $2p$ orbitals on carbon to give a set of four degenerate sp^3 ("s-p-three" or "s-p-cubed") hybrid orbitals, each with a single electron:

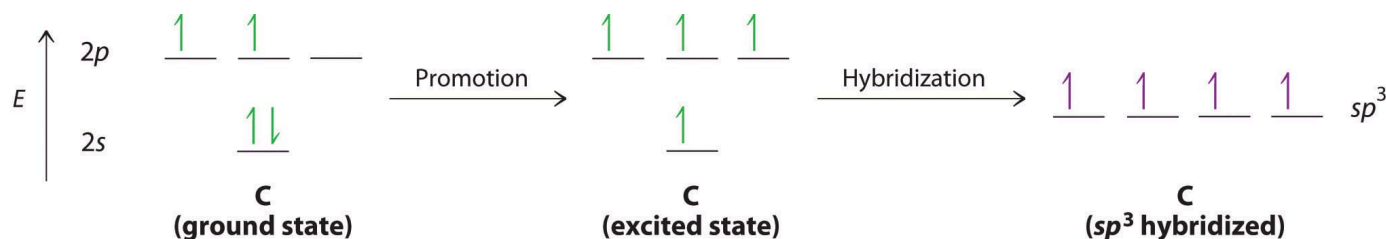


Figure 3.1.5.6). Like all the hybridized orbitals discussed earlier, the sp^3 hybrid atomic orbitals are predicted to be equal in energy. Thus, methane (CH_4) is a tetrahedral molecule with four equivalent C-H bonds.

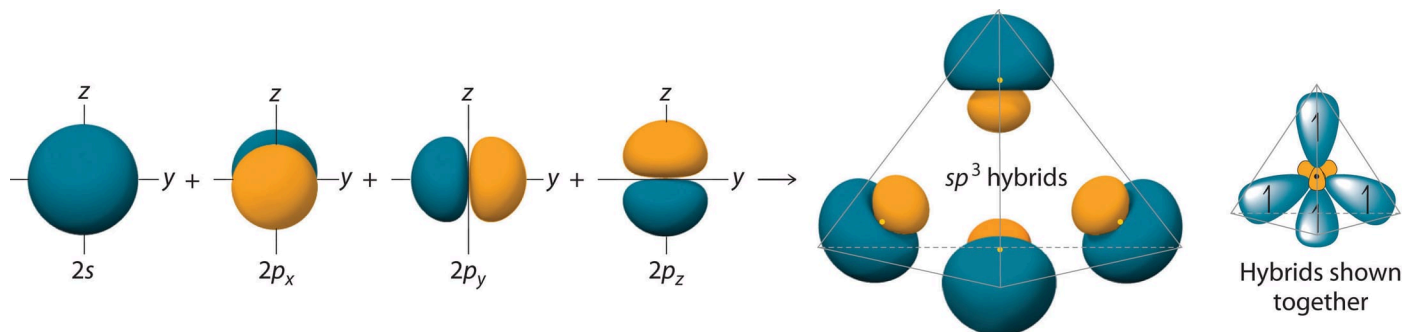


Figure 3.1.5.6: Formation of sp^3 Hybrid Orbitals. Combining one ns and three np atomic orbitals results in four sp^3 hybrid orbitals oriented at 109.5° to one another in a tetrahedral arrangement.

In addition to explaining why some elements form more bonds than would be expected based on their valence electron configurations, and why the bonds formed are equal in energy, valence bond theory explains why these compounds are so stable: the amount of energy released increases with the number of bonds formed. In the case of carbon, for example, much more energy is released in the formation of four bonds than two, so compounds of carbon with four bonds tend to be more stable than those

with only two. Carbon does form compounds with only two covalent bonds (such as CH_2 or CF_2), but these species are highly reactive, unstable intermediates that only form in certain chemical reactions.

Valence bond theory explains the number of bonds formed in a compound and the relative bond strengths.

The bonding in molecules such as NH_3 or H_2O , which have lone pairs on the central atom, can also be described in terms of hybrid atomic orbitals. In NH_3 , for example, N, with a $2s^2 2p^3$ valence electron configuration, can hybridize its $2s$ and $2p$ orbitals to produce four sp^3 hybrid orbitals. Placing five valence electrons in the four hybrid orbitals, we obtain three that are singly occupied and one with a pair of electrons:



The three singly occupied sp^3 lobes can form bonds with three H atoms, while the fourth orbital accommodates the lone pair of electrons. Similarly, H_2O has an sp^3 hybridized oxygen atom that uses two singly occupied sp^3 lobes to bond to two H atoms, and two to accommodate the two lone pairs predicted by the VSEPR model. Such descriptions explain the approximately tetrahedral distribution of electron pairs on the central atom in NH_3 and H_2O . Unfortunately, however, recent experimental evidence indicates that in NH_3 and H_2O , the hybridized orbitals are *not* entirely equivalent in energy, making this bonding model an active area of research.

YouTube Video

This interactive element is not available in this format. Visit the link or scan the QR code to access it online.

[View this YouTube Video online](#)



Example 3.1.5.1

Use the VSEPR model to predict the number of electron pairs and molecular geometry in each compound and then describe the hybridization and bonding of all atoms except hydrogen.

- H_2S
- CHCl_3

Given: two chemical compounds

Asked for: number of electron pairs and molecular geometry, hybridization, and bonding

Strategy:

- Using the VSEPR approach to determine the number of electron pairs and the molecular geometry of the molecule.
- From the valence electron configuration of the central atom, predict the number and type of hybrid orbitals that can be produced. Fill these hybrid orbitals with the total number of valence electrons around the central atom and describe the hybridization.

Solution:

- A** H_2S has four electron pairs around the sulfur atom with two bonded atoms, so the VSEPR model predicts a molecular geometry that is bent, or V shaped. **B** Sulfur has a $3s^2 3p^4$ valence electron configuration with six electrons, but by hybridizing its $3s$ and $3p$ orbitals, it can produce four sp^3 hybrids. If the six valence electrons are placed in these orbitals,

two have electron pairs and two are singly occupied. The two sp^3 hybrid orbitals that are singly occupied are used to form S-H bonds, whereas the other two have lone pairs of electrons. Together, the four sp^3 hybrid orbitals produce an approximately tetrahedral arrangement of electron pairs, which agrees with the molecular geometry predicted by the VSEPR model.

2. **A** The CHCl_3 molecule has four valence electrons around the central atom. In the VSEPR model, the carbon atom has four electron pairs, and the molecular geometry is tetrahedral. **B** Carbon has a $2s^2 2p^2$ valence electron configuration. By hybridizing its 2s and 2p orbitals, it can form four sp^3 hybridized orbitals that are equal in energy. Eight electrons around the central atom (four from C, one from H, and one from each of the three Cl atoms) fill three sp^3 hybrid orbitals to form C-Cl bonds, and one forms a C-H bond. Similarly, the Cl atoms, with seven electrons each in their 3s and 3p valence subshells, can be viewed as sp^3 hybridized. Each Cl atom uses a singly occupied sp^3 hybrid orbital to form a C-Cl bond and three hybrid orbitals to accommodate lone pairs.

Exercise 3.1.5.1

Use the VSEPR model to predict the number of electron pairs and molecular geometry in each compound and then describe the hybridization and bonding of all atoms except hydrogen.

- the BF_4^- ion
- hydrazine ($\text{H}_2\text{N}-\text{NH}_2$)

Answer a available at the end of this section.

The number of hybrid orbitals used by the central atom is the same as the number of electron pairs around the central atom.

Hybridization Using d Orbitals

Hybridization is not restricted to the ns and np atomic orbitals. The bonding in compounds with central atoms in the period 3 and below can also be described using hybrid atomic orbitals. In these cases, the central atom can use its valence $(n - 1)d$ orbitals as well as its ns and np orbitals to form hybrid atomic orbitals, which allows it to accommodate five or more bonded atoms (as in PF_5 and SF_6). Using the ns orbital, all three np orbitals, and one $(n - 1)d$ orbital gives a set of five sp^3d hybrid orbitals that point toward the vertices of a trigonal bipyramid (part (a) in Figure 3.1.5.7). In this case, the five hybrid orbitals are *not* all equivalent: three form a triangular array oriented at 120° angles, and the other two are oriented at 90° to the first three and at 180° to each other.

Similarly, the combination of the ns orbital, all three np orbitals, and *two* nd orbitals gives a set of six equivalent sp^3d^2 hybrid orbitals oriented toward the vertices of an octahedron (part (b) in Figure 9.5.6). In the VSEPR model, PF_5 and SF_6 are predicted to be trigonal bipyramidal and octahedral, respectively, which agrees with a valence bond description in which sp^3d or sp^3d^2 hybrid orbitals are used for bonding.

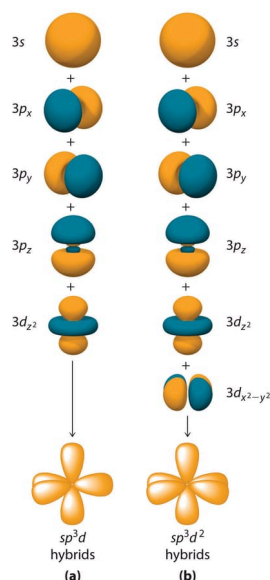


Figure 3.1.5.7: Hybrid Orbitals Involving d Orbitals. The formation of a set of (a) five sp^3d hybrid orbitals and (b) six sp^3d^2 hybrid orbitals from ns , np , and nd atomic orbitals where $n = 4$.

Example 3.1.5.2

What is the hybridization of the central atom in each species? Describe the bonding in each species.

- XeF_4
- SO_4^{2-}
- SF_4

Given: three chemical species

Asked for: hybridization of the central atom

Strategy:

- Determine the geometry of the molecule using the strategy in Example 3.1.5.1. From the valence electron configuration of the central atom and the number of electron pairs, determine the hybridization.
- Place the total number of electrons around the central atom in the hybrid orbitals and describe the bonding.

Solution:

- A** Using the VSEPR model, we find that Xe in XeF_4 forms four bonds and has two lone pairs, so its structure is square planar and it has six electron pairs. The six electron pairs form an octahedral arrangement, so the Xe must be sp^3d^2 hybridized. **B** With 12 electrons around Xe, four of the six sp^3d^2 hybrid orbitals form Xe-F bonds, and two are occupied by lone pairs of electrons.
- A** The S in the SO_4^{2-} ion has four electron pairs and has four bonded atoms, so the structure is tetrahedral. The sulfur must be sp^3 hybridized to generate four S-O bonds. **B** Filling the sp^3 hybrid orbitals with eight electrons from four bonds produces four filled sp^3 hybrid orbitals.
- A** The S atom in SF_4 contains five electron pairs and four bonded atoms. The molecule has a seesaw structure with one lone pair:



To accommodate five electron pairs, the sulfur atom must be sp^3d hybridized. **B** Filling these orbitals with 10 electrons gives four sp^3d hybrid orbitals forming S-F bonds and one with a lone pair of electrons.

Exercise 3.1.5.2

What is the hybridization of the central atom in each species? Describe the bonding.

- PCl_4^+
- BrF_3
- SiF_6^{2-}

Answer a available at the end of this section.

Hybridization using d orbitals allows chemists to explain the structures and properties of many molecules and ions. Like most such models, however, it is not universally accepted. Nonetheless, it does explain a fundamental difference between the chemistry of the elements in the period 2 (C, N, and O) and those in period 3 and below (such as Si, P, and S).

Period 2 elements do not form compounds in which the central atom is covalently bonded to five or more atoms, although such compounds are common for the heavier elements. Thus whereas carbon and silicon both form tetrafluorides (CF_4 and SiF_4), only SiF_4 reacts with F^- to give a stable hexafluoro dianion, SiF_6^{2-} . Because there are no $2d$ atomic orbitals, the formation of octahedral CF_6^{2-} would require hybrid orbitals created from $2s$, $2p$, and $3d$ atomic orbitals. The $3d$ orbitals of carbon are so high in energy that the amount of energy needed to form a set of sp^3d^2 hybrid orbitals cannot be equaled by the energy released in the formation of two additional C-F bonds. These additional bonds are expected to be weak because the carbon atom (and other atoms in period 2) is so small that it cannot accommodate five or six F atoms at normal C-F bond lengths due to repulsions between electrons on adjacent fluorine atoms. Perhaps not surprisingly, then, species such as CF_6^{2-} have never been prepared.

YouTube Video

This interactive element is not available in this format. Visit the link or scan the QR code to access it online.

[View this YouTube Video online](#)



Example 3.1.5.3: OF_4

What is the hybridization of the oxygen atom in OF_4 ? Is OF_4 likely to exist?

Given: chemical compound

Asked for: hybridization and stability

Strategy:

- Predict the geometry of OF_4 using the VSEPR model.
- From the number of electron pairs around O in OF_4 , predict the hybridization of O. Compare the number of hybrid orbitals with the number of electron pairs to decide whether the molecule is likely to exist.

Solution:

A The VSEPR model predicts that OF_4 will have five electron pairs, resulting in a trigonal bipyramidal geometry with four bonding pairs and one lone pair. **B** To accommodate five electron pairs, the O atom would have to be sp^3d hybridized. The only d orbital available for forming a set of sp^3d hybrid orbitals is a $3d$ orbital, which is *much* higher in energy than the $2s$ and $2p$ valence orbitals of oxygen. As a result, the OF_4 molecule is unlikely to exist. In fact, it has not been detected.

Exercise 3.1.5.3

What is the hybridization of the boron atom in BF_6^{3-} ? Is this ion likely to exist?

Answer is available at the end of this section.

Summary

Hybridization increases the overlap of bonding orbitals and explains the molecular geometries of many species whose geometry cannot be explained using a VSEPR approach. The *localized bonding* model (called **valence bond theory**) assumes that covalent bonds are formed when atomic orbitals overlap and that the strength of a covalent bond is proportional to the amount of overlap. It also assumes that atoms use combinations of atomic orbitals (*hybrids*) to maximize the overlap with adjacent atoms. The formation of **hybrid atomic orbitals** can be viewed as occurring via **promotion** of an electron from a filled ns^2 subshell to an empty np or $(n - 1)d$ valence orbital, followed by **hybridization**, the combination of the orbitals to give a new set of (usually) equivalent orbitals that are oriented properly to form bonds. The combination of an ns and an np orbital gives rise to two equivalent **sp hybrids** oriented at 180° , whereas the combination of an ns and two or three np orbitals produces three equivalent **sp^2 hybrids** or four equivalent **sp^3 hybrids**, respectively. The bonding in molecules with more than an octet of electrons around a central atom can be explained by invoking the participation of one or two $(n - 1)d$ orbitals to give sets of five sp^3d or six **sp^3d^2 hybrid** orbitals, capable of forming five or six bonds, respectively. The spatial orientation of the hybrid atomic orbitals is consistent with the geometries predicted using the VSEPR model.

Answers

Exercise 3.1.5.1

B is sp^3 hybridized; F is also sp^3 hybridized so it can accommodate one B-F bond and three lone pairs. The molecular geometry is tetrahedral.

Each N atom is sp^3 hybridized and uses one sp^3 hybrid orbital to form the N-N bond, two to form N-H bonds, and one to accommodate a lone pair. The molecular geometry about each N is trigonal pyramidal.

Exercise 3.1.5.2

sp^3 with four P-Cl bonds

sp^3d with three Br-F bonds and two lone pairs

sp^3d^2 with six Si-F bonds

Exercise 3.1.5.3

sp^3d^2 hybridization; no

This page titled [3.1.5: Hybrid Orbitals](#) is shared under a [CC BY-NC-SA 4.0](#) license and was authored, remixed, and/or curated by LibreTexts.

- 9.5: Hybrid Orbitals is licensed [CC BY-NC-SA 3.0](#).

3.1.6: Multiple Bonds

Learning Objectives

- To explain resonance structures using molecular orbitals.

So far in our valence bond orbital descriptions we have not dealt with polyatomic systems with multiple bonds. To do so, we can use an approach in which we describe σ bonding using localized electron-pair bonds formed by hybrid atomic orbitals, and π bonding using **molecular orbitals** formed by unhybridized np atomic orbitals.

Multiple Bonding

We begin our discussion by considering the bonding in ethylene (C_2H_4). Experimentally, we know that the H-C-H and H-C-C angles in ethylene are approximately 120° . This angle suggests that the carbon atoms are sp^2 hybridized, which means that a singly occupied sp^2 orbital on one carbon overlaps with a singly occupied s orbital on each H and a singly occupied sp^2 lobe on the other C. The sp^2 hybridization can be represented as follows:

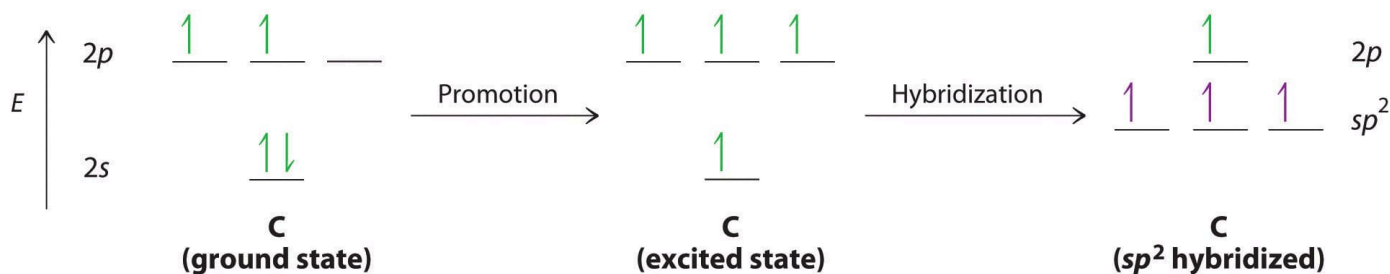


Figure 3.1.6.1). These two singly occupied $2p_z$ orbitals can overlap in a side-to-side fashion to form a π bond. The orbitals overlap both above and below the plane of the molecule but form just one bonding orbital space. The C-C π bond plus the hybridized C-C σ bond together form a double bond.

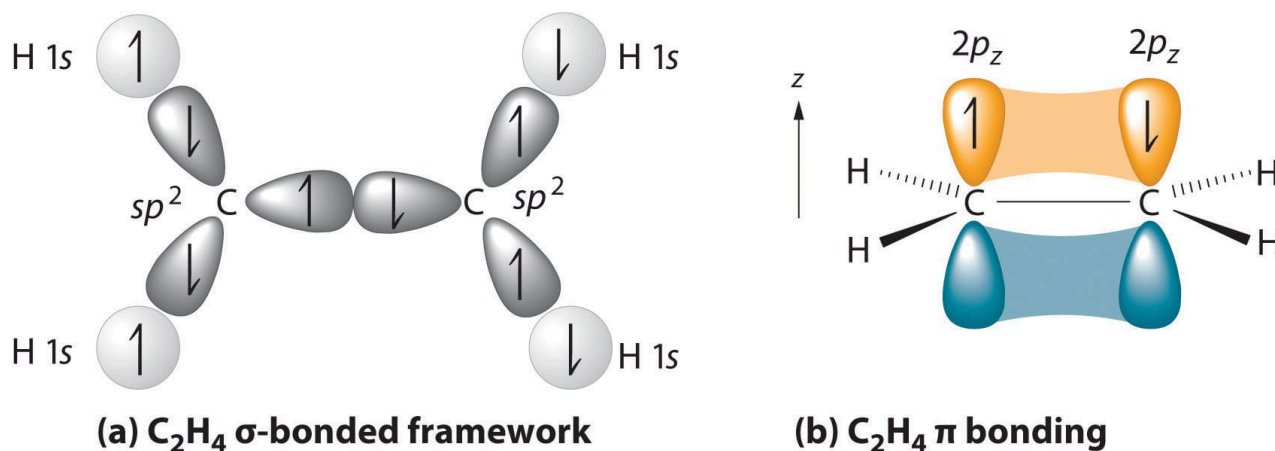


Figure 3.1.6.1: Bonding in Ethylene. (a) The σ -bonded framework is formed by the overlap of two sets of singly occupied carbon sp^2 hybrid orbitals and four singly occupied hydrogen $1s$ orbitals to form electron-pair bonds. This uses 10 of the 12 valence electrons to form a total of five σ bonds (four C-H bonds and one C-C bond). (b) One singly occupied unhybridized $2p_z$ orbital remains on each carbon atom to form a carbon-carbon π bond. (Note: by convention, in planar molecules the axis perpendicular to the molecular plane is the z -axis.)

When considering multiple bonds, we can introduce the more sophisticated **molecular orbital theory** to better understand how orbital overlap creates bonding orbitals. Recall that atomic orbitals represent *electron wavefunctions*; this implies that "orbital overlap" actually involves the combination of those wavefunctions, which can occur via both constructive and destructive interference. Thus, when the two singly occupied $2p_z$ orbitals in ethylene overlap, they actually create both a π bonding orbital

(constructive combination) and a π^* antibonding orbital (destructive combination), which produces the energy-level diagram shown in Figure 3.1.6.2. With the formation of a π bonding orbital, electron density increases in the plane between the carbon nuclei. Electrons occupying this orbital lower the potential energy of the combination and tend to hold the two nuclei together (i.e., they form a bond.) The π^* orbital lies outside the internuclear region and has a nodal plane perpendicular to the internuclear axis; electrons in this orbital would tend to push the nuclei apart, so it is called an antibonding orbital. Because each $2p_z$ orbital has a single electron, there are only two electrons, enough to fill only the bonding (π) level, leaving the π^* orbital empty. Consequently, the C–C bond in ethylene consists of a σ bond and a π bond, which together give a C=C double bond. Our model is supported by the facts that the measured carbon–carbon bond is shorter than that in ethane (133.9 pm versus 153.5 pm) and the bond is stronger (728 kJ/mol versus 376 kJ/mol in ethane). The two CH_2 fragments are coplanar, which maximizes the overlap of the two singly occupied $2p_z$ orbitals.

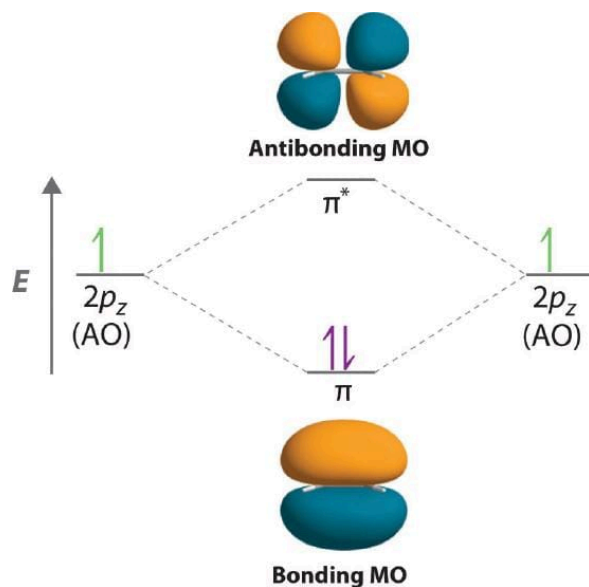


Figure 3.1.6.2: Molecular Orbital Energy-Level Diagram for π Bonding in Ethylene. As in the diatomic molecules discussed previously, the singly occupied $2p_z$ orbitals in ethylene can overlap to form a bonding/antibonding pair of π molecular orbitals. The two electrons remaining are enough to fill only the bonding π orbital. With one σ bond plus one π bond, the carbon–carbon bond order in ethylene is 2.

Triple bonds, as in acetylene (C_2H_2), can also be explained using a combination of hybrid atomic orbitals and molecular orbitals. The four atoms of acetylene are collinear, which suggests that each carbon is sp hybridized. If one sp lobe on each carbon atom is used to form a C–C σ bond and one is used to form the C–H σ bond, then each carbon will still have two unhybridized $2p$ orbitals (a $2p_{x,y}$ pair), each with one electron (part (a) in Figure 3.1.6.3).

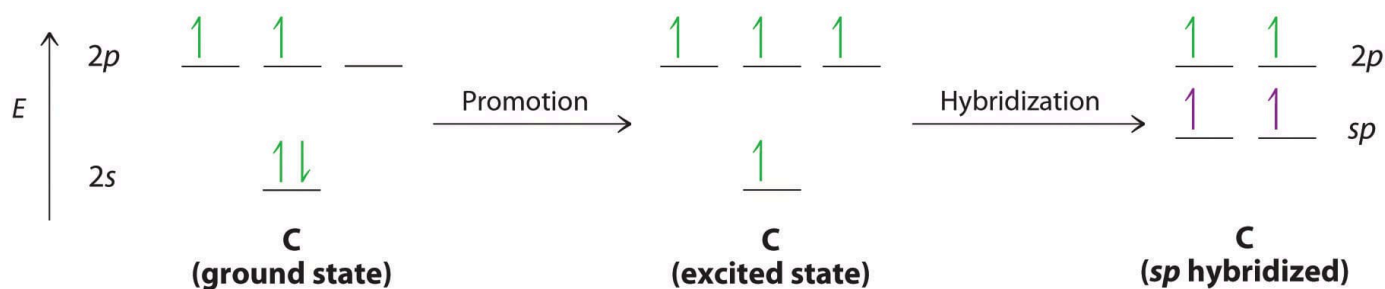


Figure 3.1.6.2). Because each of the unhybridized $2p$ orbitals has a single electron, four electrons are available for π bonding, which is enough to occupy only the bonding molecular orbitals. Acetylene must therefore have a carbon–carbon triple bond, which consists of a C–C σ bond and two mutually perpendicular π bonds. Acetylene does in fact have a shorter carbon–carbon bond (120.3 pm) and a higher bond energy (965 kJ/mol) than ethane and ethylene, as we would expect for a triple bond.

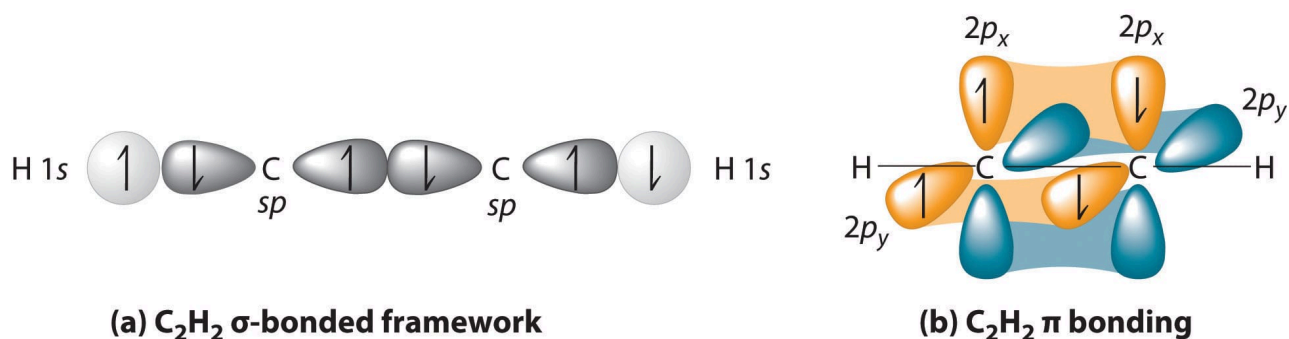


Figure 3.1.6.3: Bonding in Acetylene (a) In the formation of the σ -bonded framework, two sets of singly occupied carbon sp hybrid orbitals and two singly occupied hydrogen $1s$ orbitals overlap. (b) In the formation of two carbon-carbon π bonds in acetylene, two singly occupied unhybridized $2p_{xy}$ orbitals on each carbon atom overlap. With one σ bond plus two π bonds, the carbon-carbon bond order in acetylene is 3.

In complex molecules, *hybrid orbitals* and *valence bond theory* can be used to describe σ bonding, and unhybridized π orbitals and *molecular orbital theory* can be used to describe π bonding.

Example 3.1.6.1

Describe the bonding in HCN using a combination of hybrid atomic orbitals and molecular orbitals. The HCN molecule is linear.

Given: chemical compound and molecular geometry

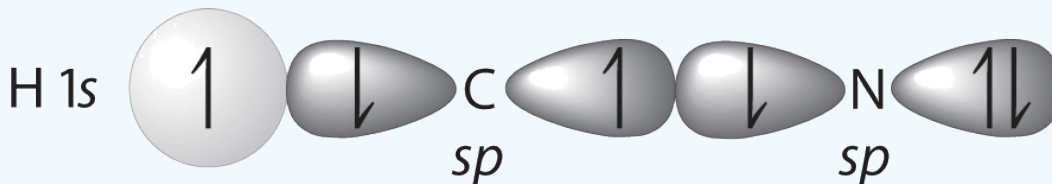
Asked for: bonding description using hybrid atomic orbitals and molecular orbitals

Strategy:

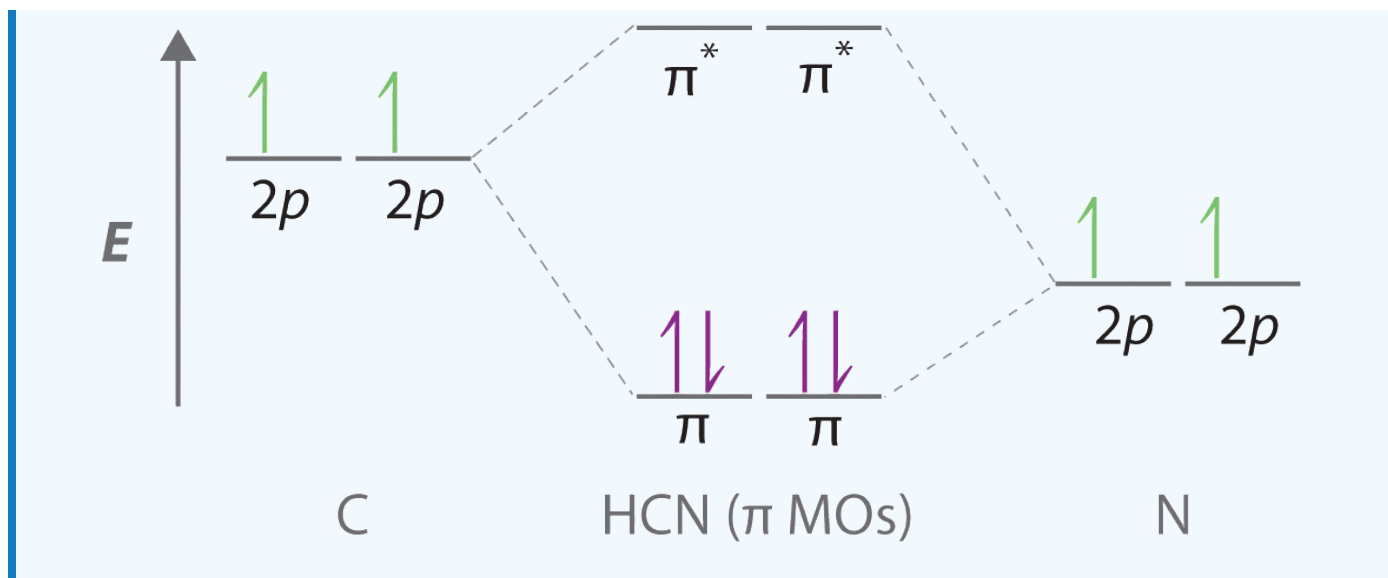
- From the geometry given, predict the hybridization in HCN. Use the hybrid orbitals to form the σ -bonded framework of the molecule and determine the number of valence electrons that are used for σ bonding.
- Determine the number of remaining valence electrons. Use any remaining unhybridized p orbitals to form π and π^* orbitals.
- Fill the orbitals with the remaining electrons in order of increasing energy. Describe the bonding in HCN.

Solution:

A Because HCN is a linear molecule, it is likely that the bonding can be described in terms of sp hybridization at carbon. Because the nitrogen atom can also be described as sp hybridized, we can use one sp hybrid on each atom to form a C-N σ bond. This leaves one sp hybrid on each atom to either bond to hydrogen (C) or hold a lone pair of electrons (N). Of 10 valence electrons (5 from N, 4 from C, and 1 from H), 4 are used for σ bonding:



B We are now left with 2 electrons on N (5 valence electrons minus 1 bonding electron minus 2 electrons in the lone pair) and 2 electrons on C (4 valence electrons minus 2 bonding electrons). We have two unhybridized $2p$ atomic orbitals left on carbon and two on nitrogen, each occupied by a single electron. These four $2p$ atomic orbitals can be combined to give four molecular orbitals: two π (bonding) orbitals and two π^* (antibonding) orbitals. **C** With 4 electrons available, only the π orbitals are filled. The overall result is a triple bond (1 σ and 2 π) between C and N.



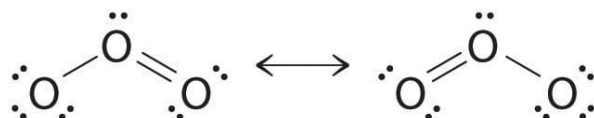
Exercise 3.1.6.1

Describe the bonding in formaldehyde ($\text{H}_2\text{C}=\text{O}$), a trigonal planar molecule, using a combination of hybrid atomic orbitals and molecular orbitals.

Answer available at the end of this section.

Molecular Orbitals and Resonance Structures

Resonance structures can be used to describe the bonding in molecules such as ozone (O_3) and the nitrite ion (NO_2^-). Ozone can be represented by either of these Lewis electron structures:



Although the VSEPR model correctly predicts that both species are bent, it gives no information about their bond orders.

Experimental evidence indicates that ozone has a bond angle of 117.5° . Because this angle is close to 120° , it is likely that the central oxygen atom in ozone is trigonal planar and sp^2 hybridized. If we assume that the terminal oxygen atoms are also sp^2 hybridized, then we obtain the σ -bonded framework shown in Figure 3.1.6.4. Two of the three sp^2 lobes on the central O are used to form O–O sigma bonds, and the third has a lone pair of electrons. Each terminal oxygen atom has two lone pairs of electrons that are also in sp^2 lobes. In addition, each oxygen atom has one unhybridized $2p$ orbital perpendicular to the molecular plane. The σ bonds and lone pairs account for a total of 14 electrons (five lone pairs and two σ bonds, each containing 2 electrons). Each oxygen atom in ozone has 6 valence electrons, so O_3 has a total of 18 valence electrons. Subtracting 14 electrons from the total gives us 4 electrons that must occupy the three unhybridized $2p$ orbitals.

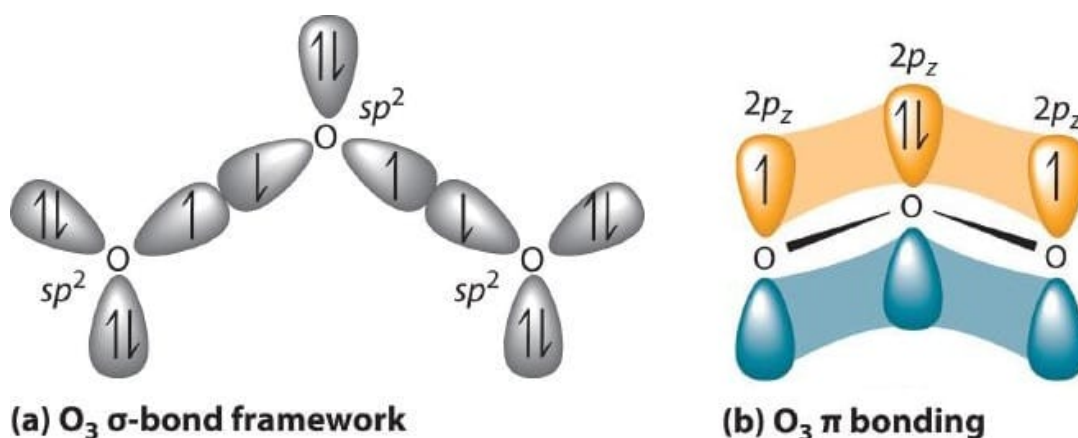


Figure 3.1.6.4: Bonding in Ozone. (a) In the formation of the σ -bonded framework, three sets of oxygen sp^2 hybrid orbitals overlap to give two O–O σ bonds and five lone pairs, two on each terminal O and one on the central O. The σ bonds and lone pairs account for 14 of the 18 valence electrons of O_3 . (b) One unhybridized $2p_z$ orbital remains on each oxygen atom that is available for π bonding. The unhybridized $2p_z$ orbital on each terminal O atom has a single electron, whereas the unhybridized $2p_z$ orbital on the central O atom has 2 electrons.

With a molecular orbital approach to describe the π bonding, three $2p$ atomic orbitals give us three molecular orbitals, as shown in Figure 3.1.6.5. One of the molecular orbitals is a π bonding molecular orbital, which is shown as a banana-shaped region of electron density above and below the molecular plane. This region has *no* nodes perpendicular to the O_3 plane. The molecular orbital with the highest energy has two nodes that bisect the O–O σ bonds; it is a π^* antibonding orbital. The third molecular orbital contains a single node that is perpendicular to the O_3 plane and passes through the central O atom; because the orbital nodes do not directly touch, this is a *nonbonding* molecular orbital. Because electrons in nonbonding orbitals are neither bonding nor antibonding, they are ignored in calculating bond orders.

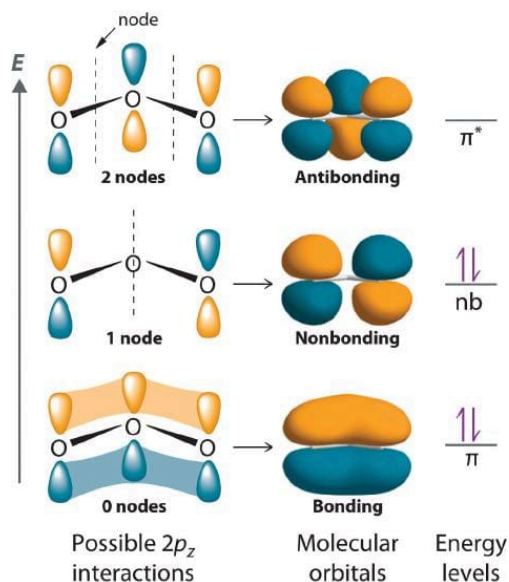


Figure 3.1.6.5: π Bonding in Ozone. The three unhybridized $2p_z$ atomic orbitals interact with one another to form three molecular orbitals: one π bonding orbital at lower energy, one π^* antibonding orbital at higher energy, and a nonbonding orbital in between. Placing four electrons in this diagram fills the bonding and nonbonding orbitals. With one filled π bonding orbital holding three atoms together, the net π bond order is $\frac{1}{2}$ per O–O bond. The combined σ/π bond order is thus $1\frac{1}{2}$ for each O–O bond.

We can now place the remaining four electrons in the three energy levels shown in Figure 3.1.6.5, thereby filling the π bonding and the nonbonding levels. The result is a single π bond holding three oxygen atoms together, or $\frac{1}{2}\pi$ bond per O–O. We therefore predict the overall O–O bond order to be $\frac{1}{2}\pi$ bond plus 1 σ bond), just as predicted using resonance structures. The molecular orbital description, however, makes it more clear that resonance really means that electrons are *delocalized* over all three atoms at once. The molecular orbital approach also shows that the π nonbonding orbital is localized on the terminal O atoms, which suggests that they are more electron rich than the central O atom (corresponding to the "extra" lone pair seen on one of the terminal O atoms in the Lewis resonance structures). The reactivity of ozone is consistent with the predicted charge localization.

Resonance structures are a crude way of describing molecular orbitals that extend over more than two atoms.

Example 3.1.6.2

Describe the bonding in the nitrite ion in terms of a combination of hybrid atomic orbitals and molecular orbitals. Lewis dot structures and the VSEPR model predict that the NO_2^- ion is bent.

Given: chemical species and molecular geometry

Asked for: bonding description using hybrid atomic orbitals and molecular orbitals

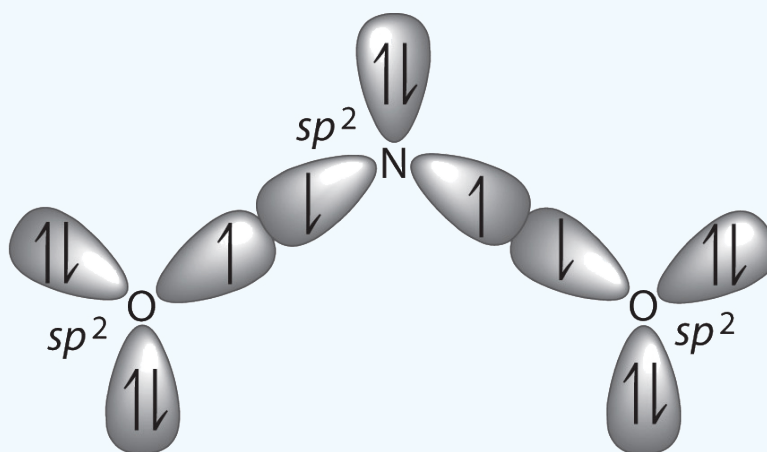
Strategy:

- Calculate the number of valence electrons in NO_2^- . From the structure, predict the type of atomic orbital hybridization in the ion.
- Predict the number and type of molecular orbitals that form during bonding. Use valence electrons to fill these orbitals and then calculate the number of electrons that remain.
- If there are unhybridized orbitals, place the remaining electrons in these orbitals in order of increasing energy. Calculate the bond order and describe the bonding.

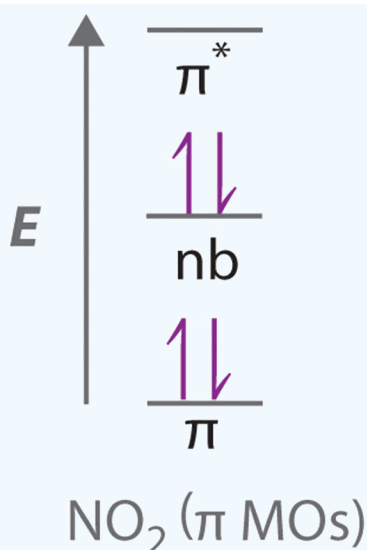
Solution:

A The lone pair of electrons on nitrogen and a bent structure suggest that the bonding in NO_2^- is similar to the bonding in ozone. This conclusion is supported by the fact that nitrite also contains 18 valence electrons (5 from N and 6 from each O, plus 1 for the -1 charge). The bent structure implies that the nitrogen is sp^2 hybridized.

B If we assume that the oxygen atoms are sp^2 hybridized as well, then we can use two sp^2 hybrid orbitals on each oxygen and one sp^2 hybrid orbital on nitrogen to accommodate the five lone pairs of electrons. Two sp^2 hybrid orbitals on nitrogen form σ bonds with the remaining sp^2 hybrid orbital on each oxygen. The σ bonds and lone pairs account for 14 electrons. We are left with three unhybridized $2p$ orbitals, one on each atom, perpendicular to the plane of the molecule, and 4 electrons. Just as with ozone, these three $2p$ orbitals interact to form bonding, nonbonding, and antibonding π molecular orbitals. The bonding molecular orbital is spread over the nitrogen and both oxygen atoms.



C Placing 4 electrons in the energy-level diagram fills both the bonding and nonbonding molecular orbitals and gives a π bond order of $1/2$ per N–O bond. The overall N–O bond order is $1 \frac{1}{2}$, consistent with a resonance structure.



Exercise 3.1.6.2

Describe the bonding in the formate ion (HCO_2^-), in terms of a combination of hybrid atomic orbitals and molecular orbitals.

Answer available at the end of this section.

The Chemistry of Vision

Hydrocarbons in which two or more carbon–carbon double bonds are directly linked by carbon–carbon single bonds (called *conjugated* structures) are generally more stable than expected because of resonance. Because the double bonds are close enough to interact electronically with one another, the π electrons are shared over all the carbon atoms, as illustrated for 1,3-butadiene in Figure 3.1.6.6. As the number of interacting atomic orbitals increases, the number of molecular orbitals increases, the energy spacing between molecular orbitals decreases, and the systems become more stable (Figure 3.1.6.7). Thus as a chain of alternating double and single bonds becomes longer, the energy required to excite an electron from the highest-energy occupied (bonding) orbital to the lowest-energy unoccupied (antibonding) orbital decreases. If the chain is long enough, the amount of energy required to excite an electron corresponds to the energy of visible light. For example, vitamin A is yellow because its chain of five alternating double bonds is able to absorb violet light. Many of the colors we associate with dyes result from this same phenomenon; most dyes are organic compounds with alternating double bonds.

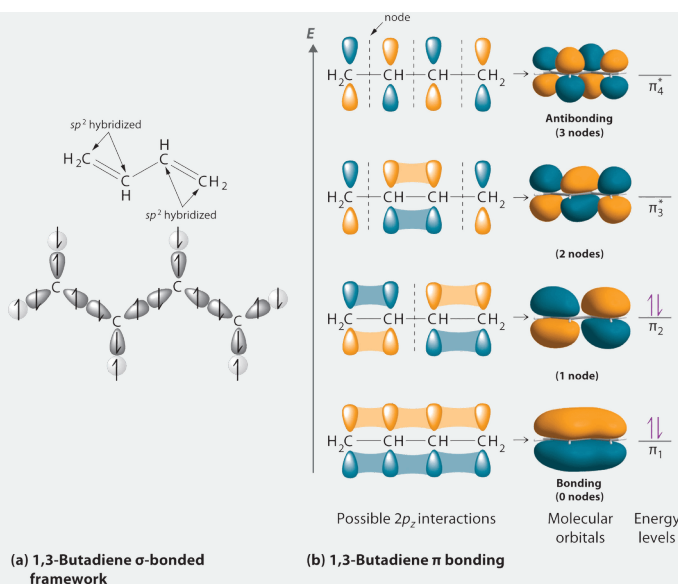


Figure 3.1.6.6: π Bonding in 1,3-Butadiene. (a) If each carbon atom is assumed to be sp^2 hybridized, we can construct a σ -bonded framework that accounts for the C-H and C-C single bonds, leaving *four* singly occupied $2p_z$ orbitals, one on each carbon atom. (b) As in ozone, these orbitals can interact, in this case to form *four* molecular orbitals. The molecular orbital at lowest energy is a bonding orbital with 0 nodes, the one at highest energy is antibonding with 3 nodes, and the two in the middle have 1 node and 2 nodes and are somewhere between bonding or antibonding and nonbonding, respectively. The energy of the molecular orbital increases with the number of nodes. With four electrons, only the two bonding orbitals are filled, consistent with the presence of two π bonds.

As the number of atomic orbitals increases, the difference in energy between the resulting molecular orbital energy levels decreases, which allows light of lower energy to be absorbed. As a result, organic compounds with long chains of carbon atoms and alternating single and double bonds tend to become more deeply colored as the number of double bonds increases.

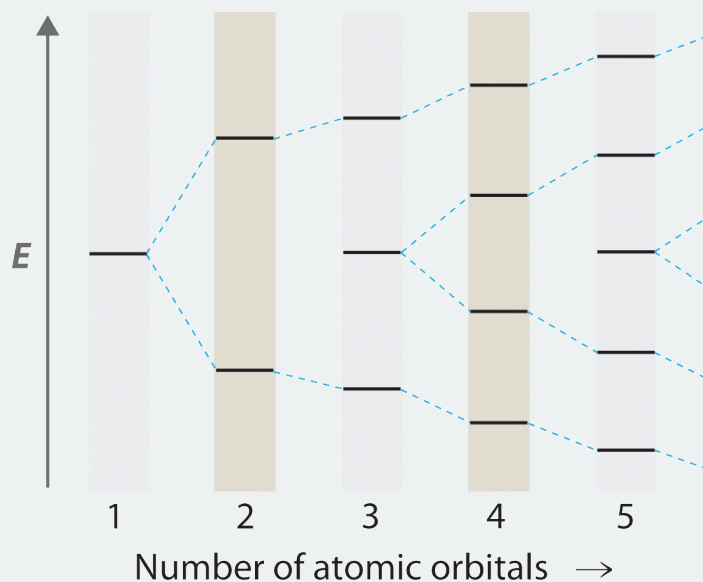


Figure 3.1.6.7: Molecular Orbital Energy-Level Diagrams for a Chain of n Like Orbitals That Interact ($n \leq 5$).

As the number of interacting atomic orbitals increases, the energy separation between the resulting molecular orbitals steadily decreases.

A derivative of vitamin A called *retinal* is used by the human eye to detect light and has a structure with alternating C=C double bonds. When visible light strikes retinal, the energy separation between the molecular orbitals is sufficiently close that the energy absorbed corresponds to the energy required to change one double bond in the molecule from *cis*, where like groups are on the same side of the double bond, to *trans*, where they are on opposite sides, initiating a process that causes a signal to be sent to the brain. If this mechanism is defective, we lose our vision in dim light. Once again, a molecular orbital approach to bonding explains a process that cannot be explained using any of the other approaches we have described.

Summary

Polyatomic systems with multiple bonds can be described using hybrid atomic orbitals for σ bonding and molecular orbitals to describe π bonding. To describe the bonding in more complex molecules with multiple bonds, we can use an approach that uses hybrid atomic orbitals to describe the σ bonding and molecular orbitals to describe the π bonding. In this approach, unhybridized np orbitals on atoms bonded to one another are allowed to interact to produce bonding, antibonding, or nonbonding combinations. For π bonds between two atoms (as in ethylene or acetylene), the resulting molecular orbitals are virtually identical to the π molecular orbitals in diatomic molecules such as O_2 and N_2 . Applying the same approach to π bonding between three or four atoms requires combining three or four unhybridized np orbitals on adjacent atoms to generate π bonding, antibonding, and nonbonding molecular orbitals extending over all of the atoms. Filling the resulting energy-level diagram with the appropriate number of electrons explains the bonding in molecules or ions that previously required the use of resonance structures in the Lewis electron-pair approach.

Answers

Exercise 3.1.6.1

- σ -bonding framework: Carbon and oxygen are sp^2 hybridized. Two sp^2 hybrid orbitals on oxygen have lone pairs, two sp^2 hybrid orbitals on carbon form C-H bonds, and one sp^2 hybrid orbital on C and O forms a C-O σ bond.
- π bonding: Unhybridized, singly occupied $2p$ atomic orbitals on carbon and oxygen interact to form π (bonding) and π^* (antibonding) molecular orbitals. With two electrons, only the π (bonding) orbital is occupied.

Exercise 3.1.6.2

Like nitrite, formate is a planar polyatomic ion with 18 valence electrons. The σ bonding framework can be described in terms of sp^2 hybridized carbon and oxygen, which account for 14 electrons. The three unhybridized $2p$ orbitals (on C and both O atoms) form three π molecular orbitals, and the remaining 4 electrons occupy both the bonding and nonbonding π molecular orbitals. The overall C-O bond order is therefore $\frac{3}{2}$.

This page titled [3.1.6: Multiple Bonds](#) is shared under a [CC BY-NC-SA 4.0](#) license and was authored, remixed, and/or curated by LibreTexts.

- [9.6: Multiple Bonds](#) is licensed [CC BY-NC-SA 3.0](#).

3.1.7: Molecular Orbitals

Learning Objectives

- To use molecular orbital theory to predict bond order

None of the approaches we have described so far can adequately explain why some compounds are colored and others are not, why some substances with unpaired electrons are stable, and why others are effective semiconductors. These approaches also cannot describe the nature of resonance. Such limitations led to the development of a new approach to bonding in which electrons are *not* viewed as being localized between the nuclei of bonded atoms but are instead delocalized throughout the entire molecule. Just as with the valence bond theory, the approach we are about to discuss is based on a quantum mechanical model.

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.

Molecular Orbital Theory: A Delocalized Bonding Approach

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 we explained in Chapter 9, electrons can behave like waves. In the molecular orbital approach, the overlapping atomic orbitals are described by mathematical equations called *wave functions*. The $1s$ atomic orbitals on the two hydrogen atoms interact to form two new molecular orbitals, one produced by taking the *sum* of the two $H\ 1s$ wave functions, and the other produced by taking their *difference*:

$$\begin{aligned} MO(1) &= AO(atom\ A) + AO(atom\ B) \\ MO(1) &= AO(atom\ A) - AO(atom\ B) \end{aligned} \quad (3.1.7.1)$$

The molecular orbitals created from Equation 3.1.7.1 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.

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

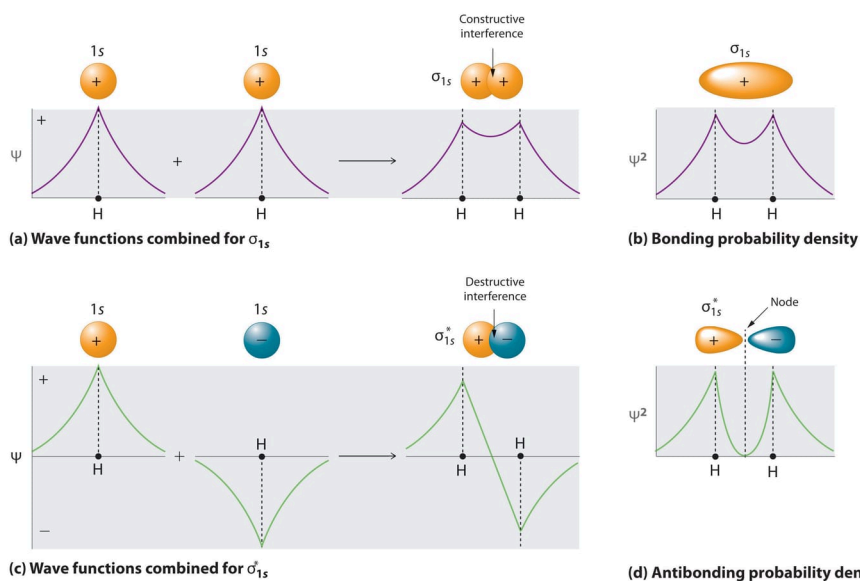


Figure 3.1.7.1: Molecular Orbitals for the H_2 Molecule. (a) This diagram shows the formation of a bonding σ_{1s} molecular orbital for H_2 as the sum of the wave functions (Ψ) of two H 1s atomic orbitals. (b) This plot of the square of the wave function (Ψ^2) for the bonding σ_{1s} molecular orbital 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.

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 1s orbitals is called a σ_{1s} combination (pronounced “sigma one ess”) (part (a) and part (b) in Figure 3.1.7.1). In a sigma (σ) orbital, (i.e., 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 1s denotes the atomic orbitals from which the molecular orbital was derived: The $\approx$ sign is used rather than an = sign because we are ignoring certain constants that are not important to our argument.

$$\sigma_{1s} \approx 1s(A) + 1s(B) \quad (3.1.7.2)$$

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 3.1.7.1). 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:

$$\sigma_{1s}^* \approx 1s(A) - 1s(B) \quad (3.1.7.3)$$

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 σ_{1s}^* orbital are generally found in the space outside the internuclear region. Because this allows the positively charged nuclei to repel one another, the σ_{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 1s atomic orbitals. Conversely, electrons in the σ_{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 1s atomic orbitals. Consequently, the σ_{1s}^* molecular orbital has a *higher* energy than either of the hydrogen 1s atomic orbitals. The σ_{1s} (bonding) molecular orbital is *stabilized* relative to the 1s atomic orbitals, and the σ_{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 3.1.7.2

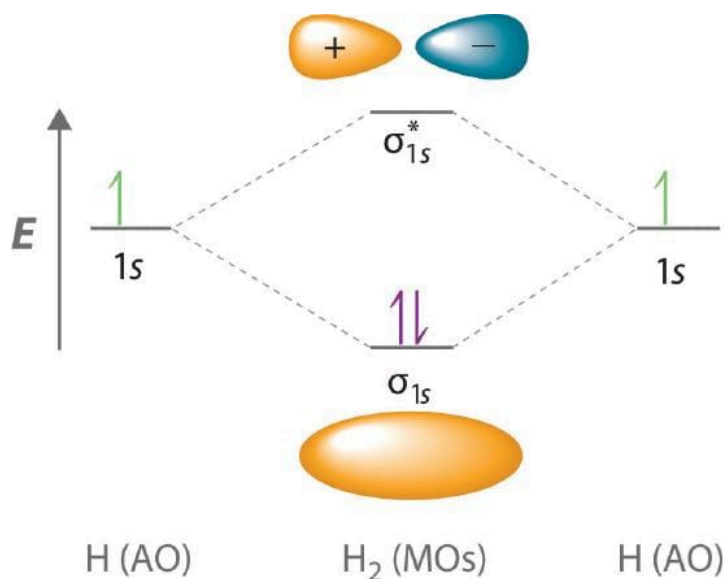


Figure 3.1.7.2: Molecular Orbital Energy-Level Diagram for H_2 . The two available electrons (one from each H atom) in this diagram fill the bonding σ_{1s} molecular orbital. Because the energy of the σ_{1s} molecular orbital is lower than that of the two H 1s atomic orbitals, the H_2 molecule is more 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 3.1.7.2). 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:

$$\text{bond order} = \frac{\text{number of bonding electrons} - \text{number of antibonding electrons}}{2} \quad (3.1.7.4)$$

To calculate the bond order of H_2 , we see from Figure 3.1.7.2 that the σ_{1s} (bonding) molecular orbital contains two electrons, while the σ_{1s}^* (antibonding) molecular orbital is empty. The bond order of H_2 is therefore

$$\frac{2-0}{2} = 1 \quad (3.1.7.5)$$

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 3.1.7.2 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](#).

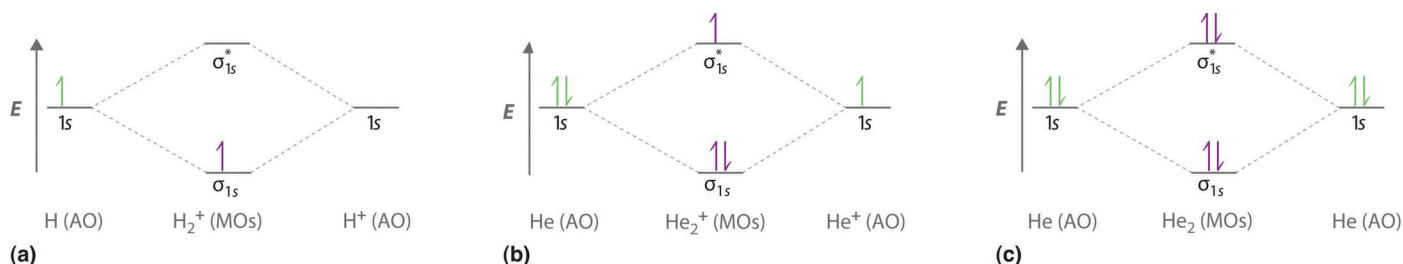


Figure 3.1.7.3: Molecular Orbital Energy-Level Diagrams for Diatomic Molecules with Only 1s Atomic Orbitals. (a) The H_2^+ ion, (b) the He_2^+ ion, and (c) the He_2 molecule are shown here.

for the H_2^+ ion the H has one unpaired electron in the 1s orbital so the H_2^+ has one unpaired electron in the σ_{1s} orbital. for He_2^+ ion,

He has a full 1s orbital and He^+ has one unpaired electron in the 1s orbital. This means that the σ_{1s} orbital is full and the σ_{1s}^* orbital has one unpaired electron. For the He_2 molecule, each He has a full 1s orbital. This means that σ_{1s} and σ_{1s}^* orbitals are full.

Figure 3.1.7.3a 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

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

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 3.1.7.1, these predictions agree with the experimental data.

Figure 3.1.7.3b 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 σ_{1s}^* antibonding orbital, giving a $(\sigma_{1s})^2(\sigma_{1s}^*)^1$ electron configuration. This electron configuration gives a bond order of

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

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 3.1.7.1).

Table 3.1.7.1: 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
H_2	$(\sigma_{1s})^2$	1	74	436
He_2^+	$(\sigma_{1s})^2(\sigma_{1s}^*)^1$	1/2	108	251
He_2	$(\sigma_{1s})^2(\sigma_{1s}^*)^2$	0	not observed	not observed

Finally, we examine the He_2 molecule, formed from two He atoms with $1s^2$ electron configurations. Figure 3.1.7.3c is the molecular orbital energy-level diagram for He_2 . With a total of four valence electrons, both the σ_{1s} bonding and σ_{1s}^* antibonding orbitals must contain two electrons. This gives a $(\sigma_{1s})^2(\sigma_{1s}^*)^2$ 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.

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

YouTube Video

This interactive element is not available in this format. Visit the link or scan the QR code to access it online.

[View this YouTube Video online](#)



Example 3.1.7.1

Use a molecular orbital energy-level diagram, such as those in Figure 3.1.7.2, to predict the bond order in the He_2^{2+} ion. Is this a stable species?

Given: chemical species

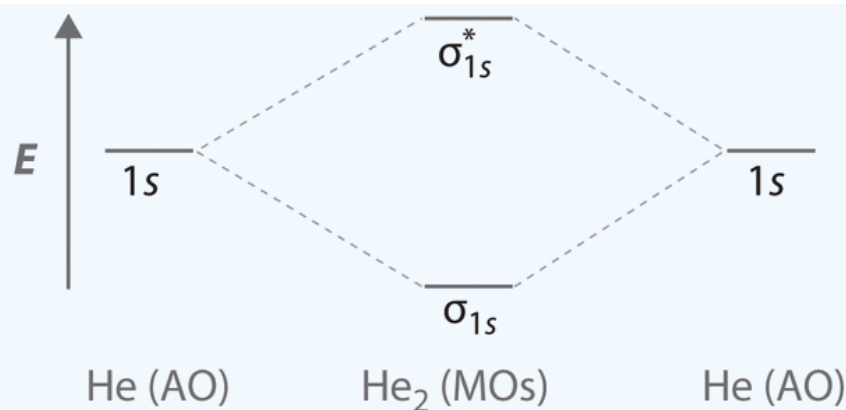
Asked for: molecular orbital energy-level diagram, bond order, and stability

Strategy:

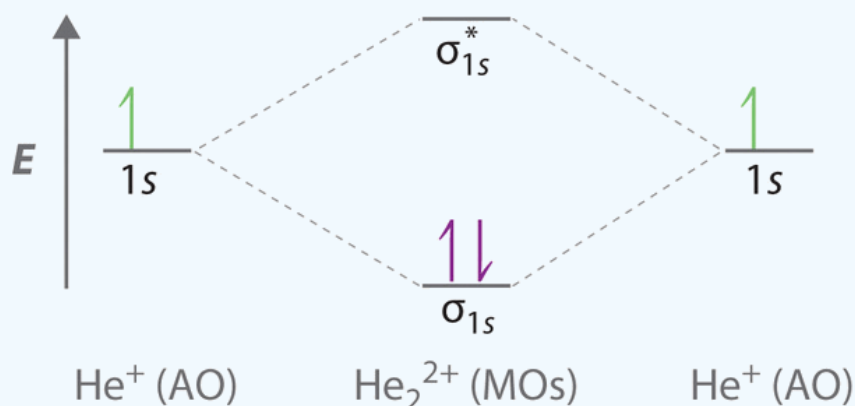
- Combine the two He valence atomic orbitals to produce bonding and antibonding molecular orbital
- Draw the molecular orbital energy-level diagram for the system.
- Determine the total number of valence electrons in the He_2^{2+} ion. Fill the molecular orbitals in the energy-level diagram beginning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

Solution:

A Two He $1s$ atomic orbitals combine to give two molecular orbitals: a σ_{1s} bonding orbital at lower energy than the atomic orbitals and a σ_{1s}^* 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 1s atomic orbital. We can now fill the molecular orbital diagram:



Each He^+ has one unpaired electron in the 1 s orbital. This means that He_2^{2+} has a full sigma 1 s orbital.

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 3.1.7.1

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 available at the end of this section.

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 3.1.7.4, 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 3.1.7.4. Experimentally, all are found to be stable in the gas phase, and some are even stable in solution.

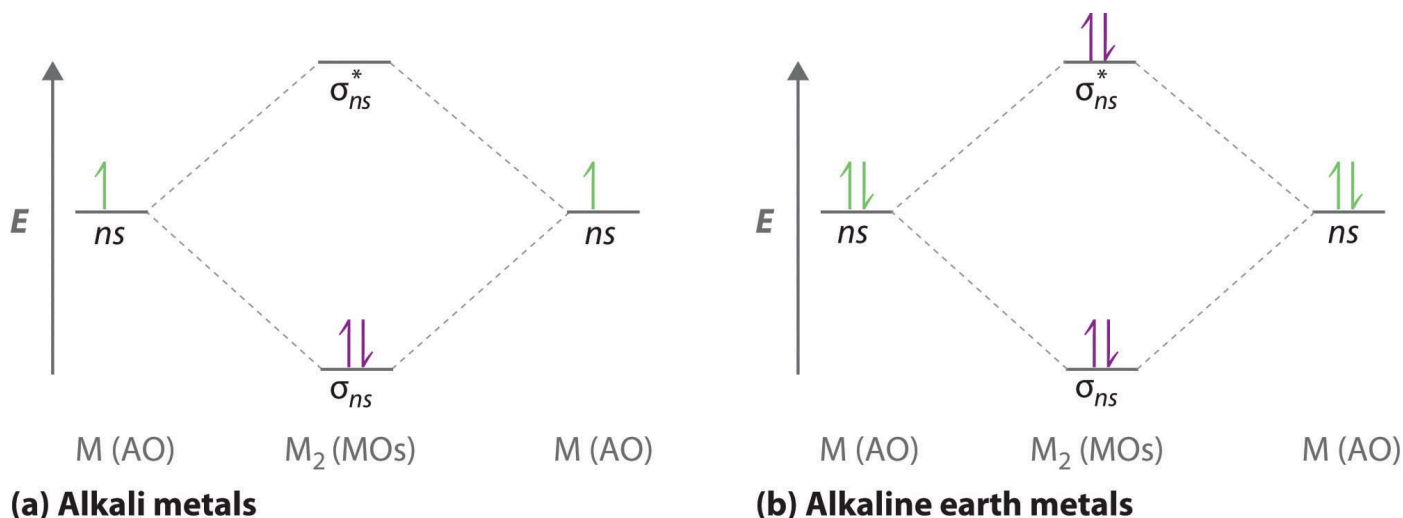


Figure 3.1.7.4 : Molecular Orbital Energy-Level Diagrams for Alkali Metal and Alkaline Earth Metal Diatomic (M_2) Molecules. (a) For alkali metal diatomic molecules, the two valence electrons are enough to fill the σ_{ns} (bonding) level, giving a bond order of 1. (b) For alkaline earth metal diatomic 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 3.1.7.2. As shown in part (b) in Figure 3.1.7.4, 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 3.1.7.2

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

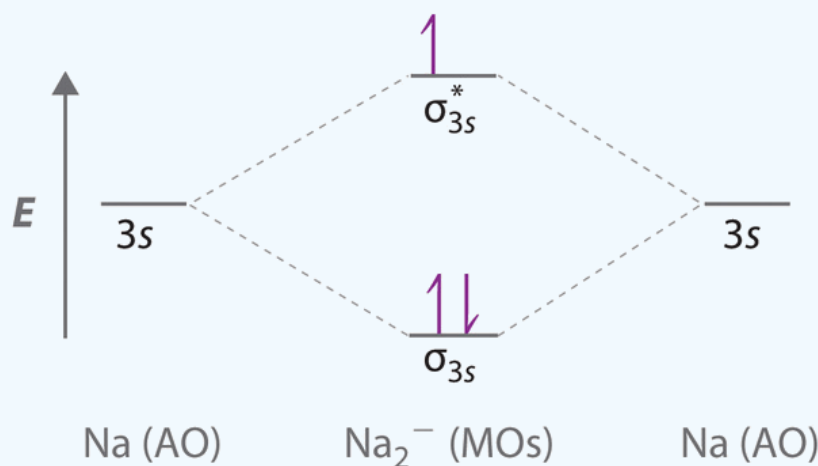
Strategy:

- 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 $[\text{Ne}]3s^1$ electron configuration, the molecular orbital energy-level diagram is qualitatively identical to the diagram for the interaction of two $1s$ 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 $(\sigma_{3s})^2 (\sigma_{3s}^*)^1$ 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 3.1.7.2

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 available at the end of this section.

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.

$$\sigma_{np_z} = np_z(A) + np_z(B) \quad (3.1.7.6)$$

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 3.1.7.5, 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):

$$\sigma_{np_z} = np_z(A) - np_z(B) \quad (3.1.7.7)$$

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

$$\sigma_{np_z} = np_z(A) + np_z(B) \quad (3.1.7.8)$$

In this combination, shown in part (b) in Figure 3.1.7.5, 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).

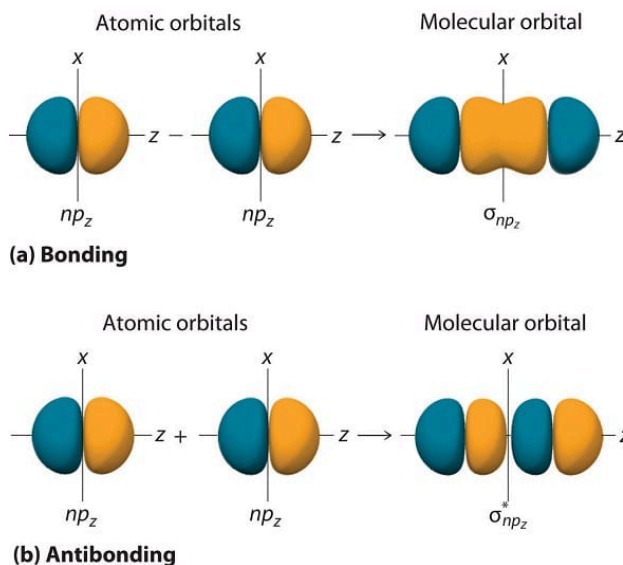


Figure 3.1.7.5 Formation of Molecular Orbitals from np_z Atomic Orbitals on Adjacent Atoms. (a) By convention, in a linear molecule or ion, the z-axis always corresponds to the internuclear axis, with +z to the right. As a result, the signs of the lobes of the np_z atomic orbitals on the two atoms alternate $- + - +$, 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 3.1.7.6, 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.

$$\pi_{np_x} = np_x(A) + np_x(B) \quad (3.1.7.9)$$

$$\pi_{np_x}^* = np_x(A) - np_x(B) \quad (3.1.7.10)$$

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 $\pi_{np_y}^*$ 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 $\pi_{np_x}^*$ and $\pi_{np_y}^*$ molecular orbitals.

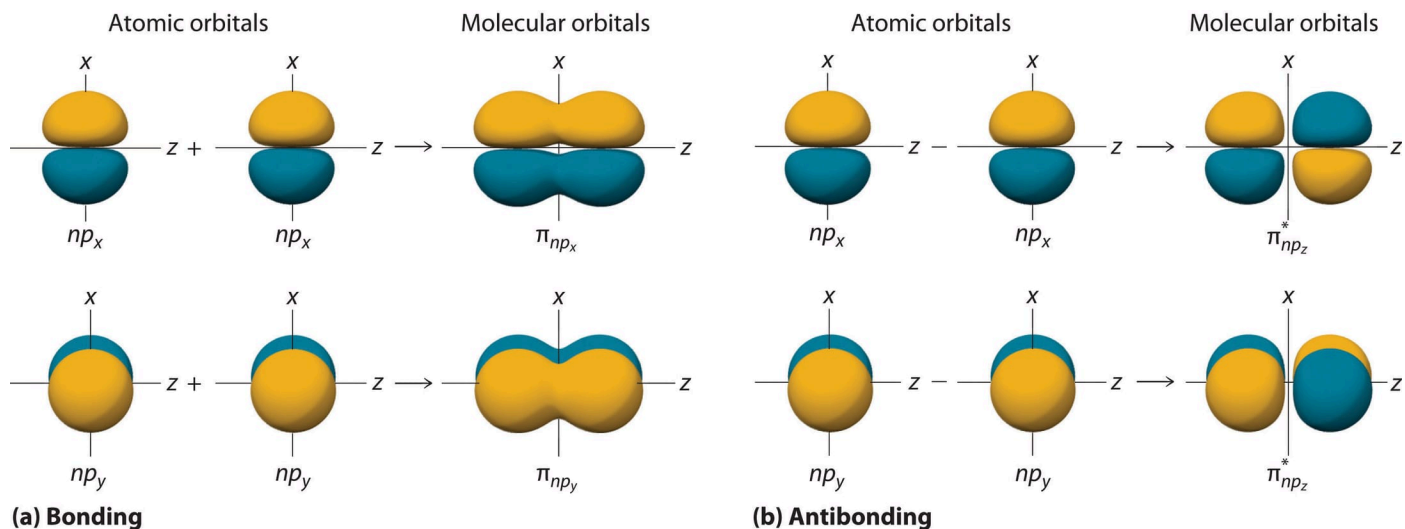


Figure 3.1.7.6: Formation of π Molecular Orbitals from np_x and np_y Atomic Orbitals on Adjacent Atoms. (a) Because the signs of the lobes of both the np_x and the np_y atomic orbitals on adjacent atoms are the same, in both cases the mathematical sum corresponds to a π (bonding) molecular orbital. (b) 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 3.1.7.7 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.

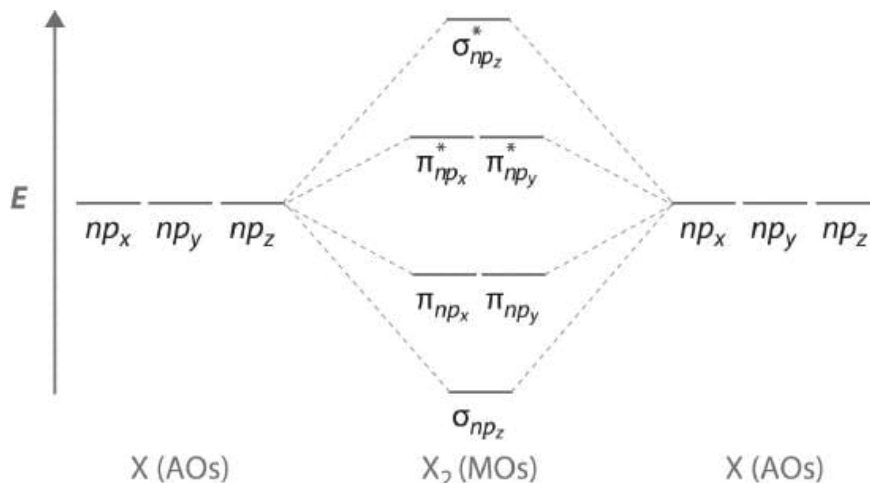


Figure 3.1.7.7 : The Relative Energies of the σ and π Molecular Orbitals Derived from np_x , np_y , and np_z Orbitals on Identical Adjacent Atoms. Because the two np_z orbitals point directly at each other, their orbital overlap is greater, so the difference in energy between the σ and σ^* molecular 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 3.1.7.8, 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.

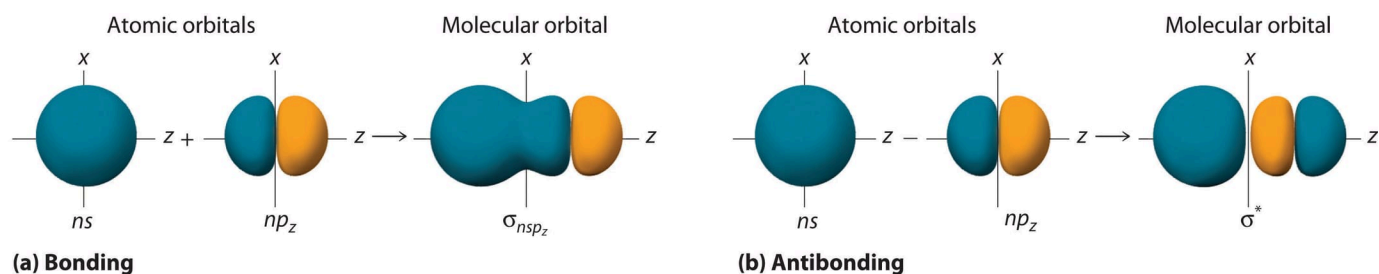


Figure 3.1.7.8 : Formation of Molecular Orbitals from an ns Atomic Orbital on One Atom and an np_z Atomic Orbital on an Adjacent Atom. (a) The mathematical sum results in a σ (bonding) molecular orbital, with increased probability density between the nuclei. (b) The mathematical difference results in a σ^* (antibonding) molecular orbital, with a nodal plane of zero probability density perpendicular to the internuclear axis.

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.

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.

Contributors and Attributions

Modified by Joshua Halpern (Howard University)

- 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.
- 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.
- 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.

Answers

Exercise 3.1.7.1

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

Exercise 3.1.7.2

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

This page titled [3.1.7: Molecular Orbitals](#) is shared under a [CC BY-NC-SA 4.0](#) license and was authored, remixed, and/or curated by LibreTexts.

- [9.7: Molecular Orbitals](#) is licensed [CC BY-NC-SA 3.0](#).

3.1.8: Second-Row Diatomic Molecules

Learning Objectives

- To apply Molecular Orbital Theory to the diatomic homonuclear molecule from the elements in the second period.

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 .

four key points to remember when drawing molecular orbital diagrams:

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.

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 3.1.8.1; 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 2p atomic orbitals because of the large difference in energy between the 2s and 2p atomic orbitals of fluorine. The lowest-energy molecular orbital derived from the three 2p 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 $\sigma_{2p_z}^*$ orbital is higher in energy than either of the degenerate $\pi_{2p_x}^*$ and $\pi_{2p_y}^*$ 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.

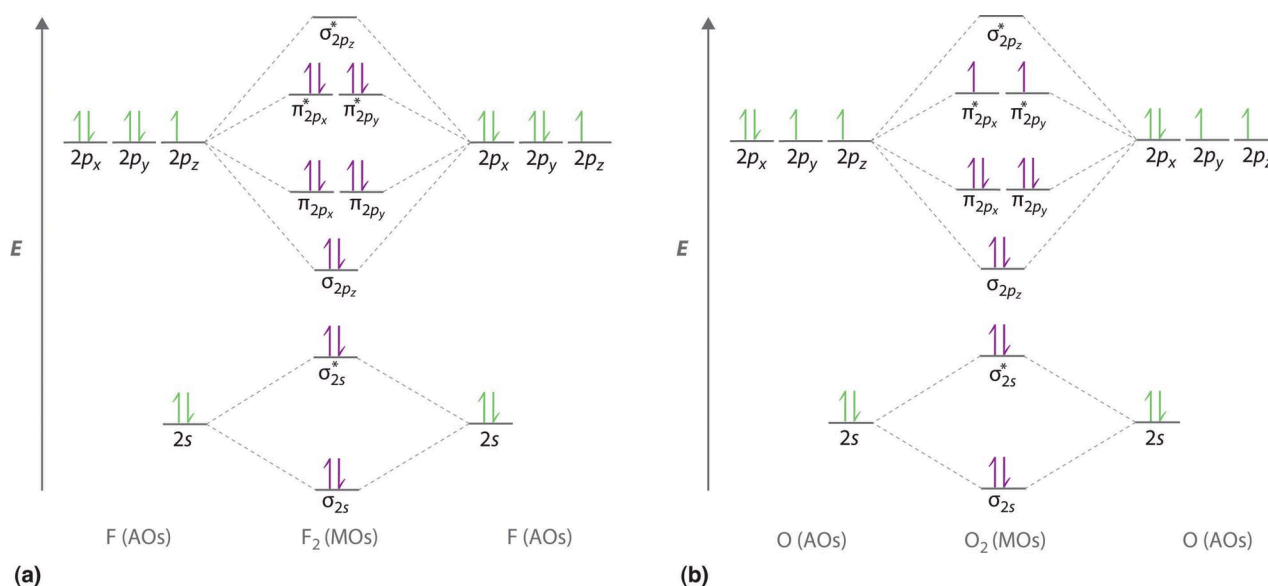


Figure 3.1.8.1: Molecular Orbital Energy-Level Diagrams for Homonuclear Diatomic Molecules. (a) For F_2 , with 14 valence electrons (7 from each F atom), all of the energy levels except the highest, $\sigma_{2p_z}^*$, are filled. This diagram shows 8 electrons in bonding orbitals and 6 in antibonding 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 $(\pi_{2p_x}^*, \pi_{2p_y}^*)$ 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 3.1.8.1. 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 $\pi_{2p_x}^*$ and $\pi_{2p_y}^*$ 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 3.1.8.2, 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.

YouTube Video

This interactive element is not available in this format. Visit the link or scan the QR code to access it online.

[View this YouTube Video online](#)

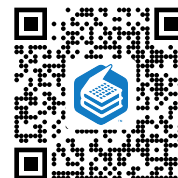


Figure 3.1.8.2: Liquid O_2 Suspended between the Poles of a Magnet. Because the O_2 molecule has two unpaired electrons, it is paramagnetic. Consequently, it is attracted into a magnetic field, which allows it to remain suspended between the poles of a powerful magnet until it evaporates. Full video can be found at www.youtube.com/watch?feature...&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 $\pi_{2p_x}^*$ and $\pi_{2p_y}^*$ orbitals. The difference in energy between the $2s$ and $2p$ atomic orbitals increases from Li_2 to F_2 due to increasing nuclear charge and poor screening of the $2s$ electrons by electrons in the $2p$ subshell. The bonding interaction between the $2s$ orbital on one atom and the $2p_z$ 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 3.1.8.3. Experimentally, it is found that the energy gap between the ns and np atomic orbitals *increases* as the nuclear charge increases (Figure 3.1.8.3). Thus for example, the σ_{2p_z} molecular orbital is at a lower energy than the $\pi_{2p_{x,y}}$ pair.

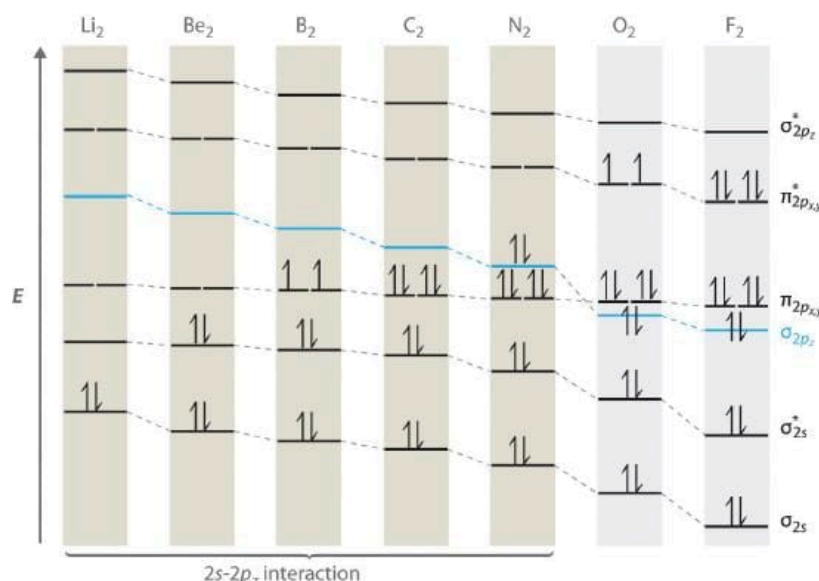


Figure 3.1.8.3: Molecular Orbital Energy-Level Diagrams for the Diatomic Molecules of the Period 2 Elements. Unlike earlier diagrams, only the molecular orbital energy levels for the molecules are shown here. For simplicity, the atomic orbital energy levels for the component *atoms* have been omitted. 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 $2s$ and $2p$ 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 3.1.8.3: Diatomic Sulfur

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

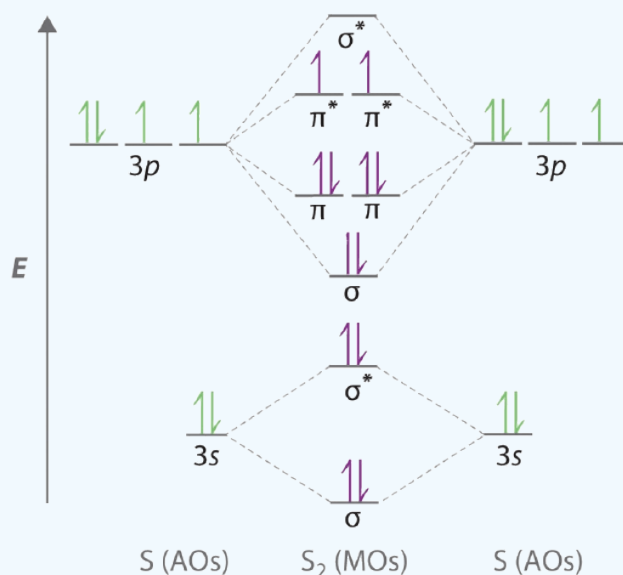
Strategy:

- 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.
- Draw the molecular orbital energy-level diagram for this system and determine the total number of valence electrons in S_2 .
- Fill the molecular orbitals in order of increasing energy, being sure to obey the Pauli principle and Hund's rule.
- 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 3.1.8.1 and Figure 3.1.8.3, we need to know how close in energy the 3s and 3p 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 3.1.8.3), 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:



Two filled sigma orbitals, one filled sigma * orbital, two filled pi orbitals, and two pi * orbitals with one unpaired electron.

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 $\pi_{3p_x}^*$ and $\pi_{3p_y}^*$ 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 $(\sigma_{3s})^2(\sigma_{3s}^*)^2(\sigma_{3p_z})^2(\pi_{3p_x,y})^4(\pi_{3p_x,y}^*)^2$ with 2 unpaired electrons. The bond order is $(8 - 4) \div 2 = 2$, so we predict an S=S double bond.

Exercise 3.1.8.3: The Peroxide Ion

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 available at the end of this section.

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 3.1.8.4. 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.

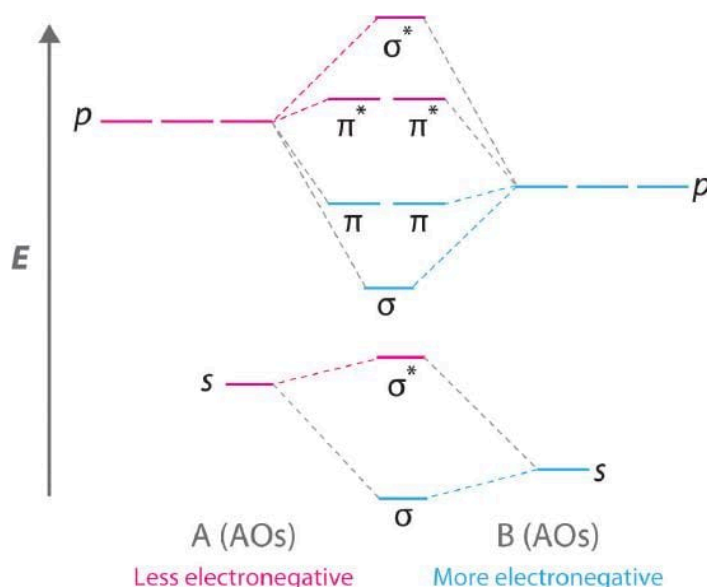


Figure 3.1.8.4: Molecular Orbital Energy-Level Diagram for a Heteronuclear Diatomic Molecule AB, Where $\chi_B > \chi_A$. The bonding molecular orbitals are closer in energy to the atomic orbitals of the more electronegative B atom. Consequently, the electrons in the bonding orbitals are not shared equally 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 3.1.8.13) shows that the general pattern is similar to that for the O_2 molecule (Figure 3.1.8.11). Because 10 electrons are sufficient to fill all the bonding molecular orbitals derived from $2p$ atomic orbitals, the 11th electron must occupy one of the degenerate π^* orbitals. The predicted bond order for NO is therefore $(8-3) \div 2 = 2 \frac{1}{2}$. 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.

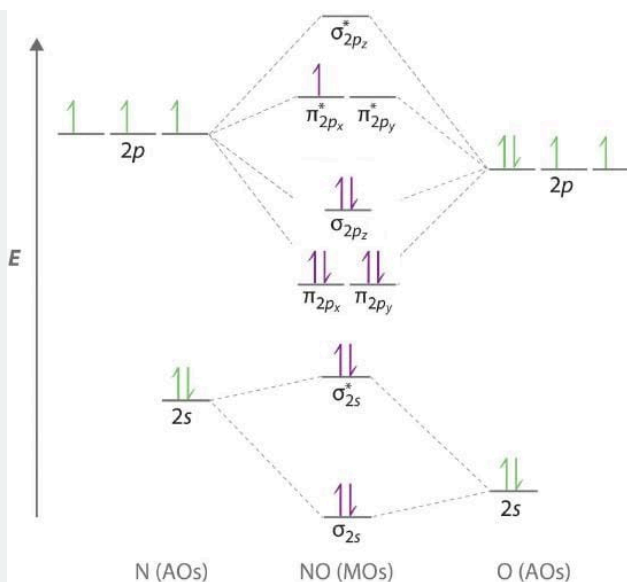


Figure 3.1.8.13: Molecular Orbital Energy-Level Diagram for NO. Because NO has 11 valence electrons, it is paramagnetic, with a single electron occupying the $(\pi_{2p_z}^*, \pi_{2p_y}^*)$ pair of orbitals.

Note that electronic structure studies show the ground state configuration of NO to be $(\sigma_{2s})^2 (\sigma_{2s}^*)^2 (\pi_{2p_{x,y}})^4 (\sigma_{2p_z})^2 (\pi_{2p_{x,y}}^*)^1$ 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 3.1.8.11).

Molecular orbital theory can also tell us something about the *chemistry* of NO. As indicated in the energy-level diagram in Figure 3.1.8.13, 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 $N \equiv O$ triple bond.

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 3.1.8.6 that the 1s orbital of atomic hydrogen is closest in energy to the 3p orbitals of chlorine. Consequently, the filled Cl 3s atomic orbital is not involved in bonding to any appreciable extent, and the only important interactions are those between the H 1s and Cl 3p orbitals. Of the three p orbitals, only one, designated as $3p_z$, can interact with the H 1s orbital. The $3p_x$ and $3p_y$ atomic orbitals have no net overlap with the 1s orbital on hydrogen, so they are not involved in bonding. Because the energies of the Cl 3s, $3p_x$, 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 $(2 - 0) \div 2 = 1$. Because the σ bonding molecular orbital is closer in energy to the Cl $3p_z$ than to the H 1s 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 $H^{\delta+} - Cl^{\delta-}$.

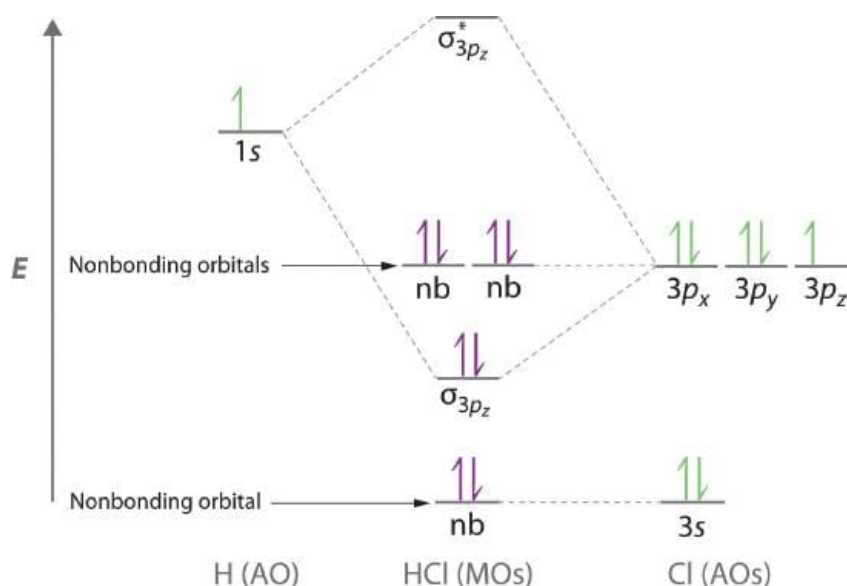


Figure 3.1.8.6: Molecular Orbital Energy-Level Diagram for HCl. The hydrogen 1s atomic orbital interacts most strongly with the $3p_z$ orbital on chlorine, producing a bonding/antibonding pair of molecular orbitals. The other electrons on Cl are best viewed as nonbonding. As a result, only the bonding σ orbital is occupied by electrons, giving a bond order of 1.

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

Example 3.1.8.4: The Cyanide Ion

Use a “skewed” molecular orbital energy-level diagram like the one in Figure 3.1.8.4 to describe the bonding in the cyanide ion (CN^-). What is the bond order?

Given: chemical species

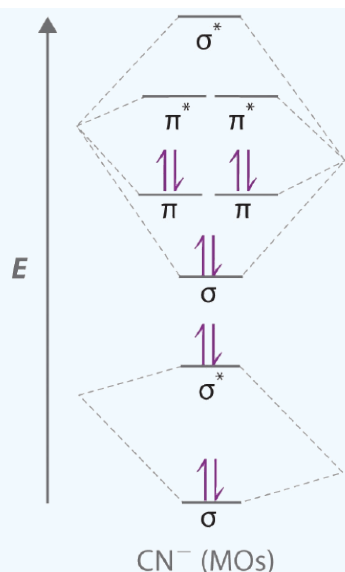
Asked for: “skewed” molecular orbital energy-level diagram, bonding description, and bond order

Strategy:

- Calculate the total number of valence electrons in CN^- . Then place these electrons in a molecular orbital energy-level diagram like Figure 3.1.8.4 in order of increasing energy. Be sure to obey the [Pauli principle](#) and [Hund's rule](#) while doing so.
- 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 3.1.8.4 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 N₂.

Exercise 3.1.8.4: The Hypochlorite Ion

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

Answer available at the end of this section.

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.

YouTube Video

This interactive element is not available in this format. Visit the link or scan the QR code to access it online.

[View this YouTube Video online](#)



Summary

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

- Modified by [Joshua Halpern \(Howard University\)](#)

Answers

Exercise 3.1.8.3: The Peroxide Ion

$(\sigma_{2s})^2 (\sigma_{2s}^*)^2 (\sigma_{2p_z})^2 (\pi_{2p_{x,y}})^4 (\pi_{2p_{x,y}}^*)^4$ bond order of 1; no unpaired electrons

Exercise 3.1.8.4: The Hypochlorite Ion

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

This page titled [3.1.8: Second-Row Diatomic Molecules](#) is shared under a [CC BY-NC-SA 4.0](#) license and was authored, remixed, and/or curated by LibreTexts.

- [9.8: Second-Row Diatomic Molecules](#) is licensed [CC BY-NC-SA 3.0](#).

3.1.E: Exercises

9.1: MOLECULAR SHAPES

9.2: THE VSEPR MODEL

Conceptual Problems

1. What is the main difference between the VSEPR model and Lewis electron structures?
2. What are the differences between molecular geometry and Lewis electron structures? Can two molecules with the same Lewis electron structures have different molecular geometries? Can two molecules with the same molecular geometry have different Lewis electron structures? In each case, support your answer with an example.
3. How does the VSEPR model deal with the presence of multiple bonds?
4. Three molecules have the following generic formulas: AX_2 , AX_2E , and AX_2E_2 . Predict the molecular geometry of each, and arrange them in order of increasing X–A–X angle.
5. Which has the smaller angles around the central atom— H_2S or SiH_4 ? Why? Do the Lewis electron structures of these molecules predict which has the smaller angle?
6. Discuss in your own words why lone pairs of electrons occupy more space than bonding pairs. How does the presence of lone pairs affect molecular geometry?
 - When using VSEPR to predict molecular geometry, the importance of repulsions between electron pairs decreases in the following order: LP–LP, LP–BP, BP–BP. Explain this order. Draw structures of real molecules that separately show each of these interactions.
 - How do multiple bonds affect molecular geometry? Does a multiple bond take up more or less space around an atom than a single bond? a lone pair?
 - Straight-chain alkanes do not have linear structures but are “kinked.” Using *n*-hexane as an example, explain why this is so. Compare the geometry of 1-hexene to that of *n*-hexane.
 - How is molecular geometry related to the presence or absence of a molecular dipole moment?
 - How are molecular geometry and dipole moments related to physical properties such as melting point and boiling point?
 - What two features of a molecule’s structure and bonding are required for a molecule to be considered polar? Is COF_2 likely to have a significant dipole moment? Explain your answer.
 - When a chemist says that a molecule is *polar*, what does this mean? What are the general physical properties of polar molecules?
 - Use the VSEPR model and your knowledge of bonding and dipole moments to predict which molecules will be liquids or solids at room temperature and which will be gases. Explain your rationale for each choice. Justify your answers.
 1. CH_3Cl
 2. PCl_3
 3. CO
 4. SF_6
 5. IF_5

6. CH_3OCH_3
 7. CCl_3H
 8. H_3COH
- The idealized molecular geometry of BrF_5 is square pyramidal, with one lone pair. What effect does the lone pair have on the actual molecular geometry of BrF_5 ? If LP-BP repulsions were *weaker* than BP-BP repulsions, what would be the effect on the molecular geometry of BrF_5 ?
 - Which has the smallest bond angle around the central atom— H_2S , H_2Se , or H_2Te ? the largest? Justify your answers.
 - Which of these molecular geometries *always* results in a molecule with a net dipole moment: linear, bent, trigonal planar, tetrahedral, seesaw, trigonal pyramidal, square pyramidal, and octahedral? For the geometries that do not always produce a net dipole moment, what factor(s) will result in a net dipole moment?

Conceptual Answers

- 1.
- 2.
3. To a first approximation, the VSEPR model assumes that multiple bonds and single bonds have the same effect on electron pair geometry and molecular geometry; in other words, VSEPR treats multiple bonds like single bonds. Only when considering fine points of molecular structure does VSEPR recognize that multiple bonds occupy more space around the central atom than single bonds.
- 4.
- 5.
- 6.
- 7.
- 8.
- 9.
- 10.
11. Physical properties like boiling point and melting point depend upon the existence and magnitude of the dipole moment of a molecule. In general, molecules that have substantial dipole moments are likely to exhibit greater intermolecular interactions, resulting in higher melting points and boiling points.
- 12.
13. The term “polar” is generally used to mean that a molecule has an asymmetrical structure and contains polar bonds. The resulting dipole moment causes the substance to have a higher boiling or melting point than a nonpolar substance.

Numerical Problems

1. Give the number of electron groups around the central atom and the molecular geometry for each molecule. Classify the electron groups in each species as bonding pairs or lone pairs.
 1. BF_3
 2. PCl_3
 3. XeF_2
 4. AlCl_4^-
 5. CH_2Cl_2
2. Give the number of electron groups around the central atom and the molecular geometry for each species. Classify the electron groups in each species as bonding pairs or lone pairs.
 1. ICl_3
 2. CCl_3^+

3. H_2Te
 4. XeF_4
 5. NH_4^+
3. Give the number of electron groups around the central atom and the molecular geometry for each molecule. For structures that are not linear, draw three-dimensional representations, clearly showing the positions of the lone pairs of electrons.
1. HCl
 2. NF_3
 3. ICl_2^+
 4. N_3^-
 5. H_3O^+
4. Give the number of electron groups around the central atom and the molecular geometry for each molecule. For structures that are not linear, draw three-dimensional representations, clearly showing the positions of the lone pairs of electrons.
1. SO_3
 2. NH_2^-
 3. NO_3^-
 4. I_3^-
 5. OF_2
5. What is the molecular geometry of ClF_3 ? Draw a three-dimensional representation of its structure and explain the effect of any lone pairs on the idealized geometry.
6. Predict the molecular geometry of each of the following.
1. ICl_3
 2. AsF_5
 3. NO_2^-
 4. TeCl_4
7. Predict whether each molecule has a net dipole moment. Justify your answers and indicate the direction of any bond dipoles.
1. NO
 2. HF
 3. PCl_3
 4. CO_2
 5. SO_2
 6. SF_4
8. Predict whether each molecule has a net dipole moment. Justify your answers and indicate the direction of any bond dipoles.
1. OF_2
 2. BCl_3
 3. CH_2Cl_2
 4. TeF_4
 5. CH_3OH
 6. XeO_4
9. Of the molecules $\text{Cl}_2\text{C}=\text{Cl}_2$, IF_3 , and SF_6 , which has a net dipole moment? Explain your reasoning.
10. Of the molecules SO_3 , XeF_4 , and $\text{H}_2\text{C}=\text{Cl}_2$, which has a net dipole moment? Explain your reasoning.

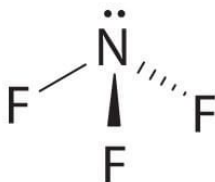
Numerical Answers

1.
 1. trigonal planar (all electron groups are bonding pairs)
 2. tetrahedral (one lone pair on P)
 3. trigonal bipyramidal (three lone pairs on Xe)
 4. tetrahedral (all electron groups on Al are bonding pairs)
 5. tetrahedral (all electron groups on C are bonding pairs)

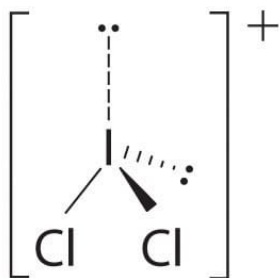
2.

1. four electron groups, linear molecular geometry

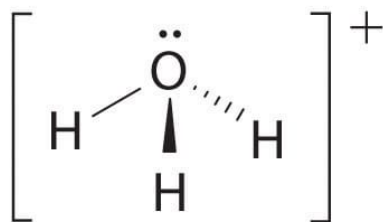
2. four electron groups, pyramidal molecular geometry



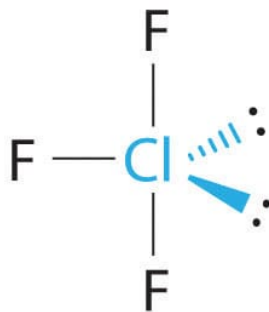
3. four electron groups, bent molecular geometry



4. two electron groups, linear molecular geometry
5. four electron groups, pyramidal molecular geometry



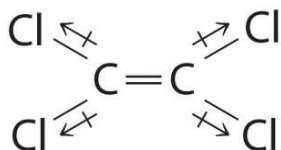
4.



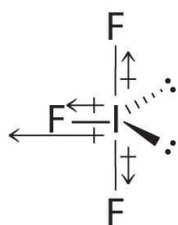
5.

The idealized geometry is T shaped, but the two lone pairs of electrons on Cl will distort the structure, making the F-Cl-F angle less than 180°.

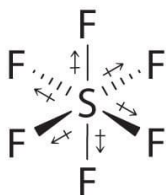
- 6.
- 7.
- 8.
9. $\text{Cl}_2\text{C}=\text{CCl}_2$: Although the C-Cl bonds are rather polar, the individual bond dipoles cancel one another in this symmetrical structure, and $\text{Cl}_2\text{C}=\text{CCl}_2$ does not have a net dipole moment.



IF_3 : In this structure, the individual I-F bond dipoles cannot cancel one another, giving IF_3 a net dipole moment.



SF_6 : The S-F bonds are quite polar, but the individual bond dipoles cancel one another in an octahedral structure. Thus, SF_6 has no net dipole moment.



9.3: MOLECULAR SHAPE AND MOLECULAR POLARITY

Conceptual Problems

1. Why do ionic compounds such as KI exhibit substantially less than 100% ionic character in the gas phase?
2. Of the compounds LiI and LiF, which would you expect to behave more like a classical ionic compound? Which would have the greater dipole moment in the gas phase? Explain your answers.

Numerical Problems

1. Predict whether each compound is purely covalent, purely ionic, or polar covalent.
 1. RbCl
 2. S_8
 3. TiCl_2
 4. SbCl_3
 5. LiI
 6. Br_2
2. Based on relative electronegativities, classify the bonding in each compound as ionic, covalent, or polar covalent. Indicate

the direction of the bond dipole for each polar covalent bond.

1. NO
 2. HF
 3. MgO
 4. AlCl_3
 5. SiO_2
 6. the C=O bond in acetone
 7. O_3
3. Based on relative electronegativities, classify the bonding in each compound as ionic, covalent, or polar covalent. Indicate the direction of the bond dipole for each polar covalent bond.
1. NaBr
 2. OF_2
 3. BCl_3
 4. the S-S bond in $\text{CH}_3\text{CH}_2\text{SSCH}_2\text{CH}_3$
 5. the C-Cl bond in CH_2Cl_2
 6. the O-H bond in CH_3OH
 7. PtCl_4^{2-}
4. Classify each species as having 0%–40% ionic character, 40%–60% ionic character, or 60%–100% ionic character based on the type of bonding you would expect. Justify your reasoning.
1. CaO
 2. S_8
 3. AlBr_3
 4. ICl
 5. Na_2S
 6. SiO_2
 7. LiBr
5. If the bond distance in HCl (dipole moment = 1.109 D) were double the actual value of 127.46 pm, what would be the effect on the charge localized on each atom? What would be the percent negative charge on Cl? At the actual bond distance, how would doubling the charge on each atom affect the dipole moment? Would this represent more ionic or covalent character?
6. Calculate the percent ionic character of HF (dipole moment = 1.826 D) if the H-F bond distance is 92 pm.
7. Calculate the percent ionic character of CO (dipole moment = 0.110 D) if the C-O distance is 113 pm.
8. Calculate the percent ionic character of PbS and PbO in the gas phase, given the following information: for PbS, $r = 228.69$ pm and $\mu = 3.59$ D; for PbO, $r = 192.18$ pm and $\mu = 4.64$ D. Would you classify these compounds as having covalent or polar covalent bonds in the solid state?

9.4: COVALENT BONDING AND ORBITAL OVERLAP

9.5: HYBRID ORBITALS

Conceptual Problems

1. Arrange sp , sp^3 , and sp^2 in order of increasing strength of the bond formed to a hydrogen atom. Explain your reasoning.
2. What atomic orbitals are combined to form sp^3 , sp , sp^3d^2 , and sp^3d ? What is the maximum number of electron-pair bonds that can be formed using each set of hybrid orbitals?

- Why is it incorrect to say that an atom with sp^2 hybridization will form only three bonds? The carbon atom in the carbonate anion is sp^2 hybridized. How many bonds to carbon are present in the carbonate ion? Which orbitals on carbon are used to form each bond?
- If hybridization did not occur, how many bonds would N, O, C, and B form in a neutral molecule, and what would be the approximate molecular geometry?
- How are hybridization and molecular geometry related? Which has a stronger correlation—molecular geometry and hybridization or Lewis structures and hybridization?
- In the valence bond approach to bonding in BeF_2 , which step(s) require(s) an energy input, and which release(s) energy?
- The energies of hybrid orbitals are intermediate between the energies of the atomic orbitals from which they are formed. Why?
- How are lone pairs on the central atom treated using hybrid orbitals?
- Because nitrogen bonds to only three hydrogen atoms in ammonia, why doesn't the nitrogen atom use sp^2 hybrid orbitals instead of sp^3 hybrids?
- Using arguments based on orbital hybridization, explain why the CCl_6^{2-} ion does not exist.
- Species such as NF_5^{2-} and OF_4^{2-} are unknown. If $3d$ atomic orbitals were much lower energy, low enough to be involved in hybrid orbital formation, what effect would this have on the stability of such species? Why? What molecular geometry, electron-pair geometry, and hybridization would be expected for each molecule?

Numerical Problems

- Draw an energy-level diagram showing promotion and hybridization to describe the bonding in CH_3^- . How does your diagram compare with that for methane? What is the molecular geometry?
- Draw an energy-level diagram showing promotion and hybridization to describe the bonding in CH_3^+ . How does your diagram compare with that for methane? What is the molecular geometry?
- Draw the molecular structure, including any lone pairs on the central atom, state the hybridization of the central atom, and determine the molecular geometry for each molecule.
 - BBr_3
 - PCl_3
 - NO_3^-
- Draw the molecular structure, including any lone pairs on the central atom, state the hybridization of the central atom, and determine the molecular geometry for each species.
 - AsBr_3
 - CF_3^+
 - H_2O
- What is the hybridization of the central atom in each of the following?
 - CF_4
 - CCl_2^{2-}
 - IO_3^-
 - SiH_4

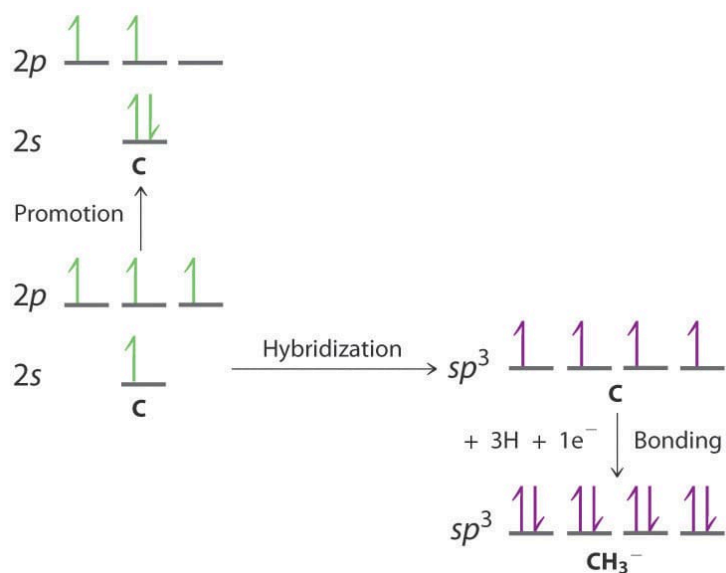
6. What is the hybridization of the central atom in each of the following?

1. CCl_3^+
2. CBr_2O
3. CO_3^{2-}
4. IBr_2^-

7. What is the hybridization of the central atom in PF_6^- ? Is this ion likely to exist? Why or why not? What would be the shape of the molecule?

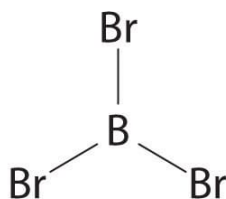
8. What is the hybridization of the central atom in SF_5^- ? Is this ion likely to exist? Why or why not? What would be the shape of the molecule?

Numerical Answers



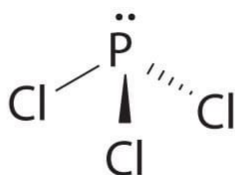
The promotion and hybridization process is exactly the same as shown for CH_4 in the chapter. The only difference is that the C atom uses the four singly occupied sp^3 hybrid orbitals to form electron-pair bonds with only *three* H atoms, and an electron is added to the fourth hybrid orbital to give a charge of 1-. The electron-pair geometry is tetrahedral, but the molecular geometry is pyramidal, as in NH_3 .

2.



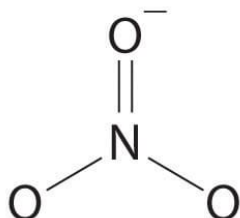
3. 1.

sp^2 , trigonal planar



2.

sp^3 , pyramidal



3.

sp^2 , trigonal planar

- 4.
5. The central atoms in CF_4 , CCl_2^{2-} , IO_3^- , and SiH_4 are all sp^3 hybridized.
- 6.
7. The phosphorus atom in the PF_6^- ion is sp^3d^2 hybridized, and the ion is octahedral. The PF_6^- ion is isoelectronic with SF_6 and has essentially the same structure. It should therefore be a stable species.

9.6: MULTIPLE BONDS

Conceptual Problems

1. What information is obtained by using the molecular orbital approach to bonding in O_3 that is not obtained using the VSEPR model? Can this information be obtained using a Lewis electron-pair approach?
2. How is resonance explained using the molecular orbital approach?
3. Indicate what information can be obtained by each method:

	Lewis Electron Structures	VSEPR Model	Valence Bond Theory	Molecular Orbital Theory
Geometry				
Resonance				
Orbital Hybridization				
Reactivity				
Expanded Valences				
Bond Order				

Numerical Problems

1. Using both a hybrid atomic orbital and molecular orbital approaches, describe the bonding in BCl_3 and CS_3^{2-} .
2. Use both a hybrid atomic orbital and molecular orbital approaches to describe the bonding in CO_2 and N_3^- .

9.7: MOLECULAR ORBITALS

9.8: SECOND-ROW DIATOMIC MOLECULES

This page titled [3.1.E: Exercises](#) is shared under a [CC BY-NC-SA 4.0](#) license and was authored, remixed, and/or curated by LibreTexts.

3.1.S: Molecular Geometry and Bonding Theories (Summary)

9.1: Molecular Shapes

The Lewis electron-pair approach described previously can be used to predict the number and types of bonds between the atoms in a substance, and it indicates which atoms have lone pairs of electrons. This approach gives no information about the actual arrangement of atoms in space, however.

- **Bond angles:** angles made by the lines joining the nuclei of the atoms in a molecule
- Bond angles determine overall shape of molecule

VSEPR Model" data-cke-saved-href="/Bookshelves/General_Chemistry/Map:_Chemistry_-_The_Central_Science_(Brown_et_al.)/09:_Molecular_Geometry_and_Bonding_9.02:_The_VSEPR_Model" href="/Bookshelves/General_Chemistry/Map:_Chemistry_-_The_Central_Science_(Brown_et_al.)/09:_Molecular_Geometry_and_Bonding_9.02:_The_VSEPR_Model" data-quail-id="12">9.2: The VSEPR Model

The VSEPR model can predict the structure of nearly any molecule or polyatomic ion in which the central atom is a nonmetal, as well as the structures of many molecules and polyatomic ions with a central metal atom. The VSEPR model is not a theory; it does not attempt to explain observations. Instead, it is a counting procedure that accurately predicts the three-dimensional structures of a large number of compounds, which cannot be predicted using the Lewis electron-pair approach.

The Valence-Shell Electron Pair-Repulsion Model

- *Valence-shell electron-pair repulsion (VSEPR) model:* model that accounts for the geometric arrangements of shared and unshared electron pairs around a central atom in terms of the repulsions between electron pairs
- Electrons repel one another; hence, *the best arrangement of a given number of electron pairs is the one that minimizes the repulsions among them.*

Predicting Molecular Geometries

- Two types of valence-shell electron pairs; *bonding pairs* and *nonbonding pairs*.
- **Electron-pair geometry:** 3-D arrangement of electron pairs around an atom according to the VSEPR model
- **Molecular geometry:** the arrangement in space of the atoms of a molecule

When describing the shapes of molecules, we always give the *molecular* geometry rather than the *electron-pair* geometry. Molecular geometries only include BONDING pairs. For example, NH_3 is a tetrahedral according to electron-pair geometry because it has 3 bonds and an unshared pair of electron. However, according to molecular geometry it is a trigonal pyramidal because it has only 3 bonds.

How to predict molecular geometries using VSEPR model:

1. Sketch the Lewis dot structure of the molecule or ion
2. Count the total number of electron pairs around the central atom and arrange them in the way that minimizes electron-pair repulsions
3. Describe the molecular geometry in terms of the angular arrangement of the *bonding* pairs

Four or Fewer Valence-Shell Electron Pairs

A double or triple bond has essentially the same effect on bond angles as a single bond and is therefore counted as one bonding pair (that is, one electron region) when predicting geometry

The Effect of Nonbonding Electrons and Multiple Bonds on Bond Angles

Bond angles decrease as the number of nonbonding electron pairs increases. Bonding pairs are attracted by the two nuclei. By contrast, nonbonding electrons move under the attractive influence of only one nucleus and thus spread out more in space.

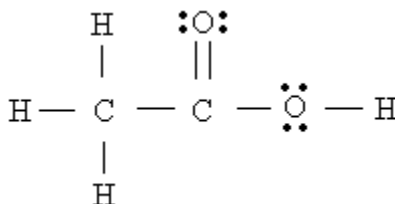
- Nonbonding electron pairs exert greater repulsive forces on adjacent electron pairs and thus tend to compress the angles between the bonding pairs
- Electrons in multiple bonds, like nonbonding pairs, exert a greater repulsive force on adjacent electron pairs than do single bonds.

Geometries of Molecules with Expanded Valence Shells

- When the central atom of a molecule or ion is from the third period of the periodic table and beyond (has *d* subshell) that atom may have more than four electron pairs around it
- The most stable electron-pair geometry for five electron pairs is the Trigonal bipyramid.
- Trigonal bipyramid geometries have two distinct types of electron pairs. They are *axial pairs* and *equatorial pairs*. In axial position, an electron pair is situated 90° from the three equatorial pairs. In an equatorial position, an electron pairs is situated 120° from the other two equatorial pairs and 90° from the two axial pairs.
- Because nonbonding pairs exert larger repulsions than bonding pairs, they always occupy the equatorial positions
- The most stable electron-pair geometry for six electron pairs is the *octahedron*.
- In an octahedron, the angles are either 90° or 180° , and all six positions are equivalent

Molecules with No Single Central Atom

Consider acetic acid molecule



Carbon bonded to three hydrogens and one carbon. Second carbon is double bonded to one oxygen and single bonded to another oxygen. The single bonded oxygen is bonded to a hydrogen.

- Notice that the leftmost C has four bonded pairs around it. Hence, it must be a tetrahedral.
- The central C has 3 bonding pairs around it (counting the double bond as a single pair), hence, it is trigonal planar
- O has two bonding pairs, and two nonbonding ones. Hence, it is bent.

9.3: Molecular Shape and Molecular Polarity

Compounds with polar covalent bonds have electrons that are shared unequally between the bonded atoms. The polarity of such a bond is determined largely by the relative electronegativities of the bonded atoms. The asymmetrical charge distribution in a polar substance produces a dipole moment, which is the product of the partial charges on the bonded atoms and the distance between them.

Polar: in a molecule, if its centers of negative and positive charge don't coincide, aka **dipole**

- If there are no charges on the opposite ends of a molecule, or if the charges have the same sign, the molecule does not have a dipole moment and is therefore *nonpolar*. Any diatomic molecule with a polar bond is a polar molecule
- Polar molecules align themselves with respect to one another. The negative end of a polar molecule is attracted to a positive ion, the positive end is attracted to a negative ion
- **Dipole moment:** measures the degree of polarity of a given molecule. The dipole moment, μ , is the product of the charge at either end of the dipole, Q , times the distance, r , between the charges.

$$\mu = Qr$$

Therefore, the dipole moment increases as the quantity of charge that is separated increases and as the distance between the positive and negative centers increases. Dipole moments are generally reported in debyes (D), a unit equaling 3.33×10^{-30} C-m.

The Polarity of Polyatomic Molecules

- The polarity of a molecule containing more than two atoms depends on both the polarities of the bonds and the geometry of the molecule
- For each polar bond in a molecule, we can consider the *bond dipole*, that is, the dipole moment due only to the two atoms bonded together. We must then ask what the overall dipole moment results from adding up the individual bond dipoles. Let's use CO₂ (linear) as an example
- In CO₂, each C – O bond is polar, and because they are identical, the bond dipoles are equal in magnitude.
- The fact that both C – O bonds are polar doesn't necessarily mean the whole CO₂ molecule is
- Bond dipoles and dipole moments are vector quantities; they have both a magnitude and direction. When calculating the overall dipole moment, both the magnitude and direction of the bond dipoles must be considered in this sum of vectors
- The two bond dipoles in CO₂, although equal in magnitude, are opposite in direction, which makes them cancel each other out. Hence, CO₂ has an overall dipole moment of zero. Even though the oxygen atoms in CO₂ carry a partial negative charge, the geometry of the molecule dictates the overall dipole moment.
- Now, let's consider H₂O. Both of its bonds are identical once again, but the geometry is bent instead of linear. Hence, the bonds do not cancel each other out, and H₂O has a dipole moment
- Molecules in which the central is symmetrically surrounded by identical atoms (BF₃, CCl₄) are nonpolar.
- For AB_{*n*} molecules in which ALL of the B atoms are the same, certain symmetrical geometries – linear (AB₂), trigonal planar (AB₃), tetrahedral and square planar (AB₄), trigonal bipyramidal (AB₅), and octahedral (AB₆) – must lead to nonpolar molecules, regardless of how polar the individual bonds are.

9.4: Covalent Bonding and Orbital Overlap

A more sophisticated treatment of bonding is needed for systems such as these. In this section, we present a quantum mechanical description of bonding, in which bonding electrons are viewed as being localized between the nuclei of the bonded atoms. The overlap of bonding orbitals is substantially increased through a process called hybridization, which results in the formation of stronger bonds.

Valence bond theory: model of chemical bonding in which an electron-pair bond is formed between two atoms by the overlap of orbitals on the two atoms

- Covalent bonding occurs when atoms share electrons. This increases the electron density between the two nuclei, and is visualized as occurring when a valence atomic orbital of one atom merges with that of another atom
- As the distance between the atoms decreases, their overlap increases. Because of the resultant increase in electron density between the nuclei, the potential energy of the system decreases, increasing the strength of the bond.
- The observed bond length is the distance at which the attractive forces between unlike charges (electrons and nuclei) are balanced by the repulsive forces between like charges (electron-electron and nucleus-nucleus)

9.5: Hybrid Orbitals

The localized valence bonding theory uses a process called hybridization, in which atomic orbitals that are similar in energy but not equivalent are combined mathematically to produce sets of equivalent orbitals that are properly oriented to form bonds. These new combinations are called hybrid atomic orbitals because they are produced by combining (hybridizing) two or more atomic orbitals from the same atom.

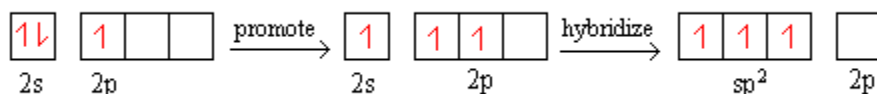
sp Hybrid Orbitals

- Use the salt BeF₂ as an example. Its geometry is linear, however it is now hard to determine which orbitals on the Be atom overlap with those of the F atoms. The electron configuration of Be is 1s² 2s². Hence, Be in its ground state has no unpaired electrons and is unable to form bonds
- Be's only option is to "promote" one of its two electrons in the 2s shell to the 2p shell. It will then have a configuration of 1s²

- $2s^1 2p^1$. Since the 2p orbital is at a higher energy level than the 2s orbital, this promotion requires energy
- The Be atom now has two unpaired electrons (2s and 2p) and would be able to form two bonds, which will not be similar. The two new orbitals are identical in shape (two lobes; one much larger than the other) but are oriented in different directions. Two hybrid orbitals have been created
- **Hybrid orbitals:** orbitals that result from the mixing of different kinds of atomic orbitals on the same atom. For example and sp^3 hybrid results from the mixing, or hybridizing, of one s orbital and three p orbitals
- **Hybridization:** mixing of different types of atomic orbitals to produce a set of equivalent hybrid orbitals
- In this case, we have hybridized one s and one p orbital, so we call each hybrid an *sp hybrid orbital*. For the Be atom of BeF_2 , the orbital diagram is written as follows: $1s^2 2sp^2$
- Hybrid orbitals have one large lobe and can therefore be directed at surrounding atoms more effectively, forming stronger bonds. The energy released by such bonds enables the promotion of a 2s electron to the 2p level.

sp^2 and sp^3 Hybrid Orbitals

- Whenever we mix a certain number of atomic orbitals, we get the same number of hybrid orbitals. Each of these hybrid orbitals is equivalent to the others but points in a different direction.
- Consider BF_3 . B has an electron configuration of $2s^2 2p^1$. It promotes one of its 2s electron to the 2p orbital to have a configuration of $2s^1 2p^2$. Then, it hybridizes into 3 sp^2 hybrid orbitals



The same process can apply to the creation of sp^3 hybrid orbitals

Hybridization Involving d Orbitals

Same process as sp^2 orbitals. For example, mixing one s orbital, three p orbitals, and two d orbitals gives six sp^3d^2 hybrid orbitals, which are directed at the vertices of an octahedron

Section Summary

The molecular geometry needs to be known first in order to use the concept of hybridization, then we can use the following rules:

1. Draw the Lewis structure for the molecule or ion
2. Determine the electron-pair geometry using the VSEPR model
3. Specify the hybrid orbitals needed to accommodate the electron pairs based on their geometrical arrangement

9.6: Multiple Bonds

To describe the bonding in more complex molecules with multiple bonds, we can use an approach that uses hybrid atomic orbitals to describe the σ bonding and molecular orbitals to describe the π bonding. In this approach, unhybridized np orbitals on atoms bonded to one another are allowed to interact to produce bonding, antibonding, or nonbonding combinations.

In each covalent bond we have considered so far, the electron density is concentrated symmetrically about the line that connects the two nuclei (*internuclear axis*). This axis passes through the middle of the overlap region

- **Sigma (σ) bond:** covalent bond in which electron density is concentrated along the internuclear axis
- **Pi (π) bond:** covalent bond in which electron density is concentrated above and below the internuclear axis. Pi bonds are generally weaker than sigma bonds (less overlap)

Usually, single bonds are σ bonds. A double bond has one σ bond and one π bond. A triple bond has one σ bond and two π bonds.

Consider C_2H_4 as an example. After hybridization, C has 3 sp^2 hybrid orbitals and one electron in the remaining unhybridized 2p

orbital. The unhybridized 2p electron is directly perpendicular to the plane that contains the three sp^2 hybrid orbitals

- The C – H σ bond is formed by the overlap of a sp^2 hybrid orbital with the 1s orbital of hydrogen. Hence, the bond uses two electrons
- The C – C σ bond is formed by the overlap of two sp^2 hybrid orbitals, one on each carbon atom, and requires two more electrons. Overall, C_2H_4 has 12 valence electrons, 10 of which are used in the formation of the bonds
- The remaining two valence electrons reside in the unhybridized 2p orbitals, one electron on each of the atoms
- The 2p orbitals can overlap with one another in a sideways fashion. This will lead to the electron density being concentrated above and below the C – C bond axis, hence being a π bond

Because π bonds require that portions of a molecule be planar, they can introduce rigidity into molecules (strongly affects the properties of substances)

Although π bonds can be formed from d orbitals, we will only consider those formed by p orbitals. They can only form if unhybridized p orbitals are present on the bonded atoms. Only atoms having sp or sp^2 hybridization can be involved in π bonding. Double and triple bonds are more common in molecules with small atoms

Delocalized Bonding

- σ and π electrons are *localized* when they are associated totally with two atoms forming the bond.
- In some molecules, particularly those with more than one resonance form, we cannot accurately describe the bonding as localized. In order to deal with this, we "smear out" the bonds (*delocalize* them) so that it fits both resonance structures as best as possible

Delocalized electrons: electrons that are spread over a number of atoms in a molecule rather than localized between a pair of atoms

Section Summary

1. Every pair of bonded atoms shares one or more pairs of electrons. In every bond, at least one pair of electrons is localized in the space between the atoms, in a σ bond. The appropriate set of hybrid orbitals used to form the σ bonds between an atom and its neighbors is determined by the observed geometry of the molecule
2. The electrons in σ bonds are localized in the region between two bonded atoms and do not make a significant contributions to the bonding between any other two atoms
3. When atoms share more than one pair of electrons, the additional pairs are in π bonds. The centers of charge density in a π bond lie above and below the bond axis.
4. Molecules with two or more resonance forms can have π bonds that extend over more than two bonded atoms. Electrons in π bonds that extend over more than two bonded atoms are said to be delocalized

9.7: Molecular Orbitals

A molecular orbital is an allowed spatial distribution of electrons in a molecule that is associated with a particular orbital energy. Unlike an atomic orbital, 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 describe overlapping atomic orbitals.

- **Molecular orbital theory:** theory that predicts that electrons in molecules exist in allowed energy states.
- **Molecular orbitals:** allowed state for an electron in a molecule. Molecular orbitals are very similar to atomic orbitals. Both hold a maximum of two electrons (with opposite spins), have definite energies, and their electron-density distribution can be visualized by using contour representations. However, molecular orbitals are associated with the *entire* molecule

The Hydrogen Molecule

Consider H_2 as an example. Whenever two atomic orbitals overlap, two molecular orbitals form. Thus, the overlap of the 1s orbitals of two hydrogen atoms to form H_2 produces two molecular orbitals.

Bonding molecular orbital: molecular orbital in which the electron density is concentrated in the internuclear region. The energy

of a bonding molecular orbital is lower than the energy of the separate atomic orbitals from which it forms.

The bonding molecular orbital results from summing the two atomic orbitals so that the atomic orbital wave functions enhance each other in the bond region. Because an electron in this molecular orbital is strongly attracted to both nuclei, the electron is more stable (lower energy) than it is in the 1s orbital of hydrogen. Because it concentrates electron density between both nuclei, the bonding molecular orbital holds the atoms together in a covalent bond.

Antibonding molecular orbital: molecular orbital in which electron density is concentrated outside the region between the two nuclei of bonded atoms. Such orbitals, designated as σ^* or π^* , are less stable (of higher energy) than bonding molecular orbitals

- An electron in the antibonding molecular orbital is repelled from the bonding region and is therefore less stable (higher energy) than it is in the 1s orbital of the hydrogen atom
- **Sigma (σ) molecular orbital:** molecular orbital that centers the electron density about an imaginary line passing through two nuclei
- **Energy level diagram:** aka **Molecular orbital diagram;** diagram that shows the energies of molecular orbitals relative to the atomic orbitals from which they are derived
- Electrons occupying a bonding molecular orbital are called *bonding* electrons

Bond Order

- **Bond order:** related to the stability of a covalent bond.

$$\text{Bond order} = \frac{1}{2}(\text{number of bonding electrons} - \text{number of antibonding electrons})$$

A bond order of 1 represents a single bond, a bond order of 2 represents a double bond, and a bond order of 3 represents a triple bond. A bond order of 0 means that no bonds exist

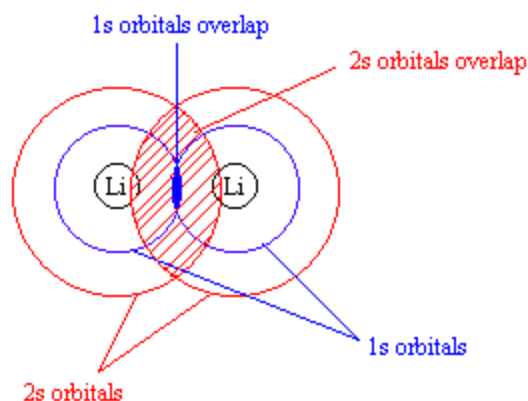
9.8: Second-Row Diatomic Molecules

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 atomic orbitals increases.

Material here applies to *homonuclear* diatomic molecules (those composed of identical atoms)

1. The number of atomic orbitals formed equals the number of atomic orbitals combined
2. Atomic orbitals combine most effectively with other atomic orbitals of similar energy
3. The effectiveness with which two atomic orbitals combine is proportional to their overlap with one another; that is, as the overlap increases, the bonding orbital is lowered in energy, and the antibonding orbital is raised in energy
4. Each molecular orbital can accommodate at most two electrons, with their spins paired (Pauli exclusion principle)
5. When molecular orbitals have the same energy, one electron enters each orbital (with parallel spins) before spin pairing occurs (Hund's rule)

Molecular Orbitals for Li_2 and Be_2



The 2 s orbitals are drawn in red whilst the 1 s orbitals are drawn in blue. There is an overlap between the two 1 s orbitals and two 2 s orbitals.

- Lithium has 1s and 2s orbitals, but both are extremely different. According to the Lewis structure of Li_2 , there is a single Li – Li bond.
- Because the 1s and 2s orbitals are so different in energy, it is likely that the 1s orbitals interact with each other. (See rule 2)
- This would create a much larger overlap between the 2s orbitals (see figure)
- As a result, the energy separation between the σ_{2s} and σ^*_{2s} is greater than that for the 1s-based orbitals.
- Each Li atom has 3 electrons; so six electrons must be placed in the molecular orbitals of Li_2
- The electrons occupy the σ_{1s} , σ^*_{1s} , and σ_{2s} orbitals (not the σ^*_{2s} orbital). There are 4 bonding orbitals and 2 nonbonding ones, so the bond order equals $\frac{1}{2} (4 - 2) = 1$. The molecule has a single bond, in accord with its Lewis structure.

Filled atomic subshells usually do not contribute significantly to bonding in molecule formation

In Be_2 , each Be has 4 electrons, for a total of eight. When we place them in molecular orbitals, we fill the σ_{1s} , σ^*_{1s} , σ_{2s} , and σ^*_{2s} orbitals. There is an equal number of bonding and antibonding electrons, so the bond order is 0. Thus, Be_2 doesn't exist.

Molecular Orbitals from 2p Atomic Orbitals

- z axis is internuclear axis (in this example). $2p_z$ orbitals face each other in a "head-to-head" fashion along the z-axis. They combine like the s orbitals, with one combination concentrating electron density between both nuclei, and the other excluding the electron density from the bonding region. In each of these combinations, the electron density lies along the internuclear axis. Hence, they are σ molecular orbitals: σ_{2p} and σ^*_{2p}
- The other 2p orbitals overlap in a sideways fashion and thus concentrate electron density on opposite sides of the internuclear axis. Molecular orbitals of this type are called **π molecular orbitals**. We get two π_{2p} molecular orbitals by combining $2p_x$ and $2p_y$ molecular orbitals. The resulting π_{2p} molecular orbitals are degenerate (same energy). Likewise, two degenerate π^*_{2p} antibonding molecular orbitals are formed.
- The $2p_z$ orbitals on two atoms point directly at one another, hence, having a greater overlap than the $2p_x$ and $2p_y$ orbitals. From rule 3, we can expect the σ_{2p} molecular orbital to be lower in energy (more stable) than the π_{2p} molecular orbitals.

Electron Configurations for B_2 Through F_2

- The elements Boron through Fluorine all have 2s and 2p valence electrons
- In the energy diagram, the σ_{2p} molecular orbital is at higher energy than the π_{2p} molecular orbitals, contrary to what we would expect from rule 3.
- This is because of interaction between the σ_{2s} and σ_{2p} molecular orbitals. It results in the σ_{2p} molecular orbital being pushed upward in energy to the point where it is above the π_{2p} orbitals, and the σ_{2s} molecular orbital is pushed down in energy. (The interaction between σ_{2p} and σ_{2s} molecular orbitals decreases as we move from left to right in the second period. As a result, the σ_{2p} is higher in energy than the π_{2p} orbitals for B_2 , C_2 , and N_2 . For O_2 , F_2 , and Ne_2 , the σ_{2p} orbital is lower in energy than the π_{2p} orbitals)
- Boron has 3 valence electrons. Thus, for B_2 , we must place 6 electrons in molecular orbitals. Four of these occupy the σ_{2s} and σ^*_{2s} molecular orbitals, leading to no net bonding. The last two electrons are put in the π_{2p} bonding molecular orbitals; one electron is put in each π_{2p} molecular orbital with the same spin (rule 5). Therefore, B_2 has a bond order of 1.

Electron Configurations and Molecular Properties

- Molecules with one or more unpaired electrons are attracted into a magnetic field. The more unpaired electrons, the stronger the force of the attraction
- **Paramagnetism:** property that a substance possesses if it contains one or more unpaired electrons. A paramagnetic substance is drawn into a magnetic field
- **Diamagnetism:** type of magnetism that causes a substance with no unpaired electrons to be weakly repelled from a magnetic field.
- Diamagnetism is a much weaker effect than paramagnetism
- As bond orders increase, bond distances decrease and bond-dissociation energies increase.
- Molecules with the same bond order do not have the same bond distances and bond-dissociation energies. There are other factors involved, such as nuclear charges and the extent of orbital overlap.

ParseError: invalid StatementList (click for details)

```
01 Callstack:
02   at (Bookshelves/General_Chemistry/Map:_Chemistry_-
   _The_Central_Science_(Brown_et_al.)/09:_Molecular_Geometry_and_Bonding_Theories/
   9.S:_Molecular_Geometry_and_Bonding_Theories_(Summary)), /content/body/div[7]/p[9]/span, line
   1, column 19
```

This page titled [3.1.S: Molecular Geometry and Bonding Theories \(Summary\)](#) is shared under a [CC BY-NC-SA 4.0](#) license and was authored, remixed, and/or curated by LibreTexts.

- [9.S: Molecular Geometry and Bonding Theories \(Summary\)](#) is licensed [CC BY-NC-SA 3.0](#).

INDEX

A

- Abegg's rule
 - 2.1.1: Chemical Bonds, Lewis Symbols, and the Octet Rule
- absorption spectrum
 - 1.1.3: Line Spectra and the Bohr Model
- amplitude
 - 1.1.1: The Wave Nature of Light
- anion
 - 2.1.2: Ionic Bonding
- antibonding molecular orbital
 - 3.1.7: Molecular Orbitals
- atomic orbital
 - 1.1.5: Quantum Mechanics and Atomic Orbitals
 - 3.1.6: Multiple Bonds
- Aufbau principle
 - 1.1.8: Electron Configurations
- azimuthal quantum number
 - 1.1.5: Quantum Mechanics and Atomic Orbitals

B

- bent
 - 3.1.2: The VSEPR Model
- blackbody radiation
 - 1.1.2: Quantized Energy and Photons
- Bohr's equation
 - 1.1.6: 3D Representation of Orbitals
- bond angle
 - 3.1.2: The VSEPR Model
- bond energy
 - 2.1.8: Strength of Covalent Bonds
 - 3.1.4: Covalent Bonding and Orbital Overlap
- bond length
 - 3.1.4: Covalent Bonding and Orbital Overlap
- bond order
 - 2.1.3: Covalent Bonding
 - 2.1.8: Strength of Covalent Bonds
 - 3.1.7: Molecular Orbitals
- bond polarity
 - 2.1.4: Bond Polarity and Electronegativity
 - 3.1.3: Molecular Shape and Molecular Polarity
- bonding molecular orbital
 - 3.1.7: Molecular Orbitals
- bonding pair
 - 2.1.5: Drawing Lewis Structures

C

- cation
 - 2.1.2: Ionic Bonding
- constructive interference
 - 1.1.4: The Wave Behavior of Matter
- coordinate covalent bond
 - 2.1.5: Drawing Lewis Structures

D

- d block
 - 1.1.9: Electron Configurations and the Periodic Table
- de Broglie wavelength
 - 1.1.4: The Wave Behavior of Matter

Debye (unit)

3.1.3: Molecular Shape and Molecular Polarity

degenerate orbitals

1.1.6: 3D Representation of Orbitals

destructive interference

1.1.4: The Wave Behavior of Matter

dipole moment

2.1.4: Bond Polarity and Electronegativity
3.1.2: The VSEPR Model
3.1.3: Molecular Shape and Molecular Polarity

double bond

2.1.3: Covalent Bonding

E

- electromagnetic radiation
 - 1.1.1: The Wave Nature of Light
- electron affinity
 - 2.1.4: Bond Polarity and Electronegativity
- electron configuration
 - 1.1.8: Electron Configurations
- electron density
 - 1.1.6: 3D Representation of Orbitals
- electron spin
 - 1.1.7: Many-Electron Atoms
- electronegativity
 - 2.1.4: Bond Polarity and Electronegativity
- emission spectrum
 - 1.1.3: Line Spectra and the Bohr Model
- endothermic
 - 2.1.3: Covalent Bonding
 - 2.1.8: Strength of Covalent Bonds
- energy level diagram
 - 3.1.7: Molecular Orbitals
- excited state
 - 1.1.3: Line Spectra and the Bohr Model
- exothermic
 - 2.1.3: Covalent Bonding
 - 2.1.8: Strength of Covalent Bonds

F

- f block
 - 1.1.9: Electron Configurations and the Periodic Table
- formal charge
 - 2.1.5: Drawing Lewis Structures
 - 2.1.6: Resonance Structures
 - 2.1.7: Exceptions to the Octet Rule
- frequency
 - 1.1.1: The Wave Nature of Light

G

- ground state
 - 1.1.3: Line Spectra and the Bohr Model

H

- Heisenberg uncertainty principle
 - 1.1.4: The Wave Behavior of Matter
- heteronuclear diatomic molecule
 - 3.1.8: Second-Row Diatomic Molecules

homonuclear diatomic molecule

3.1.7: Molecular Orbitals
3.1.8: Second-Row Diatomic Molecules

Hund's rule

1.1.8: Electron Configurations

hybrid orbital

3.1.4: Covalent Bonding and Orbital Overlap
3.1.5: Hybrid Orbitals

hybridization

3.1.4: Covalent Bonding and Orbital Overlap
3.1.5: Hybrid Orbitals

I

- insulator
 - 2.1.4: Bond Polarity and Electronegativity
- ion
 - 2.1.2: Ionic Bonding
- ionic bond
 - 2.1.2: Ionic Bonding
 - 2.1.4: Bond Polarity and Electronegativity
- ionization energy
 - 2.1.4: Bond Polarity and Electronegativity

L

- Lattice Energy
 - 2.1.2: Ionic Bonding
- LCAO
 - 3.1.7: Molecular Orbitals
- Lewis electron dot symbol
 - 2.1.1: Chemical Bonds, Lewis Symbols, and the Octet Rule
- Lewis structure
 - 2.1.5: Drawing Lewis Structures
 - 2.1.7: Exceptions to the Octet Rule
- line spectrum
 - 1.1.3: Line Spectra and the Bohr Model
- linear
 - 3.1.2: The VSEPR Model
- linear combinations of atomic orbitals
 - 3.1.7: Molecular Orbitals
- lone pair
 - 2.1.5: Drawing Lewis Structures

M

- magnetic quantum number
 - 1.1.5: Quantum Mechanics and Atomic Orbitals
- molecular geometry
 - 3.1.1: Molecular Shapes
- molecular orbital
 - 3.1.6: Multiple Bonds
 - 3.1.7: Molecular Orbitals
- molecular orbital theory
 - 3.1.7: Molecular Orbitals

N

- nonbonding molecular orbitals
 - 3.1.8: Second-Row Diatomic Molecules
- nonpolar covalent bond
 - 2.1.4: Bond Polarity and Electronegativity

O

octahedral

[3.1.2: The VSEPR Model](#)

octet rule

[2.1.1: Chemical Bonds, Lewis Symbols, and the Octet Rule](#)

[2.1.7: Exceptions to the Octet Rule](#)

orbital energy

[1.1.6: 3D Representation of Orbitals](#)

[1.1.7: Many-Electron Atoms](#)

overtones

[1.1.4: The Wave Behavior of Matter](#)

P

p block

[1.1.9: Electron Configurations and the Periodic Table](#)

Pauli exclusion principle

[1.1.7: Many-Electron Atoms](#)

[1.1.8: Electron Configurations](#)

percent ionic character

[2.1.4: Bond Polarity and Electronegativity](#)

photoelectric effect

[1.1.2: Quantized Energy and Photons](#)

photon

[1.1.2: Quantized Energy and Photons](#)

pi bond

[3.1.6: Multiple Bonds](#)

[3.1.7: Molecular Orbitals](#)

pi star bond

[3.1.7: Molecular Orbitals](#)

polar covalent bond

[2.1.4: Bond Polarity and Electronegativity](#)

[3.1.3: Molecular Shape and Molecular Polarity](#)

principle quantum number

[1.1.5: Quantum Mechanics and Atomic Orbitals](#)

principle shell

[1.1.5: Quantum Mechanics and Atomic Orbitals](#)

probability density

[1.1.6: 3D Representation of Orbitals](#)

Q

quantum

[1.1.2: Quantized Energy and Photons](#)

quantum mechanics

[1.1.5: Quantum Mechanics and Atomic Orbitals](#)

R

resonance structure

[2.1.6: Resonance Structures](#)

S

s block

[1.1.9: Electron Configurations and the Periodic Table](#)

seesaw

[3.1.2: The VSEPR Model](#)

semimetal

[2.1.4: Bond Polarity and Electronegativity](#)

shared electron pair

[2.1.3: Covalent Bonding](#)

sigma bond

[3.1.6: Multiple Bonds](#)

[3.1.7: Molecular Orbitals](#)

sigma star bond

[3.1.7: Molecular Orbitals](#)

single bond

[2.1.3: Covalent Bonding](#)

sp hybrid orbital

[3.1.5: Hybrid Orbitals](#)

sp² hybrid orbital

[3.1.5: Hybrid Orbitals](#)

sp³ hybrid orbital

[3.1.5: Hybrid Orbitals](#)

sp³d hybrid orbital

[3.1.5: Hybrid Orbitals](#)

sp³d² hybrid orbital

[3.1.5: Hybrid Orbitals](#)

speed

[1.1.1: The Wave Nature of Light](#)

speed of light

[1.1.1: The Wave Nature of Light](#)

square pyramidal

[3.1.2: The VSEPR Model](#)

standing wave

[1.1.4: The Wave Behavior of Matter](#)

subshell

[1.1.5: Quantum Mechanics and Atomic Orbitals](#)

T

tetrahedral

[3.1.1: Molecular Shapes](#)

[3.1.2: The VSEPR Model](#)

trigonal bipyramidal

[3.1.2: The VSEPR Model](#)

trigonal planar

[3.1.2: The VSEPR Model](#)

trigonal pyramidal

[3.1.2: The VSEPR Model](#)

triple bond

[2.1.3: Covalent Bonding](#)

V

valence bond theory

[2.1.6: Resonance Structures](#)

[3.1.4: Covalent Bonding and Orbital Overlap](#)

[3.1.5: Hybrid Orbitals](#)

valence electrons

[1.1.8: Electron Configurations](#)

valence shell electron pair repulsion theory

[3.1.2: The VSEPR Model](#)

VSEPR

[3.1.2: The VSEPR Model](#)

W

wave

[1.1.1: The Wave Nature of Light](#)

Wavefunction

[1.1.5: Quantum Mechanics and Atomic Orbitals](#)

wavelength

[1.1.1: The Wave Nature of Light](#)

GLOSSARY

S

Sample Word 1 | Sample Definition 1

GLOSSARY

S

Sample Word 1 | Sample Definition 1

DETAILED LICENSING

Overview

Title: Spectroscopy: Background Information on Electronic Structure of Atoms and Molecules

Webpages: 48

Applicable Restrictions: Noncommercial

All licenses found:

- [CC BY-NC-SA 4.0](#): 70.8% (34 pages)
- [Undeclared](#): 29.2% (14 pages)

By Page

- Spectroscopy: Background Information on Electronic Structure of Atoms and Molecules - *Undeclared*
 - Front Matter - *Undeclared*
 - TitlePage - *Undeclared*
 - InfoPage - *Undeclared*
 - Table of Contents - *Undeclared*
 - Licensing - *Undeclared*
 - 1: Chapter 1 - Electronic Structure of Atoms - *Undeclared*
 - 1.1: Electronic Structure of Atoms - [CC BY-NC-SA 4.0](#)
 - 1.1.1: The Wave Nature of Light - [CC BY-NC-SA 4.0](#)
 - 1.1.2: Quantized Energy and Photons - [CC BY-NC-SA 4.0](#)
 - 1.1.3: Line Spectra and the Bohr Model - [CC BY-NC-SA 4.0](#)
 - 1.1.4: The Wave Behavior of Matter - [CC BY-NC-SA 4.0](#)
 - 1.1.5: Quantum Mechanics and Atomic Orbitals - [CC BY-NC-SA 4.0](#)
 - 1.1.6: 3D Representation of Orbitals - [CC BY-NC-SA 4.0](#)
 - 1.1.7: Many-Electron Atoms - [CC BY-NC-SA 4.0](#)
 - 1.1.8: Electron Configurations - [CC BY-NC-SA 4.0](#)
 - 1.1.9: Electron Configurations and the Periodic Table - [CC BY-NC-SA 4.0](#)
 - 1.1.E: Electronic Structure of Atoms (Exercises) - [CC BY-NC-SA 4.0](#)
 - 1.1.S: Electronic Structure of Atoms (Summary) - [CC BY-NC-SA 4.0](#)
 - 2: Chapter 2 - Basics of Chemical Bonding - *Undeclared*
 - 2.1: Basic Concepts of Chemical Bonding - [CC BY-NC-SA 4.0](#)
 - 2.1.1: Chemical Bonds, Lewis Symbols, and the Octet Rule - [CC BY-NC-SA 4.0](#)
 - 2.1.2: Ionic Bonding - [CC BY-NC-SA 4.0](#)
 - 2.1.3: Covalent Bonding - [CC BY-NC-SA 4.0](#)
 - 2.1.4: Bond Polarity and Electronegativity - [CC BY-NC-SA 4.0](#)
 - 2.1.5: Drawing Lewis Structures - [CC BY-NC-SA 4.0](#)
 - 2.1.6: Resonance Structures - [CC BY-NC-SA 4.0](#)
 - 2.1.7: Exceptions to the Octet Rule - [CC BY-NC-SA 4.0](#)
 - 2.1.8: Strength of Covalent Bonds - [CC BY-NC-SA 4.0](#)
 - 2.1.E: Basic Concepts of Chemical Bonding (Exercises) - [CC BY-NC-SA 4.0](#)
 - 2.1.S: Basic Concepts of Chemical Bonding (Summary) - [CC BY-NC-SA 4.0](#)
 - 3: Chapter 3 - Molecular Shapes and Bonding Theories - *Undeclared*
 - 3.1: Molecular Geometry and Bonding Theories - [CC BY-NC-SA 4.0](#)
 - 3.1.1: Molecular Shapes - [CC BY-NC-SA 4.0](#)
 - 3.1.2: The VSEPR Model - [CC BY-NC-SA 4.0](#)
 - 3.1.3: Molecular Shape and Molecular Polarity - [CC BY-NC-SA 4.0](#)
 - 3.1.4: Covalent Bonding and Orbital Overlap - [CC BY-NC-SA 4.0](#)
 - 3.1.5: Hybrid Orbitals - [CC BY-NC-SA 4.0](#)
 - 3.1.6: Multiple Bonds - [CC BY-NC-SA 4.0](#)
 - 3.1.7: Molecular Orbitals - [CC BY-NC-SA 4.0](#)
 - 3.1.8: Second-Row Diatomic Molecules - [CC BY-NC-SA 4.0](#)
 - 3.1.E: Exercises - [CC BY-NC-SA 4.0](#)
 - 3.1.S: Molecular Geometry and Bonding Theories (Summary) - [CC BY-NC-SA 4.0](#)
 - Back Matter - *Undeclared*
 - Index - *Undeclared*

- [Glossary - Undeclared](#)
- [Glossary - Undeclared](#)
- [Detailed Licensing - Undeclared](#)